Colloids
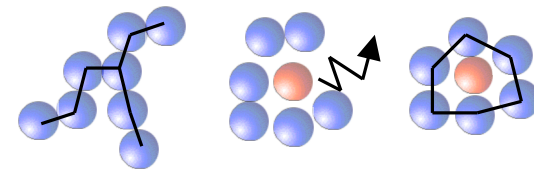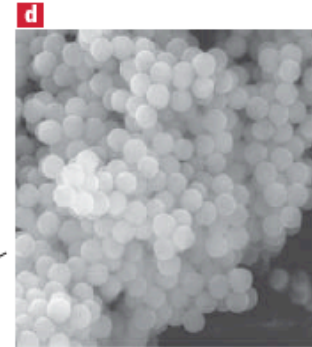
Colloids

    - what, how, why, definitions

Stability of colloidal systems

    - types of forces & interactions

    - modifying forces & interactions

Phase transitions and aggregation

Literature on colloids

- Jones - chp. 4

- Understanding foods as soft materials
  Nature Materials 4, 729 (October 2005)
  (article can be accessed via www.lib.chalmers.se)

More colloids

24/9 Colloidal dynamics and rheology,

Johan Bergenhotlz, Department of Chemistry, GU

Location: F7103   Time: 12-13

Colloidal systems

Table 3.1. Some examples of colloidal systems. *Italics* refer to industrial applications

Continuous medium	Dispersed phase		
	Solid	Liquid	Gas
Solid	Solid dispersions	Solid emulsions	Solid foams
	Composite materials	Butter, margarine	Expanded plastics (polyurethane foams)
	Photochromic glasses	Opal	
	Fillers and pigments		
	Plastic compounding and processing	*Food industry*	*Packaging* *Civil engineering*
Liquid	Suspensions	Colloidal emulsions	Foams

Colloidal systems

Liquid	Suspensions (Hydrosols and organosols)	Colloidal emulsions (Oil/water, water/oil and microemulsions)	Foams
	Muddy water	Milk	Whipped cream
	Indian ink	Mayonnaise	
		Cosmetic creams	
	Inks	*Food industry*	*Food industry*
	Papermaking		*Foam fire*
	Paints		*extinguishers*
	Production of ceramics	*Fluids for petroleum industry*	
	Used-water treatment	*Liquid/liquid extraction*	
Gas	Solid aerosols	Liquid aerosols	
	Smoke	Fog	
	Dust removal	*Cosmetics*	
		Inkjet printers	

Colloids - Size

a) Small enough to be influenced by thermal fluctuations and not dominated by gravity

b) Big enough to be treated as one body with average density, surface charge etc.

$\Rightarrow \phi$=10 - 10000 nm (or more)

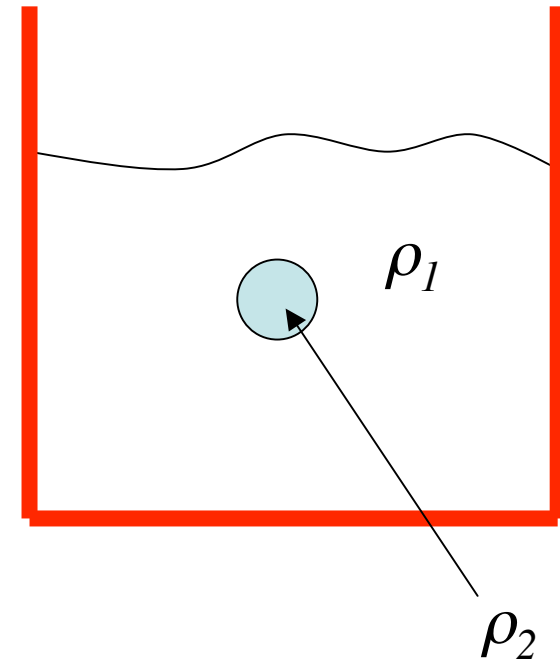Surfaces and interfaces:

Properties and behaviour controlled by surfaces
10 nm SiO_2 particle
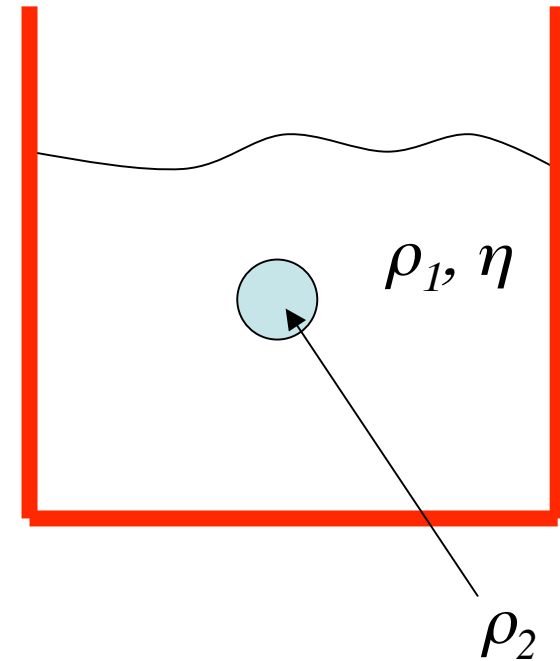$\Rightarrow$ *20% of the Si atoms are at the surface*

Forces

Force on an *individual* particle in a suspension:

- *Gravity*

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

$$\Delta\rho = \rho_2 - \rho_1$$

$\Delta\rho > 0$ sedimentation

$\Delta\rho < 0$ creaming

ρ_1

ρ_2

Forces

Force on an *individual* particle in a suspension:

- Gravity

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

$$\Delta\rho = \rho_2 - \rho_1$$

$\Delta\rho > 0$ sedimentation

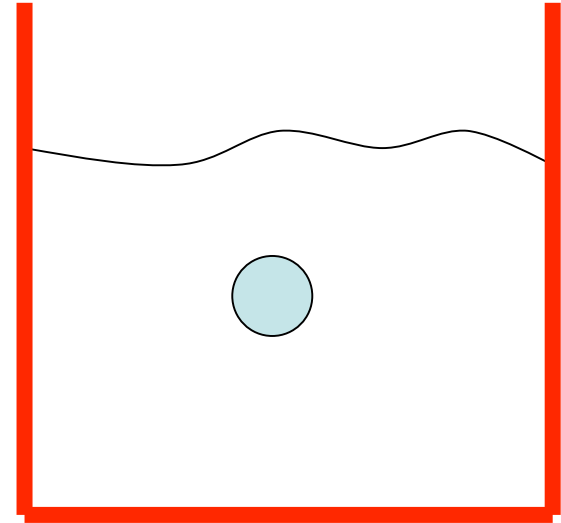$\Delta\rho < 0$ creaming

- *Drag force*

$$F_f = 6\pi\eta a v$$ Stokes law

$$v_T = \frac{2a^2\Delta\rho g}{9\eta}$$ Terminal velocity

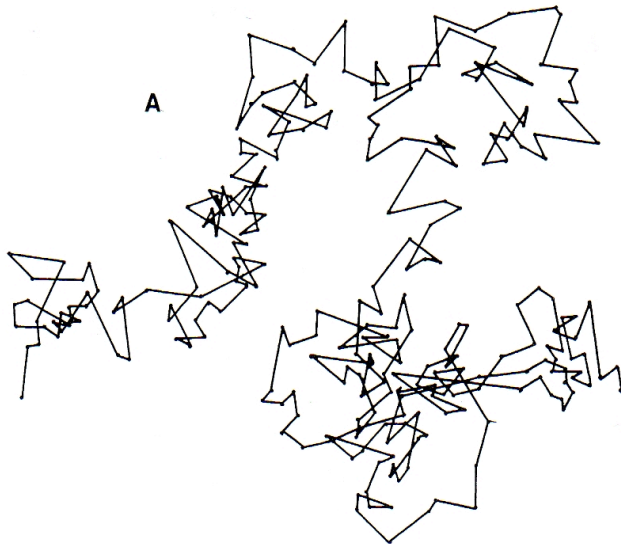ρ_1, η

ρ_2

Brownian motion

Thermal motion of the atoms/ molecules
in the liquid acts on the particle

Brownian motion

Thermal motion of the atoms/ molecules
in the liquid acts on the particle
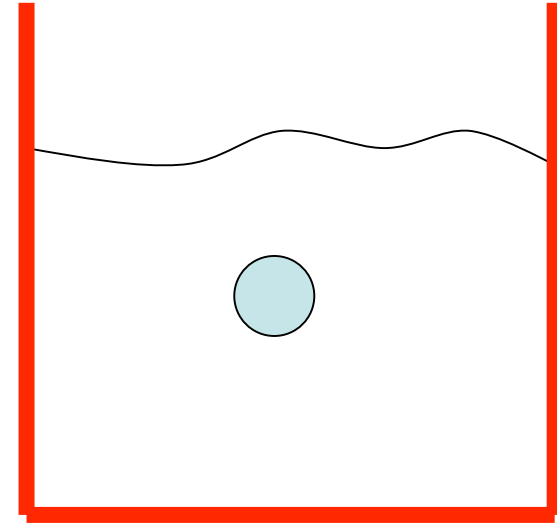
$\langle \overline{F} \rangle = 0$ *average force*

Random walk

$\langle \vec{R} \rangle = 0$

$\langle (\vec{R}(t))^2 \rangle = \alpha t$
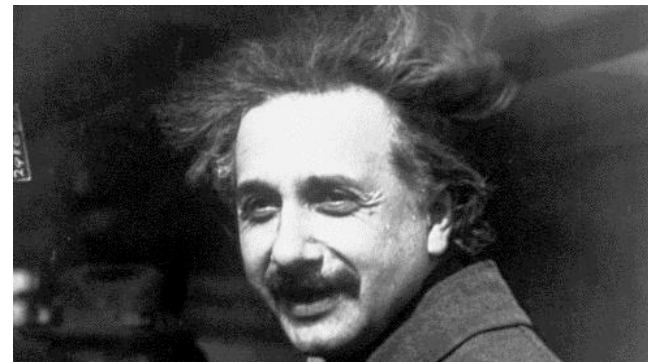
$\vec{R}(t)$ - displacement vector

Brownian motion - history

- First observed in 1827 by the botanist Robert Brown. But Brown did not understand what was happening. He only observed pollen grains under a microscope.

- Desaulx in 1877: "*In my way of thinking the phenomenon is a result of thermal molecular motion in the liquid environment (of the particles).*"

- But it was not until 1905 that the mathematical theory of Brownian motion was developed by Einstein. (It was partly for this work he received the Nobel prize 1921.)

Brownian motion

Thermal motion of the atoms/ molecules
in the liquid acts on the particle

$$\langle \overline{F} \rangle = 0 \quad \textit{average force}$$
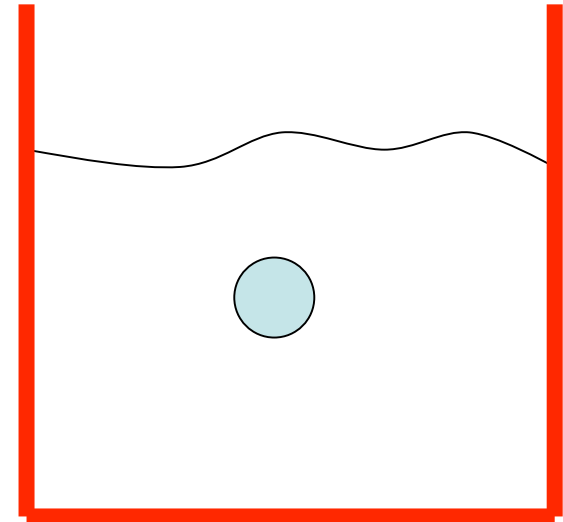

A

Random walk

$$\langle \vec{R} \rangle = 0$$
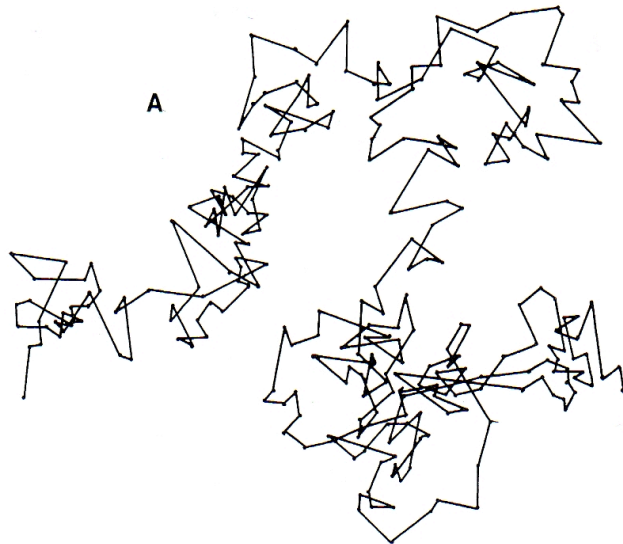
$$\langle (\vec{R}(t))^2 \rangle = \alpha t$$

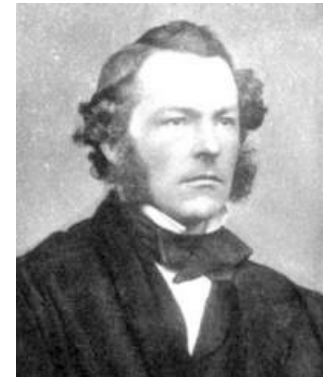$\vec{R}(t)$ - displacement vector

Diffusion constant from Stokes-Einstein
formula:

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

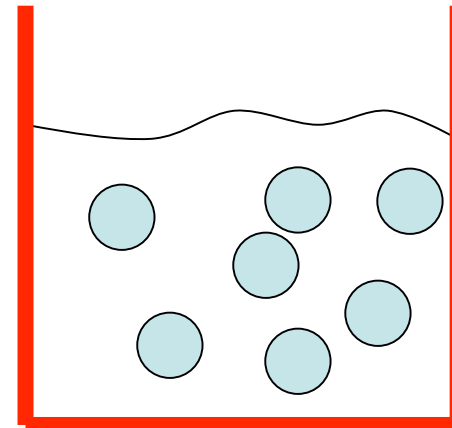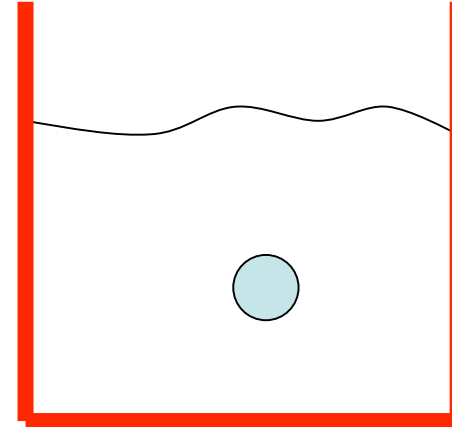η - medium viscosity

a - particle radius

Forces

Force on an individual particle:

- Gravity

- Drag force

- Brownian motion

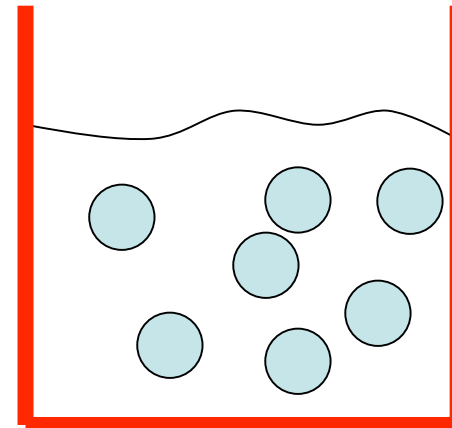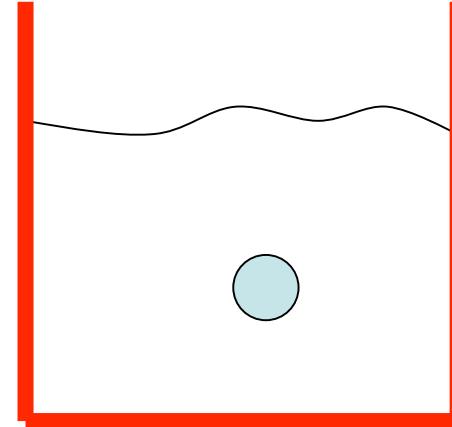Many particles ⇒ interactions

    attractive ⇔ repulsive

Forces

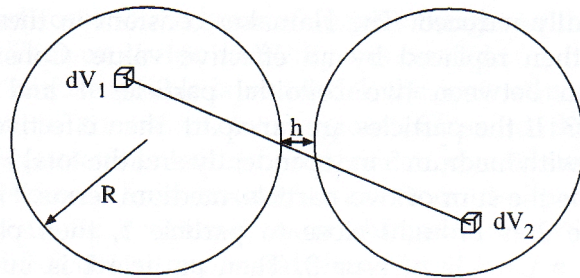Force on an individual particle:

- Gravity

- Drag force

- Brownian motion

Many particles $\Rightarrow$ interactions

- van der Waal interaction - attractive

van der Waals interaction

Figure 3.1 Illustrating the method for calculating interparticle forces between colloids. The forces between the volume elements dV of two particles are integrated

Weak interaction between individual molecules, but it is additive

Interaction between two spheres

$$U(h) = -\frac{AR}{12h} \ , \ h << R$$

A - Hamakers constant, depends on the medium

Ex: polystyrene, R=100 nm, in water:

h=1 nm -> U=8.3·10^{-20} J ≈ 20 kT

h=10 nm -> U=0.8 ·10^{-20} J ≈ 2 kT

Table 3.2. Hamaker's constant for various materials dispersed in air (A) and water (A_M)

| Material	A [10^{-20} J]	A_M [10^{-20} J] (in water)
n-pentane	3.7	0.34
n-octane	4.5	0.41
n-dodecane	5.0	0.50
Polytetrafluoroethylene	3.8	0.33
Polystyrene	6.6	1.0
Polyvinyl chloride	7.8	1.3
Acetone	4.1	–
Ethanol	4.2	–
Methanol	3.6	–
Water	3.7	–
Formamide	6.1	–
Metals	30–50	20–40

Forces

Force on an individual particle:

- Gravity $\Leftrightarrow$ Brownian motion & drag force

Interactions between particles:

- van der Waal interaction - attractive $\Rightarrow$ aggregation

- electrostatic $\Rightarrow$ repulsive

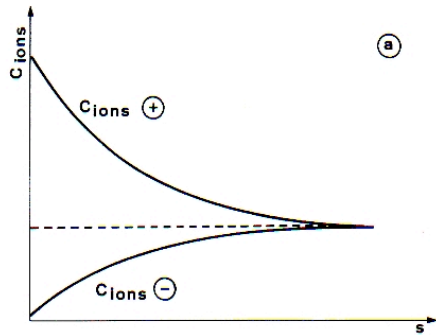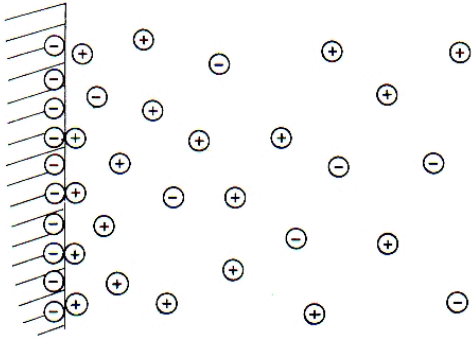# Electrostatic interaction
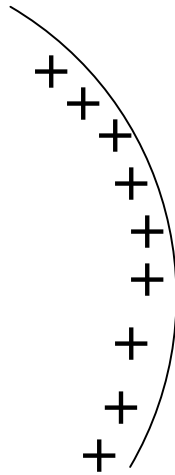
Surfaces often charged (or made to be):

- Structural origin

- Surface groups

- Selective adsorption

$\Rightarrow$ Manipulate and control through surface chemistry

Electrostatic interaction

Screening effect due to presence of ions in the medium

Charge neutrality preserved by a layer of counter ions:

- tightly bound -Stern layer

- decreasing concentration

Electrostatic interaction

Fig. 3.2. Distribution of counter-ions and co-ions near the surface of a material which, in this case, carries a negative charge excess. (a) Variation of the concentration of each ionic species with distance from the wall. (b) Variation of the electric potential Ψ created by the charges with distance from the wall
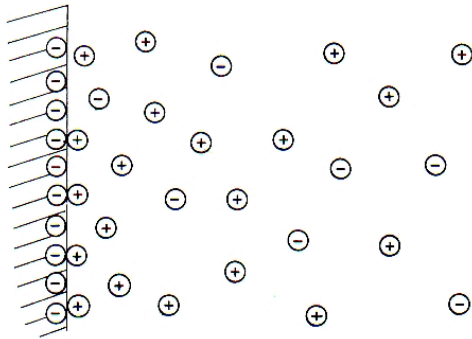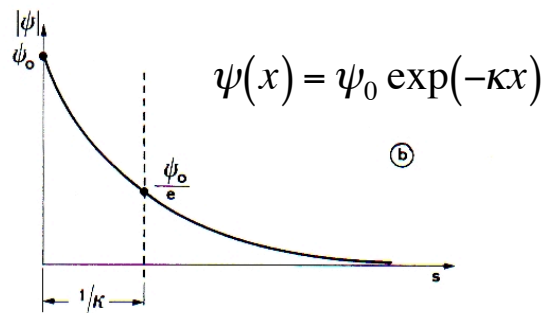
Screening effect due to presence of ions in the medium

Charge neutrality preserved by a layer of counter ions:

- tightly bound -Stern layer

- decreasing concentration

Debye screening length:
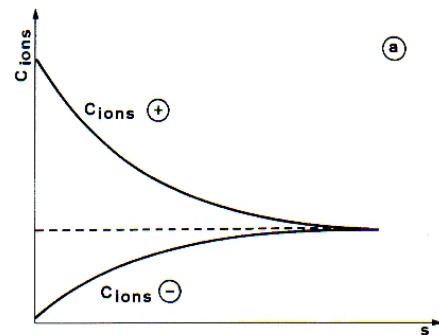
$$\psi(x) = \psi_0 \exp(-\kappa x)$$

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2 e^2 n_0 z^2} \right)^{1/2}$$

n_0 - ionic concentration in medium

ze - ionic charge

At $h \gg \kappa^{-1}$ electrostatic interaction -> 0

Forces

Force on an individual particle:

- Gravity $\Leftrightarrow$ Brownian motion & drag force
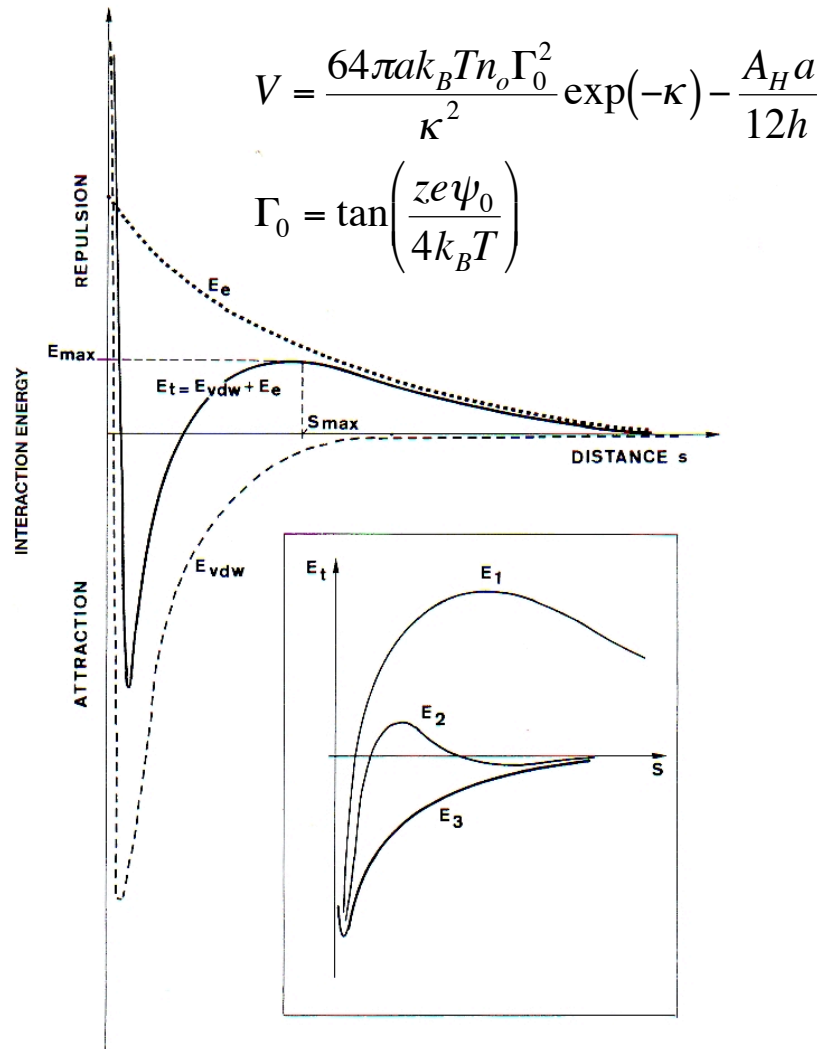
Interactions between particles:

- van der Waal interaction - attractive $\Rightarrow$ aggregation

- electrostatic $\Rightarrow$ repulsive, but screened

    stability depends on salt concentration

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2 e^2 n_0 z^2} \right)^{1/2}$$

Energy variation with distance

$$V = \frac{64\pi a k_B T n_o \Gamma_0^2}{\kappa^2} \exp(-\kappa) - \frac{A_H a}{12h}$$

$$\Gamma_0 = \tan\left(\frac{ze\psi_0}{4k_B T}\right)$$

DLVO - theory: $V = V_R + V_A$

Attractive - van der Waals
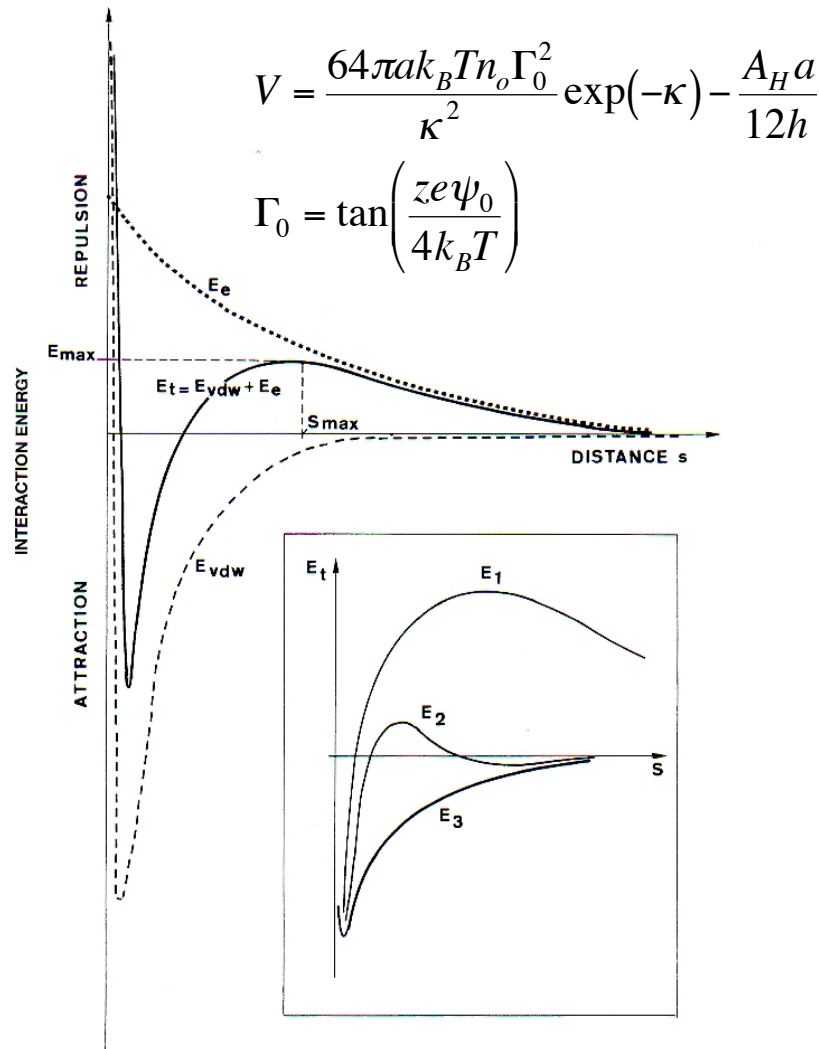(but repulsive at very short distances)

Repulsive - electrostatic, double layer

- large separation - no aggregation $\Rightarrow$
  meta-stable

- small separation - particles aggregates
  are very stable

(DLVO - Derjaguin-Landau-Verwey-Overbeek)

Fig. 3.3. Variation of energy (E) with distance for two spheres separated by distance (s). The total energy E_t is represented by the *continuous curve*

Energy variation with distance

$$V = \frac{64\pi a k_B T n_o \Gamma_0^2}{\kappa^2} \exp(-\kappa) - \frac{A_H a}{12h}$$

$$\Gamma_0 = \tan\left(\frac{ze\psi_0}{4k_B T}\right)$$

DLVO - theory: $V = V_R + V_A$

Attractive - van der Waals
(but repulsive at very short distances)

Repulsive - electrostatic, double layer

$E_t \gg k_B T \Rightarrow$ stable solution

$E_t \approx$ or $< k_B T \Rightarrow$ aggregation

only repulsive term dependent on salt concentration

Fig. 3.3. Variation of energy (E) with distance for two spheres separated by distance (s). The total energy E_t is represented by the *continuous curve*

Dependence on salt concentration

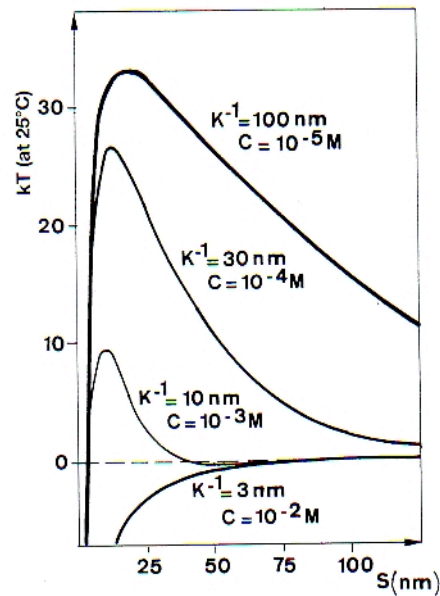Addition of salt $\Rightarrow$ destabilisation

Fig. 3.4. The curve of energy E against separ
for two particles of radius 100 nm and surface po
26 mV. The calculation has been made for variou
strengths and a value of 10^{-19} J for Hamaker
stant. For easier comparison with the energy of t
motions, E has been given in units of kT for $T =$

Dependence on salt concentration

Addition of salt $\Rightarrow$ destabilisation
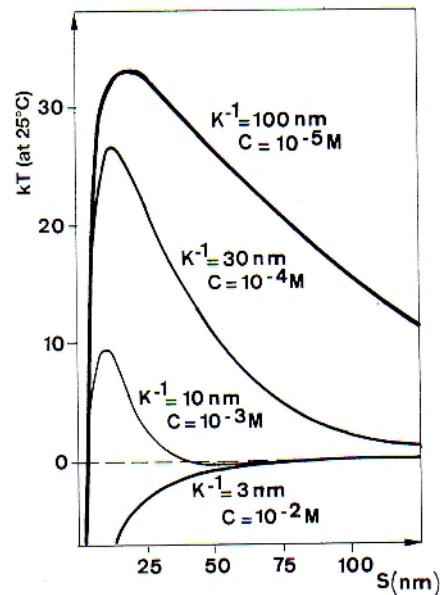

Fig. 3.4. The curve of energy E against separ
for two particles of radius 100 nm and surface po
26 mV. The calculation has been made for variou
strengths and a value of 10^{-19} J for Hamaker
stant. For easier comparison with the energy of t
motions, E has been given in units of kT for $T =$

Ex: Formation of a delta.

Muddy river water - colloidal suspension. Salt
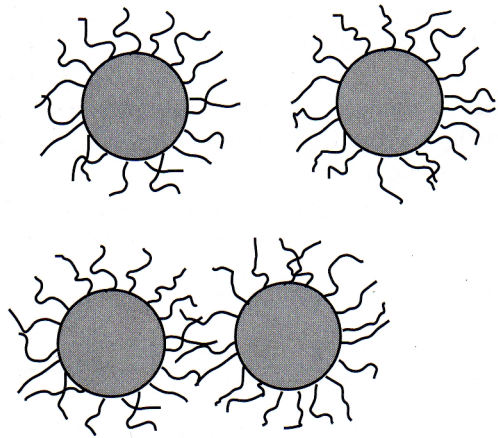sea water -> aggregation of particles   ->
sedimentation

Forces

Force on an individual particle:

- Gravity $\Leftrightarrow$ Brownian motion & drag force

Interactions between particles:

- van der Waal interaction - attractive $\Rightarrow$ aggregation

- electrostatic $\Rightarrow$ repulsive

- steric, entropic, osmotic $\Rightarrow$ repulsive

Stabilisation with polymers

Fig. 4.4 Stabilisation of colloids with grafted polymers. When the particles come close enough for the grafted polymers to overlap, a local increase in polymer concentration leads to a repulsive force of osmotic origin.

Need to stabilise to decrease sensitivity to salt concentration

$\Rightarrow$ coating with a polymer layer

$\Rightarrow$ repulsive force if the polymer chains start to overlap if no attractive interaction between polymer chains

$\Rightarrow$ range of repulsion depend on size and density of polymers
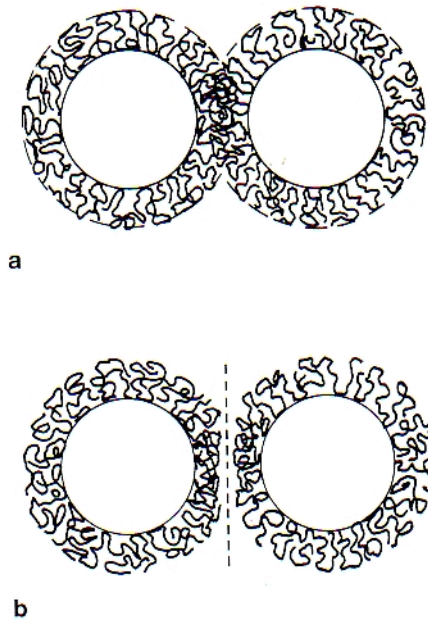
Stabilisation with polymers

Fig. 3.14. Stabilisation of particles by steric repulsion. (a) Osmotic effect, (b) volume restriction effect

Repulsive interaction

i) Osmotic effect - polymer concentration increases at the interface, solvent dependent

ii) Entropic effect - reduction in degrees of freedom

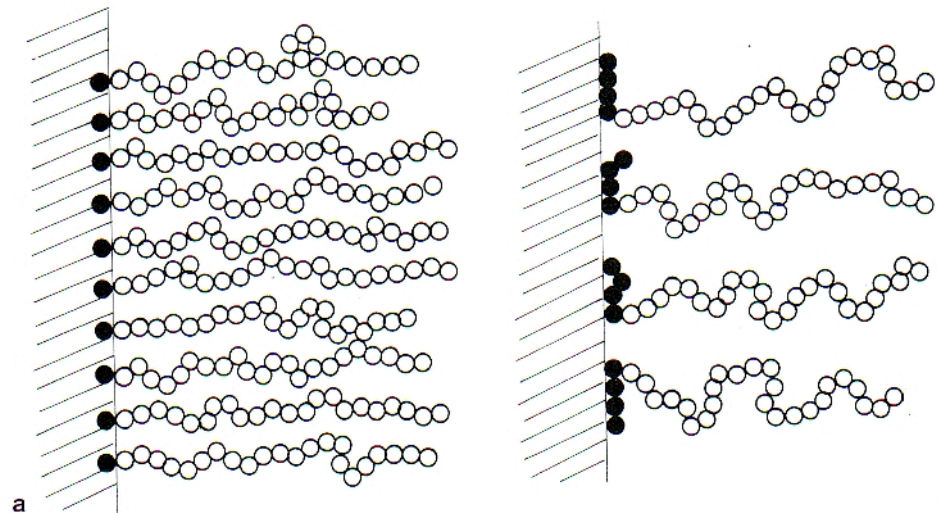# Adsorbed polymers

Polymers easily adsorbed

Interaction $> k_B T$
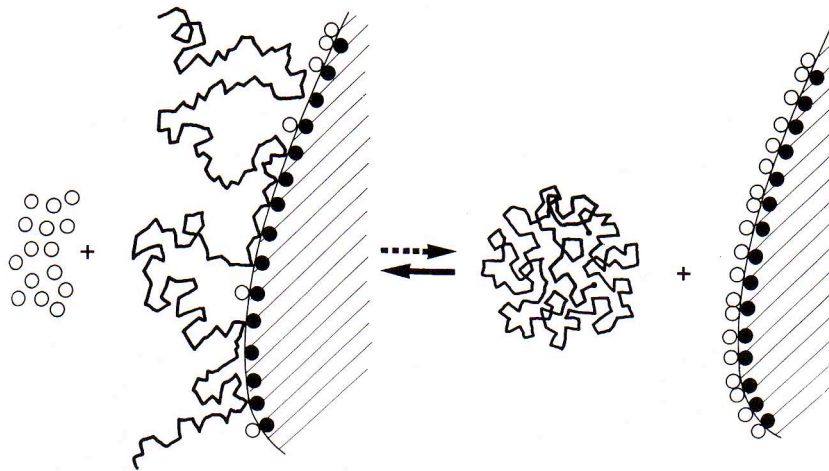
Fig. 3.11. Adsorption of a macromolecule onto a surface. Adsorption sites on the surface are represented by *black dots* and solvent molecules specifically adsorbed onto the surface are shown as *white circles*

Grafted polymers

Fig. 3.15. (a) A layer of polymer chains grafted at one end onto an interface. For high grafting densities, the chains are uncoiled. (b) Diblock copolymer adsorbed onto an interface. The *black sequence* (or anchor block) has a strong affinity for the surface, whereas the *white sequence* (or buoy block) is repelled by the surface and stretches out into the liquid

Polymers chemically attached to the surface

Strong interaction and good control

Practically expensive & difficult

Interactions of modified surfaces
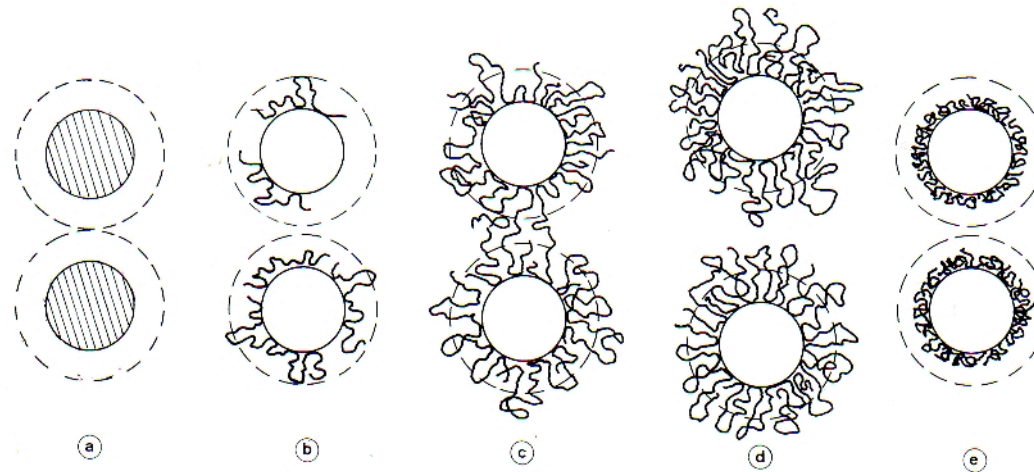
Fig. 3.13. Flocculation and stabilisation of suspensions by neutral polymers. (a) Lone particles. The range of electrostatic repulsion has been represented (*dotted line*). (b) When a small quantity of polymer is added, the adsorbed layer remains thin since the chain conformation is highly flattened. (c) When the quantity of polymer is such that the size of loops becomes greater than twice the range of electrostatic repulsion, links can be established between particles. Aggregates form in the solution and precipitate out. (d) The particles are saturated with polymer and repel each other via steric effects. (e) The saturation of particle surfaces by polymers with low molecular weight can favour stability, without increasing the risk of flocculation

Polymers on surface can also cause destabilisation

- low concentration of polymers ⇒ formation of bridges
  causing aggregation, *polymer bridging flocculation*
                              (purifying water, clearing wine)

Depletion - attractive interaction
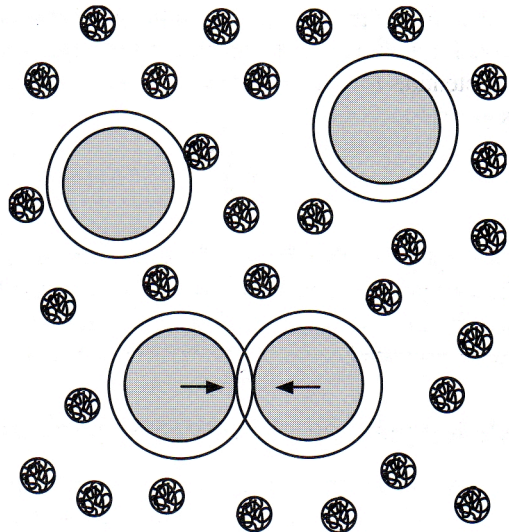
Fig. 4.5 The depletion interaction. Polymer coils are excluded from a depletion zone near the surface of the colloidal particles; when the depletion zones of two particles overlap there is a net attractive force between the particles arising from unbalanced osmotic pressures.
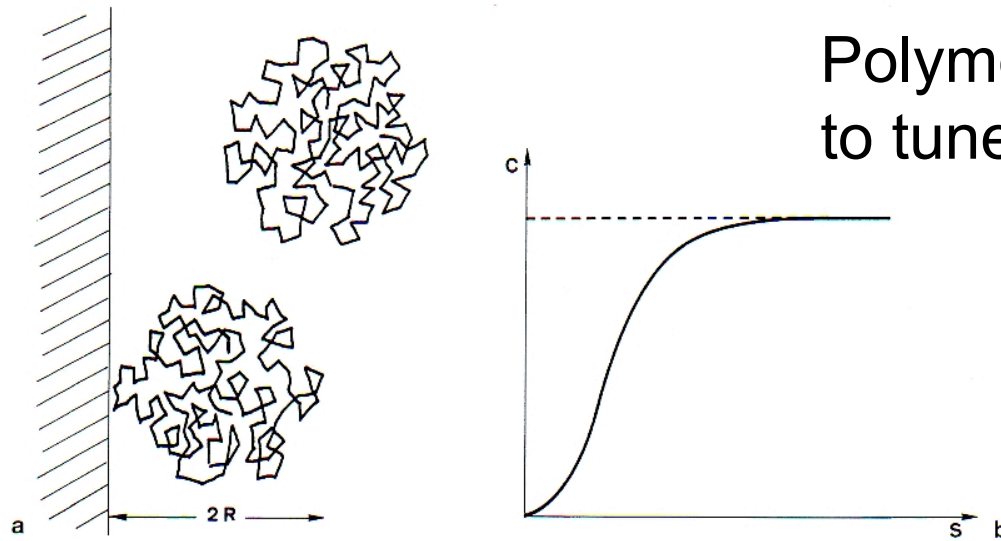
Depletion - reducing the repulsive force

- Addition of second particle in the suspension, $r_2 < r_C$

- non-adsorbing polymer

- osmotic pressure effect due to excluded volume

Depletion - attractive interaction
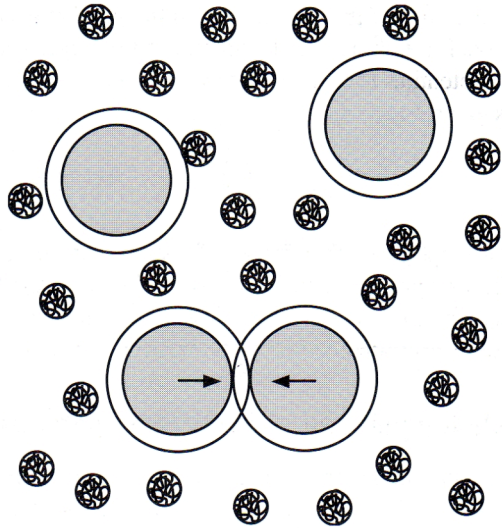
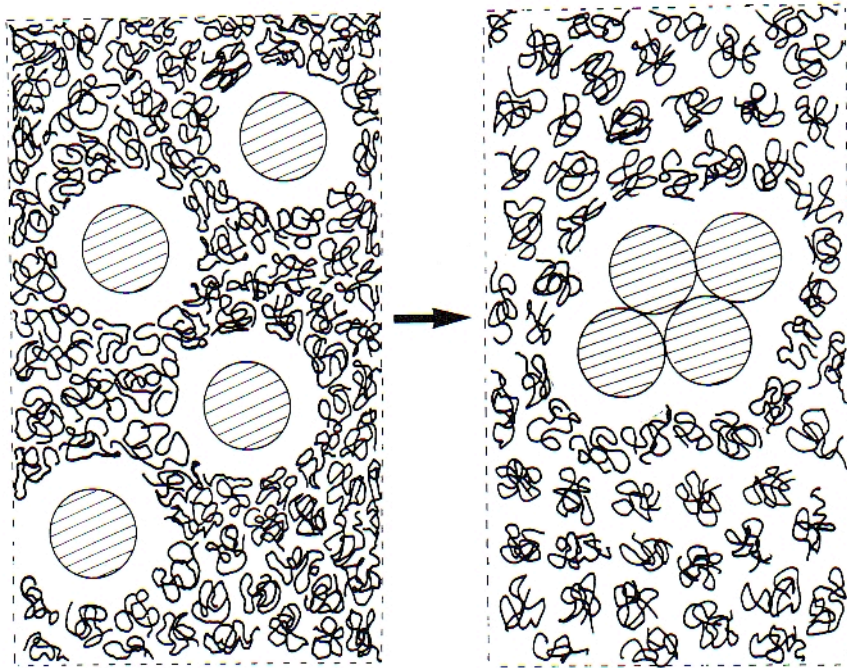Centre of mass of polymer cannot come closer to the surface than R

$\Rightarrow$ concentration gradient near the surface

Polymer concentration can be used to tune the interaction

Fig. 3.16. (a) Macromolecular chains not adsorbed onto a wall. (b) Corresponding variation in the concentration c of macromolecular segments with distance s from the wall

Depletion - attractive interaction

Fig. 3.17. (a) The polymer does not adsorb onto the particles in a suspension. When these particles are separated, the volume forbidden to the polymer is large. (b) Particle aggregation through the depletion effect minimises the excluded volume and reduces the average concentration in solution

High polymer concentration

$\Rightarrow$ supersaturation

Decreased effective concentration by aggregation
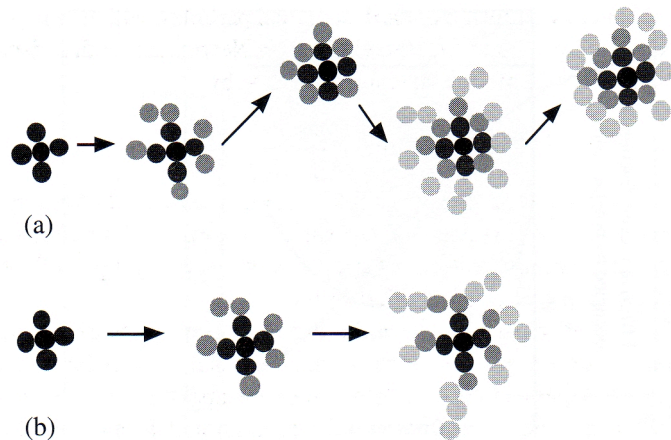
$\Rightarrow$ Depletion flocculation

Tuning the interaction

From repulsive to attractive:

i)   add salt $\Rightarrow$ reduce screening length

ii) add poor solvent $\Rightarrow$ increase polymer/polymer interaction

iii) add non-adsorbing polymer $\Rightarrow$ depletion

iv) remove grafted polymers (chemically)

Colloidal aggregation

Fig. 4.10 Aggregation with and without rearrangement. In (a) the attraction is weak enough to allow the particles to rearrange following aggregation—this produces relatively compact aggregates. In (b) the attractive energy is so strong that once particles make contact, they remain stuck in this position. Particles arriving later tend to stick on the outside of the cluster, as access to its interior is blocked, resulting in much more open aggregates with a fractal structure.

Strong attraction
$\Rightarrow$ irreversible aggregation
(compared to $k_B T$)
$\Rightarrow$ fractal structure
$\Rightarrow$ open aggregates

Weak attraction
$\Rightarrow$ dense aggregates due to
time for rearrangement

Phase transitions

Changing particle concentration $\Rightarrow$ phase transitions
(ϕ corresponding to T for molecular systems)

Hard sphere system:
- liquid $\Rightarrow$ crystal transition at $\phi=0.494$ (volume fraction)
to a a phase $\phi=0.545$, $0.494 <\phi<0.545$ co-existence

- $\phi\approx0.58$ glass transition (kinetically controlled, viscosity is
so high that crystallization is inhibited)
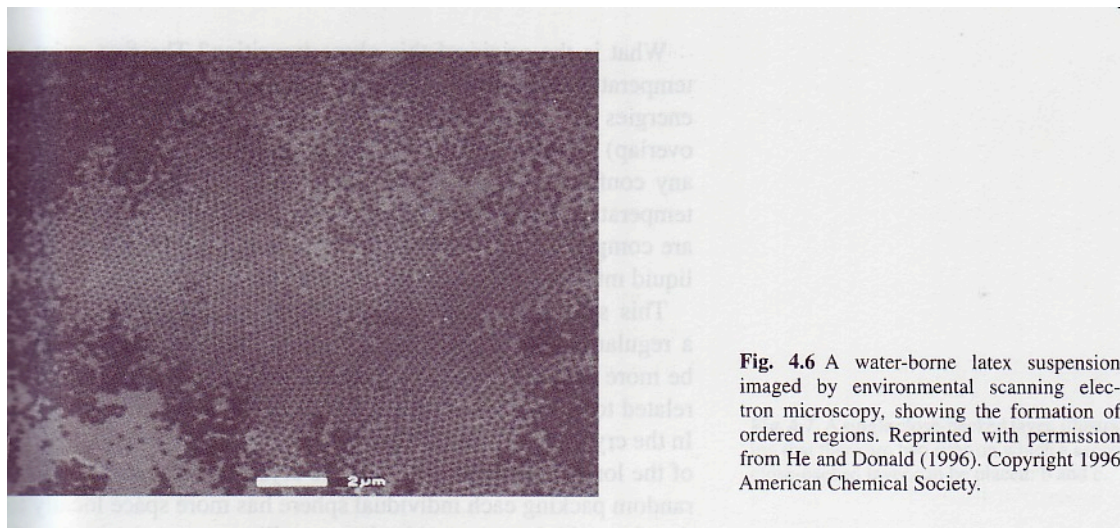
Fig. 4.6 A water-borne latex suspension imaged by environmental scanning electron microscopy, showing the formation of ordered regions. Reprinted with permission from He and Donald (1996). Copyright 1996 American Chemical Society.
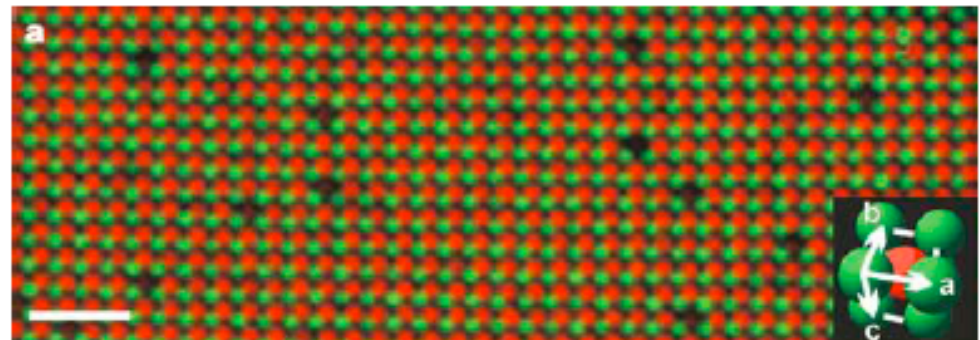
Phase transitions

Changing particle concentration $\Rightarrow$ phase transitions
(ϕ corresponding to T for molecular systems)

Hard sphere system:
- liquid $\Rightarrow$ crystal transition at ϕ=0.494 (volume fraction)
to a a phase ϕ=0.545, 0.494 <ϕ <0.545 co-existence

- ϕ≈0.58 glass transition (kinetically controlled, viscosity is so high that crystallization is inhibited)

- phase transition is driven by entropy - packing of spheres

Phase transitions

Changing particle concentration $\Rightarrow$ phase transitions
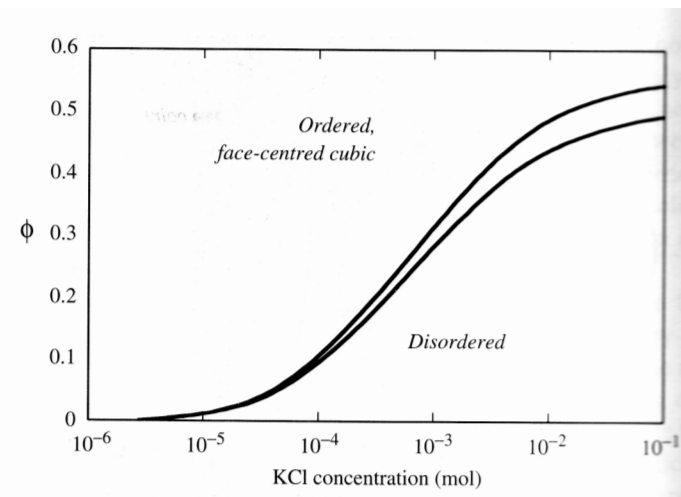(ϕ corresponding to T for molecular systems)

Hard sphere system:
- liquid $\Rightarrow$ crystal transition at ϕ=0.494 (volume fraction)
to a a phase ϕ=0.545, 0.494<ϕ<0.545 co-existence

Long range repulsion:
- the transition concentration is lowered with
  longer ranged repulsion

Fig. 4.8 Phase diagram for charged spheres in a polyelectrolyte solution as a function of the volume fraction of spheres ϕ and the concentration of salt, as calculated for spheres of radius 0.1 μm with surface charge 5000e. After Russel *et al.* (1989).

Phase transitions

Changing particle concentration -> phase transitions
(ϕ corresponding to T for molecular systems)

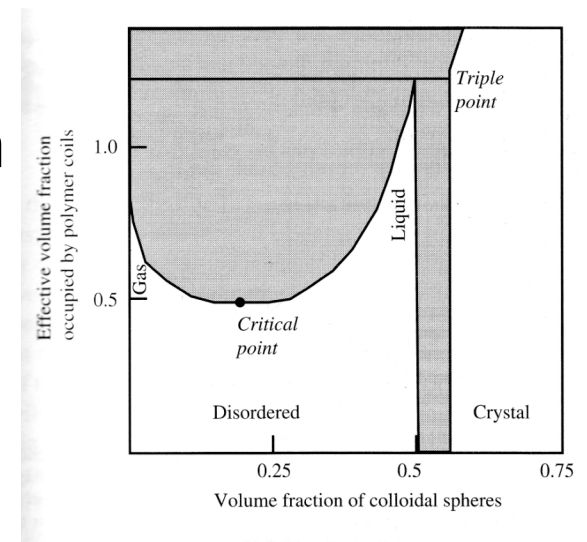Hard sphere system:
- liquid -> crystal transition at ϕ=0.494 (volume fraction)
to a a phase ϕ=0.545, 0.494<ϕ<0.545 co-existence

Long range repulsion:
- the transition concentration is lowered

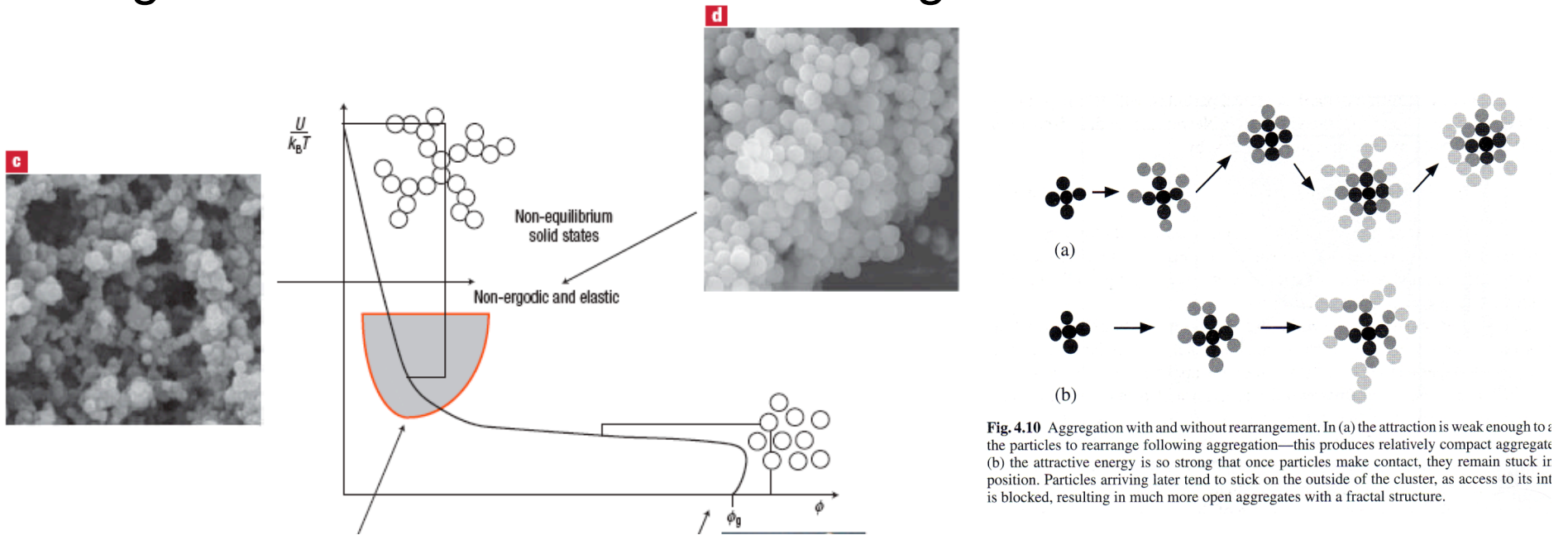Weak attraction: fluid-type phase diagram
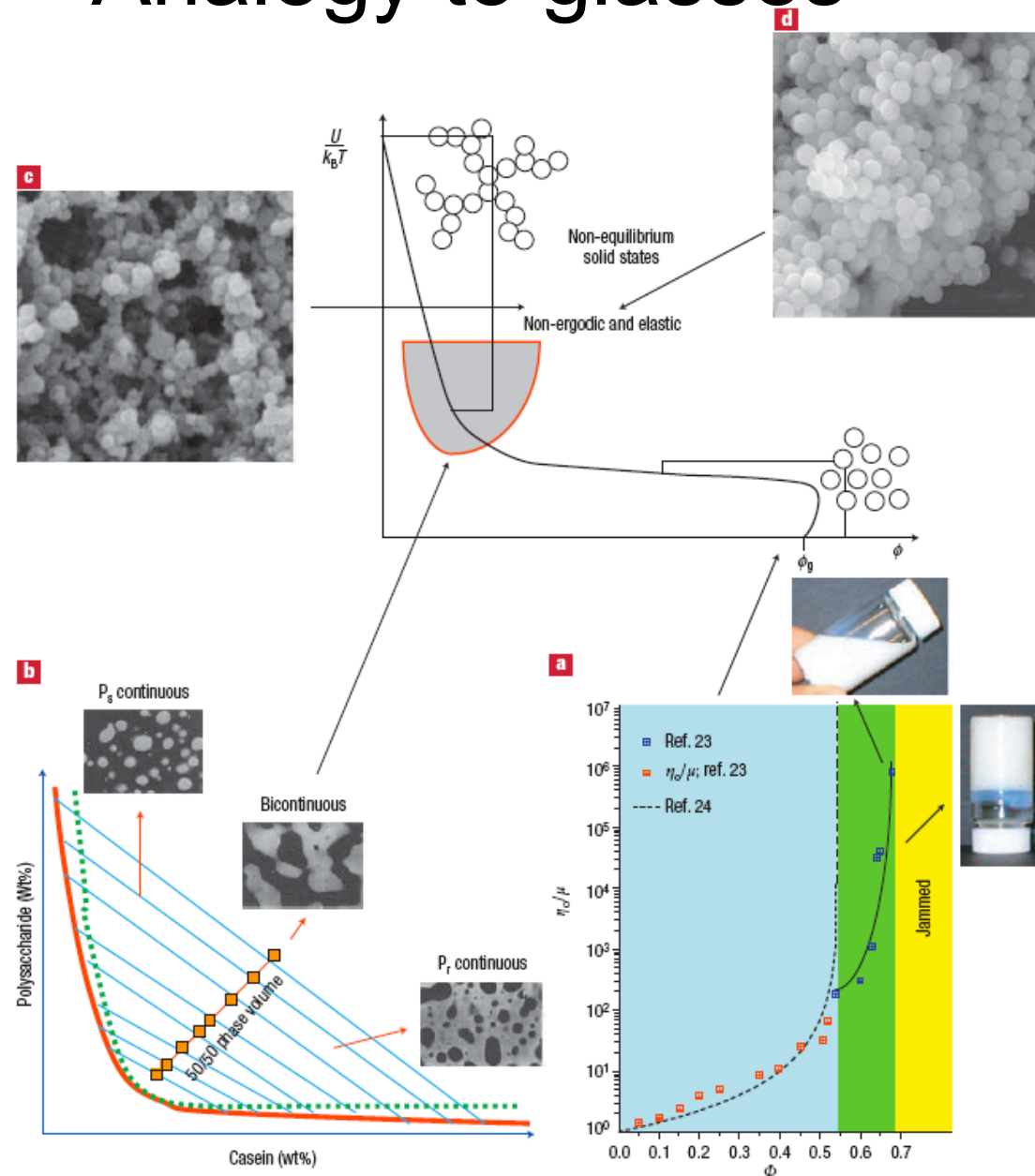
Phase diagram of attractive colloids
- disordered phases

Short range potentials:

- low concentration - high U $\Rightarrow$ fractal gel like structures

- high concentrations - low $\Rightarrow$ dense glasses

Fig. 4.10 Aggregation with and without rearrangement. In (a) the attraction is weak enough to a the particles to rearrange following aggregation—this produces relatively compact aggregate (b) the attractive energy is so strong that once particles make contact, they remain stuck in position. Particles arriving later tend to stick on the outside of the cluster, as access to its int is blocked, resulting in much more open aggregates with a fractal structure.

Analogy to glasses

Example

Milk a colloidal suspension (emulsion)

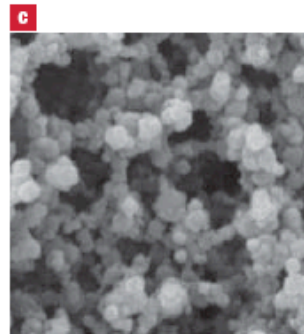

Casein (protein) micelles
(around 100 nm)

Aggregation
(pH, T)

Yoghurt

Colloidal gels

Aggregation $\Rightarrow$ Sedimentation

Cheese

Next lecture

25/9 13.00 N6115

Problem solving class: Polymers II

Johan Hedström