

ISM05

Properties of Colloids II

Topics

- DLVO theory
- Polymer adsorption/ steric stabilization
- Electrokinetic effects
- Special colloids: clay, foam, emulsions

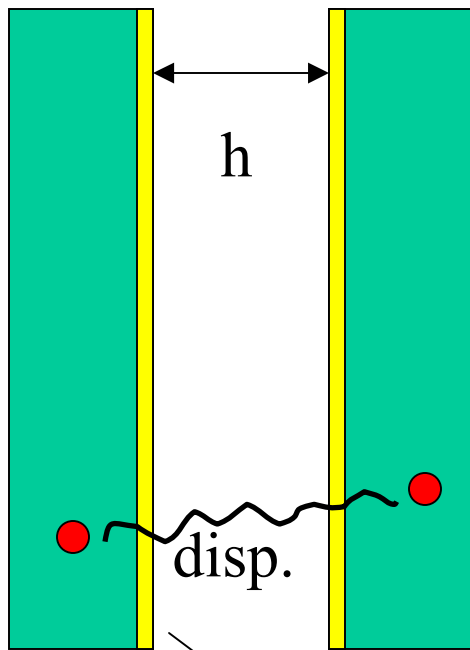
Additional information from the book

Intermolecular and surface forces

Jacob Israelachvili

DLVO theory

Derjaguin-Landau-Verwey-Overbeek



$$V = V_R + V_A \quad \text{potential energy}$$

$$V_R \quad \text{repulsive (electrostatics)}$$

$$V_A \quad \text{attractive (dispersion)}$$

$$V(h) = cst_1 e^{-\kappa h} - \frac{cst_2}{h^2} \quad \text{flat plates}$$

$$F(h) \equiv -\frac{dV}{dh} \quad \text{force}$$

Surface charge

Potential energy curves

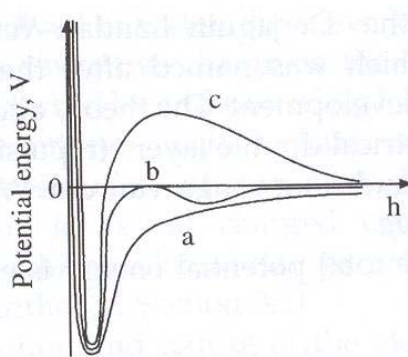


Figure 3.5 Curves of potential energy versus separation between the surfaces of charged colloidal particles. The electrolyte concentration decreases from a to c

- a: high salt concentration
- b: intermediate
- c: low salt concentration

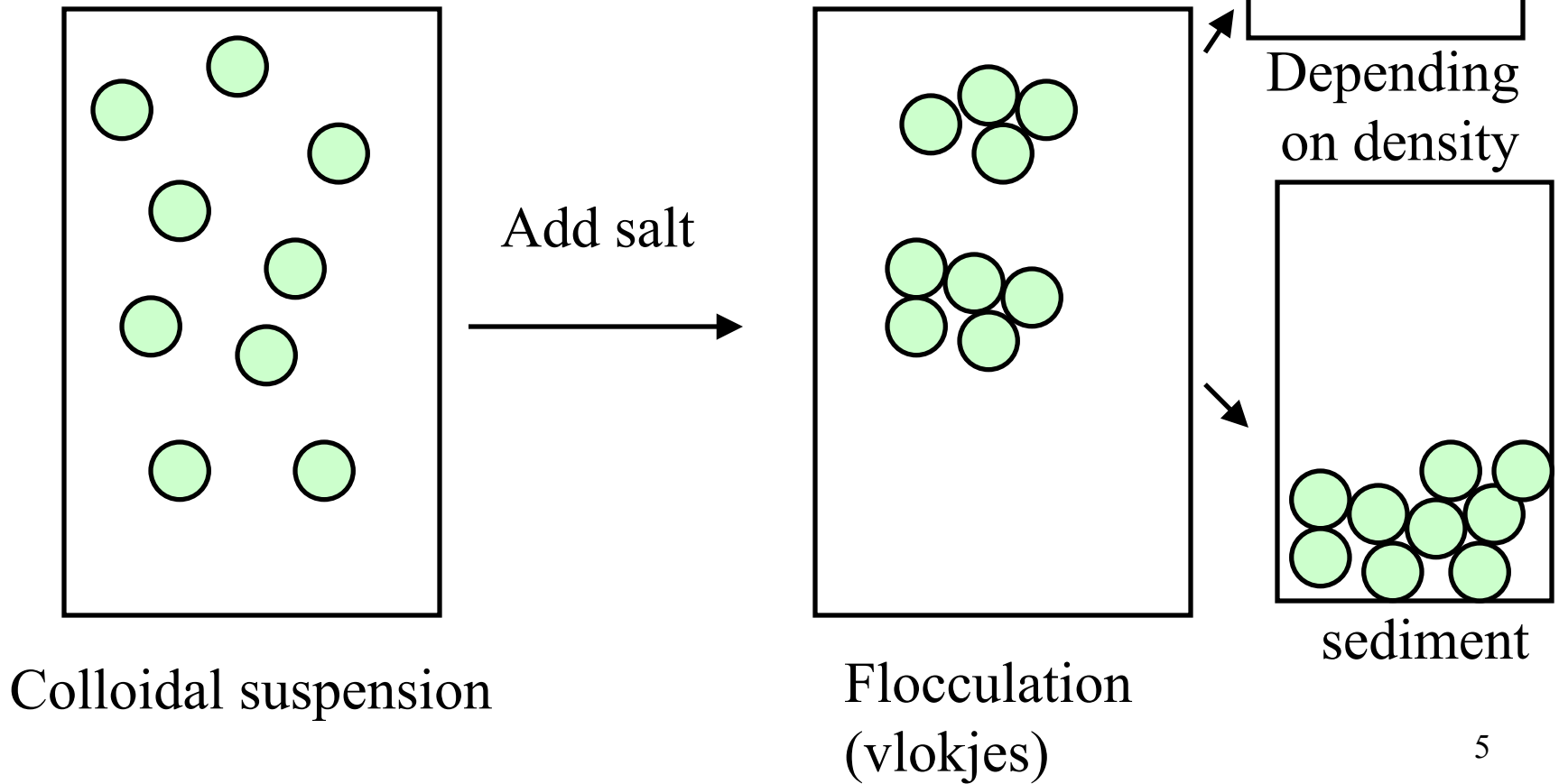
The system is unstable at high and intermediate salt concentration

Notice the secondary minimum in curve b

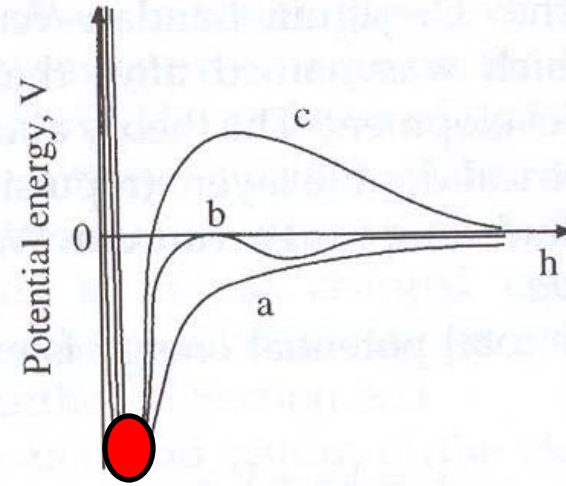
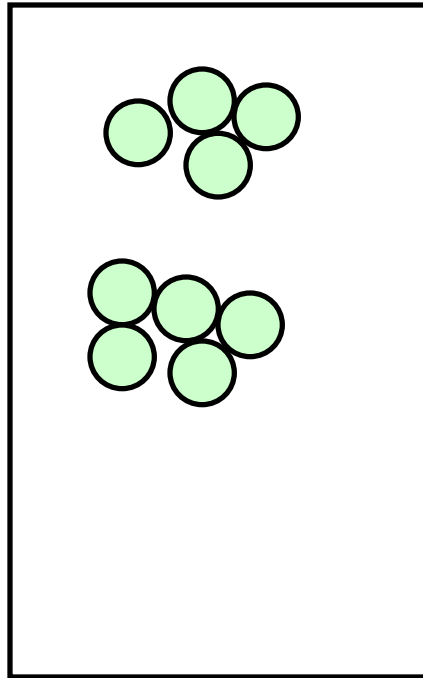
The system flocculates, but the aggregates are weak

This may imply *reversible* flocculation

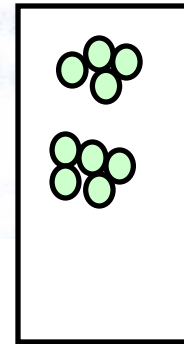
Experiment



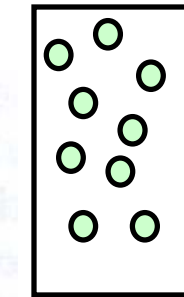
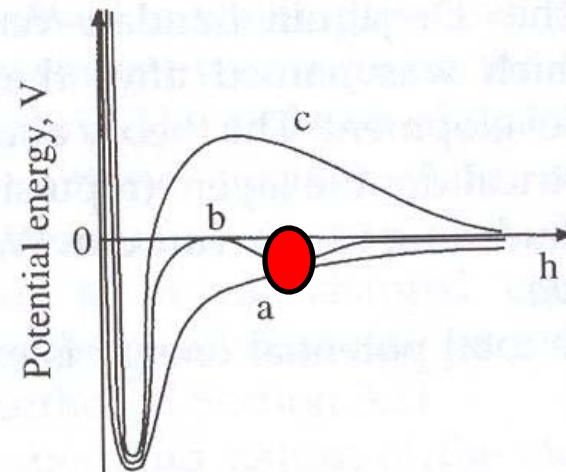
Experiment



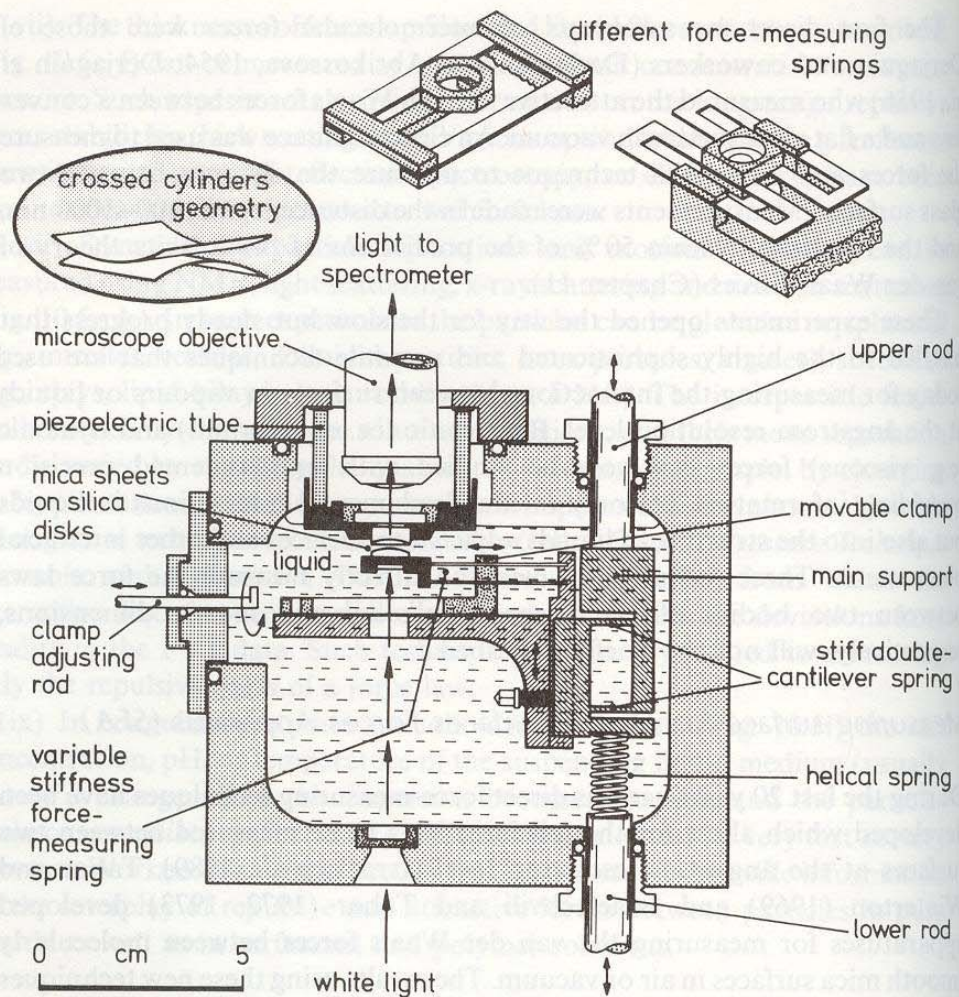
Remove salt



Irreversible
flocculation



Reversible flocculation



Surface force apparatus (Israelachvili)

Fig. 10.7. Surface Forces Apparatus (SFA) for directly measuring the force laws between surfaces in liquids or vapours at the ångström resolution level. With the SFA technique two atomically smooth surfaces immersed in a liquid can be brought towards each other in a highly controlled way (the surface separation being controlled to 1 \AA). As the surfaces approach each other they trap a very thin film of liquid between them and the forces between the two surfaces (across the liquid film) can be measured. In addition, the surfaces can be moved laterally past each other and the shear forces also measured during sliding. The results on many different liquids have revealed ultrathin film properties that are profoundly different from those of the bulk liquids, for example, that liquids can support both normal loads and shear stresses, and that molecular relaxations can take 10^{10} times longer in a 10 \AA film than in the bulk liquid. Only molecular theories, rather than continuum theories, can explain such phenomena. However, most long-range interactions are adequately explained by continuum theories.

Measured DLVO forces

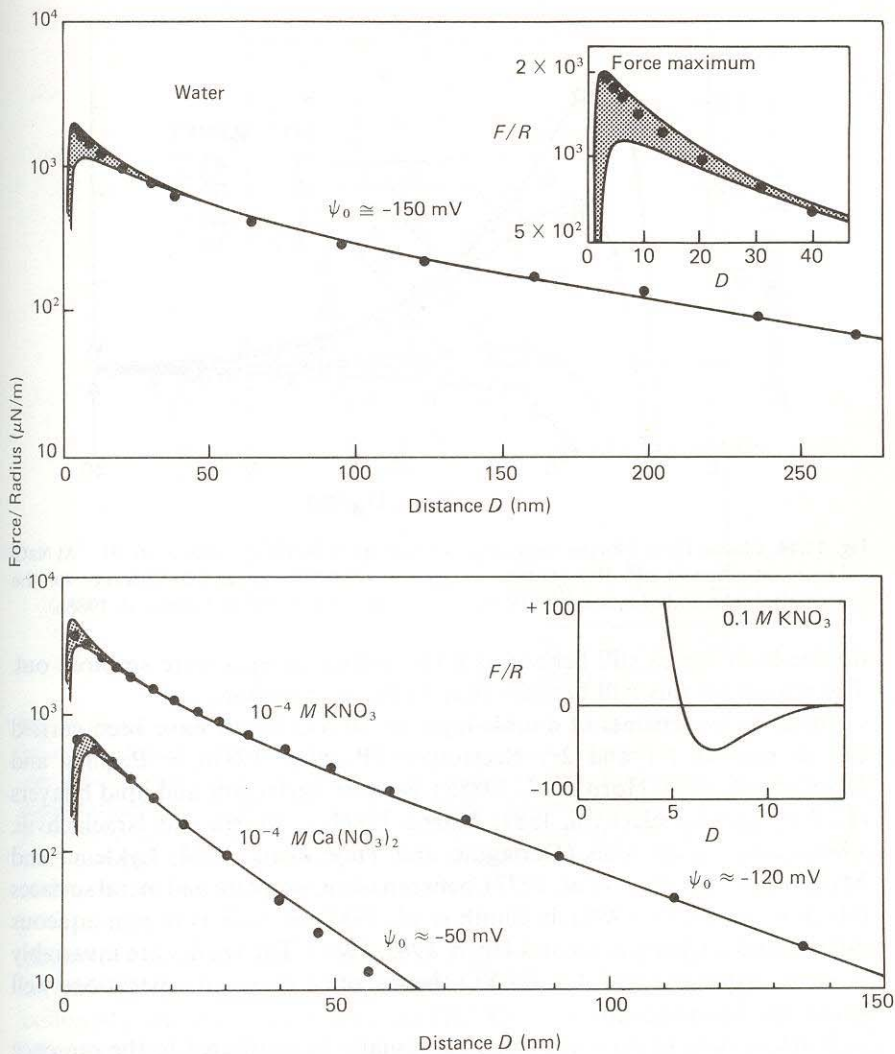


Fig. 12.13. Measured double-layer and van der Waals forces between two curved mica surfaces of radius R ($\sim 1 \text{ cm}$) in water and in dilute $\sim 10^{-4} \text{ M KNO}_3$ and $\sim 10^{-4} \text{ M Ca(NO}_3)_2$ solutions. The continuous curves are the theoretical DLVO forces (using a Hamaker constant of $A = 2.2 \times 10^{-20} \text{ J}$) showing the constant charge and constant potential limits. Theoretically, we expect the interactions to fall between these two limits. (Note that for this geometry the Derjaguin approximation gives $F/R = 2\pi W$, where W is the corresponding interaction energy per unit area between two planar surfaces, as plotted in Figs 12.10 and 12.11.) The inset in the lower part of the figure is the measured force in concentrated 0.1 M KNO_3 showing the emergence of a secondary minimum. (From Israelachvili and Adams, 1978; Pashley, 1981a; Israelachvili, 1982.)

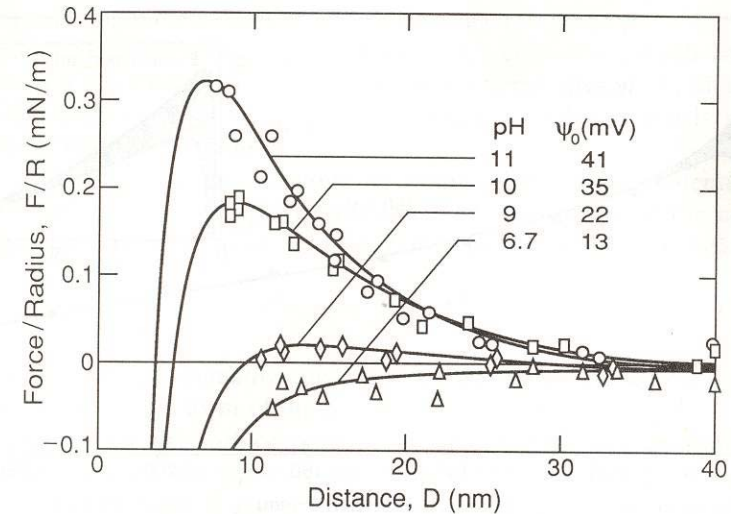


Fig. 12.14. Classic DLVO forces measured between two sapphire surfaces in 10^{-3} M NaCl solutions at different pH. The continuous lines are the theoretical DLVO forces for the potentials shown and a Hamaker constant of $A = 6.7 \times 10^{-20} \text{ J}$ (from Horn *et al.*, 1988a).

(from Israelachvili's book)

Notice logarithmic scale

DLVO theory

The derivation of the repulsive interactions in DLVO theory is ...
Something for later. But the attractive part we already know!

$$V_R = 64kTc_0A \tanh^2\left(\frac{e\psi_0}{4kT}\right)e^{-\kappa h} \quad (\text{flat plates, surface area } A)$$

$$V_R = 64kTc_0R \tanh^2\left(\frac{e\psi_0}{4kT}\right)e^{-\kappa h} \quad (\text{spheres, radius } R)$$

ψ_0 surface potential

when $e\psi_0 < kT$ ($\psi_0 < 25$ mV), this is simplified to

$$V_R = \frac{2\sigma^2 A}{\kappa\epsilon} e^{-\kappa h} \quad (\text{flat plates})$$

$$V_R = \frac{2\pi\sigma^2 R}{\kappa^2\epsilon} e^{-\kappa h} \quad (\text{spheres})$$

σ surface charge density

(Hamley eq. 3.21 contains mistake, it misses $\exp(-\kappa h)$)

Polymer adsorption/ steric stabilization

The *advantage* of electrostatic stabilization is that it is easy to prepare: just introduce a few surface charges.

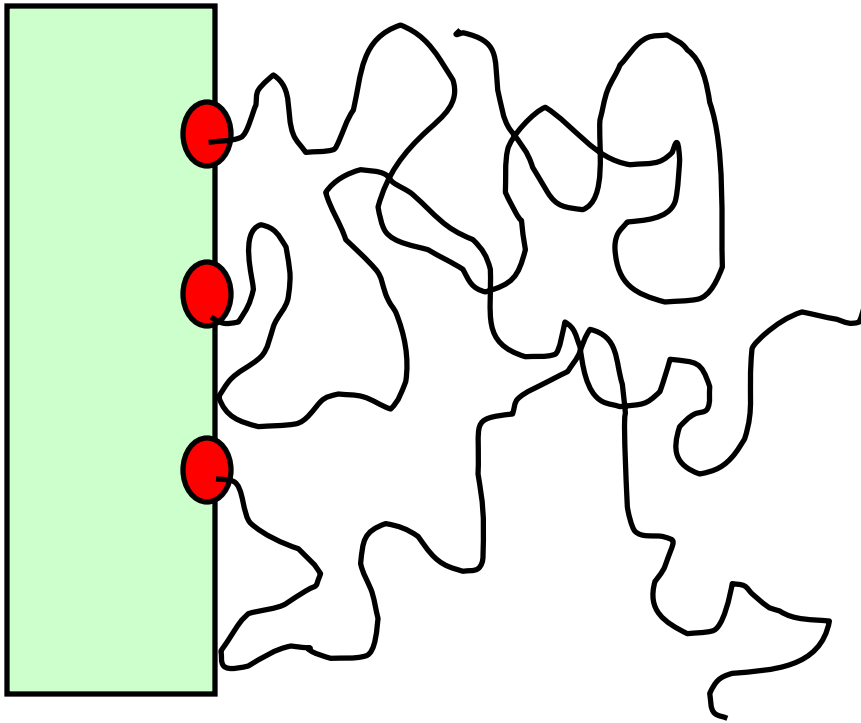
A (very big) *disadvantage* of electrostatic stabilization is that it is highly sensitive with respect to surface charge (pH) and salt concentration

Steric stabilization by surface bound polymers is

1. not sensitive to surface charge and salt concentration
2. works also in non-aqueous media
3. (and works also in concentrated dispersions)

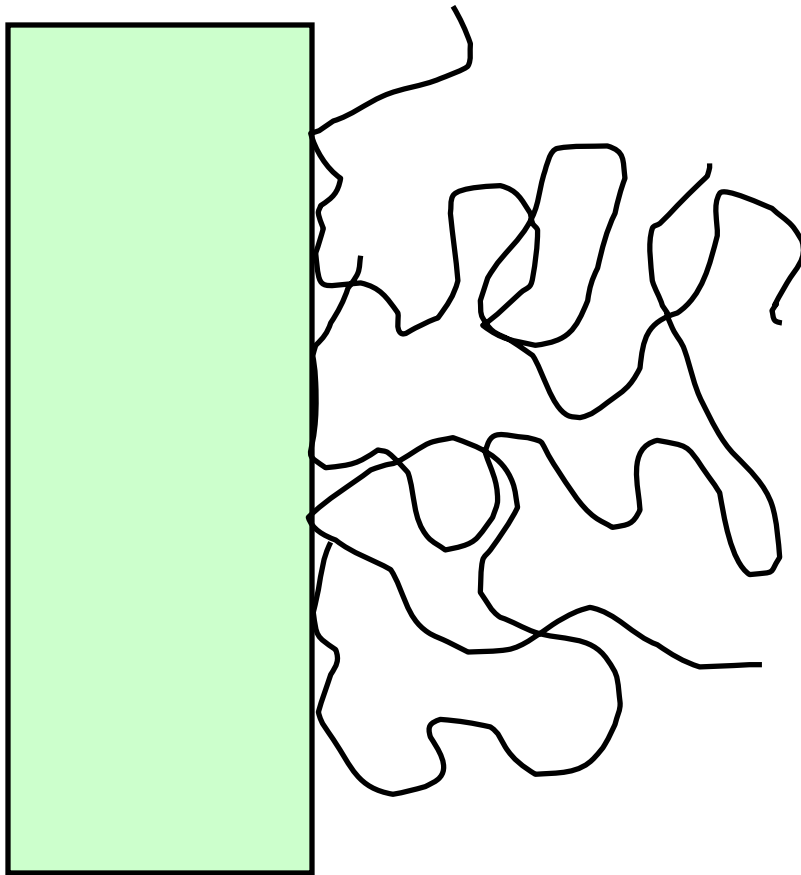
Disadvantage: more difficult to prepare

Types of polymer layers



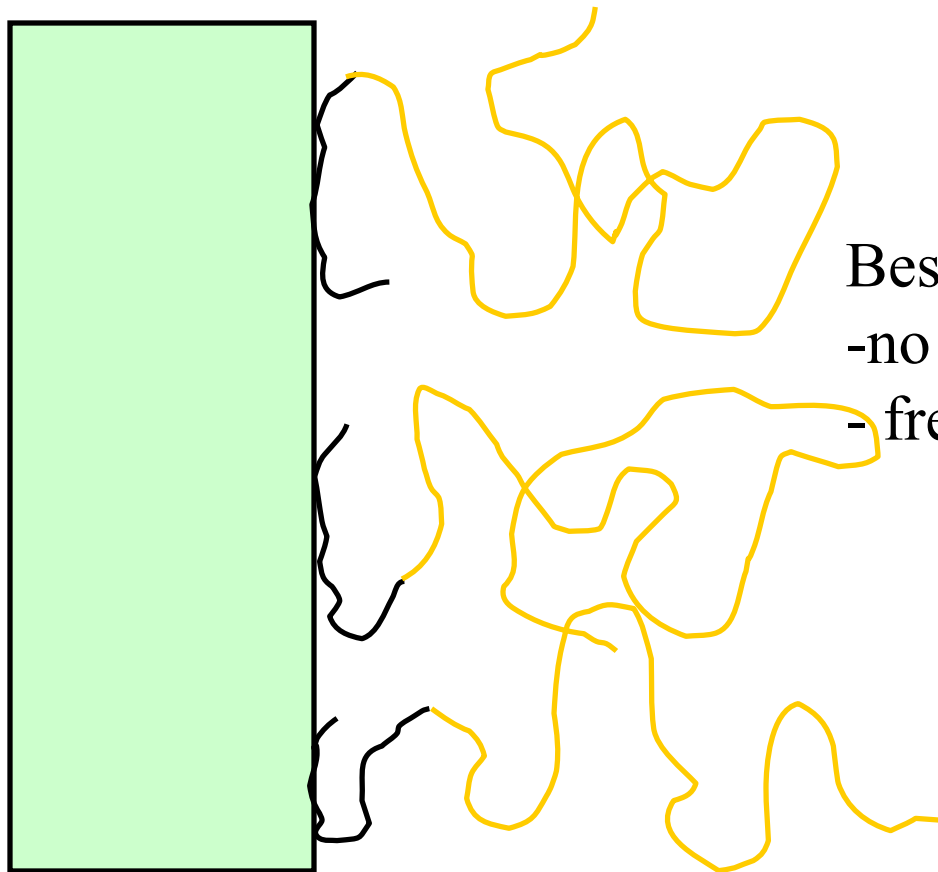
Chemical adsorption
(grafted polymers)

Types of polymer layers



Physical adsorption
Homopolymers
You need: Good solvent
and a Bad surface

Types of polymer layers

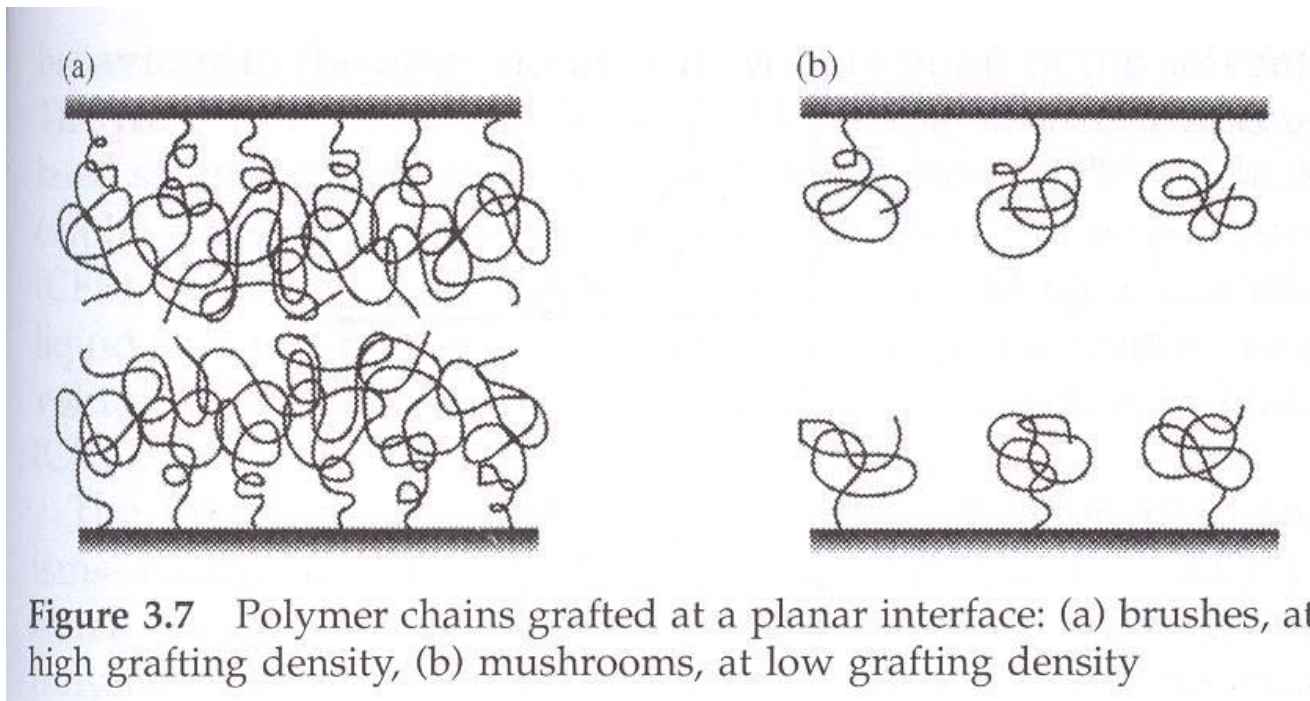


Physical adsorption
Block copolymer

Best choice:

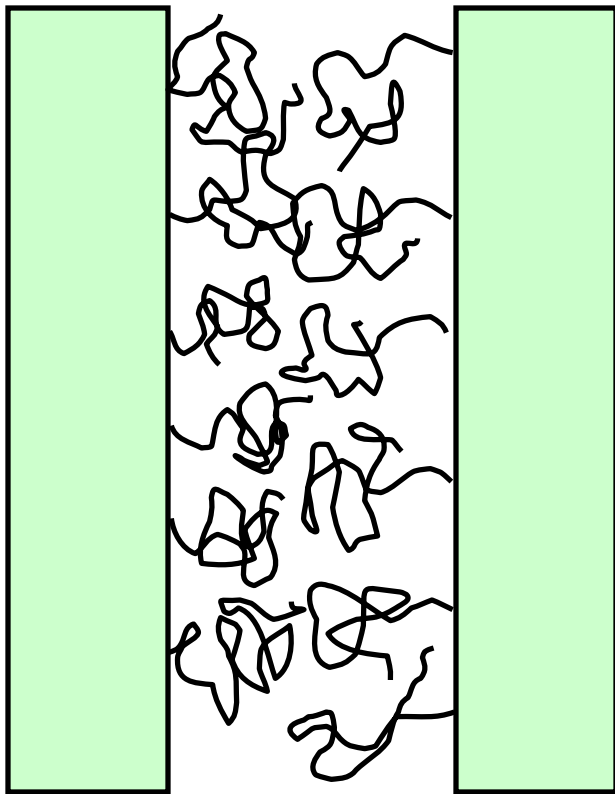
- no chemical synthesis required
- free design of anchoring block

Morphologies of grafted polymer layers



stabilization

Good solvent, adsorbed polymers



The chains are swollen

When the two layers come into contact

- the osmotic pressure rises, because the concentration of monomers increases
- the configurational entropy decreases, because the polymers can sample fewer conformations

The two colloids are kept apart, on the scale of the swollen polymer layer.

When the van der Waals interactions of the colloids on this scale of separation is small (depends on length of polymers, grafting density etc.)
The colloidal dispersion is stable

The higher the load with polymers,
The higher the repulsion

Free energy curves

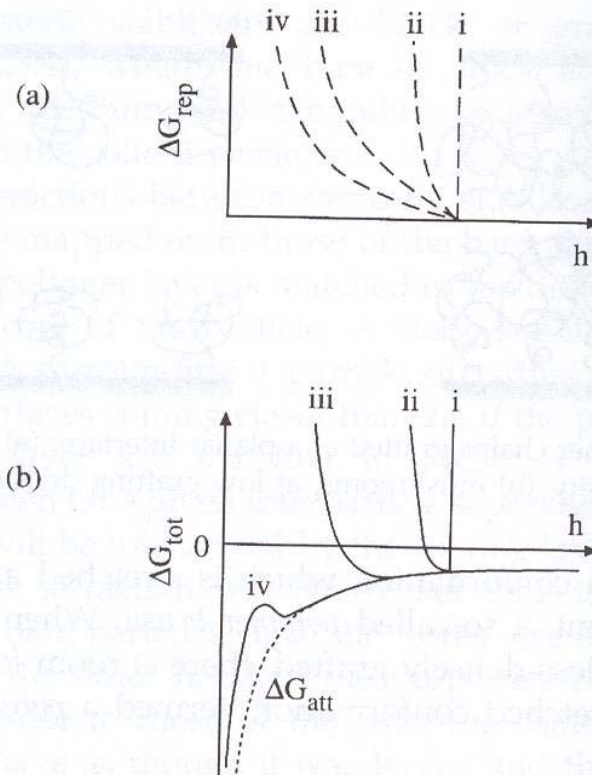
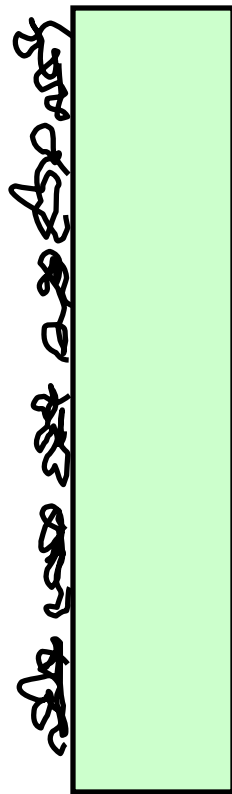
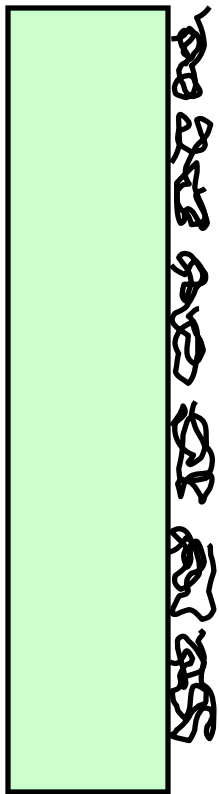


Figure 3.8 Potential energy curves for a pair of sterically stabilized colloid particles, separated by a distance h . (a) Repulsive contribution to the free energy, (b) attractive contribution and total free energy. The grafting density decreases from i to iv

Flocculation

Bad solvent, adsorbed polymers



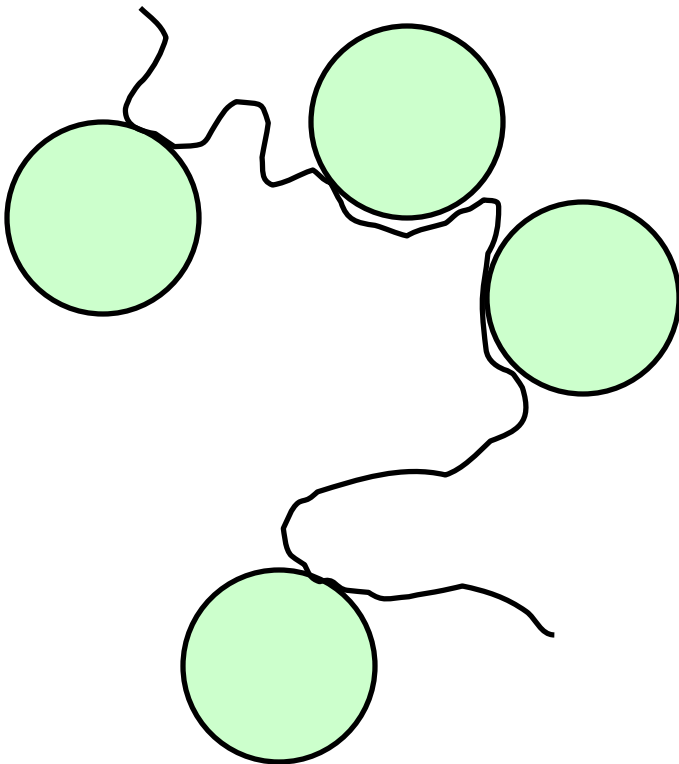
The chains are collapsed, in order to avoid solvent-monomer interactions. When the polymer layers come into close contact, they will stick together

**The worse the solvent,
The more unstable the colloidal dispersion**

Cross-over from stabilization to flocculation:
theta solvent

Bridging flocculation

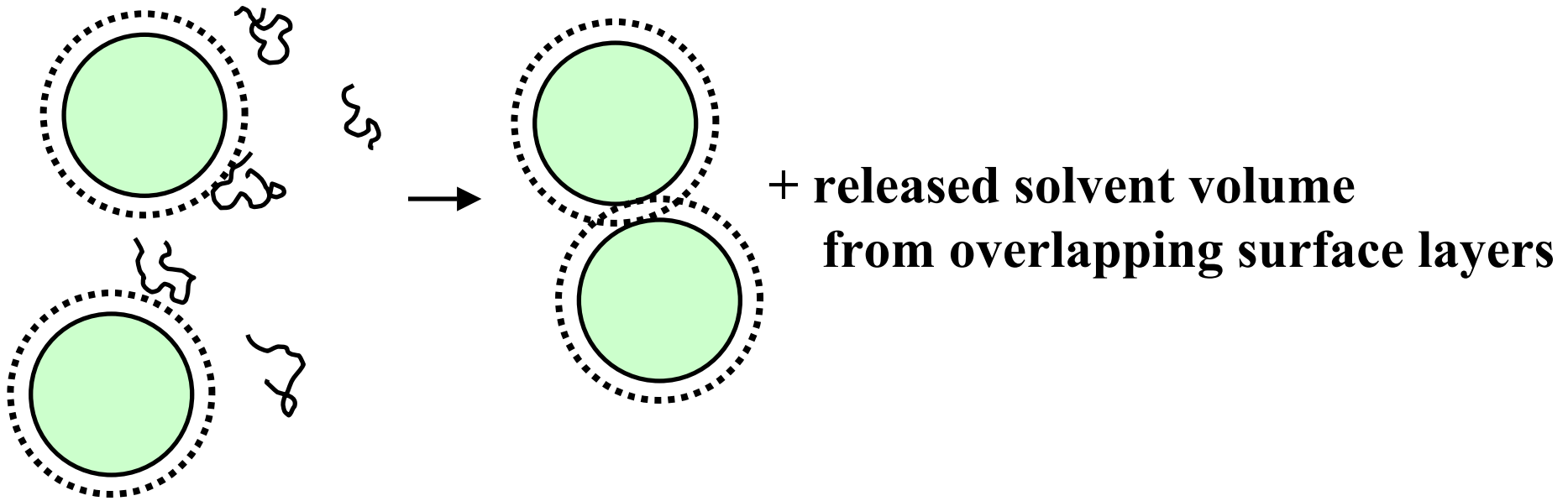
Good adsorbers, good solvent, (very) low polymer density,
(very) long polymers



The long polymers ‘bind’
the colloids together in open flocs.
Application: water purification
(in practice, a few ppm of cationic
polyelectrolyte is added, since most
natural colloid surfaces are negative)

Depletion flocculation

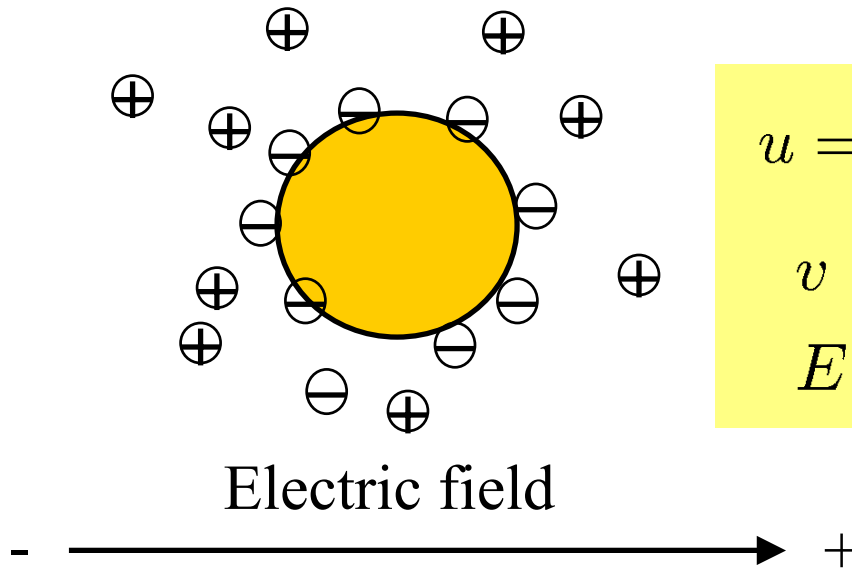
Good solvent, non-adsorbing polymers



Chains are expelled from surface layer with thickness $\sim R_g$

When two colloids meet in close contact, the total amount of accessible volume (for the polymer) is increased, hence the translational entropy is increased, and thus the colloidal dispersion is destabilized

Electrophoresis



$$u = \frac{v}{E} \quad \text{mobility}$$

v velocity

E electric field strength

The surface bound ions pull the colloid along the electric field

$$\mathbf{E} \equiv -\nabla V$$

V applied potential

$$E = -\frac{dV}{dx} \quad \text{potential gradient in 1 dimension}$$

Mobility

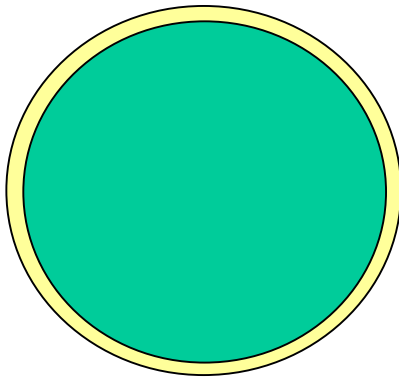
ion



Charge is in the center

$$F_{pull} = qE \quad \text{small ions and spherical colloids}$$
$$q = 4\pi R^2 \sigma \quad \text{colloids}$$

colloid



Charge is on the surface

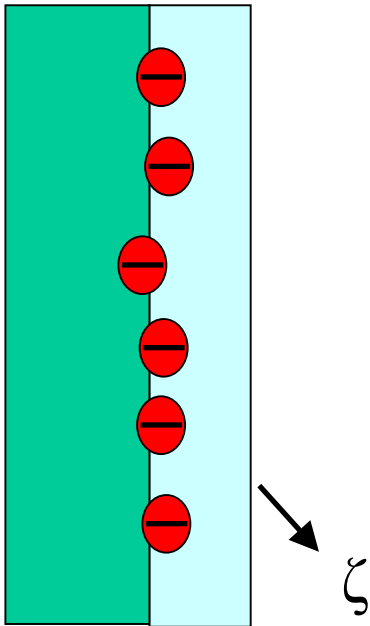
$$F_{friction} = 6\pi\eta Rv \quad \text{Stokes}$$

$$F_{pull} = F_{friction} \quad \text{stationary state}$$

$$u = \frac{q}{6\pi\eta R}$$

Whether the charge is on the surface or in the middle, does not matter

Advanced topic: zeta-potential



The colloid surface is hydrated,
and the mobile ions do not penetrate
the *Stern* layer (see ISM04)

The potential at the surface of the Stern layer
is the zeta-potential ζ

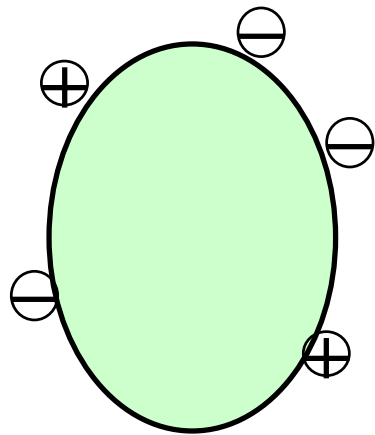
In the colloid and surface chemistry literature,
electrokinetic phenomena are usually explained in
terms of the zeta-potential.

In the bio(chemical) literature, electrokinetics
is explained with charges

Bonus for exam: 0.5 point

What is the relation between surface charge density and zeta-potential
for a flat surface?

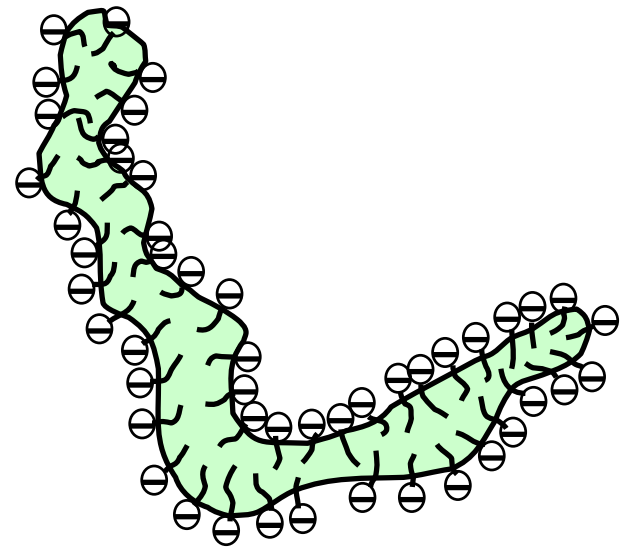
Application: SDS gel electrophoresis



Proteins:
variable mass,
variable charge



Denaturate with
surfactant SDS

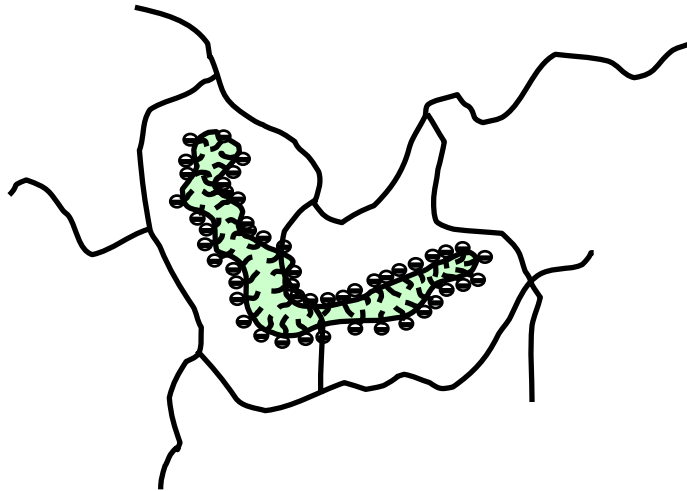


When the
chain is completely unfolded

$$q \approx q_{SDS} \approx cst. \times M$$

mmm....rather rough model

Gel electrophoresis



$$q \approx q_{SDS} \approx cst. \times M$$

In the gel,
the friction coefficient is (much) larger due to the physical polymer barriers.
The net mobility is in first approximation a function of the protein mass *only* (and the pore size)

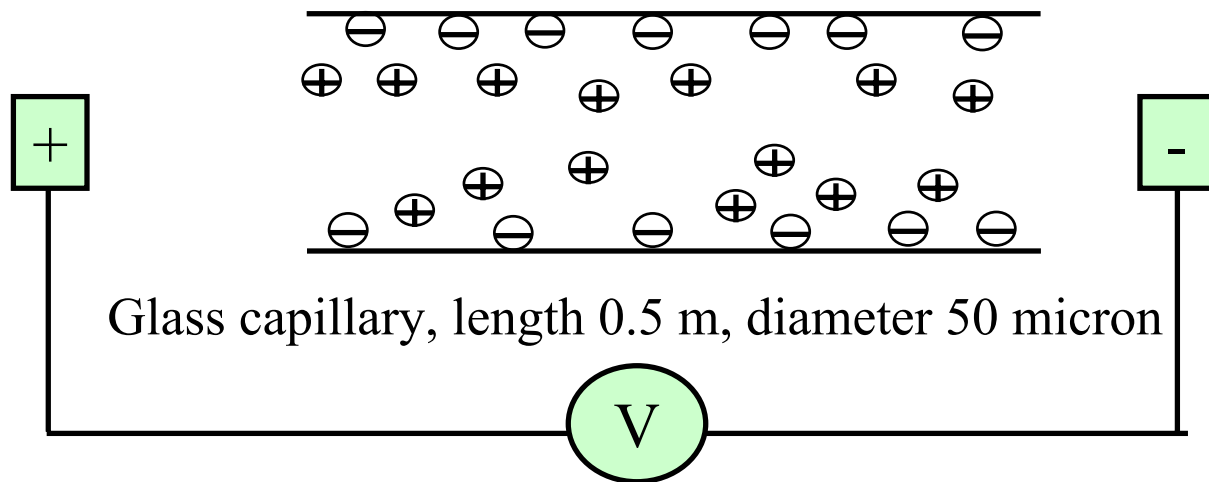
$$F_{friction} = \eta f(M, gel)$$

$$F_{pull} = F_{friction} \quad \text{stationary state}$$

$$u = \frac{cst.}{\eta} \times \frac{M}{f(M, gel)}$$

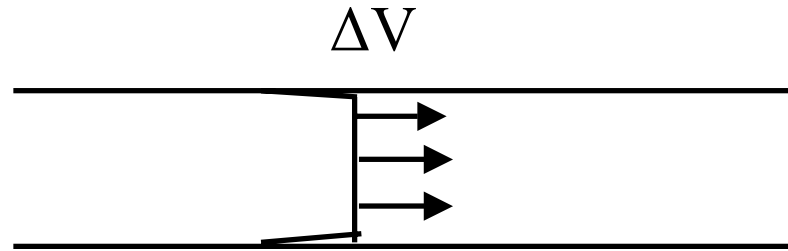
In the experiments, the mobility (or distance traveled after given amount of time) is plotted versus $\log M$: more or less a straight line, there is no satisfactory model why this should be so!

Electro-osmosis and capillary electrophoresis



The mobile positive counter-ions move in the applied electric field
They drag the solvent towards the anode
Hence the electric field generates a flow
The higher the surface charge, the more mobile counter-ions, and the larger the flow.

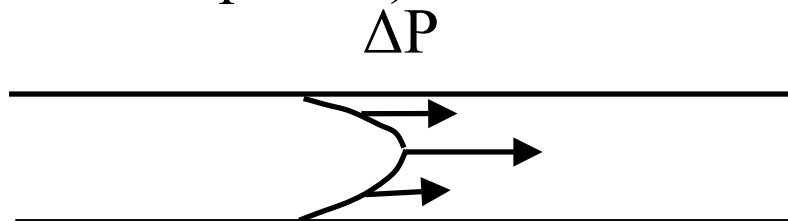
Capillary electrophoresis



Since the pull on the solvent is located at the boundaries (in the double layer $O(1\text{nm})$), the flow-profile is that of a *plug*

$$v_{EOS} = \frac{E\epsilon\zeta}{\eta}$$

Compare with flow profile in response to pressure gradient (parabolic Poiseuille profile)



Electro-osmotic velocity

$$v_{EOS} = \frac{E\epsilon\zeta}{\eta}$$

Derived from combination of (Navier-)Stokes equation and Poisson Boltzmann equation
Very difficult!

We will try a simple dimensional analysis

$$v_{EOS} = E^\alpha r_D^\beta \sigma^\gamma \eta^\delta \quad \text{m s}^{-1}$$

These are the factors we think are important

$$\alpha = 1$$

$$\beta = 1$$

$$\gamma = 1$$

$$\delta = -1$$

Trick: match dimensions
left hand side
and right hand side

Exercise: is the velocity
dependent of the
length of the capillary?

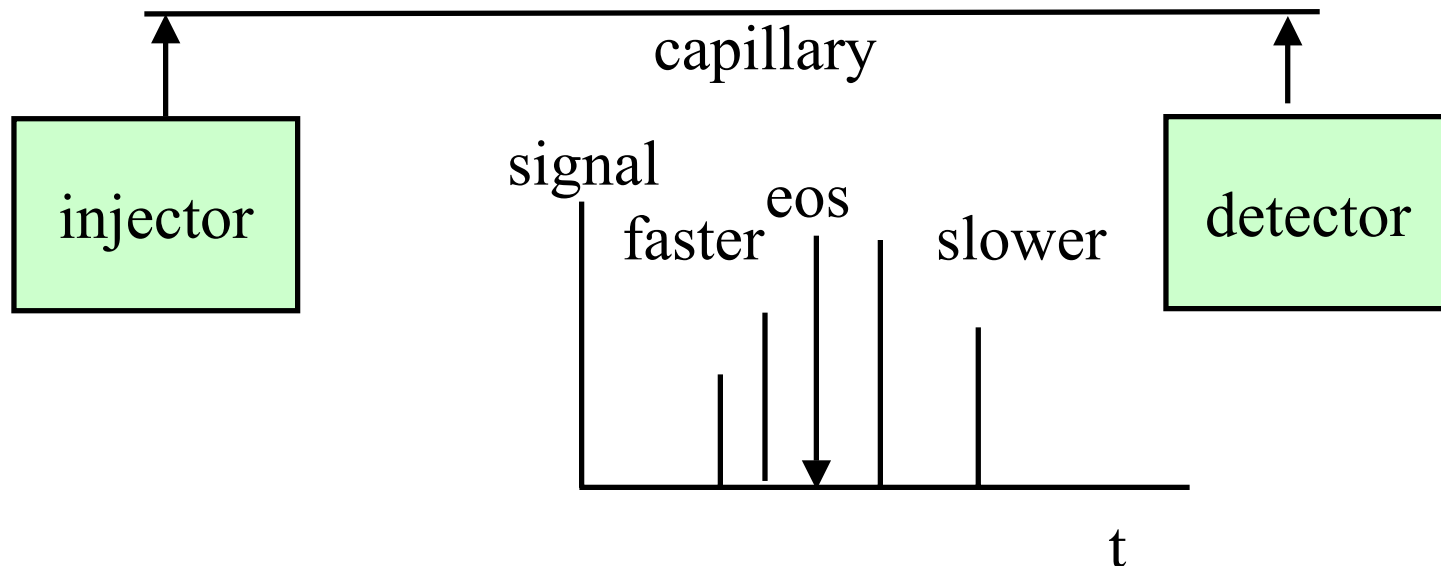
$$v_{EOS} = \frac{1}{\eta} E r_D \sigma = \frac{1}{\eta} E \epsilon \frac{\sigma}{\epsilon \kappa} = \frac{E \epsilon \zeta}{\eta}$$

Capillary electrophoresis

Added charged analytes will

- move with the background solvent flow
- and on top of that, move faster or slower depending on the additional pull by the electric field

Very fast and efficient separation



Special colloids: clay

Diameter: O(microns)

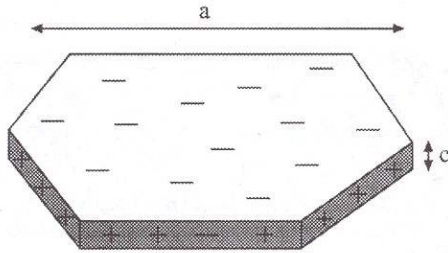


Figure 3.10 A clay particle, typical of kaolinite. The aspect ratio a/c is typically about 10. [Reproduced with permission from R. J. Hunter, *Foundations of Colloid Science*, Vol. I, Oxford University Press, Oxford (1989)]

Mica,
Kaolinite,
Bentonite,
Montmorillonite,

...

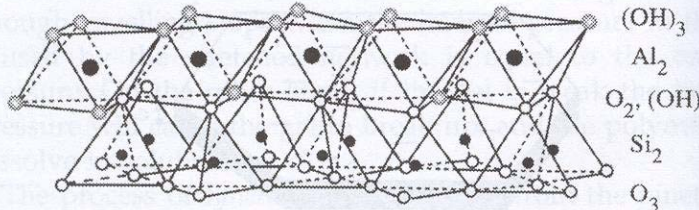


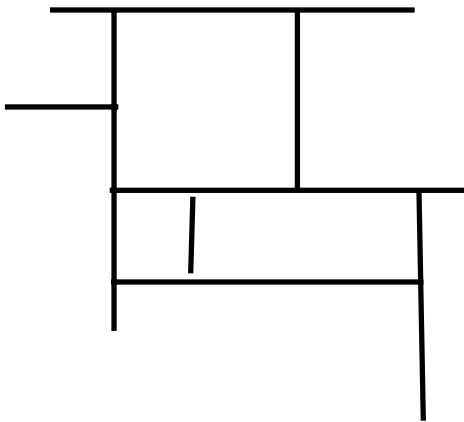
Figure 3.11 Structure of one layer of the ideal kaolin structure, $(\text{Al}(\text{OH})_2)_2 \cdot \text{O} \cdot (\text{SiO}_2)_2$. [Reproduced with permission from R. J. Hunter, *Foundations of Colloid Science*, Vol. I, Oxford University Press, Oxford (1989)]

Applications:

- bricks/ceramics
- fillers
- drilling muds
- clay 'detergents'
- The Netherlands

Stacking of clays

Some clays may stack like a card house (or Mondriaan): positive edges in contact with negative plate surface with lots of open space for the solution



When softly shaken, such a structure behaves like a *gel*, ...but when vigorously shaken, it behaves like a fluid: catastrophic avalanche effect

In drilling mud, negative (poly)electrolyte is added to stabilize the edges, this is called ‘peptization’

Quick clay: very dangerous!

‘a type of clay formed by glaciers that loses its shape when shaken’

The quick clay landslide in Rissa, Norway

Available from [NGI, Norway](#)---

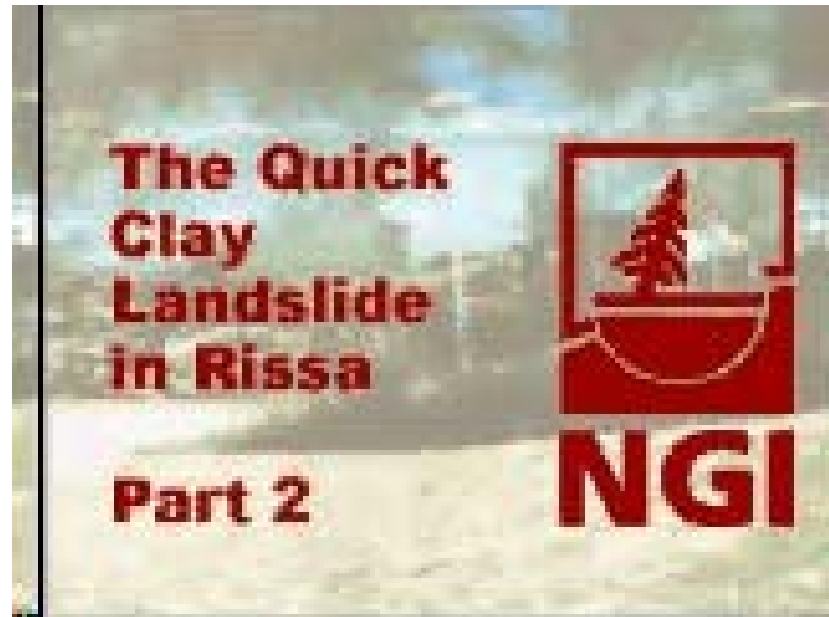
See [this Web page](#) for a browser video clip.

This is one landslide video you should see!

It was taken on the spot by someone who happened to be there with a camcorder in his hand! Very dramatic scenes...

A tiny excavation triggered the slide

<http://www.ejge.com/iGEM/videos.htm>



Special colloid: casein micelles

Of, hoe je kaas maakt. Op het werkcollege!

This concludes file ISM05