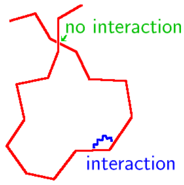
Polymer solutions
1/16 *col13*

Model of the **ideal chain**:



- beads are connected by flexible bonds/angles/torsions
- beads far enough do not interact (by solvent-mediated effective interaction)

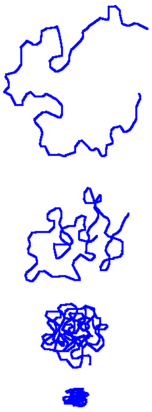
= random walk = trajectory of Brownian motion

Brownian motion: $\langle r^2 \rangle = 6D$, time corresponds to the number of beads N
$\Rightarrow$ coil size $\propto N^{1/2}$

Better models:

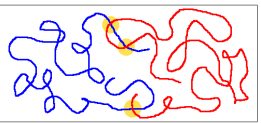
- repulsive forces → excluded volume (beads do not overlap)
- attractive forces → "negative excluded volume" (beads are "sticky")

Polymer solutions II
2/16 *col13*



good solvent – (lyophilic polymer), beads effectively repel each other, the chain partly unwinds = self-avoiding random walk
coil size $\propto N^{1/1.7}$

entropic (steric) repulsion – the coils in a good solvent repel each other because of excluded volumes

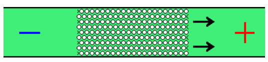


theta-solvent – beads interact with the solvent in the same way as mutually (effectively repulsion = attraction) ≈ ideal chain
coil size $\propto N^{1/2}$

bad solvent – (lyophobic polymer), chain shrinks and packs to a smaller volume, some solvent between chains
coil size $\propto N^{1/3}$

non-solvent – no solvent between chains, size $\propto N^{1/3}$

Electrokinetic phenomena
[vlc show/hgheart.mov] 3/16 *col13*

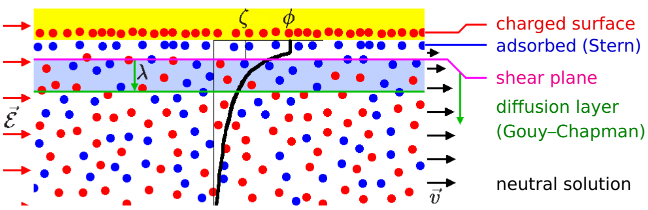


- electroosmosis – motion of an ionic solution through a porous material or capillary induced by an applied electric field (electroosmotic flow); if pressure is applied against: electroosmotic pressure
- reversed: flow of the solution produces an electroosmotic potential
- electrophoresis – motion of a colloid particle in an ionic solution induced by an applied electric field
- reversed: sedimentation potential or current

Different is the **electrocapillarity**, change of the surface tension with applied voltage (e.g., mercury)
movie: jchemed.chem.wisc.edu

Electroosmosis
4/16 *col13*

Shear plane, slipping plane = approximative plane dividing the moving liquid from the stationary liquid close to the surface



Surface charge = σ, el. field intensity = $\mathcal{E}$, viscosity = η

Tangent el. force per area: $\sigma\mathcal{E} = \eta\frac{v}{\lambda} \Rightarrow$ velocity $v = \frac{\sigma\mathcal{E}\lambda}{\eta}$

Double layer capacity (per area) $C/\mathcal{A} = \epsilon/\lambda$

$$\sigma = \frac{C}{\mathcal{A}}\zeta = \frac{\epsilon}{\lambda}\zeta \quad \Rightarrow \quad v = \frac{\epsilon\mathcal{E}}{\eta}\zeta$$

potential at the shear plane = ζ = **zeta-potential** = electrokinetic potential

Electroosmosis
5/16 *col13*

Smoluchowski (also Helmholtz–Smoluchowski) equation:

$$v = \frac{\epsilon\zeta\mathcal{E}}{\eta} \quad \text{or using mobility: } u = \frac{\epsilon\zeta}{\eta} \tag{1}$$

El. current across area $\mathcal{A}_\oslash$: $\mathcal{A}_\oslash$: $I = \mathcal{A}_\oslash\mathcal{E}\kappa = \mathcal{A}_\oslash\frac{U}{L}\kappa$ (κ = conductivity)
Volume flow: $\frac{dV}{d\tau} = v\mathcal{A}_\oslash$

$$\frac{dV/d\tau}{I} = \frac{\epsilon\zeta}{\eta\kappa} \tag{2}$$

Eq. (1) also holds for electrophoresis with coefficient 2/3 provided that the particles are large enough and distant ($\gg \lambda$). For small particles → ionic conductivity, $u \propto 1/\eta$.

Eqs. (1) and (2) are used to measure the ζ potential

Colloid stability requires $|\zeta| > 40$ mV.

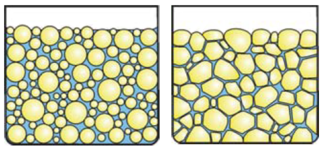
Isoelectric point: the concentration of ions or pH so that $\zeta = 0$ (≈ a particle is not charged) – typical for polyelectrolytes (proteins with both -NH_2 and -COOH). Smallest repulsion – best folded

Example. Small cavities in a solution of soap move towards the anode

Emulsions
6/16 *col13*

Types:

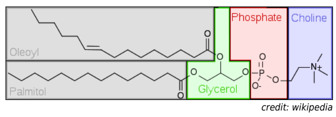
- O/W (*oil-in-water*): less polar liquid (oil) in a more polar liquid (water)
- W/O (*water-in-oil*)



Examples: milk, mayonnaise, cutting fluids (for metals)

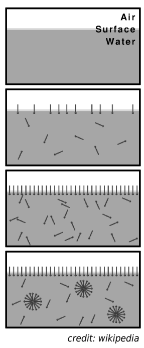
Most properties given by the continuous phase (medium): el. conductivity, wetting, dissolution of dyes

Concentrated emulsions must be stabilized by an **emulsifier** – surfactant, e.g., lecithin (phosphatidylcholine)



Instability: flocculation (aggregation – bound by elst. forces), coalescence (of droplets), creaming (sedimentation), Ostwald ripening

Micelles
7/16 *col13*

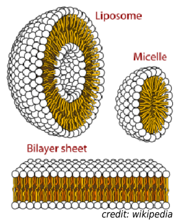


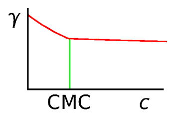
Micelle = usually spherical composed of a surfactant and stabilized:
– lyophilic interaction (w. the solvent)
– lyophobic interaction (inside)

Creation: solution → microaggregation $\xrightarrow{\text{CMC}}$ micelle → cylindric or laminar micelles, liquid crystals, ...

CMC = **critical micelle concentration**: "Surface too crowded". Slope change on the curve γ vs. c (is not a phase transition – not abrupt)

Inverse micelle (butter)





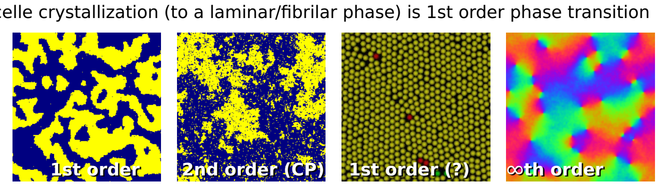
Solubilization – ability of micelles do absorb lyophobic substances

Detergency – washing

Phase transition classification
[showvid pic/harddisks.vid] + 8/16 *col13*

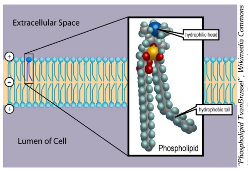
- 1st order: slope change of G, discontinuity in enthalpy, density (crystallization, vaporization, ...)
- 2nd order: Ehrenfest: discontinuity in enthalpy, density; higher derivatives
  modern: higher derivatives diverge ("continuous")
  (critical point [CP], Curie point, lambda-transition He)
- ∞th order ("continuous"): e.g., Kosterlitz–Thouless (some 2D systems):
  all derivatives continuous ($f(x) = \begin{cases} e^{-1/x} & \text{pro } x > 0 \\ 0 & \text{pro } x <= 0 \end{cases}$)

Glass transition = viscosity > 10^{12} Pa s – not a phase transition
Micellization (at CMC) is not a phase transition
Micelle crystallization (to a laminar/fibrilar phase) is 1st order phase transition



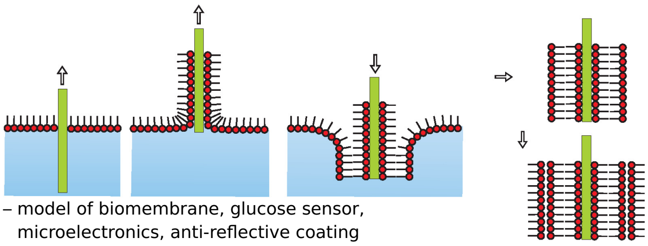
Double layer

Two layers of a surfactant; cell membrane = phospholipide double layer ("glued" together by the hydrophobic ends, usually 2D liquid)



vesicle – liquid inside
vacuoles, lysosomes, transport vesicles...
artificial liposomes: drug transport

Langmuir–Blodgett films: more (double) layers, usu. 2D crystal

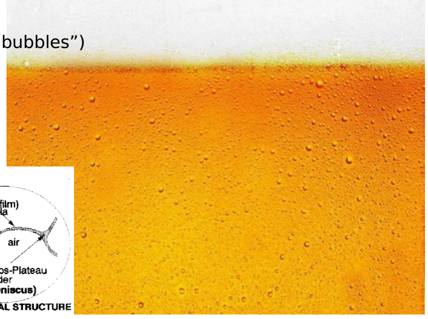


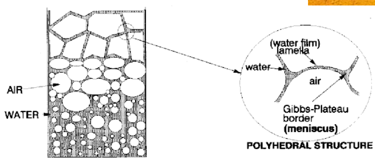
– model of biomembrane, glucose sensor, microelectronics, anti-reflective coating

Foams

Gas in liquid

- wet foams (spherical cavities, "bubbles")
- dry foams (polyhedra, 12–14)
- Gibbs–Plateau channels
- Plateau rules (see lecture 10)





Stabilized by surfactants

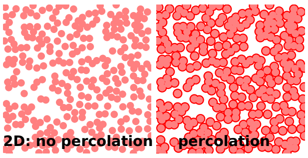
destabilization: gravity, evaporation, Ostwald ripening, film rupture

Dry foams (styrofoam)

credits: http://galerie.albumfotek.cz (krvavy dedek), Kim&Kim

Gels

Connected 3D network of the disperged phase (and the medium), do not flow

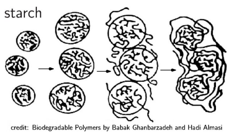


Generally **lyogel**, in water **hydrogel**, (dried) **xerogel**

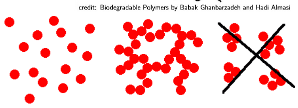
reversible gel: gel $\underset{\text{swelling}}{\overset{\text{drying}}{\rightleftarrows}}$ xerogel

sometimes reversibility refers to the sol ⇄ gel process

- gelatinization of macromolecule solutions:
  - cross-linking by chemical bonds
  - association (vdW, H-bonds)
  - crystalline links
  - geometric (entanglement)



- destabilization of (lyophobic) sols with linking (not coagulation)

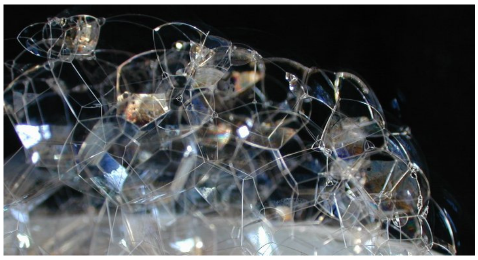


older gels: syneresis
(swelling of the structure – yoghurt)

Foams: Plateau rules

By Joseph Plateau (1801–1883)*

- smooth surfaces
- constant curvature $1/R_x + 1/R_y$
- surfaces meet at angle 120°
- channels meet at tetrahedral angles $\arccos(-1/3) = 109.47°$

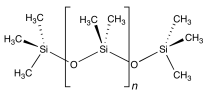


*known also for "phenakistiscope" and Plateu–Rayleigh instability

Gels II

Mechanical properties:

Credits: Polydimethylsiloxane: Wikipedia "Sol-Gel Scheme": Claudionico, see wikipedia «sol–gel»



- elasticity (a few covalent links)
- thixotropy (reversible weak links)

Hydrogels:

- contact lenses (polyacrylamides, "silicone" – oxygen-permeable)
- diapers (sodium polyacrylate, [-CH_2-CH(COONa)-]$_n$)
- biomaterials – silicon implants, scaffolding for tissue growth

Aerosols

Liquid dispersion: fog (10 nm – 10 μm)
Solid dispersion: smoke (to 10 μm), dust (above 10 μm)

Destabilization:

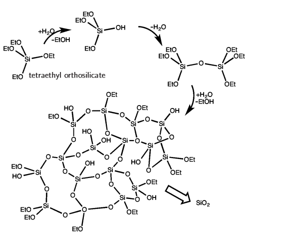
- sedimentation (stabilized by sun radiation: heated)
- coagulation (stabilized by el. charge)

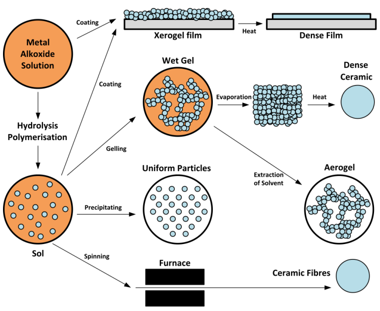
Particle charge: (electro)spraying (nozzle, wind+sea), ionization by UV, grinding of ionic crystals

Aerosol of flamable dust may explode (flour, coal)

Gels III

Sol–gel process: Synthesis of colloid particles followed by gelatinization and production of solid materials (ceramics, layers, fibers)





Aerogel = xerogel with a very low density (supercritical drying), silica gel to 1.9 g dm^{-3}; alumina; aerographite 0.18 g dm^{-3} – ultimate tensile strength 1 kPa
Use: insulation, adsorbent, Cherenkov detector

Atmospheric aerosols

troposphere

- clouds
  nucleation of droplets around dust, ions, salts ($(NH_4)_2SO_4$ most typical)
  polarizable anions at surface of droplets
- solid aerosols
  most stable ≈ 300 nm: PM = Particulate Matter
  – smaller particles diffuse fast and get adsorbed
  – larger particles sediment
  particles < 10 μm (PM10, = aerodynamic diameter) are not filtered in the nose, may penetrate to alveoli and (smaller ones) to the blood
- smog (< *smoke and fog*): VOC = Volatile Organic Compound
  – London (reduction) type (smoke, fog, SO_2); vog = volcanic smog
  – photochemical (ox.) smog (L.A.): NO_2 + VOC + $h\nu \to O_3$ + ...

stratosphere

- soot (does not sediment because heated)
- volcanic ash, $SO_2 \to SO_4{}^{2-}$ (→ cooling)

nuclear winter (soot), volcanic winter (ash, SO_x)