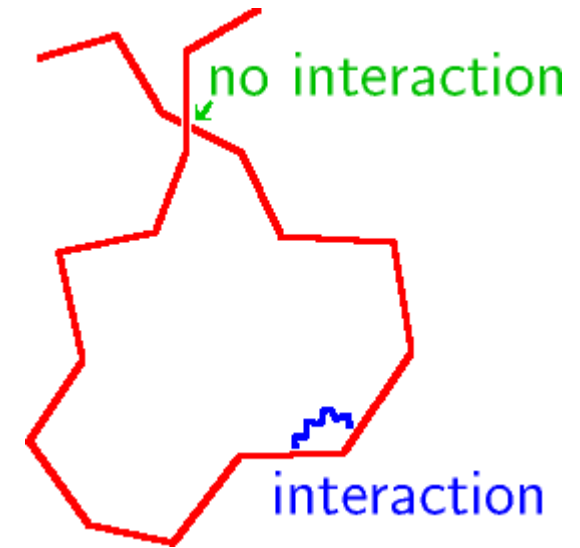# Polymer solutions

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

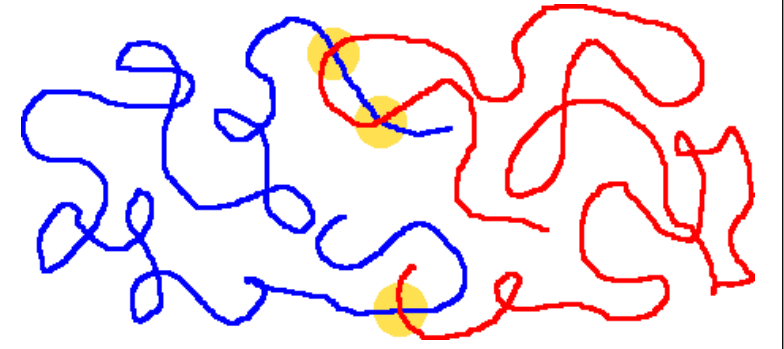$\Rightarrow$ coil size $\propto N^{1/2}$

Better models:

🟣 repulsive forces $\rightarrow$ excluded volume (beads do not overlap)

🟣 attractive forces $\rightarrow$ "negative excluded volume" (beads are "sticky")
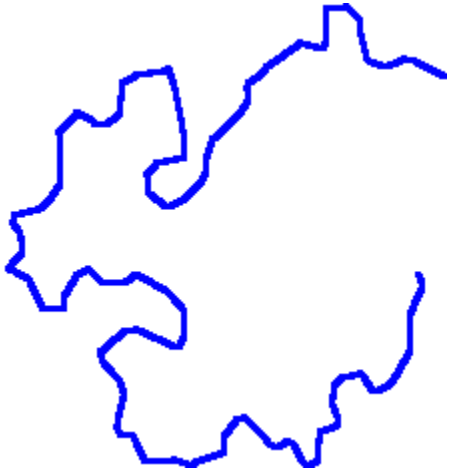
good solvent – (lyophilic polymer), beads effectively repel each other, the chain partly unwinds = self-avoiding random walk
coil size $\propto N^{1/1.7}$

entropic (steric) repulsion – the coils in a good solvent repel each other because of excluded volumes
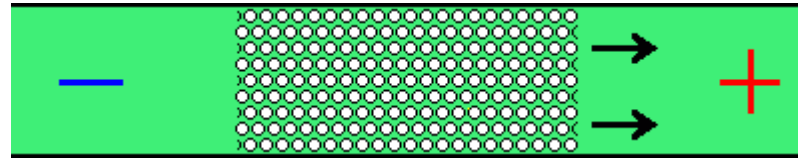
theta-solvent – beads interact with the solvent in the same way as mutually (effectively repulsion = attraction) $\approx$ ideal chain
coil size $\propto N^{1/2}$

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 $\propto N^{1/3}$
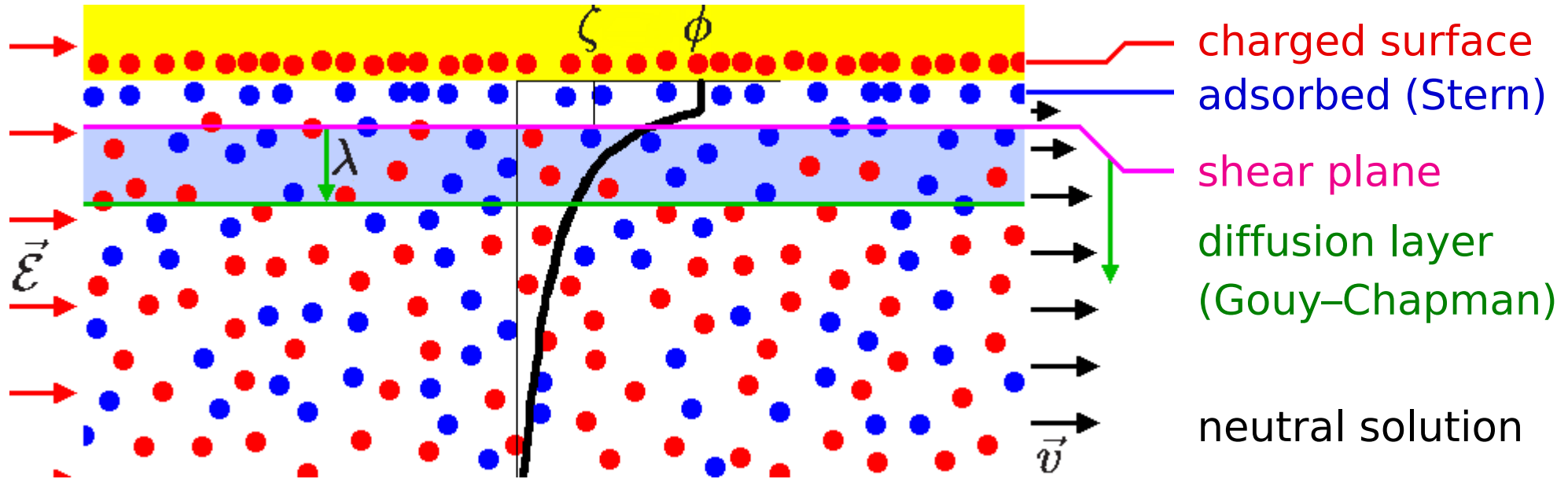
Electrokinetic phenomena

🔴 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

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

— charged surface
— adsorbed (Stern)

— shear plane

diffusion layer
(Gouy–Chapman)

neutral solution

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

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

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

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 $\mathcal{A}_\varnothing$: $\mathcal{A}_\varnothing$: $I = \mathcal{A}_\varnothing \mathcal{E} \kappa = \mathcal{A}_\varnothing \frac{U}{L} \kappa$ (κ = conductivity)

Volume flow: $\frac{dV}{d\tau} = v \mathcal{A}_\varnothing$

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

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 $\zeta = 0$ ($\approx$ 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

Types:

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

- 🟣 W/O (*water-in-oil*)
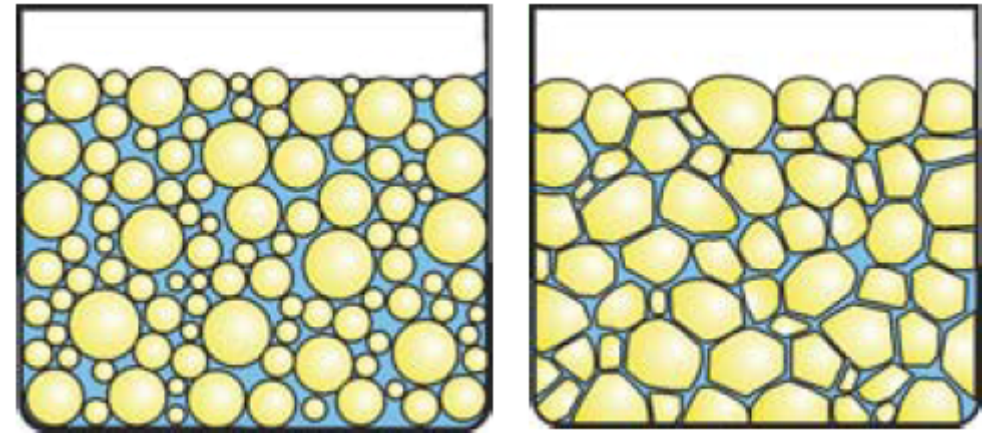
Examples: milk, mayonnaise, cutting fluids (for metals)

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)
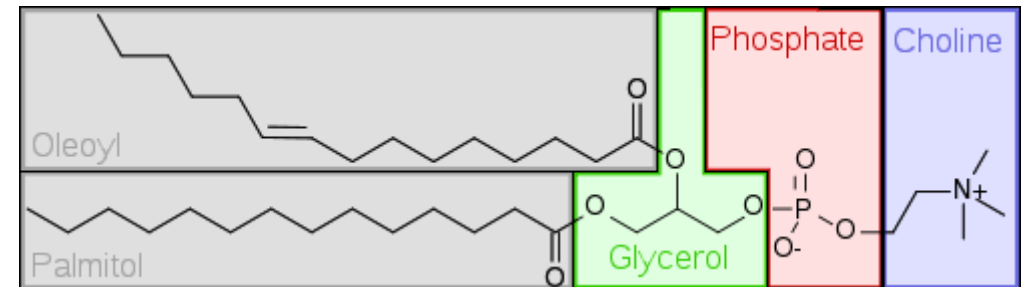
credit: wikipedia

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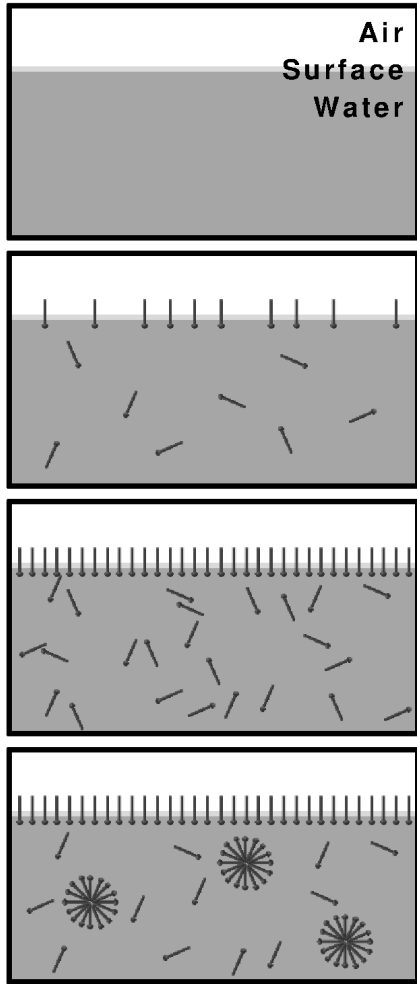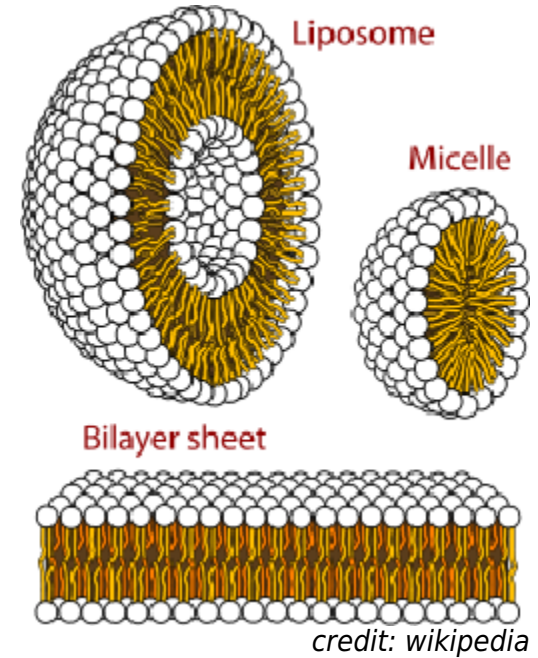
credit: wikipedia

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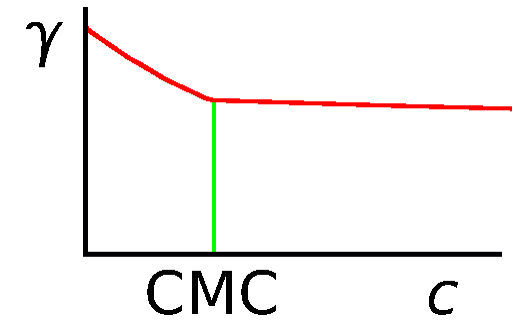– lyophobic interaction (inside)

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)

credit: wikipedia

Solubilization – ability of micelles do absorb lyophobic substances

Detergency – washing

Phase transition classification

+

- 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
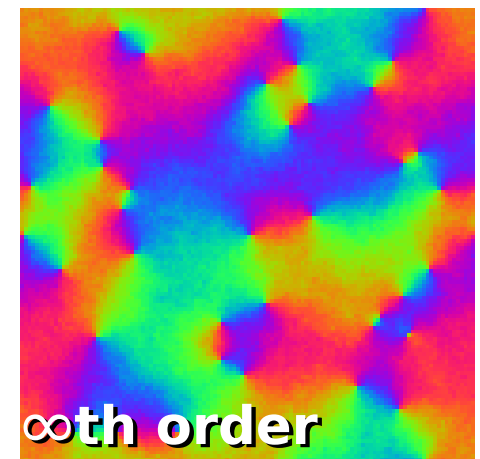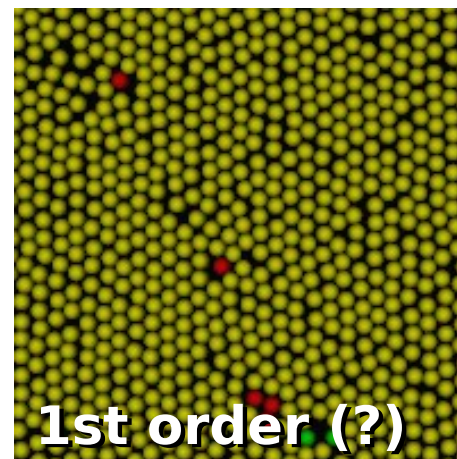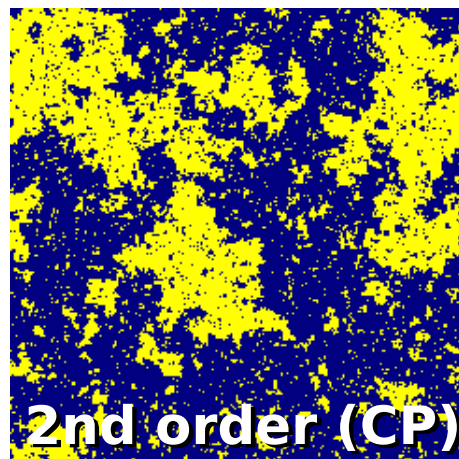
1st order   **2nd order (CP)**   **1st order (?)**   **∞th order**

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

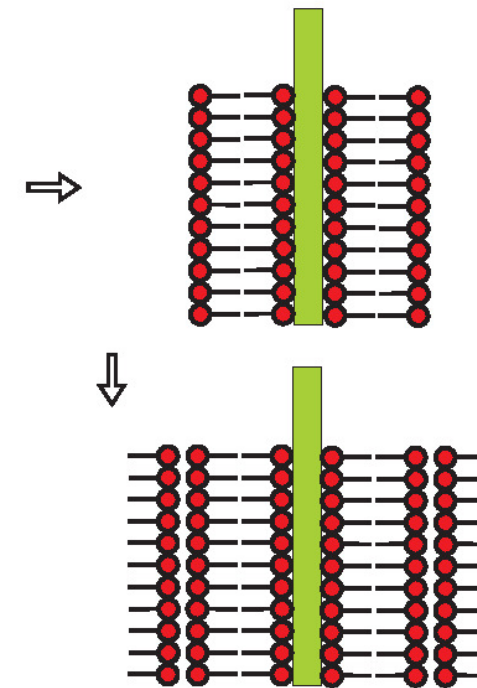**vesicle** – liquid inside
vacuoles, lysosomes, transport vesicles. . .
artificial liposomes: drug transport

"Phospholipid TvanBrussel", Wikimedia Commons
(file Phospholipid_TvanBrussel.jpg)
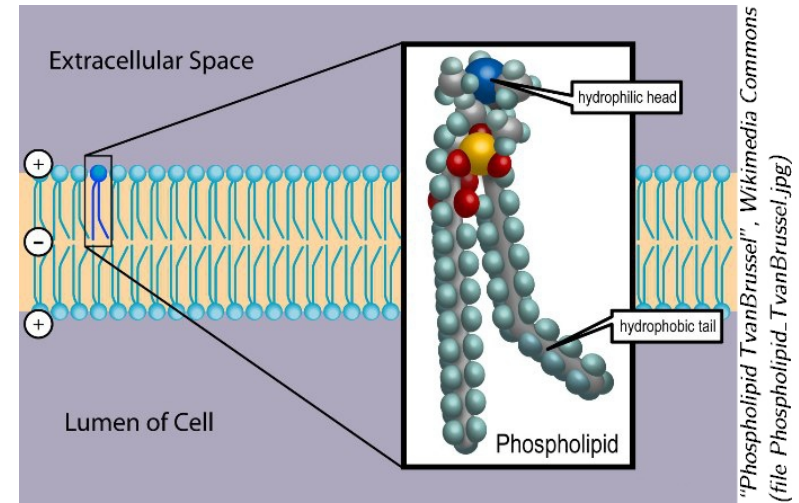
Langmuir–Blodgett films: more (double) layers, usu. 2D crystal
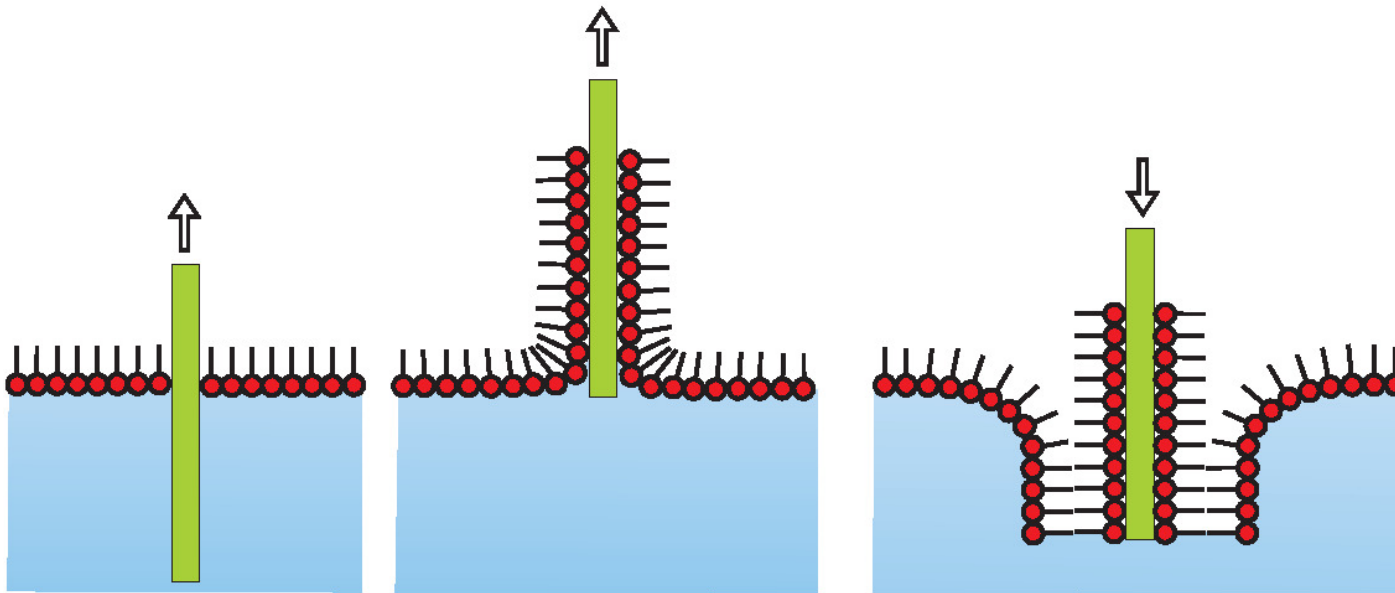
– model of biomembrane, glucose sensor,
microelectronics, anti-reflective coating

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

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

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

sometimes reversibility refers to the sol ⇌ gel process

2D: no percolation   **percolation**

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

starch

credit: Biodegradable Polymers by Babak Ghanbarzadeh and Hadi Almasi

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

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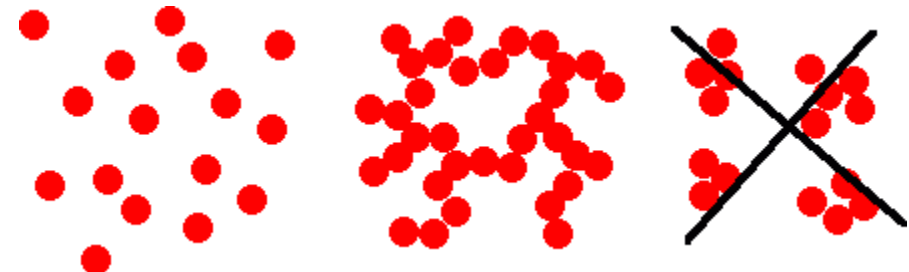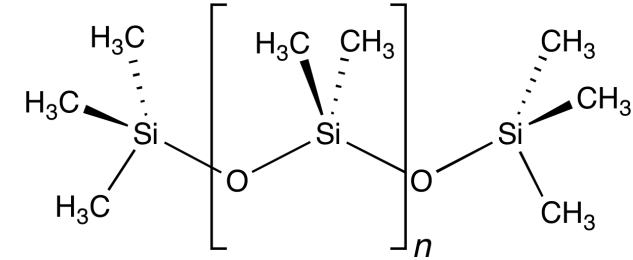
Mechanical properties:

● elasticity (a few covalent links)

● thixotropy (reversible weak links)

Hydrogels:
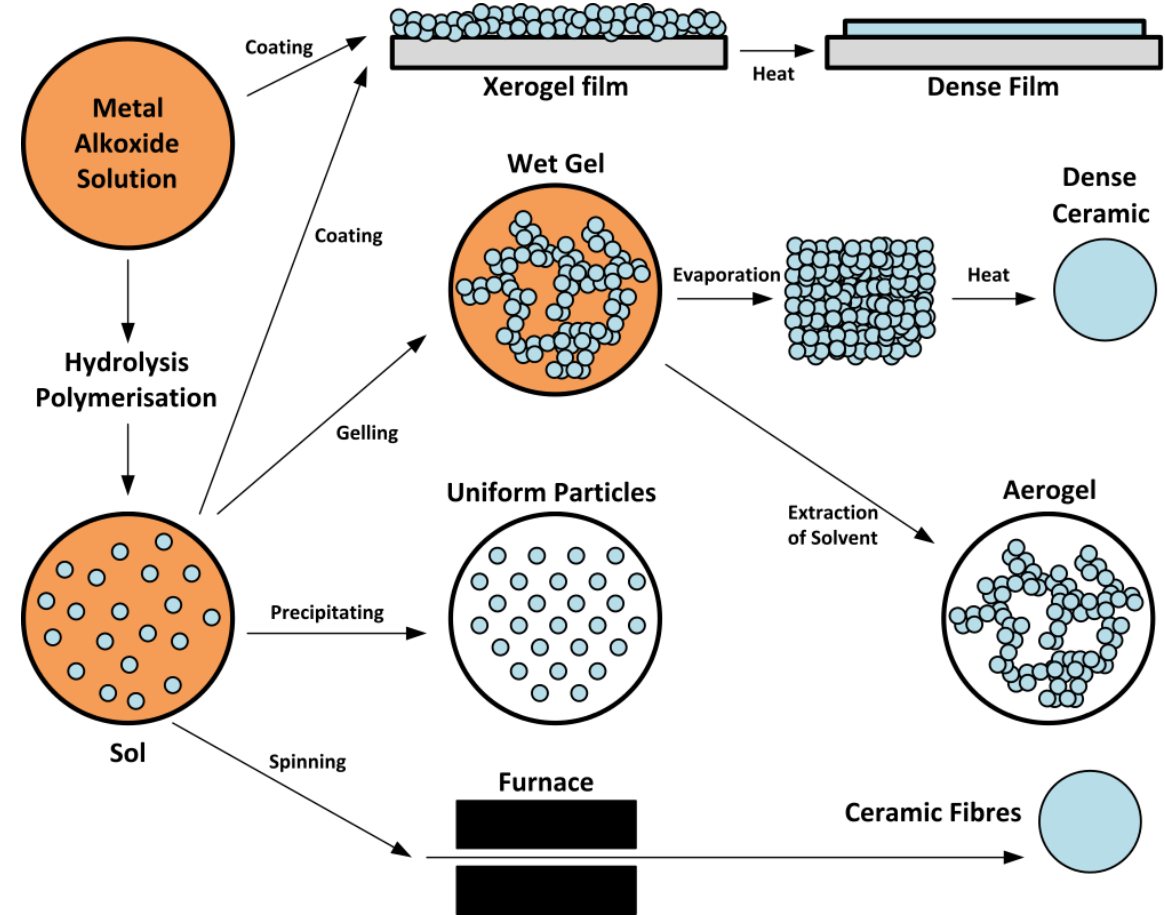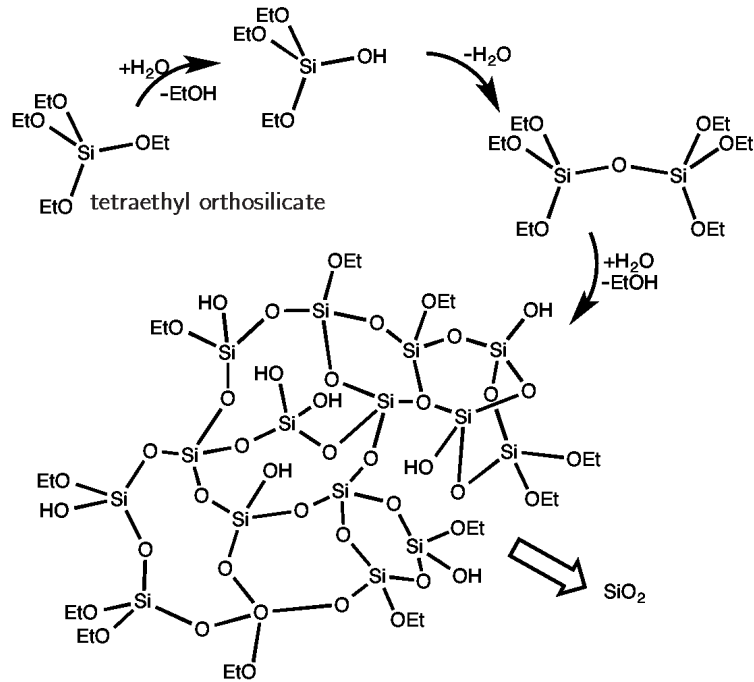
● contact lenses (polyacrylamides, "silicone" – oxygen-permeable)

● diapers (sodium polyacrylate, [-CH_2-CH(COONa)-]$_n$)

● biomaterials – silicon implants, scaffolding for tissue growth

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

tetraethyl orthosilicate
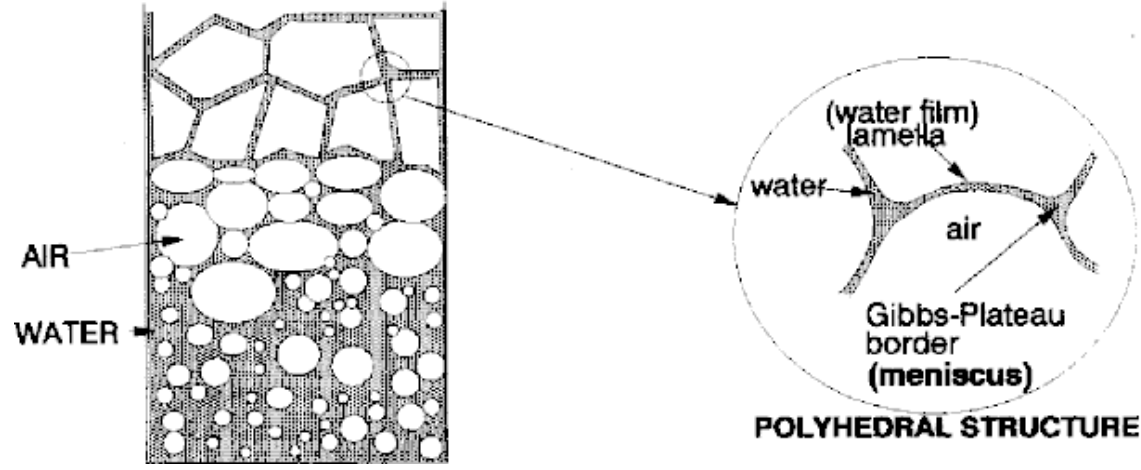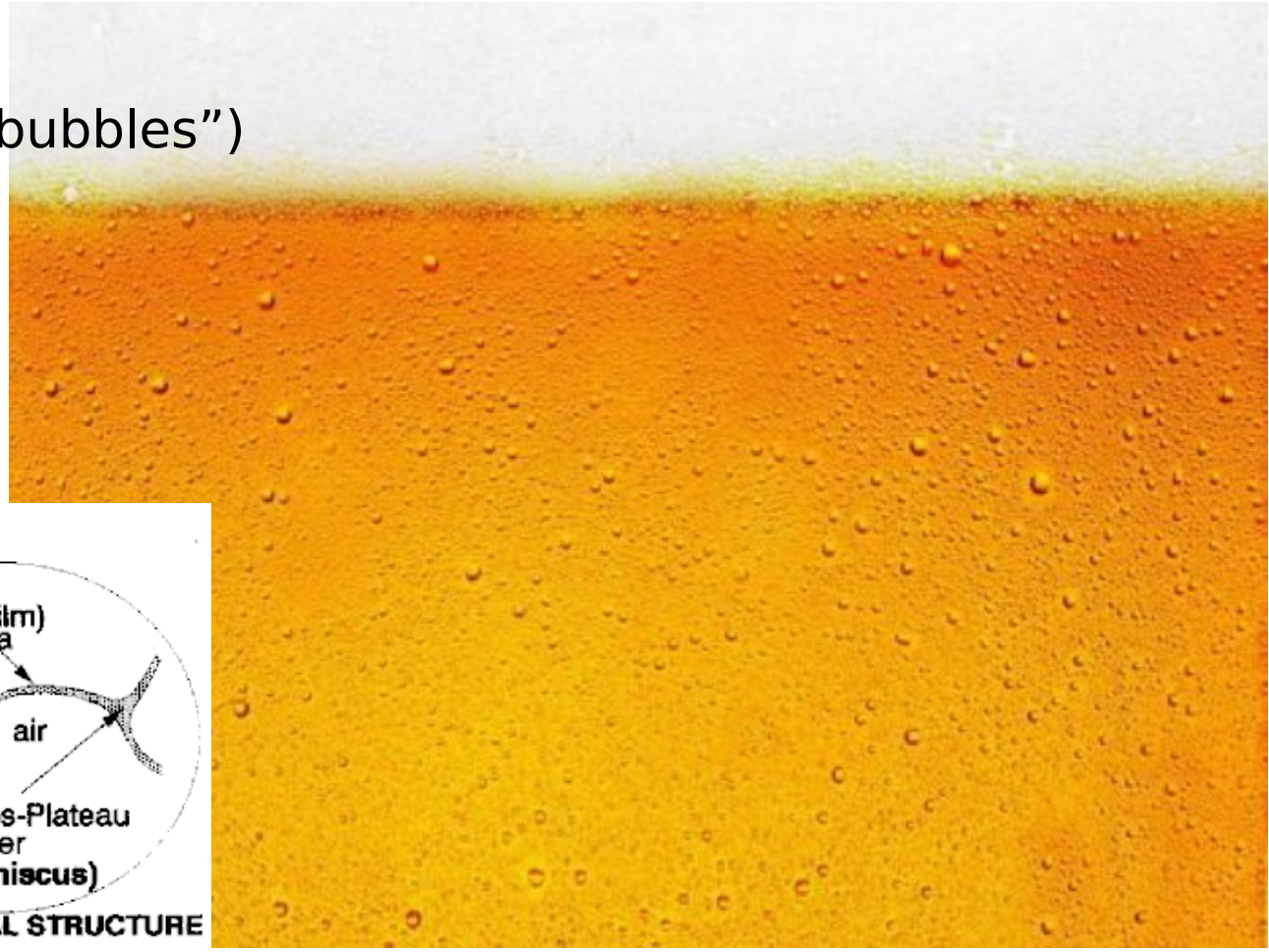

Aerogel = xerogel with a very low density (supercritical drying), silica gel to $1.9\,\mathrm{g\,dm^{-3}}$; alumina; aerographite $0.18\,\mathrm{g\,dm^{-3}}$ – ultimate tensile strength 1 kPa

Use: insulation, adsorbent, Cherenkov detector

Gas in liquid

🟣 wet foams (spherical cavities, "bubbles")

🟣 dry foams (polyhedra, 12–14)

🟣 Gibbs–Plateau channels

🟣 Plateau rules (see lecture 10)

POLYHEDRAL STRUCTURE

Stabilized by surfactants

destabilization: gravity, evaporation, Ostwald ripening, film rupture

Dry foams (styrofoam)

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

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)

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 $< 10\,\mu m$ (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.): $NO_2 + VOC + h\nu \rightarrow O_3 + \ldots$

stratosphere

⬤ soot (does not sediment because heated)

⬤ volcanic ash, $SO_2 \rightarrow SO_4^{2-}$ ($\rightarrow$ cooling)

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