Lecture 13

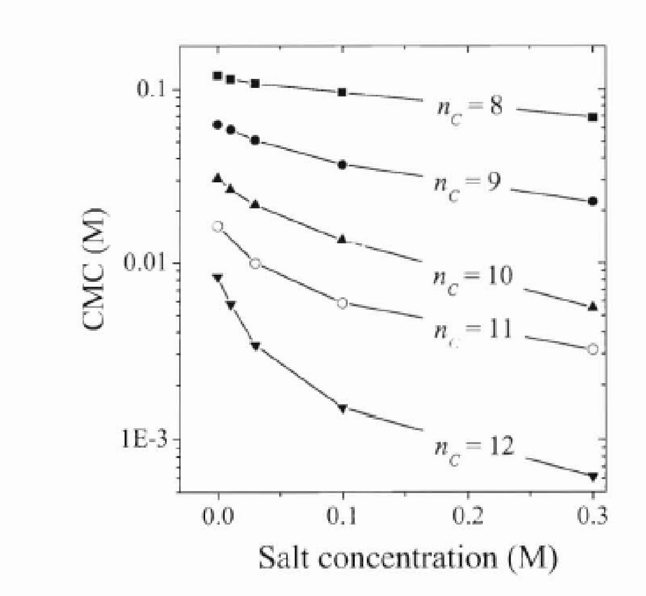
Micelles formation.

Factors affecting the CMC

- Hydrophobic interaction:
  - entropy lowered due to arranging of surfactants into the micelles
  - entropy increased due to removal hydrocarbon chains from water (much higher gain!)
- Head group interaction:
  - hydration repulsion: head group needs to be dehydrated to a approach
  - steric effects: due to reduction of fluctuations (entropy reduction)
  - electrostatic repulsion

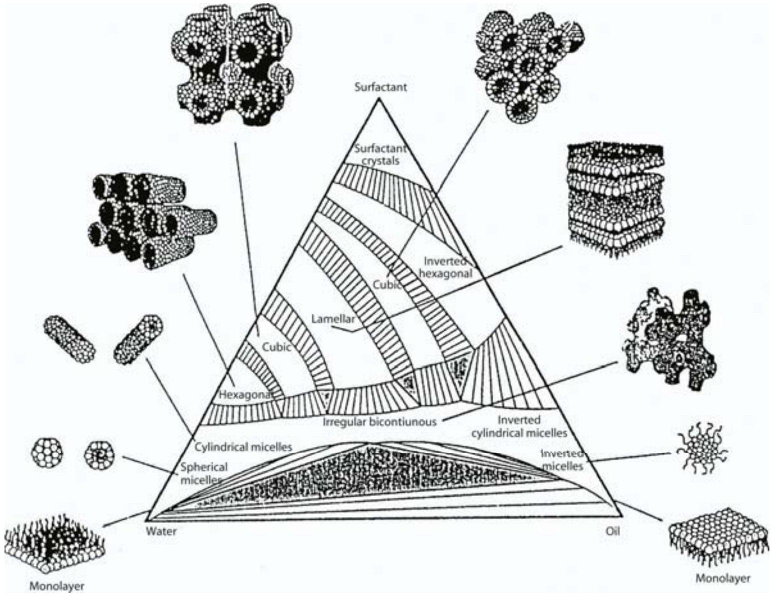
longer hydrophobic chain leads to lower CMC

increase in ionic strength leads to lower CMC



Micelle structure considerations

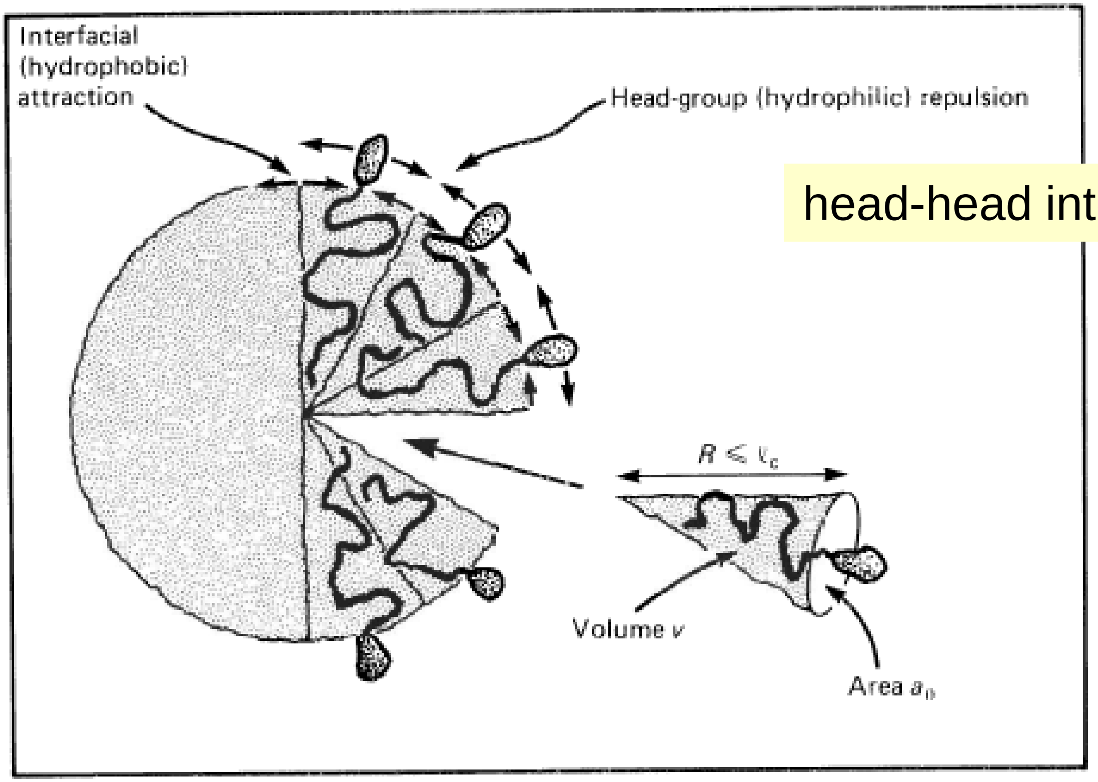
- The structure of a micelle depends on:
  - thermodynamics of self-assembly
  - forces within the aggregate
  - intra-aggregate forces
- Size and shape of the micelles are defined as a distribution (no exact size or shape!)
- The distribution might have several equilibrium values at the same time



Optimal head group area

- We can express the energy factors through the geometrical parameters of the micelle

energy gain due to decrease of water-oil surface tension.
Thus it can be written as : γ=20-50 mJ/m^2.



head-head interaction: K/a

Optimal head group area

$$\mu_N = \gamma a + K / a$$

- minimizing:

$$\mu_{N\_\min} = 2\gamma a_0;\;\; a_0 = \sqrt{K/\gamma}$$

optimal head group area,
mainly depends on the head (not the tail length)

$$\mu_N = 2\gamma a_0 + \frac{\gamma}{a}\left(a - a_0\right)^2$$

Optimal headgroup area

Optimal headgroup area approach:

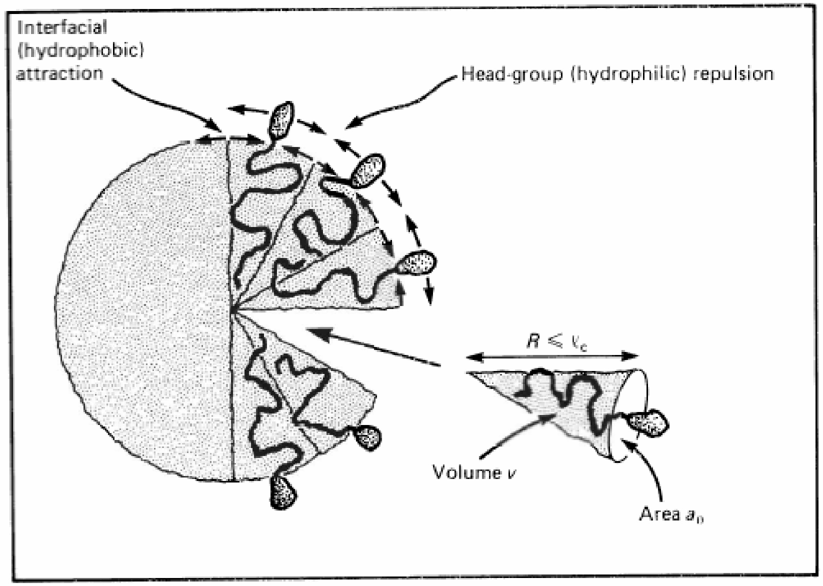
- contains essential features of interlipid interaction
- explains an energy minimum about which the energy varies parabolically (equilibrium N!)
- doesn’t include into account
  - specific headgroup interaction, e.g. ionic bridging
  - specific chain-chain interaction
  - effect of surface curvature on the energy

Geometric packing

- The geometry of aggregate is defined by the following factors:
  - optimal headgroup area $\boldsymbol{a_0}$;
  - maximum effective length of the chain, “critical chain length” $\boldsymbol{l_c}$;
  - volume of the hydrocarbon chain $\boldsymbol{v}$.

$$l_c \le l_{\max} \approx \left(0.154 + 0.1265 \cdot n\right) nm$$

$$v \approx \left(27.4 + 26.9 \cdot n\right) \times 10^{-3} nm^{-3}$$



- packing parameter (shape factor): $\dfrac{v}{a_0 l_c}$
- minimal possible size corresponds to equilibrium (entropy)

Spherical micelles

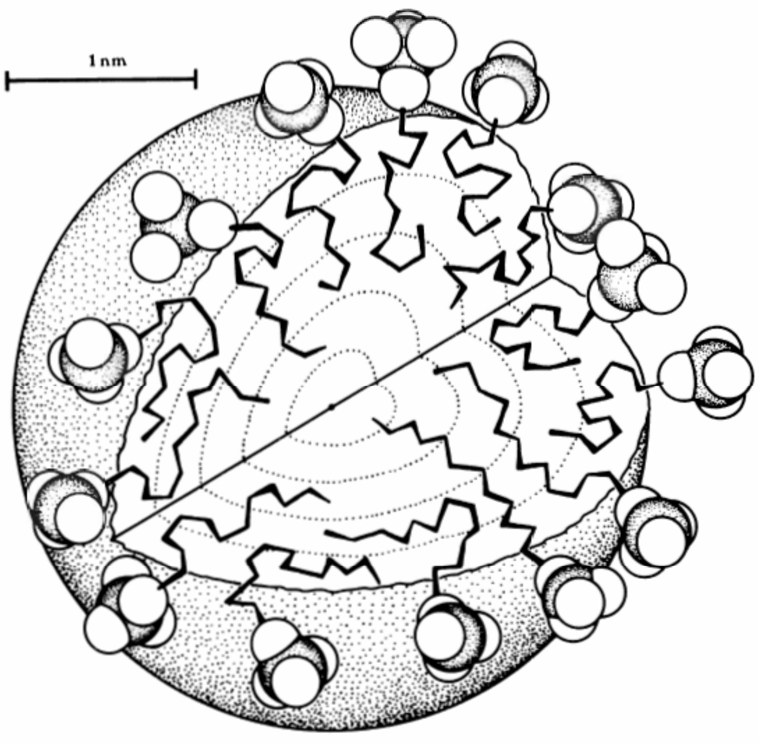
- For a spherical micelle of radius R with aggregation number M:

$$M = \frac{4\pi R^2}{a_0} = \frac{4\pi R^3}{3v} \Rightarrow R = 3v/a_0$$

$$\frac{v}{l_c a_0} < \frac{1}{3}$$

Example: SDS-micelle
M=74; 12 carbon chain;
from equation we get:
$v=0.35$ nm^3; $l_c=1.67$ nm; $a0=0.57$ nm^2; $R=1.84$ nm
$v/a_0 l_c=0.37$

slightly non-spherical shape



Cylindrical micelles

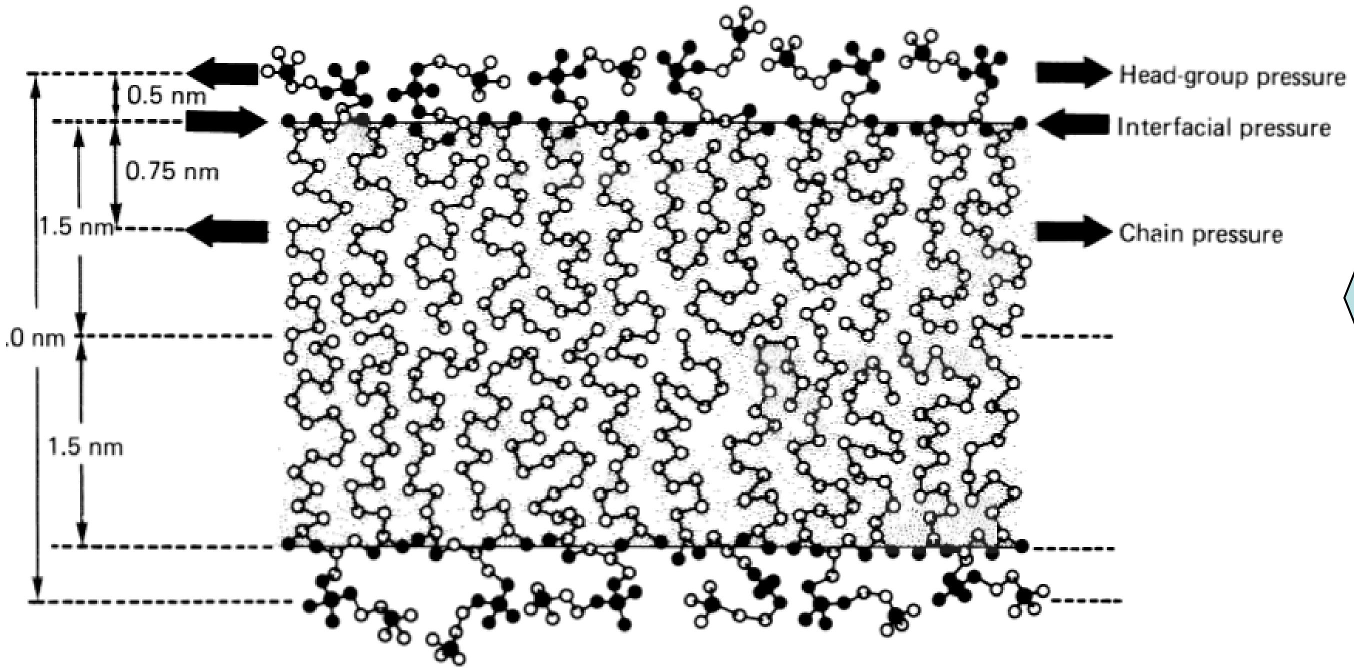
$$\frac{1}{3} < \frac{v}{a_0 l_c} < \frac{1}{2}$$

- lipids forming spherical micelles at low salt concentration might switch to cylindrical at higher ionic strength;
- from thermodynamics, the cylindrical micelles are **large** and **polydisperse,** mean aggregation number $\sim \boldsymbol{C}^{1/2}$.
- most energy is associated with ends of the micelle (spherical caps are unfavorable)

Bilayers

$$\frac{1}{2} < \frac{v}{a_0 l_c} \leq 1$$

- formed when the headgroup is small or chain is bulky, e.g. lipids with two chains



lecitin bilayer

Bilayer: Some estimates

- residence time inside the membrane

$$\tau_R = \tau_0 / \exp(-\Delta E / kT) = 55\tau_0 / \mathrm{CMC}$$

time between colliding the interface

$$\tau_0 = 10^{-9} - 10^{-7} s$$

$$\tau_R(micelles) \sim 55 \cdot 10^{-9} / 10^{-3} \sim 10^{-4} s;$$

$$\tau_R(bilayers) \sim 55 \cdot 10^{-7} / 10^{-10} \sim 10^{4} s;$$

Bilayer: Some estimates

- elastic energy (stretching) of bilayer

$$\text{elastic energy} = \frac{1}{2} k_a (a - a_0)^2 / a$$

compare: $$\mu_N^0 = 2\gamma a_0 + \frac{\gamma}{a}(a - a_0)^2$$

$$k_a \approx 2\gamma \text{ per monolayer;}$$

$$k_a \approx 4\gamma \text{ per bilayer}$$

Vesicles

- at some condition it could be energetically favorable to eliminate the edges of a bilayer forming ***vesicles***
- however it requires curvature, so lipids in the outer layer should pack into truncated cones:

$$\frac{v}{a_0 l_c} \leq 1$$

- for a vesicle:

$$R_c \approx \frac{l_c}{1 - v/\left(a_0 l_c\right)}; N \approx 4\pi\left[R_c{}^2 + \left(R_c - t\right)^2\right]/a_0$$

Lipid bilayers

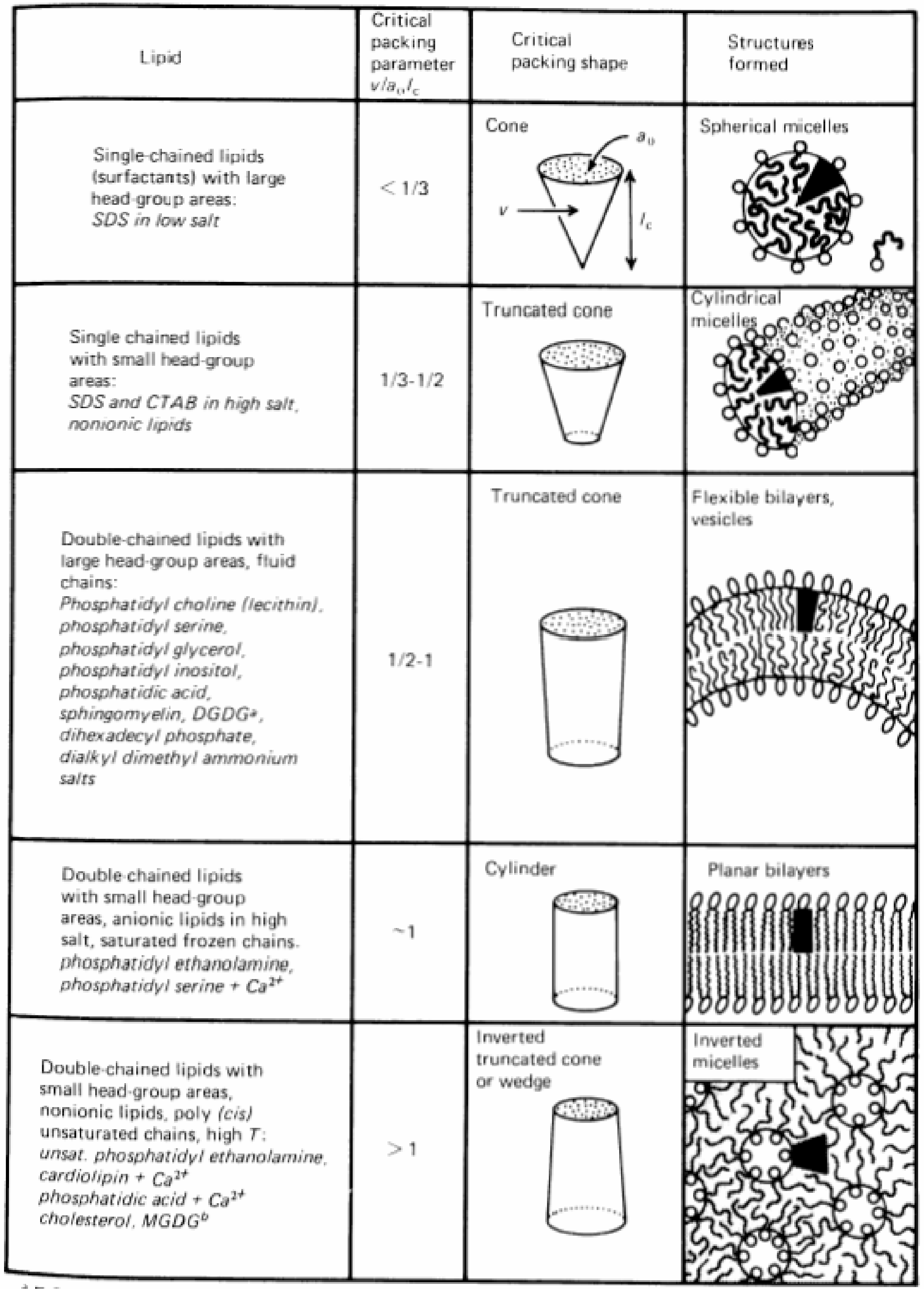
- biological membrane are formed by lipid bilayers
- prevent diffusion of polar molecules (possess a high resistance for ionic currents)

$$\frac{e^2}{8\pi\varepsilon_0 \underset{\underset{0.2\text{nm}}{\nearrow}}{R}}\left(\frac{1}{\underset{\underset{4}{\uparrow}}{\varepsilon_2}}-\frac{1}{\underset{\underset{78}{\uparrow}}{\varepsilon_1}}\right)=1.37\cdot 10^{-19}\,J \approx 33kT$$

typical resistance ~ 10^8 Ohm/cm^2.

Factors affecting structure changes

- factors affecting headgroup area: ionic strength, pH
- factors affecting chain packing (e.g. chain branching and unsaturation)
- effect of temperature, affects both $\boldsymbol{a_o}$ and $\boldsymbol{l_c}$.
- lipid mixtures



Lipid	Critical packing parameter v/a_0l_c	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	$< 1/3$	Cone	Spherical micelles
Single chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3-1/2	Truncated cone	Cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin,* DGDG^a*, dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2-1	Truncated cone	Flexible bilayers, vesicles
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains. *phosphatidyl ethanolamine, phosphatidyl serine +* Ca^{2+}	~1	Cylinder	Planar bilayers
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high *T*: *unsat. phosphatidyl ethanolamine, cardiolipin +* Ca^{2+} *phosphatidic acid +* Ca^{2+} *cholesterol,* MGDG^b	> 1	Inverted truncated cone or wedge	Inverted micelles

Emulsions

- Emulsion – dispersion of two immiscible liquids. **Outer** (continuous) and **inner** phases are distinguished.
- Emulsion are stabilized by addition of surfactants
- Macro- and micro-emulsions can be distinguished:
- Macro-emulsions:
  - concentration of surfactant just above CMC
  - spherical droplets 0.1-10µm, highly polydispersed
  - thermodynamically unstable
- Microemulsions:
  - high concentration of surfactant
  - thermodynamically stable
  - typical sizes 2-50nm

Evolution of macroemulsions

- we expect that from the thermodynamics prospective the emulsions will eventually coalesce
- this is delayed by
  - reducing surface tension (surfactants)
  - repulsive forces
  - kinetics

Emulsion stability

- selection of emulsifier determines which type of emulsion will be formed

Bancroft rule: the phase the emulsifier is more soluble in will be the continuous phase

Harkins wedge theory: larger end of the emulsifier lies in the continuous phase

Winsor theory: based on ratio of cohesive energies

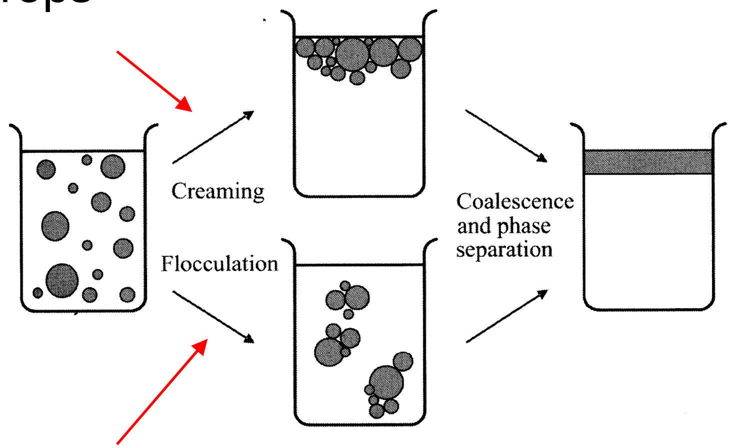
$$R = \frac{E_{LO}}{E_{HW}}$$

R<1 O/W emulsion is formed
R>1 W/O emulsion is formed

Griffin’s hydrophile-lipophile balance (HLB) theory:
Surfactants with low HLB (3-6) stabilize water-in-oil emulsions
Surfcatants with high HLB(8-18) stabilize oil-in-water emulsion

Evolution of macroemulsions

- Kinetics of demulsification



separation of drops
by gravity

forming loose clusters
without loosing identity of
drops (secondary
minimum)

Evolution of macroemulsions

- Kinetics of demulsification
  - Diffusion limited encounter of droplets (Smoluchowski)

$$\frac{dc}{dt} = -8\pi DRc^2 = \frac{-8\pi k_B TR}{6\pi\eta R}c^2 = -\frac{4k_B T}{3\eta}c^2$$

$$\frac{dc}{dt} = -k_f c^2 \qquad k_f = \frac{4k_B T}{3\eta}$$

⇦ rate of flocculation,
depends only on T and viscosity

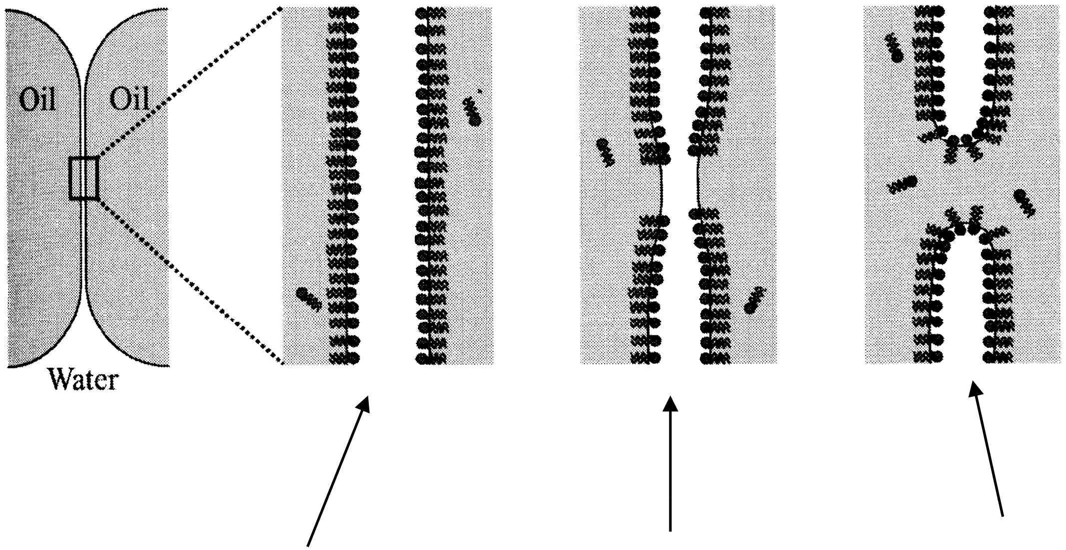
  - If a barrier E* for coalescence exists:

$$\frac{dc}{dt} = -k_f \exp\left(-\frac{E^*}{k_B T}\right)c^2$$

$$\frac{1}{c} = \frac{1}{c_0} + k_f^* t, \quad k_f^* = k_f \exp\left(-\frac{E^*}{k_B T}\right)$$

Evolution of macroemulsions

- Stages of droplet coalescence



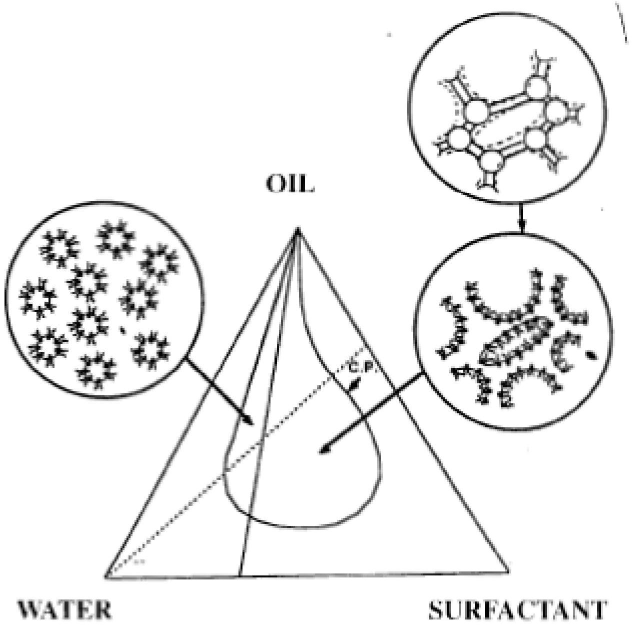
stability of lamella depends on the repulsion forces between the surfactants

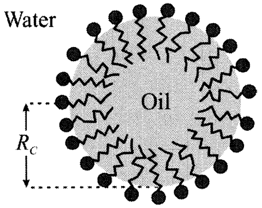
formation of bare spots depends of surfactant density

area and curvature of the surfactant film changes

Microemulsions

- Microemulsions (discovered in 1950s) are
  - thermodynamically stable;
  - formed spontaneously
  - react reversibly on the change in temperature and composition
  - consist of submicron size droplets





Microemulsions

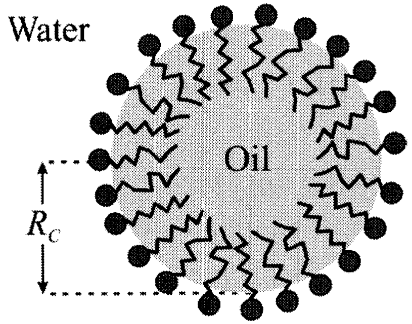
- The radius of the droplet (in case of complete coverage by a surfactant)

volume fraction

dispersed phase: $$V\phi_d = n\frac{4}{3}\pi R^3$$

surfactant: $$V\phi_s = n4\pi R^2 L_s$$

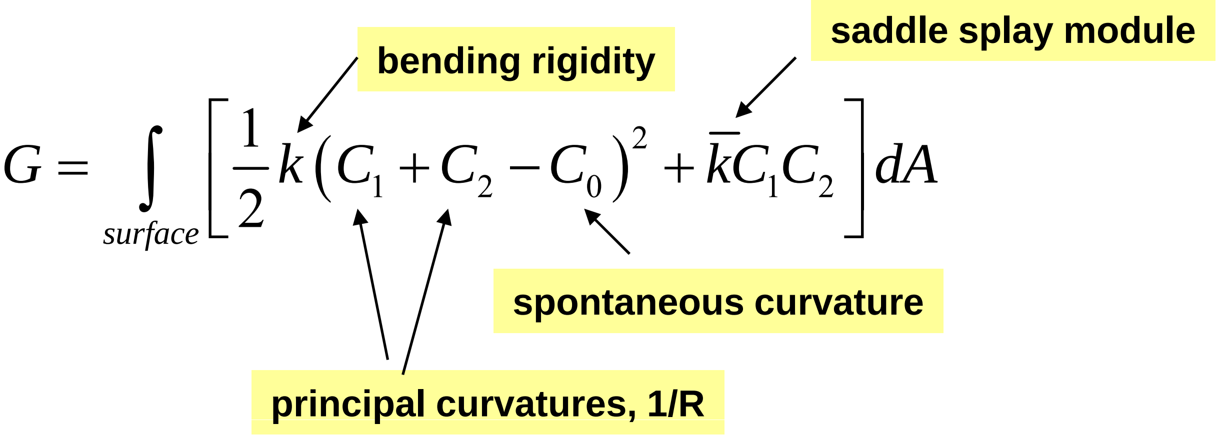
$$R = \frac{3L_s\phi_d}{\phi_s}$$



R_c - core radius –
radius of “neutral surface”

Elastic properties of surfactant films

- Laplace pressure is relatively small due to small surface tension
- Gibbs free energy of a curved surface:



saddle splay module

bending rigidity

$$G = \int_{surface} \left[\frac{1}{2} k \left(C_1 + C_2 - C_0 \right)^2 + \bar{k} C_1 C_2 \right] dA$$

spontaneous curvature

principal curvatures, 1/R

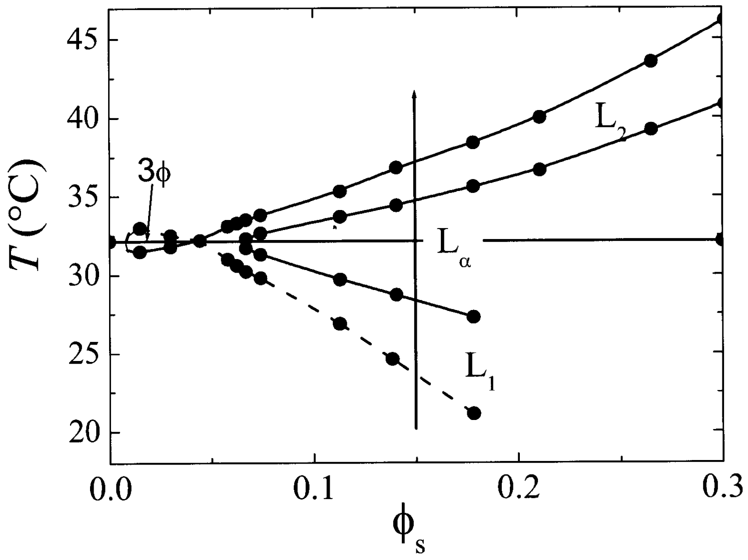
Minimum in Gibbs free energy corresponds to “equilibrium” curvature

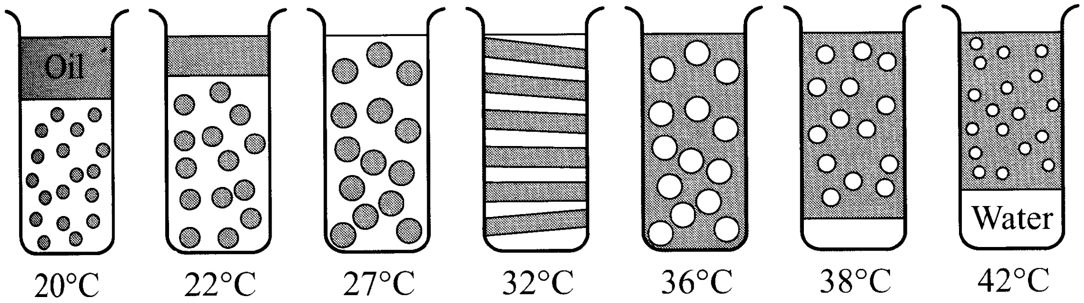
$$C_1 = C_2 = kC_0 \Big/ \left(2k + \bar{k} \right)$$

Microemulsions

- emulsion evolution with temperature

Phase diagram of 50:50 water-octane mixture with $C_{12}E_5$ surfactant





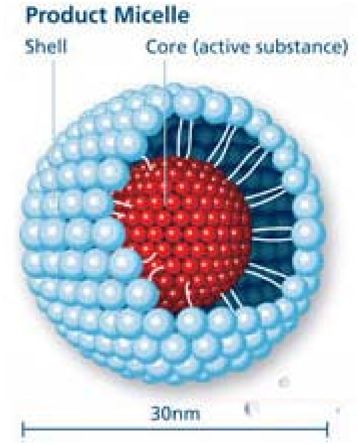
PIT

decrease in spontaneous curvature

Microemulsion applications

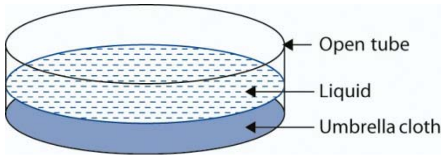
- delivery of water insoluble vitamins and medicine

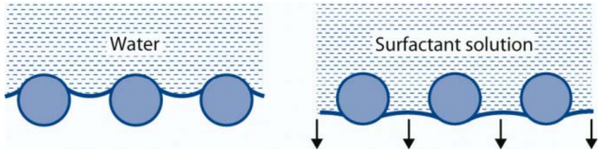
Example: AquaNova GmbH produces 30nm size micelle system suitable e.g. for delivery of vitamin E and vitamin A. Micelles are thermally, mechanically and pH stable

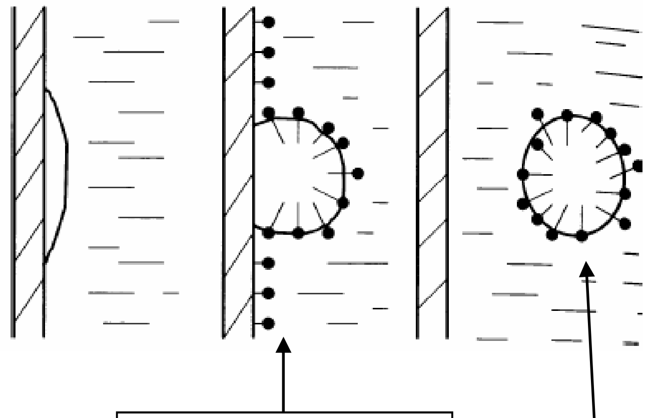


Application of surfactants

- Wetting: contact angle is reduced.
- Detergency:
  - detergent: mixture of surfactants with other additives for effective cleansing (builders, brighteners and bleaches, electrolyte filler)
  - cleansing efficiency grows with the concentration up to cmc
- Water repulsion
  - hydrophilic surface can be made hydrophobic
- Emulsification
- Froth flotation in ore treatment:
  - particles with hydrophobic surface stick to bubbles and are carried upwards when foam is formed (lead and copper sulfide ores, oxides, coal etc.)
- Oil recovery
- Membrane disruption





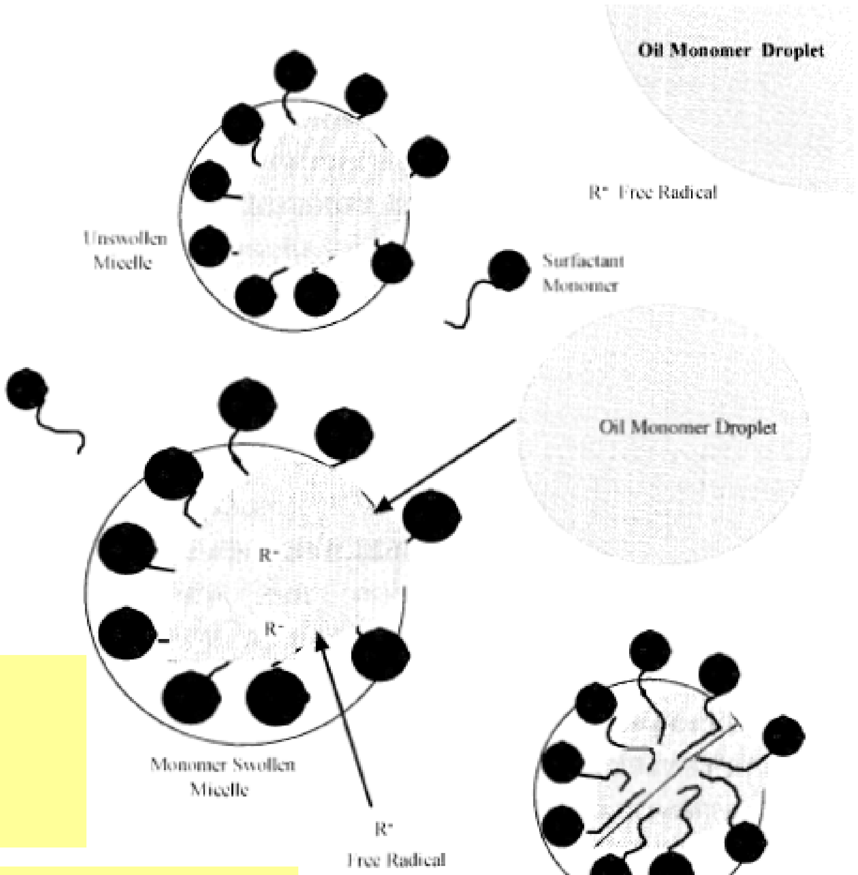


absorption on the interface

emulsifying soil

Emulsion polymerization

- monomer is prepared as emulsion in water stabilized by surfactants
- initiator is dissolved in water
- polymerization starts in the aqueous phase



$$\left.\begin{array}{l} I* + M \longrightarrow M* \\ M* + M \longrightarrow MM* \end{array}\right\}$$

initial polymerization in aqueous phase

$$...MM* + M \longrightarrow ...MMM*$$

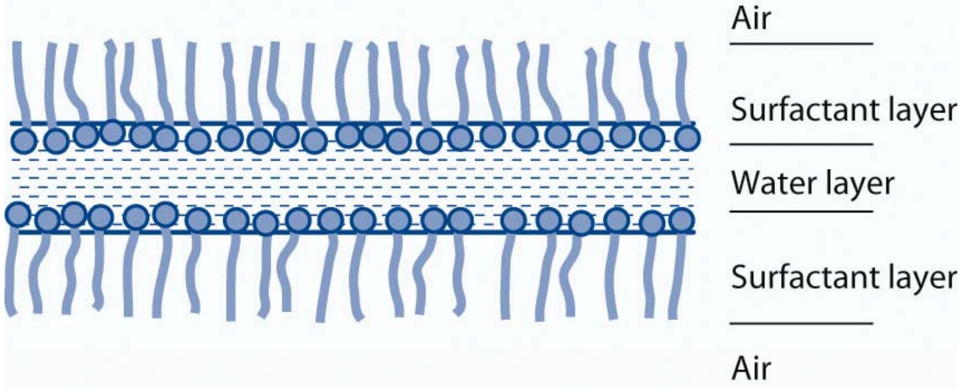
oligomers solubilized in the micelles

$$...MM* + ...MMM* \longrightarrow ...MMM...$$

termination

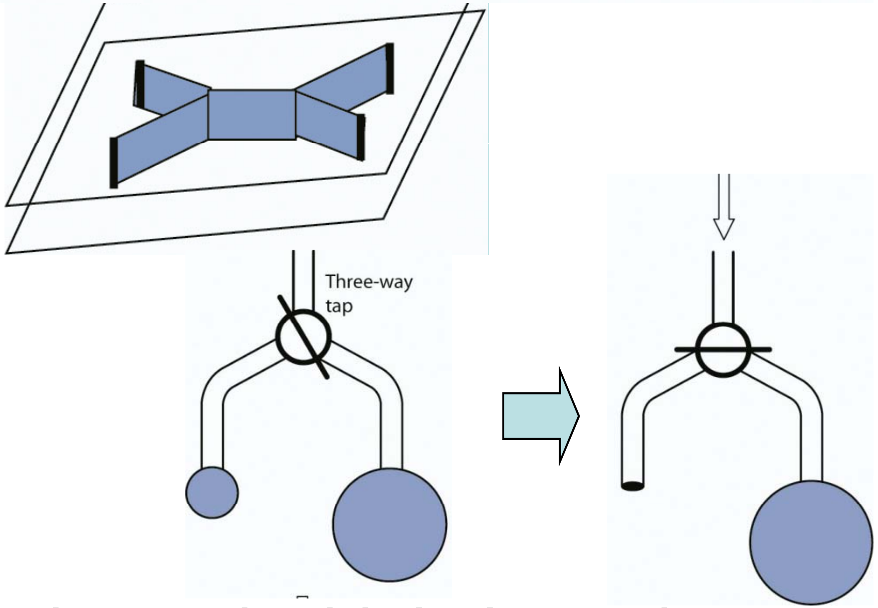
Films and Foams

Structure of a foam layer:



Foam layer has a surface tension, therefore foam film tries to minimize the area:

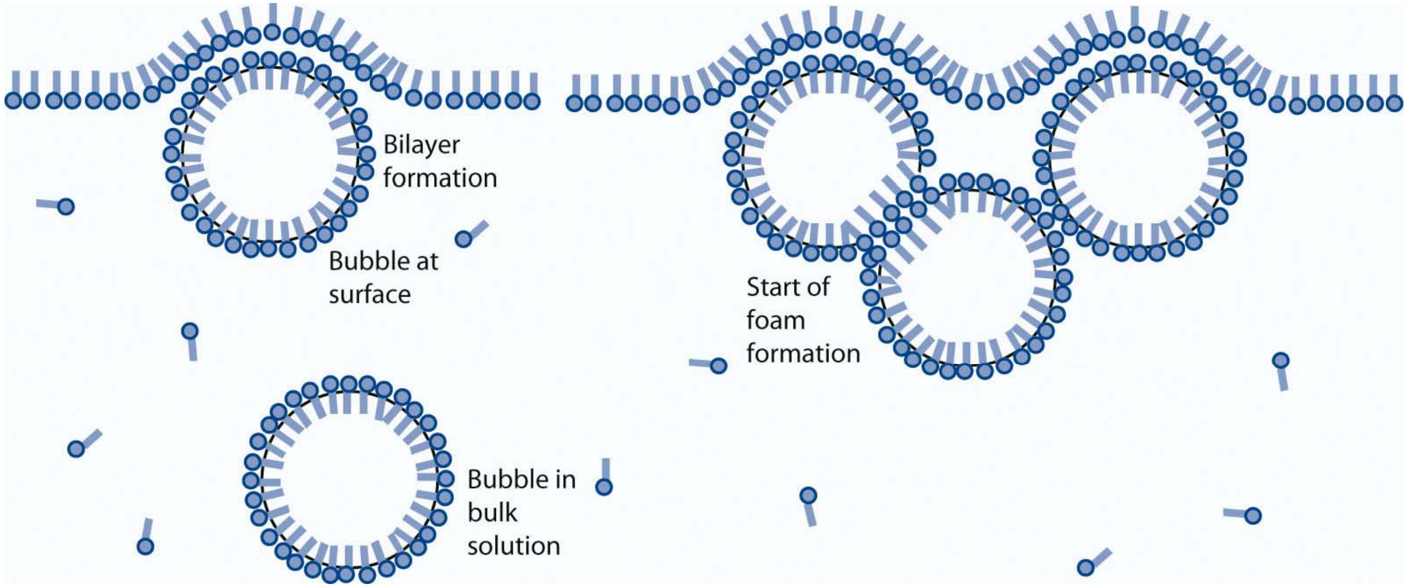
Laplace equation is applicable as well:



- when a foam thickness decreases due to liquid drainage it forms **black** films: **common black film** (liquid core) and **Newton black film** (no liquid core)

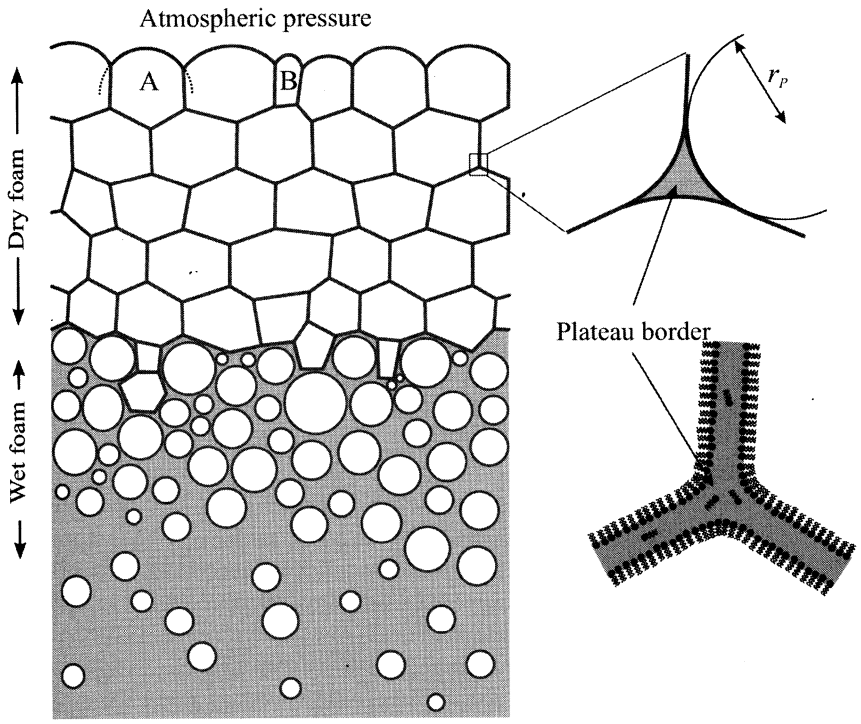
Films and Foams

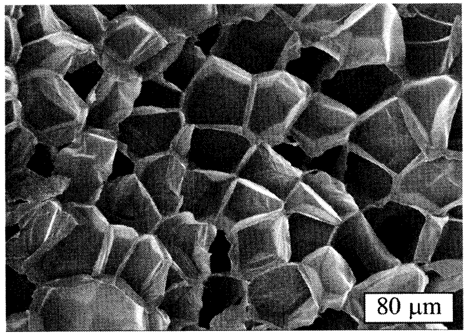
- Foam formation (by bubbling)

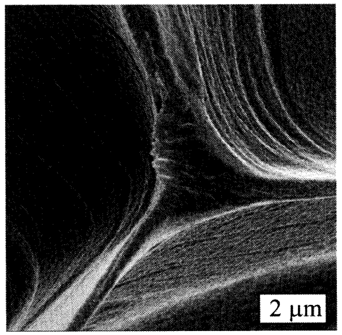


Foams

- Wet foam: bubbles are spherical separated by thick liquid films
- Dry foam:
  mostly gas separated by thin lamellas. Individual cells are polyhedra.
  - three flat sides of poplyhedra meet at an angle of 120º.
  - configuration of 4 or more sides connecting at one line is unstable
  - at all corners the 4 edges meet in a tetrahedral arrangement

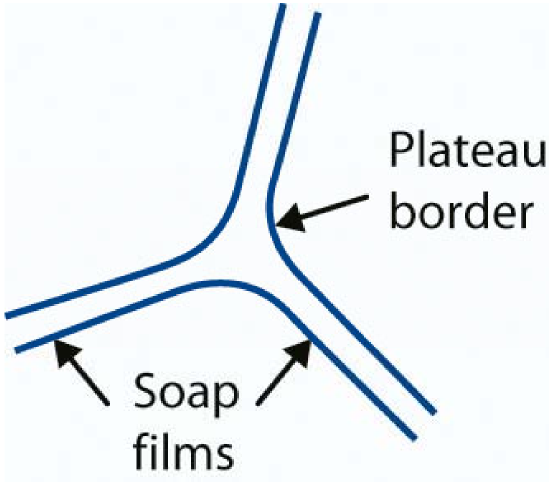






Films and Foams

- the Plateau border
  - as the curvature radius is smaller at the triple point, the pressure will be lower and the liquid will flow there dirupting the foam
  - foam can be stabilized by repulsive pressure between the adsorbed layers: **disjoining pressure**



Films and Foams

- Permeability to gases

monolayer permeation: $J = k_m \Delta c_m$

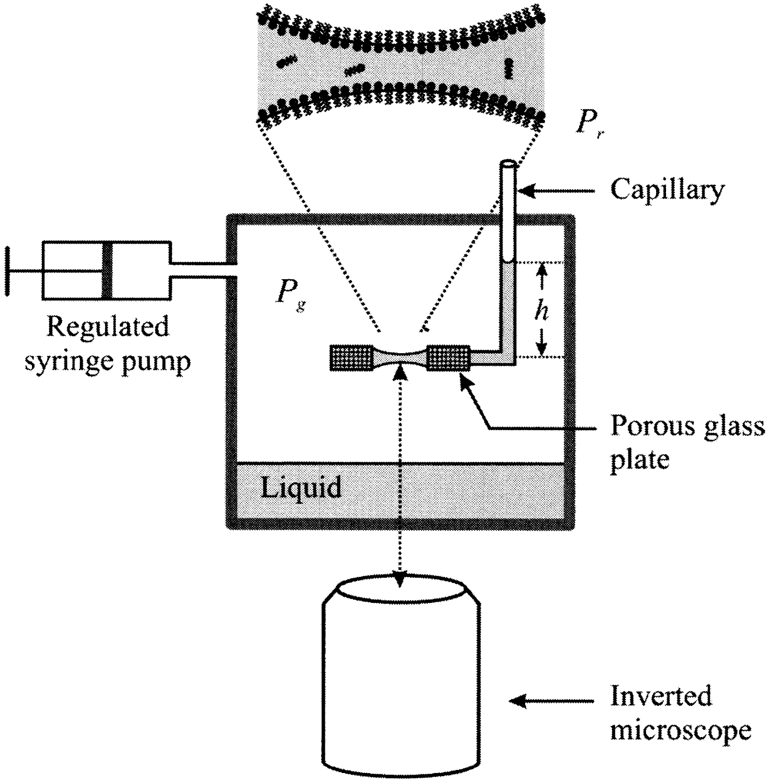
diffusion through the solution: $J = \frac{DH}{z_b} \Delta c_b$

$$J \underbrace{\left(\frac{1}{k_m} + \frac{z_b}{DH} + \frac{1}{k_m} \right)}_{k_i} = \Delta c$$

Measuring pressure in foam: Thin Film Balance

- Pressure inside the liquid film:

$$\Pi = P_g - P_r + \frac{2\gamma}{r_C} - \rho g h$$



Problems

- Below what aggregation number SDS micelles can be spherical?
- Estimate CMC for Hexane in water. Surface tension of Hexane-Water interface is 51.1mN/m
- End-of chapter problems: 12.2, 5, 6