Surfaces, surfactants & self-assembly

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Outline

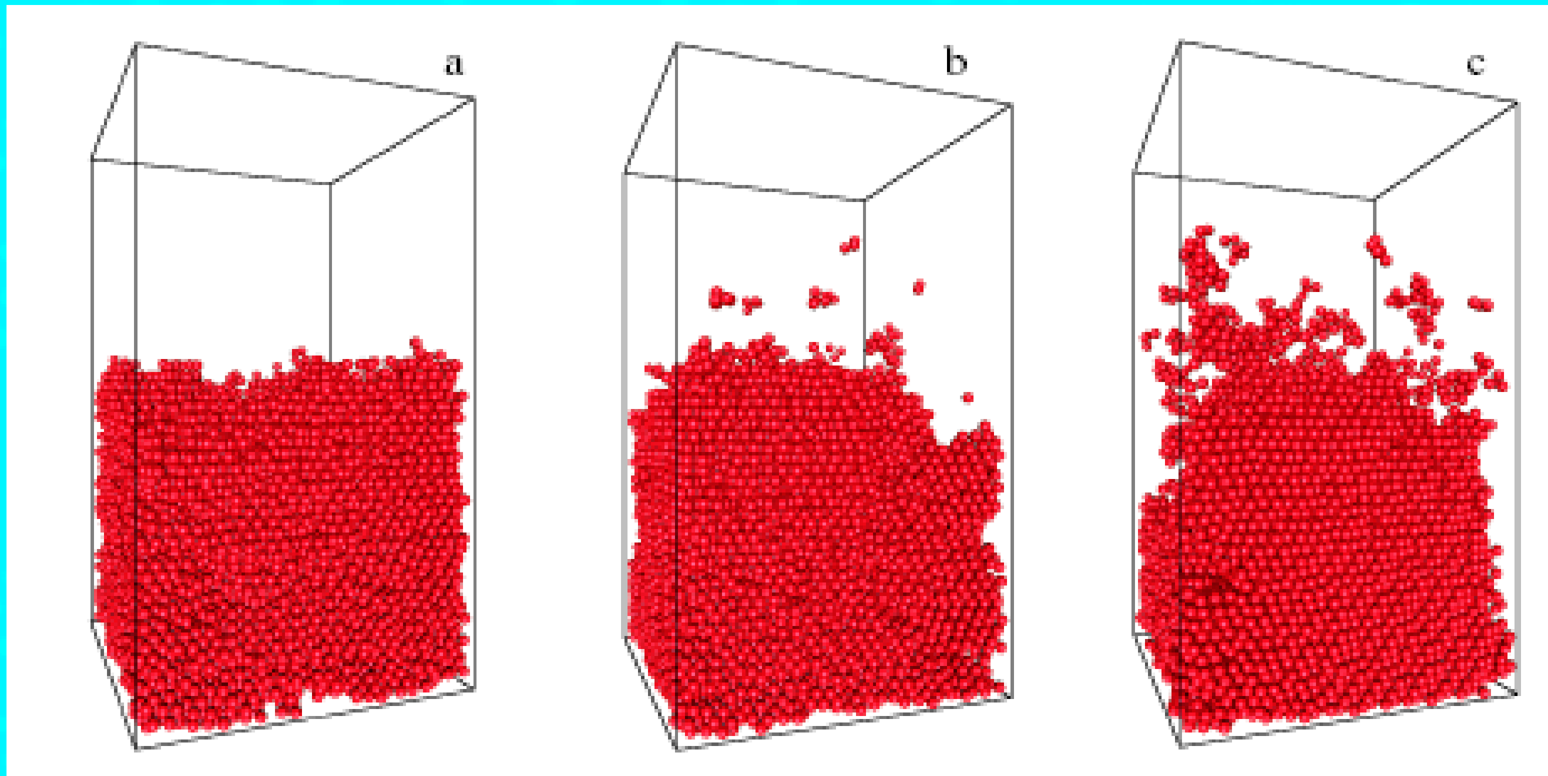
I. Wed 18 April: Interfaces p.125-138

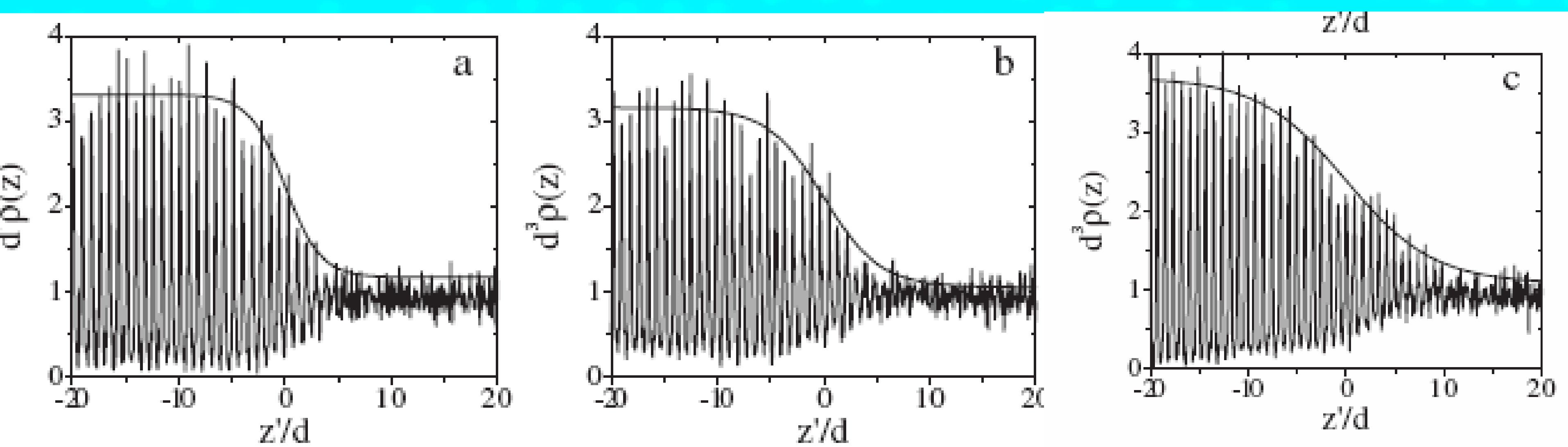
- (Molecular) origin of interfacial tension
- Interface thermodynamics:
  Gibbs Adsorption eq / adsorption isotherms
  Excess properties
- Interfacial density profile

II. Th 19th: Surfactants & association colloids p.139-161

- Surfactants
- Micelles – critical micelle concentration
- Microemulsions – curvature elasticity

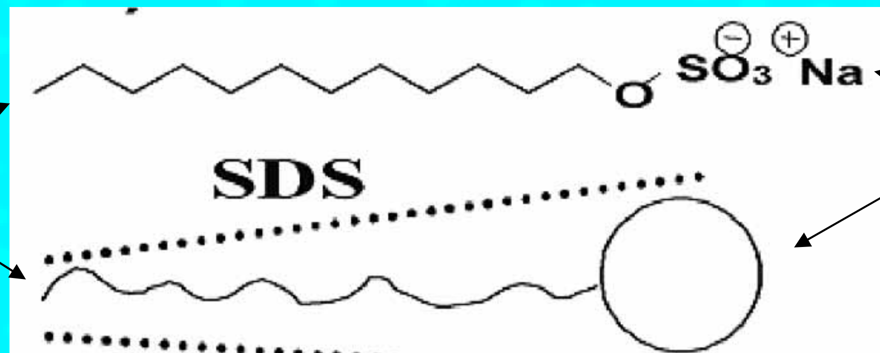
Fluid-crystal interface [RPA Dullens, DGAL Aarts, WKK, Phys. Rev. Lett **97,** 228301, (2006)]





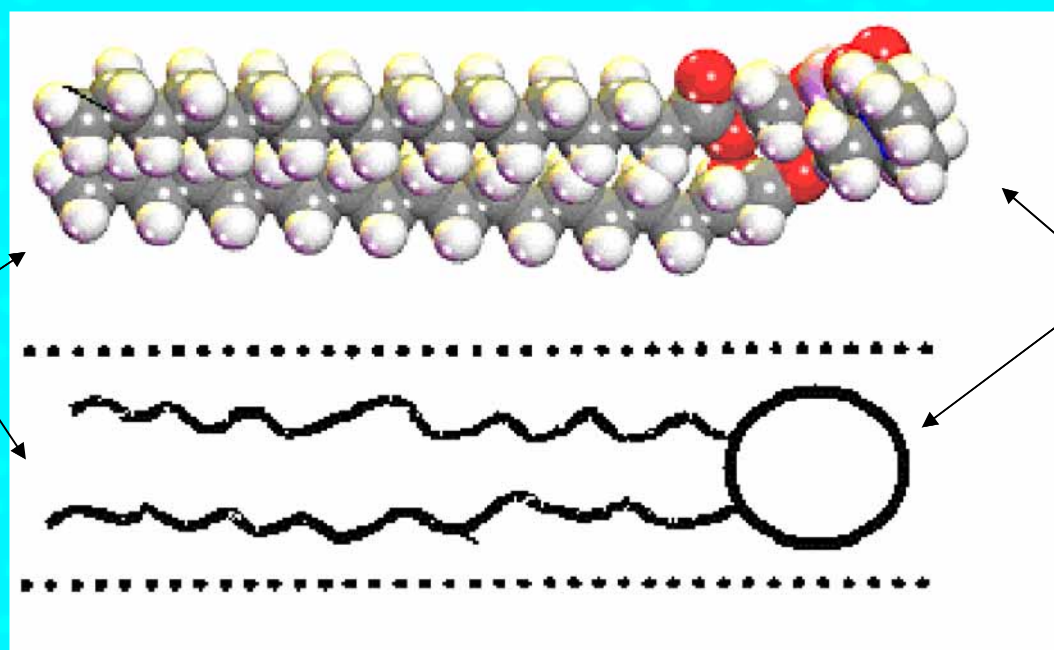
Surfactant molecules

Hydrophobic
(C_{12})
“tail”



Hydrophilic
(ionic)
“head”

Two
hydrophobic
“tails”



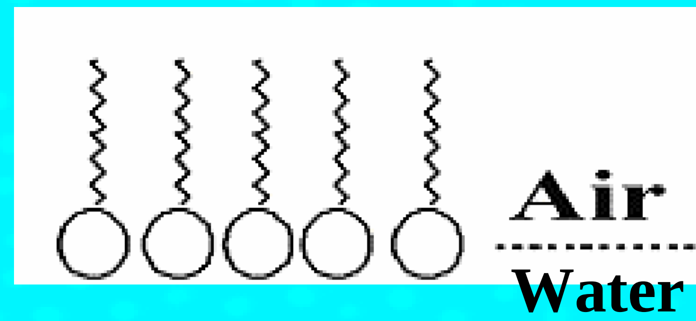
Hydrophilic
(nonionic)
“head”

Some commonly used surfactants

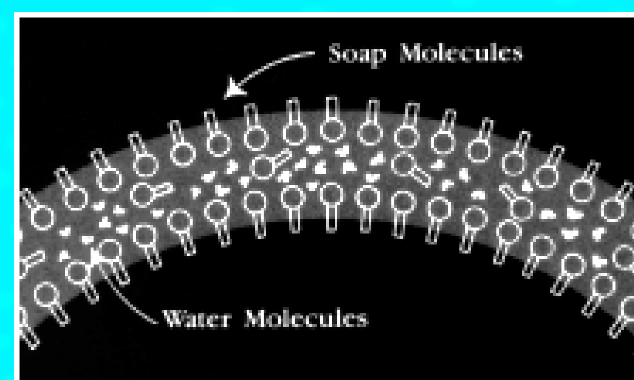
Name and Type	*Chemical structure*	*Short*	*CMC / M (25 °C)*
Anionic			
sodium dodecyl sulfate	$C_{12}H_{25}$–OSO_3^- Na^+	SDS, $C_{12}SO_4Na$	8.1×10^{-3}
sodium dodecanoate	$C_{11}H_{23}$–C(=O)O^- Na^+	$C_{11}CO_2Na$	2.5×10^{-3}
Cationic			
hexadecyl trimethylammonium Bromide	$C_{16}H_{33}$–$N(CH_3)_3^+$ Br^-	CTAB	9.2×10^{-4}
Nonionic			
decyl octaethylene Glycol	$C_{10}H_{21}(OCH_2CH_2)_8OH$	$C_{10}E_8$	1.0×10^{-3}
dodecyl hexaethylene Glycol	$C_{12}H_{25}(OCH_2CH_2)_6OH$	$C_{12}E_6$	8.7×10^{-5}

Surfactants tend to sit at interfaces

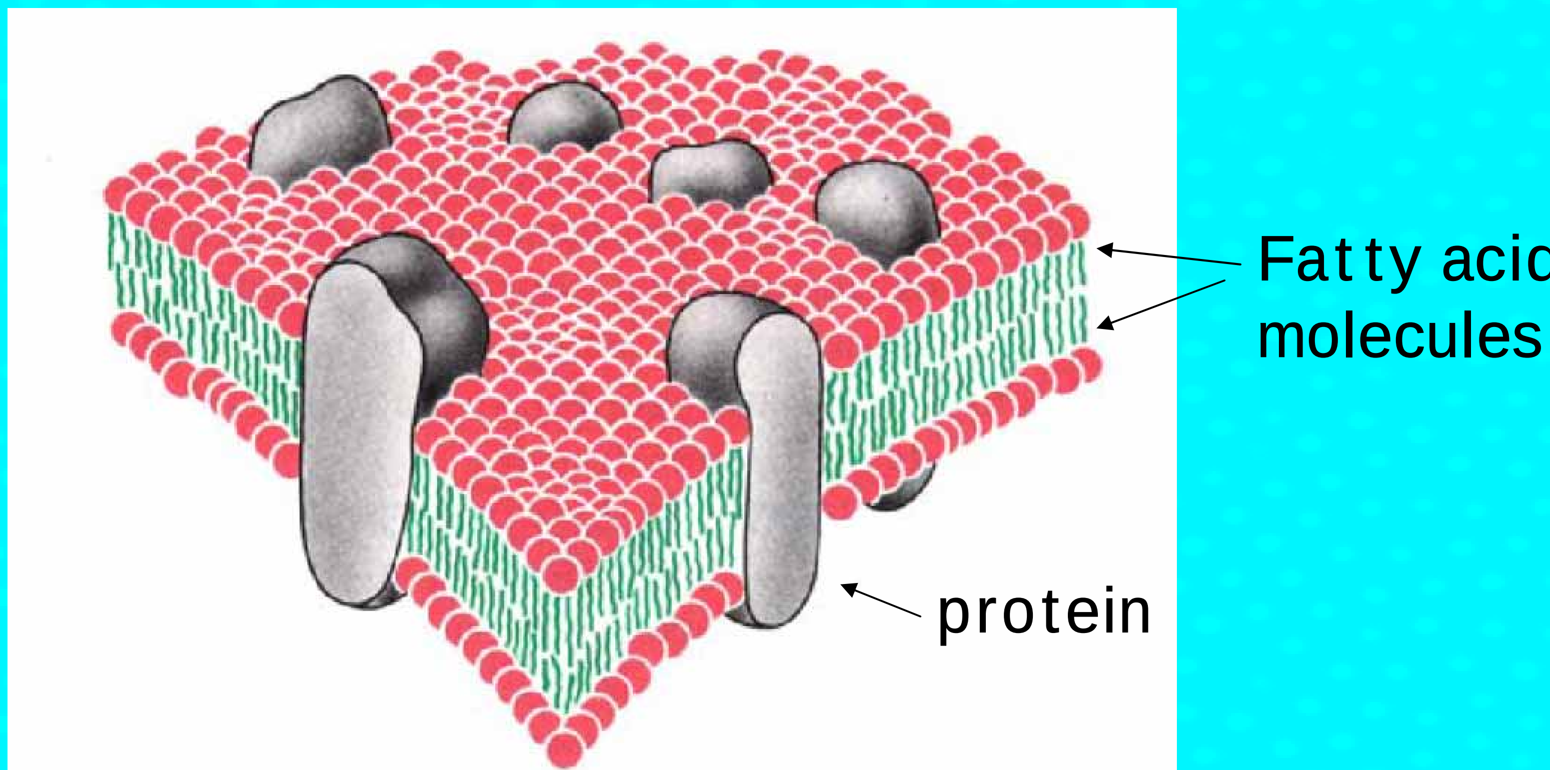
monolayer



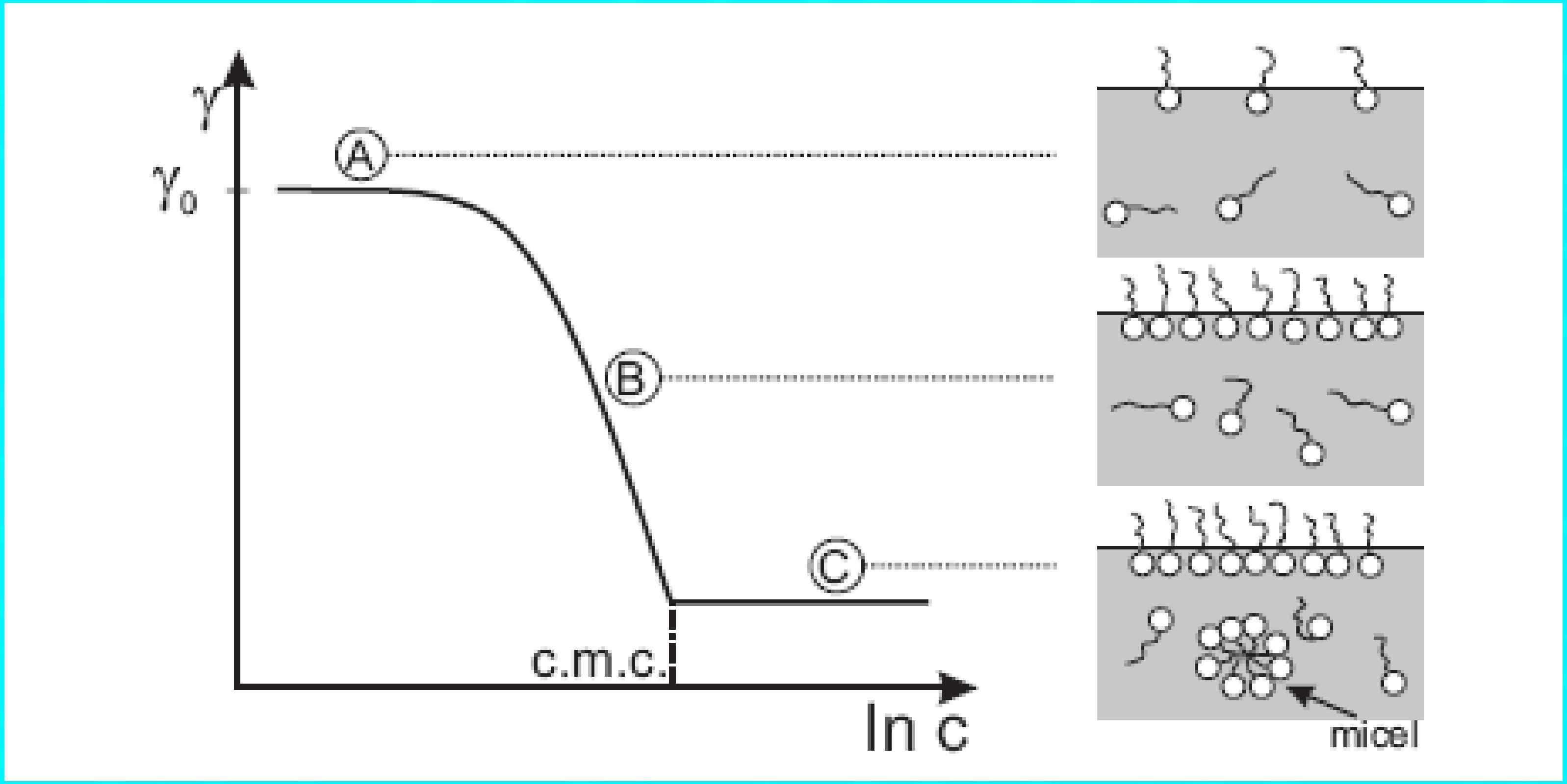
bubble / soap film

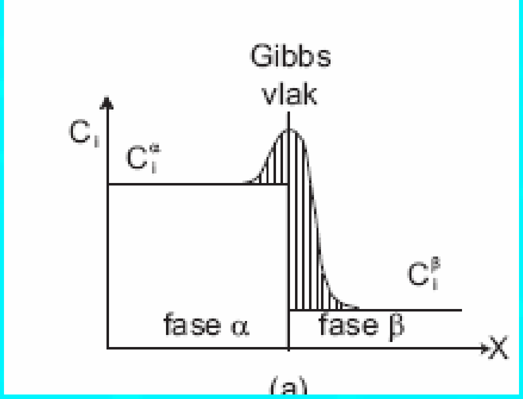


Celmembranes are (mainly) surfactant bilayers



Adsorption of surfactants at interfaces





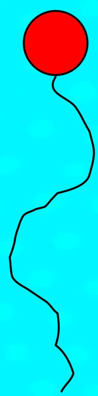
micelles (archetypical self-assembly)

LIGHT SCATTERING IN SOAP SOLUTIONS

By P. Debye*

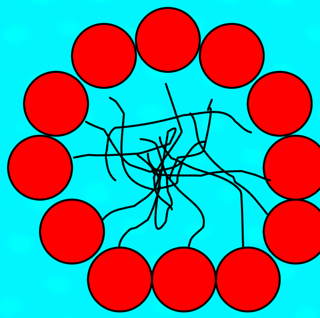
Baker Laboratory, Cornell University, Ithaca, New York

[Ann. NY Acad. Sci. **51**, 575, (1949)]



Consider the following idealized reaction between fatty ions A and micelles A_n, where n is the number of fatty ions per micelle:

$$nA \rightleftarrows A_n \tag{9}$$



If we let c_n be the concentration of micelles, c_1 the concentration of unaggregated paraffin chains, and c the total concentration of fatty ions the following relationships hold:

$$\frac{c_1^n}{c_n} = K \tag{10}$$

$$c = c_1 + nc_n \tag{11}$$

K is the equilibrium constant. It has been assumed that, for this simple treatment, activity coefficients are equal to unity.

The equilibrium constant K has the dimension of a concentration to the power $(n - 1)$. We write $K = c_0^{n-1}$ and express our concentrations as multiples of c_0. For the relative concentrations

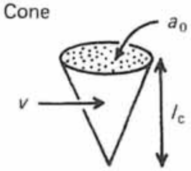
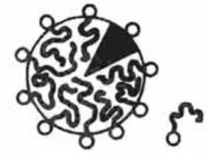
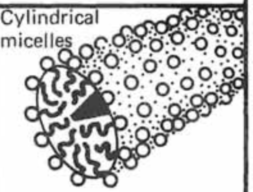
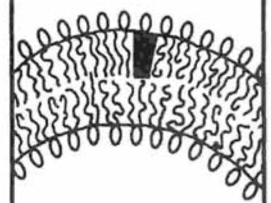
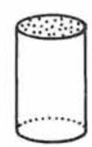
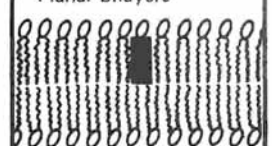
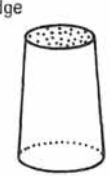
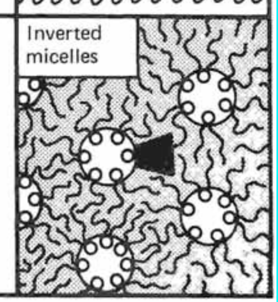
$$\gamma_1 = \frac{c_1}{c_0}, \qquad \gamma_n = \frac{cn}{c_0}, \qquad \gamma = \frac{c}{c_0}, \tag{12}$$

the relations

$$\gamma_1^n = \gamma_n, \qquad \gamma_1 + n\gamma_n = \gamma \tag{13}$$

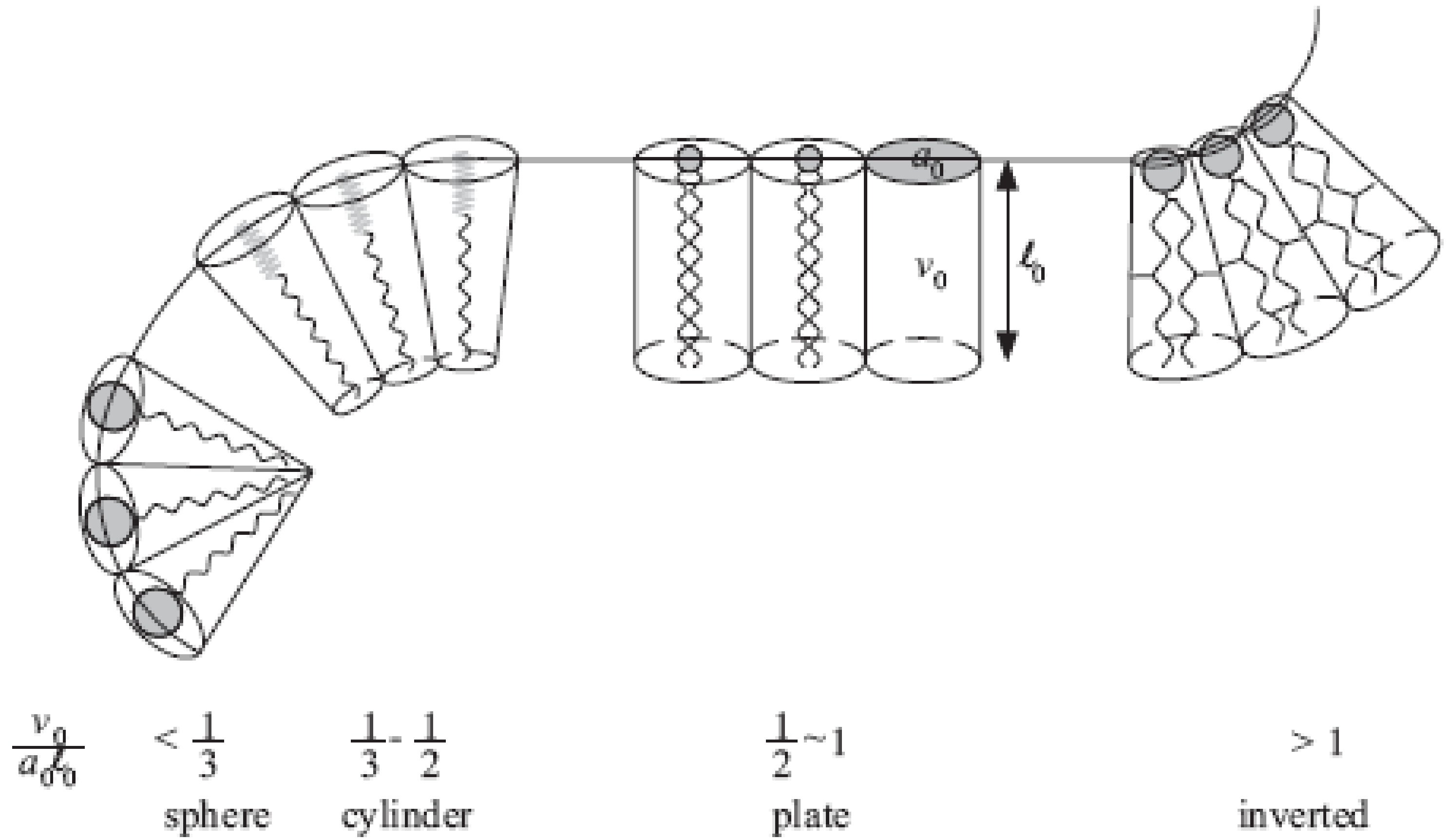
hold.

For very large values of n, it turns out that the relative concentration γ_1 of the monomer is equal to γ for $\gamma < 1$. From $\gamma = 1$ on the concentration γ_1 remains constant. The relative concentration of the polymeric particle, on the other hand, is 0 from $\gamma = 0$ to $\gamma = 1$ and equal to $\gamma - 1$ from there on. It is seen that $\gamma = 1$ corresponds to a critical point and we shall have to identify c_0 with the critical concentration.

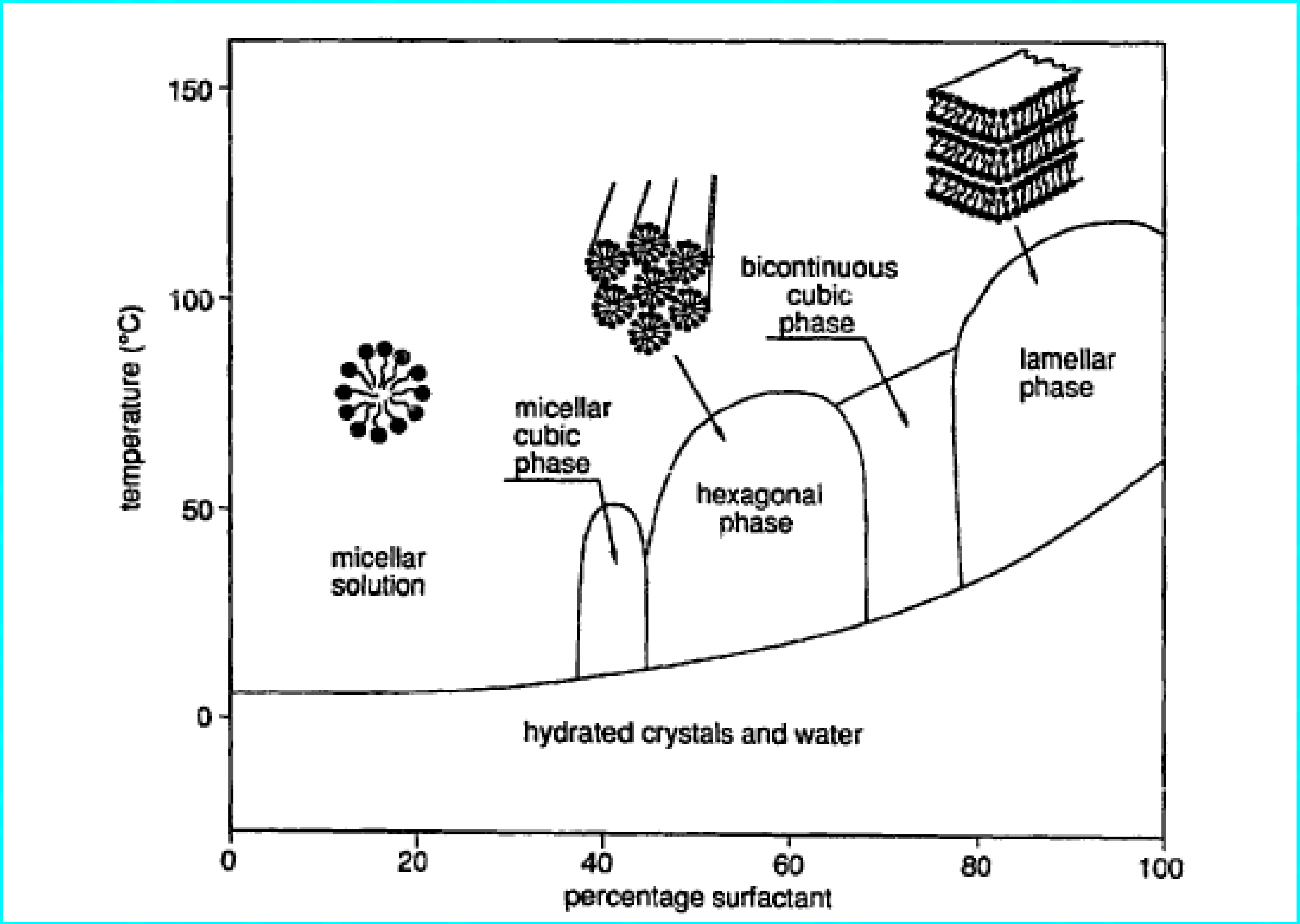
Lipid	Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone 	Spherical micelles 
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3–1/2	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 

[a] DGDG, digalactosyl diglyceride, diglucosyl diglyceride.
[b] MGDG, monogalactosyl diglyceride, monoglucosyl diglyceride.

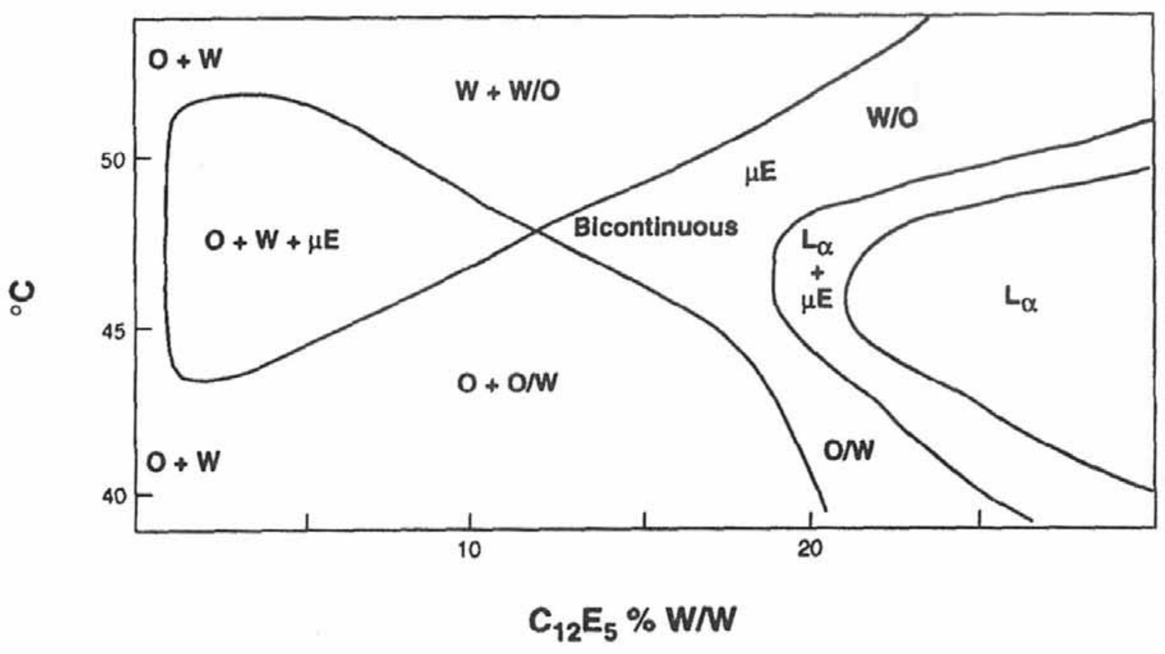
'Surfactant parameter' & micelle shape

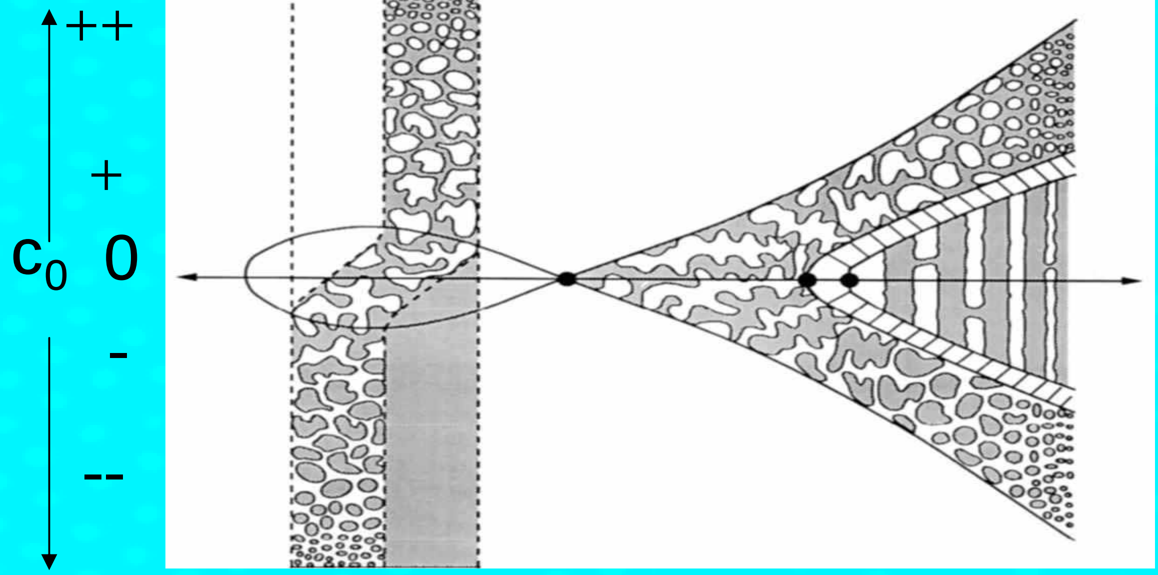


High(er) surfactant concentrations: (liquid) crystals



Microemulsions





‘Plumbers nightmare’ (Schwartz minimal surface)