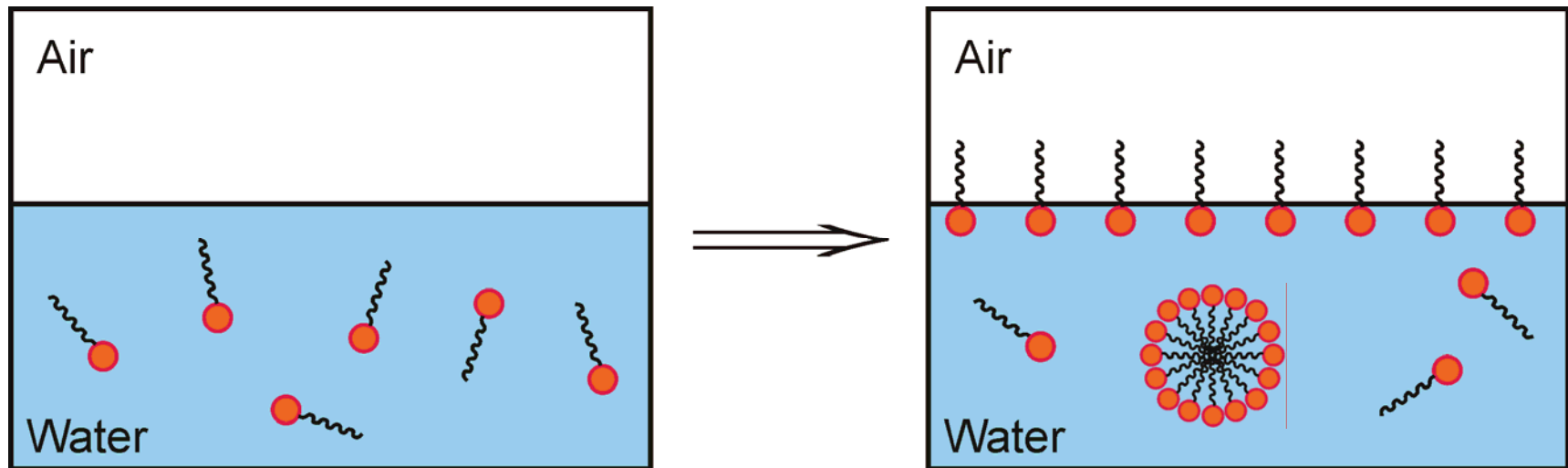


SURFACTANT ADSORPTION

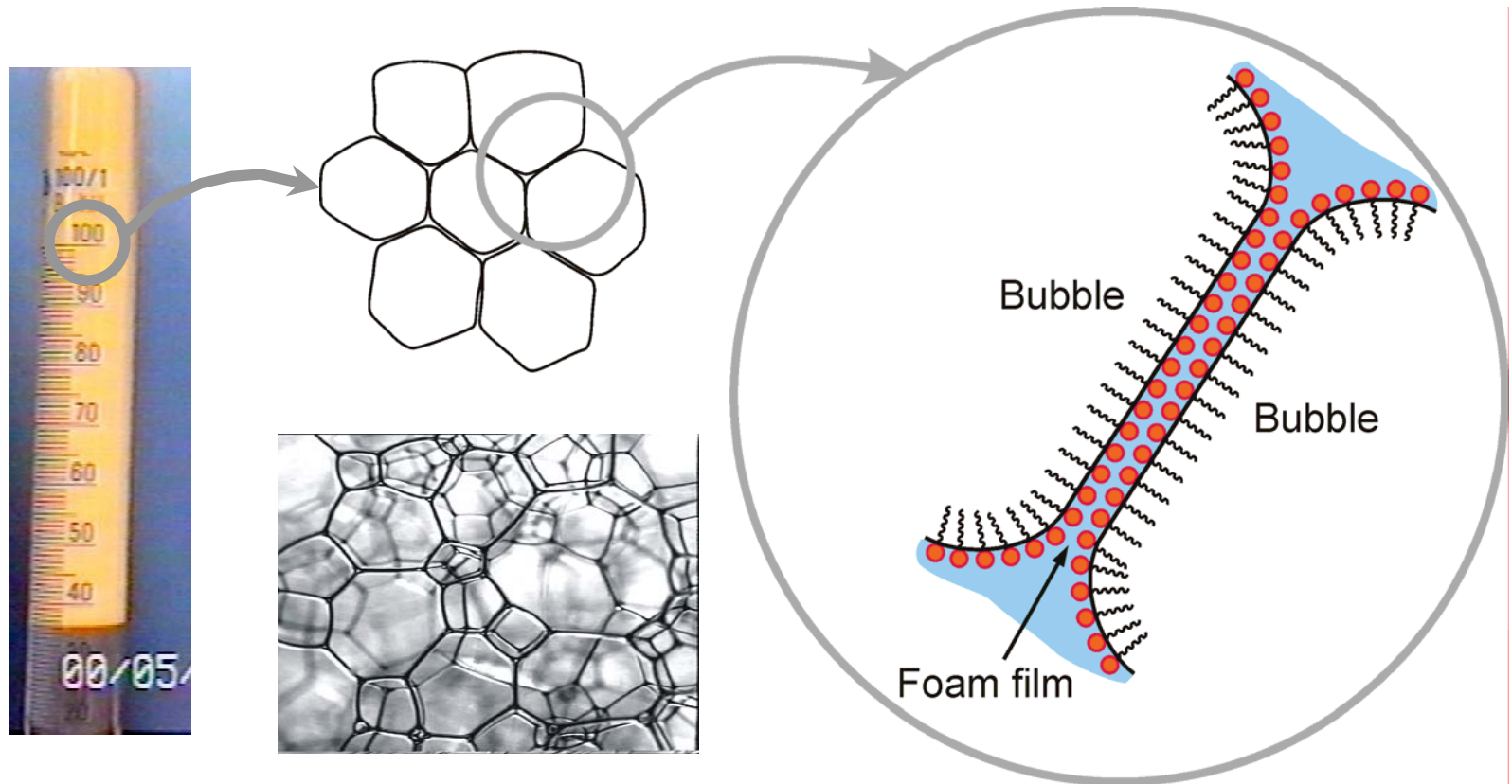
Surfactant =

substance composed of surface active molecules
(spontaneously adsorb and decrease surface tension)



Why are the surfactants so important ?

Ensure foam stability:



Affect all foam properties!

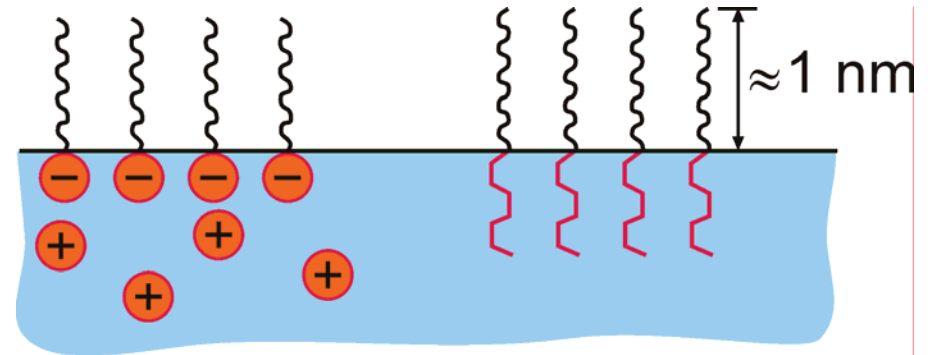
Can be used for control of foam behavior!

Types of surfactant

1. Low molecular mass (≈ 200 to 1000)

Ionic 

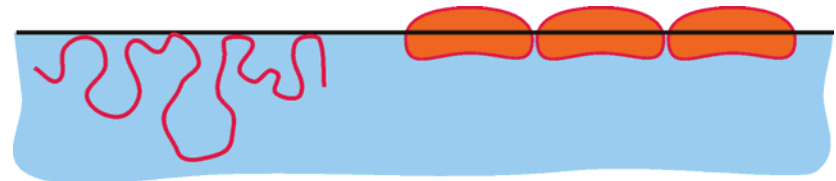
Nonionic 



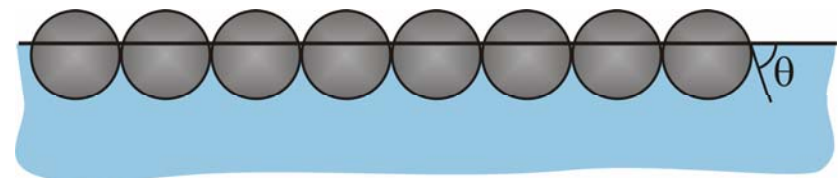
2. Polymeric (including proteins)

Fibrillar

Globular



3. Solid particles



Aims of presentation:

- 1. To describe the phenomena of surfactant adsorption and aggregation in solutions.**
- 2. Role of surfactants in foams (introduction).**

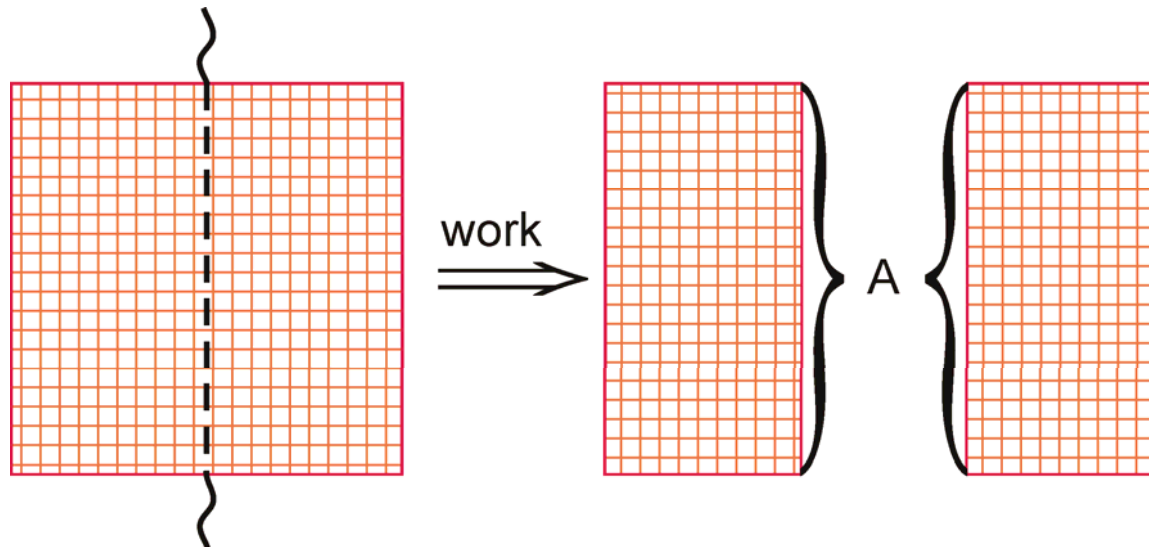
CONTENTS

- A. Surface tension and surfactant adsorption.**
- B. Kinetics of surfactant adsorption.**
- C. Surfactants in foams – illustrative examples.**

A. Surface tension and surfactant adsorption

Surface tension - energetical and force approaches.

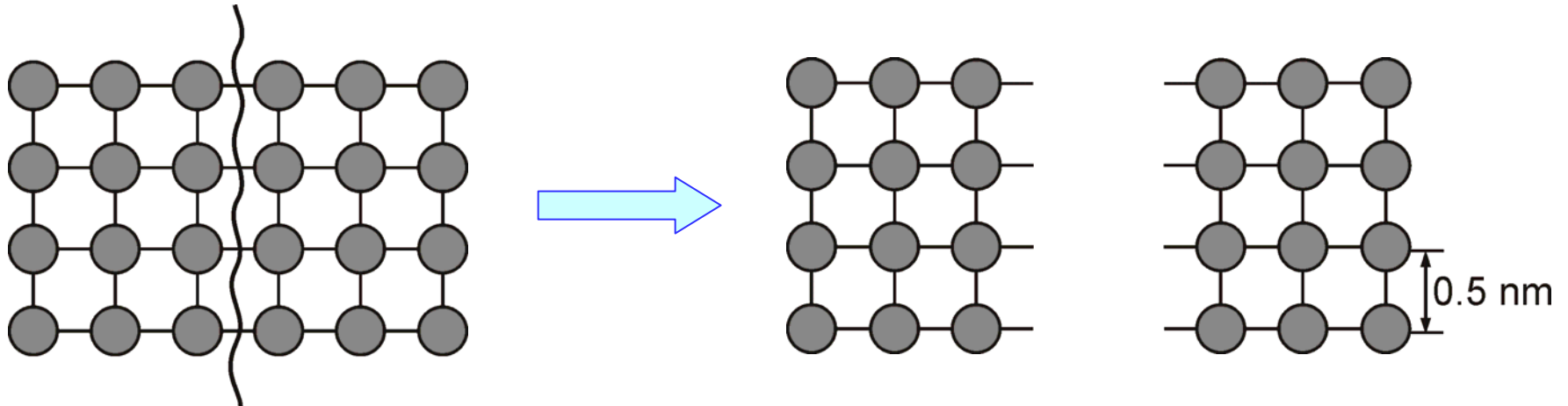
1. Energetical approach



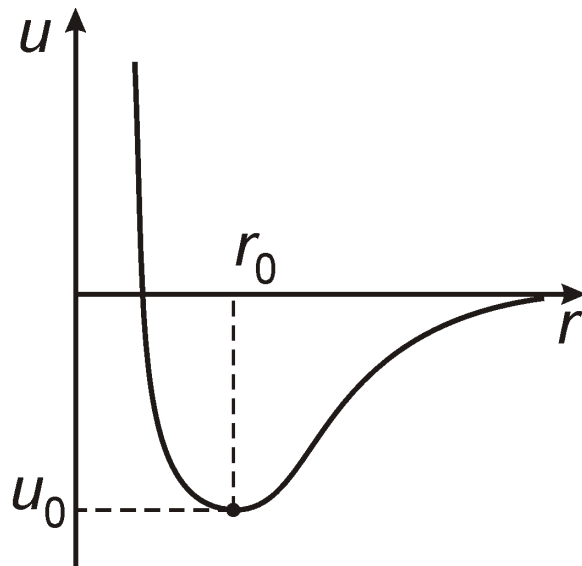
$$\text{Work} = 2\sigma A$$

σ - interfacial energy per unit area [J/m^2]

Molecular interpretation of energetical approach



Intermolecular interaction energy



Surface energy as an excess energy

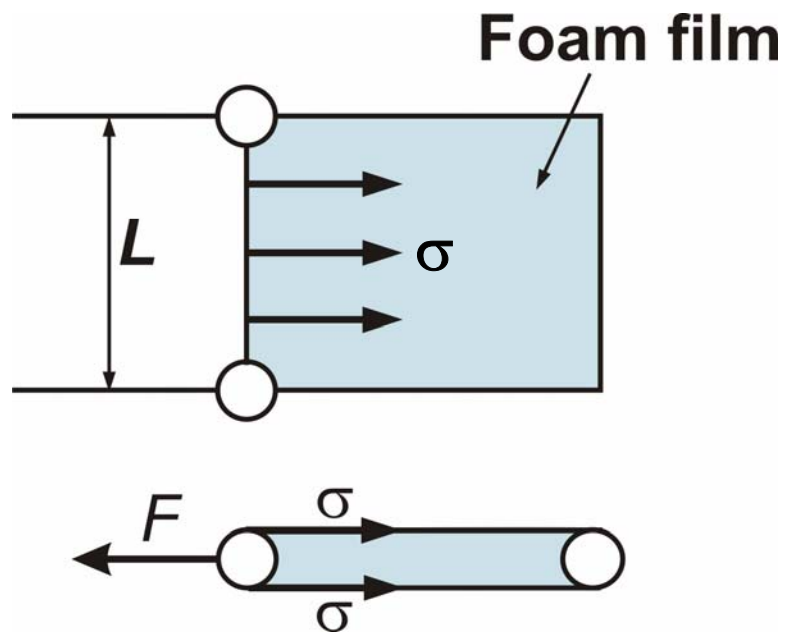
$$G = N_B (\mu_0 - 6u_0) + N_S (\mu_0 - 5u_0)$$

$$= N_{TOT} \underbrace{(\mu_0 - 6u_0)}_{\mu_B} + \underbrace{N_S u_0}_{\text{surface energy} = \sigma A}$$

$$\sigma \approx N_S u_0 / A \approx 200 \text{ mJ/m}^2$$

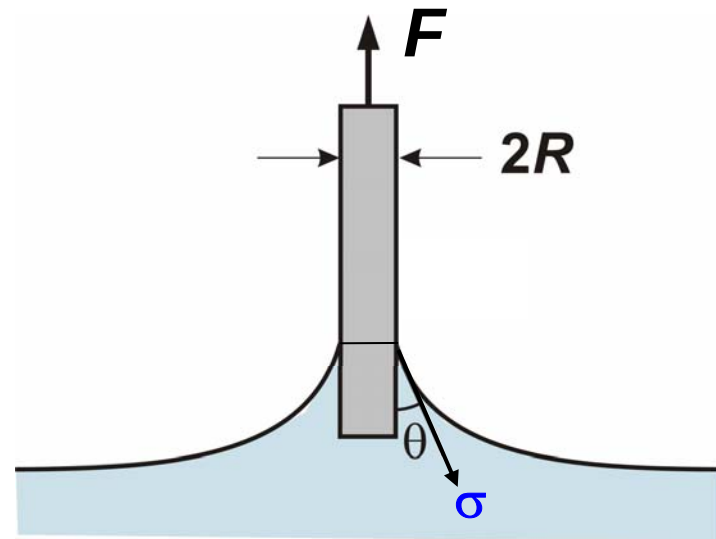
2. Force approach

Surface tension of liquids as a tangential force



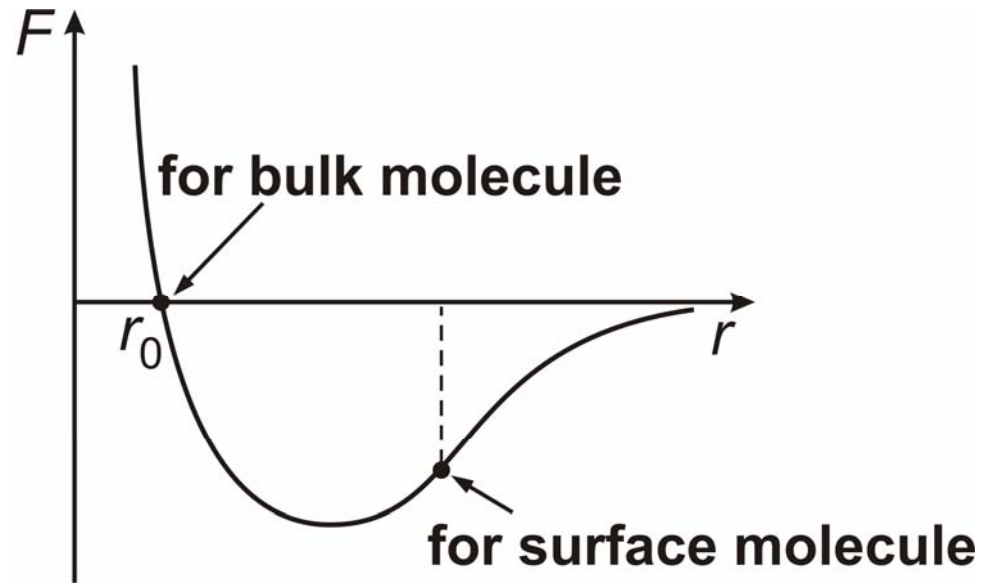
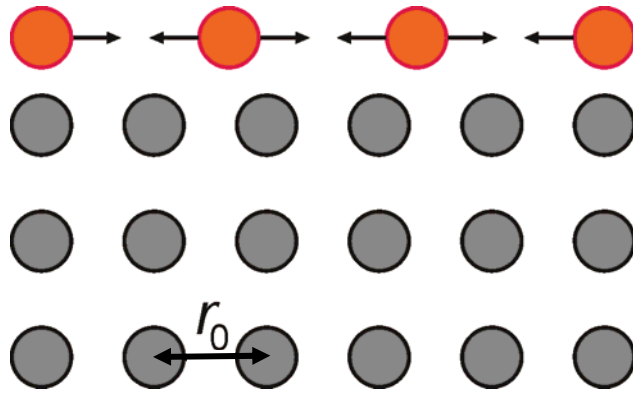
$$F = 2\sigma L$$

$$\sigma = (F / 2L) \text{ [N/m]}$$



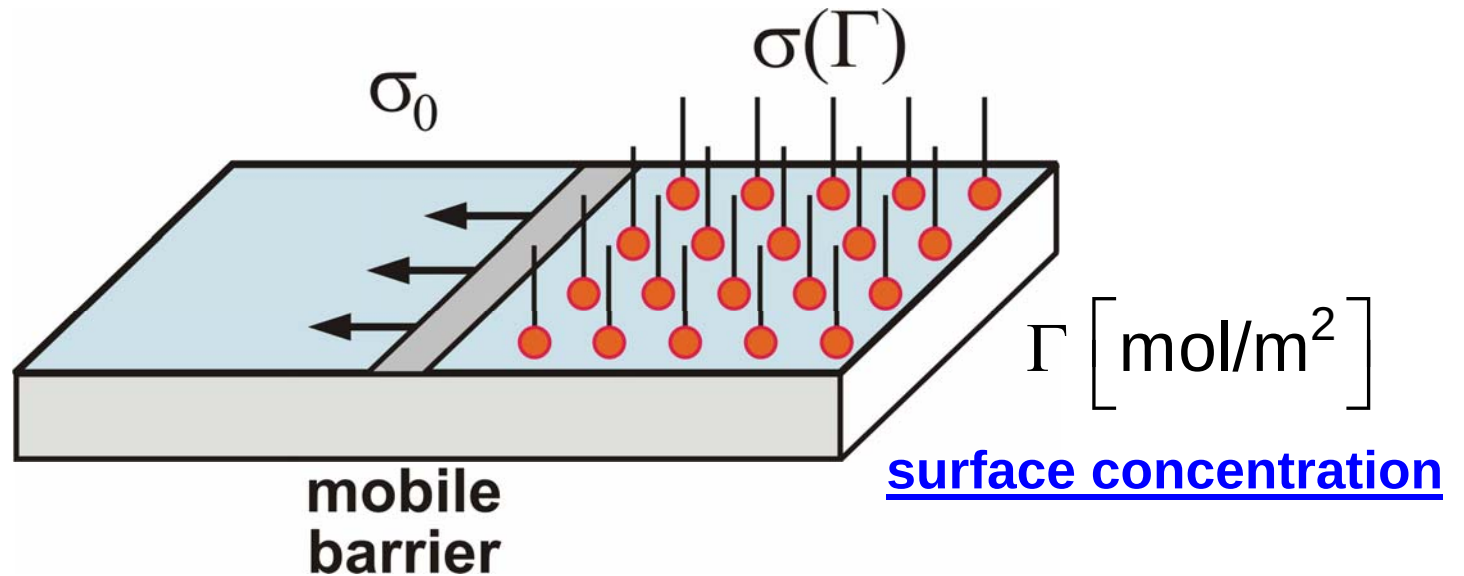
$$F = mg + 2\pi R\sigma \cos \theta$$

Where does this tangential force come from?

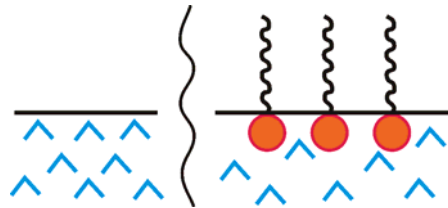


Surface tension of spread surfactant monolayers (Langmuir-trough)

$$F = (\sigma_0 - \sigma)L$$



Effect of
surfactants



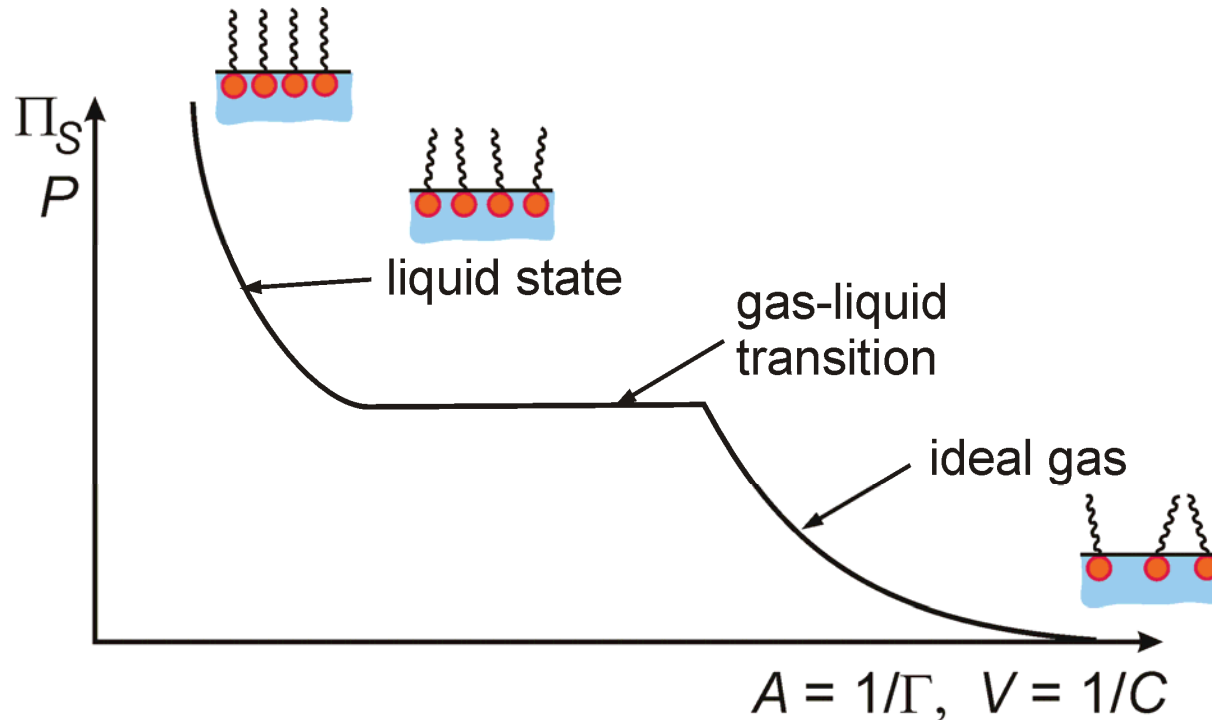
$W/A \Rightarrow W/S/A$

Surface pressure

$$\Pi_S \equiv (\sigma_0 - \sigma)$$

Related to
Marangoni effect

Analogy between surface and bulk pressures



Dilute monolayers

Ideal adsorption layer

$$\Pi_S(\Gamma) = \Gamma k_B T$$

Ideal gas

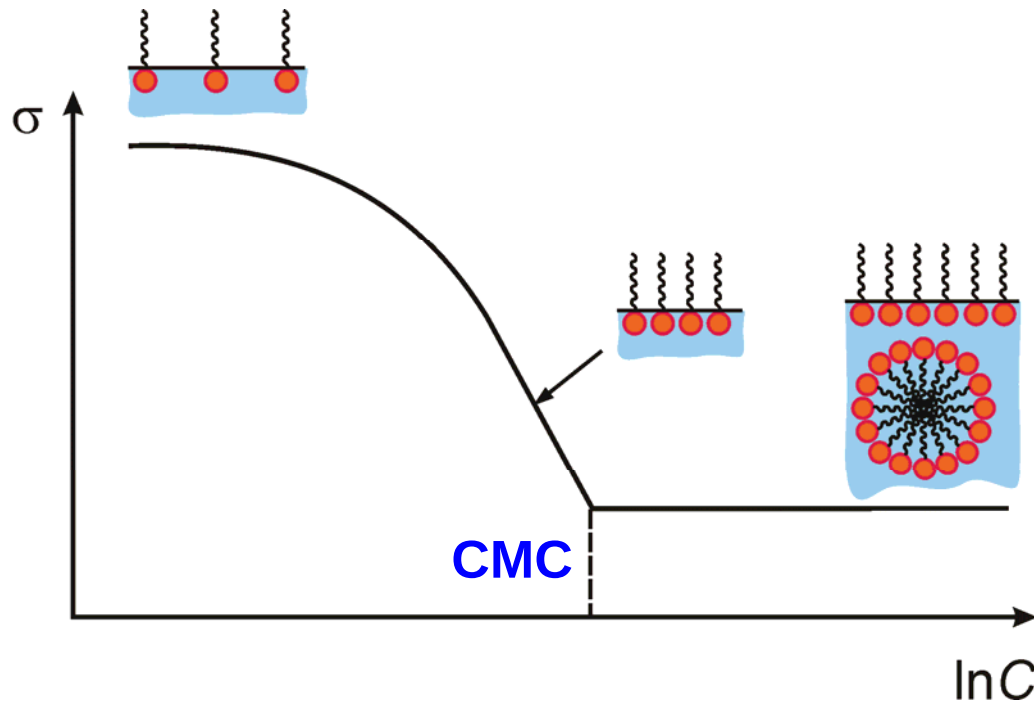
$$P(C) = C k_B T$$

Concentrated monolayers

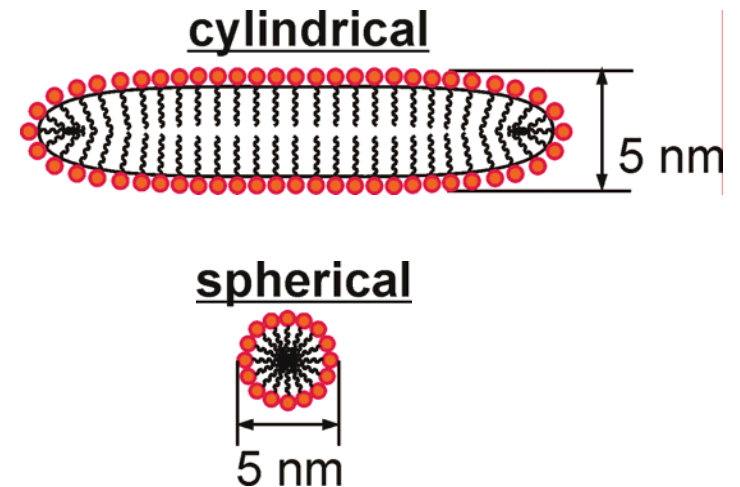
$$(\Pi_S - \beta/A^2)(A - A_\infty) = k_B T \quad - \text{2D van der Waals}$$

$$(P - a/v^2)(v - v_\infty) = k_B T \quad - \text{3D van der Waals}$$

Typical results for soluble surfactants and data interpretation



Micelle formation



Gibbs adsorption isotherm

$$d\sigma = -\Gamma d\mu \approx -\Gamma k_B T d \ln C$$

$$\mu = \mu_0 + k_B T \ln C$$

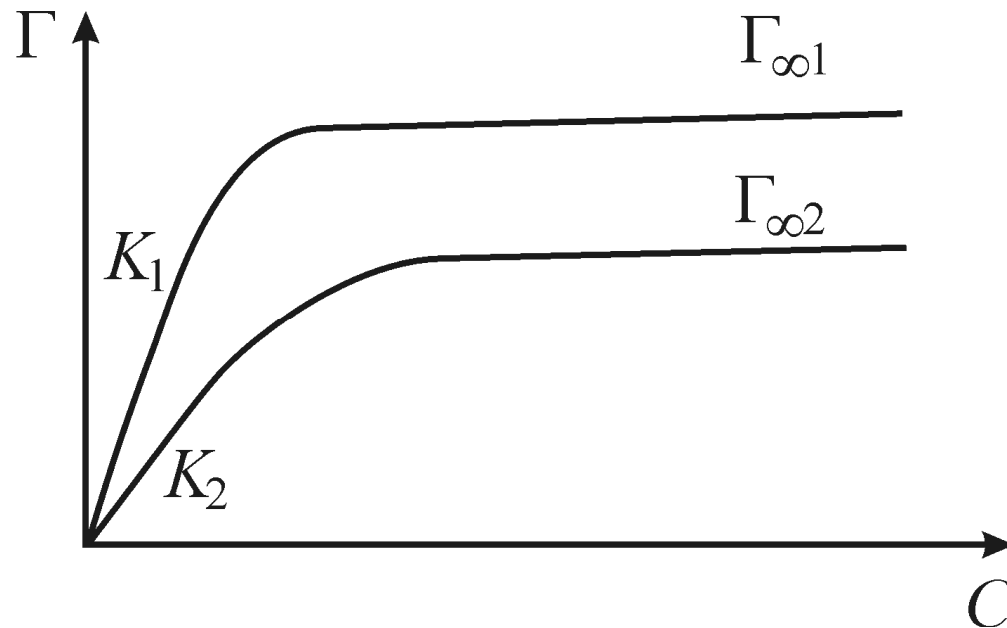
(Gibbs-Duhem for the surface phase)

Model adsorption isotherms

Langmuir $\Gamma(C) = \Gamma_{\infty} \frac{KC}{1+KC}$ $d\sigma = -k_B T \Gamma d \ln C$

Surface tension isotherm

$$\sigma(C) = \sigma_0 - \int_0^C k_B T \Gamma_{\infty} \frac{K}{1+KC} dC = \sigma_0 - k_B T K \Gamma_{\infty} \ln(1+KC)$$



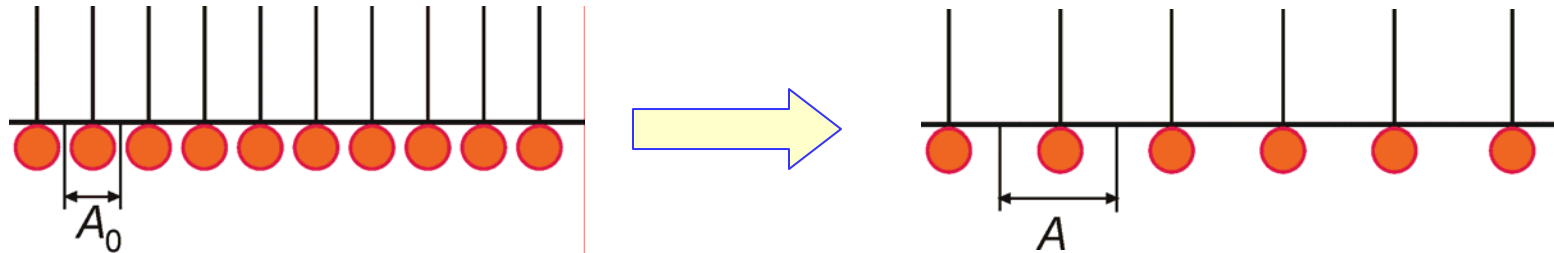
Assumptions:

- Localized adsorption.
- Non-interacting molecules.

Model adsorption isotherms

Type of isotherm	Surfactant adsorption isotherm	Surface equation of state
Henry	$KC = \frac{\Gamma}{\Gamma_{\infty}}$	$\Pi_S = \sigma_0 - \sigma = k_B T \Gamma$
Langmuir	$KC = \frac{\Gamma}{\Gamma_{\infty} - \Gamma}$	$\Pi_S = k_B T \Gamma_{\infty} \ln \left(\frac{\Gamma_{\infty}}{\Gamma_{\infty} - \Gamma} \right)$
Volmer	$KC = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp \left(\frac{\Gamma}{\Gamma_{\infty} - \Gamma} \right)$	$\Pi_S = k_B T \Gamma_{\infty} \frac{\Gamma}{\Gamma_{\infty} - \Gamma}$
Frumkin	$KC = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp \left(-\frac{2\beta\Gamma}{k_B T} \right)$	$\Pi_S = k_B T \Gamma_{\infty} \ln \left(\frac{\Gamma_{\infty}}{\Gamma_{\infty} - \Gamma} \right) - \beta\Gamma^2$
van der Waals	$KC = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp \left(\frac{\Gamma}{\Gamma_{\infty} - \Gamma} - \frac{2\beta\Gamma}{k_B T} \right)$	$\Pi_S = k_B T \Gamma_{\infty} \frac{\Gamma}{\Gamma_{\infty} - \Gamma} - \beta\Gamma^2$

Gibbs elasticity of adsorption monolayers



Insoluble monolayer

$$E_G = + \frac{d\sigma}{d \ln A}$$

Soluble monolayer

$$E_G = - \frac{d\sigma}{d \ln \Gamma} = \frac{d\Pi_S}{d \ln \Gamma}$$

Examples

Henry

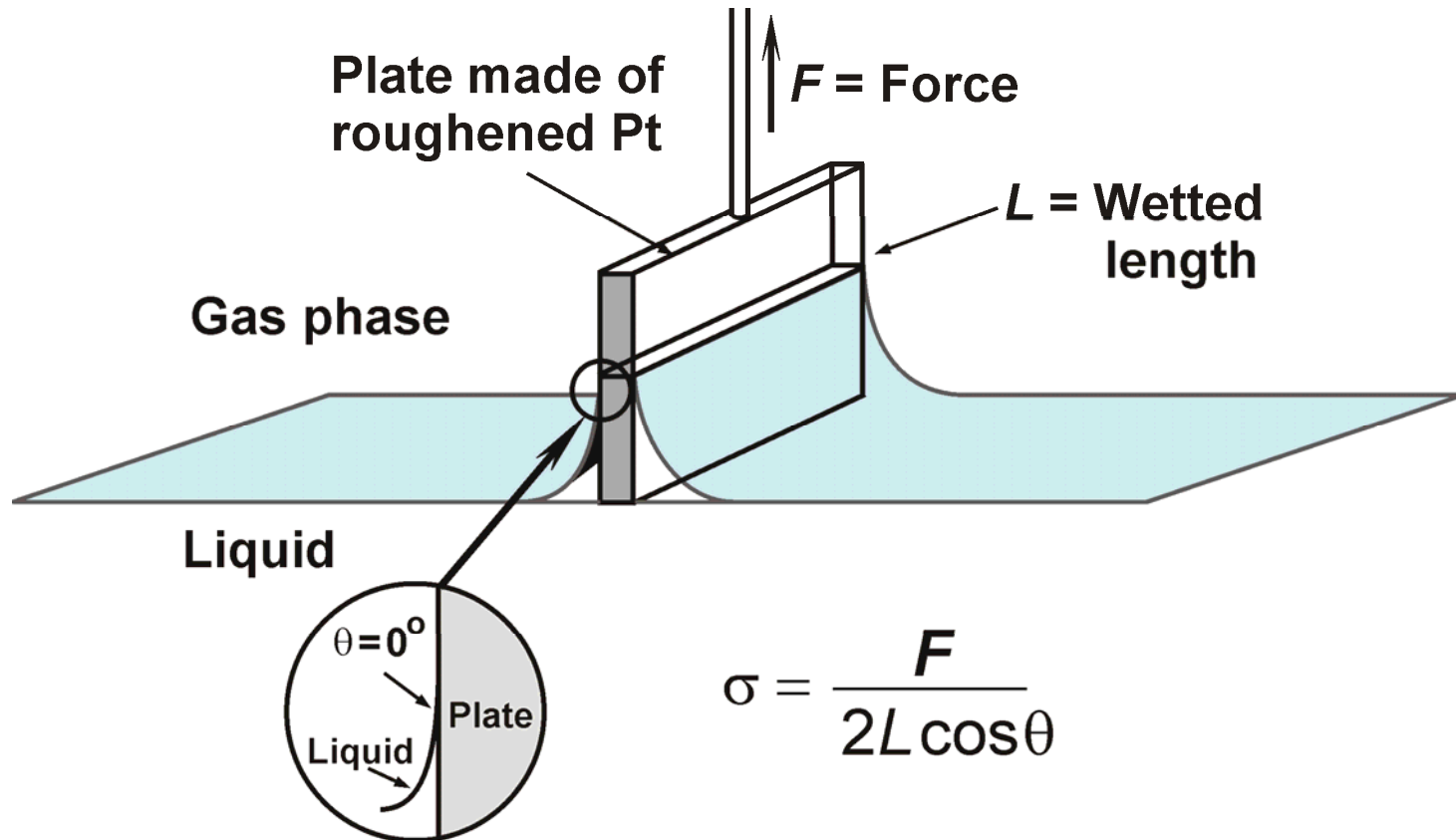
$$\Pi_S = k_B T \Gamma \Rightarrow E_G = k_B T \Gamma$$

Volmer

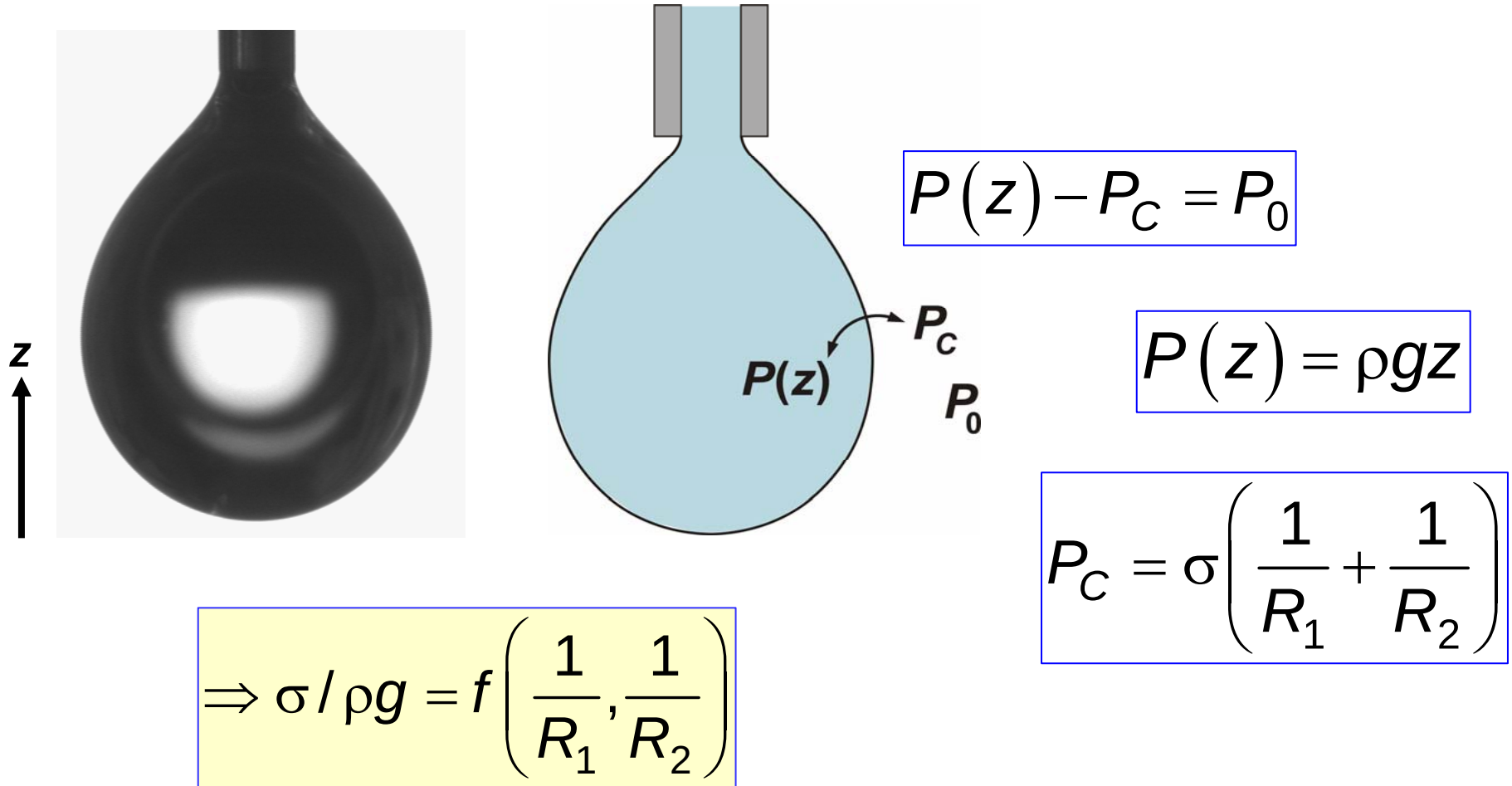
$$\Pi_S = k_B T \Gamma_\infty \frac{\Gamma}{\Gamma_\infty - \Gamma} \Rightarrow E_G = k_B T \Gamma \frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma)^2}$$

Methods for measuring the surface tension

1. Wilhelmy plate



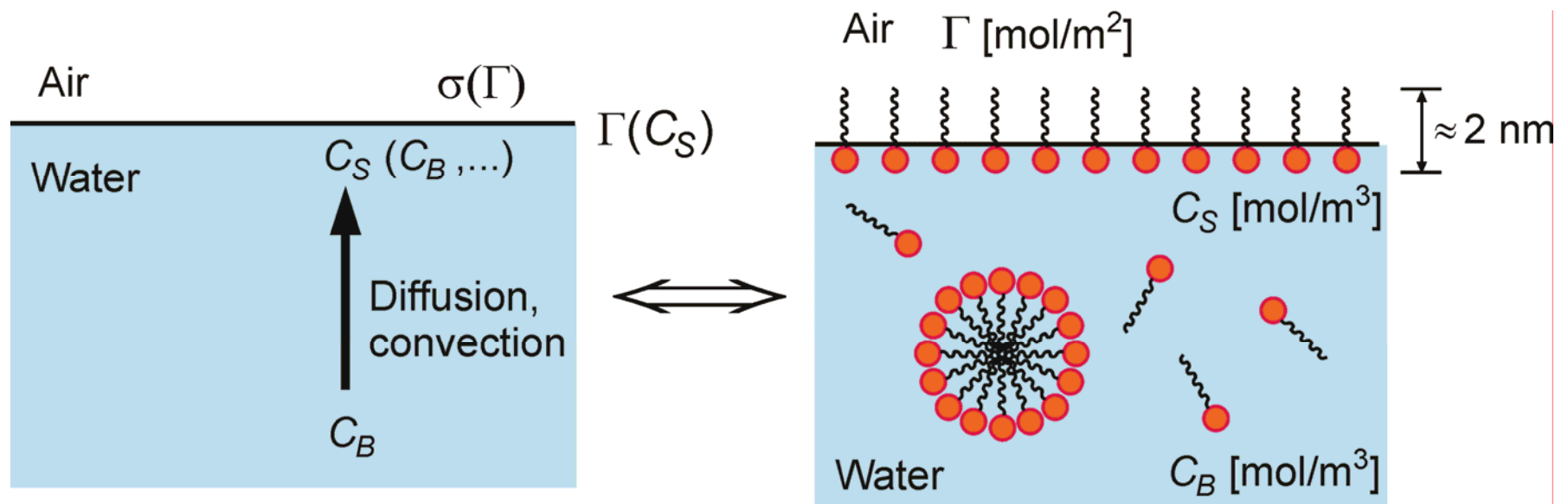
2. Pendant drop method



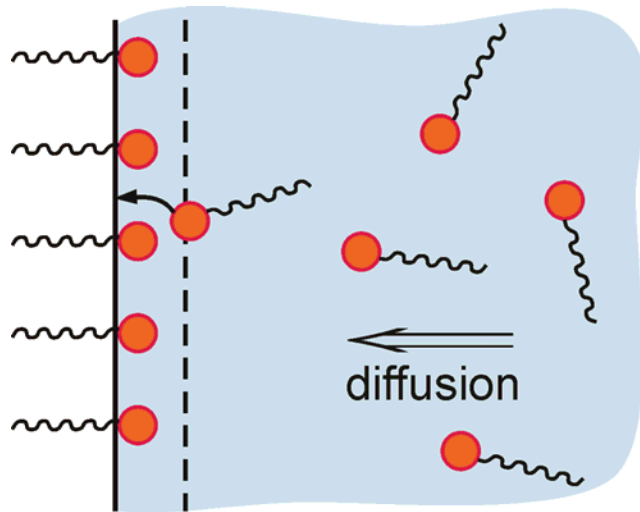
Experimental determination of $\Gamma(C)$:
ellipsometry, neutron reflection, radioactivity...

B. Kinetics of surfactant adsorption

Interrelation between macroscopic and molecular levels of description



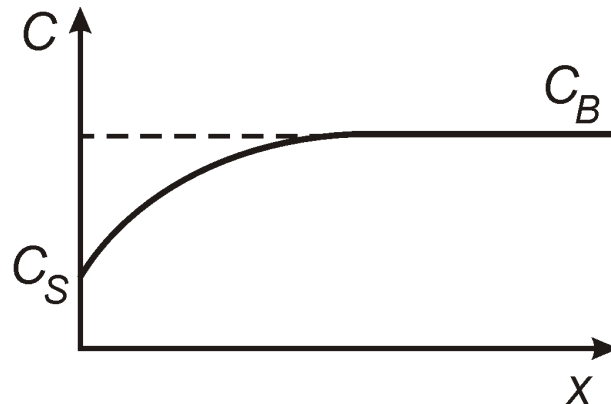
Stages of dynamic adsorption



Two consecutive stages

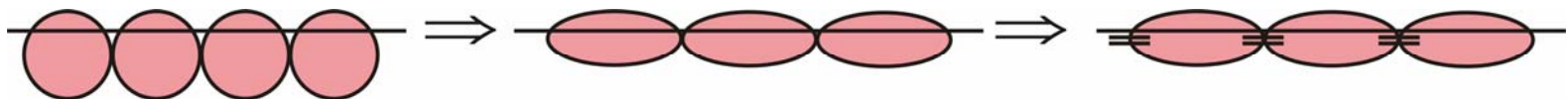
Stage 1 - adsorption from the "subsurface layer" onto surface.

Stage 2 - diffusion from the bulk to the subsurface layer



Possible additional stages

- Molecule rearrangement
- Formation of intermolecular bonds



Diffusion control of adsorption: large deviation from equilibrium

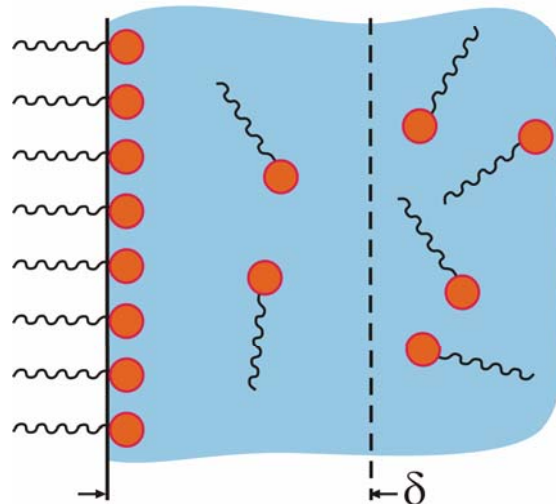
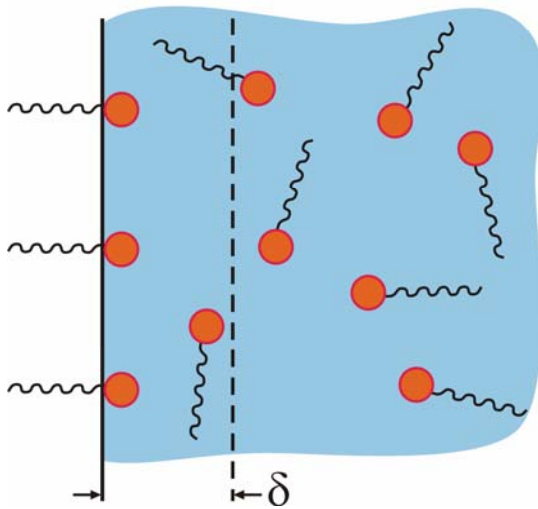
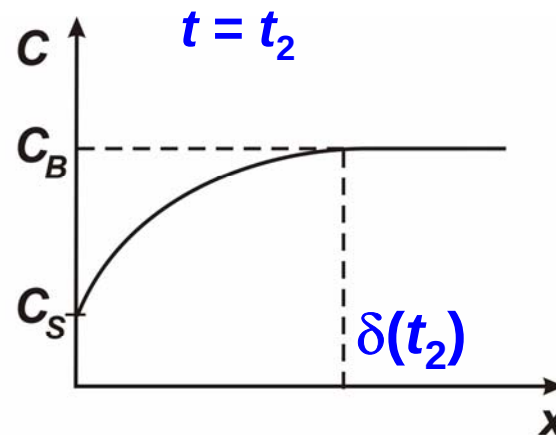
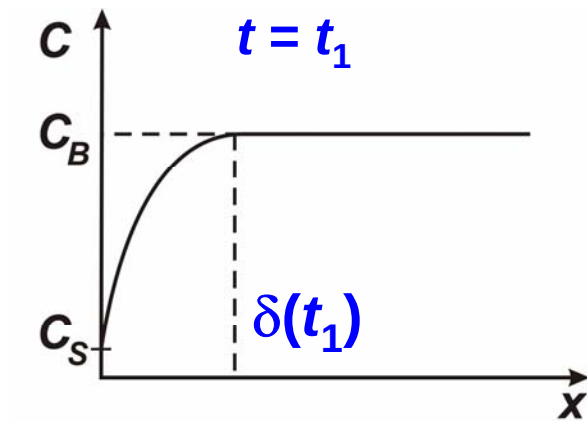
$$\Gamma = \Gamma(C_S)$$

Diffusion time

$$\delta^2(t) \sim 2Dt$$

$$\Gamma_{\infty} \sim C_B \delta_{\max}$$

$$\tau_{\text{diff}} \sim \frac{1}{D} \left(\frac{\Gamma_{\infty}}{C_B} \right)^2$$



Diffusion control of adsorption: exact solution and asymptotics

Diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Surface mass balance

$$\frac{d\Gamma}{dt} = D \left. \frac{\partial C}{\partial x} \right|_{x=0}$$

Adsorption isotherm

$$\Gamma = \Gamma(C_S)$$

Solution (Ward & Tordai)

$$\Gamma(t) = \Gamma(0) + \sqrt{\frac{D}{\pi}} \left[2C_b \sqrt{t} - \int_0^t \frac{C_S(\tau)}{\sqrt{t-\tau}} d\tau \right]$$

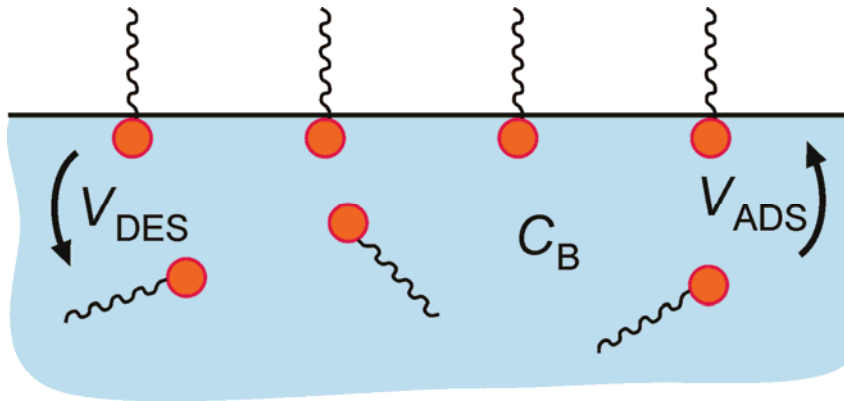
$$t \rightarrow 0$$

$$\Gamma(t) \approx 2C_B \sqrt{\frac{Dt}{\pi}} \propto \sqrt{t}$$

$$t \rightarrow \infty$$

$$\Delta\sigma(t) = \left(\frac{d\sigma}{d\Gamma} \right) \Delta\Gamma(t) = \Delta\Gamma(0) \sqrt{\frac{\tau_d}{\pi t}} \propto \frac{1}{\sqrt{t}}$$

Barrier control of adsorption



Surface mass balance

$$\frac{d\Gamma}{dt} = V_{ads}(C_B, \Gamma) - V_{des}(\Gamma)$$

Example: Langmuir adsorption

Rate of adsorption

$$V_{ads} = k_{ads} C_B (1 - \Gamma/\Gamma_{\infty})$$

Rate of desorption

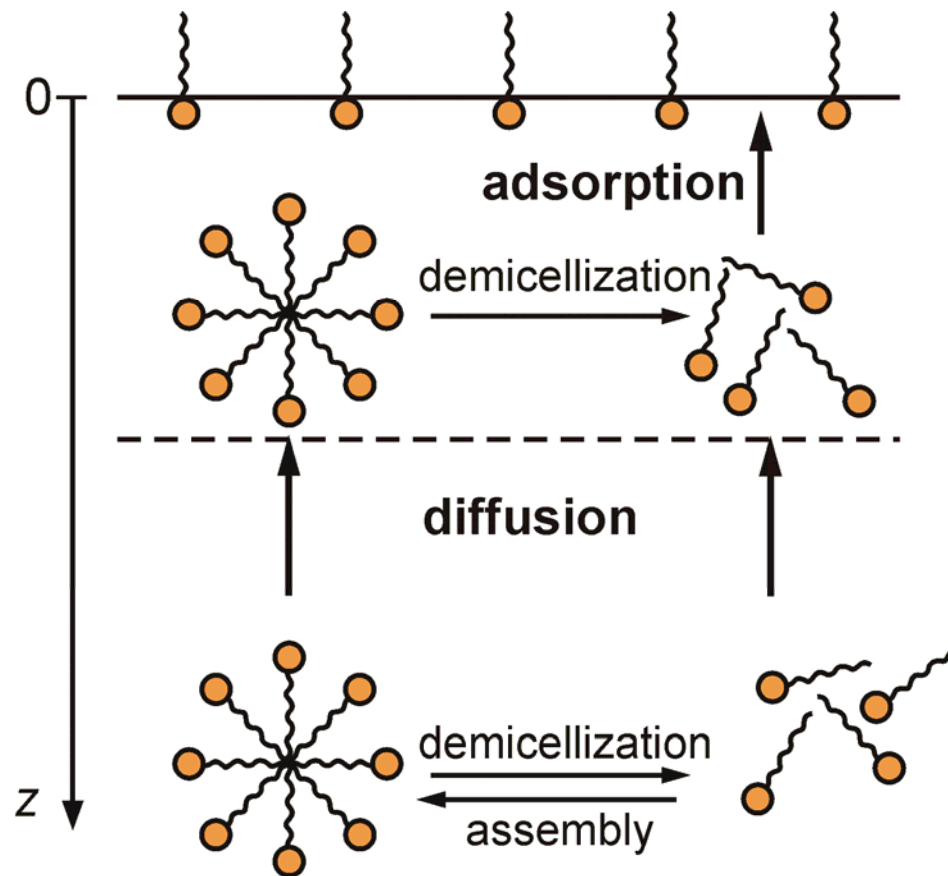
$$V_{des} = k_{des} \Gamma$$

$$\frac{d\Gamma}{dt} = k_{ads} C_B - (k_{ads} C_B / \Gamma_{\infty} + k_{des}) \Gamma$$

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} = \frac{\Delta\Gamma(t)}{\Delta\Gamma(0)} = \exp\left(-\frac{t}{\tau_b}\right)$$

$$\tau_b = \frac{\Gamma_{\infty}}{k_{des} \Gamma_{\infty} + k_{ads} C_B}$$

Adsorption from micellar solutions



Characteristic times

τ_d – diffusion of monomers

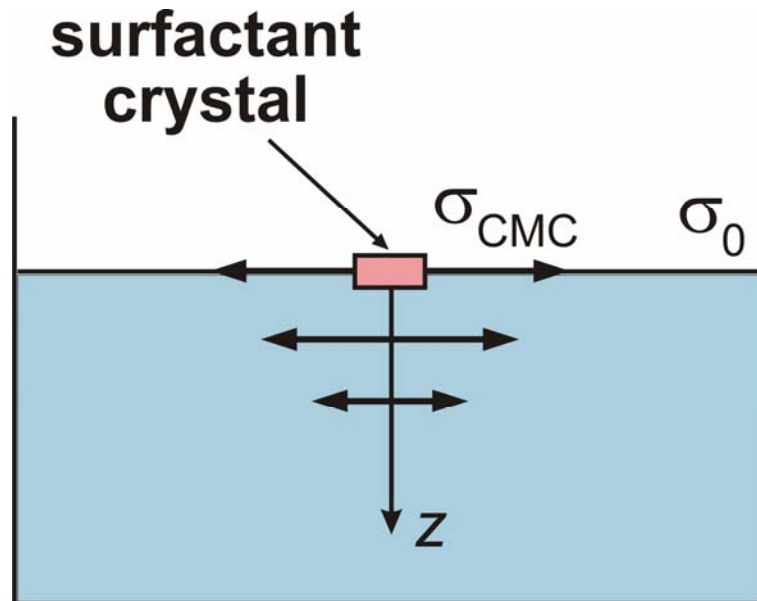
τ_{dm} - diffusion of micelles

τ_{mic} - supply of monomers
from the micelles

For ionic surfactants – msec

For nonionic surfactants - sec

Surfactant spreading and Marangoni effect



Stress balance

$$\underbrace{\tau_{surf}}_{\text{surface stress}} = \underbrace{\tau_{visc}}_{\text{viscous stress}}$$

Viscous stress

$$\tau_{visc} = \mu \left(\frac{dV_r}{dz} \right)_{z=0}$$

Surface stress

$$\tau_{surf} = \frac{d\sigma}{dr} \approx \frac{\sigma_0 - \sigma}{r}$$



Spreading velocity

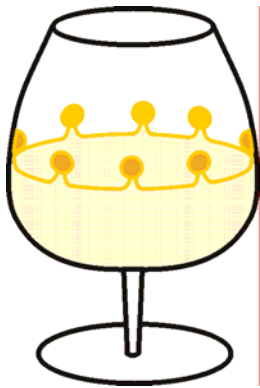
$$V_r = \left[\frac{3(\sigma_0 - \sigma)}{4\rho^{1/2}\mu^{1/2}} \right]^{1/2} t^{-1/4}$$

Marangoni effect

“Tears of wine” and Marangoni effect

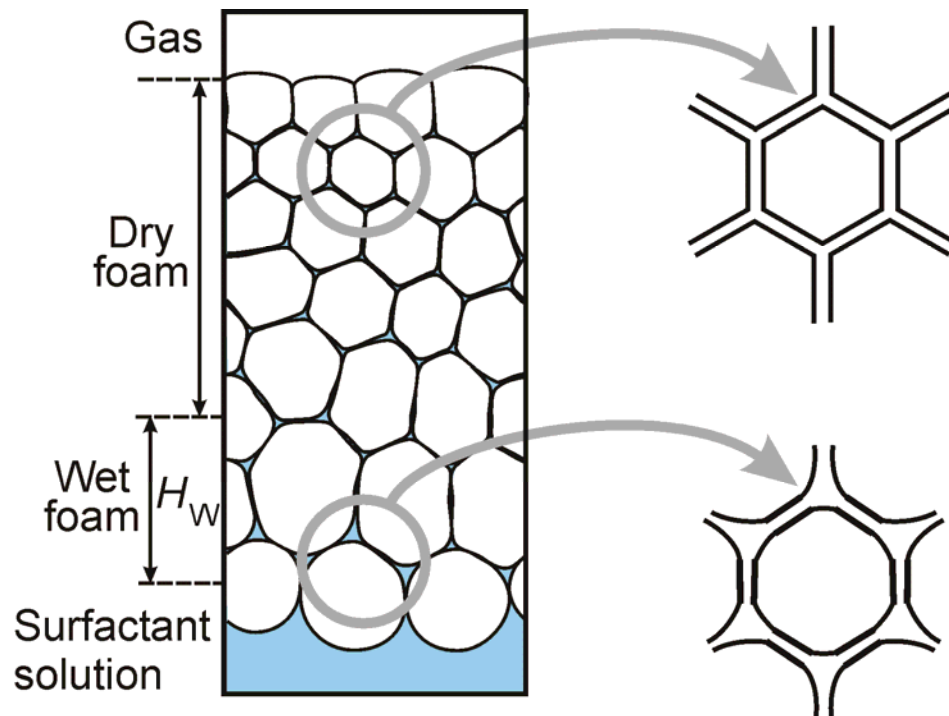
Carlo Marangoni

- James Thomson, "On certain curious motions observable on the surfaces of wine and other alcoholic liquours," *Philosophical Magazine*, 10, 330 (1855).
- Carlo Marangoni, "On the expansion of a drop of liquid floating in the surface of another liquid", PhD Thesis, Pavia, Italy, 1865.



C. Role of surfactants in foams

1. Determine the equilibrium surface tension
 $\Rightarrow$ the static foam structure.



Capillary pressure

$$P_C = 2\sigma / R_B$$

Hydrostatic pressure

$$P_H = \rho g H$$

Height of the wet foam

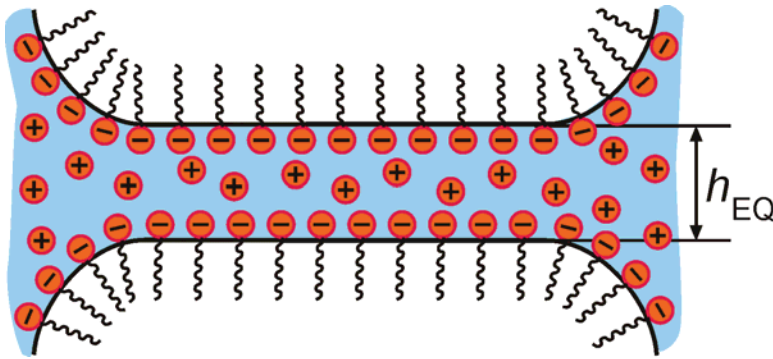
$$H_W = \frac{2\sigma}{\rho g R_B}$$

Water drainage:
(ASJ, SCA – next week)

Proteins: $\sigma \sim 50$ mN/m
Fluoro-surfactants: $\sigma \sim 15$ mN/m

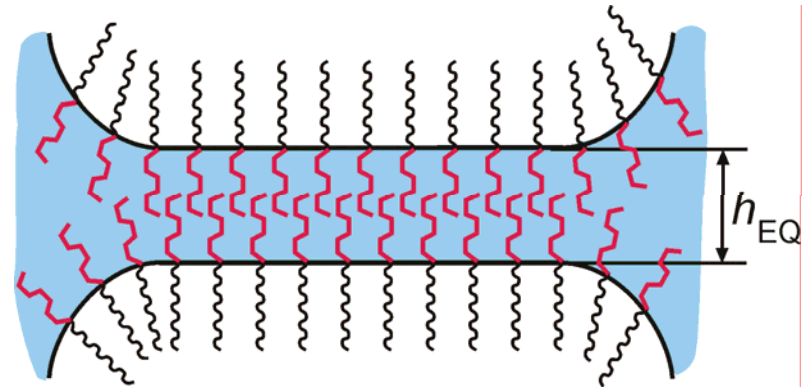
2. Static stabilization of foam films

Ionic surfactants



**Electrostatic stabilization
by ionic surfactants**

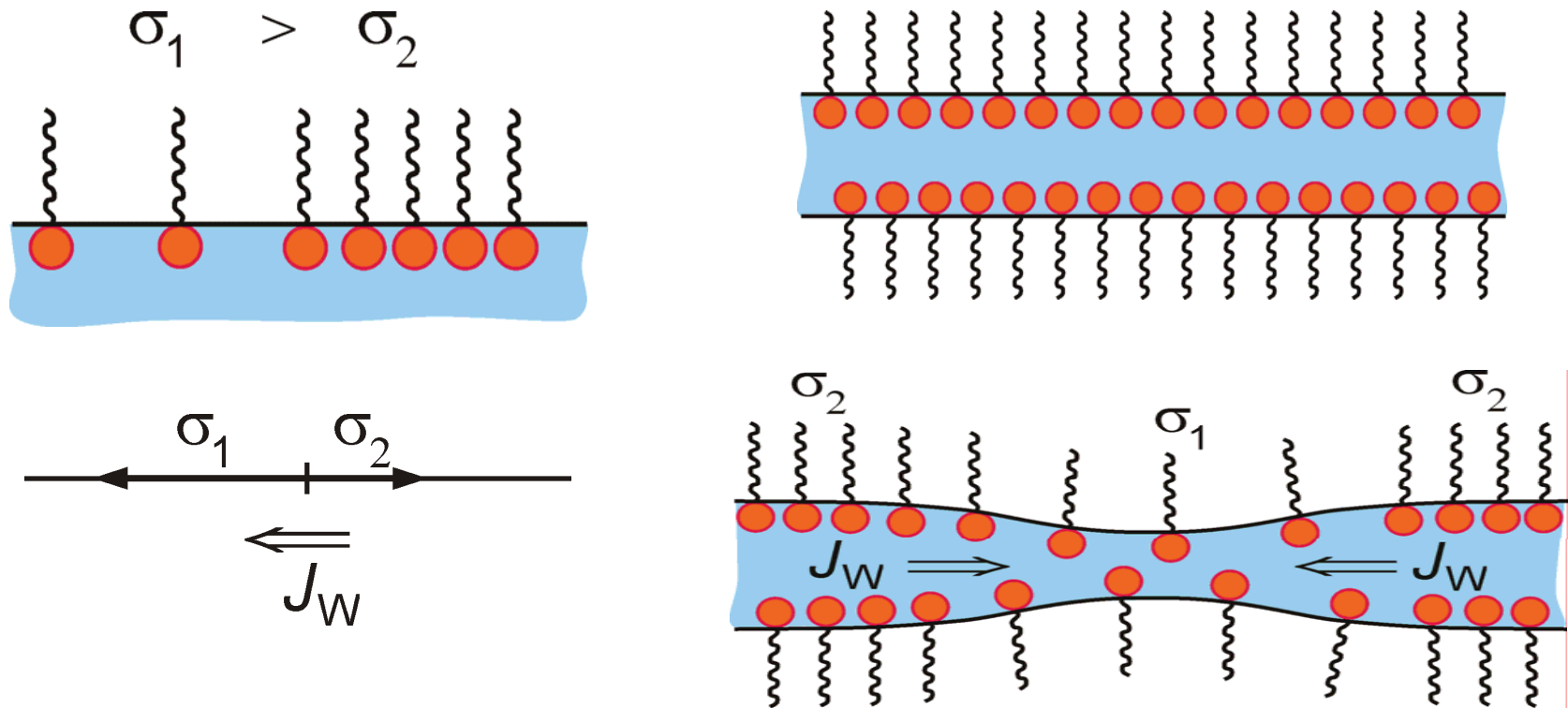
Nonionic surfactants



**Steric stabilization by
nonionic surfactants**

Static stabilization: ASJ and ND in Thursday

3. Dynamic stabilization of the foam films by Marangoni effect



**Damped local perturbations in the film thickness
due to Marangoni effect
 $\Rightarrow$ Slower film drainage and higher stability**

4. Effect of surfactants on the dynamic phenomena in foams

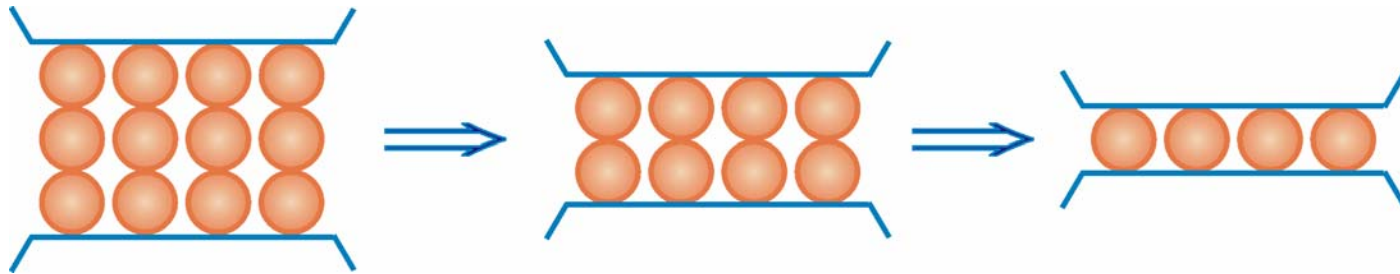
- **Foaming – foam volume and bubble size.**
- **Rate of water drainage from foams.**
- **Rate of foam film thinning.**
- **Viscous dissipation in foams.**
- **Foam-wall friction.**
- **Ostwald ripening.**

Important role of dynamic surface tension and interfacial rheology!

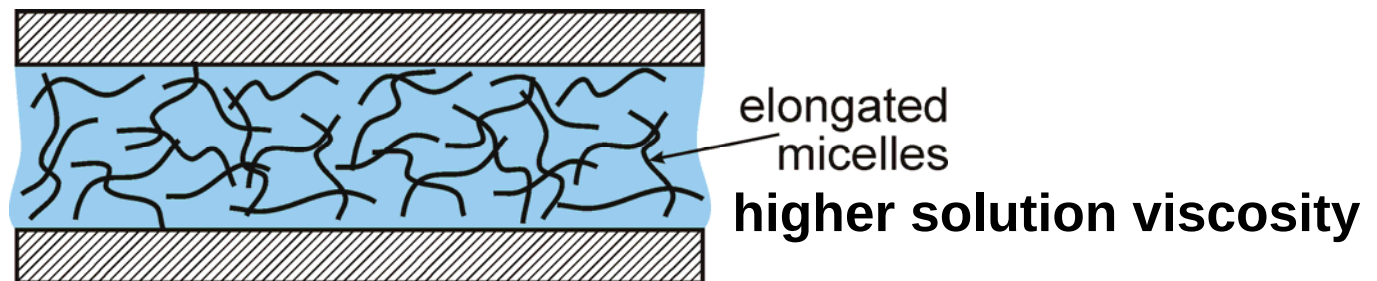
5. Role of micelles in foams

(a) Reservoir of surfactant – dynamic surface tension.

(b) Oscillatory forces in foam films (stratification).



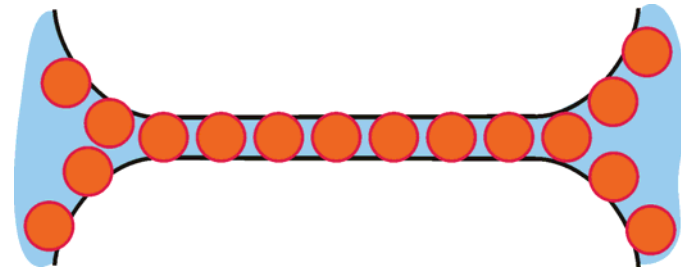
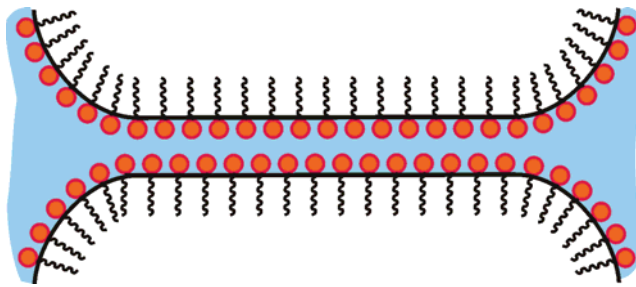
(c) Solution rheology (shampoos, dish-washing gels)



Following related presentations:

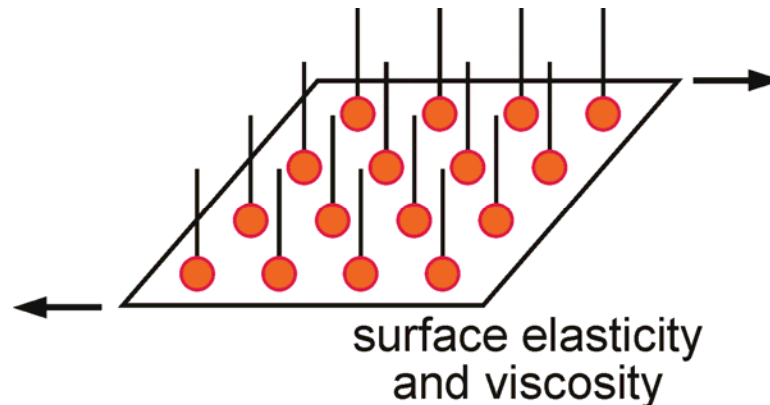
Thursday

Role of surfactants in foam stabilization (including antifoams)



Friday

- Interfacial rheology



SINCERE THANKS

Dr. S. Tcholakova

Help in preparation of the presentation.

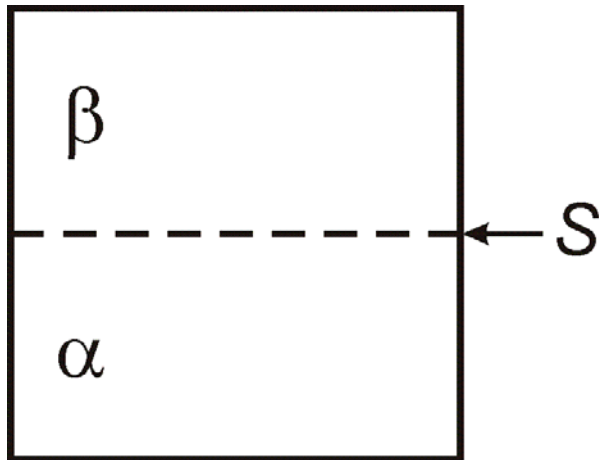
Miss M. Paraskova

Preparation of some of the figures.

Other colleagues

**The Laboratory of Chemical Physics & Engineering
Faculty of Chemistry, University of Sofia, Sofia, Bulgaria**

Derivation of Gibbs adsorption isotherm



Surface excess quantities

$$f^S = \int_{-\infty}^0 [f(z) - f^\alpha] dz + \int_0^{\infty} [f(z) - f^\beta] dz$$

$$\Gamma_i = \int_{-\infty}^0 [n_i(z) - n_i^\alpha] dz + \int_0^{\infty} [n_i(z) - n_i^\beta] dz$$

$$\sigma = - \int_{-\infty}^0 [P_T(z) - P^\alpha] dz - \int_0^{\infty} [P_T(z) - P^\beta] dz$$

$$V = V^\alpha + V^\beta$$

$$N_i = N_i^\alpha + N_i^\beta + N_i^S$$

$$F = F^\alpha + F^\beta + F^S$$

$$U = U^\alpha + U^\beta + U^S$$

For the total system:

$$dF = -SdT - pdV + \sigma dA + \sum \mu_i dN_i$$

$$\sigma = \left(\frac{\partial F}{\partial A} \right)_{T,V,N}$$

$$F = -PV + \sigma A + \sum \mu_i N_i$$

Conditions for
equilibrium:

$$T = \text{const}$$

$$\mu_i = \text{const}$$

For the subsystems

$$S = S^\alpha + S^\beta + S^S \quad F^\alpha = -pV^\alpha + \sum \mu_i N_i^\alpha; \quad F^\beta = -pV^\beta + \sum \mu_i N_i^\beta$$

$$F^S = U^S - TS^S \quad \Rightarrow F^S = \sigma A + \sum \mu_i N_i^S$$

$$dF^\alpha = -s^\alpha dT - pdV^\alpha + \sum \mu_i dN_i^\alpha; \quad dF^\beta = -s^\beta dT - pdV^\beta + \sum \mu_i dN_i^\beta$$

$$\Rightarrow dF^S = -S^S dT + \sigma dA + \sum \mu_i dN_i^S$$

$$d\sigma = -S^S dT - \sum \Gamma_i d\mu_i$$