Soft Matter

Lecture 4

Interfaces and surfactants

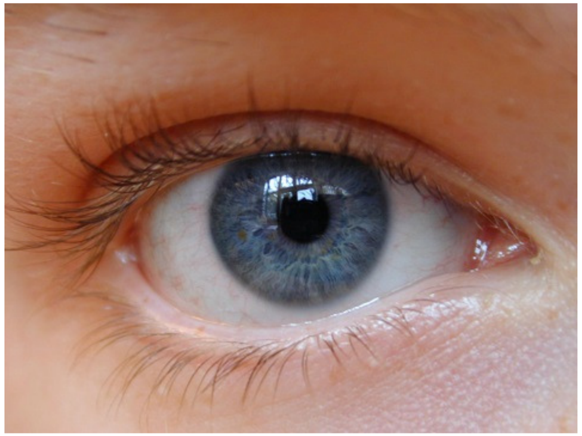
- Interfacial tension
- Wetting: Laplace and Young equations
- Capillary rise
- Surfactants: micelles and Gibbs adsorption equation

Soft matter interfaces in daily life

food

foam

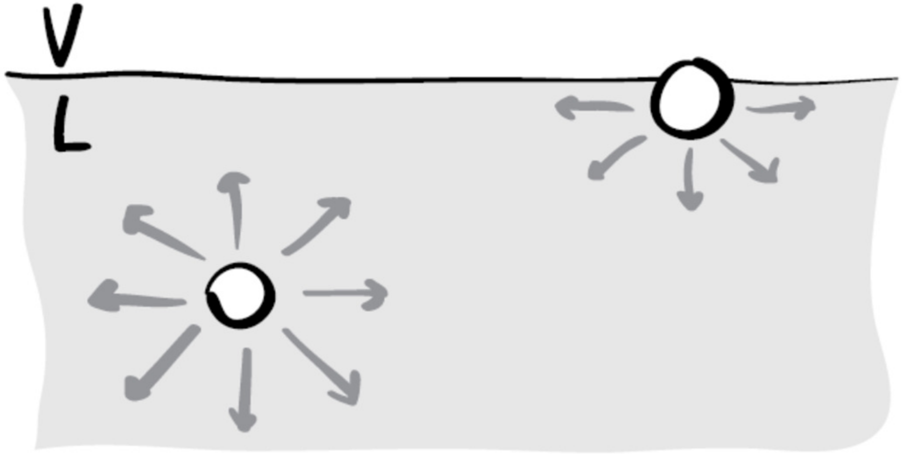
cosmetics



human body

Interfacial tension

- Molecules at an interface are different from molecules in the bulk
  - Asymmetric interactions
  - Energy cost of being at the interface
  - Consequence: density of molecules at the interface is lower than in bulk



Marchand et al., Am. J. Phys. ***79****, 999 (2011)*

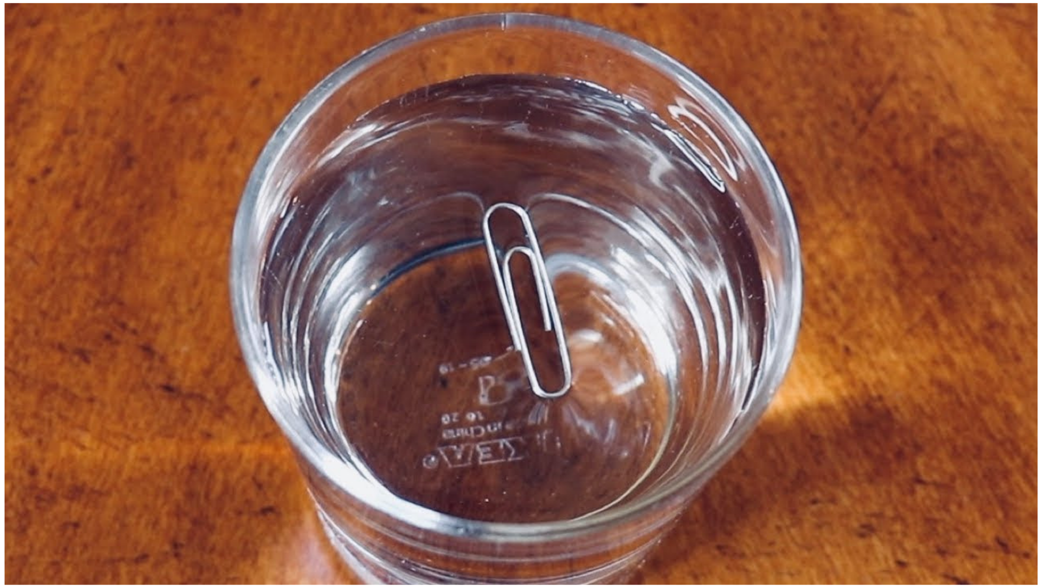
Boltzmann distribution:

$$\frac{n_2}{n_1} = e^{-\Delta U/kT}$$

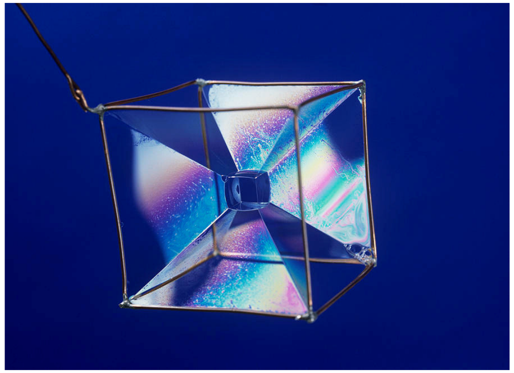
n_1, n_2 = number of molecules in state 1,2
ΔU = energy difference between 1 and 2
k = Boltzmann's constant
T = absolute temperature

Interfacial tension

- The surface of a liquid acts as an “elastic skin” that does not want to be deformed and tends to minimize the surface area: this property is called surface tension (for liquid-air/vapor interfaces), or: interfacial tension (more generally).



Interfacial tension

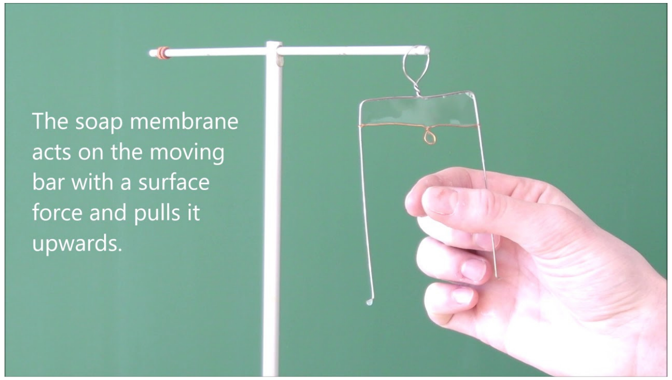


- Mechanical definition:

Surface tension is force per unit length:

$$\gamma = \frac{f}{2\ell}$$

γ = interfacial tension [N/m] or [J/m^2]
f = force



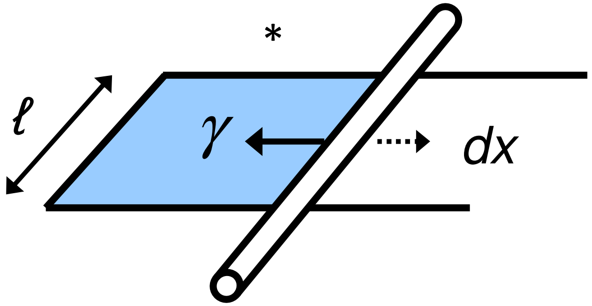
The soap membrane acts on the moving bar with a surface force and pulls it upwards.

Work (d*w*) that must be done to move barrier and stretch a film* by an area (d*A*):

$$dw = f dx = 2\gamma\ell dx \quad = \gamma dA$$

A = interfacial area
w = work

$$\gamma = \frac{dw}{dA}$$



*Note that this film has 2 sides

Interfacial tension

- Thermodynamic definition

Interfacial work: $dw = \gamma dA$

Work depends on the way a process is done, so conditions must be specified!

Reversible process at constant *N, V, T*:

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

Reversible process at constant *N, p, T*:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{N,p,T}$$

Enthalpic and Entropic component:

$$G = H - TS$$

enthalpy entropy

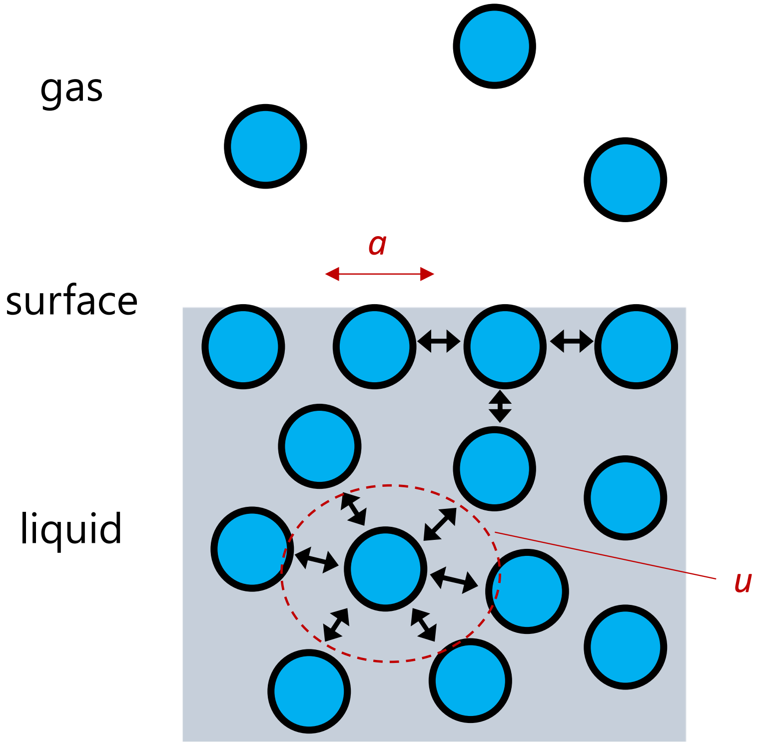
$$\gamma = \left(\frac{\partial H}{\partial A}\right)_{N,p,T} - T\left(\frac{\partial S}{\partial A}\right)_{N,p,T}$$

$$= h_a - Ts_a$$

Interfacial entropy is usually > 0

Magnitude of the interfacial tension

- Use the missing interactions at the interface picture



Energy of molecule in bulk: *u*
Missing interactions at surface: *u*/2

$$\gamma^{S} \approx \frac{u}{2a^2}$$

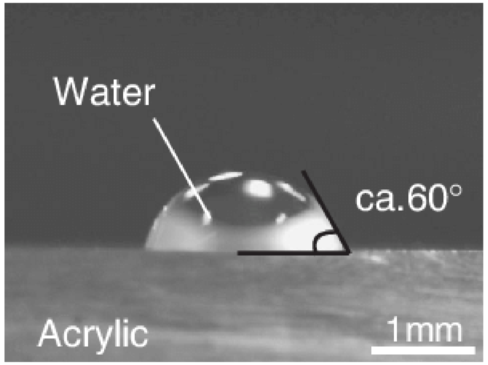
u ≈ 1 *kT*
a ≈ 0.2 nm
γ ≈ 0.05 J/m^2

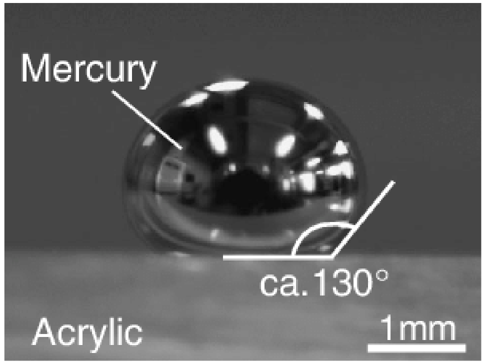
In reality, surface tensions are somewhat lower

Magnitude of the interfacial tension

- Use the missing interactions at the interface picture to explain these magnitudes

	γ (mN/m)	Type interactions
helium (4 K)	0.1	Van der Waals
n-propane	18	
n-butane	20	
n-hexane	22	
n-octane	26	
ethanol	23	
acetone	24	
toluene	29	π electron
glycerol	63	H-bonds
water	72	
mercury	485	metallic

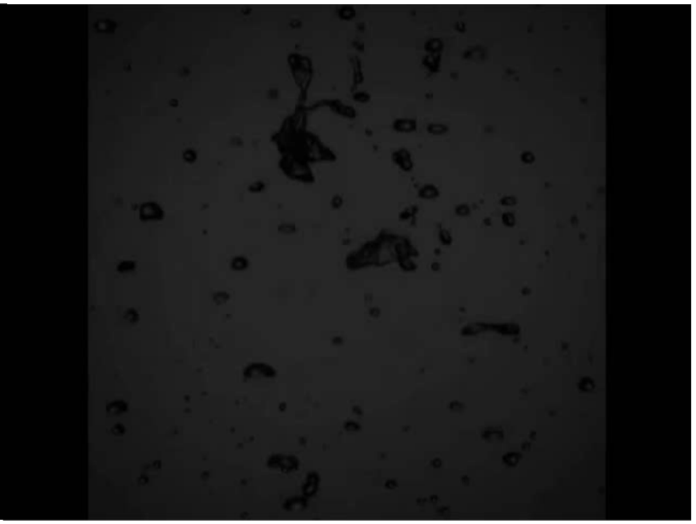




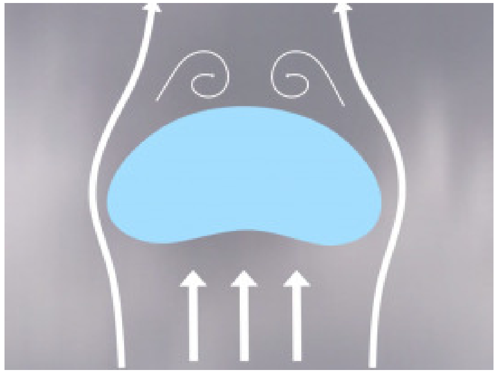
What is the shape of a rain drop?

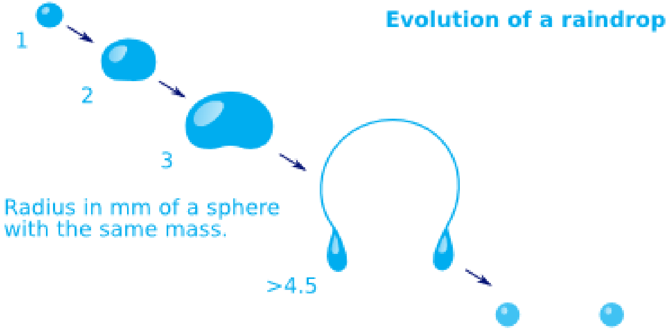
- Interfacial tension!

Model rain (slow)



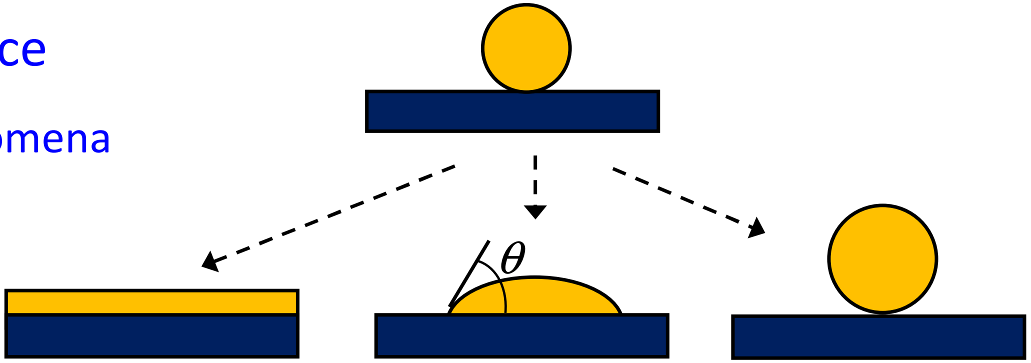
Real rain



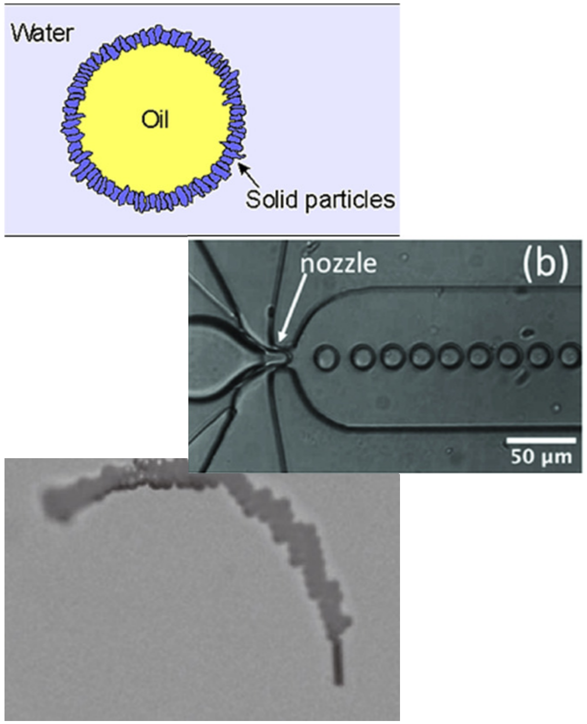


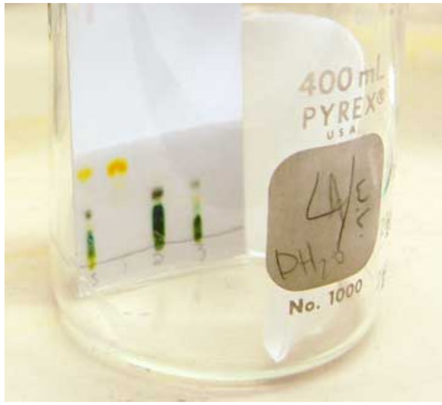
Wetting

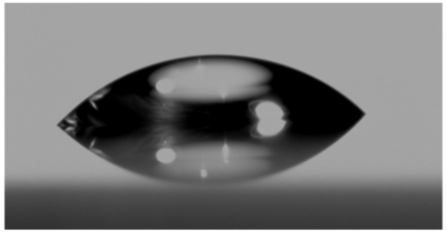
- Shape of a liquid on a solid surface
  - Relevant for many colloidal phenomena

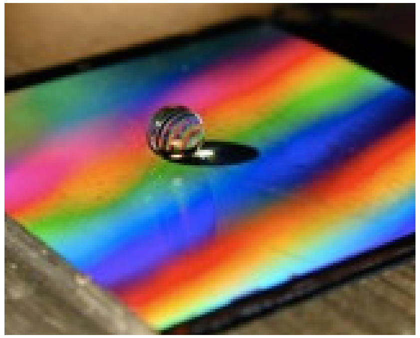


complete wetting partial wetting completely dry



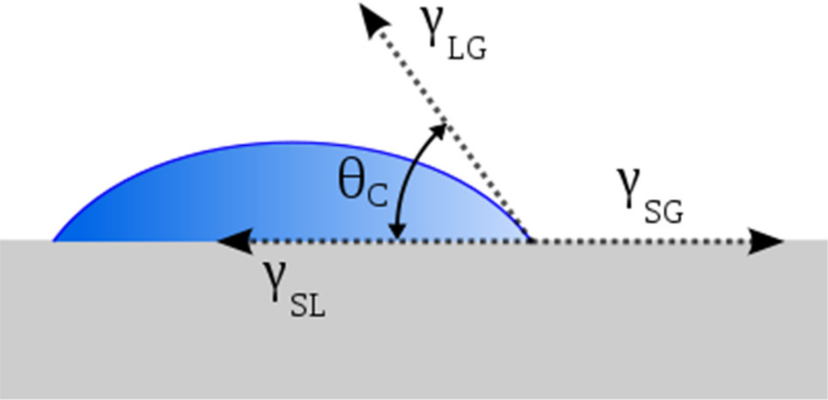






Young’s law

- Balance of surface energies
- Spreading parameter S : $S = \gamma_{\mathrm{SV}} - (\gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}})$
  - S > 0 -> Complete or total wetting
  - S < 0 -> Partial wetting, nonwetting, Young’s law:
  - $\theta < 90^{\circ}$ hydrophilic
  - $\theta > 90^{\circ}$ hydrophobic

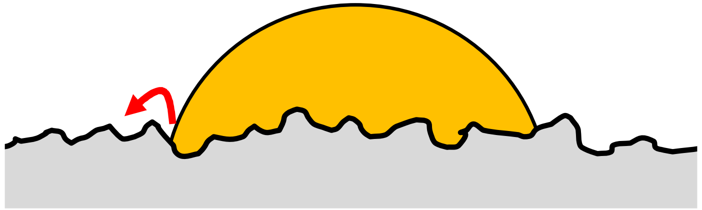


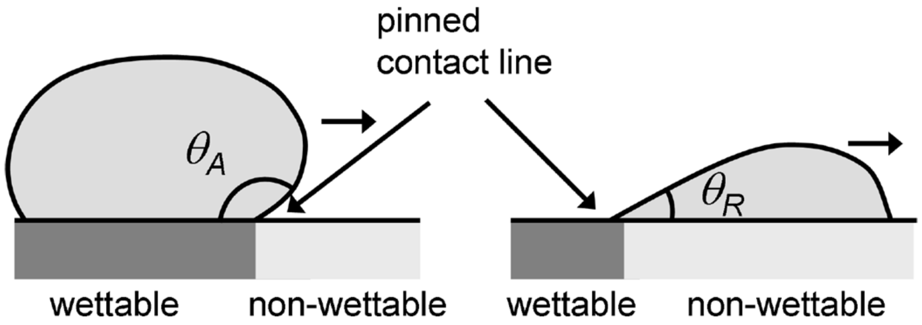
$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta$$

$$\cos\theta = \frac{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}}{\gamma_{\mathrm{LV}}}$$

Why is this not a good prediction for many real surfaces?

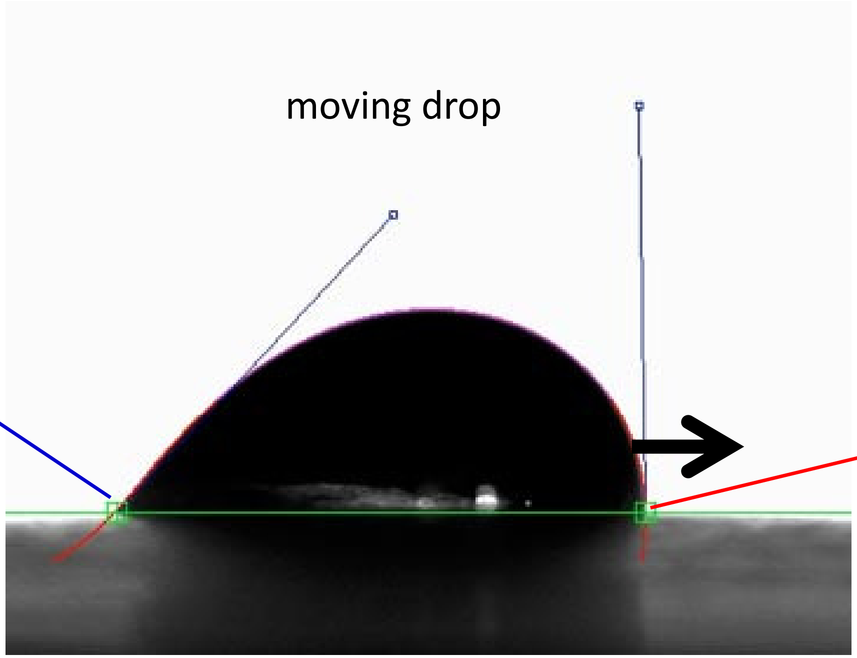
- Real surfaces are rough
- Real surfaces are heterogeneous
- -> Contact line pinning





Contact angle hysteresis

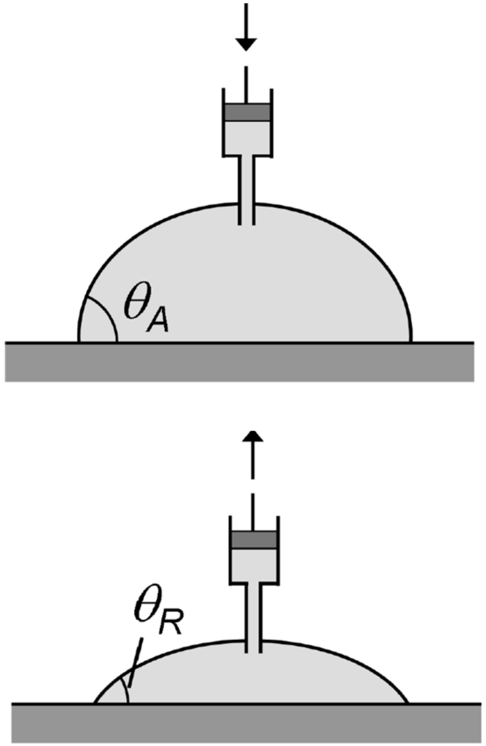
- Advancing and receding contact angles



receding
contact angle

advancing
contact angle

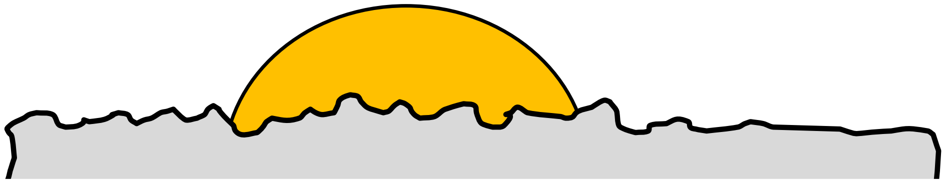
$$\theta_A > \theta_R$$

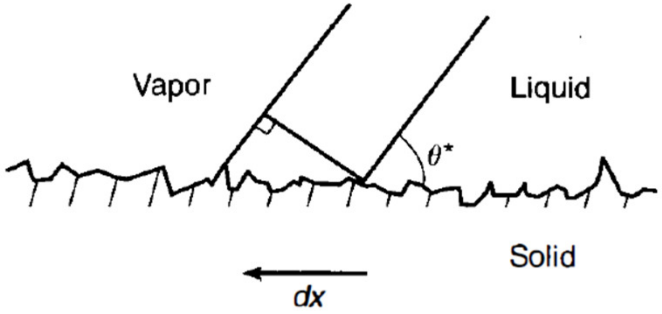


Pinning force:

$$f = 2\pi R\,\gamma_{LV}(\cos\theta_R - \cos\theta_A)$$

Wetting on rough surfaces





- Displacement of contact line by d*x*:

$$dU/l = r(\gamma_{SL} - \gamma_{SV}) \cdot dx + \gamma_{LV} \cos\theta^* \cdot dx$$

Roughness (*r*) = ratio of actual and apparent (projected) surface area

$$r = \frac{A_{real}}{A_{app}}$$

Equilibrium position: d*U*/d*x* = 0

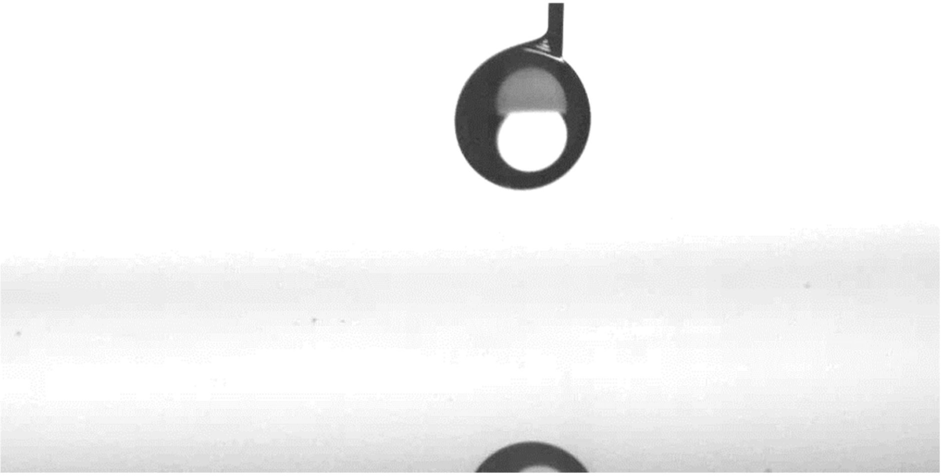
$$\frac{\cos\theta^*}{r} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

$$\cos\theta^* = r\cos\theta$$ (Wenzel)

Surface roughness enhances underlying chemistry!

- Superhydrophobicity and superhydrophilicity

$$\cos\theta^* = r\cos\theta_E$$



(real time)

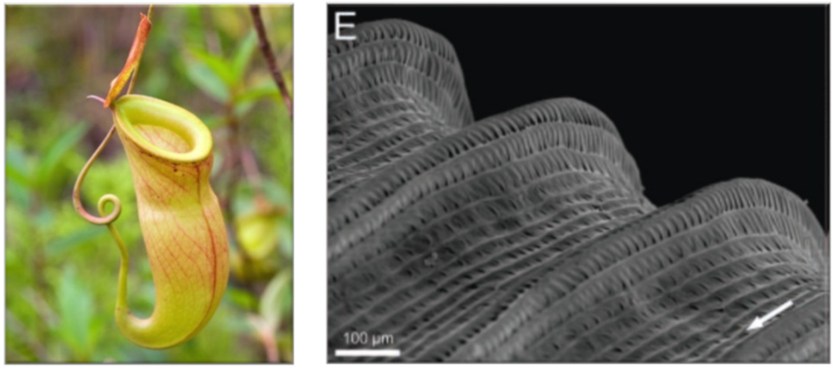
Same roughness!

(670x slowed down)

Credits: Philippe Bourrianne (ESPCI, Paris)

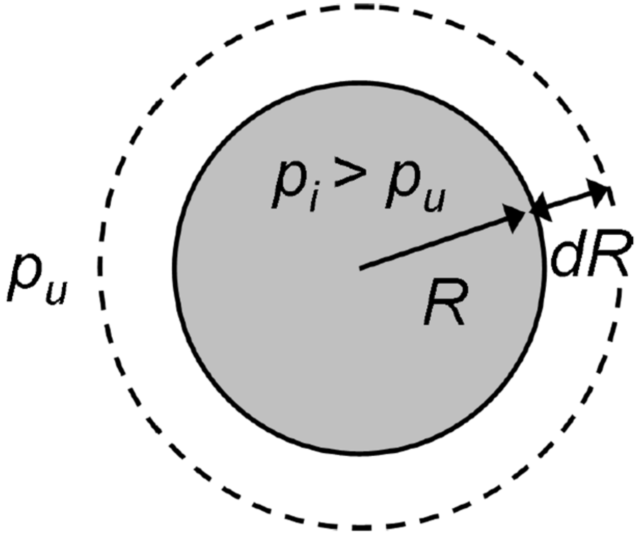
Superhydrophilic and superhydrophobic surfaces

- Double roughness



Curved interfaces: Young-Laplace equation

- Interfacial tension causes an increase in internal pressure below curved interface
- Laplace pressure



$$\Delta p = \frac{2\gamma}{R}$$

– General: $\Delta p = \gamma C$ C = curvature

$$C = \frac{1}{R_1} + \frac{1}{R_2}$$

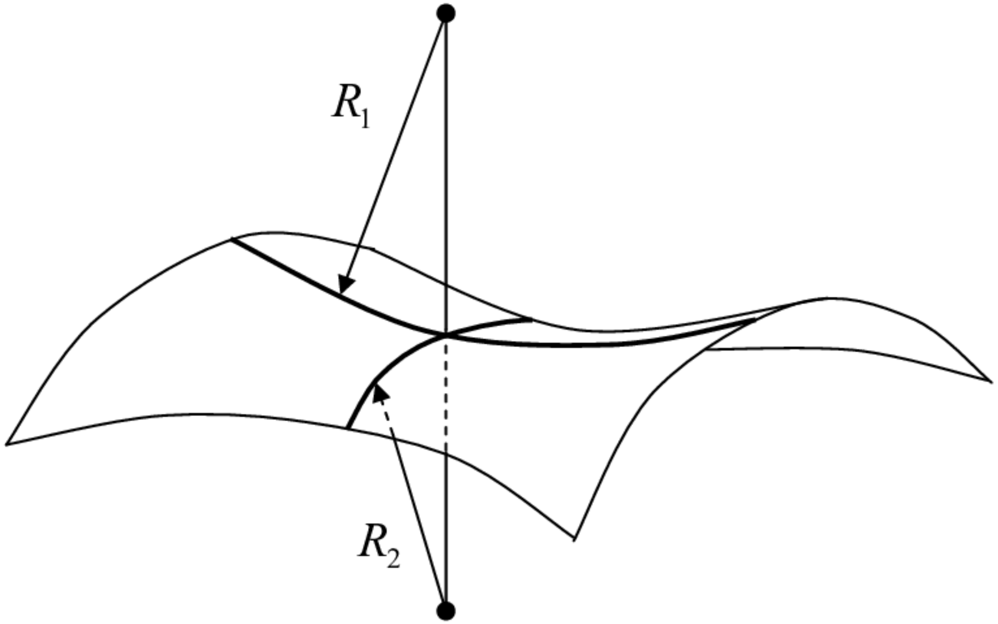
R_1, R_2 are principal radii of curvature

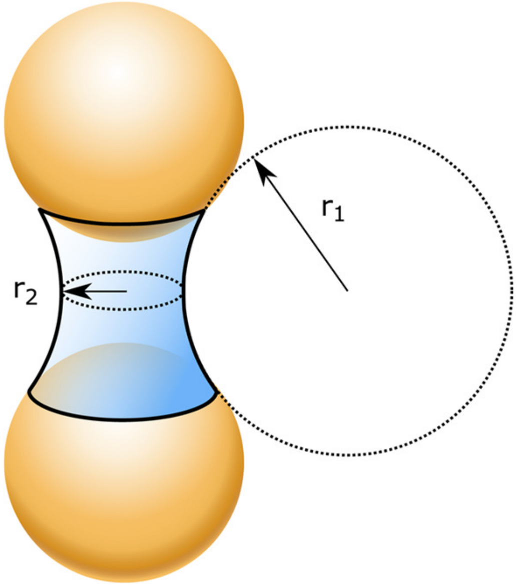
Curved interfaces: Young-Laplace equation

- Interfacial tension causes an increase in internal pressure below curved interface
- Laplace pressure

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

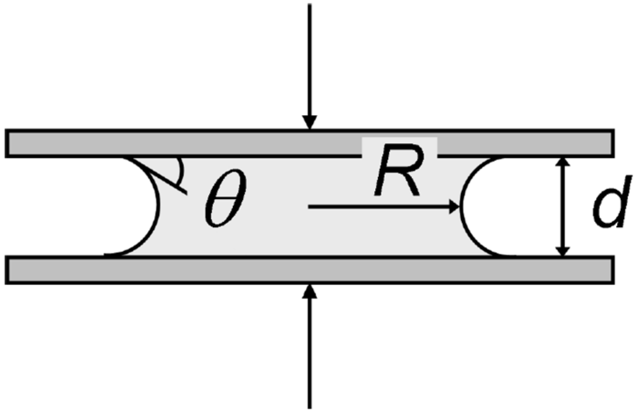
R_1, R_2 are principal radii of curvature





Capillarity

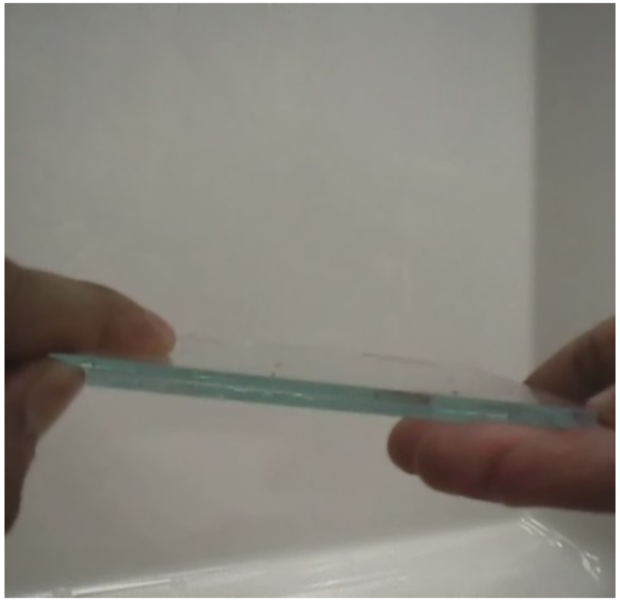
- Capillary adhesion



$$\Delta p = \gamma \left(\frac{1}{R} - \frac{2\cos\theta}{d} \right)$$

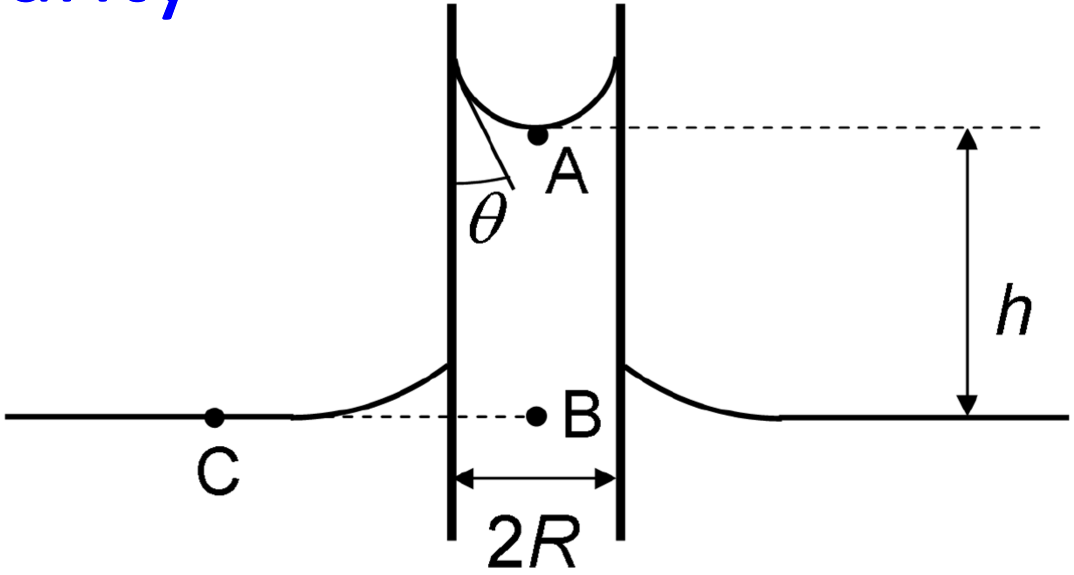
$$f = A\Delta p$$

$$f = \pi R^2 \frac{2\gamma\cos\theta}{d}$$



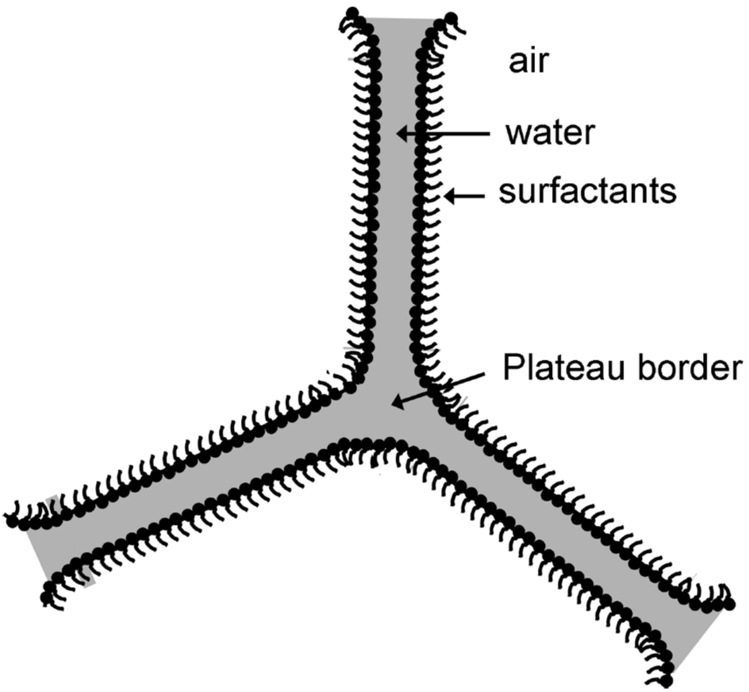
Capillarity

- Capillary adhesion
- Capillary rise



$$h = \frac{2\gamma\cos\theta}{\rho g R}$$

Foam drainage



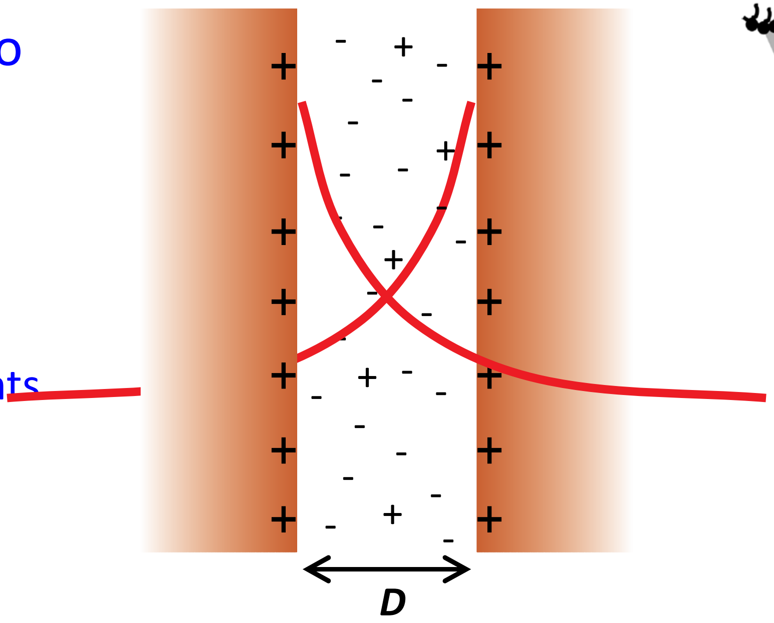
- Why are foams stable?
- Laplace pressure difference drives liquid out of films

- Thinning stops due to disjoining pressure:

$$\Pi(h) = -\left(\frac{\partial G_{\text{int}}}{\partial h}\right)_{p,T}$$

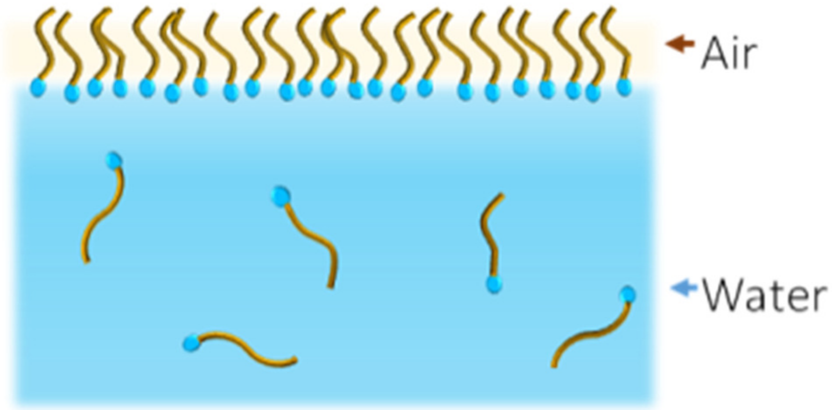
E.g., charged surfactants

(Lecture 2)

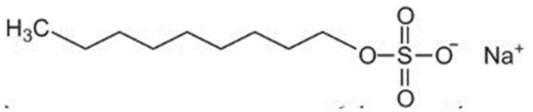


Surfactants

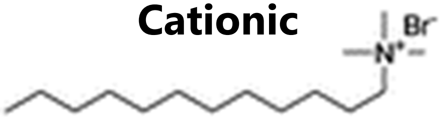
- Surface active agents
  - Schizophrenic molecules:
  - One part hydrophilic, one part hydrophobic
  - Accumulate at interfaces
  - Self-assemble into micelles (and vesicles, lamella, etc)

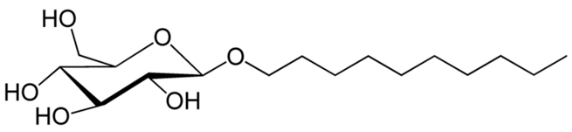


Anionic



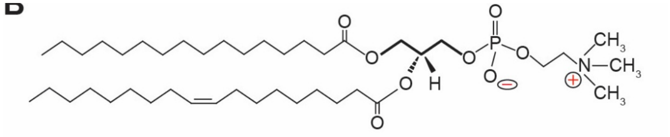
Cationic

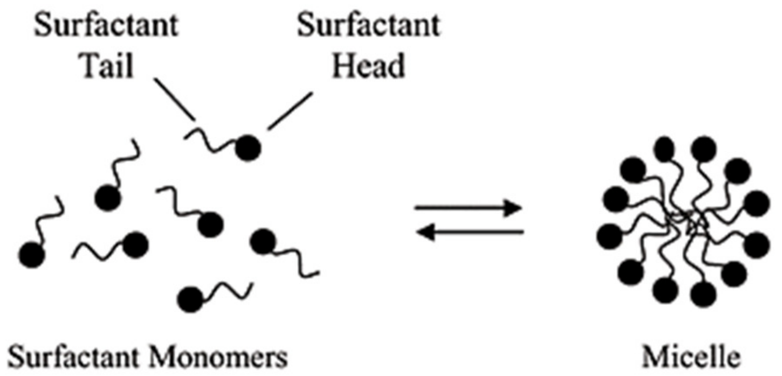




Nonionic

Zwitterionic

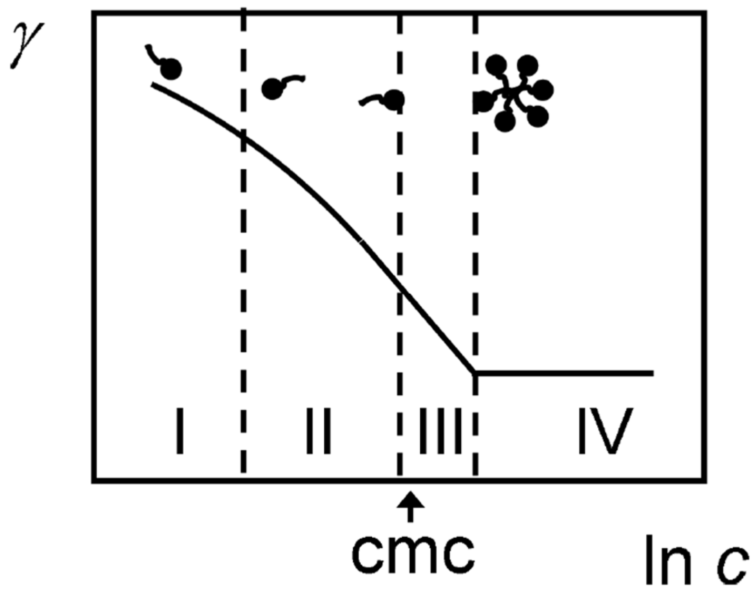


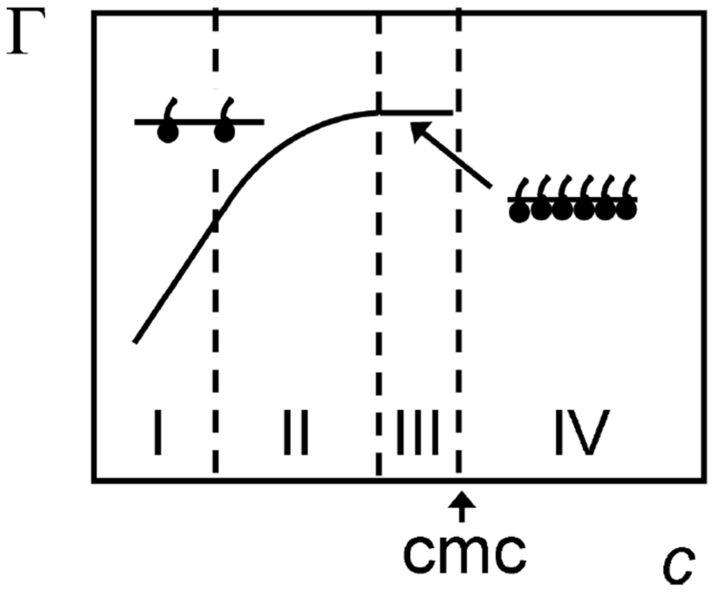


Adsorption of surfactants

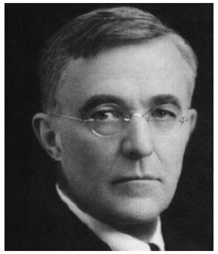
- Gibbs law: $$\mathrm{d}\gamma = -\sum_i \Gamma_i \; \mathrm{d}\mu_i$$

$$\mu_i = \mu_i^0 + RT \ln c_i \qquad \mathrm{d}\gamma = -RT \sum_i \Gamma_i \; \mathrm{d}\ln c_i \qquad \Gamma_i = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c_i} = \frac{c_i}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c_i}$$





Adsorption of surfactants



- Langmuir isotherm (*monolayer adsorption, accounts for saturation*)

$$S_{\text{free}} + X_{\text{sol}} \rightleftarrows SX_{\text{ads}}$$

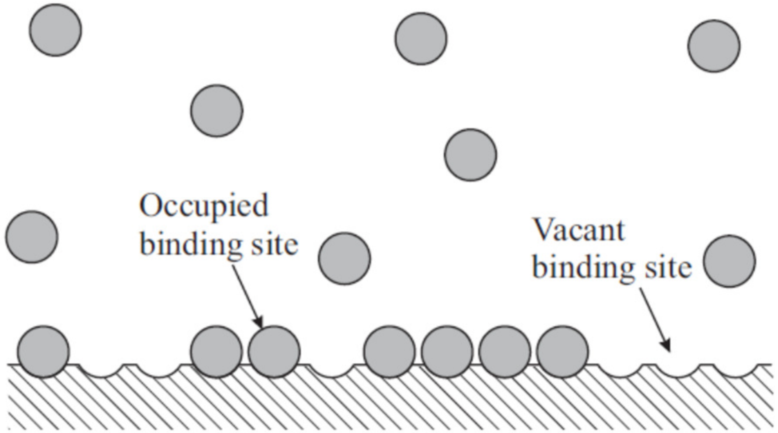
fraction of occupied sites: $\theta = [SX_{\text{ads}}]/[S_{\text{tot}}]$
total number of sites: $S_{\text{tot}} = S_{\text{free}} + SX_{\text{ads}}$

$$K_L = \frac{[SX_{\text{ads}}]}{[S_{\text{free}}]\cdot[X_{\text{sol}}]} = \frac{\theta}{c(1-\theta)}$$

$$\theta = \frac{K_L \cdot c}{1 + K_L \cdot c} = \frac{c}{K_d + c}$$

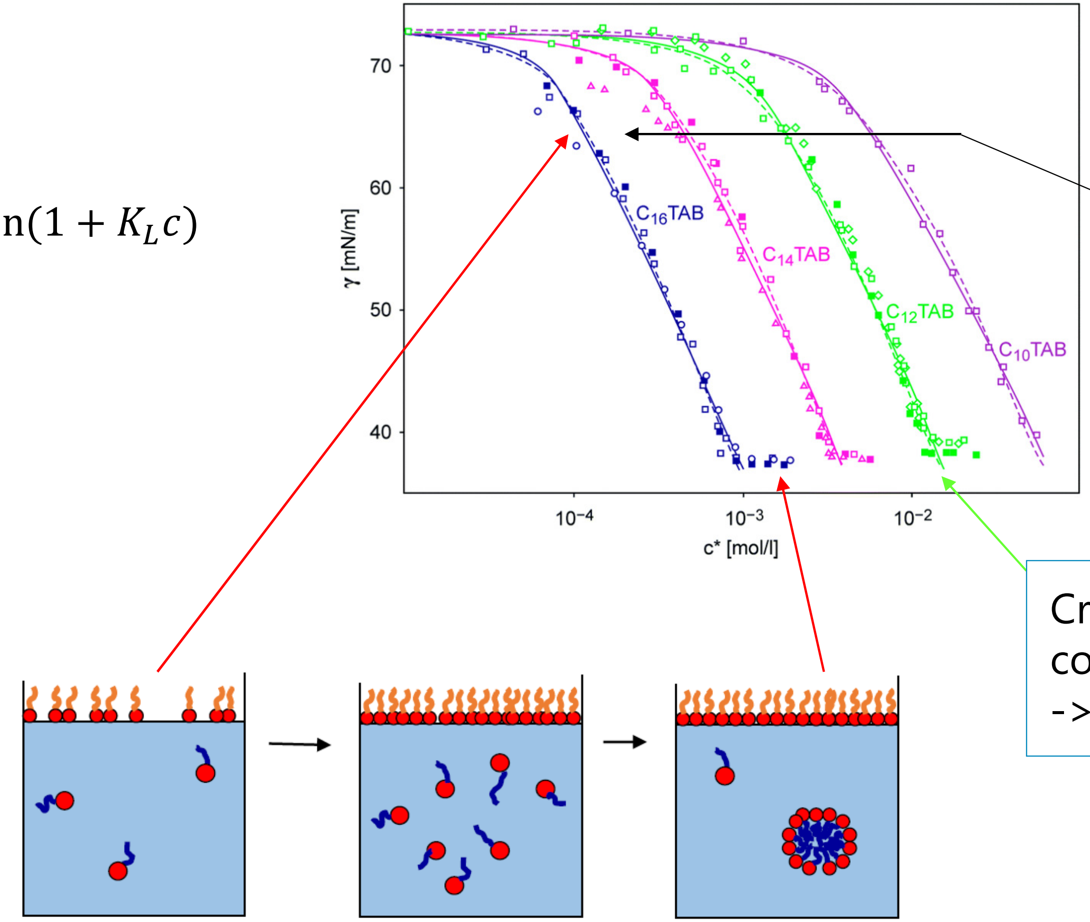
$$\Gamma = \theta \cdot [S_{\text{tot}}]$$

Assumptions:
- Adsorption on distinct sites
- All sites are equal
- All molecules occupy single site
- Adsorption does not affect neighbouring site
- Competition possible



Adsorption of surfactants

$$\gamma = \gamma^* - RT[S]_{\text{tot}} \ln(1 + K_L c)$$

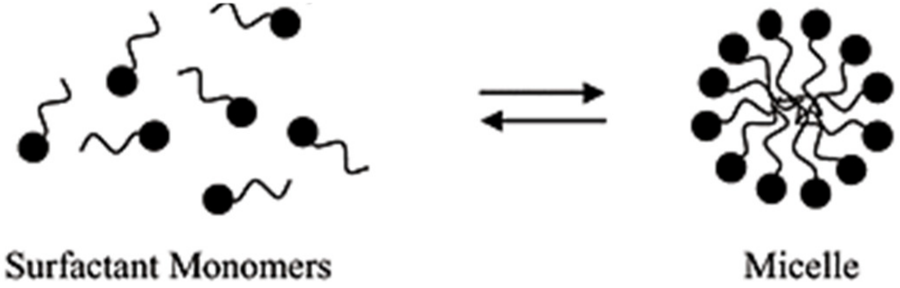


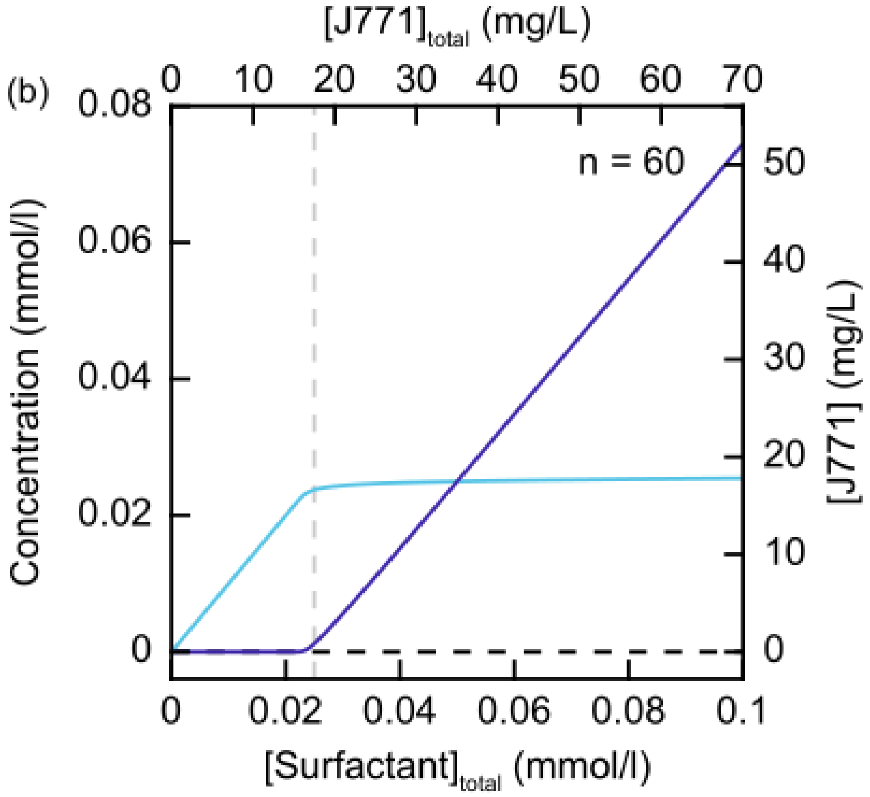
- Increasing length of hydrophobic tail
- Increasing salt concentration

Critical micelle concentration (CMC)
-> at kink

Self-assembly of surfactants: micelles

- Equilibrium between monomers and aggregate of size *n*





$$nA \longleftrightarrow A_n$$

$$n\mu_1^\circ + nk_BT\ln x_1 = \mu_{agg}^\circ + k_BT\ln x_{agg}$$

$$\mu_1^\circ + k_BT\ln x_1 = \mu_n^\circ + \frac{k_BT}{n}\ln\left(x_n/n\right)$$

$$x_n = nx_1^n e^{n\left(\mu_1^\circ - \mu_n^\circ\right)/k_BT} = nK_nx_1^n$$