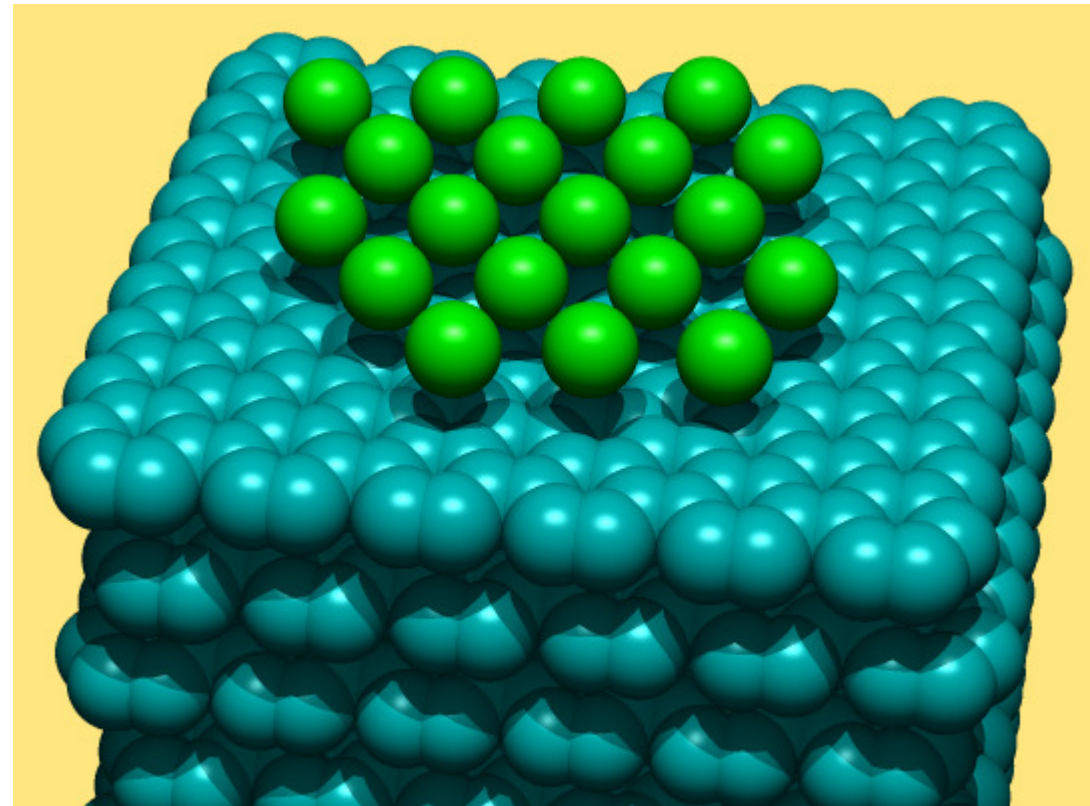


↑ Ar on graphite →

- adsorption: on surface (interface)
- absorption: inside (bulk)
- sorption: both

- molecular adsorption
(g) → (s), (l) → (s)/(l), . . .
- ion adsorption
Paneth-Fajans rule
- exchange ion adsorption,
counterions in aluminosilicates



	physical adsorption	chemisorption
forces	physical (weak: van der Waals, H-bonds)	covalent bonds
specificity	non-specific (easy to liquefy – easily adsorbed)	specific
adsorption heat	-20 to -40 kJ mol^{-1} (\approx condensation heat)	-40 to -400 kJ mol^{-1} (\approx reaction heat)
number of layers	several layers possible (as condensation)	one layer
activation energy	0	> 0
rate	high (seconds)	slow at low T , fast at high T
amount adsorbed	large below T_c , small above T_c	small; usually given by kinetics
reversibility	easy (vacuum, temperature)	not so easy (vacuum + higher T)

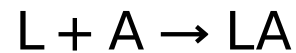
Langmuir adsorption isotherm

- Good for chemisorption, adsorption in small cavities (zeolites); limited for physical adsorption ($p \ll p^s$)
- Independent (noninteracting) adsorption centers of one kind
- Max 1 molecule/center (one layer)

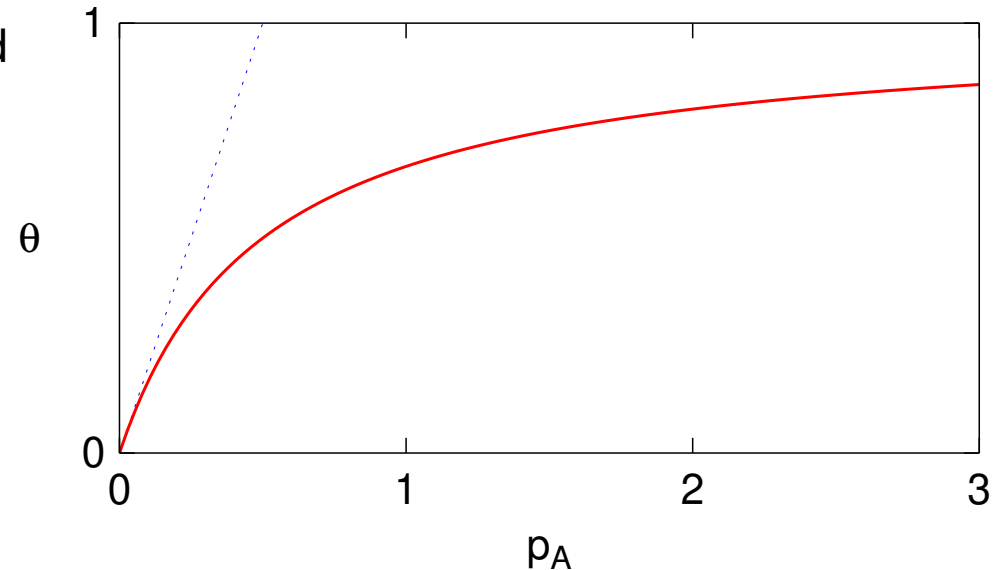
Known: Activity of the adsorbate: $a_A = \frac{p_A}{p^{st}}$, or from solution: $a_A = \frac{c_A(\odot)}{c^{st}}$

Equilibrium constant of adsorption K_{ad}

Adsorption equilibrium:



$$[LA] + [L] = c_{L0}, \quad \frac{[LA]}{a_A[L]} = K_{ad}$$

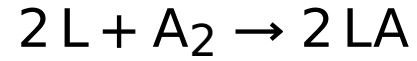


Coverage (saturation):

$$\theta = \frac{\text{adsorbed amount}}{\text{maximum amount (monolayer)}} = \frac{[LA]}{c_{L0}} = \frac{K_{ad}a_A}{1 + K_{ad}a_A}$$

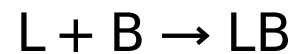
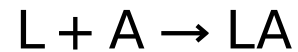
Gas: $\theta = \frac{bp_A}{1 + bp_A}, \quad b = \frac{K_{ad}}{p^{st}}$

● Dissociative adsorption



$$\theta = \frac{b p_A^{1/2}}{1 + b p_A^{1/2}}$$

● Competitive adsorption (2 compounds):



$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B}$$

Heterogeneous catalysis

A catalyst in solid phase, large specific surface area.
The rate-determining process may be:

- diffusion (in solution: k drops if we increase the viscosity)
- chemisorption (T -dependent)
- surface diffusion

Example – chemisorption determines the rate, $A \rightarrow B$
Independent active centers L , adsorption equilibrium



If not $k_2 \ll k_{-1}$, follow the Michaelis-Menten kinetics

for $k_2 \ll k_{-1}$ use pre-equilibrium, $K_{ad} = k_1/k_{-1}$

$$-\frac{dc_A}{d\tau} = \frac{dc_B}{d\tau} = k_2 c_{L0} \theta = k_2 c_{L0} \frac{K_{ad} c_A}{1 + K_{ad} c_A} \stackrel{\text{gas}}{\propto} \frac{bp_A}{1 + bp_A}$$

● small c_A : $-\frac{dc_A}{d\tau} = k_2 K_{ad} c_{L0} c_A \stackrel{\text{gas}}{\propto} p_A$ (**1st order**)

● large c_A : $-\frac{dc_A}{d\tau} = k_2 c_{L0} \stackrel{\text{gas}}{=} \text{const}$ (saturated catalyst – **0th order**)

E.g., decomposition of phosphane (phosphine, PH_3) on tungsten (W).

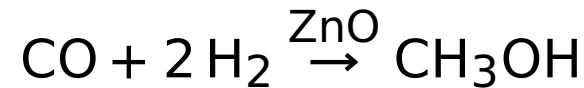
Reaction in (g) or (less typically) in (l):



Langmuir-Hinshelwood mechanism: both A and B are adsorbed and then react

$$-\frac{dc_P}{d\tau} = k\theta_A\theta_B = k\frac{b_A\rho_A b_B\rho_B}{(1 + b_A\rho_A + b_B\rho_A)^2}$$

Most common type for heat-activated reactions on a solid catalyst, e.g.:



Complex rate/temperature dependence.

Eley-Rideal mechanism: A is adsorbed, then directly reacts with B in (g)

$$-\frac{dc_P}{d\tau} = k\theta_A\rho_B = k\frac{b_A\rho_A\rho_B}{1 + b_A\rho_A}$$

E.g., $\text{H} + \text{H} \rightarrow \text{H}_2$ on dust grains in the interstellar space

Stephen Brunauer
Paul Hugh Emmet
Edward Teller*

Usage: determining the specific surface area of adsorbent

● independent adsorption centers of the same kind
simple but problematic assumption

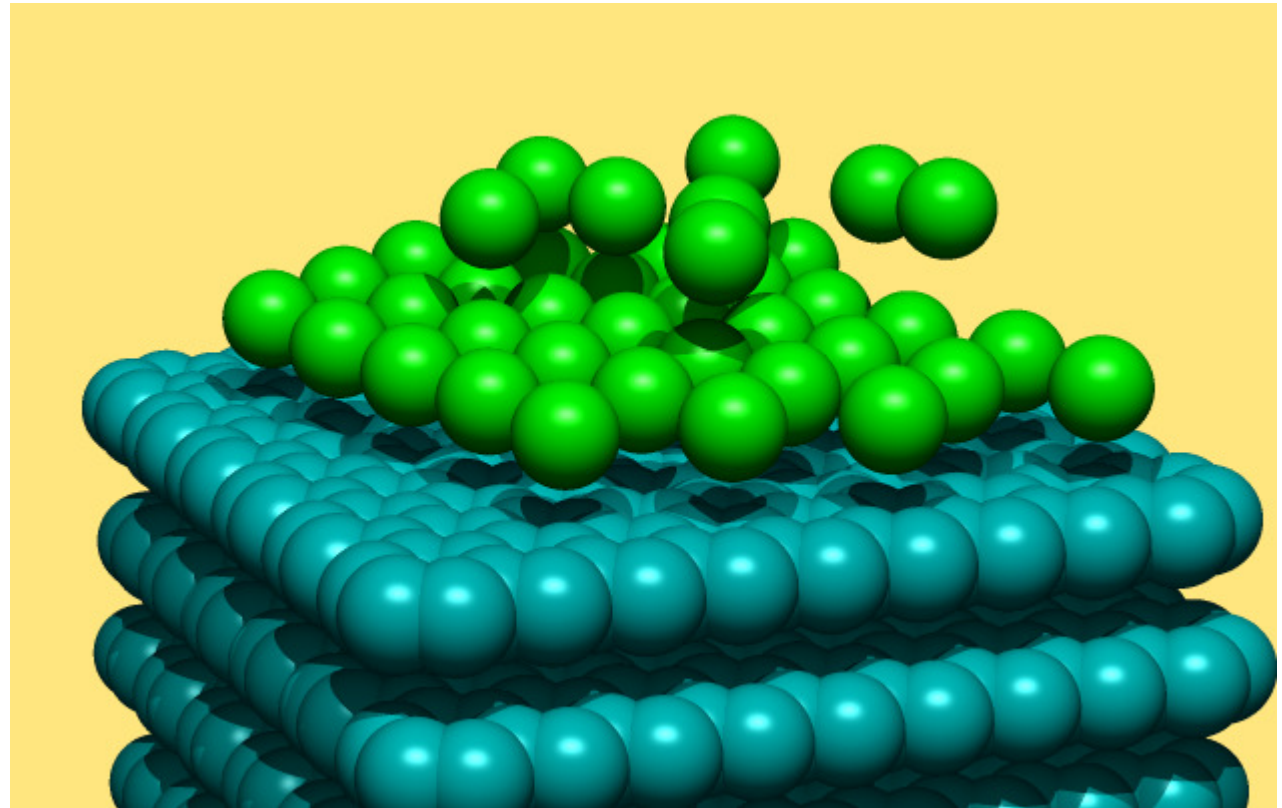
● several layers

● 1st layer as in the Langmuir isotherm

● additional layers bound in the same way as in a liquid

Known: Activity of the adsorbate: α_A

Equilibrium constants of adsorption: K_{ad} (1st layer), K (more layers)



* also known as “the father of the hydrogen bomb”

Adsorption center = L, molecule = A, complexes LA, LA₂, ...

Balance: $\sum_{n=0}^{\infty} [LA_n] = c_{L0}$, coverage: $\theta = \frac{1}{c_{L0}} \sum_{n=0}^{\infty} n[LA_n] \in (0, \infty)$



$$c_{L0} - [L] = K_{ad}a_A[L] + Ka_A(c_{L0} - [L])$$

$$\Rightarrow [L] = \frac{c_{L0}(1 - Ka_A)}{1 - K_{ad}a_A - Ka_A}$$

$$\theta = \frac{1}{c_{L0}} K_{ad}a_A[L] \left[1 + 2Ka_A + 3(Ka_A)^2 + \dots \right] = \frac{K_{ad}a_A[L]}{(1 - Ka_A)^2}$$

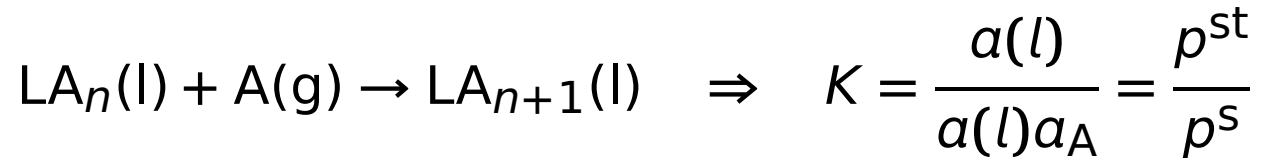
$$S_1 = 1 + x + x^2 + x^3 + \dots = 1 + xS_1 \Rightarrow S_1 = 1/(1 - x)$$

$$S_2 = 1 + 2x + 3x^2 + \dots = S_1 + xS_2 \Rightarrow S_2 = 1/(1 - x)^2 \text{ or } S_2 = dS_1/dx$$

BET Isotherm II

$$\theta = \frac{K_{\text{ad}} a_{\text{A}}}{(1 - K a_{\text{A}})[1 + (K_{\text{ad}} - K) a_{\text{A}}]}$$

K describes the adsorption to 2nd, 3rd, ... layers = condensation.
From the equilibrium at the saturated vapor pressure p^{S} :



Let us replace $a_{\text{A}} = \frac{p}{p^{\text{st}}}$ and let us define $C = \frac{K_{\text{ad}}}{K}$. The common form of BET is:

$$\theta = \frac{Cp/p^{\text{S}}}{(1 - p/p^{\text{S}})[1 + (C - 1)p/p^{\text{S}}]}$$

For C it holds:

$$C = \frac{K_{\text{ad}}}{K} = \exp \left[-\frac{\Delta_{\text{ad},1} G_{\text{m}}^{\ominus} - \Delta_{\text{ad},n} G_{\text{m}}^{\ominus}}{RT} \right] \approx \exp \left[-\frac{\Delta_{\text{ad},1} H_{\text{m}}^{\ominus} - \Delta_{\text{ad},n} H_{\text{m}}^{\ominus}}{RT} \right]$$

where $\Delta_{\text{ad},n} = -\Delta_{\text{vap}}$

$C \gg 1$: forces adsorbent–adsorbate are much stronger than adsorbate–adsorbate
e.g., very hydrophilic surface

$C \approx 1$: similar forces, bad adsorbent

$C \ll 1$: poor adsorption (hydrophobic surface)

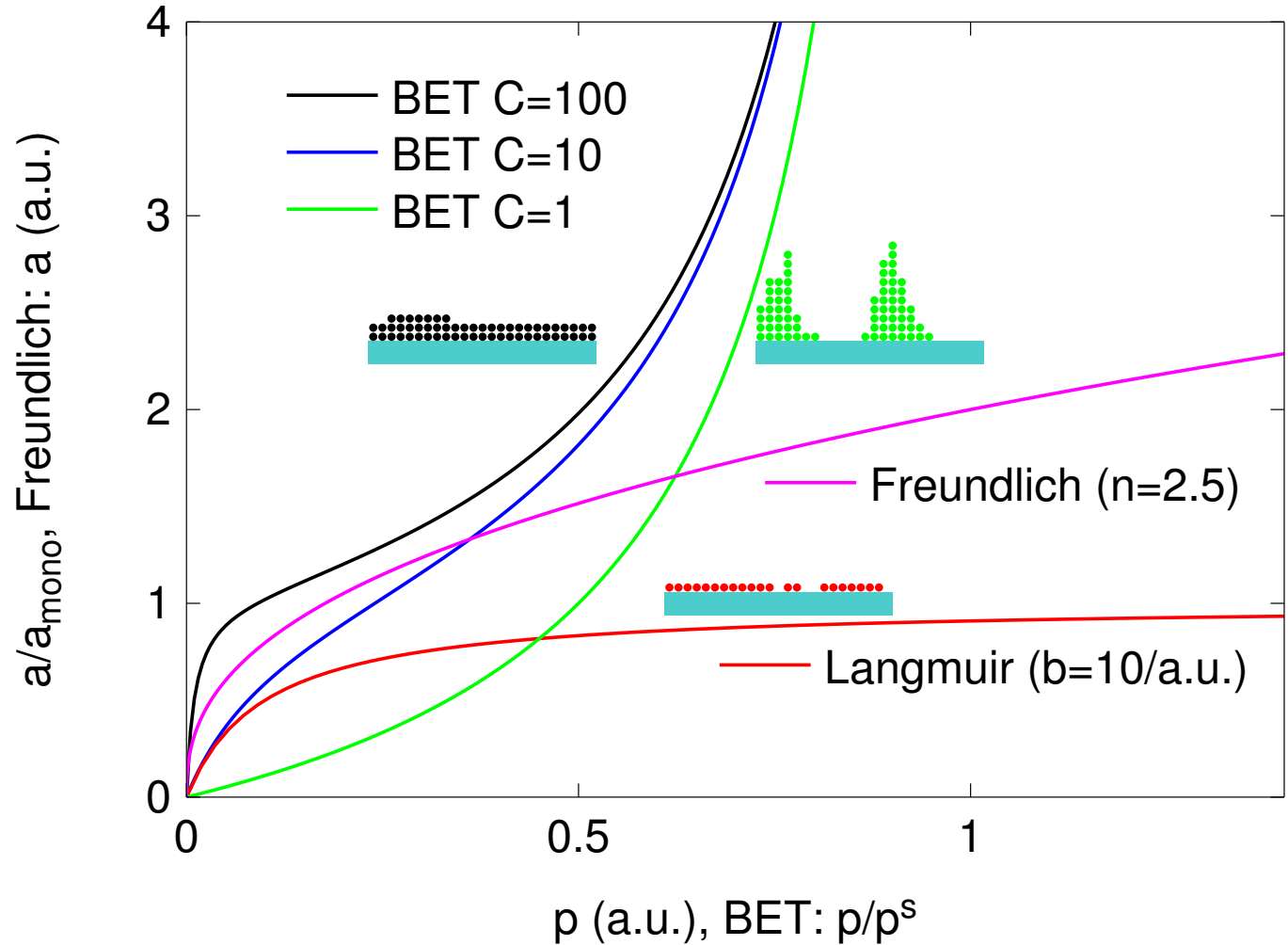
Freundlich isotherm

- empirical
- heterogeneous surfaces
- fails close to $p_A = p^s$

$$a = k p^{1/n}$$

a = amount adsorbed
 k = constant (decreasing with increasing T)
 n = constant, $n > 1$ ($n \approx 1$ for high T)

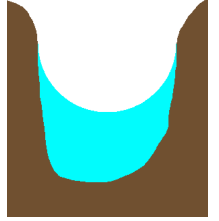
Isotherms compared



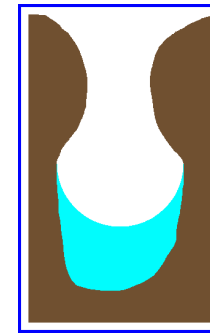
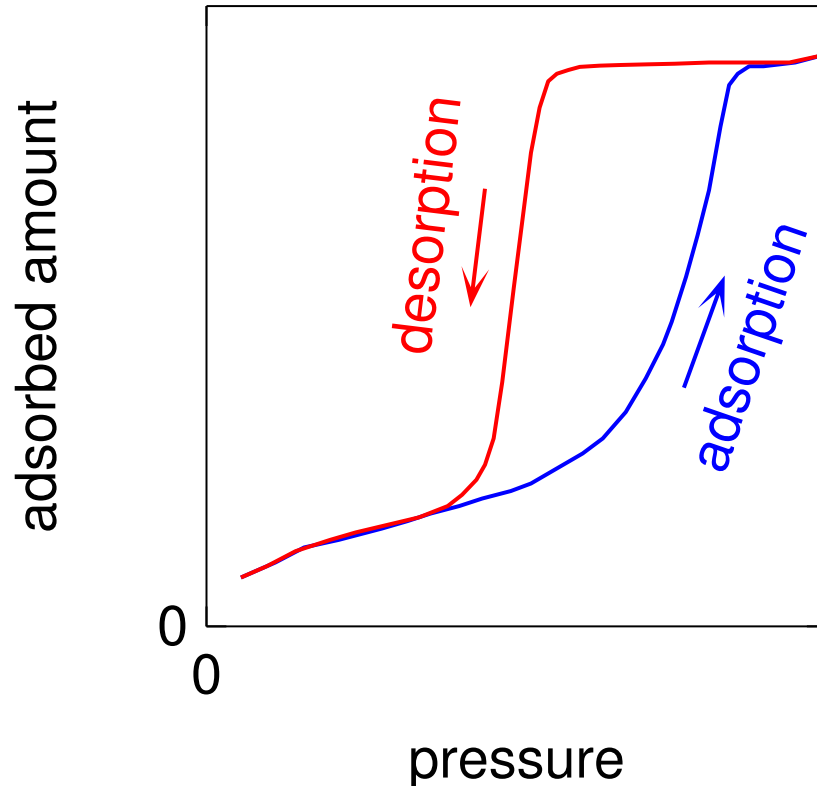
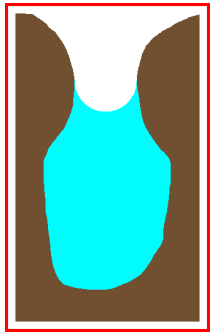
Capillary condensation and hysteresis

It follows from the Kelvin equation that there is a lower saturated pressure above the meniscus in hydrophilic/lyophilic pores (contact angle $< 90^\circ$). Therefore, the pores get filled already at $p < p^s$, hence the amount adsorbed (a) increases.

$$p_r^s < p_\infty^s$$



Complex pore shape (cavities, bottle-like), open cylinders (curvatures for adsorption/desorption differ) \Rightarrow hysteresis (different shape for adsorption/desorption)



Example

The adsorption of ethylene on activated carbon at 273 K, expressed as the mass of ethylene per mass of charcoal (α) in dependence on pressure (p), is shown in the table below. Determine the constants of the Langmuir isotherm and the specific surface area of the adsorbent. One molecule of ethylene covers $19 \text{ \AA}^2 = 0.19 \text{ nm}^2$.

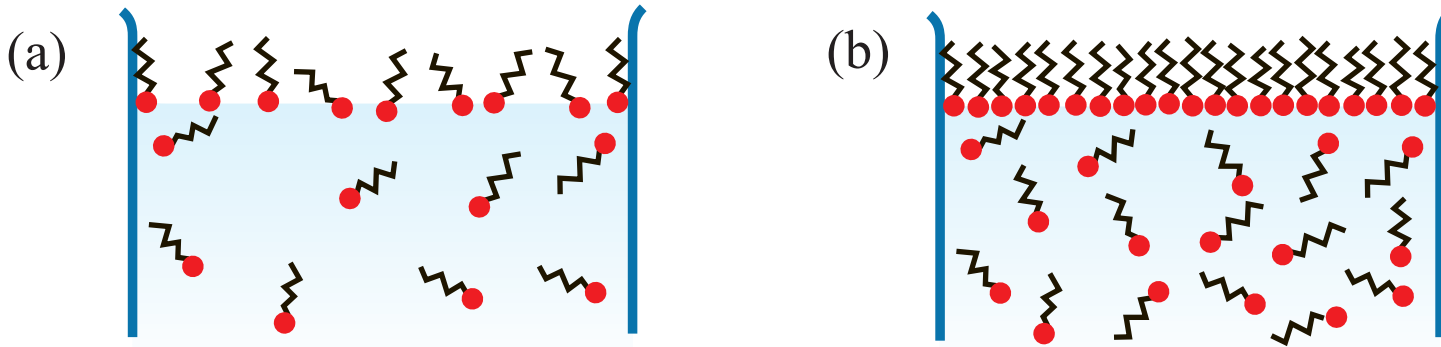
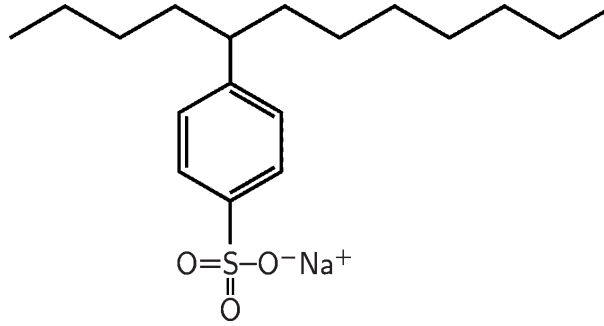
$\frac{p}{\text{MPa}}$	0.1	0.2	0.28	0.41	0.98	1.39	1.93	2.75	3.01	3.51
α	0.089	0.127	0.144	0.163	0.189	0.198	0.206	0.208	0.209	0.210

$$\alpha_{\max} = 0.219, b = 6.84 \text{ MPa}^{-1}, A_{\text{spec}} = 900 \text{ m}^2 \text{ g}^{-1}$$

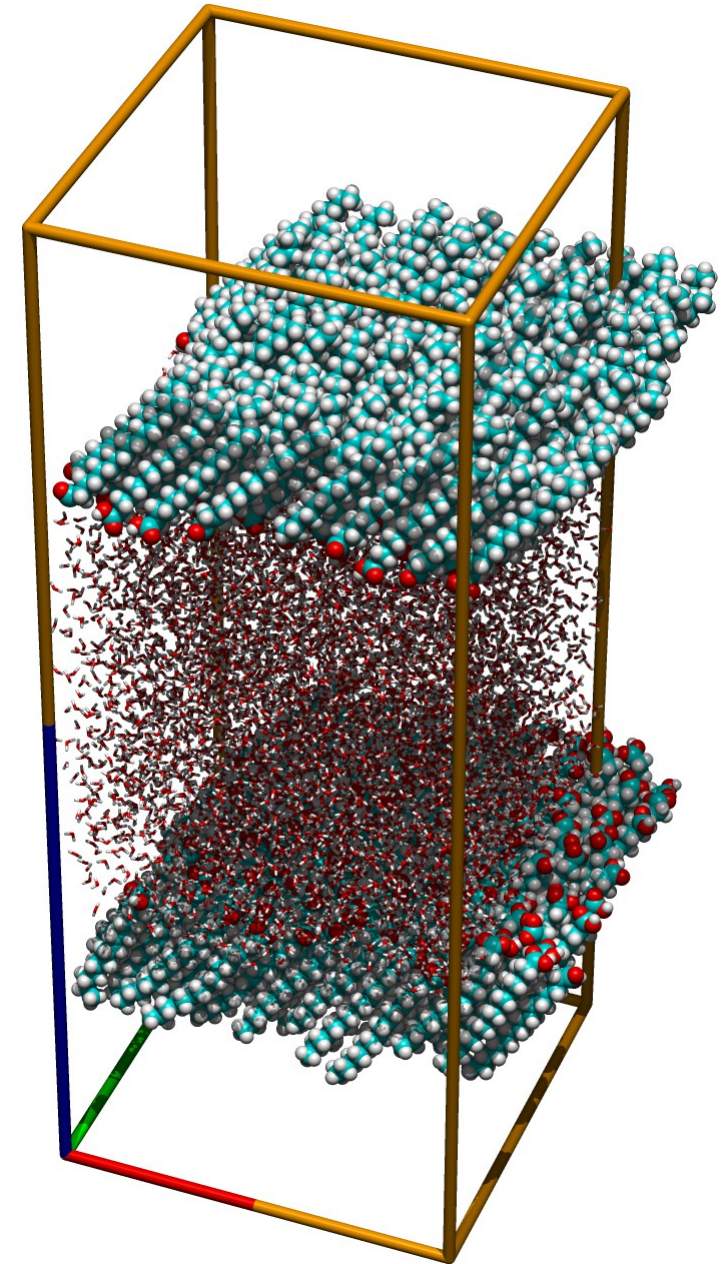
Surfactants

surface active (acting) agent

- adsorbed at the solvent surface
- decreases the surface tension
- usually a hydrophilic “head” (-COOH, -SO₃H) and a hydrophobic “tail” (aliphatic: 0.205 nm²/molecule)

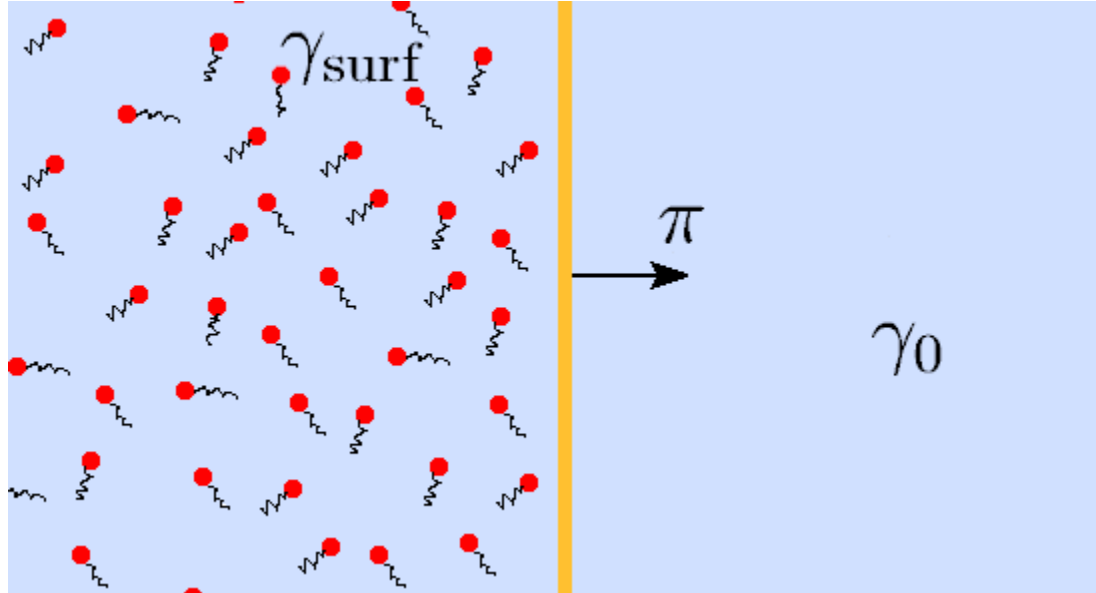


- longer molecules are not dissolved, but can compose films at a surface



Surface pressure

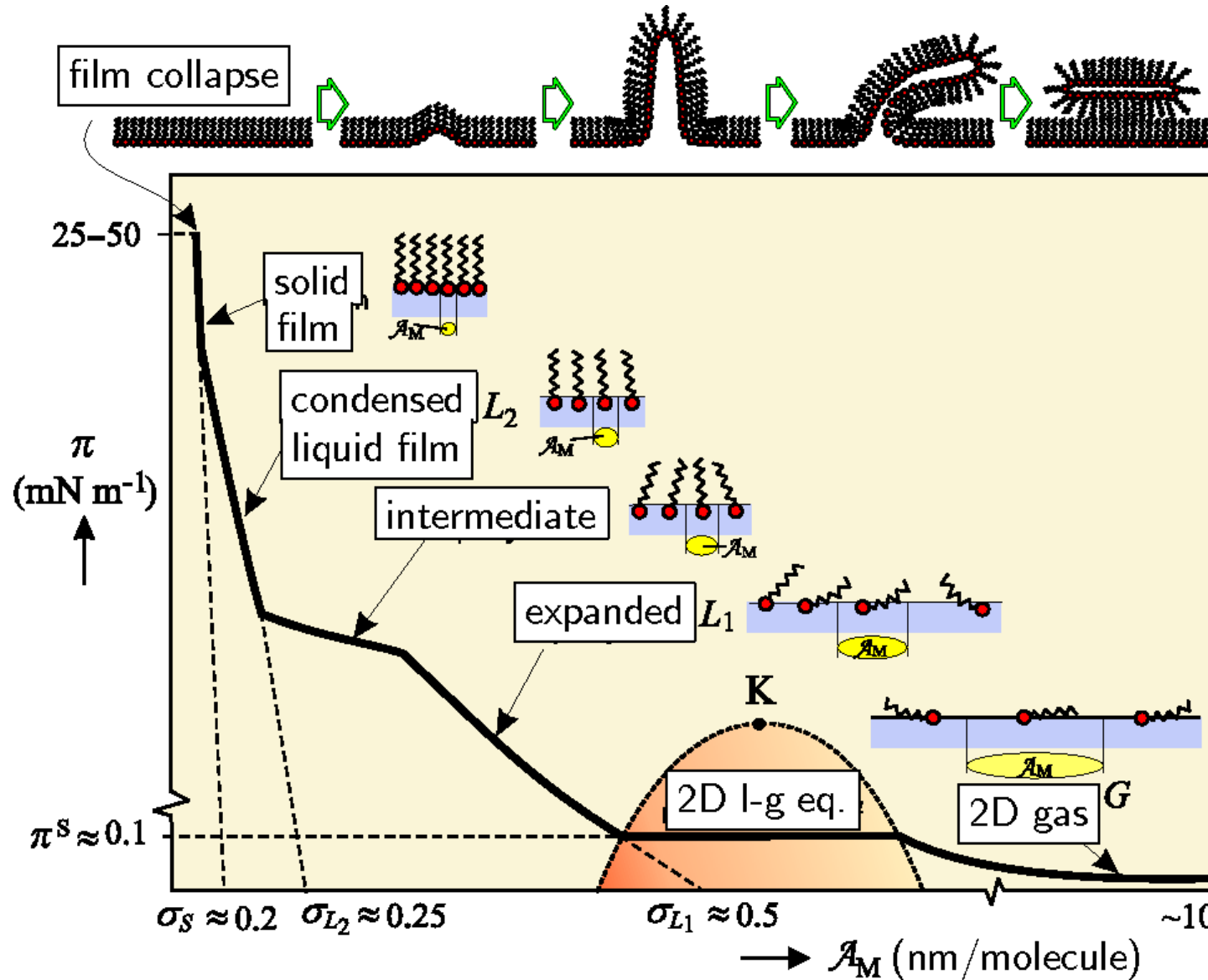
Experiment. Throw matches to water, touch the surface with soap or other detergent.



Lowering surface (Gibbs) energy \Rightarrow increase the surface covered by a surfactant \Rightarrow surface pressure

$$\pi = \gamma_0 - \gamma_{surf} > 0$$

Unit: N/m



credit: L. Bartovská

hexadecanol, palmitate: 2D crystal
phospholipides (less regular): 2D liquid film

1 = solvent

2 = surfactant

Surface excess:

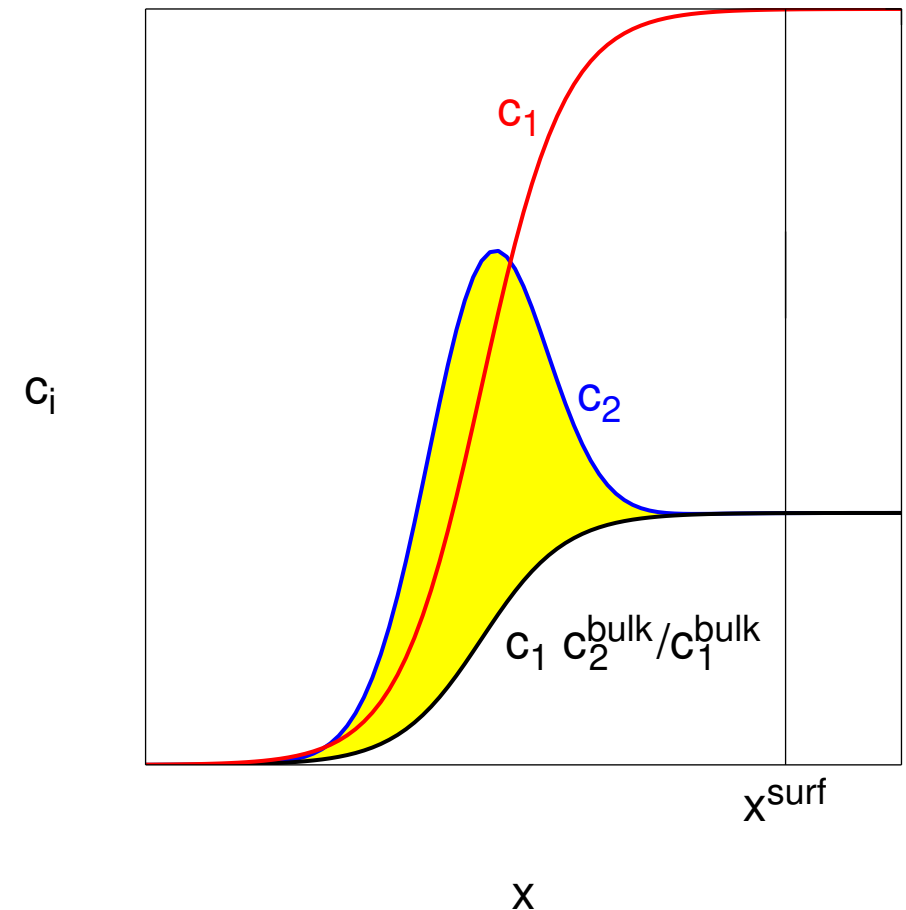
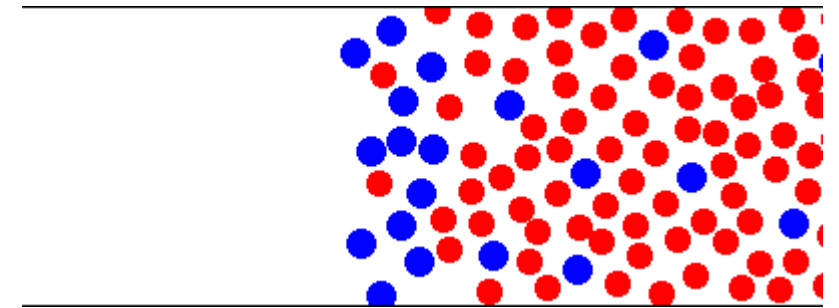
$$\Gamma_{2,1} = \int_{-\infty}^{\infty} \left[c_2(x) - \frac{c_2^{\text{bulk}}}{c_1^{\text{bulk}}} c_1(x) \right] dx$$

$$= \frac{1}{\mathcal{A}} \left[n_2^{\text{surf}} - \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} n_1^{\text{surf}} \right]$$

$c_i(x)$ = concentration of compound i at x

c_i^{bulk} = concentration of i in the bulk

$n_i^{\text{surf}} = \mathcal{A} \int_{-\infty}^{x^{\text{surf}}} c_i(x) dx$ for x^{surf} far away



Gibbs–Duhem equation in the bulk at constant $[p, T]$:

$$\begin{aligned}dG^{\text{bulk}} &= \mu_1 dn_1^{\text{bulk}} + \mu_2 dn_2^{\text{bulk}} = d(\mu_1 n_1^{\text{bulk}} + \mu_2 n_2^{\text{bulk}}) \\ \Rightarrow d\mu_1 n_1^{\text{bulk}} + d\mu_2 n_2^{\text{bulk}} &= 0 \Rightarrow d\mu_1 = -d\mu_2 \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}}\end{aligned}\quad (1)$$

Similarly for the surface (to x^{surf}):

$$\begin{aligned}dG^{\text{surf}} &= \mu_1 dn_1^{\text{surf}} + \mu_2 dn_2^{\text{surf}} + \gamma d\mathcal{A} = d(\mu_1 n_1^{\text{surf}} + \mu_2 n_2^{\text{surf}} + \gamma \mathcal{A}) \\ \Rightarrow d\mu_1 n_1^{\text{surf}} + d\mu_2 n_2^{\text{surf}} + d\gamma \mathcal{A} &= 0\end{aligned}\quad (2)$$

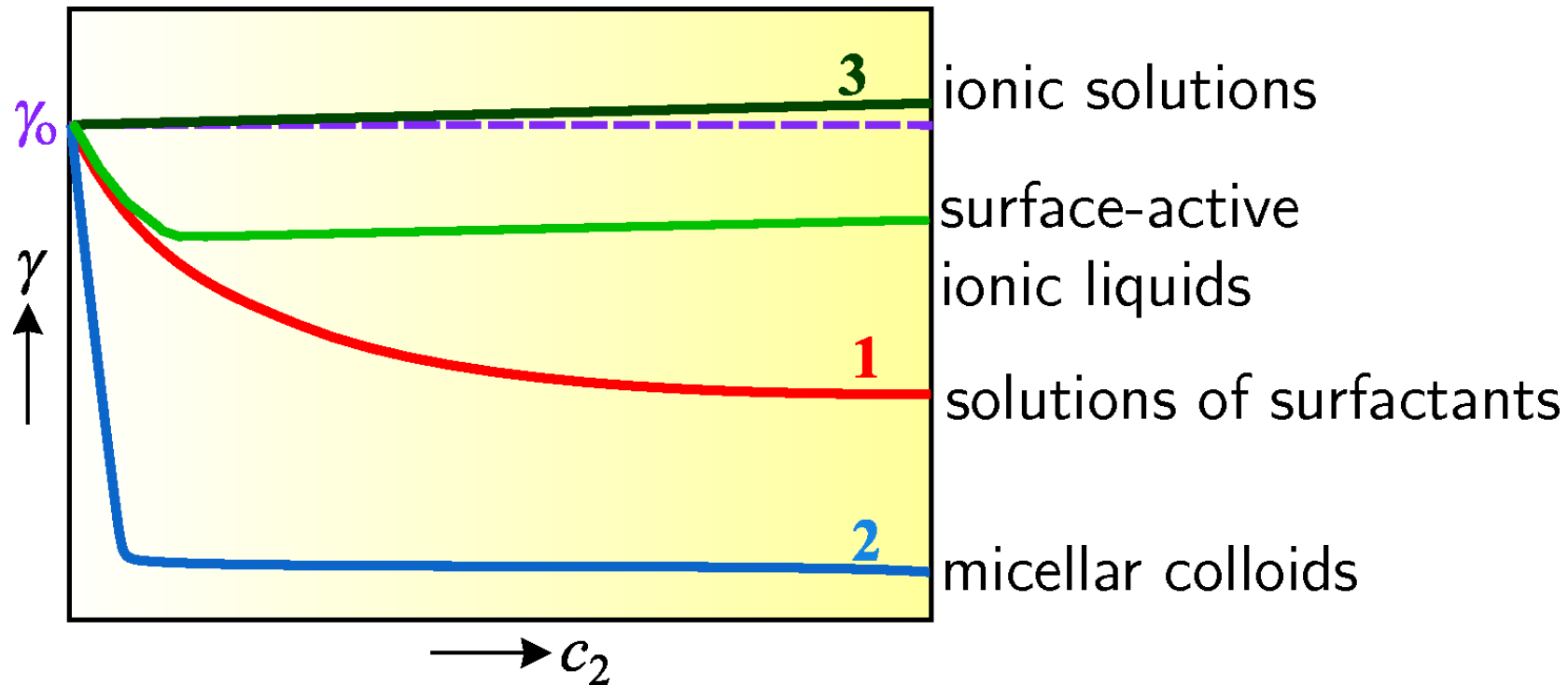
The chemical potentials are the same! On inserting (1) to (2):

$$-d\mu_2 \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} n_1^{\text{surf}} + d\mu_2 n_2^{\text{surf}} + d\gamma \mathcal{A} = d\mu_2 \left(n_2^{\text{surf}} - \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} n_1^{\text{surf}} \right) + d\gamma \mathcal{A} = 0$$

$\Gamma_{2,1}$ ←

$$\Gamma_{2,1} = - \left(\frac{\partial \gamma}{\partial \mu_2} \right)_{p,T} \approx - \frac{c_2}{RT} \left(\frac{\partial \gamma}{\partial c_2} \right)_{p,T}$$

A surfactant (decreasing the surface energy) exhibits a positive surface excess



Atomic Layer Deposition (ALD)

A precursor adsorbed to a monomolecular layer. Example:

- vapor of $\text{Al}_2(\text{CH}_3)_6$ (trimethylaluminium dimer): dissociative chemisorption
- remove vapor (vacuum, nitrogen)
- water vapor $\rightarrow \text{Al}_2\text{O}_3$
- remove vapor