EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering
sunmil.epfl.ch

SuNMiL
Supramolecular NanoMaterials and Interfaces Laboratory

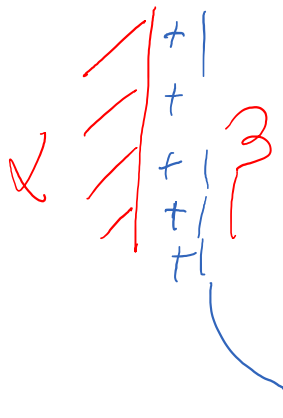
Adsorption at Interfaces
Lesson 7

MSE 304

Francesco Stellacci

桑缪 썬밀 सानमिल ΣouNMιΛ سنمل CaHMПЛ

Key Topics in the Previous Class



$$\gamma_{\alpha\beta} = \frac{1}{2}W_{\alpha\alpha} + \frac{1}{2}W_{\beta\beta} - W_{\alpha\beta} =$$

$$\gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

ψ_1

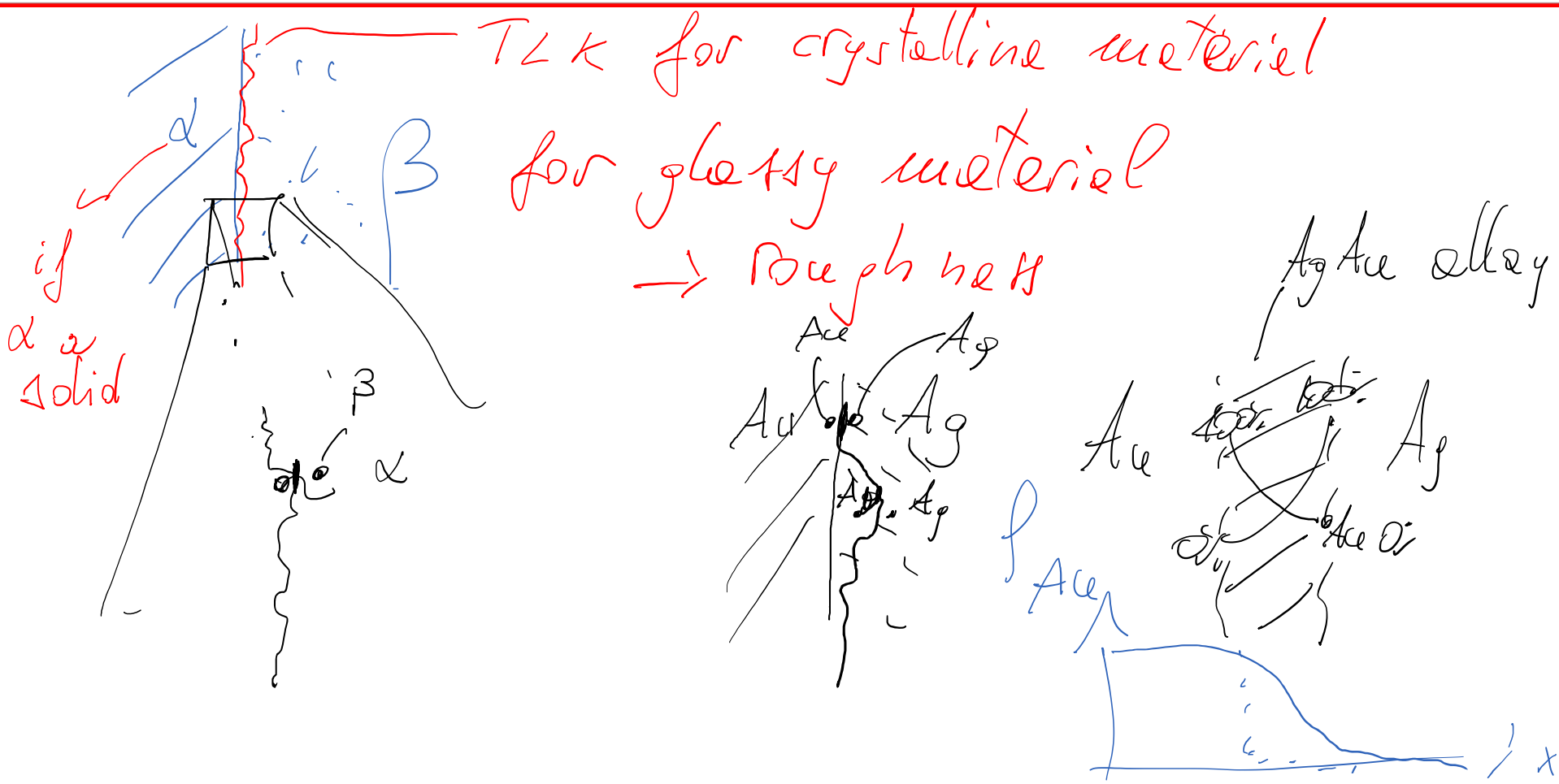
ζ zeta potential

Debey length

Reading for this Class

Butt Ch. 9

Challenges in Defining an Interface



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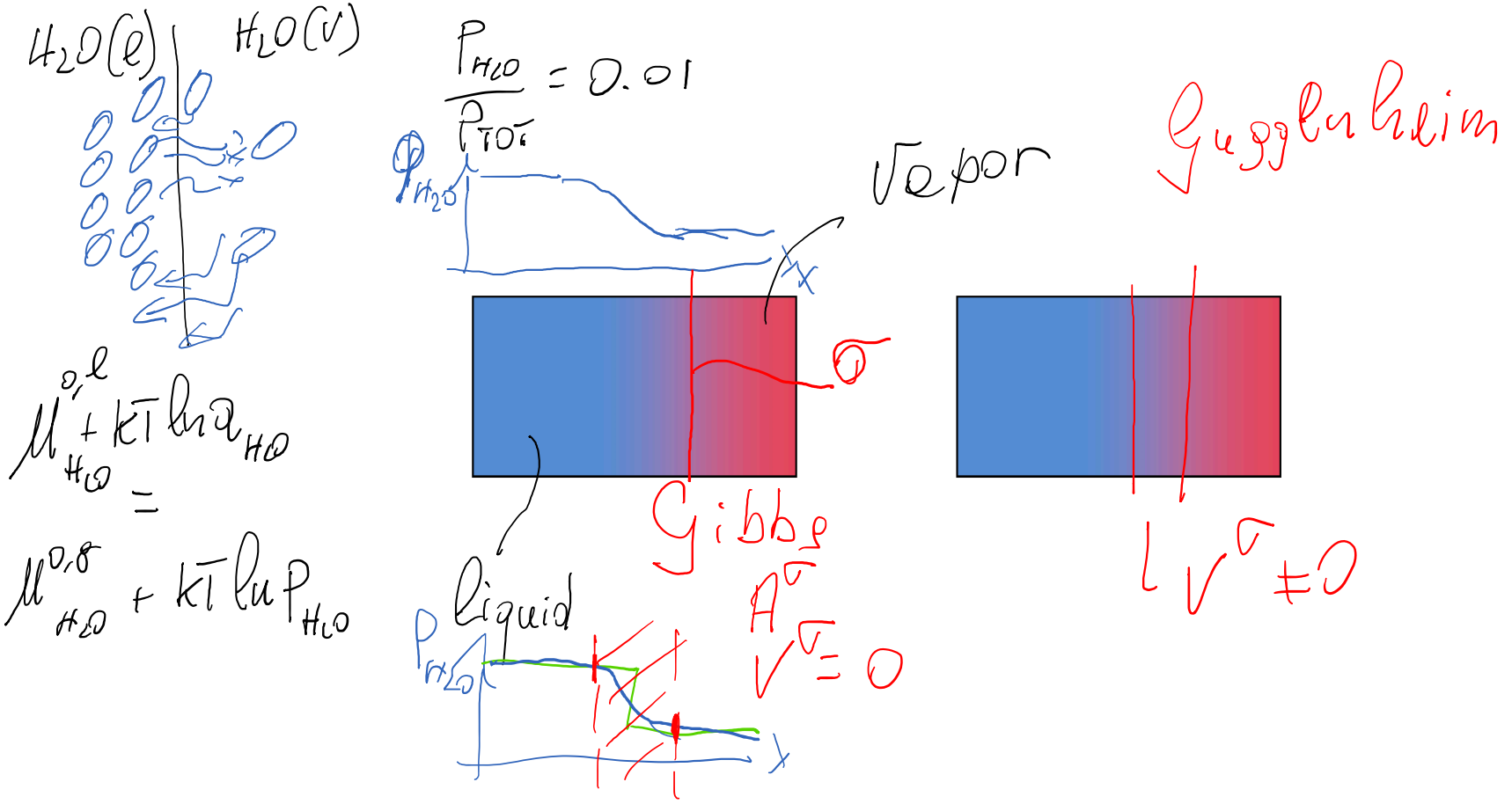
Challenges in Defining an Interface



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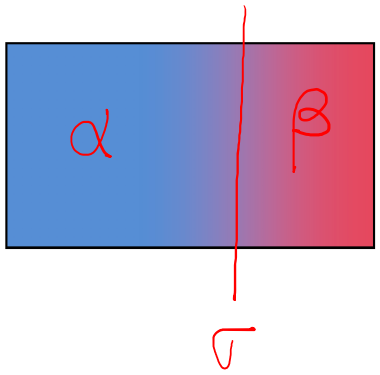
Gibbs Definition



$$N_i = N^\alpha + N^\beta + N^\sigma$$

$$U_i = U_i^\alpha + U_i^\beta + U_i^\sigma$$

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

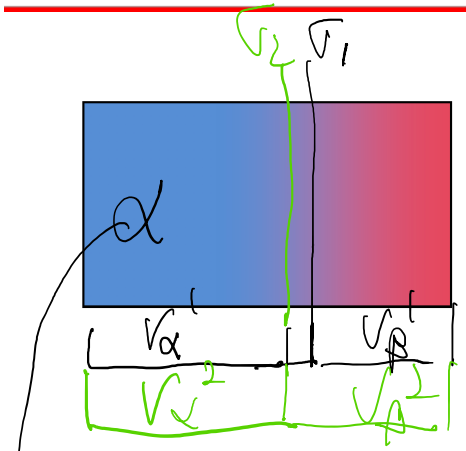
$$V = V^\alpha + V^\beta \qquad V^\sigma = 0$$

$$N_i = N^\alpha + N^\beta + N^\sigma = c_i^\alpha \cdot V^\alpha + c_i^\beta V^\beta + N^\sigma$$

$$N_i^\sigma = N_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta$$

$$\Gamma_i^\sigma = \frac{N_i^\sigma}{A^\sigma}$$

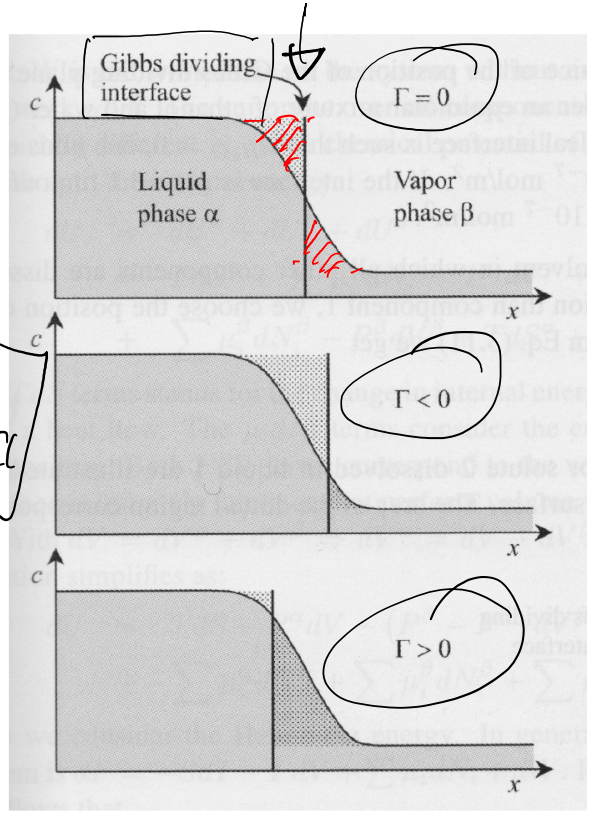
Gibbs Definition



liquid → solvent [example H_2O or LiCl]

main component

↳ ≡ $\Gamma = 0$



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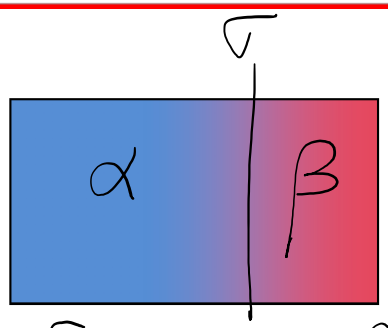
Gibbs Isotherm

MAIN COMPONENT => 1

ANY OTHER COMPONENT => i



$V^\sigma = 0 \qquad V = V^\alpha + V^\beta \Rightarrow V^\alpha = V - V^\beta$

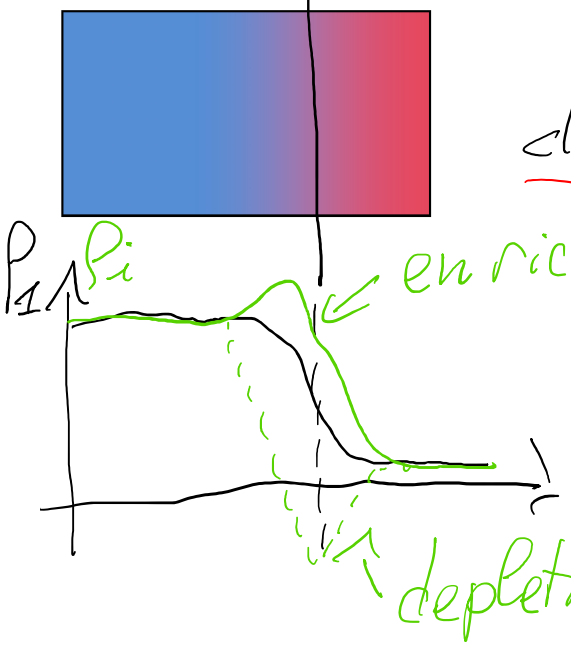
$N_i^\sigma = N_i - C_i^\alpha V^\alpha - C_i^\beta V^\beta = N_i - C_i^\alpha V - (C_i^\beta - C_i^\alpha) V^\beta$

$N_1^\sigma = N_1 - C_1^\alpha V - (C_1^\beta - C_1^\alpha) V^\beta \rightarrow V^\beta = \frac{1}{C_1^\alpha - C_1^\beta}\left(N_1^\sigma - N_1 - C_1^\alpha V\right)$

$\frac{N_i^\sigma}{A} - \frac{N_1^\sigma}{A}\left(\frac{C_i^\alpha - C_i^\beta}{C_1^\alpha - C_1^\beta}\right) = \left\{N_i - C_i^\alpha V - \left(N_1^\sigma - C_1^\alpha\right)\left(\frac{C_i^\alpha - C_i^\beta}{C_1^\alpha - C_1^\beta}\right)\right\}\frac{1}{A}$

$\Gamma_i^\sigma - \Gamma_1^\sigma \cdot \frac{\Delta^{\alpha\beta}}{\Delta^{\alpha\beta}} = \Gamma_i^{1,\sigma} \rightarrow \Gamma_1^\sigma = 0 \rightarrow \Gamma_i^\sigma = \Gamma_i^{(1)}$

Gibbs Isotherm



$$V^\sigma \equiv 0$$

$$U^\sigma \equiv TS^\sigma - pV^\sigma + \sum_i \mu_i N_i^\sigma + \gamma A^\sigma$$

$$dU^\sigma = T\,dS^\sigma + S^\sigma dT - p\,dV^\sigma - V^\sigma dp + \sum_i \mu_i\, dN_i^\sigma + \sum_i N_i^\sigma d\mu_i + \gamma\, dA^\sigma + A^\sigma d\gamma$$

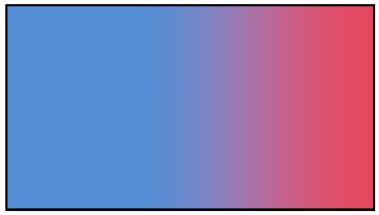
$$\rightarrow dU^\sigma \equiv T\,dS^\sigma - p\,dV^\sigma + \sum_i \mu_i\, dN_i^\sigma + \gamma\, dA$$

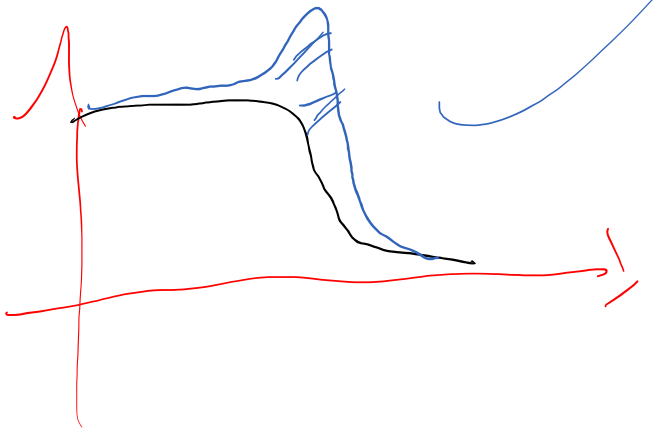
$$S^\sigma dT + \sum_i N_i^\sigma d\mu_i^\sigma + A^\sigma d\gamma = 0$$

$$dT = 0$$

$$d\gamma = -\sum_i \Gamma_i\, d\mu_i^\sigma$$

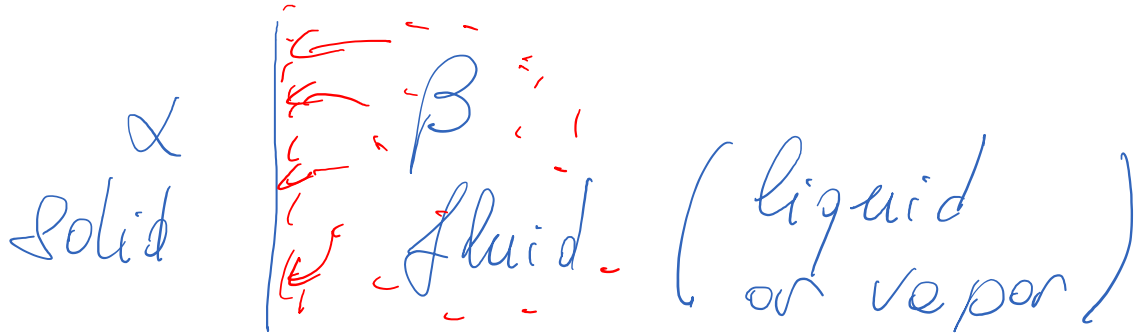
Gibbs Isotherm





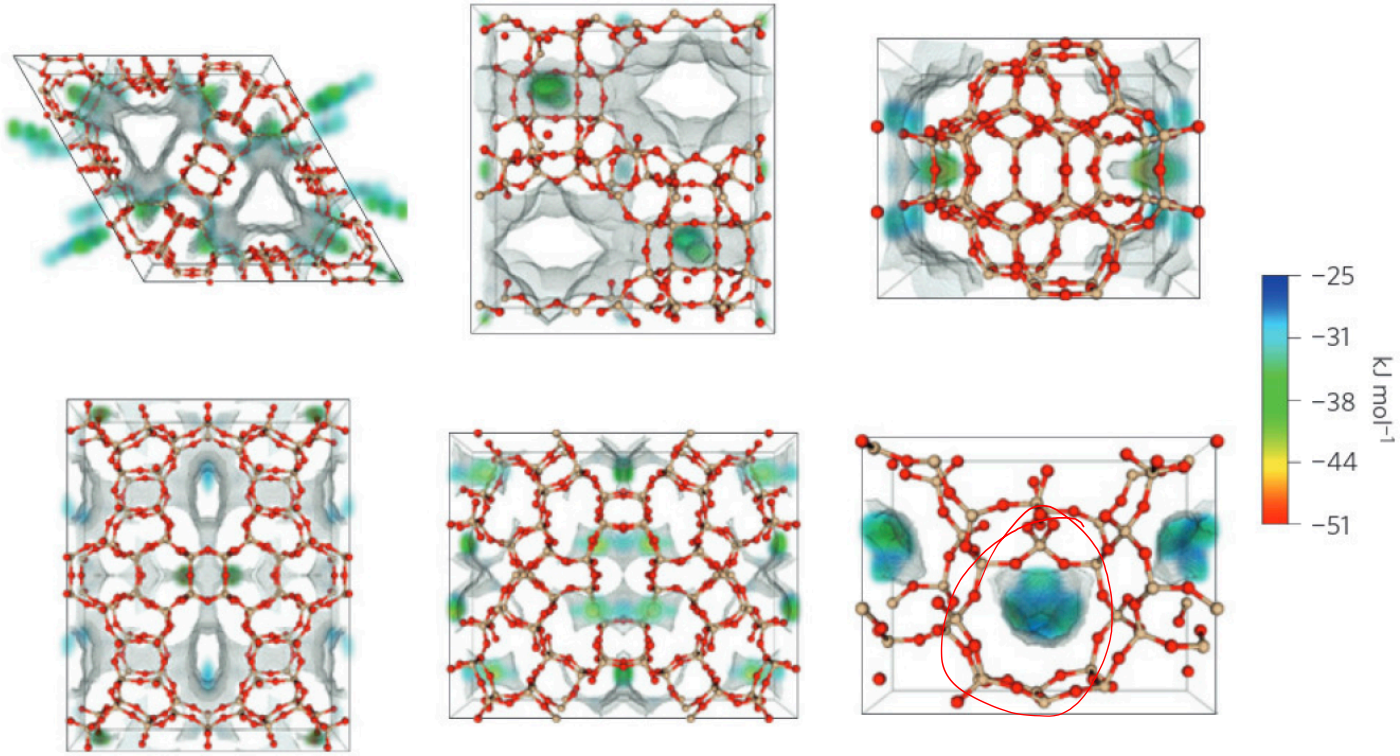
$$d\gamma = -\sum \Gamma_i \, d\mu_i$$

Adsorption at Interfaces



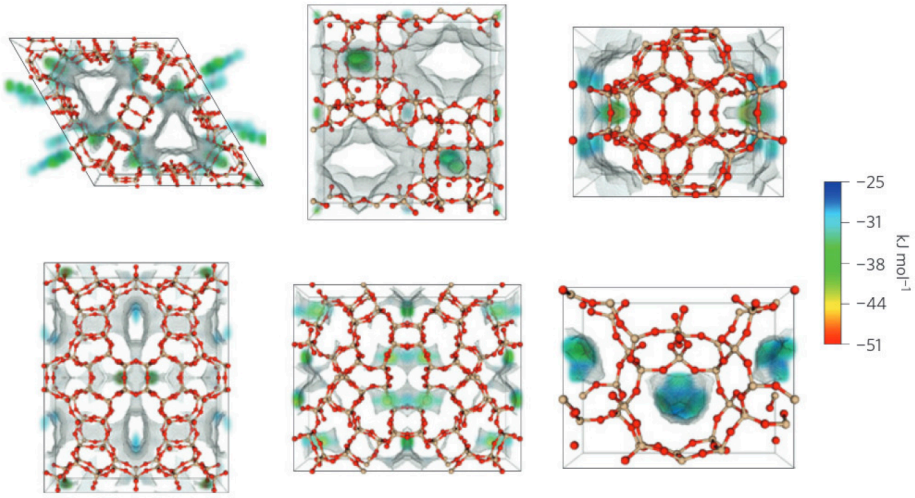
isotherms

Adsorption at Interfaces

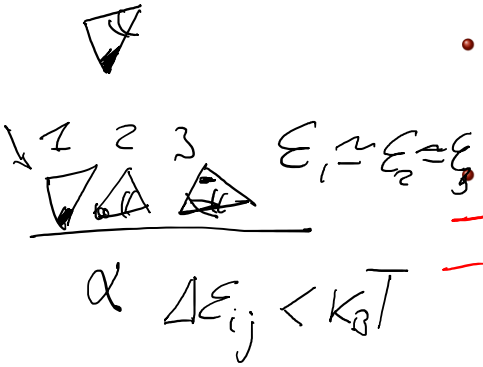


Adsorption at Interfaces

- Adsorption is crucial for catalysis, and storage of gases!
- Phenomenology of adsorption
- Langmuir adsorption interface: one species and competitive
- Different kinds of adsorption isotherms: FFG (correlated), BET (multilayer)



Chemisorption and Physisorption



- Real surfaces are often covered in molecules, often with complex/regular arrangements
  - Adsorption lowers the surface energy
- Conventional classification as a function of the adsorption enthalpy
  - **physisorption**: reversible, weak binding (< 40 kcal/mol), mobile species
  - **chemisorption**: irreversible, strong binding (> 40kcal/mol), immobile species

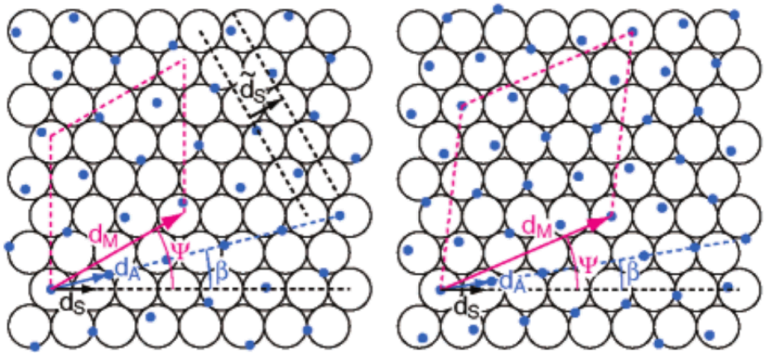
$\Delta\varepsilon_{ij} \gtrsim 2 k_B T$

physisorption → adsorption (adsorbates)

chemisorption → absorption (absorbates)
- preferential geometry
- with no preferential geometry

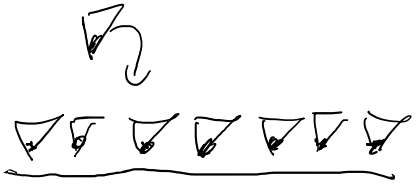
Monolayers

chemisorption



reconstruction crystallography

ordered monolayers



full packing of these molecules is called a monolayer

Key Definitions in Adsorption

- An adsorbate molecule often resides in specific adsorption sites (not necessarily one per surface unit cell).
- **Coverage** θ measures the number of occupied sites n relative to the maximum possible number N
- Adsorption energy ϵ: stabilization relative to the gas-phase molecule.
  Residence time: $\tau \sim \tau_0 e^{\epsilon / k_B T}$
- Experimental measure: **adsorption isotherm**

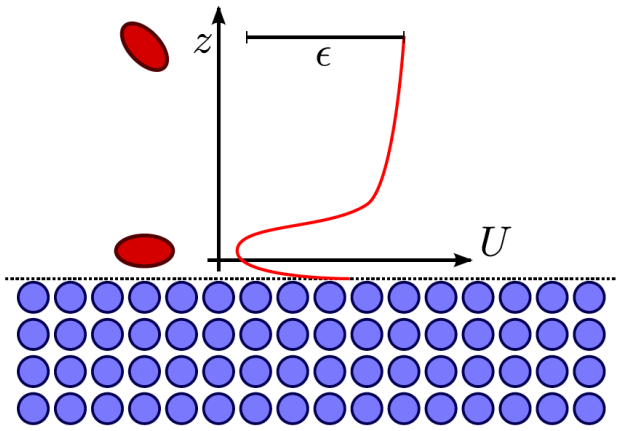
$\theta = \frac{n}{N}$

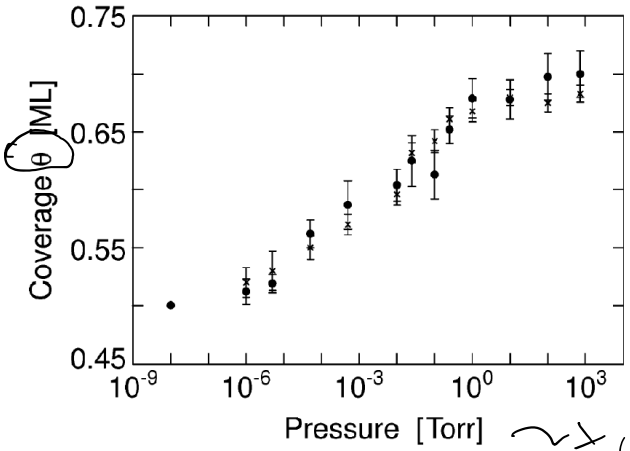
$\theta = 1$ monolayer

$\theta < 1$ submol.

$\theta > 1$ multilayer

ϵ = energy of adsorption





→ for gas

concentration → for liquid

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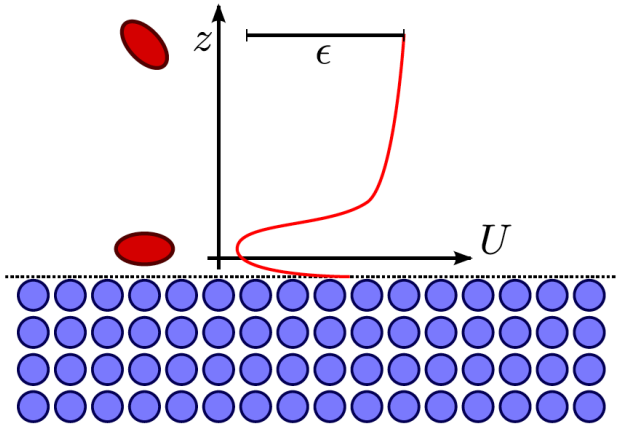

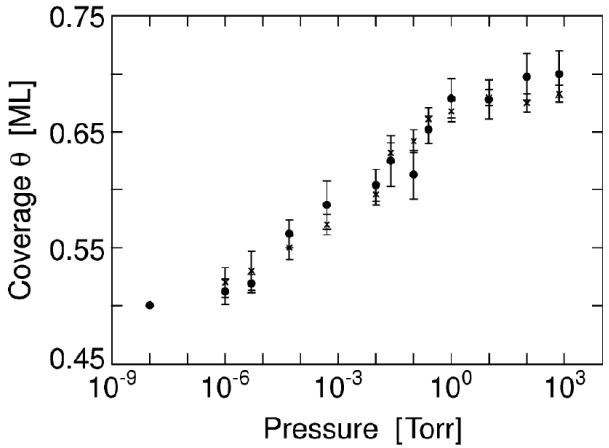

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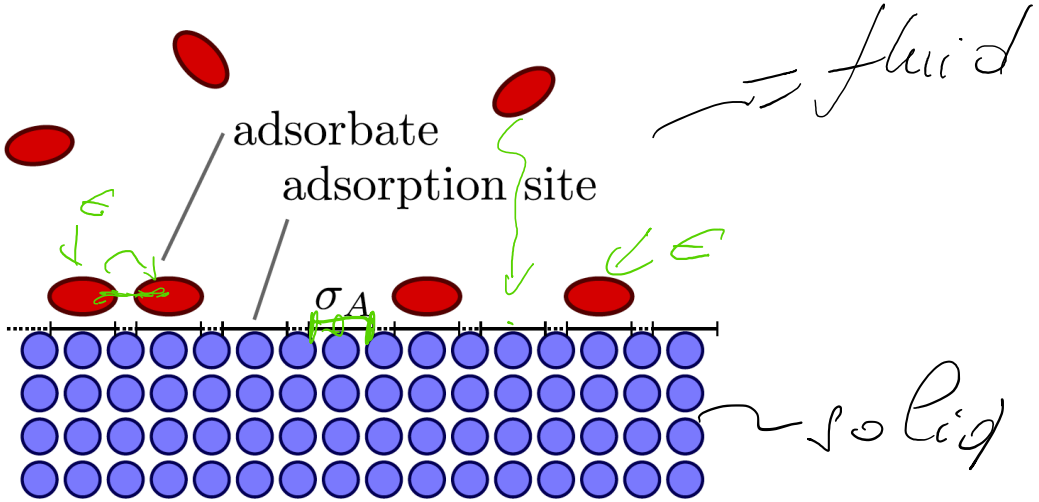
Langmuir Isotherm – Initial Hypotheses

- A simple model for adsorption that leads to the **Langmuir adsorption isotherm**:
  - The surface is covered by *equivalent* adsorption sites, with area σ_A
  - The adsorption energy ϵ is *independent* on the site and on the occupation of nearby adsorption sites
  - The *sticking coefficient* (probability on binding upon a collision with the surface) on an empty site is one



Langmuir Isotherm – Equilibrium Derivation

- Equilibrium between adsorption rate K_{AD} and desorption rate K_{DE}
  - **Desorption rate** proportional to the fraction of occupied sites and the rate for one site
  - **Adsorption rate** proportional to the fraction of empty sites and the collision rate (assuming *sticking coefficient* is one)

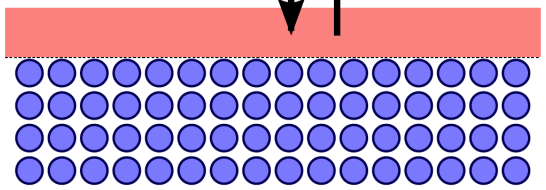
$$K_{DE} = K_{AD}$$

$$K_{DE} = \theta \cdot k_{DE} \qquad K_{AD} = (1-\theta) \cdot P \cdot k_{AD}$$

$$\theta\, k_{DE} = (1-\theta) \cdot P \cdot k_{AD}$$

$$\theta \left(k_{DE} + P k_{AD}\right) = P k_{AD}$$

$$K_{AD} = (1-\theta) P k_{AD} \qquad K_{DE} = \theta k_{DE}$$



$$\theta = \frac{P k_{AD}/k_{DE}}{k_{DE} + P k_{AD}}$$

$$\frac{k_{AD}}{k_{DE}} = k_c$$

Langmuir Isotherm

$$K_L = \frac{1}{P_0}$$

$$\theta = \frac{PK_L}{PK_L + 1},$$

$$\frac{\theta}{1-\theta} = \frac{P}{P_0} = k_L P = \frac{k_{AD}}{k_{DE}} P,$$

$$P K_L = \frac{\theta}{1-\theta}$$

$$\frac{\theta}{1-\theta} = \frac{P}{P_0}$$

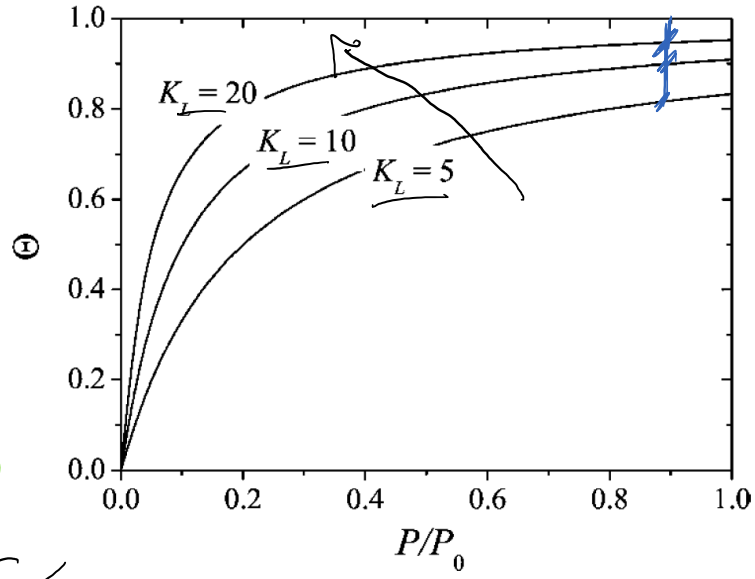
$$k_L = \frac{1}{P_0} = \frac{k_{AD}}{k_{DE}} = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} e^{\epsilon / k_B T}$$

$$K_{AD} = \tau_0 e^{E/k_B T}$$

$$\lim_{P \to \infty} \theta = 1$$

$$K_{DE} = \frac{\sigma_A}{\sqrt{2\pi m K_B T}} \cdot S$$

$S = 1$



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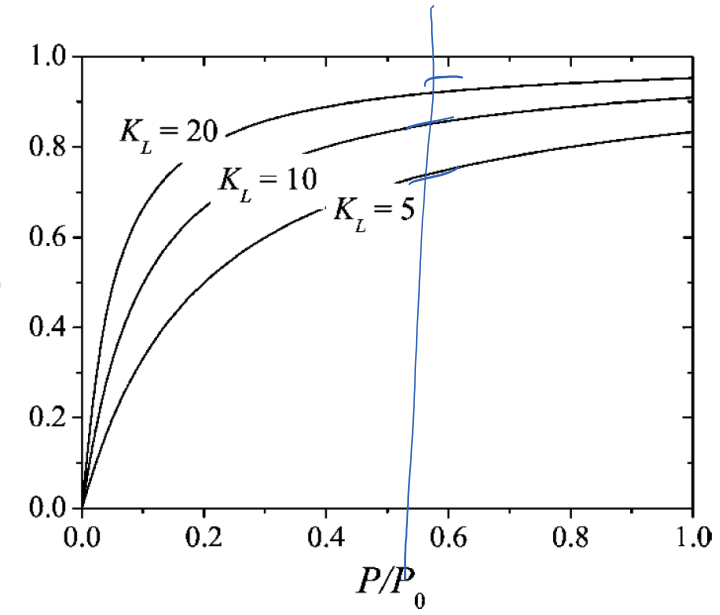
Langmuir Isotherm - Considerations

Vacancies

K_L

is this compatible with the TLK model?



absorption
adsorption
} to be reversible

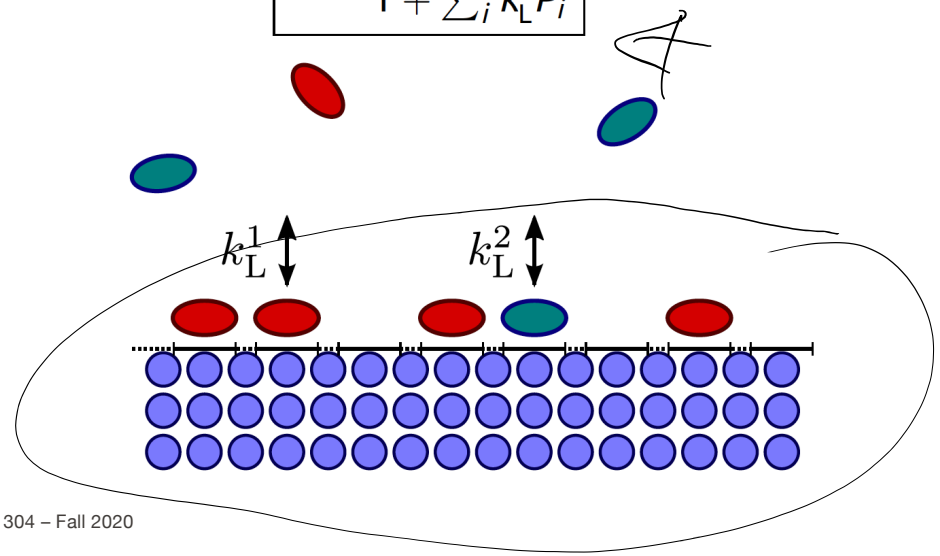
Langmuir Isotherm – Competitive Adsorption

- What if we have multiple molecules in the gas phase? $\theta = \sum_i \theta_i$
- At equilibrium one must have mass balance for each specie separately

$$\theta_i k^i_{DE} = K^i_{DE} = K^i_{AD} = (1-\theta)\, k^i_{AD} P_i$$

$$\frac{\theta}{1-\theta} = \sum_i k^i_L P_i \rightarrow \theta = \frac{\sum_i k^i_L P_i}{1+\sum_i k^i_L P_i} \rightarrow 1-\theta = \frac{1}{1+\sum_i k^i_L P_i}$$

$$\boxed{\theta_i = \frac{k^i_L P_i}{1+\sum_i k^i_L P_i}}$$



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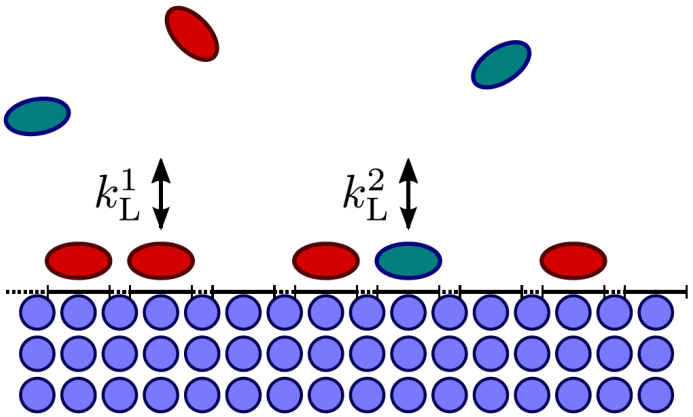
$$\theta_i k^i_{DE} = K^i_{DE} = K^i_{AD} = (1-\theta)\, k^i_{AD} P_i$$

$$\frac{\theta}{1-\theta} = \sum_i k^i_L P_i \rightarrow \theta = \frac{\sum_i k^i_L P_i}{1+\sum_i k^i_L P_i} \rightarrow 1-\theta = \frac{1}{1+\sum_i k^i_L P_i}$$

$$\boxed{\theta_i = \frac{k^i_L P_i}{1+\sum_i k^i_L P_i}}$$



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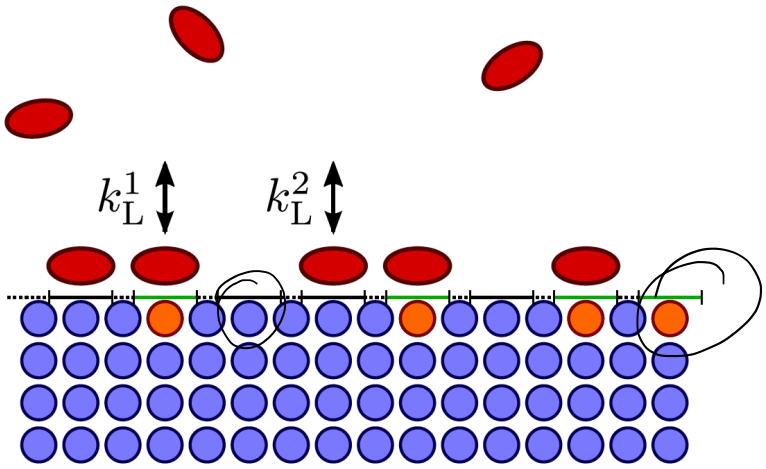
Langmuir Isotherm – Competitive Adsorption

- Multiple adsorption sites, with fraction x_i and different adsorption energies ϵ_i
- Can treat as independent adsorption problems, but $\theta = \sum_i x_i \theta_i$

$$\theta_i x_i k^i_{DE} = K^i_{DE} = K^i_{AD} = x_i \left(1 - \theta_i\right) k^i_{AD} P$$

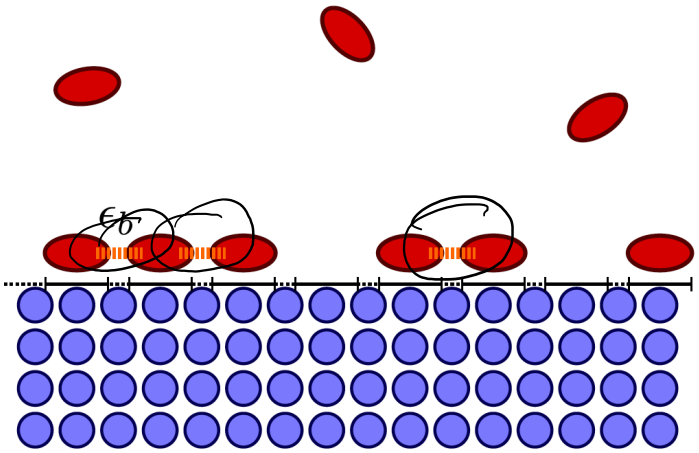
$$\boxed{\theta_i = \frac{k^i_L P}{1 + k^i_L P}, \quad \theta = \sum_i \frac{x_i k^i_L P}{1 + k^i_L P}}$$



Collaborative Adsorption – FFG Isotherm

- Consider the possibility of bonding between molecules.
- The number of bonds per molecule at full coverage is n, and the energy per bond ϵ_b
- The probability of one neighbor being occupied is θ, so the mean energy of an adsorbed molecule becomes $\epsilon \leftarrow \epsilon + n\theta\epsilon_b$
- Isotherm is given by the (physical) solutions to the implicit equation

$$\frac{\theta}{1-\theta} = k_L e^{\frac{n\epsilon_b\theta}{k_B T}} P$$



$$k_L = \frac{1}{P_0} = \frac{k_{AD}}{k_{DE}} = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} e^{\epsilon/k_B T}$$

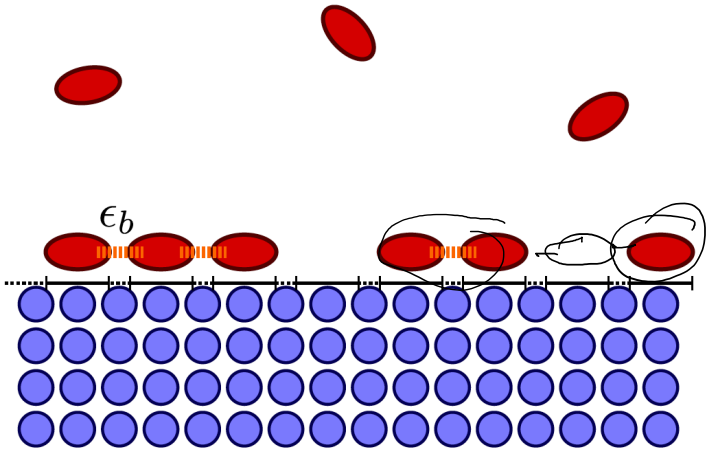
$$K_L = \alpha e^{\epsilon/k_B T}$$

$$K_L^{FFG} = \alpha e^{\epsilon'/k_B T} =$$

$$= \alpha e^{\frac{\epsilon + n\epsilon_b\theta}{k_B}} = \underbrace{\alpha e^{\epsilon/k_B}}_{K_L} \cdot e^{\beta}$$

Collaborative Adsorption – FFG Isotherm

$$\frac{\theta}{1-\theta} = k_L e^{\frac{n\epsilon_b \theta}{k_B T}} P$$



$\beta > 4$

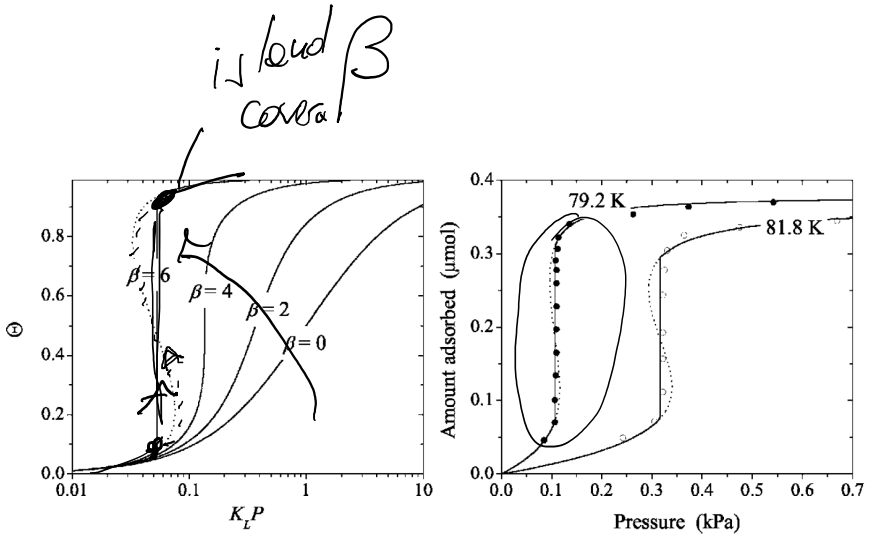
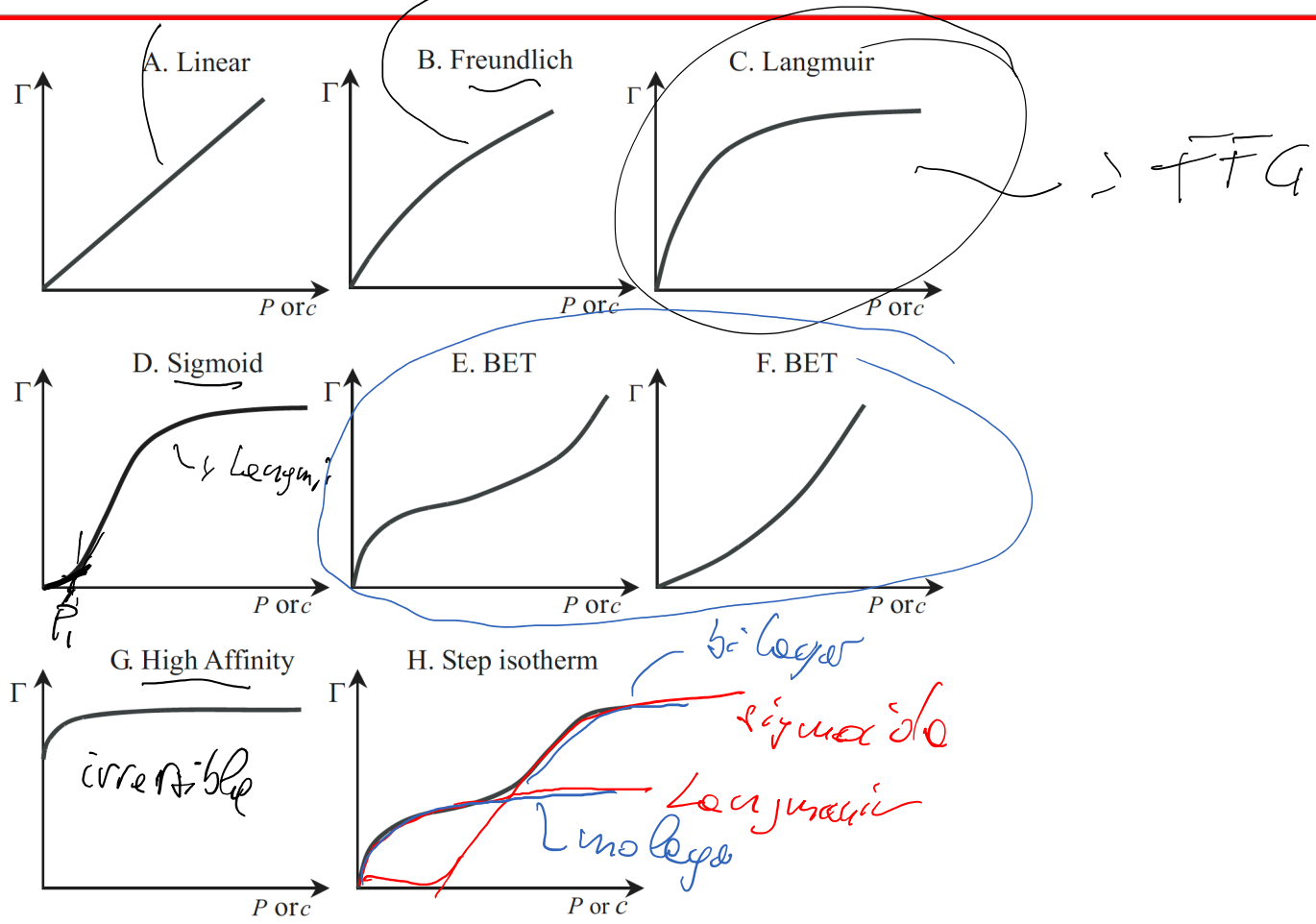


Figure 9.7: Left: Frumkin–Fowler–Guggenheim (FFG) adsorption isotherms (coverage θ versus the pressure in units of K_L^{-1}). The curves were calculated using Eq. (9.35) with $\beta = 0, 2, 4, 6$. For $\beta = 6$ the physically correct adsorption curve is plotted as a continuous curve while the one calculated with Eq. (9.35) is plotted as a dotted curve. Right: Adsorption isotherms for krypton adsorbing to the (0001) plane of graphite at two different temperatures. The dotted curves were fitted using Eq. (9.35) with $\beta = 4.5$. Experimental results were taken from Ref. [377].

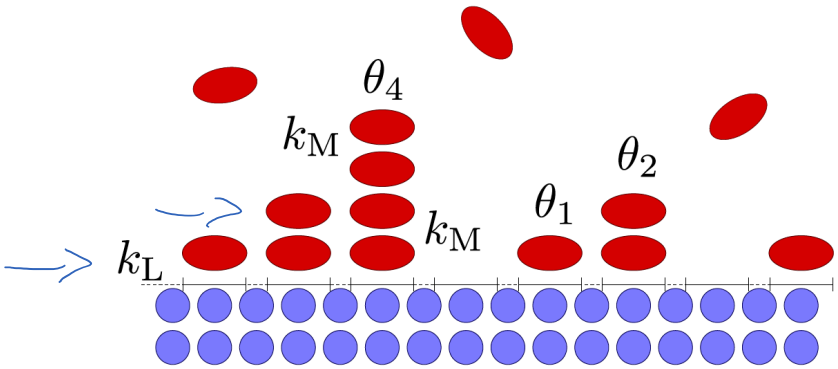
Isotherms


A. Linear
B. Freundlich
C. Langmuir
D. Sigmoid
E. BET
F. BET
G. High Affinity
H. Step isotherm
Γ
P or c

BET

- Random adsorption on multiple layers. Langmuir constant for the first layer is k_L, other layers bind on the previous with $k_M = k_L e^{(\epsilon_M - \epsilon_1)/k_B T}$
- One must equate ad/desorption rate from the sites covered by i layers
- The sums of θ_i's are geometric series.
- Total coverage (number of molecules per number of *surface* sites)

$$\theta_1 = k_L P \left(1 - \sum_i \theta_i\right), \qquad \theta_i = \theta_{i-1} k_M P = \theta_1 \left[k_M P\right]^{i-1}$$



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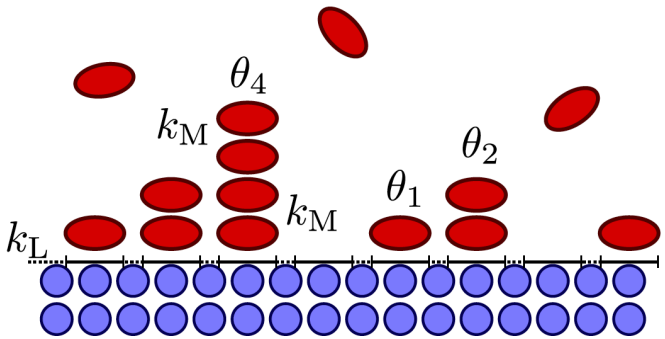
BET - Multilayers

$$\sum_{i=1}^{\infty} [k_M P]^{i-1} = \frac{1}{1 - k_M P}, \qquad \sum_{i=1}^{\infty} i\,[k_M P]^{i-1} = \frac{1}{(1 - k_M P)^2}$$

$$\theta = \theta_1 \sum_{i=1}^{\infty} i\,[k_M P]^{i-1} = \theta_1 \frac{1}{(1 - k_M P)^2} = \frac{k_L P\,(1 - k_M P)}{1 + k_L P - k_M P} \frac{1}{(1 - k_M P)^2}$$

$$\theta \approx \frac{1}{(1 - x_B)} \frac{x_B c_B}{1 + x_B\,(c_B - 1)}, \qquad x_B = k_M P,\ c_B = k_L / k_M$$

$$\boxed{\theta = \frac{k_L P}{1 + k_L P - k_M P} \frac{1}{1 - k_M P}}$$



SuNMIL EPFL

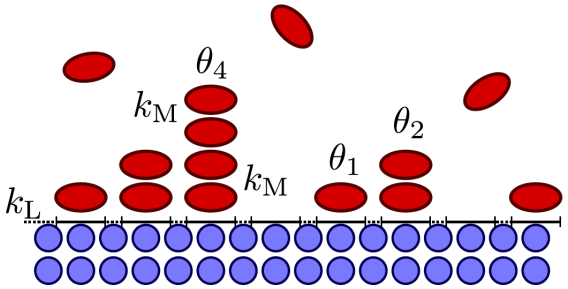
BET - Multilayers

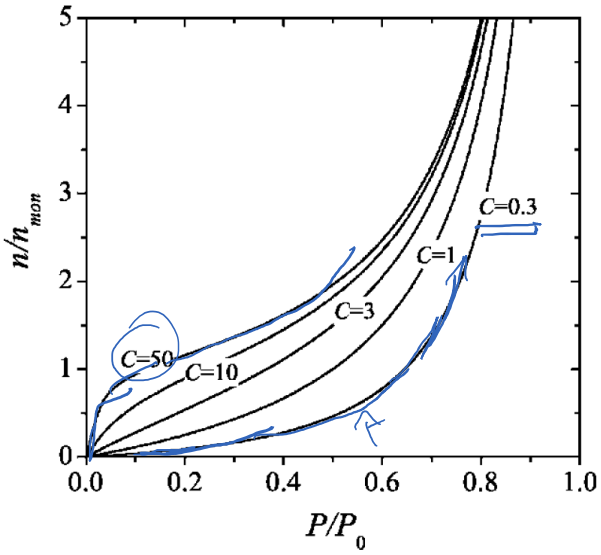
$$\theta = \frac{k_L P}{1 + k_L P - k_M P} \frac{1}{1 - k_M P}$$

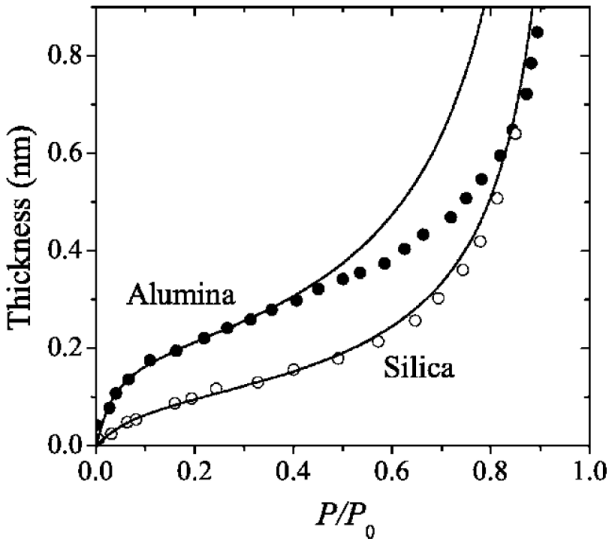
$\to \infty$

$P = \frac{1}{k_H}$

$\frac{1}{k_H}$ condensation pressure







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Conclusions

isotherm

↳ $d\gamma = -\sum_i \Gamma_i \, d\mu_i$

→ Langmuir → BET