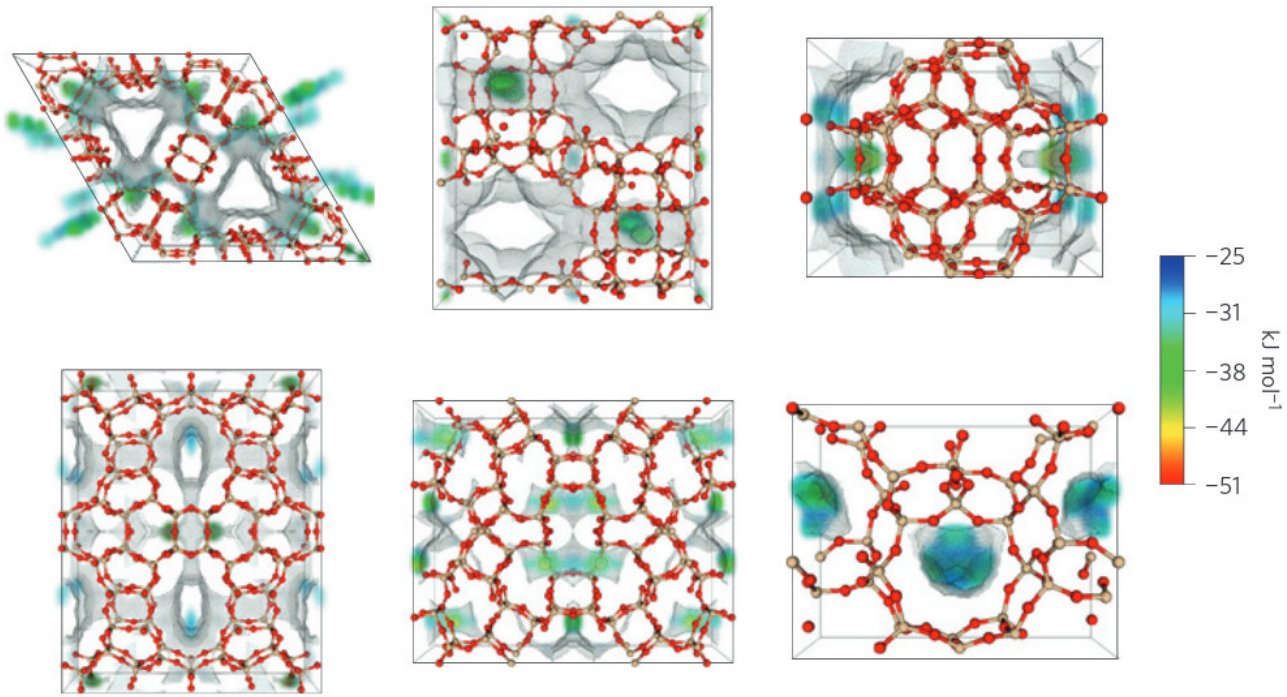
Adsorption at interfaces

M. Ceriotti - MX304

EPFL

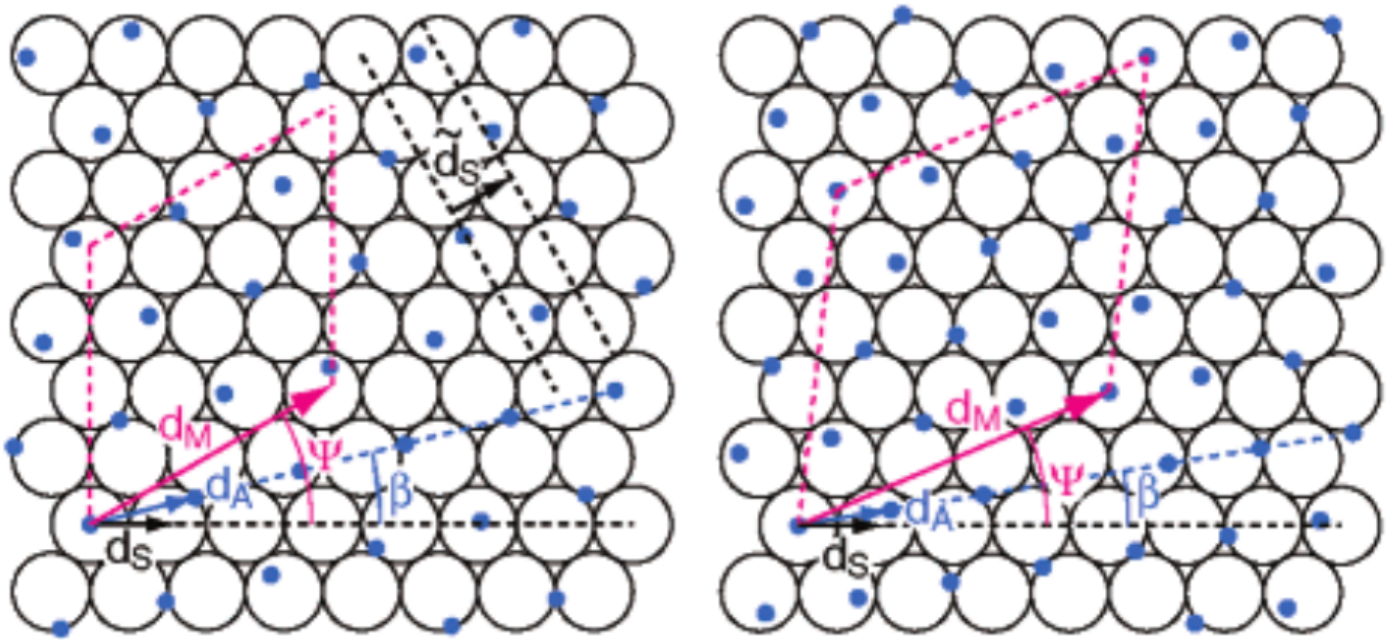
Outline

- 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)



Atoms and molecules on surfaces

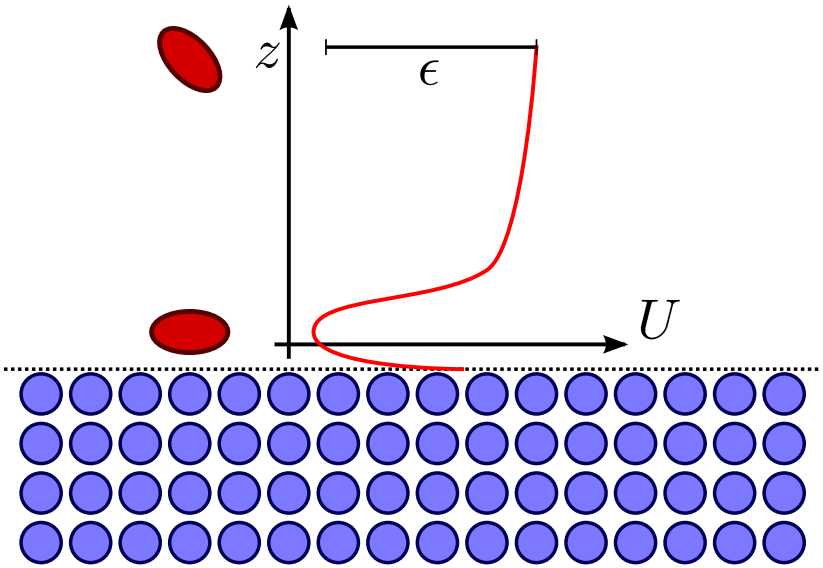
- Real surfaces are often covered in molecules, often with complex/regular arrangements
  - Adsorption lowers the surface energy
- Conventional classification as a function of the adsorption enthalpy
  - **physisorption**: reversible, weak binding ($<$ 40 kcal/mol), mobile species
  - **chemisorption**: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

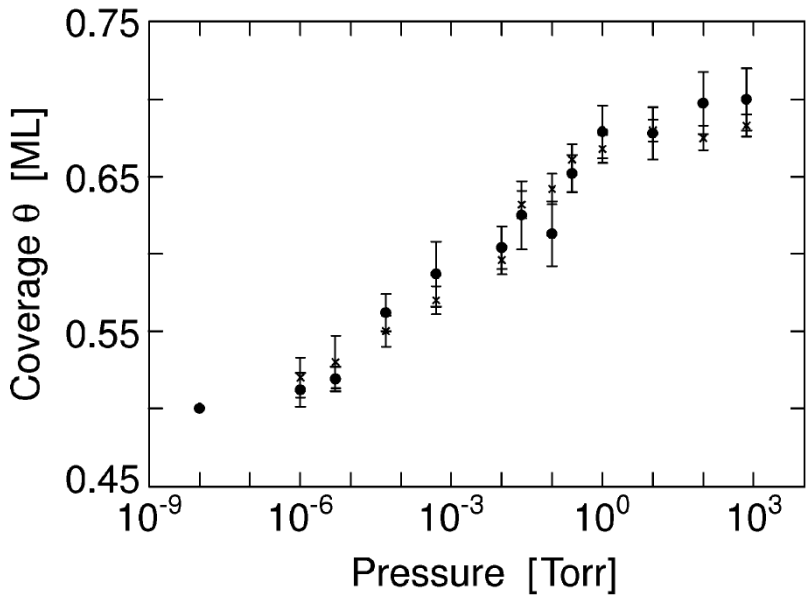


S. Longwitz et al., J. Phys. Chem. B 108, 14497 (2004)

Residence time, coverage, isotherms

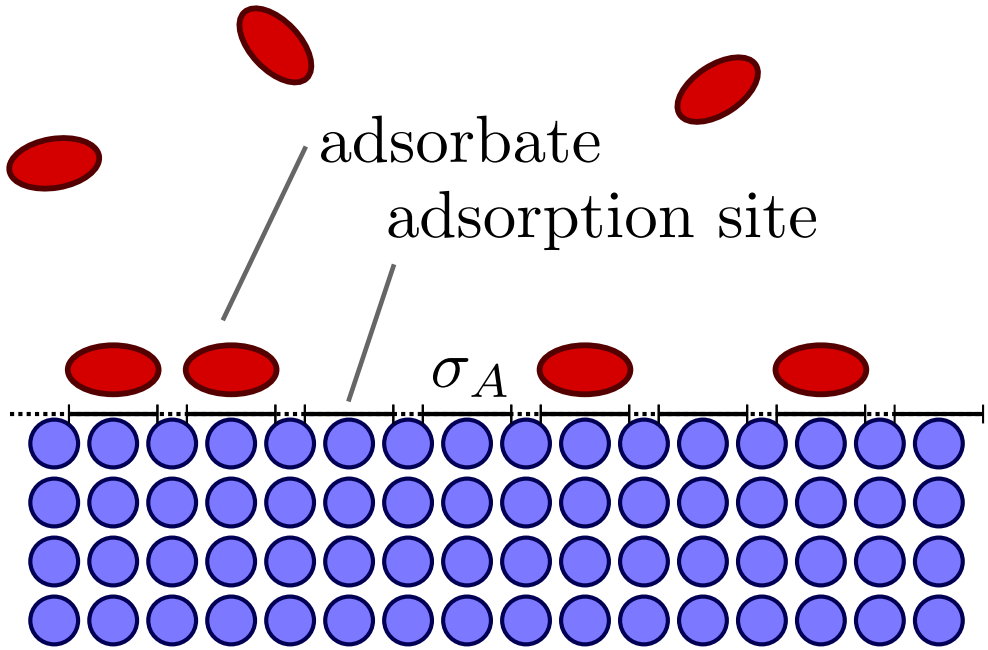
- An adsorbate molecule often resides in specific adsorption sites (not necessarily one per surface unit cell).
- **Coverage** θ measures the number of occupied sites n relative to the maximum possible number N
- Adsorption energy ϵ: stabilization relative to the gas-phase molecule. **Residence time**: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





Langmuir adsorption model

- 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



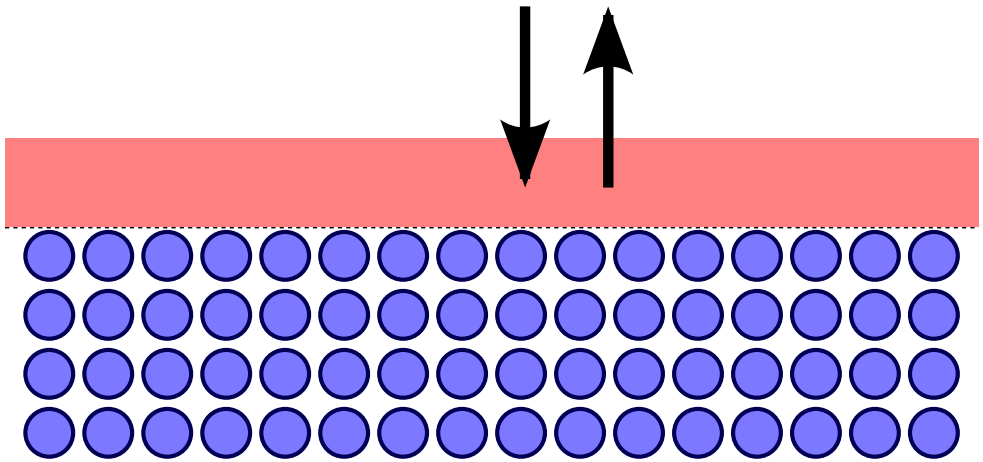
Langmuir isotherm: a chemical equilibrium

- 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)

$$K_{DE} = \theta k_{DE} = \frac{\theta}{\tau_0} e^{-\epsilon/k_B T}, \quad K_{AD} = (1-\theta)\, k_{AD} P = (1-\theta)\, \frac{\sigma_A P}{\sqrt{2\pi m k_B T}}$$

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

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



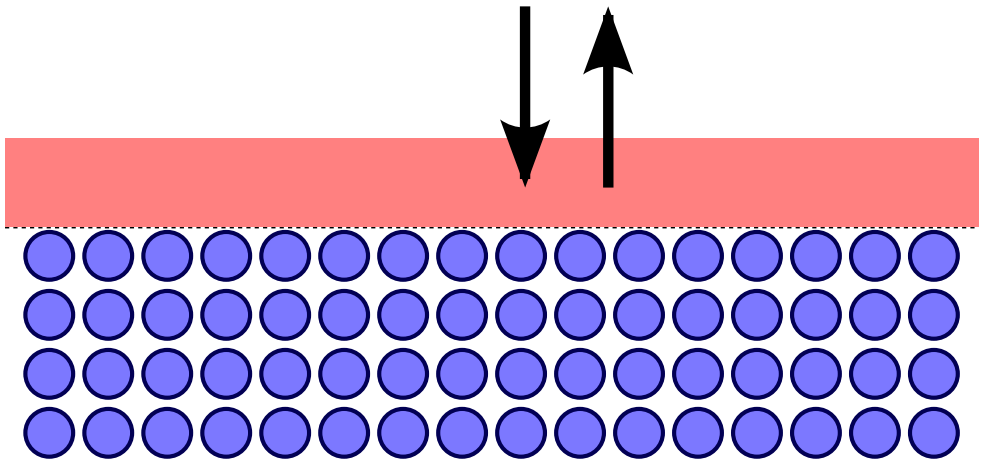
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$$k_L = \frac{1}{P_0} = \frac{k_{AD}}{k_{DE}} = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} e^{\epsilon / k_B T}$$

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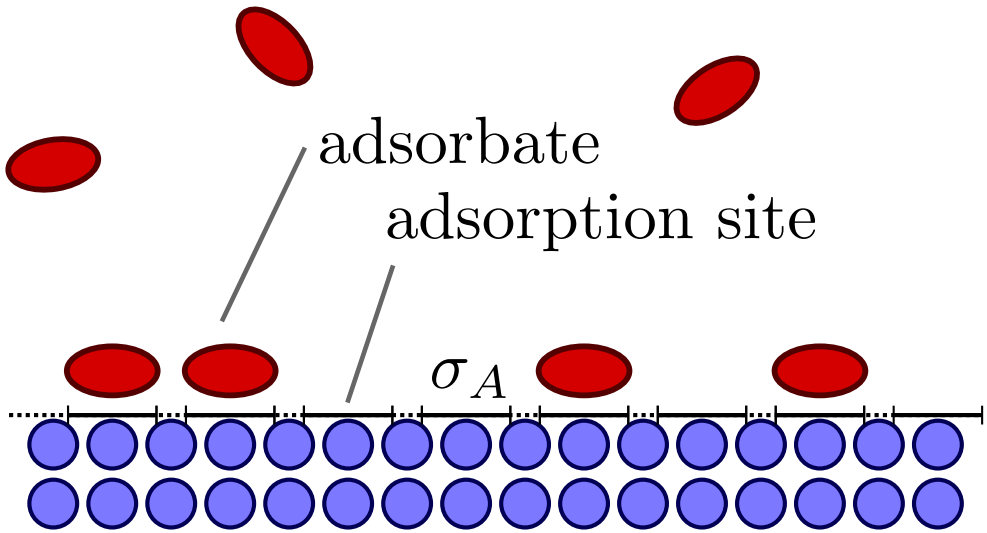


Langmuir isotherm: the stat-mech approach

- Let's look at the statistical mechanics of a mono-layer:
  - N available *sites*, n adsorbed molecules (coverage $\theta = n/N$), adsorption energy ϵ
  - The chemical potential must equal that in the gas phase $\mu_G = \mu_G^{\ominus} + RT \ln \frac{P}{P^{\ominus}}$
  - Putting all the "unknown terms" into an effective P_0 gives us the **Langmuir isotherm**

$$G = G_0 + n\epsilon - RT\left[N \ln N - (N-n)\ln(N-n) - n \ln n\right]$$

Chemical potential: $\mu_{ADS} = \dfrac{\partial G}{\partial n} = -\epsilon + RT\left[1 + \ln n - \ln(N-n) - 1\right]$

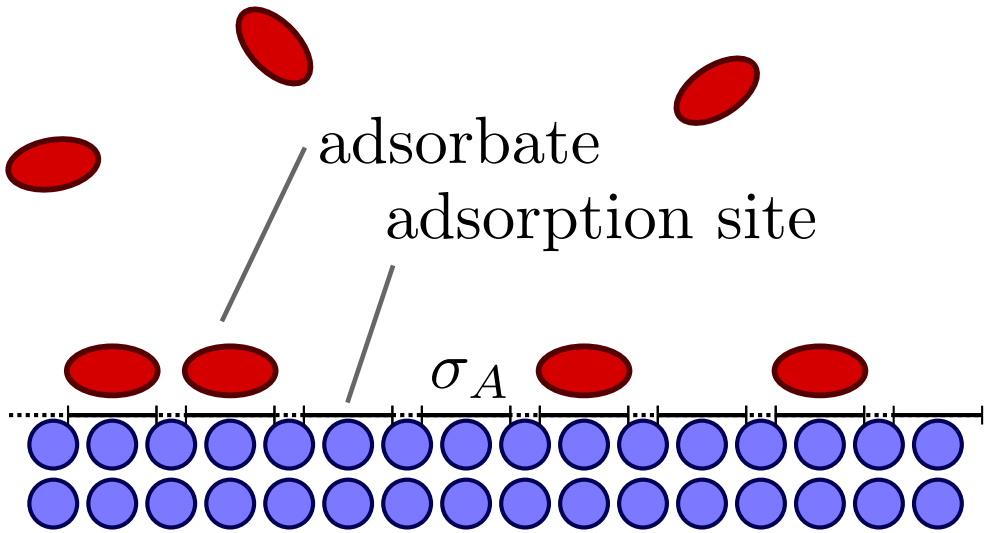


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$$\mu_G^{\ominus} + RT \ln \frac{P}{P^{\ominus}} = -\epsilon + RT \ln \frac{\theta}{1-\theta}$$

$$\boxed{\frac{P}{P_0} = \frac{\theta}{1-\theta} \qquad \theta = \frac{P}{P+P_0}}$$



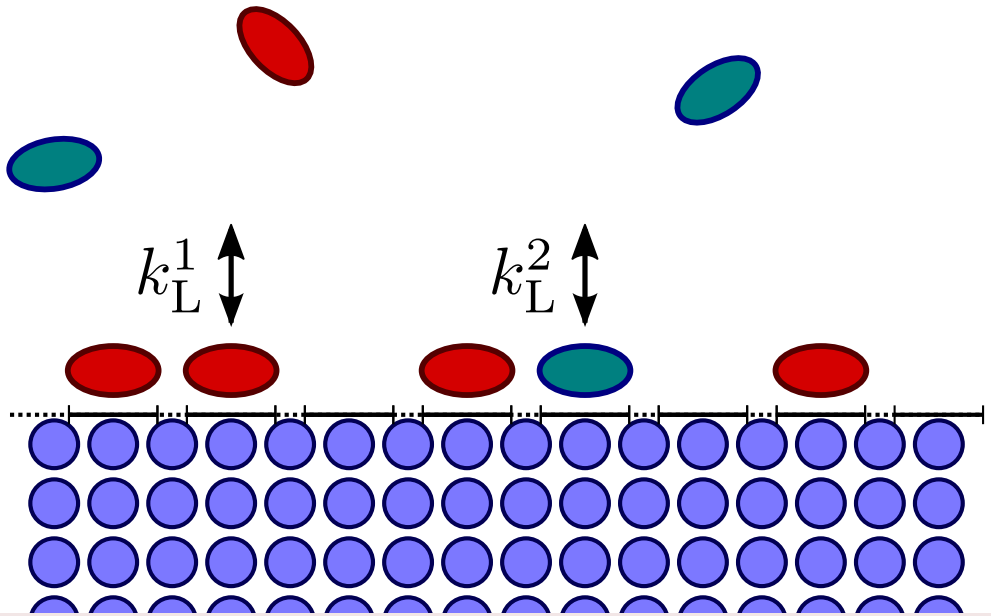
Competitive adsorption

- 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

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

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

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

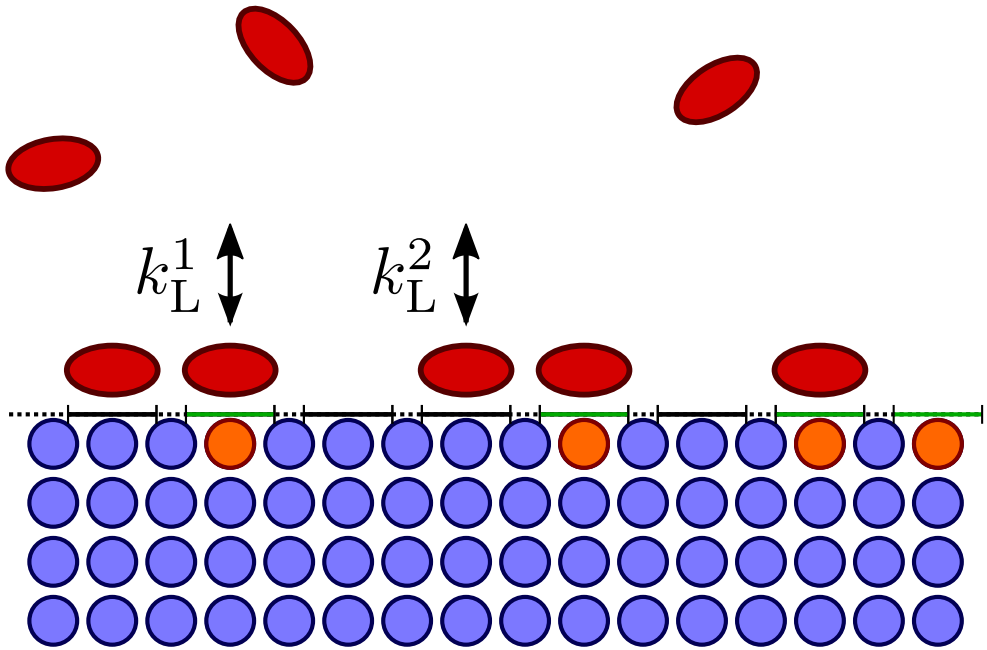


Competing adsorption sites

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

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

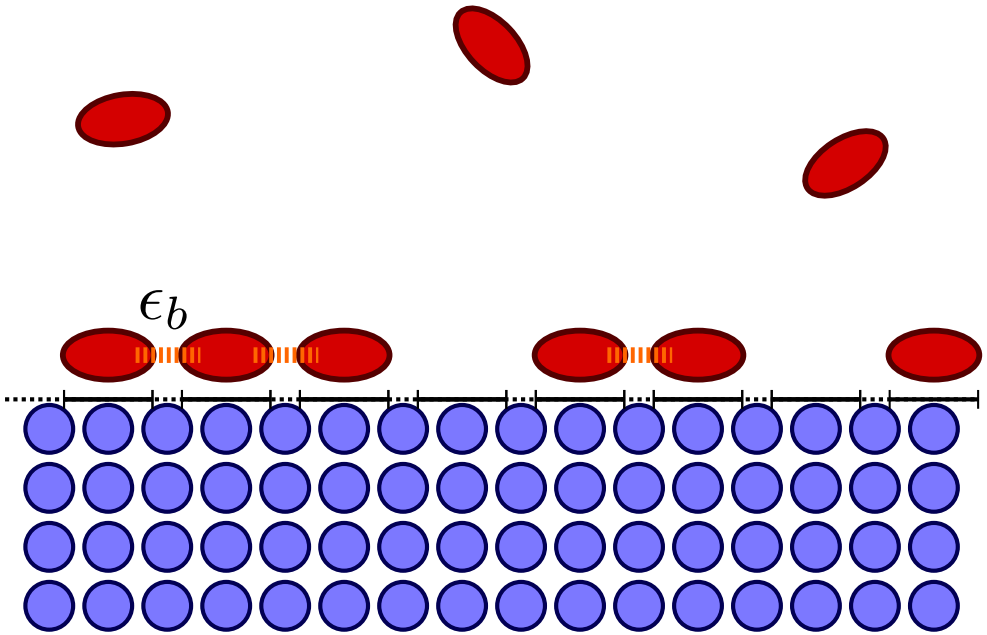
$$\theta_i = \frac{k^i_{\mathrm{L}} P}{1 + k^i_{\mathrm{L}} P}, \quad \theta = \sum_i \frac{x_i k^i_{\mathrm{L}} P}{1 + k^i_{\mathrm{L}} P}$$



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

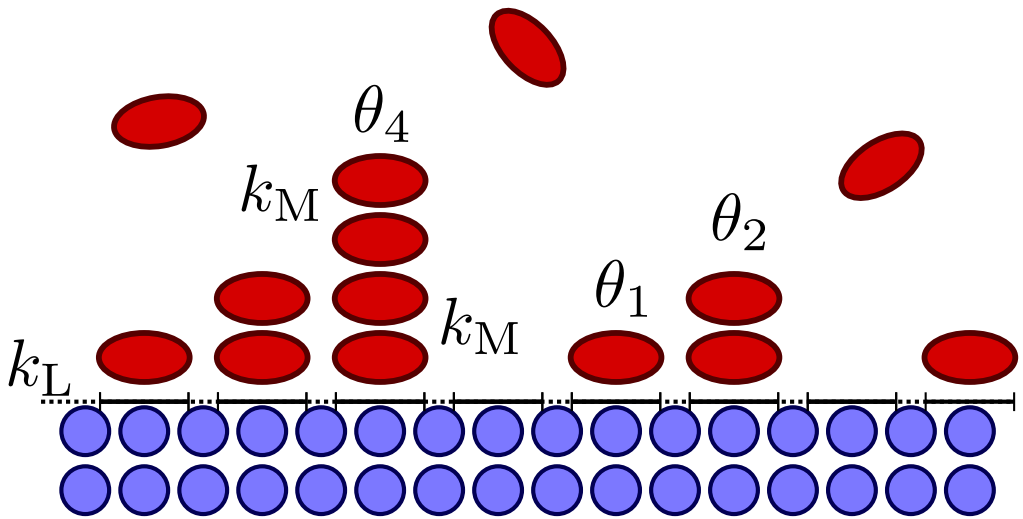
$$\frac{\theta}{1-\theta} = k_L e^{\frac{n\epsilon_b\theta}{k_B T}} P$$



Multi-layer adsorption (BET isotherm)

- 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)

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

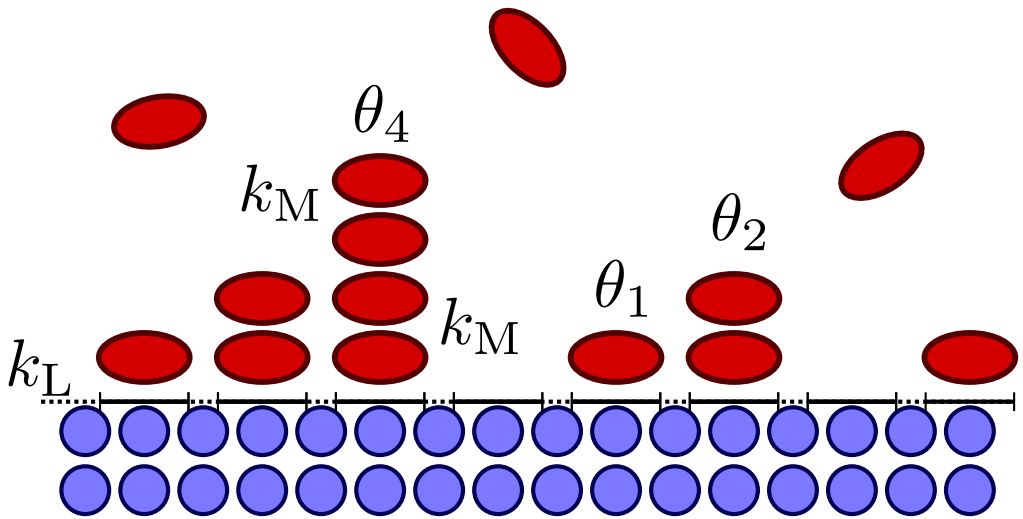


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$$\sum_{i=1}^{\infty} [k_M P]^{i-1} = \frac{1}{1 - k_M P}, \qquad \sum_{i=1}^{\infty} i\,[k_M P]^{i-1} = \frac{1}{(1 - k_M P)^2}$$

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



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- 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)

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

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

