$\Omega_{mn} = \sigma_m k_{mn}$

$\Omega_{nm} = \sigma_n k_{nm}$

microstates obey LDB:

$$\frac{k_{mn}}{k_{nm}} = e^{-\beta(H_m - H_n - W_{mn})}$$

(W_{mn}: other work)

$$\frac{\Omega_{nm}}{\Omega_{mn}} = \frac{\sigma_n k_{nm}}{\sigma_m k_{mn}} = \frac{\sigma_n}{\sigma_m} e^{-\beta(H_n - H_m - W_{nm})}$$

$$= e^{-\beta\left(H_n - H_m - k_B T \ln \frac{\sigma_n}{\sigma_m} - W_{nm}\right)}$$

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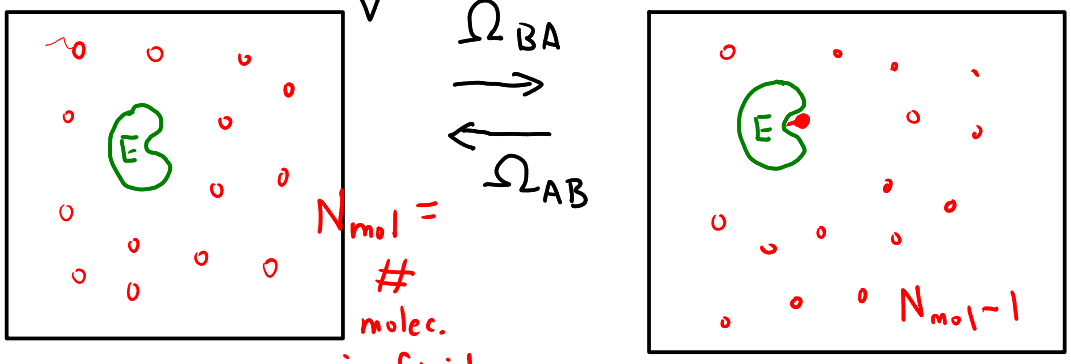
example:

enzyme E w/ fixed position



macrostate A ⇒ includes all config's of molec. in fluid

macrostate B ⇒ molec. bound to enzyme

binding / unbinding $\frac{\Omega_{BA}}{\Omega_{AB}} = e^{-\beta\left(\underbrace{H_B - H_A}_{<0 \text{ for molec. forming a bond}} - k_B T \ln \frac{\sigma_B}{\sigma_A}\right)}$ $W_{BA} = 0$ (no other work terms)

(if binding thermodyn. favorable)

σ_A = # of configs of N_{mol} molecules in a box of volume V (ignore vol. of E $\ll$ V)

divide up volume V into small volumes V_{mol} = vol. of molecule (big enough to fit one)

$$\# \text{ boxes} = N_{pos} = \frac{V}{V_{mol}}$$

how many ways to arrange N_{mol} molec. into N_{pos} possible positions?

$$\Omega_A = \binom{N_{pos}}{N_{mol}} = \frac{N_{pos}!}{N_{mol}!\,(N_{pos}-N_{mol})!}$$

$$\Omega_B = \binom{N_{pos}}{N_{mol}-1} = \frac{N_{pos}!}{(N_{mol}-1)!\,(N_{pos}-N_{mol}+1)!}$$

$$\frac{\Omega_B}{\Omega_A} = \frac{N_{mol}}{N_{pos}-N_{mol}+1} \approx \frac{N_{mol}}{N_{pos}}$$

when $N_{pos} \gg N_{mol}$ (dilute sol'n)

$$k_B T \ln \frac{\Omega_B}{\Omega_A} \approx k_B T \ln \frac{N_{mol}}{N_{pos}}$$

$$= k_B T \ln c\, V_{mol}$$

$$= \underbrace{k_B T \ln V_{mol}}_{\mu_0 = \text{const.}} + k_B T \ln c$$

$= $ "standard" chem. potential

$$N_{pos} = \frac{V}{V_{mol}}$$

$$c = \frac{N_{mol}}{V}$$

$=$ concentration

chemical potential $\equiv$ $\mu = k_B T \ln \frac{\sigma_B}{\sigma_A} = \mu_0 + k_B T \ln c$

binding / unbinding $\frac{\Omega_{BA}}{\Omega_{AB}} = e^{-\beta(H_B - H_A - \mu)}$ (Eq. 1)

when $N_{pos} >> N_{mol} \Rightarrow \mu < 0$

increasing $c \Rightarrow \mu$ less negative

$\Rightarrow$ make Ω_{BA} larger relative to Ω_{AB}

$\Rightarrow$ larger conc. favor more binding

compare this to the FAR-NEAR-BOUND model from earlier in the course: $0 \leq \alpha_b \leq 1$

Eq. 2: $\frac{\Omega_{BA}}{\Omega_{AB}} = \frac{\text{binding}}{\text{unbinding}} = \frac{k_b}{k_u} = \frac{\alpha_b K_s c}{k_u}$

both Eq. 1 + Eq. 2 are $\propto c \Rightarrow$ consistent!

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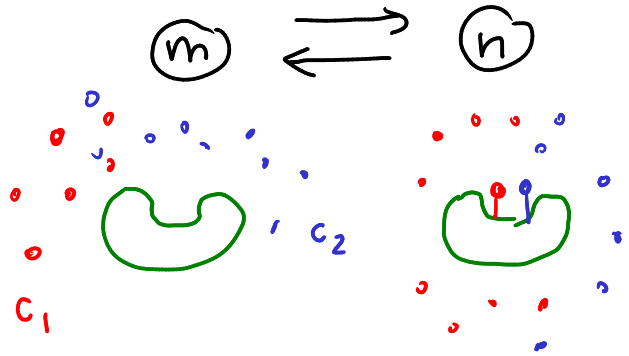
generalize to many types of particles in fluid around system

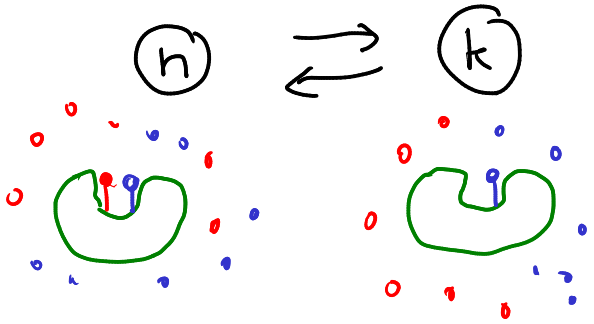
type j molec: $\mu_j = \mu_0^j + k_B T \ln c_j$

↳ conc. of type j



$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(H_n - H_m - \mu_1 - \mu_2)}$$

for every molec. that binds we get a μ_j term w/ minus sign

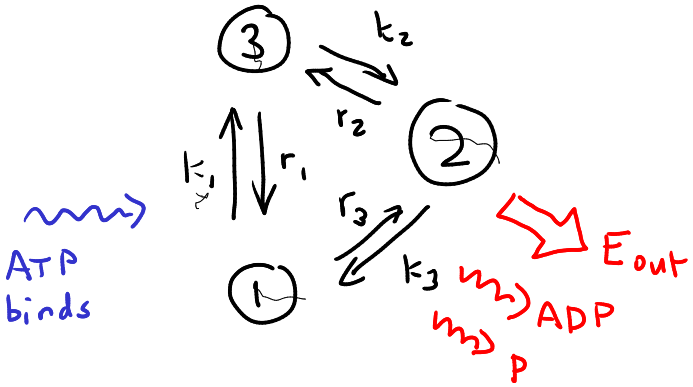


$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(H_n - H_m + \mu_1)}$$

numerator: unbinding of type j: $+\mu_j$ term

numerator trans.

example:



ATP = A-P-P-P

ADP = A-P-P