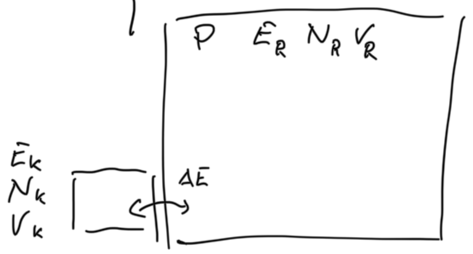
Boltzmann



$E_R N_R V_R \gg E_k N_k V_k$

ΔE does not change R

$T_k = T_R$

$\Rightarrow K:$ (NVT), not NVE

$E = E_0 = E_R + E_k \qquad N = N_R + N_k \quad V = V_R + V_k$

Microstate with $E_k = \varepsilon_i \qquad \Omega_K(i) = 1$ (one single microstate)

$E_R = E_0 - \varepsilon_i \qquad \Omega_R(i) \gg 1$

Likelihood of i?
$$P(i) = \frac{\Omega_R \Omega_K}{\sum \Omega_B \Omega_K} = C \cdot \Omega_B(E_0 - \varepsilon_i)$$

$\varepsilon_i \ll E_0$
$$\ln P(i) = \ln C + \ln \Omega_R \approx \ln C + \ln \Omega_R(E_0) + \frac{\partial \ln \Omega_R(E_0)}{\partial E} \cdot (-\varepsilon$$

$S = k \ln \Omega$
$$= -\ln Z - \frac{\varepsilon_i}{k} \underbrace{\frac{\partial S_R(E_0)}{\partial E}}_{1/T}$$

$$= -\ln Z - \frac{\varepsilon_i}{kT}$$

$$\Rightarrow P(i) = \frac{1}{Z} \boxed{e^{-\varepsilon_i/kT}} \text{ Boltzmann factor}$$

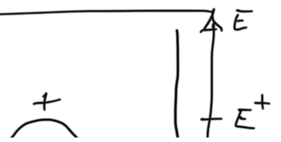
$$Z = \sum_i e^{-\varepsilon_i/kT}$$

Simple two-state system: $\qquad S_1, S_2 \qquad \Delta E = E_2 - E_1$

$$\frac{P_1}{P_2} = \frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_2/kT}} = e^{(E_2 - E_1)/kT} = e^{-\Delta E/kT}$$

$$P_1 + P_2 = 1 \Rightarrow P_1 = \frac{1}{1 + e^{-\Delta E/kT}} \quad P_2 = \frac{1}{1 + e^{\Delta E/kT}}$$

Rates



$$S_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} S_2$$

$$\frac{N_1}{N_2} = \frac{P_1}{P_2} = e^{-\Delta E/kT} \quad \text{equil}$$

Probability to get over + $\quad P_{2+} = c\, e^{-(E_+ - E_2)/kT}$

Rate $\quad N_2 \cdot P_{2+} = N_2\, e^{-(E_+ - E_2)/kT}$

$$\frac{k_{12}}{k_{21}} = e^{-\Delta E/kT}$$

Complex two-state system

Ensemble S_1 : open conformation $\quad \Omega_1$

— " — S_2 : closed — " — $\quad \Omega_2$

If all $S_{1,2}$ have $E_{1,2}$ $\Rightarrow$ $\dfrac{P_1}{P_2} = \dfrac{\Omega_1 e^{-E_1/kT}}{\Omega_2 e^{-E_2/kT}}$

Often long time in 1 then jump $\to$ 2.

Define $\quad F_i = \langle E \rangle_i - T S_i$

$$\Delta F = F_1 - F_2 = \langle E_1 - E_2 \rangle - T(S_1 - S_2)$$

$$\frac{P_1}{P_2} = \frac{\Omega_1}{\Omega_2}\, e^{-(E_1 - E_2)/kT}$$

$$\Omega_i = e^{\ln \Omega_i} = e^{S_i/k} = e^{TS_i/kT}$$

$$\frac{P_1}{P_2} = e^{T(S_1 - S_2)/kT} \cdot e^{-(E_1 - E_2)/kT} = e^{-\Delta F/kT}$$

$$\frac{k_{12}}{k_{21}} = e^{-\Delta F/kT}$$
