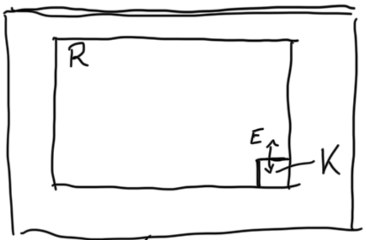
Boltzmann statistics

NVE



Ω - multiplicity

$S = k \ln \Omega$

N_K, V_K - constant

N_R, V_R, E_R - constant

K is small $\quad N_K \ll N_R$, $\quad V_K \ll V_R$, $\quad E_K \ll E_R$

$\Delta E_K \ll E_R \approx$ const.

Thermal equil. $\quad T_K = T_R$ $\qquad E_R + E_K = E = E_0$

$E_R = E_0 - E_K$

Reservoir : E_R const, R is large $\Rightarrow T_R$ = stable

Probability of a microstate i in K , $\varepsilon_i = E_K$, $\Omega_K(i) = 1$

$$P(i) = \frac{\Omega_R \Omega_K}{\sum_i \Omega_R(i)\, \Omega_K(i)} = C \cdot \Omega_R(E_0 - \varepsilon_i) \qquad \Omega_R(i) \gg 1$$

$\varepsilon_i \ll E_0$

$$\ln P(i) = \boxed{\ln C + \ln \Omega_R(E_0)} + \frac{\partial \ln \Omega_R(E_0)}{\partial E} \cdot (-\varepsilon_i) \;,$$

$S k \ln \Omega$

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

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

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

Boltzmann factor

$$\underbrace{\sum_i P(i) = 1}$$

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

Partition function (all possible states)

$\Delta E = \varepsilon_1 - \varepsilon_2$

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

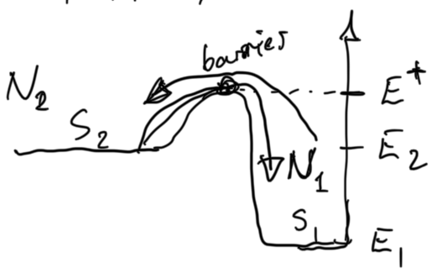
Simple two state system $\quad S_1 : E_1 \quad S_2 : E_2 \quad \Delta E = E_1 - E_2$

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

S_2 $\quad \uparrow E$

$S_1 \quad \left.\right] \Delta E \lesssim kT$

$$\boxed{\frac{P_1}{P_2} = \frac{N_1}{N_2}} \quad \text{equilibrium}$$



Probability to cross barrier

$$\Delta E = E^+ - E_2$$

$$P_{2+} = C\, e^{-(E^+ - E_2)/kT}$$

$$P_{1+} = C\, e^{-(E^+ - E_1)/kT}$$

Rate $\quad S_1 \underset{R_{21}}{\overset{R_{12}}{\rightleftharpoons}} S_2$

$$R_{12} = N_1 P_{12} = N_1 \cdot C e^{-(E^+ - E_1)/kT}$$

$$\frac{R_{12}}{R_{21}} = 1$$

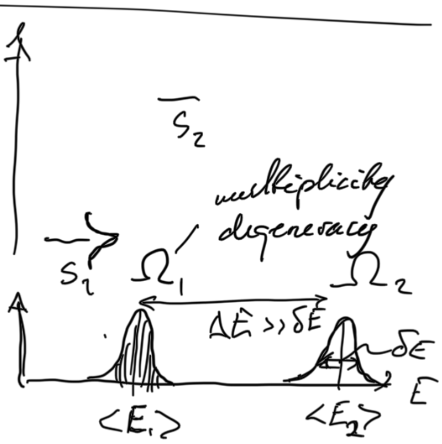
Complex two state

closed conformation

S_1

open conform.

S_2



$$\frac{P_1}{P_2} = \frac{\Omega_1 e^{-\langle E_1 \rangle/kT}}{\Omega_2 e^{-\langle E_2 \rangle/kT}}$$

$S = k \ln \Omega$

$\Omega = e^{S/k}$

$$\frac{P_1}{P_2} = \frac{e^{TS_1/Tk - \langle E_1 \rangle/kT}}{e^{TS_2/Tk - \langle E_2 \rangle/kT}} = e^{-(\Delta E - T\Delta S)/kT}$$

$\Delta E = E_1 - E_2 \quad \Delta S = S_1 - S_2$

$$F = E - TS \Rightarrow \Delta F = \Delta E - T\Delta S - \cancel{S\Delta T} \quad T = \text{const.}$$

Helmholtz f.e.

$$\boxed{\frac{P_1}{P_2} = e^{-\Delta F/kT}}$$

NVT $\quad$ F minimized

$\quad$ ↳ natural variables