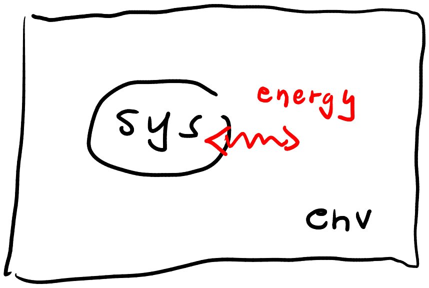


system states w/

energies E_n $\quad n = 1, \ldots, N$

LDB: $$\frac{W_{nm}}{W_{mn}} = e^{-\beta (E_n - E_m)}$$

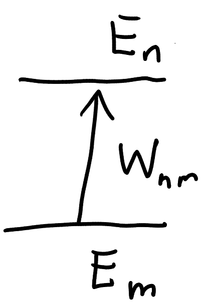
$$\beta = \frac{1}{k_B T} \equiv \left. \frac{\partial \ln \Theta}{\partial E} \right|_{E_{tot}}$$

Counting func. $$\Theta(E) = c\, \Theta_0(E)$$

$$\ln \Theta(E) = \ln c + \ln \Theta_0(E)$$

$$\left. \frac{\partial \ln \Theta}{\partial E} \right|_{E_{tot}} = \left. \frac{\partial \ln \Theta_0}{\partial E} \right|_{E_{tot}}$$

$k_B T = \frac{1}{\beta}$ = units of energy $\Rightarrow$ sets the basic energy scale for "generosity" of environment



$$\frac{W_{nm}}{W_{mn}} = \frac{\text{uphill}}{\text{downhill}} = e^{-\frac{(E_n - E_m)}{k_B T}}$$

transitions $E_n - E_m \gg k_B T$ are exp. unlikely

for room temp. $k_B T \approx \frac{1}{40}$ eV $\simeq 0.025$ eV for any $T > 0$: $\frac{\text{uphill}}{\text{downhill}} < 1$

$\uparrow$
kelvin

everyday experience

env. is "stingy": less likely to give energy to sys. than take away

$T \to 0^+$: $\beta \to \infty$ $\quad \frac{\text{uphill}}{\text{downhill}} \to 0$ all uphill forbidden

$\beta \to 0^+$ $(T \to +\infty)$ $\quad \frac{\text{uphill}}{\text{downhill}} \to 1$ equally likely to give or take energy

untypical case: $\beta < 0$: $T < 0$

$\frac{\text{uphill}}{\text{downhill}} > 1$ extremely "generous" environment

hotter than $T = +\infty$

consequences: $$p_n^s = \frac{\Theta_n}{\Theta_{tot}} = \frac{\Theta_n}{\sum_m' \Theta_m}$$

$$\ln \Theta_n = \ln \Theta(E_{tot} - E_n) \approx \ln \Theta(E_{tot}) - \beta E_n$$

$$= \frac{e^{\ln \Theta_n}}{\sum_m e^{\ln \Theta_m}}$$

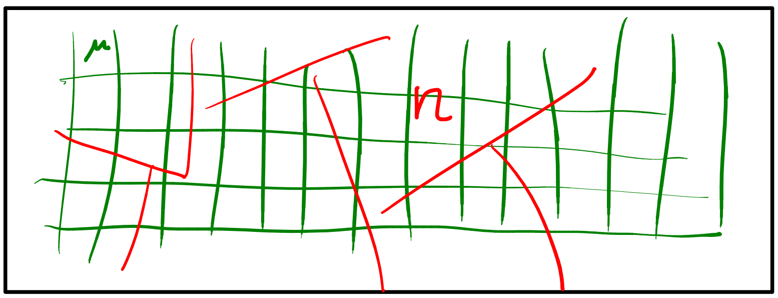
$$p_n^s = \underbrace{\frac{\Theta(E_{tot})}{\sum_m e^{m}\Theta_m}}_{1/Z} e^{-\beta E_n} = \boxed{\frac{1}{Z} e^{-\beta E_n}}$$

const. indep. of n

Boltz. equilibrium distribution

Z = norm. const. $\quad \sum_n p_n^s = 1$

$$\Rightarrow Z = \sum_m e^{-\beta E_m}$$



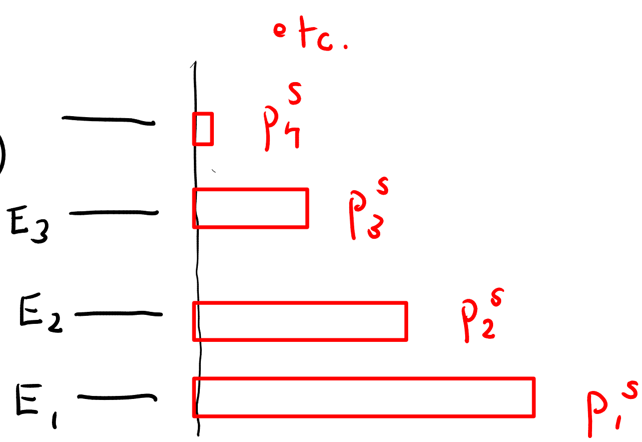
$p_\mu^s = \dfrac{1}{\Theta_{tot}}$ microcanonical ensemble

$p_n^s = \dfrac{e^{-\beta E_n}}{Z}$ canonical ensemble

$\Rightarrow$ Same story, diff. perspectives

$T > 0$

$(\beta > 0)$



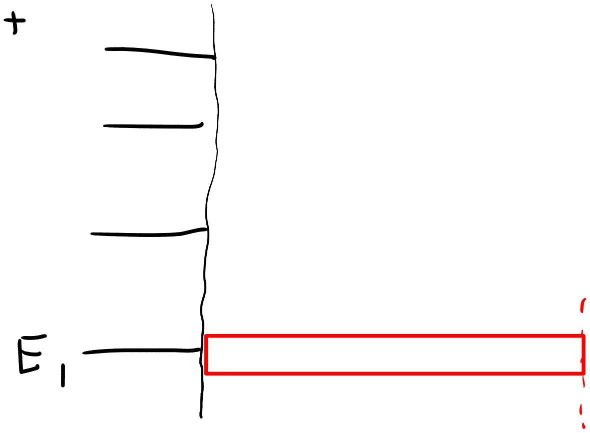
stat. dist. biased toward lower energies b/c of "stingy" environ.

Same stationary distrib. for any matrix W at same temp. T

$T \to 0^+$

$\beta \to \infty$

$E_1 < E_2 < E_3 < \dots$



$p_1^s = 1$

$$p_1^s = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2} + \dots} \xrightarrow[\beta \to \infty]{T \to 0^+} 1$$

decay faster

$E_2 > E_1$

$$p_2^s = \frac{e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2} + \dots} \xrightarrow[\beta \to \infty]{T \to 0^+} e^{-\beta(E_2 - E_1)} \to 0$$

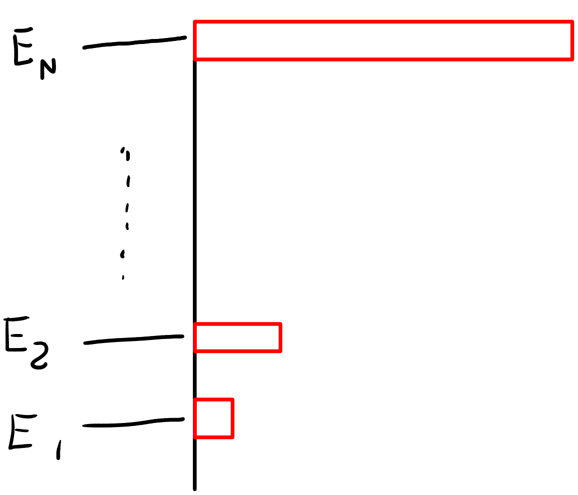
$$\beta = \frac{1}{k_B T} \to 0^+ \qquad p_n^s \to \frac{1}{N} \qquad N = \#\ \text{states}$$

$T \to +\infty$

all macrostates equally likely when $T \to \infty$

$\beta < 0$

$(T < 0)$



this $\beta < 0$ stationary state only makes sense (properly normalized) when there is a maximum energy E_N

$\Longleftarrow$ usually requires quantum