$$\Theta_n = \Theta(E_n^{env}, N_n^{part,env}, \ldots)$$

\# microstates in macrostate n

focus on case where only energy is conserved.

LDB = $W_{nm} p_m^s = W_{mn} p_n^s$

$$p_m^s = \Theta_m / \Theta_{tot} \qquad p_n^s = \Theta_n / \Theta_{tot}$$

$$\frac{W_{nm}}{W_{mn}} = \frac{\Theta_n}{\Theta_m} = \frac{\Theta(E_n^{env})}{\Theta(E_m^{env})} = \frac{\Theta(E_{tot} - E_n)}{\Theta(E_{tot} - E_m)}$$

assume: env >> system $E_{tot} \gg E_n$

$$\frac{W_{nm}}{W_{mn}} = \exp\left[\ln \Theta(E_{tot} - E_n) - \ln \Theta(E_{tot} - E_m)\right]$$

$$\ln \Theta(E_{tot} - E_n) \approx \ln \Theta(E_{tot}) - \overbrace{\left.\frac{\partial \ln \Theta}{\partial E}\right|_{E_{tot}}}^{\beta} E_n + \ldots$$

$$\approx \ln \Theta(E_{tot}) - \beta E_n + \ldots$$

$$\Rightarrow \frac{W_{nm}}{W_{mn}} = \exp\left[-\beta(E_n - E_m) + \ldots\right]$$

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

$\beta =$ inverse energy units $= J^{-1}$

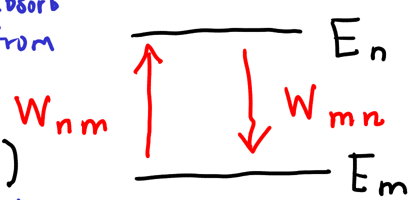
$k_B =$ Boltzmann's constant $= 1.38 \times 10^{-23}\ J/K$

$T =$ units of Kelvin (K)

$k_B T =$ units of J

"how easy it is to absorb energy from env."

$$\frac{W_{nm}}{W_{mn}} = \frac{\text{uphill}}{\text{downhill}} = e^{-\beta \underbrace{(E_n - E_m)}_{\text{energy diff. that needs to be absorbed from env.}}}$$



$E_n > E_m$

$\beta > 0$

$\underbrace{\beta > 0 \quad (T > 0)}_{\text{our everyday experience}}$: $\dfrac{\text{uphill}}{\text{downhill}} < 1$

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

: typical when env >> sys

$\beta \to +\infty \quad (T \to 0^+)$ $\quad \dfrac{\text{uphill}}{\text{downhill}} \to 0$

all uphill trans. are forbidden (abs. zero temp.)

$\beta \to 0^+ \quad (T \to +\infty)$ $\quad \dfrac{\text{uphill}}{\text{downhill}} \to 1$

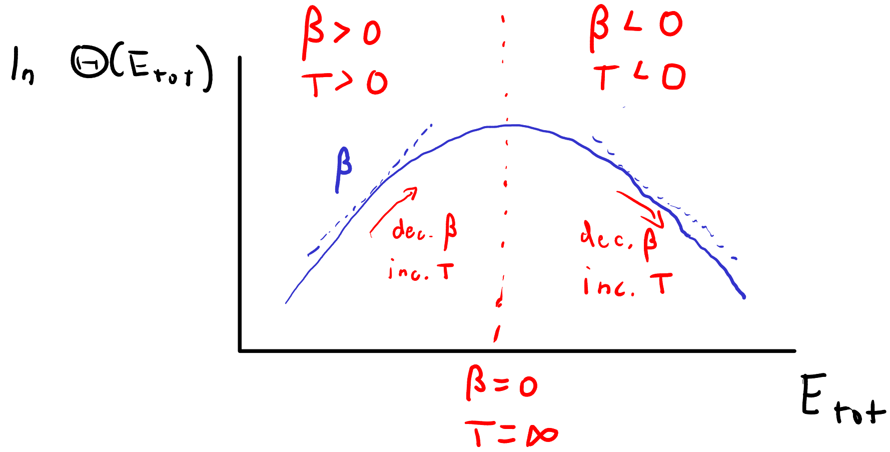
equally likely to gain or lose energy to env.

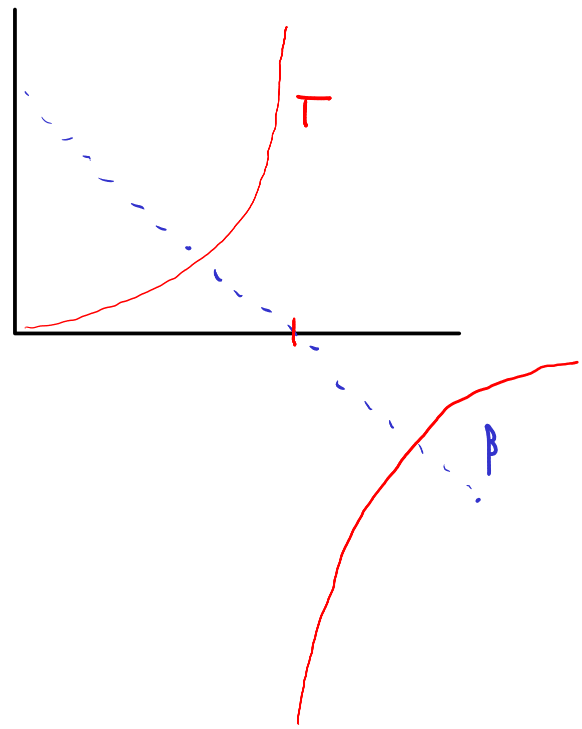
really hot! hotter than $T=+\infty$

untypical case:

$$\beta < 0 \quad (T<0): \quad \frac{\text{uphill}}{\text{downhill}} > 1$$

extremely "generous" environment!





Consequences:

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

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

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

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

note:

$\Theta_{tot} \neq \Theta(E_{tot})$

$\Theta_{tot} = \sum_m \Theta(E_{tot} - E_m)$

$$= \underbrace{\frac{\Theta(E_{tot})}{\sum_m \Theta_m}}_{\text{const. indep. of } n \;=\; \frac{1}{Z}} e^{-\beta E_n} \Rightarrow \boxed{p_n^s = \frac{e^{-\beta E_n}}{Z}}$$

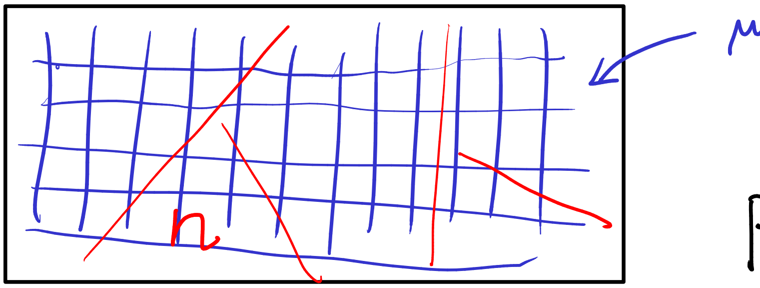
Boltzmann equil. distrib.

Z = "partition func" = normaliz. const.

$$\sum_n p_n^s = 1 \Rightarrow Z = \sum_m e^{-\beta E_m}$$

ensemble: microcanonical

ergodic & mixing



$$p_\mu^s = \frac{1}{\Theta_{tot}}$$

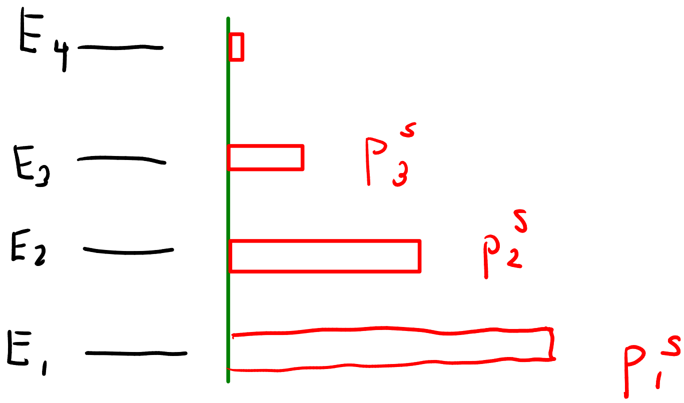
canonical ensemble

$$p_n^s = \frac{e^{-\beta E_n}}{Z}$$

$\Rightarrow$ same story, different perspectives

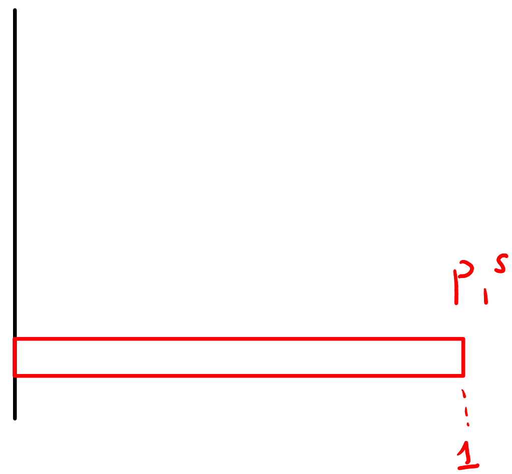
$T > 0$

$\beta > 0$



$T \to 0^+$

$\beta \to \infty$



$E_1 < E_2 \dots$

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

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