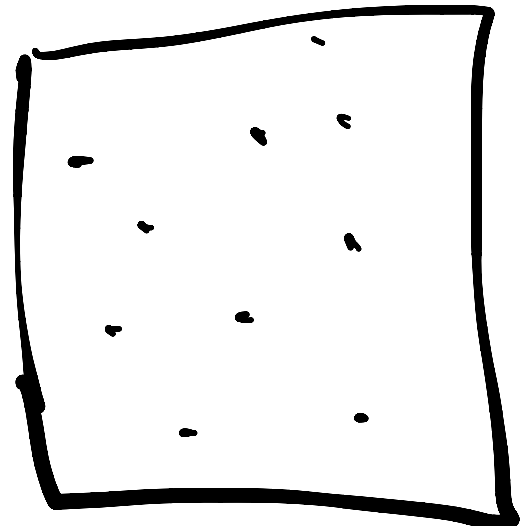
Partition functions / "Ensemble"

Constant energy

(microcanonical ensemble)



Reminder:

maximizes $S = k_B \ln \Omega$

isolated

N, V, E ← constant

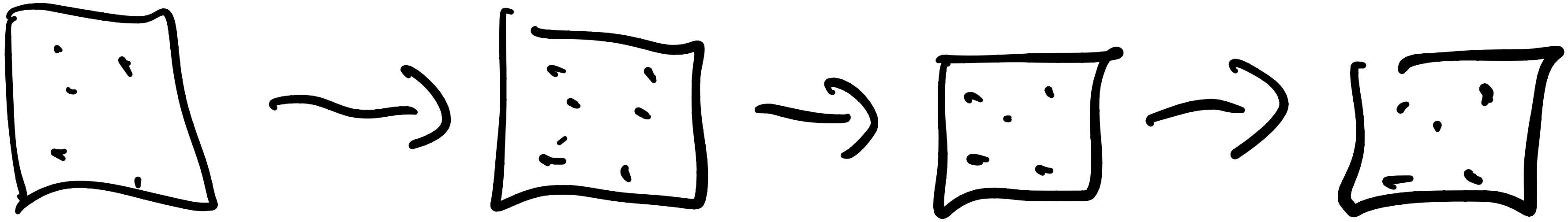
Ensemble:

name for the situation: (N, V, E)

(N, V, T)

(N, P, T)

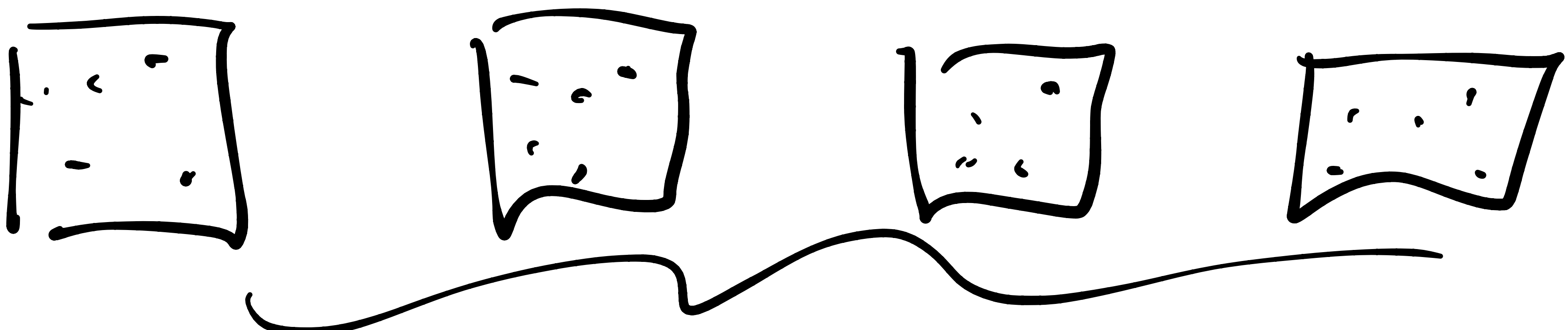
time avg vs "ensemble" average



time

time T

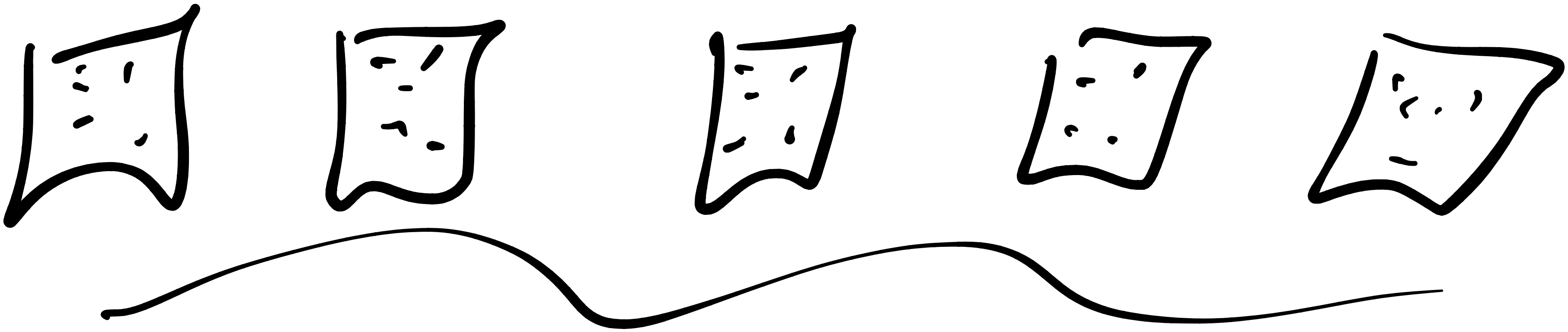
averages over a "movie"



M copies

ensemble of "microstates" with same thermody. bulk properties

Constant E



M copies

assert all valid cfgs are equally likely @ const E

$$S = k_B \ln \Omega(N,V,E)$$

$$P(\bar{X}) = \frac{1}{\Omega(N,V,E)}$$

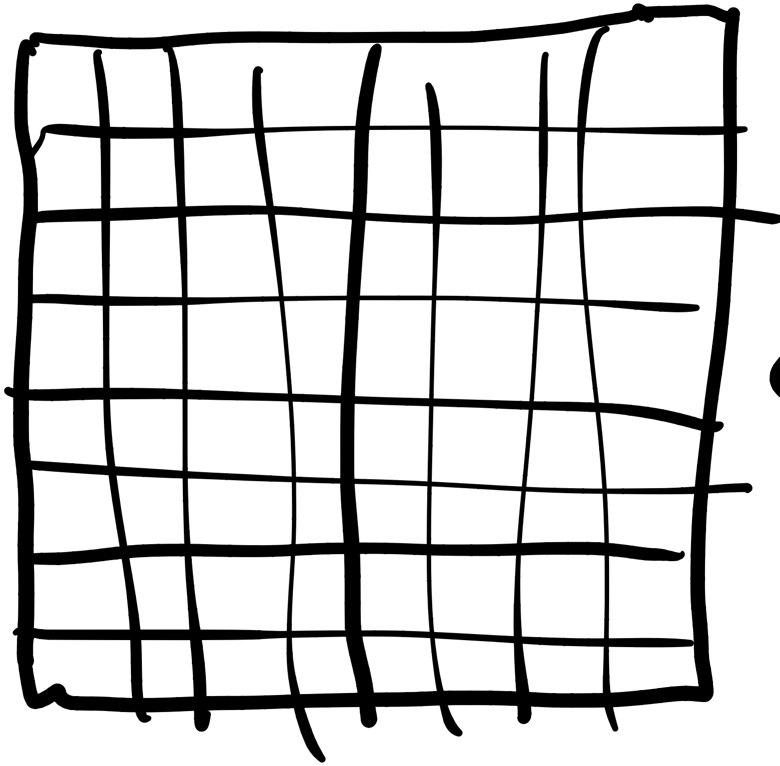
arrangement of atoms with energy E

$$S = -k_B \ln P$$

$$\langle S \rangle = \sum_{i=1}^{\Omega} P_i S_i = +\frac{1}{\Omega} \sum_{i=1}^{\Omega} k_B \ln \Omega$$

$$= k_B \ln \Omega = S$$

Gibbs Entropy: $S = -k_B \sum_{i=1}^{\Omega} P_i \ln P_i$



if q can flow
then each one is constant
(N, V, T)

In total constant
N, V, E

Result will be $\frac{n_i}{M} = \frac{e^{-\varepsilon_i/k_B T}}{Z}$

M copies

Assume that energies are discrete

$\varepsilon_i \quad i = 0, \ldots, \infty$

m_i of M total copies are in state ε_i

$$S = k_B \ln \Omega_{total}, \quad \Omega_{total} = \frac{M!}{m_0!\, m_1! \cdots m_\infty!}$$

wants to be maximized

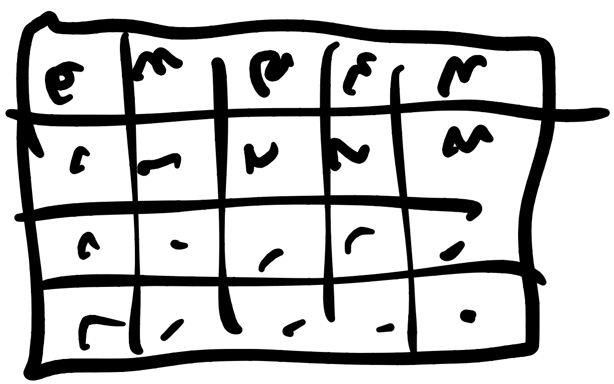
there is some j for which $\varepsilon_j > \varepsilon_{total}$

want to maximize this, but...

maximize S w/ constraints

$$\sum_{i=0}^{\infty} m_i = M \qquad \sum_{i=0}^{\infty} m_i \varepsilon_i = \mathcal{E}$$

[1 h.o., $\varepsilon_{\text{possible}} = \hbar\omega(n + 1/2)$



Eg million copies $= M$

$$\mathcal{E}_{\text{total}} = 400\,\hbar\omega + \frac{\hbar\omega}{2} M.$$

Lagrange multipliers

maximize $f(a,b,c)$

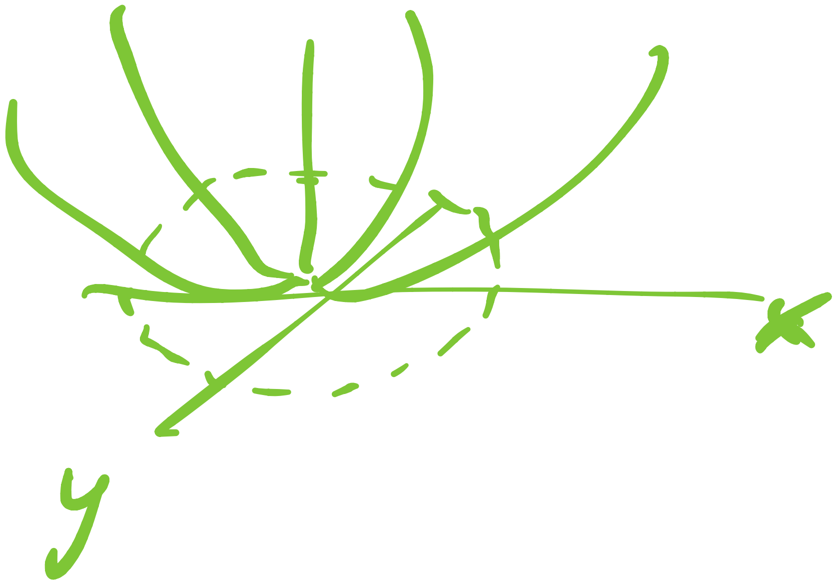
with constraint $g(a,b,c) = 0$

$$f(a,b,c) + \alpha g = h$$

$$\frac{\partial f}{\partial a} = 0 \quad \frac{\partial f}{\partial b} = 0 \quad \frac{\partial f}{\partial c} = 0$$

$$\frac{\partial h}{\partial a} = 0 \quad \frac{\partial h}{\partial b} = 0 \quad \frac{\partial h}{\partial c} = 0 \ \& \ \frac{\partial h}{\partial \alpha} = 0$$

when is x^2+y^2 maximum, on a circle



if $x^2+y^2=c$

want to maxime:

$$\ln \Omega + \alpha\left(\sum m_i - M\right) + \beta\left(\sum m_i \epsilon_i - E\right)$$

interested in $\dfrac{m_i}{M} = P(\epsilon_i)$

$$h = \ln\left(\frac{M!}{m_1!\,m_2!\ldots m_\alpha!}\right) - \alpha\left(\sum m_i - M\right) - \beta\left(\sum m_i \epsilon_i - E\right)$$

what is $\dfrac{\partial h}{\partial m_j}$

Only care about $h = -\ln m_j! - \alpha m_j - \beta m_j \epsilon_j + \text{stuff}$

$$0 = \frac{\partial h}{\partial m_j} = -\ln m_j - \alpha - \beta \epsilon_j \Rightarrow m_j = e^{-\alpha} e^{-\beta \epsilon_j}$$

$$m_j = e^{-\alpha} e^{-\beta \epsilon_j}$$ true for all j

use our constraints, to find α

$$\sum m_j = M$$

$$\sum \underbrace{e^{-\alpha}}_{=} e^{-\beta \epsilon_j} = M$$

$$e^{-\alpha} \sum e^{-\beta \epsilon_j} = M$$

$$e^{-\alpha} = M / \sum e^{-\beta \epsilon_j}$$

$$m_j = M \frac{e^{-\beta \epsilon_j}}{\sum e^{-\beta \epsilon_j}}$$

$$\boxed{p_j = \frac{e^{-\beta \epsilon_j}}{\sum_j e^{-\beta \epsilon_j}}}$$

$\beta = \frac{1}{k_B T}$, why?

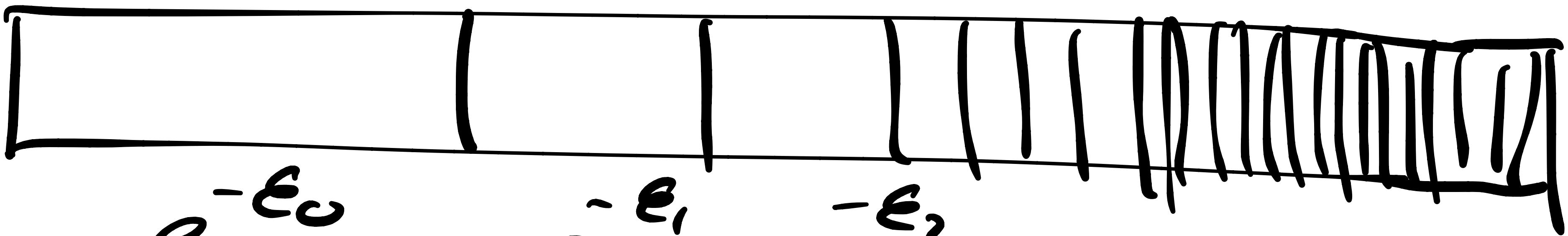
$\frac{\partial S}{\partial \varepsilon} = \frac{1}{T}$, what is S, ε ?

$$\varepsilon = \langle \varepsilon \rangle = \sum_{i=0}^{\infty} \varepsilon_i P_i$$

define $Z = \sum_{i=0}^{\infty} e^{-\beta \varepsilon_i}$, partition function

equivalent of Ω

break into states w/ weight $e^{-\beta \varepsilon_i} / Z$



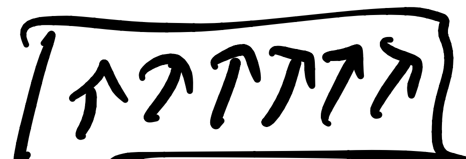
$e^{-\varepsilon_0}$ $e^{-\varepsilon_1}$ $e^{-\varepsilon_2}$ . . . . . Z

note: Z is just a #

$Z(N, V, T)$ the way it changes with these parameters

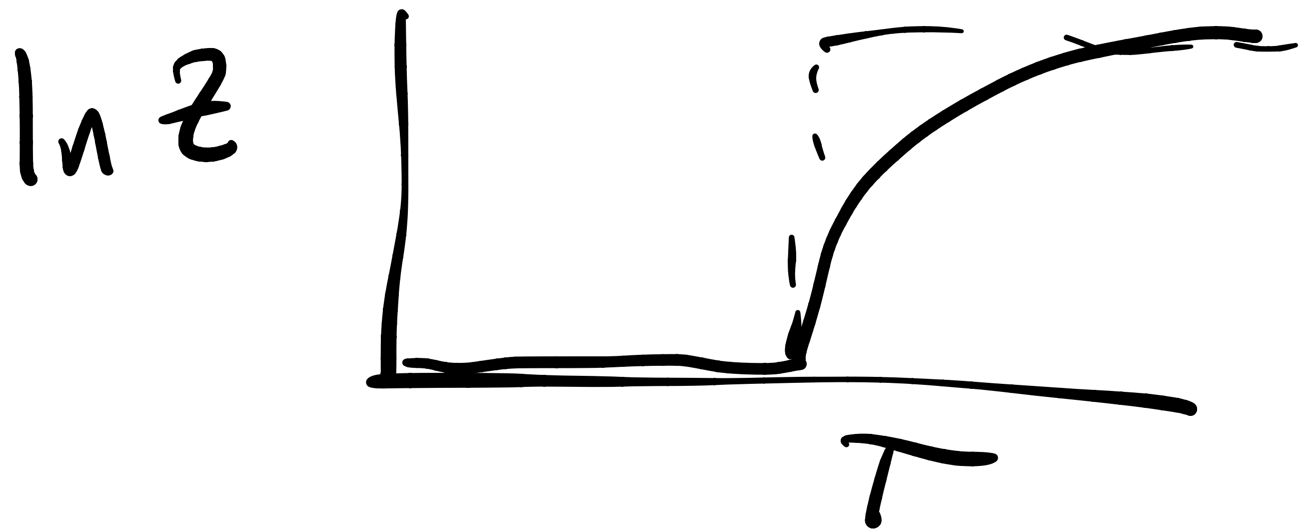
at high T

$Z(\text{high } T)$



low T

$Z(\text{low } T)$



normally we can't calculate Z
but sometimes we can calculate relative Z

$$A = -k_B T \ln Z$$

analagous to how $S = k_B \ln \Omega$

$$S = -k_B \sum_j p_i \ln p_j \quad , \quad p_j = \frac{e^{-\beta \epsilon_j}}{Z}$$

$$= -k_B \sum_j p_i \left[-\beta \epsilon_j - \ln Z \right]$$

$$= k_B \beta \langle \varepsilon \rangle + k_B \ln Z \underbrace{\sum p_j}_{1}$$

$$S = k_B \beta \langle \varepsilon \rangle + k_B \ln Z$$

$$\frac{\partial S}{\partial \langle \varepsilon \rangle} = \frac{1}{T} = k_B \beta \Rightarrow \beta = \frac{1}{k_B T}$$

$$ST = \langle \varepsilon \rangle + k_B T \ln Z \Rightarrow -k_B T \ln Z = \overset{\overset{A}{\parallel}}{\varepsilon - TS}$$

$$\langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$C_V = \left(\frac{\partial \varepsilon}{\partial T}\right)_V$$

(next time)