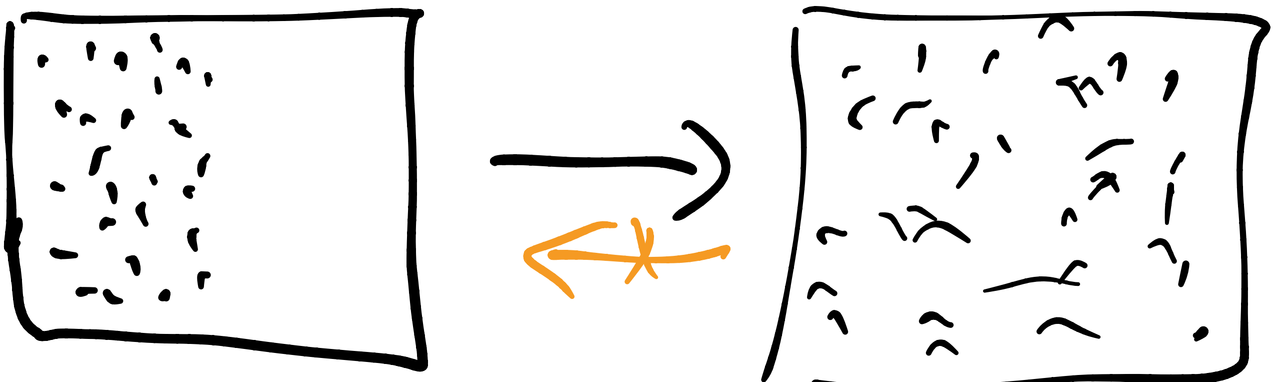
Molecular origin of Entropy

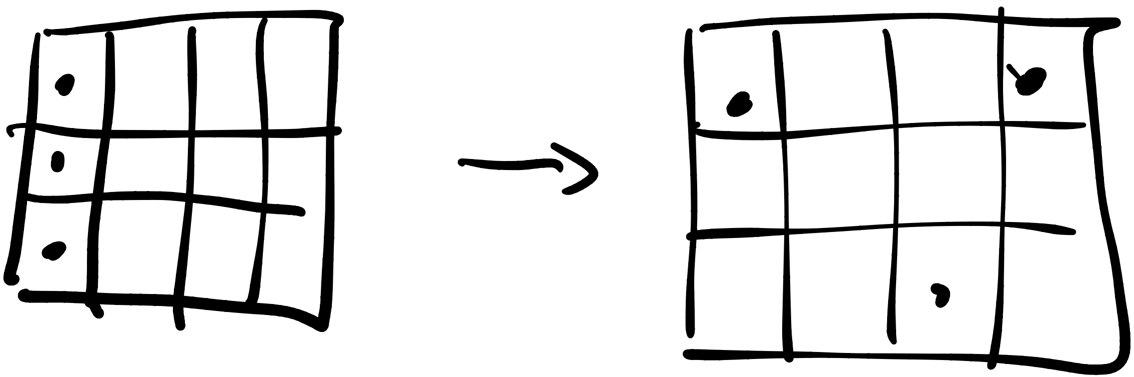
Boltzmann Entropy

Entropy = Disorder (?)



Contradict newton's equations

How can we measure take into account # states of system



non uniform → uniform

W - # microstates accessible to the system

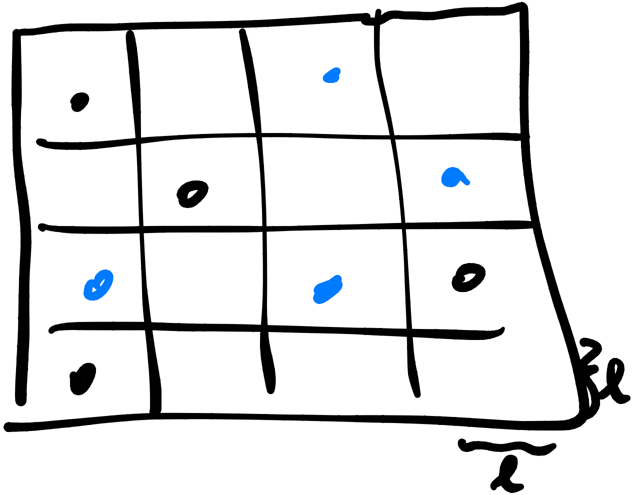
$$S = k_B \ln W \qquad (\Omega)$$

[eg state - (N, V, T)]

[constant N, V, E isolated system]

microstate - arrangement of molecules consistent with the state

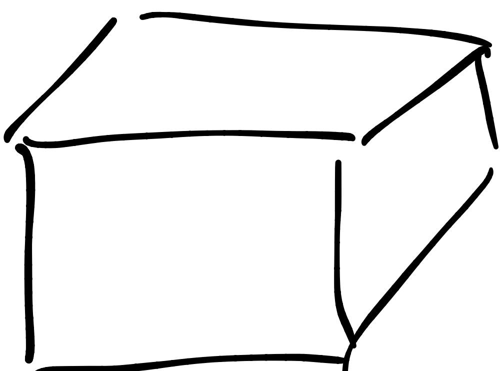
lattice gas



N molecules

$V = N_{squares} \cdot l^2$

$$\varepsilon = \begin{cases} 0 & \text{if no overlap} \\ \infty & \text{if is 2 particles in same box} \end{cases}$$



$V = N l^3$

What is W?

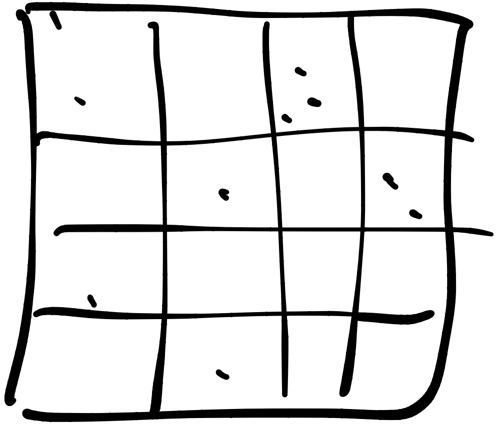
lattice gas

$$W = \binom{N_{sites}}{N_{molecules}} = \binom{N_c}{m}$$

$$= \frac{N_c!}{m!(N_c - m)!}$$

16

4



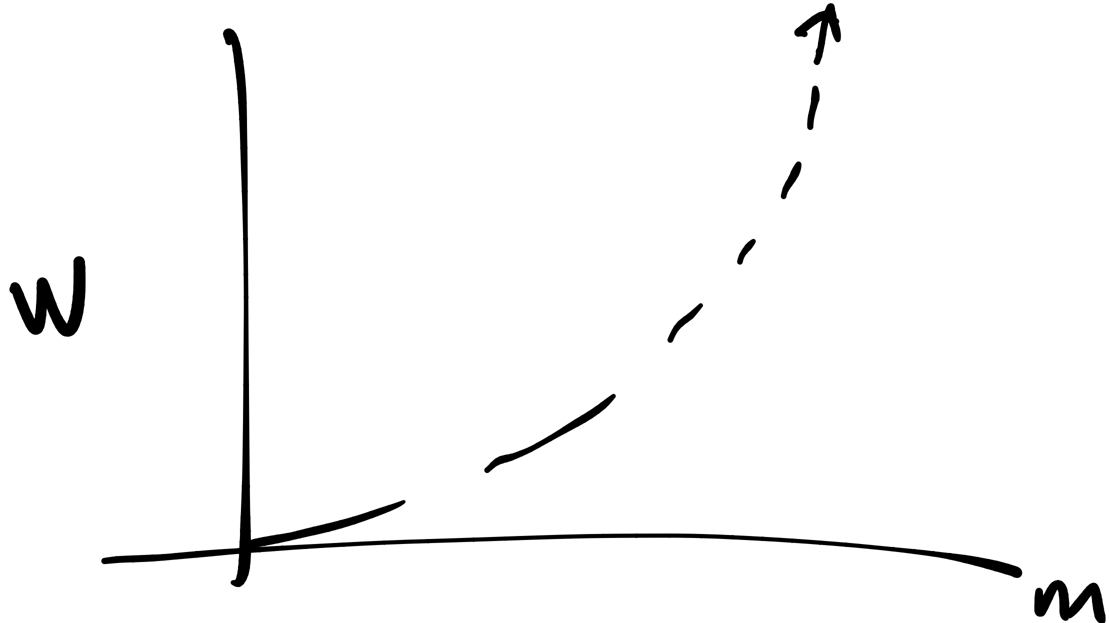
fully ideal gas

$\varepsilon = 0$ for any config.

$W = ?$ # ways arrange

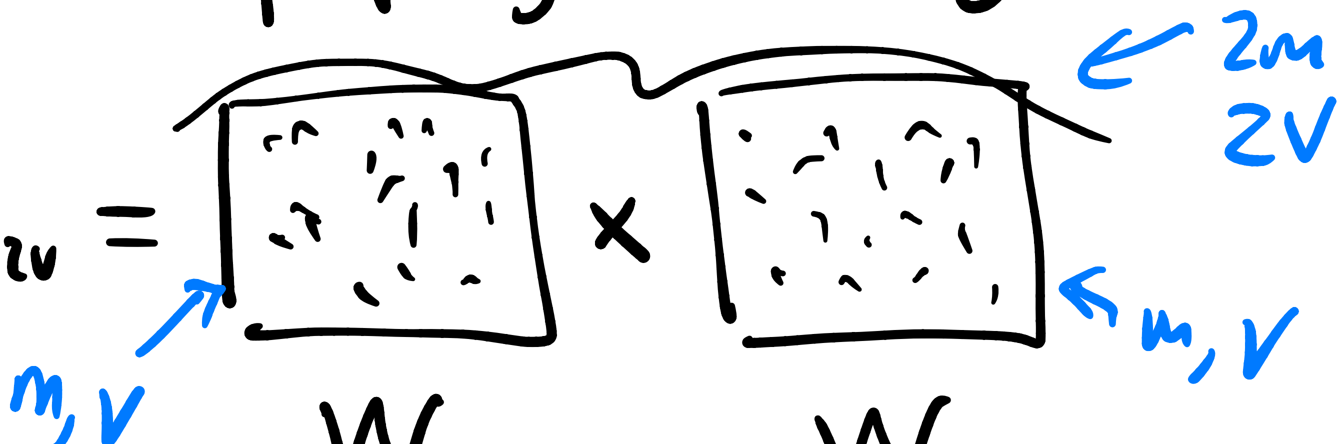
$$W = \underset{\uparrow \atop \text{1st}}{N_c} \cdot \underset{\uparrow \atop \text{2nd}}{N_c} \cdots \underset{\uparrow \atop \text{mth}}{N_c} = N_c^{\,m} = e^{m(\ln N_c)}$$

$* \; / m!$ (see next lecture)


w
m

Why does S have to be logarithmic?

S has property of being extensive



$$W_{2m,2V} = W \times W$$

$$\ln(W \times W) = \ln(W) + \ln(W)$$
$$= 2 \ln W$$

Entropy for lattice gas?

$$S = k_B \ln \binom{N_c}{m}$$

$$\frac{N_c!}{(N_c - m)!\, m!}$$

$m = N_c$

$$K_B = R/N_A \sim \frac{8.314\ J/K\,mol}{6.022\times 10^{23}\ /mol}$$

$$S \approx q/T \qquad [E]/[T]$$

1	0	0	1	0	0	0	0	0

$$S = k \ln\left(\frac{N_c!}{m!\,(N_c-m)!}\right)$$

Stirling's approximation

for big N

$$N! = N\cdot(N-1)(N-2)\cdots\cdot$$
$$= N^N\cdot(\text{smaller})$$

$$\ln(N!) \approx \underbrace{N\ln N - N}_{} + \frac{1}{2}\ln(2\pi N) + \cdots$$

$$N! \approx N^N e^{-N} \cdot \sqrt{2\pi N}$$

$$S = k_B \ln\left(\frac{N_c!}{m!\,(N_c-m)!}\right)$$

$$= k_B\left[\ln(N_c!) - \ln(m!) - \ln((N_c-m)!)\right]$$

big big big

$$\underline{1 \text{ billion}} - \underline{\tfrac{1}{2} \text{ billion}} = \underline{\tfrac{1}{2} \text{ billion}}$$

$$= k_B\left[N_c \ln N_c - \underline{N_c} - (m\ln m - \underline{m}) - \left[(N_c-m)\ln(N_c-m) - \underline{(N_c-m)}\right]\right]$$

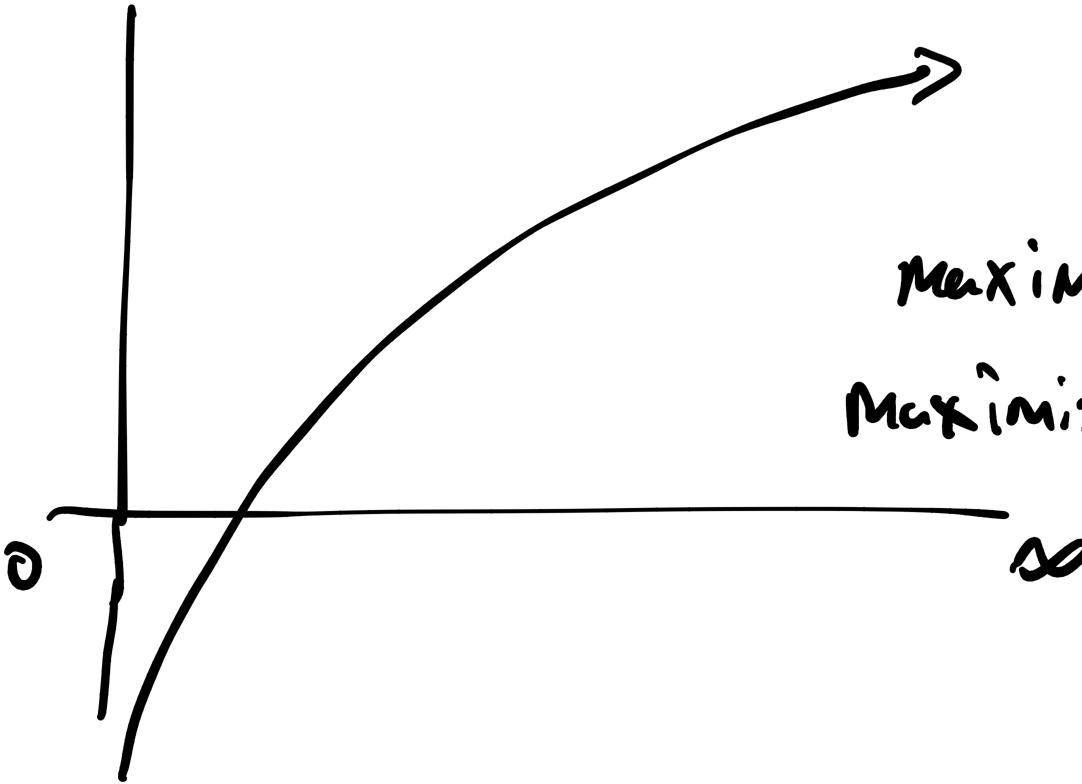
$$S = k_B \ln\left[\frac{N_c^{N_c}}{m^m (N_c - m)^{N_c - m}}\right]$$

maximum for $m = N_c/2$

$\left[\frac{\partial S}{\partial m} = 0 \quad \text{solve for } m\right]$

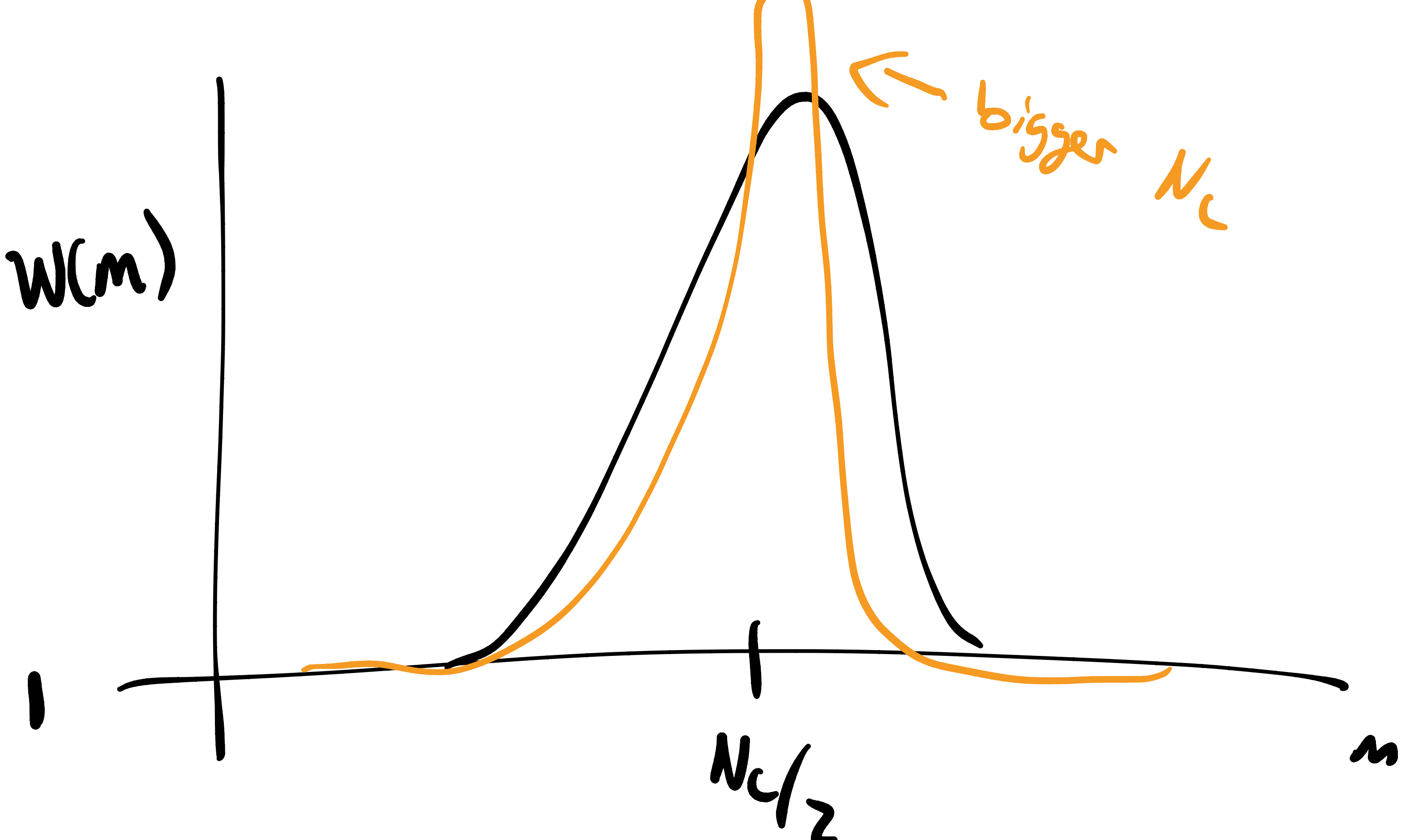
$$= k_B\left[N_c \ln N_c - m \ln m - (N_c - m)\ln(N_c - m)\right]$$

ln is a monotonically increasing function



maximize $f(x)$

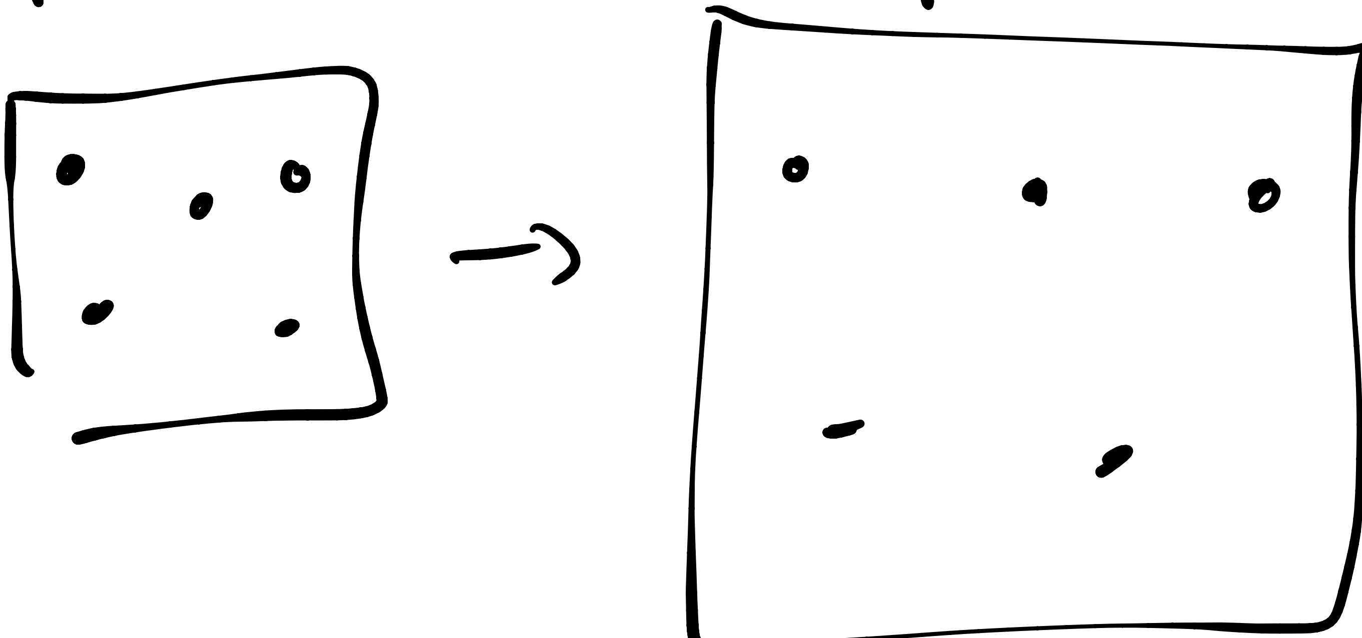
Maximize $\ln(f(x))$



W(n)
1
N_c/2
n
bigger N_c

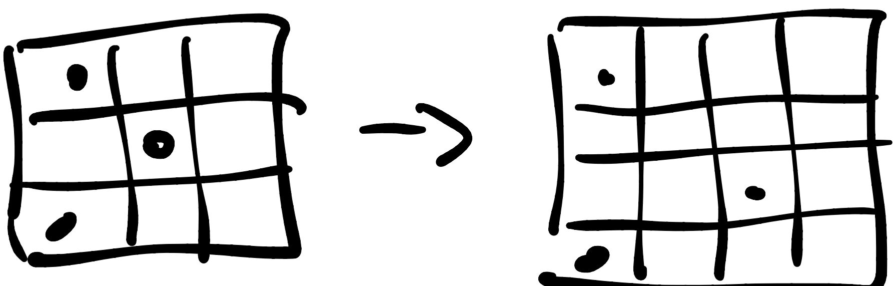
Change in entropy for "isothermal expansion"

expansion where $V_i \to V_f$



$$S(N_c) = k_B \ln\left(\frac{N_c^{N_c}}{m^m \, (N_c - m)^{N_c - m}}\right)$$

$$V = N_c \cdot l^2 \qquad N_i \rightarrow N_f$$



$$\Delta S = k_B \ln\left(\frac{N_f^{\,N_f}}{m^m\,(N_f - m)^{N_f - m}}\right) - k_B \ln\left(\frac{N_i^{\,N_i}}{m^m\,(N_i - m)^{N_i - m}}\right)$$

$$= k_B\Big[N_f \ln N_f - N_i \ln N_i - (N_f - m)\ln(N_f - m) + (N_i - m)\ln(N_i - m)\Big]$$

$$\approx k_B m \ln\left({}^{N_f}/_{N_i} \right)$$

${}^{m}/_{N_f}$ is small

$$\longleftrightarrow \; nR \ln\left({}^{V_f}/_{V_i} \right)$$

[check ideal gas]