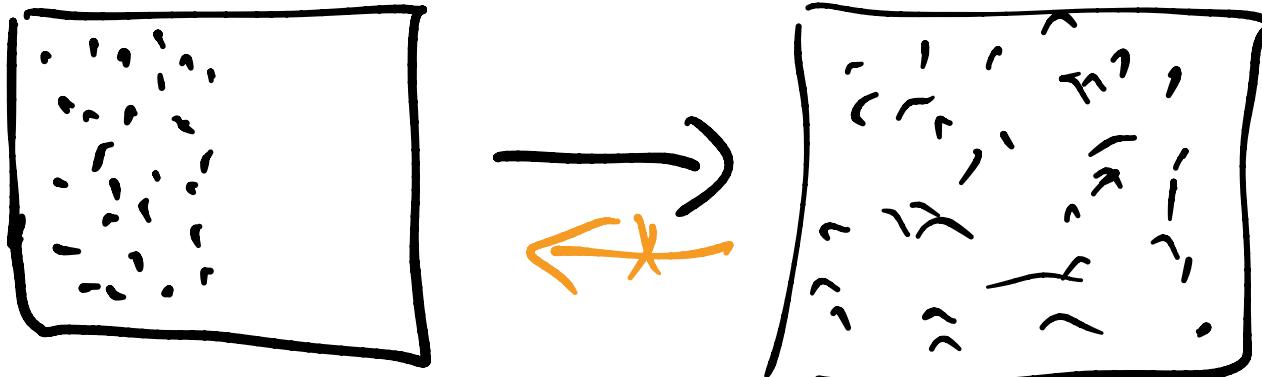


# Molecular origin of Entropy

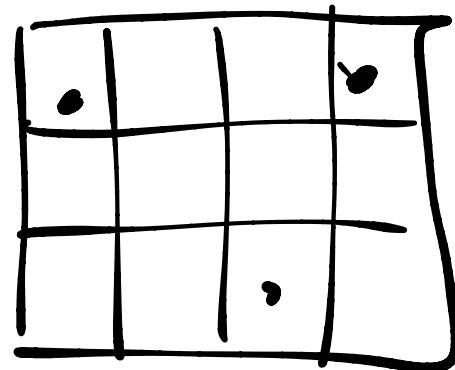
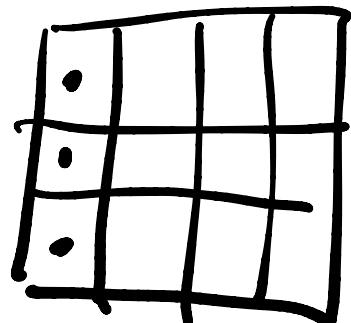
Boltzmann Entropy

Entropy = Disorder (?)



Contradict Newton's equations

How can we measure take into account # states of system



Non unif. Form

Uniform

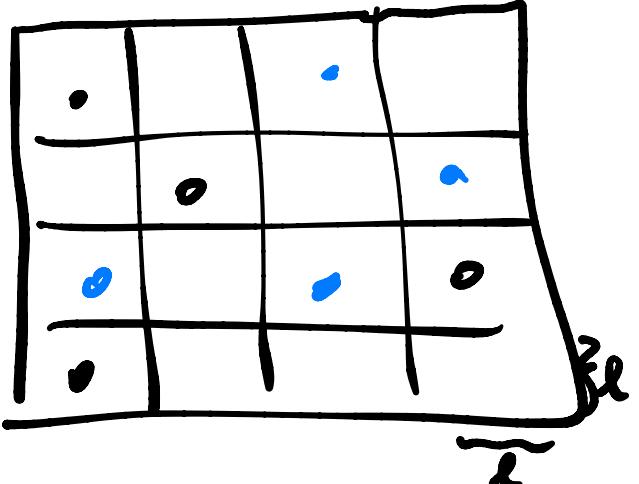
$W$  - # microstates accessible to the system

$$S = K_B \ln W \quad (\text{R})$$

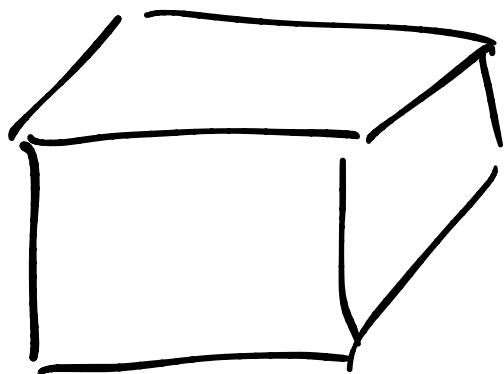
[<sub>eg</sub> state -  $(N, V, T)$ ]

[constant  $N, V, E$   
isolated system]

microstate - arrangement of molecules  
consistent with the state



$\pi$



$$V = Nl^3$$

lattice gas

$N$  molecules

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

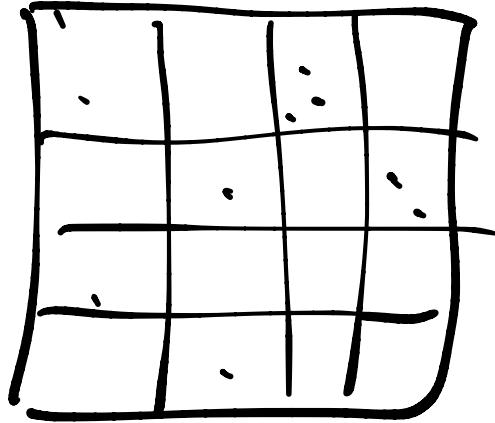
$E = \begin{cases} 0 & \text{if no overlap} \\ \infty & \text{if } \geq 2 \text{ particles} \end{cases}$   
in same box

What is  $W$ ? lattice gas

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

$$= \frac{N_c!}{m!(N_c-m)!} \quad \leftarrow ^{16}$$

4 →



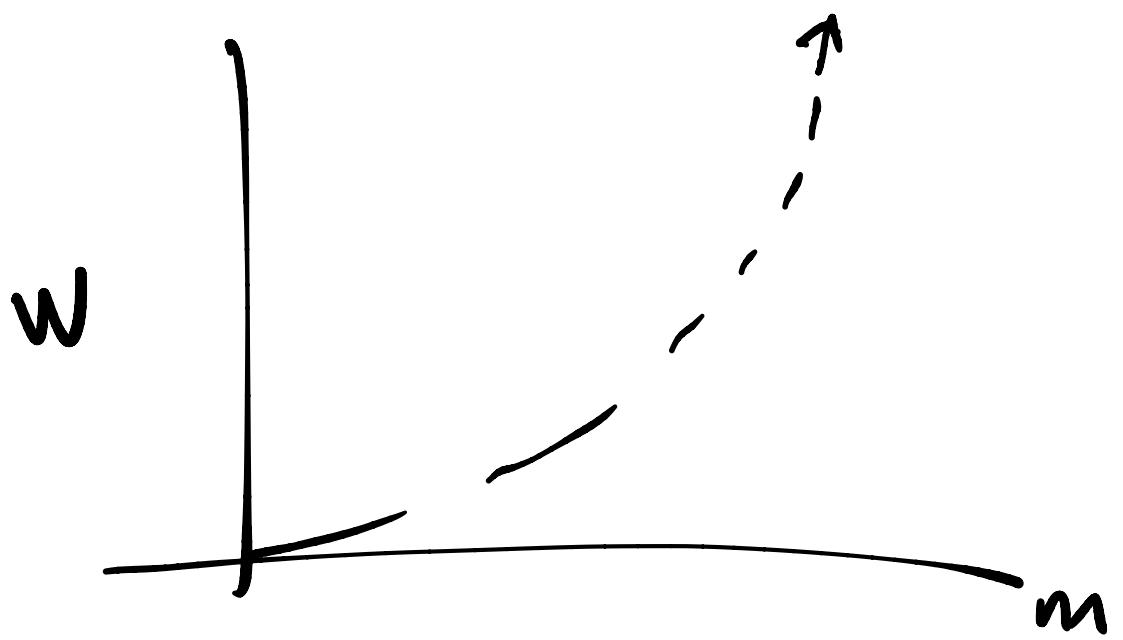
fully  
ideal gas

$E = 0$  for any config.

$W = ?$       # ways arrange

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

$+ 1/m!$  (see next lecture)



Why does  $S$  have to be logarithmic?

$S$  has property of being extensive

$$W_{2m,2v} = \underbrace{\text{[Diagram of a system with } m, v\text{]}}_{W} \times \underbrace{\text{[Diagram of a system with } m, v\text{]}}_W$$

Diagram illustrating the extensivity of entropy  $S$ . It shows two identical systems, each represented by a rectangle divided into smaller regions, with labels  $m, v$  at the bottom left and  $W$  at the bottom center. An arrow points from the label  $W$  to the first system. To the right of the second system, there are two blue arrows pointing towards it: one labeled  $2m$  above and one labeled  $2v$  below, indicating that the entropy of the combined system is the sum of the entropies of the individual systems.

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

Entropy for lattice gas?

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

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

$$m = N_c$$

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

$$\sigma \approx \frac{\delta/T}{[\epsilon]/[T]}$$

110101110101010

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

Stirling's approximations

for big  $N$

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

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

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

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

$$= k_B \left[ \ln(N_c!) - \underbrace{\ln(m!)}_{\text{big}} - \underbrace{\ln((N_c-m)!)}_{\text{big}} \right]$$

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

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

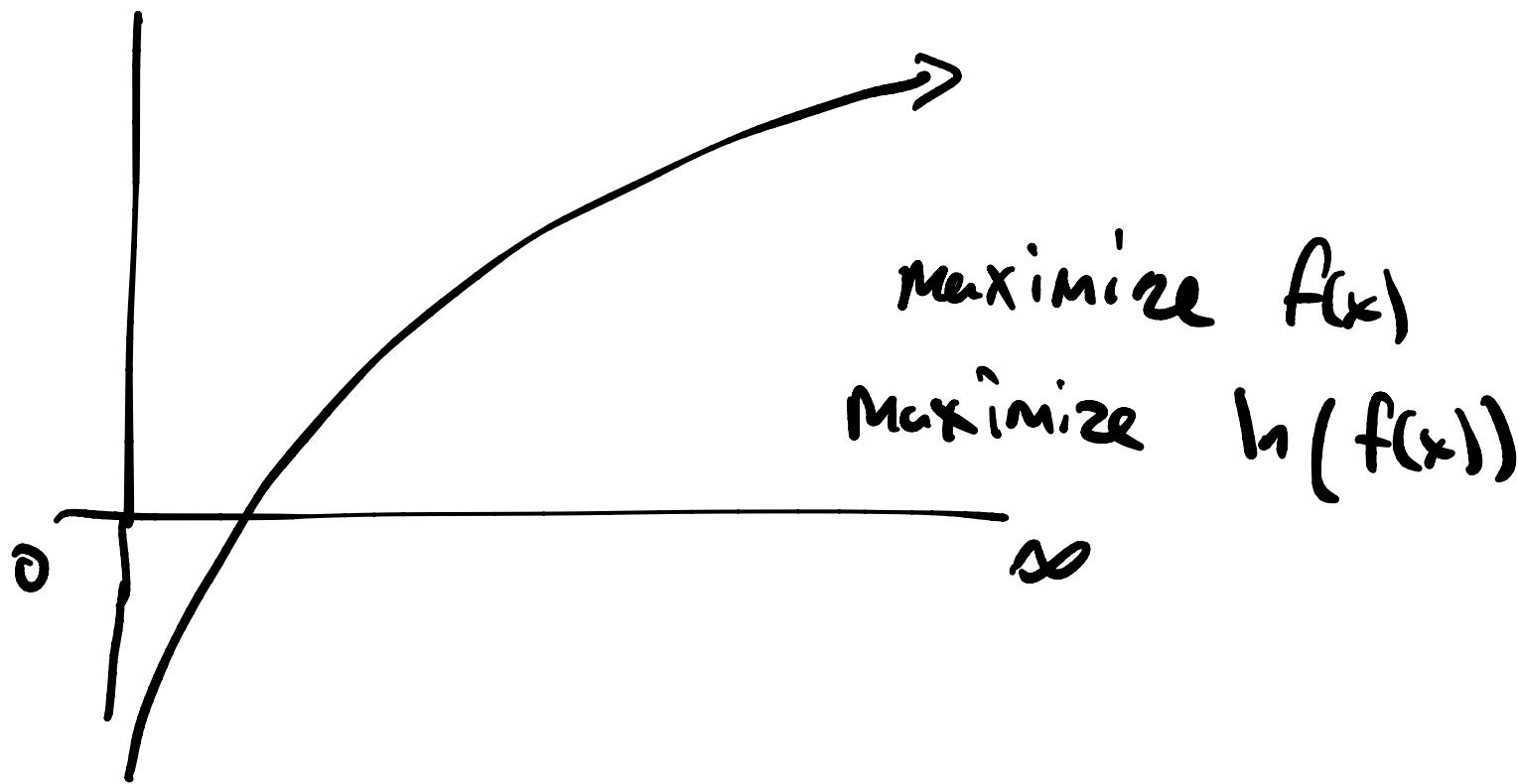
$$S = k_B \ln \left[ \frac{N_c^N c}{m^m (N_c - m)^{N_c - m}} \right]$$

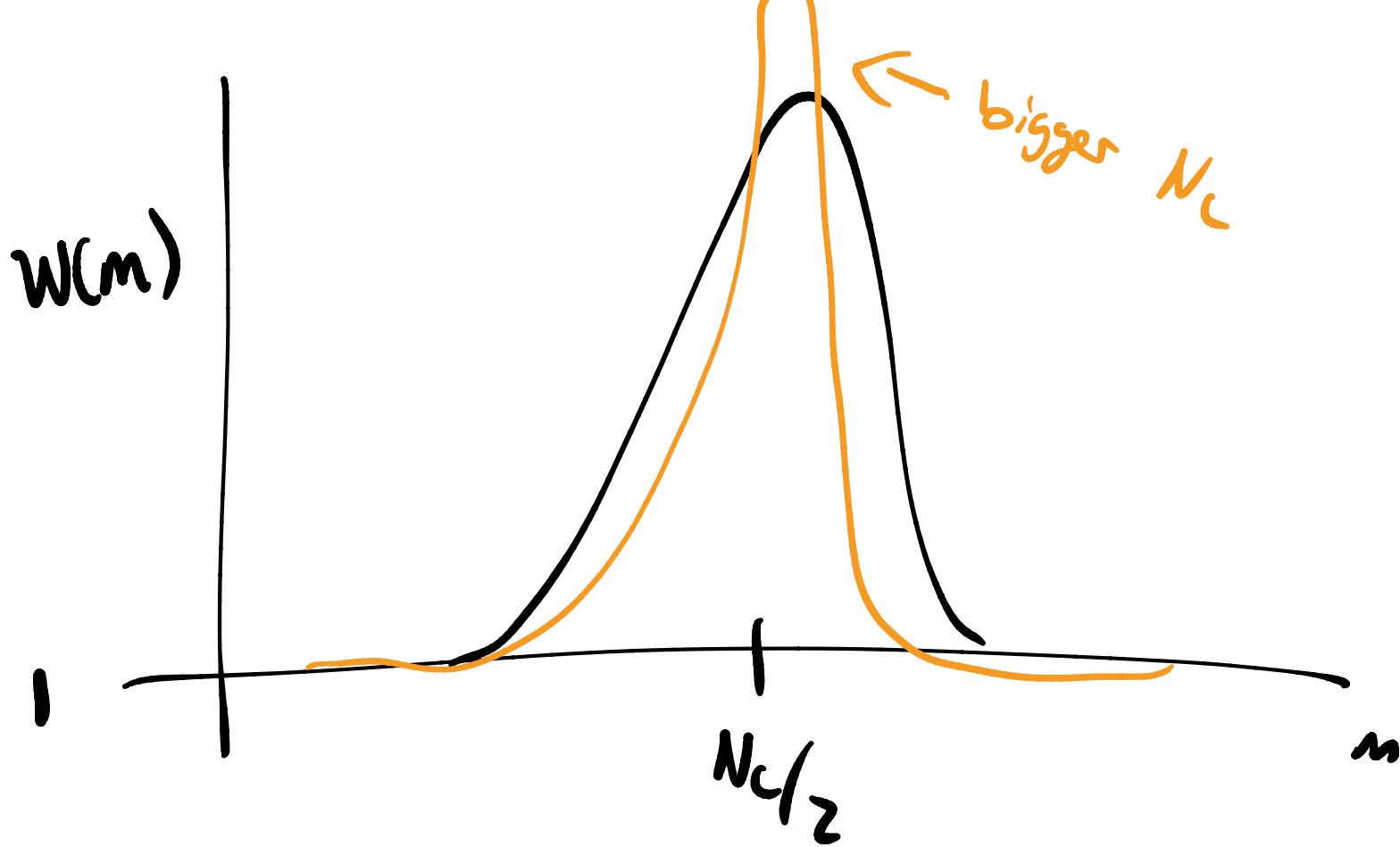
maximum for  $m = N_c/2$

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

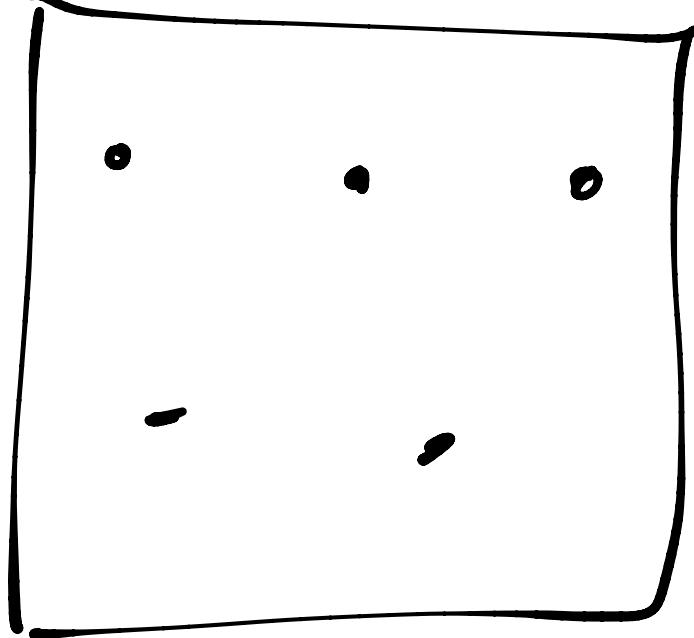
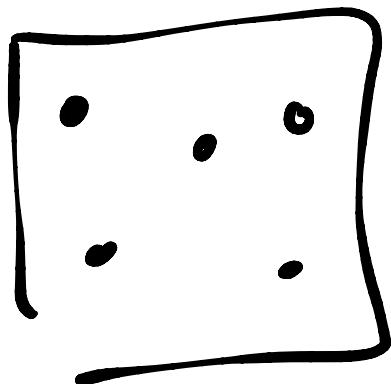
$$= k_B [N_c \ln N_c - m \ln m - (N_c - m) \ln (N_c - m)]$$

$\ln$  is a monotonically increasing function



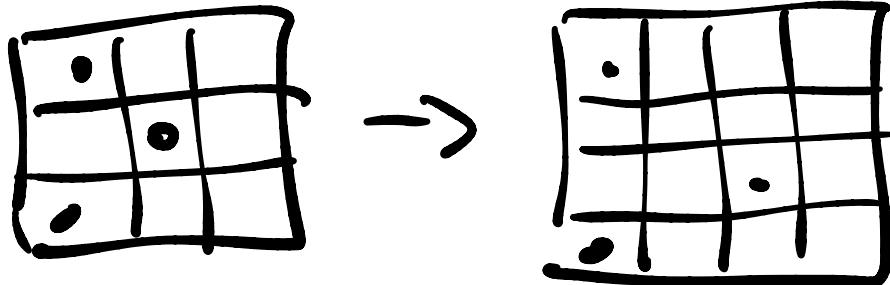


Change in entropy for "isothermal expansion"  
expansion where  $V_i \rightarrow V_f$



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

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



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

$$- k_B \ln \left( \frac{N_i^{N_i}}{m^m (N_i - m)^{N_i - m}} \right)$$

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

$$\tilde{n} \approx k_B m \ln\left(\frac{N_f}{N_i}\right)$$

$n/N_f$  is small

$$\Leftrightarrow n R \ln\left(\frac{v_f}{v_i}\right)$$

[check ideal gas]