


## Microscopic definition of entropy

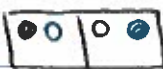
We mentioned that entropy characterizes disorder in a system.

Each macroscopic state can be realized with a number of microscopic configurations


Example: 4 beads in 2 boxes

#1 #2

 - 1 configuration with #2 empty



} 6 configurations with equal numbers in both sides

 - 1 configuration with #1 empty

$W$  - statistical weight (not work, just the same letter)

$$W_{4-0} = 1$$

$$W_{2-2} = 6$$

$$W_{0-4} = 1$$

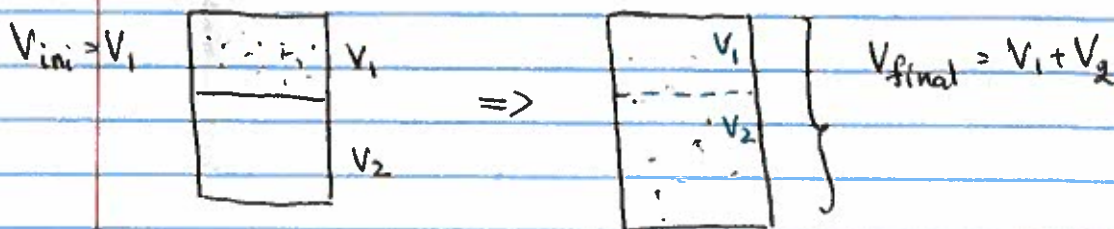
Entropy  $S = k_B \ln W$  Boltzmann definition

So  $S_{4-0} = 0$  and  $S_{0-4} = 0$  but  $S_{2-2} = k_B \ln 6$

The quote I really like: Boltzmann showed that the laws of physics are mostly accurate.

Arrow of time appears not because of fundamental laws of physics, but because every <sup>complex</sup> system evolves from ~~an~~ more ordered (<sup>less</sup> probable) to less ordered (more probable) state  $\rightarrow$  entropy grows

We calculated the entropy growth when gas expands using macroscopic description. We can do the same with microscopic description as well.



Probability of a single molecule

For a given volume  $V_i$  let's break it into small "cells" of volume  $V_{min}$ , and count how many possible "locations" a single molecule can have

$$W_i = \frac{V_i}{V_{min}}$$

If we have  $N$  molecules, each one has the same # of options, so

$$W_i = \left( \frac{V_i}{V_{min}} \right)^N$$

$$S_i = k_B \ln W_i = k_B \cdot N \ln \frac{V_i}{V_{min}}$$

If volume is increased  $\rightarrow w_2 = \frac{V_{f,2}}{V_{min}}$

$$W_{f,2} = \left( \frac{V_{f,2}}{V_{min}} \right)^N \quad S_{f,2} = k_B \ln W_{f,2} = k_B N \ln \frac{V_{f,2}}{V_{min}}$$

$$\Delta S = S_{f,2} - S_{f,1} = k_B \cdot N \left( \ln \frac{V_{f,2}}{V_{min}} - \ln \frac{V_{f,1}}{V_{min}} \right) = k_B N \cdot \ln \frac{V_{f,2}}{V_{f,1}}$$

same as  $\Delta S = nR \ln \frac{V_{f,2}}{V_{f,1}}$  we got last time