Microscopic origin of Entropy

$dS = \delta Q^{rev}/T$ → "macroscopic" definition

Boltzmann, 1872 clarified microscopic basis

$$\boxed{S = k_B \ln \Omega}$$

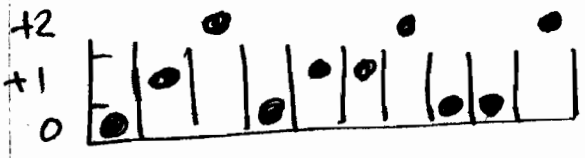
[at const. N, V, U]

$S : \frac{J}{\text{molecule K}}, \frac{J}{K}$

$$k_B = \frac{R}{N_{Av}} = 1.38 \cdot 10^{-23} \frac{J}{K}$$

Ω (omega): number of microscopic states (microstates) of a system with given energy U, number of molecules N, volume V

Example: 10 spheres, 3 energy levels for each energy measured in units of $k_B T_0$, where T_0 is a characteristic temperature



$\Omega(U=0) = 1$ $\quad S(0) = 0$

$\Omega(U=1) = 10$ $\quad S(1) = k_B \ln 10$

$\Omega(U=2) = 10 + \binom{10}{2} = 10 + \frac{10 \cdot 9}{2} = 55$ $\quad S(2) = k_B \ln 55$

10: each sphere at +2

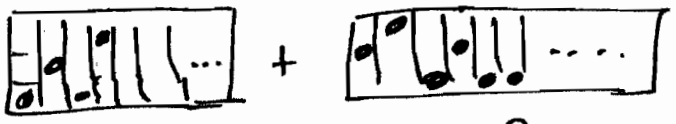
$\binom{10}{2}$: two at +1

etc

Properties of $k_B \ln \Omega$

(1) Extensive: $S_{A+B} = k_B \ln \Omega_{A+B} =$

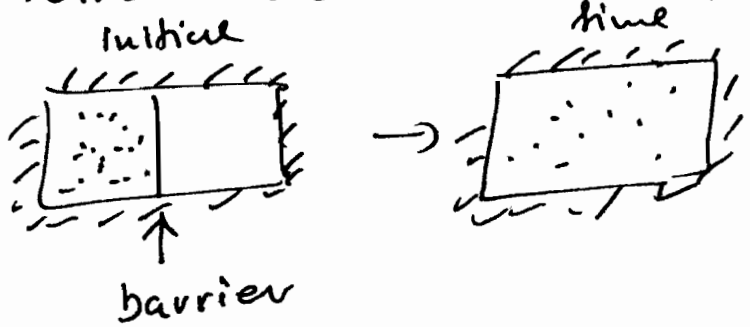
$= k_B \ln (\Omega_A \cdot \Omega_B) = k_B \ln \Omega_A + k_B \ln \Omega_B$



each microstate for A combined with each of B

(2) Maximized at equilibrium:

For spontaneous processes resulting from removal of constraints, number of states increases



$\ln \Omega_{final} > \ln \Omega_{initial}$

An important difference: microscopically defined S is <u>absolute</u> (Third Law) entropy, goes to 0 for $T \to 0$ when all systems exist in their ground state!

Basic Postulate of Statistical Mechanics } At const. N, V, U each microstate occurs with the <u>same</u> probability

$$p_i = \frac{1}{\Omega} \quad \text{at const. } N, V, U$$

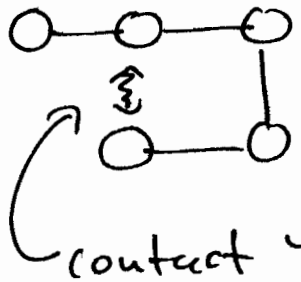
$$S = k_B \ln \Omega = k_B \ln \frac{1}{p_i} = -k_B \ln p_i \Rightarrow$$

$$\boxed{S = -k_B \sum_{\substack{\text{all} \\ \text{States}}} p_i \ln p_i}$$

Gibbs entropy formula valid for all ensembles, (when system is not at const N, V, U not all p_i's are the same → Ch. 5)

Example 3.9 - Flory lattice polymer

* each bead occupies lattice site
* excluded volume + nearest-neighbor attraction



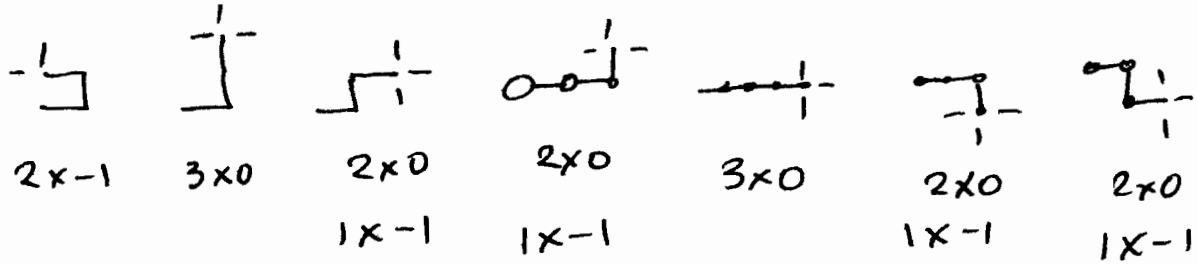
sample configuration of 2D lattice chain of 5 beads

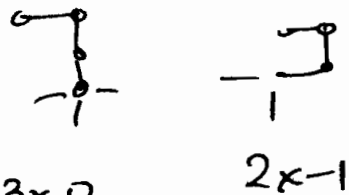
energy $= -1\ k_B T_0$ for this configuration

$\Omega(u=0) = ?$

$\Omega(u=-1) = ?$

Counting microstates:





$\Omega(0) = 17$

$\Omega(-1) = 8$