Microscopic origin of Entropy
\[ ds = \frac{\delta q}{T} \rightarrow \text{"macroscopic" definition} \]

\[ S = k_B \ln \Omega \]

(at const. \(N, V, U\))

\[ s : \frac{0}{\text{molecule}} = \frac{1}{k} \]

\[ k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} \]

\(\Omega\) (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.

\[ \Omega (U=0) = 1 \]
\[ \Omega (U=1) = 10 \]
\[ \Omega (U=2) = 1 \times 2 \]

\[ S(0) = 0 \]
\[ S(1) = k_B \ln 10 \]
\[ S(2) = k_B \ln (2) = 10 + \frac{10.9}{2} = 55 \]

\(\downarrow\) each sphere at \(+2\)
\(\uparrow\) two at \(+1\) etc.
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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 increase
   
   ![Diagram showing increase in entropy over time]

   Initial state $\ln \Omega_{\text{initial}} > \ln \Omega_{\text{final}}$

An important difference: microscopically defined $S$ is absolute (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 same probability

$$ P_i = \frac{1}{\Omega} $$ at const. $N, V, U$
### CBE 2+6 Microscopic S

\[ S = k_B \ln \Omega = k_B \ln \frac{1}{P_i} = -k_B \ln P_i \rightarrow \]

\[ S = -k_B \sum_{\text{all states}} P_i \ln P_i \]

Gibbs entropy formula valid for all ensembles, (when system is not at constant $N, V, u$ not all $P_i$'s are the same $\rightarrow$ 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: $-1$ $k_B T \Omega$ for this configuration

- $\Omega (u=0) = ?$
- $\Omega (u=-1) = ?$

**Counting microstates:**

\[
\begin{array}{ccccccc}
- & 1 & 1 & 1 & 1 & 1 & 1 \\
2x-1 & 3x0 & 2x0 & 2x0 & 3x0 & 2x0 & 2x0 \\
1x-1 & 1x-1 & 1x-1 & 1x-1 \\
3x0 & 2x-1 \\
\end{array}
\]

- $\Omega (0) = 17$
- $\Omega (-1) = 8$