
- What is Statistical Mechanics?
- Brief Review of probability and combinatorics
- $S=k \ln\Omega$ and $S = -k \sum p_i \ln p_i$

• What is Statistical Mechanics?

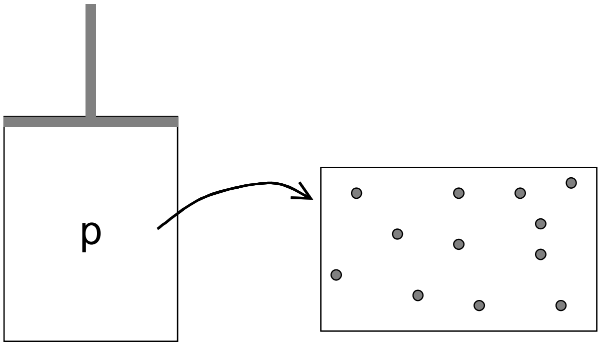
Spontaneous processes:

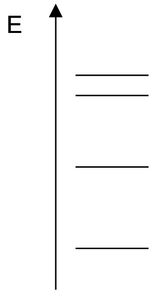
under certain conditions, know what system would like to maximize/minimize:

$$
\begin{array}{ll}
U(S,V,n_i) & (dU)_{S,V,n_i} \le 0 \\
A(T,V,n_i) & (dA)_{T,V,n_i} \le 0 \\
H(S,P,n_i) & (dH)_{S,P,n_i} \le 0 \\
G(T,P,n_i) & (dG)_{T,P,n_i} \le 0
\end{array}
$$

These tell you which way a reaction will go, and when it will stop or reach equilibrium.

Want these thermodynamic properties, now in terms of **molecular level picture**.





Before: ignore molecular properties

Now want to account for it: molecule exists in states, has energy levels (recall 5.111)

If have large number of molecules ($N_A = 6\times 10^{23}$), it is nearly impossible to track all of the states. Mind boggling!

How?: use probability to describe molecule instead of tracking each one

p_i = probability that molecule will be in i^{th} state. The link between microscopic and macroscopic:

Boltzmann Equation

Ω = multiplicity

k=Boltzmann constant, = 1.38×10^{-23} J/K

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

Another form:

p_i = probability that molecule will be in ith state

t = number of states

$$\boxed{S = -k \sum_{i=1}^{t} p_i \ln p_i}$$

Probabilistic description of entropy!

Then relate these microscopic properties to macroscopic ones: U, S, etc. (Driving forces). Explain:

unfolded protein → folded protein

Do not need to know exactly how many molecules are in a state, just the probability that it is.

Ludwig Boltzmann (1844-1906)

Image removed due to copyright reasons.

<u>Approach</u>:

- make model to represent problem
- describe the states a system can be in
- use statistics and probability to average
- relate to a thermodynamic property (U, S, etc)

DEMYSTIFYING S

• Brief Review of Probability and Combinatorics

Combinatorics: counting the number of available states (conformations, energy levels)

Multiplicity (Ω): Number of possible arrangements

For a set of N **distinguishable** objects:

$$\boxed{\Omega = N\cdot(N-1)\cdot(N-2)\cdot\ldots\cdot 3\cdot 2\cdot 1 = N!}$$

Example: 4 mer, A, T, G, C

How many different ways can these 4 nucleotides be arranged?

Write out all possible arrangements:

ACGT	CAGT	GACT	TACG
ACTG	CATG	GATC	TAGC
AGCT	CGAT	GCAT	TCAG
AGTC	CGTA	GCTA	TCGA
ATCG	CTAG	GTAC	TGAC
ATGC	CTGA	GTCA	TGCA

Ω=24 ways

Using equation:

4 available slots: __ __ __ __

$\Omega = 4 \times 3 \times 2 \times 1 = 4! = 24$ possible arrangements

(remember: 0! =1)

Indistinguishability: What if two of the letters are the same?:

Example: 3mer with A, A, G

Two of the nucleotides are **indistinguishable** (can't tell them apart)

First: pretend A and A are **distinguishable:** A_1 A_2

G A_1 A_2	G A_2 A_1
A_1 G A_2	A_2 G A_1
A_1 A_2 G	A_2 A_1 G

Ω = 6 ways

Then: take away labels. Both columns same. Ω = 3 ways

To account for indistinguishability, divide by N_A = number of A's

$$\Omega = \frac{N!}{N_A!} = \frac{3\times 2\times 1}{2\times 1} = 3$$

N_A = number of A's = 2

<u>**General equation**</u>:

N objects

t categories

n_i = number of objects in i^{th} category (**degeneracy**)

$$\boxed{\Omega = \frac{N!}{n_1!\times n_2!\times \ldots n_t!}}$$

<u>**Binomial case**</u>: only two possibilities (Heads/Tails, On/off, spin up/spin down, ground state/excited state)

then, t=2

$n_H + n_T = N$

need to specify only $n_H \equiv n$

then $n_T = N-n$

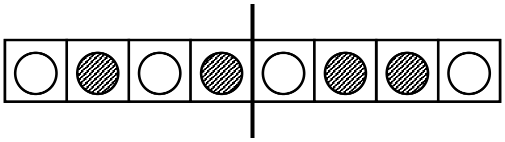
$$\boxed{\Omega(n,N) = \binom{N}{n} = \frac{N!}{n!(N-n)!}}$$

Let's utilize Ω in an example:

Example 1: Entropy of mixing

This example will show that maximum Ω indicates a maximum S. Well choose a model for to demonstrate the entropy of mixing. This will illustrate the driving force behind mixing based on entropy.

Lattice model: 8 slots, separated by a wall. Total volume is fixed. 4 black particles and 4 white ones, which can be placed one per slot in any configuration:



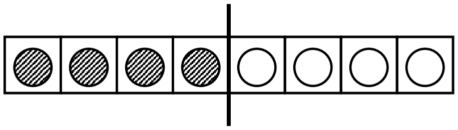
Degree of freedom: is the # of black particles and # white particles on either side of the wall.

$$\Omega = \frac{N!}{n_B! \times n_w!} = \frac{8!}{4!4!} = 70$$

Now: count number of ways each configuration is possible for each configuration (number of B on Left) Use

$$\Omega_{tot} = \Omega_{left} \cdot \Omega_{right}$$

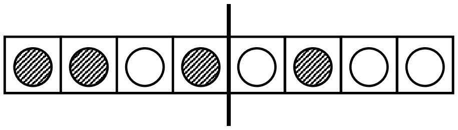
A



4B | 0B

$$\Omega = \frac{4!}{4!0!} \cdot \frac{4!}{0!4!} = 1$$

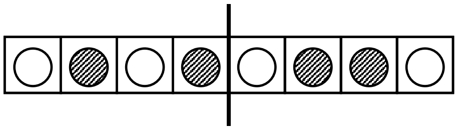
B



3B | 1B

$$\Omega = \frac{4!}{3!1!} \cdot \frac{4!}{1!3!} = 16$$

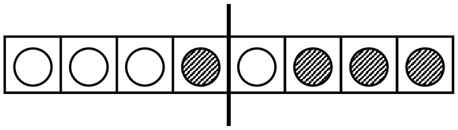
C



2B | 2B

$$\Omega = \frac{4!}{2!2!} \cdot \frac{4!}{2!2!} = 36$$

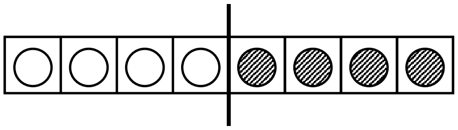
D



1B | 3B

$$\Omega = \frac{4!}{1!3!} \cdot \frac{4!}{3!1!} = 16$$

E



0B | 4B

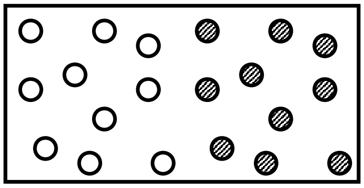
$$\Omega = \frac{4!}{0!4!} \cdot \frac{4!}{4!0!} = 1$$

Ω_{tot}=70 ways

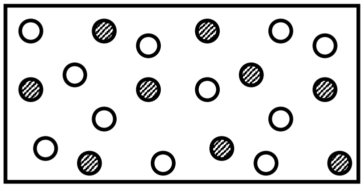
Case C has the **highest entropy** because it has the **highest multiplicity**. Therefore, this is the state the system is most likely to be in. This also is confirmed by our intuition of the problem, in that C is the most disordered case.

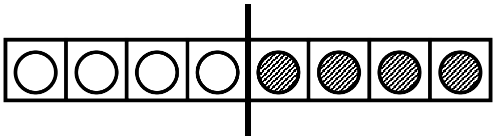
$$\boxed{S = k \ln \Omega}$$

This is akin to:

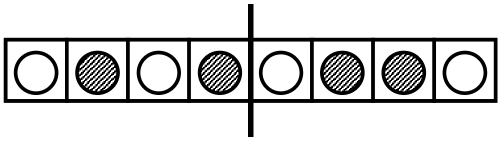


vs





Ω=1



Ω =36

maximizing Ω maximizes S

tendency towards disorder

<u>Probability</u>: likelihood that the system is occupying that state

N = number of total outcomes

n_A = number of outcomes of category A

$$p_A = \frac{n_A}{N}$$

p_A = probability of obtaining outcome of type A

Example: Die

N = 6

n_{odd} = 3

$$p_{\text{odd}} = \frac{n_{\text{odd}}}{N} = \frac{3}{6} = \frac{1}{2}$$

Addition Rule:

Probability of outcome A OR outcome B:

$$p_A + p_B$$

Multiplication Rule:

Probability of outcome A AND outcome B

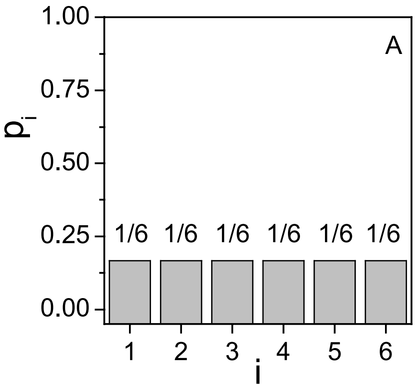
$$p_A \cdot p_B$$

If outcomes are collectively exhaustive:

$$\boxed{\sum_{i=1}^{t} p_i = 1}$$

Probability Distributions

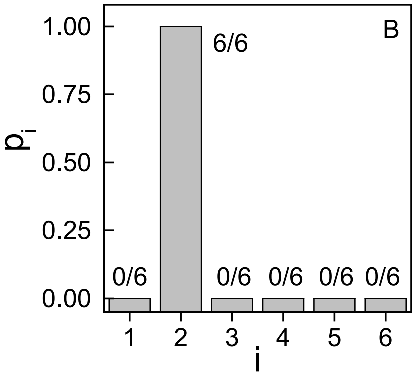
Plotting pi vs. i gives you a probability distribution. For example, the probabilities of rolling a die may look like either case A or case B:



$$S = -k\sum_{i=1}^{6} p_i \ln p_i$$

$$= -k\left[\tfrac{1}{6}\ln\left(\tfrac{1}{6}\right) + \tfrac{1}{6}\ln\left(\tfrac{1}{6}\right) + \tfrac{1}{6}\ln\left(\tfrac{1}{6}\right) + \tfrac{1}{6}\ln\left(\tfrac{1}{6}\right) + \tfrac{1}{6}\ln\left(\tfrac{1}{6}\right) + \tfrac{1}{6}\ln\left(\tfrac{1}{6}\right)\right]$$

$$= k\left[\ln 6\right] = 1.79k$$



$$S = -k\sum_{i=1}^{6} p_i \ln p_i$$

$$= -k\left[0\ln(0) + 1\ln(1) + 0\ln(0) + 0\ln(0) + 0\ln(0) + 0\ln(0)\right]$$

$$= 0$$

Let's use this to calculate S for two different probability distributions. Of the two above, can guess that the case a) has the higher entropy. More disordered. But let's calculate a number using:

$$\boxed{S = -k\sum_{i=1}^{t} p_i \ln p_i}$$

Can see that **flatter distributions** have **higher entropy.** What does this mean? If you are distributing particles in energy levels, evenly distributing them leads to the highest entropy.

But what we usually observe is that things tend to have lower energies. Why is that? We have placed **no constraints** on the system. But don't worry, we will!

Given a probability distribution, can compute the average values of some property X

$$\boxed{< X >= \sum_{\substack{all\\states}} X_i p_i}$$

For example, if we wanted to computer the average score for this probability distribution:

$$< \text{score} >= \sum_{\substack{all\\states}} \text{score}_i p_i = 1\left(\frac{1}{6}\right) + 2\left(\frac{1}{6}\right) + 3\left(\frac{1}{6}\right) + 4\left(\frac{1}{6}\right) + 5\left(\frac{1}{6}\right) + 6\left(\frac{1}{6}\right) = 3.5$$

We will be using average energy a lot:

$$\boxed{< \varepsilon >= \sum_{\substack{all\\states}} \varepsilon_i p_i}$$

This is our constraint: that the total energy has to sum up to a particular value.

Stirling's approximation:

S = k ln Ω

Ω=N! or N!/(n_1!n_2!….)

then need to do ln N! for large N (N >10)

$$\boxed{\begin{gathered} n! \approx \left(\frac{n}{e}\right)^n \\ \ln n! \approx n \ln n - n \end{gathered}}$$