Entropy and Probability

(A statistical view)

Entropy ~ a measure of the disorder of a system.

A state of high order = low probability
A state of low order = high probability

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.

We will illustrate the concepts by considering the free expansion of a gas from volume V_i to volume V_f.

The gas always expands to fill the available space. It never spontaneously compresses itself back into the original volume.

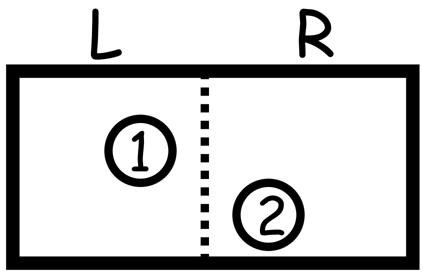
First, two definitions:

Microstate: a description of a system that specifies the properties (position and/or momentum, etc.) of each individual particle.

Macrostate: a more generalized description of the system; it can be in terms of macroscopic quantities, such as P and V, or it can be in terms of the number of particles whose properties fall within a given range.

In general, each macrostate contains a large number of microstates.

An example: Imagine a gas consisting of just 2 molecules. We want to consider whether the molecules are in the left or right half of the container.



There are 3 macrostates: both molecules on the left, both on the right, and one on each side.

There are 4 microstates: LL, RR, LR, RL.

How about 3 molecules? Now we have:

LLL, (LLR, LRL, RLL), (LRR, RLR, RRL), RRR

(all L) (2 L, 1 R) (2 R, 1 L) (all R)

i.e. 8 microstates, 4 macrostates

How about 4 molecules? Now there are 16 microstates and 5 macrostates

(all L)	(3L, 1R)	(2L, 2R)	(1L, 3R)	(all R)
1	4	6	4	1

number of microstates

In general:

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

1 6 15 20 15 6 1

1 7 21 35 35 21 7 1

1 8 28 56 70 56 28 8 1

N	W	M
1	2	2
2	4	3
3	8	4
4	16	5
5	32	6
6	64	7
7	128	8
8	256	9
	↑ 2^N	↑ $N+1$

This table was generated using the formula for # of permutations for picking n items from N total:

$$W_{N,n} = \frac{N!}{N!\,(N-n)!}$$

i.e. $W_{6,2} = \frac{6!}{2!\,4!} = 15$

"multiplicity"

Fundamental Assumption of Statistical Mechanics: All microstates are equally probable.

Thus, we can calculate the likelihood of finding a given arrangement of molecules in the container.

E.g. for 10 molecules:

Conclusion: Events such as the spontaneous compression of a gas (or spontaneous conduction of heat from a cold body to a hot body) are not impossible, but they are so improbable that they never occur.

We can relate the # of microstates W of a system to its entropy S by considering the probability of a gas to spontaneously compress itself into a smaller volume.

If the original volume is V_i, then the probability of finding N molecules in a smaller volume V_f is

$$\text{Probability} = W_f/W_i = (V_f/V_i)^N$$

- $\ln(W_f/W_i) = N \ln(V_f/V_i) = n N_A \ln(V_f/V_i)$

We have seen for a free expansion that

$$\Delta S = n R \ln(V_f/V_i) ,$$

so

$$\Delta S = (R/N_A) \ln(W_f/W_i) = k \ln(W_f/W_i)$$

or

$$S_f - S_i = k \ln(W_f) - k \ln(W_i)$$

Thus, we arrive at an equation, first deduced by Ludwig Boltzmann, relating the entropy of a system to the number of microstates:

$$S = k \ln(W)$$

He was so pleased with this relation that he asked for it to be engraved on his tombstone.