Multiplicity and the second law

We have seen:

> *Energy tends to rearrange itself such that the multiplicity is at (or very near) its maximum value.*

A formulation of the *second law of thermodynamics*:

> *Any large system in equilibrium will be found in the macrostate with the greatest multiplicity.*

or

> *Multiplicity tends to increase.*

Entropy

Introduce the entropy:

$$S = k_B \ln \Omega$$

- Ω — a very large number,
- $\ln \Omega$ — a large number,
- $k_B \ln \Omega$ — an ordinary number.

The entropy increases with...

- increasing number of particles,
- increasing energy,
- increasing volume,
- breaking apart of larger molecules into smaller.

Additive property of entropy

Additive property: For two parts A and B with $\Omega_{\text{total}} = \Omega_A \Omega_B$:

$$
\begin{aligned}
S_{\text{total}} &= k_B \ln \Omega_{\text{total}} \\
&= k_B \ln(\Omega_A \Omega_B) \\
&= k_B \ln \Omega_A + k_B \ln \Omega_B \\
&= S_A + S_B.
\end{aligned}
$$

Example: Entropy of an Einstein solid

Einstein solid with N oscillators and $q \gg N$ energy units.

$$\Omega = \left(\frac{eq}{N}\right)^N,$$

$$S = k_B \ln \left(\frac{eq}{N}\right)^N = N k_B \ln \left(\frac{eq}{N}\right).$$

With $N = 10^{22}$ and $q = 10^{24}$ in $S = k_B \ln \Omega$:

$$
\begin{aligned}
S &= N k_B \ln(271.8) = N k_B \times 5.6 \\
&= 10^{22} \times 1.38 \cdot 10^{-23} \times 5.6 \\
&= 0.77 \ \mathrm{J/K}.
\end{aligned}
$$

Entropy and disorder!

Often an helpful analogy:

> *A shuffled deck of cards is more disordered—higher entropy.*

However:

> *A glass of crushed ice appears more disordered, but actually has a lower entropy than a glass with the same amount of water.*

Entropy and the second law

Restate the *second law of thermodynamics* in terms of the entropy:

> *Any large system in equilibrium will be found in the macrostate with the greatest entropy.*

or

> *Entropy tends to increase.*

Maxwell's demon

Is it really generally true that all processes lead to the increase of entropy?

Maxwell suggested that a "very observant and neat-fingered being" could deflect faster particles in one direction and slower particles in the other.

However,

- devices for doing this have been found to be ineffective since each such a device has to process the information needed to sort the molecules and this creates entropy.
- The entropy will thus increase and the second law is not violated.