

Chapter 2 - The second law of thermodynamics

Two-State Systems

Each different outcome is called a *microstate* (often specified by each individual particle). If the state is specified more generally, we have a *macrostate*. The number of microstates for a given macrostate is called the multiplicity, and is given by

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

This can be read as the number of ways of choosing n objects out of N . The probability of any particular macrostate $\Omega(n)$ can be written

$$P(n) = \frac{\Omega(n)}{\Omega(all)}$$

where $\Omega(all)$ is the total multiplicity of the system.

The two-state paramagnet

A paramagnet is a material in which the constituent particles tend to have spins that align *parallel* to any external magnetic field. Each of these spin-elements is called a dipole. One dipole could be an electron, a group of electrons in an atom or an atomic nucleus. If the particle interaction is strong enough so that the material can magnetise without an external field, it's a *ferromagnet*. The multiplicity of the paramagnet, where the only option for the dipoles' spin direction is parallel or antiparallel, is given by

$$\Omega(N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

An up-dipole has less energy than a down-dipole. Since the energy of the system is determined by the total number of up and down dipoles, by looking at the multiplicity of the system, we also know the energy. This type of paramagnet is called a *two state paramagnet*.

The Einstein Model of a solid

Here particles in a solid are modelled as harmonic oscillators, a so-called *Einstein-Solid*. Since all oscillators can move in three dimensions, there are $N/3$ atoms for every N oscillator. The general formula for an Einstein solid with N oscillators and q energy units is

$$\Omega(N, q) = \binom{q + N - 1}{1} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

The actual energy in such a system is $E = hf = \hbar\omega$, where f is the frequency of the system and ω is the angular frequency. h and \hbar should be known by now.

Interacting systems

We now consider two Einstein solids that can exchange energy units q (exchange heat). We now assume that the energy transfer is random, such that each microstate is equally probable. This is the **fundamental assumption of statistical mechanics**:



In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

Although each microstate is equally probable, not all macrostates are. In fact, the higher the multiplicity of a certain configuration, the more probable it is to find the system in this configuration. This is where *heat* comes from. It's an irreversible behaviour based on probabilities. It is far more probable that energy flows from a warm system to a cold system than the other way around. The total multiplicity of a composite system, Ω_{total} , is the multiplicities of each constituent multiplied by each other, $\Omega_{total} = \Omega_A \cdot \Omega_B \cdot \Omega_C \cdots \Omega_N$.

For large systems, we use the *Stirling approximation*

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

For very big N s, we can omit the square root. This gives us the following multiplicity for large Einstein solids:

$$\ln(\Omega) = (q + N) \ln(q + N) - q \ln q - N \ln N$$

when $q \gg N$, we get that

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

and when $q \ll N$

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

If we graph the multiplicity of the two Einstein-solids, A and B , as a function of energy units in one of them, q_A , we will see that the width of the graph is narrow around the most probable microstate. When the graph falls to $1/e$ of the maximum value, the width is q/\sqrt{N} . As the number of particles in the system increases, the spike gets sharper.

The ideal gas

The multiplicity of a monatomic ideal gas can be written as follows

$$\Omega(U, V, N) = \frac{1}{N!} \frac{1}{h^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} V^N \left(\sqrt{2mU}\right)^{3N-1} \approx f(N) V^N U^{3N/2}$$

where $f(N)$ is the complicated function of N as shown above. N is the number of particles, h is Planck's constant, V is the volume of the gas, m is the mass of the constituents of the gas, and U is the total kinetic energy of the gas.

For two interacting gases separated by a barrier that only allows energy to be transferred, populated by the same species of atoms, we have that the total multiplicity is the product of the multiplicities of the two gases:

$$\Omega_{tot} = \Omega_A \cdot \Omega_B = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2}$$

Entropy

A generalisation of the second law of thermodynamics is that *multiplicity tends to increase*. The quantity **entropy** is defined as

$$S \equiv k \ln \Omega$$

where k is the Boltzmann constant and Ω is the multiplicity. So for the large Einstein solid with N oscillators and q units of energy, where $q \gg N$ (the high temperature limit), we have that the entropy is $S = k \ln(eq/N)^N = Nk[\ln(q/N) + 1]$.

The entropy of a composite system is the entropy of the sum of its parts, i.e.: $S_{tot} = S_A + S_B$. The second law of thermodynamics now can be rephrased as *Entropy tends to increase*. The **Sackur-Tetrode equation** gives us the entropy of an ideal gas:

$$S = NK \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

For fixed U and N , we can say that the increase in entropy when an ideal gas expands from V_i to V_f is

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

You have two gases with the same N , U , and V , but different compositions, in a box separated by a barrier in the middle. If we then remove the barrier so the gases mix, we get a change in entropy

$$\Delta S_{tot} = \Delta S_A + \Delta S_B = Nk \ln 2 + Nk \ln 2 = 2Nk \ln 2$$

The 2 in the logarithm is there due to the final volume being twice as large as the initial volume. If the particles are indistinguishable, however, the entropy does not change when the barrier is removed.

Reversible and irreversible processes

If a reaction increases a system's entropy, it cannot happen in reverse; it would then break the second law of thermodynamics and decrease the entropy of the system. Such processes are **irreversible**. If the change in entropy is $\Delta S = 0$, then the process may be reversed. Heat flow, for example, is always irreversible. One may hear the phrase "reversible heat flow". This simply means that the heat flow is so slow, and goes between two systems in approximate thermal equilibrium, such that the change in entropy is negligible. Any change in volume have to be quasistatic $W = -PdV$, if it is to be reversible. Generally, a reversible process is one that can be reversed by changing the conditions infinitesimally.