

Chapter 3 - Interactions and implications

Temperature

When two systems are in thermal equilibrium, they are in the states with highest entropy, $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, but they also have the same temperature. Temperature is defined, among other things, as:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

Entropy and heat

We have the following definition:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

From this, we can deduce the heat capacities of the Einstein solid (with $q \gg N$) and a monatomic ideal gas, respectively:

$$C_V = \frac{\partial}{\partial T}(NkT) = Nk \quad C_V = \frac{\partial}{\partial T} \left(\frac{3}{2}NkT \right) = \frac{3}{2}Nk$$

We remember that $dS = dU/T = Q/T = C_V dT/T$. This allows us to formulate the following equation, using the integral

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT = C_V \ln \left(\frac{T_f}{T_i} \right)$$

If you have a system where N and V are constant, and you add heat, the entropy will increase in this fashion. If you fix $T_i = 0$, then you can theoretically find the total entropy of the system at any given temperature (given that you have C_V for all temperatures). This due to the fact that the system will settle in its unique lowest energy state, where $\Omega = 1 \Rightarrow S = 0$. This is often called the *Third law of thermodynamics*. In practise, this might not be as easy. If this is the case, we call the lowest obtainable entropy the *residual entropy*. Another interesting observation is that $C_V \rightarrow 0$ as $T \rightarrow 0$.

Paramagnetism

Here we have N spin-1/2 particles pointing in the z -direction, all in a constant magnetic field $\vec{B} = B\hat{z}$. These particles are called dipoles, and they do not interact; we have an ideal paramagnet. The total energy of the system is

$$U = \mu B(N_{\uparrow} - N_{\downarrow}) = \mu B(N - 2N_{\uparrow})$$

The net magnetisation can be written

$$M = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B}$$

with the multiplicity

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

From this, we can get the entropy as a function of energy. This turns out to have a maximum at $U = 0$, meaning that the entropy is maximum when we have as many down-states as up-states. μ is a number with dimension eV/T.

Mechanical equilibrium

We now imagine a system in a box with a divider somewhere in that box. The box is filled with gas. For mechanical equilibrium, we have that

$$\left(\frac{\partial S_A}{\partial V_A}\right)_{N_A, U_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B, U_B}$$

In addition, the pressure must be equal on both sides, and from this we can derive that

$$P = T \left(\frac{\partial S}{\partial V}\right)_{U, N}$$

Diffusive equilibrium and chemical potential

We now consider the same box as before, but with a membrane as a divider, such that particles and energy can be exchange between system A and B . Both systems consist of the same species of particles. We can hereby take a giant intuitive leap and say that

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

which we can use (alongside some more hocus pocus) to deduce

$$\mu \equiv -T \left(\frac{\partial}{\partial N}\right)_{U, V}$$

In diffusive equilibrium, we have that $\mu_A = \mu_B$. With a bit of maths, we arrive at the *thermodynamic identity*:

$$dU = TdS - PdV + \mu dN$$