Lecture_13

November 4, 2022

1 Distinguishability

In the last lecture, we discussed the partition function in the case of a 3 particle system. Let's now generalise it to N particles. So to generalise this to N particles:

$$Z = \sum_r e^{-N\beta(\epsilon_r)} + ... + \frac{1}{N!}(\sum_{r_1} \cdots \sum_{r_n})_{r1 \neq ... \neq rn} e^{-\beta(\epsilon_{r1}+...+\epsilon_{rn})}$$

where the ... represent terms where we have multiple particles in different states. Now, we make an important assumption: the number of states in a given energy interval is much larger than the number of particles with an energy in that interval. In the classical regime, the probability that any state r is occupied by more than one particle is very low. This means only the last term is significantly different from 0.

The partition function then becomes

$$Z = \frac{1}{N!} \sum_{r_1} \cdots \sum_{r_n} e^{-\beta(\epsilon_{r1}+...+\epsilon_{rn})} \tag{1}$$

$$Z = \frac{1}{N!} \sum_{r_1} e^{-\beta\epsilon_{r1}} \cdots \sum_{r_N} e^{-\beta\epsilon_{rn}} \tag{2}$$

$$Z = \frac{1}{N!} \left(\sum_{r_1} e^{-\beta\epsilon_{r1}} \right)^N \tag{3}$$

$$Z = \frac{1}{N!} Z_1^N \tag{4}$$

This is true for the perfect, classical gas. Here, perfect means the particles are weakly/non-interacting (which let's us to write down the energies as $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 ... \leq \epsilon_r \leq ...$), and classical means there is a very low probability that there are multiple particles in any state. When is this last condition valid?

There will only be one particle occupying each state if the system is in a regime where the number of states is much larger than the number of particles. For an ideal gas, this means we require that the number of thermally accessible states is larger than the number of particles. As such, we require that the number density of molecules be much less than the quantum concentration:

$$n << n_Q$$

2   Functions of state of an ideal gas

So now that we know how to calculate the partition function for N indistinguishable particles, let's apply the techniques we have developed to understand an ideal gas. The partition function for N particles in a gas is

$$Z_N = \frac{1}{N!} \left(\frac{V}{\lambda_{\text{th}}^3} \right)^N$$

Using the expression for λ_{th}, we then get that

$$Z_N = \frac{1}{N!} V^N \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$$

This means that

$$\ln Z_N = N \ln V + \frac{3}{2} N \ln T + C$$

The internal energy is then given by

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = k_B T^2 \frac{\partial \ln Z_N}{\partial T} = \frac{3}{2} N k_B T$$

The Helmholtz free energy is

$$F = -k_B T \ln Z_N = -k_B T N \ln V - k_B T \frac{3}{2} N \ln T - k_B T C$$

such that if we use (from Lecture 7)

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V}$$

which is the equation of state for an ideal gas! In order to work out the other thermodynamic quantities, we need to be a bit more careful with those constants in earlier equations. Returning to the partition function, we can write it instead as.

$$\ln Z_N = N \ln V - 3N \ln \lambda_{\text{th}} - N \ln N + N$$

after using Stirlings approximation of $\ln N! \sim N \ln N - N$. This further simplifies to

$$\ln Z_N = N \ln \left(\frac{V e}{N \lambda_{\text{th}}^3} \right)$$

and so the Helmholtz free energy is given by

$$F = -N k_B T \ln \left(\frac{V e}{N \lambda_{\text{th}}^3} \right) \tag{5}$$

$$= N k_B T [\ln(n \lambda_{\text{th}}^3) - 1] \tag{6}$$

from which all other thermodynamic quantities of an ideal gas can be derived.

3   The Maxwell Boltzmann Distribution

The next question we want to ask is, given a gas at a certain temperature, what is the distribution of particle velocities within that gas?

First, we will ignore all rotational or vibrational energies associated with any particles (that is, we will assume a monatomic gas where the energy only arises due to translational motion of the particles, see Lecture 9). As such, the energy of a single particle can be written as

$$\epsilon = \frac{p^2}{2m}$$

The probability that a particle is in a particular state s with translational energy ϵ is then given by

$$P_s = \frac{1}{Z_1} e^{-\beta \epsilon}$$

If the gas consisits of N particles, the mean number $\bar{n}_s$ of particles which are in the translational state s is given by

$$\bar{n}_s = N P_s$$

Now, substituting for Z_1 and ϵ then gives

$$\bar{n}_s(p) = \frac{\hbar^3 N}{V} \left(\frac{2\pi}{mk_{\mathrm{B}}T} \right)^{3/2} \exp\left(\frac{-p^2}{2mk_{\mathrm{B}}T} \right)$$

We now need to figure out what the appropriate expression is for particles which have momenta between $\mathbf{p}$ and $\mathbf{p} + \mathrm{d}\mathbf{p}$. Fortunately, we can get this from the density of states equation

$$g(k)\mathrm{d}k = \frac{V k^2 \mathrm{d}k}{2\pi^2}$$

and using the relation that $p = \hbar k$. This gives

$$f(p)\mathrm{d}p = \frac{V p^2}{2\pi^2 \hbar^3} \mathrm{d}p$$

This means that the probability that a particle will possess a momentum with magnitude between $\mathbf{p}$ and $\mathbf{p} + \mathrm{d}\mathbf{p}$ is given by

$$P(p)dp = \frac{1}{N} f(p) \, dp \, \bar{n}(p)$$

Plugging in our above expressions thus gives

$$P(p)dp = \frac{4\pi p^2}{(2\pi m k_{\mathrm{B}}T)^{3/2}} \exp\left(\frac{-p^2}{2mk_{\mathrm{B}}T} \right) dp$$

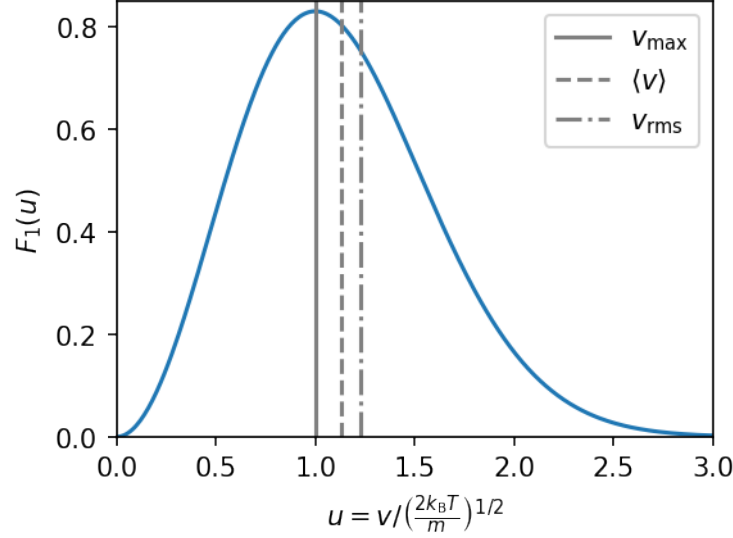The normalisation for this equation is the condition that

$$\int_0^\infty P(p)dp = 1$$

So, what does this equation tell us? If we let $p = mv$, then the expression above becomes

$$P(v)dv = 4\pi v^2 \left(\frac{m}{2\pi k_{\mathrm{B}}T} \right)^{3/2} \exp\left(\frac{-mv^2}{2k_{\mathrm{B}}T} \right) dv$$

which, if we then let $u = v/\left(\frac{2k_BT}{m}\right)^{1/2}$, becomes

$$P(u)du = \frac{4}{\sqrt{\pi}}u^2 \exp(-u^2)du = F_1(u)du$$

This equation describes a Maxwell velocity distribution, and is plotted below.

4 The Chemical Potential and Phase transitions

The next part of this course will focus on what happens if the particle number within a system is no longer kept constant, and what happens when systems of two or more phases are in equilibrium. Here, a phase is a homogenous part of a system bounded by surfaces, across which the properties of the system change discontinuously (say for example a container which has both water which is boiling at 100 degrees, above which we have water vapour also at 100 degrees). We will restrict ourselves to a sginle component (that is, we won't consider a mixture of water and acid) as this would be a complex task.

In this setup, we will be able to transfer matter between the different states. For different phases to be in equilibrium, certain conditions must hold such that no matter transfer occurs.

4.1 Equilibrium conditions

Imagine we have a one component system, and we want to determin the conditions for which 2 phases can exist in equilibrium. First, let's assume the system is totally isolated, such that

$$U_1 + U_2 = U \tag{7}$$
$$V_1 + V_2 = V \tag{8}$$
$$N_1 + N_2 = N \tag{9}$$
$$\tag{10}$$

The entropy of the system is given by

$$S(U, V, N, U_1, V_1, N_1) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2).$$

To be in equilibrium, the entropy must be maximised, giving

$$dS = dS_1 + dS_2$$

Now,

$$dS_1 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} dN_1$$

and

$$dS_2 = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} dU_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2} dN_2$$

Using

$$U_2 = U - U_1 \rightarrow dU_2 = -dU_2$$

gives

$$dS_2 = -\left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} dU_1 - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2} dV_1 - \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2} dN_1$$

which finally gives

$$dS = \left[\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}\right] dU_1 + \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2}\right] dV_1 + \left[\left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} - \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2}\right] dN_1$$

Since U_1, V_1, and N_1 are all independant, each of terms must go to 0 for equilibrium to be achieved. The first two terms equate to saying that both states must be at the same temperature and pressure (refer to the definition of entropy in Lecture 5 if this isn't clear). The last term implies that

$$\left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} = \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2}$$

is the condition for particle equilibrium. If we noiw define the chemical potential as

$$\mu_i = -T_i \left(\frac{\partial S_i}{\partial N_i}\right)_{V_i,U_i}$$

then the condition becomes

$$\mu_1 = \mu_2.$$

That is, the chemical potentials of the two phases must be the same when the phases are in equilibrium.

So what does this do to the fundamental thermodynamic relation? Consider again

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN.$$

Using our known substitutions, we get

$$dS = \frac{1}{T} dU + \frac{1}{T} P dV - \frac{1}{T} \mu dN.$$

Tidying up gives

$$dU = T dS - P dV + \mu dN.$$