9. Ideal gas and indistinguishability

Blundell and Blundell chapter 21

So far we have applied the Boltzmann theory for weakly interacting systems to solids and their magnetic and vibrational properties. We now turn to the other example of a weakly interacting system mentioned earlier- the ideal gas. In fact we have to modify the theory a little to cope with this system due to the property of indistinguishability.

9.1 Indistinguishability

Since atoms of some element or molecules of the same type all have the same chemical make-up they are truly identical.

In solids we can still tell which atom is which because they are localised at the lattice sites of the crystal structure. So we can label the atom nearest to site 1, as atom number 1 and know that basically it will always be the same atom.

However in gases, or liquids, the identity of the particles is problematic. The problem stems from quantum mechanics. In quantum mechanics to correctly describe a many particle system one has to consider a many-particle wavefunction. We will not delve into the issues here, but will just argue that we cannot treat particles individually because we cannot keep track of their identities.

> 💡 Key point 14
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> Identical non-localised particles must be treated as indistinguishable.

9.2 Semi-classical treatment

We seek to modify in a simple way the Boltzmann theory to take into account indistinguishability.

Roughly speaking, the number of microstates of a system of indistinguishable particles is less by a factor of $1/N!$ compared to the case where the particles are treated distinguishably. Thus to correct for the overcounting due to indistinguishability, we divide the partition function by $N!$:

$$Z_{\text{indist.}} = \frac{1}{N!} \sum_{i_1 = i_2 \cdots = i_N} \exp(-\beta[\epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N}]) = \frac{1}{N!}[Z(1)]^N$$

where i_n is the state of particle n.

9.3 Calculation of $Z(1)$

We now have to evaluate $Z(1)$ the single particle partition function. Here the single particle is simply a free particle in a box (container for the ideal gas) which we take to be a cube of side L.

The time independent Schrödinger's equation for the free particle ($V = 0$) reduces to the equation for standing waves:

$$\left(-\frac{\hbar^2}{2M} \nabla^2 - \epsilon \right) \psi = 0$$

Consider first the one-dimensional case which becomes:

$$\psi'' = -k^2 \psi \quad \text{where} \quad k^2 = \frac{2M\epsilon}{\hbar^2} = 0$$

We have to fit the boundary conditions that ψ vanishes at the boundaries $x = 0, L$. Thus:

$$\psi = A \sin kx \quad \text{with} \quad k = \frac{n\pi}{L} \quad \text{and} \quad n = 1, 2, 3, ...$$

The generalisation to three dimensions with the boundary conditions that ψ vanishes at $x, y, z = 0, L$ is straightforward:

$$\psi = A \sin k_x x \sin k_y y \sin k_z z \quad \text{with} \quad k_x = \frac{n_x \pi}{L}, \; k_y = \frac{n_y \pi}{L}, \; k_z = \frac{n_z \pi}{L}$$

$$\epsilon = \frac{\hbar^2}{2M}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2ML^2}(n_x^2 + n_y^2 + n_z^2)$$

The task now is to sum over all allowed values of n_x, n_y, n_z:

$$Z(1) = \sum_{n_x, n_y, n_z} \exp(-\beta \epsilon(n_x, n_y, n_z)) = \exp(-\beta \epsilon(1, 1, 1)) + \exp(-\beta \epsilon(2, 1, 1)) + ...$$

In principle this looks quite difficult but the way to simplify matters is to convert the sum into an integral.

Referring to Figure 2 we see that n-space contains points, which represent the allowed quantum states of the particle, distributed with unit density. Since the energy depends only on the magnitude n of the position vector of a point in n-space:
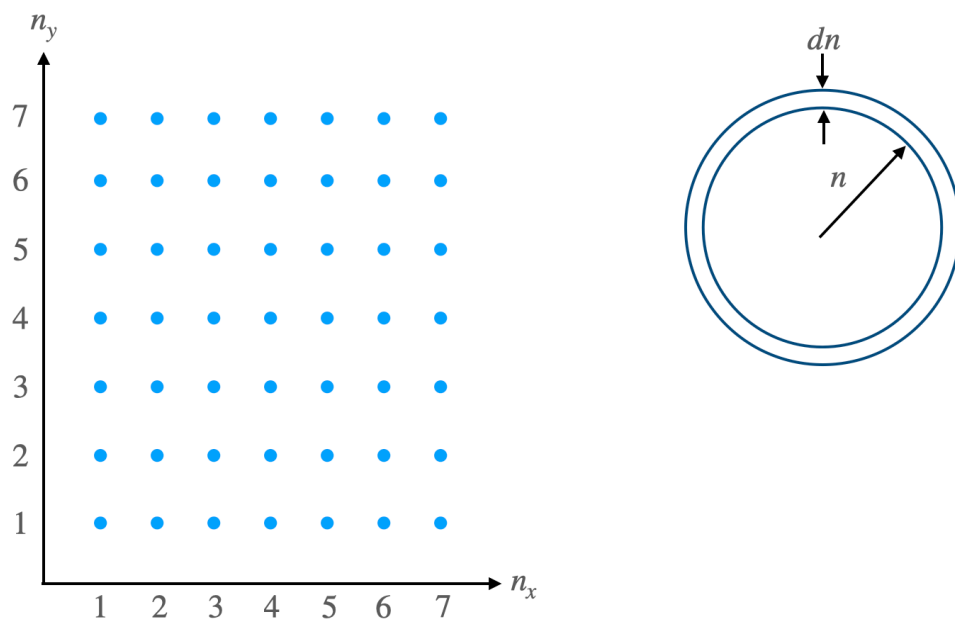
Figure 1: A 2-d representation of 'n-space'. The density of points is one. An integration shell of radius n and thickness dn is indicated.

$$n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$$

we convert to an integral with respect to n. We think of adding up shells of constant n whose volume are $\frac{1}{8}4\pi n^2 dn$ and which, since the density of points is one, contain on average $\frac{1}{8}4\pi n^2 dn$ points. The volume is of a spherical shell of radius n and thickness dn; the division by 8 is because we are restricted to the octant where all components of n are positive.

$$\sum_{n_x,n_y,n_z} [\cdots] \to \frac{1}{8} \int [\cdots] 4\pi n^2 dn$$

In particular:

$$Z(1) \to \frac{\pi}{2} \int_0^\infty \exp\left(-\beta\frac{\hbar^2\pi^2 n^2}{2ML^2}\right) n^2 dn$$

This is of course an approximation. It is a good approximation when:

$$\frac{\hbar^2\pi^2}{2ML^2} \ll kT$$