9. Ideal gas and indistinguishability

Indistinguishability

- Let us review the arguments of key point 13 for weakly interacting particles.

- Identification of a microstate as a specification of the state of each and every particle, $i_1 \ldots i_N$ of particles $1 \ldots N$.

- Reorganisation of the partition function as

$$Z = \sum_r e^{-\beta E_r} = \left[\sum_{i_1} e^{-\beta \epsilon_{i_1}} \right] \cdots \left[\sum_{i_N} e^{-\beta \epsilon_{i_N}} \right]$$

- We must now recognise that these steps presuppose that the constituent particles are at least, in principle, **distinguishable** from one another, so that each may be thought of as carrying a personal identifying label.

Indistinguishability

- Specifically:

- The interpretation of 'microstate' presupposes that we can (in principle) point to each particle in turn and identify its state ('particle 33 is in state $i_{33} = 4$').

- The reformulated Z counts the contributions of many microstates which are in fact identical unless the particles are in some sense distinguishable. Thus for example a microstate with $i_1 = 1$ and $i_2 = 2$ is 'different' from a microstate with $i_1 = 2$ and $i_2 = 1$ only if we can distinguish between 'particle 1' and 'particle 2'.

Indistinguishability

- In the context of models of solids or crystalline magnets, there is nothing for us to worry about: the atoms in a solid are **localised** (nailed down!) in space; their 'addresses' in space provide, in principle, the ingredients of a labelling scheme.

- In the case of a gas, **within a classical world view**, there is also no problem. We may envisage 'christening' the atoms at some point and, with the aid of an army of willing assistants, keeping track of their identities.

- But quantum physics tells us that particles should not be thought of as having 'trajectories'; they are at best characterised by wave functions whose overlap makes it impossible to 'keep track of' which particle is which.

- We reach a profound conclusion:

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

Accounting for indistinguishability

- We seek to modify in a simple way the Boltzmann theory to take into account indistinguishability that arises from non-localisation.

- Roughly speaking (see Blundell-Blundell for full argument), the number of microstates of a system of non-localised 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.

- This simple correction for non-localisation is only valid at low densities

Calculation of $Z(1)$

- The single particle partition function $Z(1)$ for a free particle in a cubic box of side L.

- Schrödinger's equation for a free particle: $\left(-\dfrac{\hbar^2}{2M}\nabla^2 - \epsilon \right)\psi = 0$

- In $1d$: $\psi'' = -k^2\psi$ where $k^2 = \dfrac{2M\epsilon}{\hbar^2}$

  $\psi = A\sin kx$ with $k = \dfrac{n\pi}{L}$ and $n = 1,2,3,\ldots$

  Standing wave solutions.
  ψ vanishes at $x = 0, L$

- In $3d$: $\psi = A\sin k_x x \sin k_y y \sin k_z z$ with $k_x = \dfrac{n_x\pi}{L}, k_y = \dfrac{n_y\pi}{L}, k_z = \dfrac{n_z\pi}{L}$

  $\epsilon = \dfrac{\hbar^2}{2M}(k_x^2 + k_y^2 + k_z^2) = \dfrac{\hbar^2\pi^2}{2ML^2}(n_x^2 + n_y^2 + n_z^2)$
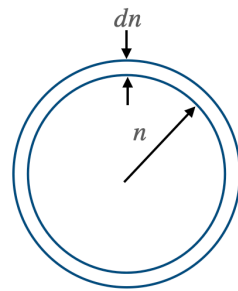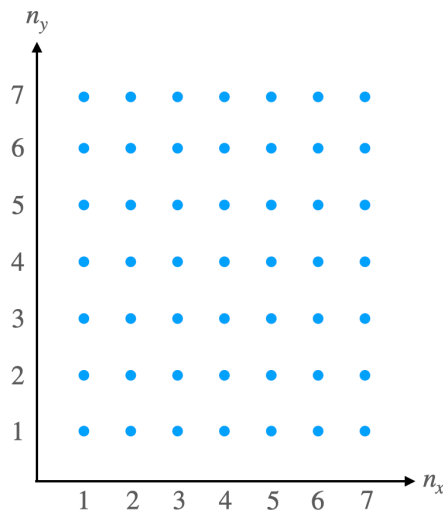
(See Chapter 11 of quantum mechanics notes)

Calculation of $Z(1)$

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

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

- Approach: convert the sum into an integral in n-space.

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

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

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

- This is of course an approximation. It is a good approximation when $\dfrac{\hbar^2 \pi^2}{2ML^2} \ll kT$