



9. Ideal gas and indistinguishability

Indistinguishability



- Let us review the arguments of key point 13.
- Identification of a microstate as a specification of the state of each and every particle, $i_1 \dots i_N$ of particles $1 \dots N$.
- Reorganisation of the partition function as

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

- 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



- 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 $N!$

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

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

- In 1d: $\psi'' = -k^2 \psi$ where $k^2 = \frac{2M\epsilon}{\hbar^2} = 0$

$$\psi = A \sin kx \quad \text{with} \quad k = \frac{n\pi}{L} \quad \text{and} \quad n = 1, 2, 3, \dots \quad \bullet \psi \text{ vanishes at } x = 0, L$$

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

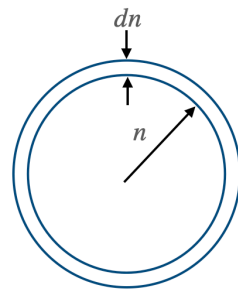
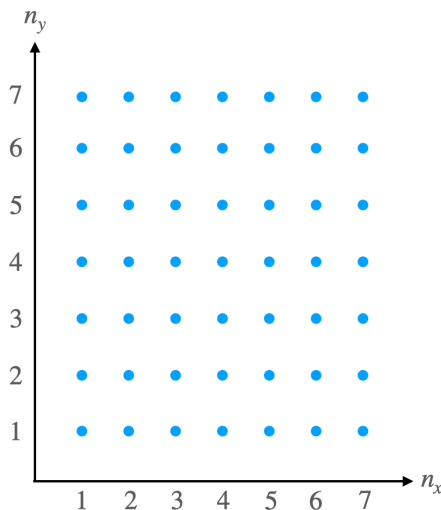
$$\epsilon = \frac{\hbar^2}{2M} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2)$$



Calculation of $Z(1)$

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

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



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

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

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

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

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