



10. Ideal gas in the low density limit



Calculation of $Z(1)$

- We now do the required integral for $Z(1)$

$$Z(1) = \pi \int_0^{\infty} \exp(-an^2) n^2 dn \quad \text{where} \quad a = \frac{\hbar^2 \pi^2}{2kTML^2}$$

Use the standard result $\int_{-\infty}^{\infty} \exp(-an^2) dn = \left(\frac{\pi}{a}\right)^{1/2}$

to find $Z(1) = -\frac{1}{2} \frac{d}{da} \left(\int_{-\infty}^{\infty} \exp(-an^2) dn \right) = -\frac{1}{2} \frac{d}{da} \left(\frac{\pi}{a} \right)^{1/2} = \frac{\sqrt{\pi}}{4a^{3/2}}$

want limit 0 to ∞

- Substitute for $a \Rightarrow Z(1) = \frac{\pi^{3/2}}{8} \left(\frac{2ML^2}{\beta \hbar^2 \pi^2} \right)^{3/2}$
 $= V \left(\frac{2\pi M k T}{h^2} \right)^{3/2}$

Density of states



- Return to our approximation of a 3d sum of some function of n by an integral over n space.

$$\sum_{n_x, n_y, n_z} A(n) \rightarrow \frac{1}{8} \int_0^\infty A(n) 4\pi n^2 dn$$

- Now change variables $n \rightarrow k$: $n = \frac{L}{\pi}k \quad dn = \frac{dn}{dk}dk = \frac{L}{\pi}dk$

to find

$$\begin{aligned} \sum_{n_x, n_y, n_z} A(n) &\rightarrow \frac{1}{8} \int A(k) \frac{4\pi L^2 k^2}{\pi^2} \frac{L}{\pi} dk \\ &= \int A(k) \Gamma(k) dk \end{aligned} \quad \text{where} \quad \Gamma(k) dk = \frac{k^2}{2\pi^2} V dk$$

- $\Gamma(k)$ is known as the **density of states** (here, in k space).



Density of states

- Similarly, we can change variables to energy ϵ :

$$\epsilon = \frac{\hbar^2 k^2}{2M},$$

$$\Rightarrow k = \left(\frac{2M\epsilon}{\hbar^2} \right)^{1/2}$$

$$\Rightarrow dk = \frac{dk}{d\epsilon} d\epsilon = \frac{1}{2} \left(\frac{2M}{\hbar^2} \right)^{1/2} \epsilon^{-1/2} d\epsilon$$

- To obtain the density of states in energy space, $g(\epsilon)$, equate: $g(\epsilon)d\epsilon = \Gamma(k)dk$

$$\begin{aligned} g(\epsilon)d\epsilon &= \frac{k^2}{2\pi^2} V dk \\ &= \left(\frac{2M}{\hbar^2} \right)^{3/2} \frac{V}{4\pi^2} \epsilon^{1/2} d\epsilon \end{aligned}$$

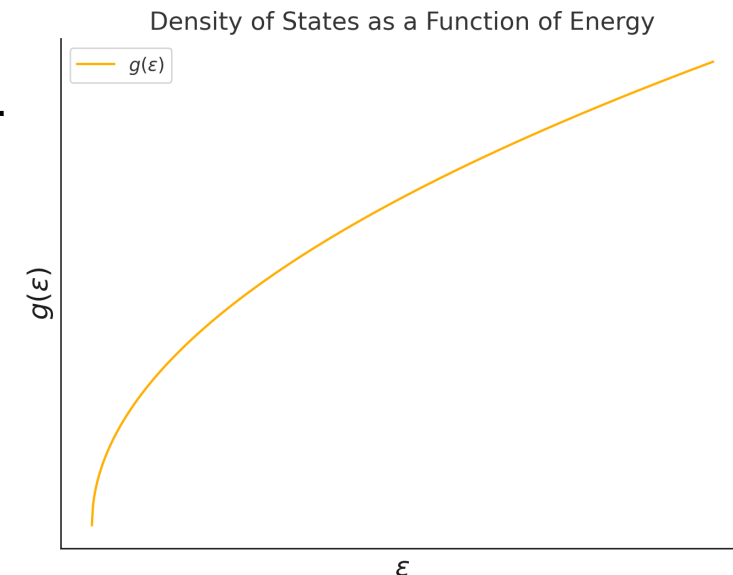
Density of states



- The meaning of the density of states $g(\epsilon)$ is that $g(\epsilon)d\epsilon$ is the number of states with energy between ϵ and $\epsilon + d\epsilon$
- In terms of the density of states we can rewrite the partition function

$$Z(1) = \int_0^{\infty} g(\epsilon) \exp(-\beta\epsilon) d\epsilon$$

- Essentially we are grouping all states of a given energy into a weight $g(\epsilon)$ for that energy so that we can sum over energies rather than states.
- Notice that the density of states increases with energy, meaning that at higher energies, more states are available to the particle.



Thermodynamic variables



- For indistinguishable particles at low density:

$$Z = \frac{Z(1)^N}{N!} = \frac{V^N}{N!} \left(\frac{2\pi M k T}{h^2} \right)^{3N/2}$$

$$F = -kT \ln Z = NkT \left[\ln \left(\frac{N}{V} \right) - 1 - \frac{3}{2} \ln \left(\frac{2\pi M k T}{h^2} \right) \right]$$

$$\bar{E} = kT^2 \frac{\partial \ln Z}{\partial T} = \frac{3}{2} NkT$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{NkT}{V} \quad (\text{ideal gas equation of state})$$

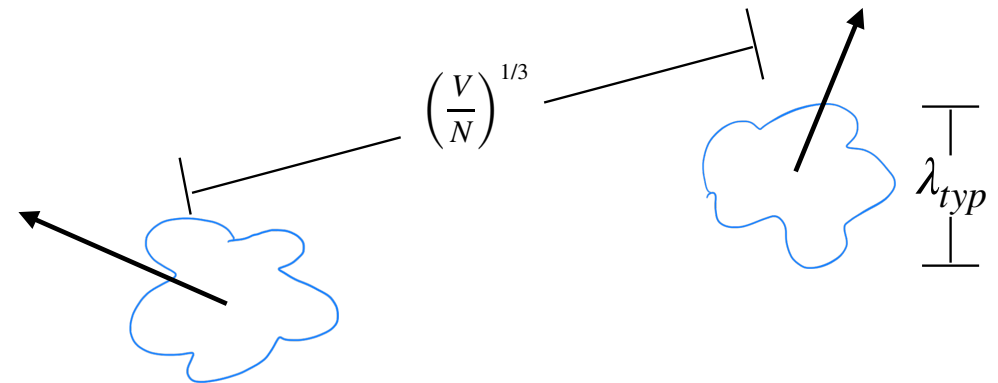
$$C_V = \frac{3}{2} Nk \quad (\text{Accords with equipartition theorem})$$

Validity of semi-classical approximation



- The approximation that allows us to write $Z(N) = \frac{Z(1)^N}{N!}$ for non-localised weakly interacting particles is that the particle density is low. Then we can treat the correction for indistinguishability classically (the $N!$ correction)
- At high density particle wave functions overlap and quantum indistinguishability must be taken into account.
- For an ideal gas, we require $n\lambda_{typ} \ll 1$
- Using $\lambda_{typ} = \frac{h}{\sqrt{3MkT}}$, this condition becomes:

$$n \left(\frac{h}{\sqrt{3MkT}} \right)^3 \ll 1 \quad \Rightarrow \quad n \left(\frac{h^2}{2\pi MkT} \right)^{3/2} \ll 1$$



(after Baierlein)