10. Ideal gas in the low density limit

Calculation of $Z(1)$

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

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

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

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

want limit 0 to ∞

- Substitute for $a \Rightarrow$

$$Z(1) = \frac{\pi^{3/2}}{8}\left(\frac{2ML^2}{\beta\hbar^2\pi^2}\right)^{3/2}$$

$$= V\left(\frac{2\pi MkT}{h^2}\right)^{3/2} \quad \text{where } V = L^3$$

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 $n \rightarrow k$: $\quad n = \frac{L}{\pi}k \quad dn = \frac{dn}{dk}dk = \frac{L}{\pi}dk$

to find

$$\sum_{n_x,n_y,n_z} A(n) \rightarrow \frac{1}{8}\int A(k)\frac{4\pi L^2 k^2}{\pi^2}\frac{L}{\pi}dk$$

$$= \int A(k)\Gamma(k)dk$$

where $\Gamma(k)dk = \frac{k^2}{2\pi^2}Vdk$

- $\Gamma(k)$ is known as the **density of states** (here, in k space - experimentally relevant).
- Counts number of wavevector states between k and $k + dk$ (not to be confused with Boltzmann's constant). See Atoms and Matter course for more use of k-space.

Density of states

- Similarly, we can change variables to energy ϵ:

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

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

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

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

$$g(\epsilon)d\epsilon = \frac{k^2}{2\pi^2}Vdk$$

$$= \left(\frac{2M}{\hbar^2}\right)^{3/2} \frac{V}{4\pi^2}\epsilon^{1/2}d\epsilon$$

Number of energy states between ϵ and $\epsilon + d\epsilon$ = number of wave vector states between k and $k + dk$

Density of states

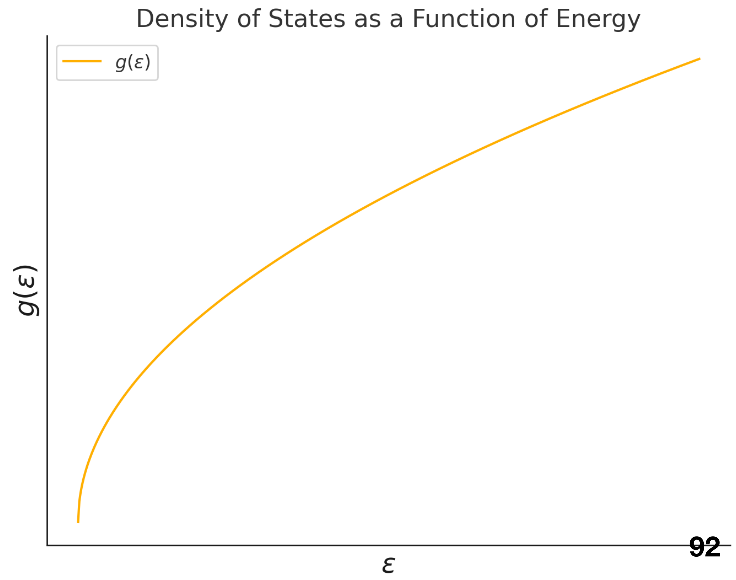
- The meaning of the density of states $g(\epsilon)$ is that $g(\epsilon)d\epsilon$ is the number of states with energy between ϵ and $\epsilon + d\epsilon$

- 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 ideal gas particles at low density:

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

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

$$\overline{E} = kT^2\frac{\partial \ln Z}{\partial T} = \frac{3}{2}NkT$$ (Accords with equipartition theorem)

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

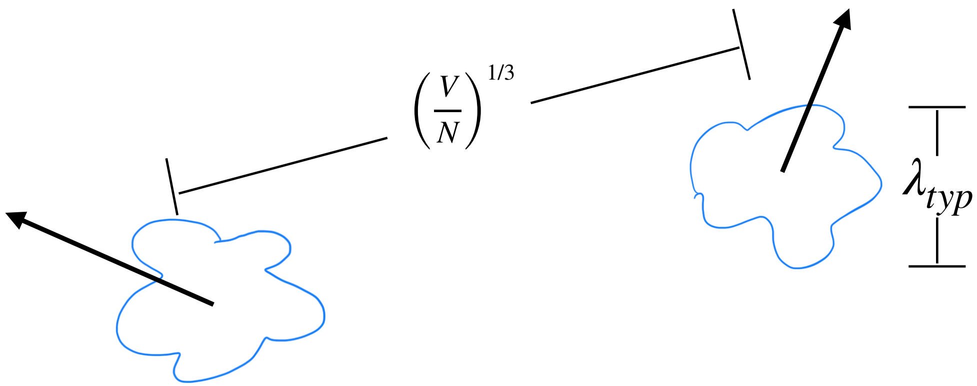
$$C_V = \frac{3}{2}Nk$$ (Accords with equipartition theorem)

- Exercise: Confirm these results using expression for Z and Stirling's approximation

Validity of semi-classical approximation

- The approximation that allows us to write $Z(N) = \dfrac{Z(1)^N}{N!}$ 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 number density $\rho = N/V$, particle wave functions overlap and further aspects of quantum indistinguishability must be taken into account.
- Approximations is valid when typical particles separation $d_{typ} \gg \lambda_{typ}$ the typical thermal de Broglie wavelength
- For an ideal gas, we require $\rho \lambda_{typ} \ll 1$
- Using $\lambda_{typ} = \dfrac{h}{\sqrt{3MkT}}$, this condition becomes:

$$\rho \left(\frac{h}{\sqrt{3MkT}} \right)^3 \ll 1$$



(after Baierlein)