Ideal Monoatomic Gas

Here, ideal implies that the gas is dilute enough to neglect the intermolecular interactions. The results derived here will be applicable to monoatomic real gases at pressure below 1 atmosphere and temperature greater than room temperature.

A monoatomic gas has translational, electronic and nuclear degrees of freedom. The translational motion can be treated independently from the electronic and nuclear motion. Thus,

$$q = q_{trans}\, q_{elec}\, q_{nucl}$$

Aim: To derive the translational partition function.

Energy of a particle in a box (3-D).

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

where $n_x, n_y, n_z \rightarrow$ principal quantum no. along x, y, z axis respectively

$m \rightarrow$ mass of the particle

$h \rightarrow$ Planck's constant

$L \rightarrow$ Dimension of the box

$$q_{trans} = \sum_i e^{-\beta E_{trans}}$$

Substituting the value of energy,

$$q_{trans} = \sum_{n_x, n_y, n_z = 1}^{\infty} e^{-\beta E_{n_x n_y n_z}}$$

$$= \sum_{n_x=1}^{\infty} e^{-\frac{\beta h^2 n_x^2}{8mL^2}} \sum_{n_y=1}^{\infty} e^{-\frac{\beta h^2 n_y^2}{8mL^2}} \sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2 n_z^2}{8mL^2}}$$

$$= \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8mL^2}} \right)^3$$

The above summation cannot be evaluated in closed form as it cannot be expressed in terms of any simple analytic function. Although the successive terms of the summation differ so little from each other that they vary essentially continuously and thus it is possible to replace the summation by integration for all practical purposes. This is also to say that translational energy levels are very closed spaced.

$$q_{trans} = \int_0^{\infty} dn_x \, e^{-\frac{\beta h^2}{8mL^2} n_x^2} \int_0^{\infty} dn_y \, e^{-\frac{\beta h^2}{8mL^2} n_y^2} \int_0^{\infty} dn_z \, e^{-\frac{\beta h^2}{8mL^2} n_z^2}$$

Using the standard integral

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\therefore q_{trans} = \frac{1}{2} \sqrt{\frac{8mL^2\pi}{\beta h^2}} \times \frac{1}{2} \sqrt{\frac{8mL^2\pi}{\beta h^2}} \times \frac{1}{2} \sqrt{\frac{8mL^2\pi}{\beta h^2}}$$

$$= \frac{1}{8} \left(\frac{8mL^2\pi}{\beta h^2} \right)^{3/2} = 2\sqrt{2} \left(\frac{8mL^2\pi}{\beta h^2} \right)^{3/2}$$

$$= \left(\frac{2\pi mkT}{h^2} \right)^{3/2} L^3 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Where V is the volume of the box; L^3.

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$$q_{trans} = \frac{V}{\Lambda^3}$$

where $\Lambda = \left(\frac{h^2}{2\pi mKT}\right)^{1/2}$

Λ is known as the thermal De Broglie Wavelength.

Λ has the units of length i.e. dimension of [L].
The quantity Λ can be given the following interpretation.
Firstly calculate the average translational energy of the gas.

Average Energy, $\langle E \rangle$

$$\langle E \rangle = NKT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

$$q_{trans} = \left(\frac{2\pi mKT}{h^2}\right)^{3/2} V$$

$$\ln q_{trans} = \frac{3}{2} \ln\left(\frac{2\pi mKT}{h^2}\right) + \ln V$$

$$\frac{d \ln q_{trans}}{dT} = \frac{3}{2} \frac{h^2}{2\pi mKT} \times \frac{2\pi mK}{h^2} = \frac{3}{2T}$$

$$\therefore \langle E \rangle = NKT^2 \left(\frac{3}{2T}\right) = \frac{3}{2} NKT$$

$\langle E \rangle = \frac{3}{2} RT$ (where $NK = R$) $\rightarrow$ Average translational energy

$\langle E \rangle = \frac{3}{2} KT$ when $N = 1$.

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$\langle E \rangle = \frac{3}{2} KT$ (when Principle of equipartition of energy is applied).

$$\frac{\langle p^2 \rangle}{2m} = \frac{3}{2} KT$$

$$\Rightarrow \quad p \propto \sqrt{(mKT)}$$

$$\Rightarrow \quad \Lambda = \left(\frac{h^2}{2\pi m KT}\right)^{1/2} \propto \frac{h}{p}$$

$$\Lambda \propto \frac{h}{p} \Rightarrow \Lambda \propto \underset{\text{De Broglie wavelength}}{\lambda}$$

Thus $\Lambda \Rightarrow$ Thermal De-Broglie wavelength

$\Rightarrow (\Lambda^3/V) \lll 1$ i.e. Thermal De-Broglie Wavelength must be small compared to the dimensions of the container.