

18.1: Translational Partition Functions of Monatomic Gases

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L . The particle inside the box has translational energy levels given by:

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

where n_x , n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \quad (18.1.1)$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \quad (18.1.2)$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 18.1.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \quad (18.1.3)$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \quad (18.1.4)$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 18.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}}$$

We then use the following solved Gaussian integral:

$$\int_0^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2 kT}$$

we get:

$$q_x = \frac{1}{2} \sqrt{\frac{\pi}{a}} = \frac{1}{2} \sqrt{\frac{\pi 8m kT}{h^2}} L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi m kT}}$$

Multiplying the expressions for q_x , q_y and q_z (Equation 18.1.1) and using V as the volume of the box L^3 , we arrive at:

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi mkT}}{h} \right)^3 V = \frac{V}{\Lambda^3} \quad (18.1.5)$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2} nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

✓ Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} \text{ kg}$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27} \text{ kg}) \times 1.3807 \times 10^{-23} \text{ J/K} \times 300 \text{ K} \\ &= 1.0969 \times 10^{-44} \text{ J kg} \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34} \text{ J s}}{\sqrt{1.0969 \times 10^{-44} \text{ J kg}}} = 6.326 \times 10^{-12} \text{ m} \end{aligned}$$

The via Equation 18.1.5

$$q_{\text{trans}} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} \text{ m}^3}{(6.326 \times 10^{-12} \text{ m})^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

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