

# Translational Partition Functions of Monatomic Gases

Let consider the translational partition function of a monatomic gas. Consider a molecule confined to a cubic box. A molecule inside a cubic box of length  $L$  has the translational energy levels given by

$$E_{tr} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2} \quad (18.1.1)$$

where  $n_x$ ,  $n_y$  and  $n_z$  are the [quantum numbers in the three directions](#). The translational partition function is given by

$$q_{tr} = \sum_i e^{-\epsilon_i/k_B T} \quad (18.1.2)$$

which is the product of translational partition functions in the three dimensions.

$$q_{tr} = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/k_B T} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/k_B T} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/k_B T} \quad (18.1.3)$$

$$q_{tr} = q_x q_y q_z \quad (18.1.4)$$

Since the levels are very closely spaced, we can replace each sum in Equation 18.1.3 with an integral, for example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/k_B T} \approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/k_B T} \quad (18.1.5)$$

and after substituting the energy for the relevant dimension

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2} \quad (18.1.6)$$

we can extend the lower limit of integration in the approximation of Equation 18.1.5

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 k_B T}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 k_B T}} \quad (18.1.7)$$

we then use the following solved Gaussian integral

$$\int_0^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}} \quad (18.1.8)$$

with the following substitution

$$a = \frac{h^2}{8mL^2k_B T} \quad (18.1.9)$$

we get,

$$q_x = \frac{1}{2} \sqrt{\frac{\pi}{a}} = \frac{1}{2} \sqrt{\frac{\pi 8m k_B T}{h^2}} L \quad (18.1.10)$$

or more commonly presented as

$$q_x = \frac{L}{\Lambda} \quad (18.1.11)$$

where  $\Lambda$  is the [de Broglie thermal wavelength](#) and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8m k_b T}} \quad (18.1.12)$$

Multiplying the expressions for  $q_x$ ,  $q_y$  and  $q_z$  (Equation 18.1.4) and using  $V$  as the volume of the box  $L^3$ , we arrive at

$$q_{tr} = \left( \frac{\sqrt{2\pi 8m k_b T}}{h} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad (18.1.13)$$

This is usually a very large number ( $10^{20}$ ) for volumes of  $1 \text{ cm}^3$  for a typical small molecular masses. This means that such a large number of translational states are accessible 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 should read as

$$U = \frac{3}{2} nRT \quad (18.1.14)$$

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.

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

**Solution**

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

$$2\pi mkBT = 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27} \text{ kg}) \times 1.3807 \times 10^{-23} \text{ J/K} \times 300 \text{ K} \quad (18.1.15)$$

$$= 1.0969 \times 10^{-44} \text{ J kg} \quad (18.1.16)$$

$$\Lambda = \frac{h}{\sqrt{2\pi mkBT}} \quad (18.1.17)$$

$$= \frac{6.6262 \times 10^{-34} \text{ J s}}{\sqrt{1.0969 \times 10^{-44} \text{ J kg}}} = 6.326 \times 10^{-12} \text{ m} \quad (18.1.18)$$

$$q_{tr} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} \text{ m}^3}{(6.326 \times 10^{-12} \text{ m})^3} = 3.95 \times 10^{30} \quad (18.1.19)$$

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