24.3: Occupancy Probabilities for Translational Energy Levels

The particle in a box is a quantum mechanical model for the motion of a point mass in one dimension. In Section 18.3, we find that the energy levels are

$$\epsilon_n = \frac{n^2 h^2}{8m\ell^2}$$

so that the partition function for a particle in a one-dimensional box is

$$z = \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 h^2}{8mkT\ell^2}\right)$$

When the mass approximates that of a molecule, the length of the box is macroscopic, and the temperature is not extremely low, there are a very large number of energy levels for which $\epsilon_n < kt >$. When this is the case, we find in Section 22-4 that this sum can be approximated by an integral to obtain an expression for z in closed form:

$$z \approx \int_0^{\infty} \exp\left(\frac{-n^2 h^2}{8mkT\ell^2}\right)\, dn = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} \ell$$

A particle in a three-dimensional rectangular box is a quantum mechanical model for an ideal gas molecule. The molecule moves in three dimensions, but the component of its motion parallel to any one coordinate axis is independent of its motion parallel to the others. This being the case, the kinetic energy of a particle in a three-dimensional box can be modeled as the sum of the energies for motion along each of the three independent coordinate axes that describe the translational motion of the particle. Taking the coordinate axes parallel to the faces of the box and labeling the lengths of the sides ℓ_x, ℓ_y, and ℓ_z, the energy of the particle in the three-dimensional box becomes

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z$$

and the three-dimensional partition function becomes

$$\begin{aligned} z_t &= \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[\left(\frac{-h^2}{8mkT}\right)\left(\frac{n_x^2}{\ell_x^2}+\frac{n_y^2}{\ell_y^2}+\frac{n_z^2}{\ell_z^2}\right)\right] \\ &= \sum_{n_x=1}^{\infty} \exp\left(\frac{-n_x^2 h^2}{8mkT\ell_x^2}\right) \sum_{n_y=1}^{\infty} \exp\left(\frac{-n_y^2 h^2}{8mkT\ell_y^2}\right) \sum_{n_z=1}^{\infty} \exp\left(\frac{-n_z^2 h^2}{8mkT\ell_z^2}\right) \end{aligned}$$

or, recognizing this as the product of three one-dimensional partition functions,

$$z_t = z_x z_y z_z.$$

Approximating each molecular partition function as integrals gives

$$z_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \ell_x \ell_y \ell_z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

where the volume of the container is $V = \ell_x \ell_y \ell_z$.

Let us estimate a lower limit for the molecular partition function for the translational motion of a typical gas at ambient temperature. The partition function increases with volume, V, so we want to select a volume that is near the smallest volume a gas can have. We can estimate this as the volume of the corresponding liquid at the same temperature. Let us calculate the molecular translational partition function for a gas whose molar mass is 0.040 kg in a volume of 0.020 L at 300 K. We find $z_t = 5 \times 10^{27}$.

Given z_t, we can estimate the probability that any one of the energy levels available to this molecule is occupied. For any energy level, the upper limit to the term $\exp(-\epsilon_i/kT)$ is one. If the quantum numbers n_x, n_y, and n_z are different from one another, the corresponding molecular energy is non-degenerate. To a good approximation, we have $g_i = 1$. We find

$$\frac{N_i}{N} = \frac{g_i \exp(-\epsilon_i/kT)}{z_t} < \frac{1}{z_t} = 2 \times 10^{-28}$$

We calculate $N_i \approx 1 \times 10^{-4}$. When a mole of this gas occupies $0.020\,\mathrm{L}$, the system density approximates that of a liquid. Therefore, even in circumstances selected to minimize the number of energy levels, there is less than one gas molecule per ten thousand energy levels.

For translational energy levels of gas molecules, it is an excellent approximation to say that each molecule occupies a different translational energy level. This is a welcome result, because it assures us that the translational partition function for a system containing a gas of N indistinguishable non-interacting molecules is just

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

So that Z_t is the translational partition function for a system of N ideal gas molecules.

We derive Z_t from the assumption that every equilibrium population number, $N_i^\bullet$, for the molecular energy levels satisfies $N_i^\bullet \leq 1$. We use Z_t and the ensemble-treatment results that we develop in Chapter 23 to find thermodynamic functions for the N-molecule ideal-gas system. The ensemble development assumes that the number of systems, $\hat{N}_i^\bullet$, in the ensemble that have energy E_i is very large. Since the ensemble is a creature of our imaginations, we can imagine that $\hat{N}$ is as big as it needs to be in order that $\hat{N}_i^\bullet$ be big enough. The population sets $N_i^\bullet$ and $\hat{N}_i^\bullet$ are independent; they characterize different distributions. The fact that $N_i^\bullet \leq 1$ is irrelevant when we apply Lagrange's method to find the distribution function for $\hat{N}_i^\bullet$, the partition function Z_t, and the thermodynamic functions for the system. Consequently, the ensemble treatment enables us to find the partition function for an ideal gas, Z_{IG}, by arguments that avoid the questions that arise when we apply Lagrange's method to the distribution of molecular translational energies.