

4.4: Partition Functions and Average Energies at High Temperatures

It is enlightening to find the integral approximations to the partition functions and average energies for our simple quantum-mechanical models of translational, rotational, and vibrational motions. In doing so, however, it is important to remember that the use of integrals to approximate Boltzmann-equation sums assumes that there are a large number of energy levels, ϵ_i , for which $\epsilon_i \ll kT$. If we select a high enough temperature, the energy levels for any motion will always satisfy this condition. The energy levels for translational motion satisfy this condition even at sub-ambient temperatures. This is the reason that Maxwell's derivation of the probability density function for translational motion is successful.

Rotational motion is an intermediate case. At sub-ambient temperatures, the classical-mechanical derivation can be inadequate; at ordinary temperatures, it is a good approximation. This can be seen by comparing the classical-theory prediction to experimental values for diatomic molecules. For diatomic molecules, the classical model predicts a constant-volume heat capacity of $5k/2$ from 3 degrees of translational and 2 degrees of rotational freedom. Since this does not include the contributions from vibrational motions, constant-volume heat capacities for diatomic molecules must be greater than $5k/2$ if both the translational and rotational contributions are accounted for by the classical model. For diatomic molecules at 298 K, the experimental values are indeed somewhat larger than $5k/2$. (Hydrogen is an exception; its value is $2.47k$.)

Vibrational energies are usually so big that only a minor fraction of the molecules can be in higher vibrational levels at reasonable temperatures. If we try to increase the temperature enough to make the high-temperature approximation describe vibrational motions, most molecules decompose. Likewise, electronic partition functions must be evaluated from the defining equation.

The high-temperature limiting average energies can also be calculated from the Boltzmann equation and the appropriate quantum-mechanical energies. Recall that we find the following quantum-mechanical energies for simple models of translational, rotational, and vibrational motions:

Translation

$$\epsilon_{\text{trans}}^{(n)} = \frac{n^2 h^2}{8m\ell^2}$$

($n = 1, 2, 3, \dots$ Derived for a particle in a box)

Rotation

$$\epsilon_{\text{rot}}^{(m)} = \frac{m^2 h^2}{8\pi^2 I}$$

($m = 1, 2, 3, \dots$ Derived for rotation about one axis—each energy level is doubly degenerate)

Vibration

$$\epsilon_{\text{vibration}}^{(n)} = h\nu \left(n + \frac{1}{2} \right)$$

($n = 0, 1, 2, 3, \dots$ Derived for simple harmonic motion in one dimension)

When we assume that the temperature is so high that many ϵ_i are small compared to kT , we find the following high-temperature limiting partition functions for these motions:

$$\begin{aligned} z_{\text{translation}} &= \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 h^2}{8m\ell^2 kT}\right) \approx \int_0^{\infty} \exp\left(\frac{-n^2 h^2}{8m\ell^2 kT}\right) dn = \left(\frac{2\pi mkT\ell^2}{h^2}\right)^{1/2} \\ z_{\text{rotation}} &= \sum_{m=1}^{\infty} 2 \exp\left(\frac{-m^2 h^2}{8\pi^2 I kT}\right) \approx 2 \int_0^{\infty} \exp\left(\frac{-m^2 h^2}{8\pi^2 I kT}\right) dm = \left(\frac{8\pi^3 I kT}{h^2}\right)^{1/2} \\ z_{\text{vibration}} &= \sum_{n=0}^{\infty} \exp\left(\frac{-h\nu}{kT} \left(n + \frac{1}{2}\right)\right) \approx \int_0^{\infty} \exp\left(\frac{-h\nu}{kT} \left(n + \frac{1}{2}\right)\right) dn = \frac{kT}{h\nu} \exp\left(\frac{-h\nu}{2kT}\right) \end{aligned}$$

We can then calculate the average energy for each mode as

$$\langle \epsilon \rangle = z^{-1} \int_0^{\infty} \epsilon_n \exp\left(\frac{-\epsilon_n}{kT}\right) dn$$

and find

$$\begin{aligned} \langle \epsilon_{\text{translation}} \rangle &= z_{\text{translation}}^{-1} \int_0^{\infty} \left(\frac{n^2 h^2}{8m\ell^2} \right) \exp\left(\frac{-n^2 h^2}{8m\ell^2 kT}\right) dn \\ &= \frac{kT}{2} \\ \langle \epsilon_{\text{rotation}} \rangle &= z_{\text{rotation}}^{-1} \int_0^{\infty} 2 \left(\frac{m^2 h^2}{8\pi^2 I} \right) \exp\left(\frac{-m^2 h^2}{8\pi^2 I kT}\right) dm \\ &= \frac{kT}{2} \\ \langle \epsilon_{\text{vibration}} \rangle &= z_{\text{vibration}}^{-1} \times \int_0^{\infty} h\nu \left(n + \frac{1}{2} \right) \exp\left(\frac{-h\nu}{kT} \left(n + \frac{1}{2} \right)\right) dn \\ &= kT + \frac{h\nu}{2} \\ &\approx kT \end{aligned}$$

where the last approximation assumes that $h\nu/2 \ll kT$. In the limit as $T \rightarrow 0$, the average energy of the vibrational mode becomes just $h\nu/2$. This is just the energy of the lowest vibrational state, implying that all of the molecules are in the lowest vibrational energy level at absolute zero.

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