Chem 457: Lecture 16

The Maxwell-Boltzmann Distribution

Reading Assignment: McQuarrie and Simon 27-3,

Derivation of the Maxwell-Boltzmann Distribution

Previously, we were able to state from the equipartition theorem that the average translational energy of a monatomic gas was 3/2kT. This gives us an idea what the total energy is, but it does not tell us how this energy is distributed. Do all gas molecules have the same translational energy and thus travel at the same speed? What is the distribution of speeds for a gas? This distribution is given by the Maxwell-Boltzmann distribution.

To derive this distribution, we begin by asking, “What is the fraction of molecules with translational energy $\varepsilon$?” Using our knowledge of statistical mechanics, we write:

$$f(\varepsilon) =$$

and the energy is given by the 3-dimensional particle in a box model:

$$\varepsilon = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

We define

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

(the square of $n$ is taken to eliminate directionality), then

$$\varepsilon_i = \frac{n^2 \hbar^2}{8mL^2}$$

where we have let the lengths of each side of the box be equal.
As we previously saw, the energy spacing between translational energy states is very small such that we can describe the states as forming a continuum in energy space (indexed by n). In determining the distribution of energies, we can think of this density of translational states as a sphere in space. The volume of the sphere determined over a given interval of n is the density of translational states. The figure below depicts the sphere octet of interest (why only and octet?):

\[
\zeta = \frac{4\pi}{8} \int_0^n n^2 \, dn
\]

such that:

\[
d\zeta = \frac{\pi}{2} n^2 \, dn
\]

We now need an expression for n. We can get this by equating the kinetic energy to the translational energy derived above:

\[
\varepsilon = \frac{n^2 h^2}{8mL^2} = \frac{n^2 h^2}{8mV^{2/3}} = \frac{1}{2} mu^2
\]
\[ dn = \frac{2mV^{1/3}}{h} du \]

We can then use these expressions for \( n \) and \( dn \) with the differential expression for our sphere as follows:

\[ d\zeta = \frac{\pi}{2} n^2 \, dn = \]

We now modify the relationship stated at the beginning of this lecture that gave the fraction of molecules at a specific energy to be the fraction of molecules in a given region of energy space:

\[ \frac{dN_i}{N} = \frac{d\zeta}{q} e^{-\beta \epsilon_i} = \]

substituting in for the thermal wavelength, we get
\[
\frac{1}{N} \frac{dN}{du} = 4\pi u^2 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mu^2}{2kT}}
\]

This is the Maxwell-Boltzmann distribution.

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**Aspects of the Maxwell-Boltzmann Distribution**

First, note that the distribution is not Gaussian. As the speed of the molecules approaches zero, the \(v^2\) part of the distribution dominates the expression such that the distribution grows quadratically, but at higher speeds the distribution decays in a Gaussian fashion due to the exponential.

As the temperature of the gas increases, we would expect that higher translational energy states should be populated such that higher velocities are achieved. Therefore, the distribution should shift to higher velocities with an increase in temperature. This is exactly what happens as the following graph demonstrates for CO\(_2\) gas at \(T = 100\) and 600 K:
Characterizing Distributions

To get a general accounting of the velocity of a gas, rather than plot the entire distribution, we use the Maxwell-Boltzmann distribution to provide information on the average and root-mean-squared (rms) speeds as follows. First, the average is defined as:

$$\langle f(u) \rangle = \int_0^\infty \frac{f(u)}{N} dn_u$$

where $f(v)$ represents some function of velocity (or speed in our case since we have not defined the direction of translation) and $N$ is the total number of molecules. For example, the rms average speed would be the square root of the average speed squared:

$$\langle u^2 \rangle = \int_0^\infty \frac{u^2}{N} dn_u$$

Now

$$dN =$$

such that the integral becomes:

$$\langle u^2 \rangle = \int_0^\infty \frac{u^2}{N} \left(4\pi u^2 \left(\frac{m}{2\pi kT}\right) \frac{3}{2} \left(\frac{-mu^2}{e^{2kT}}\right) du\right)$$
Now

\[
\int_{0}^{\infty} x^4 e^{-ax^2} \, dx = \frac{3}{8} \sqrt{\frac{\pi}{a^5}}
\]

such that

and

\[
u_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3kT}{m}}
\]

In addition, we could do the same development for the average speed except that now:

\[
f(u) = u
\]

and we would find that:

\[
u_{ave} = \sqrt{\frac{8kT}{\pi m}}
\]

Finally, we can calculate the most-probably speed (see homework):

\[
u_{mp} = \sqrt{\frac{2kT}{m}}
\]

Inspection of the above demonstrates that:

\[
u_{rms} > \nu_{ave} > \nu_{mp}
\]