6.8: Statistics for Molecular Speeds

Expected values for several quantities can be calculated from the Maxwell-Boltzmann probability density function. The required definite integrals are tabulated in Appendix D.

The ***most probable speed***, v_{mp}, is the speed at which the Maxwell-Boltzmann equation takes on its maximum value. At this speed, we have

$$\begin{aligned} 0 &= \frac{d}{dv}\left(\frac{df(v)}{dv}\right) = \frac{d}{dv}\left[4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2kT}\right)\right] \\ &= \left[4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mv^2}{2kT}\right)\right]\left[2v - \frac{mv^3}{kT}\right] \end{aligned}$$

from which

$$v_{mp} = \sqrt{\frac{2kT}{m}} \approx 1.414\sqrt{\frac{kT}{m}}$$

The ***average speed***, $\bar{v}$ or $\langle v\rangle$, is the expected value of the scalar velocity ($g(v) = v$). We find

$$\bar{v} = \langle v\rangle = \int_0^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^3 exp\left(\frac{-mv^2}{2kT}\right) dv = \sqrt{\frac{8kT}{\pi m}} \approx 1.596\sqrt{\frac{kT}{m}}$$

The ***mean-square speed***, $\overline{v^2}$ or $\langle v^2\rangle$, is the expected value of the velocity squared ($g(v) = v^2$):

$$\overline{v^2} = \langle v^2\rangle = \int_0^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^4 exp\left(\frac{-mv^2}{2kT}\right) dv = \frac{3kT}{m}$$

and the ***root mean-square speed***, v_{rms} , is

$$v_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}} \approx 1.732\sqrt{\frac{kT}{m}}$$

Example 6.8.1

Figure 6 shows the velocity distribution 300 K for nitrogen molecules at 300 K.

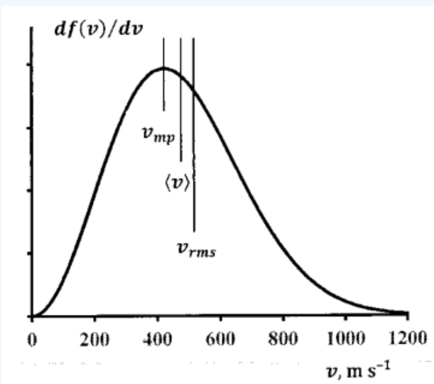

Figure 6. The Maxwell-Boltzmann distribution function for N_2 at 300K.

Solution

Finally, let us find the variance of the velocity; that is, the expected value of $(v - \langle v\rangle)^2$:

$$\text{variance}(v) = \sigma_v^2$$

$$
\begin{aligned}
&= \int_0^\infty (v - \langle v \rangle)^2 \left(\frac{df(v)}{dv} \right) dv \\
&= \int_0^\infty v^2 \left(\frac{df}{dv} \right) dv - 2\langle v \rangle \int_0^\infty v \left(\frac{df}{dv} \right) dv + \langle v \rangle^2 \int_0^\infty \left(\frac{df}{dv} \right) \\
&= \left\langle v^2 \right\rangle - 2\langle v \rangle \langle v \rangle + \langle v \rangle^2 \\
&= \left\langle v^2 \right\rangle - \langle v \rangle^2
\end{aligned}
$$

For N_2 at $300\,\mathrm{K}$, we calculate:

$$v_{mp} \ = 422 \text{ m s}^{-1}$$

$$\langle v \rangle = \bar{v} = 476 \text{ m s}^{-1}$$

$$v_{rms} = 517 \text{ m s}^{-1}$$

$$\text{Variance}\,(v) = \sigma_v^2 = 40.23 \times 10^{-3} \text{ m s}^{-1}$$

$$\sigma_v = 201 \text{ m s}^{-1}$$