

## 4.8: 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

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

$$= \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( \frac{-mv^2}{2kT} \right) \right] \left[ 2v - \frac{mv^3}{kT} \right]$$

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 4.8.1

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

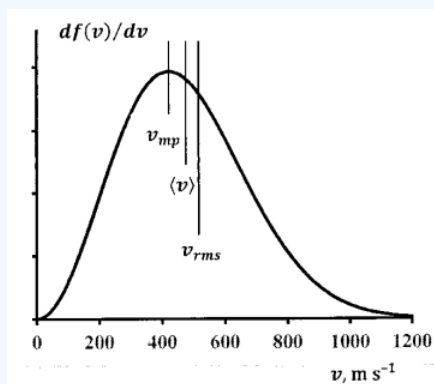


Figure 6. The Maxwell-Boltzmann distribution function for  $N_2$  at 300K.

### Solution

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

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

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

For  $N_2$  at 300 K, we calculate:

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

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

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

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

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

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