Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution of molecular speeds in a gas is actually a probability density function of a continuous variable, *v*, the speed of a molecule. You may be familiar with probability distribution functions for discrete variables. For example, the probability of getting heads by flipping a fair coin is $\frac{1}{2}$; the probability of rolling snake-eyes (two ones) with a pair of dice is $\frac{1}{36}$; and the probability of rolling a seven is $\frac{1}{6}$. For continuous variables, you can *not* obtain the probability of a molecule having a specific velocity from the probability density function. Rather, you must determine the probability of a molecule's speed being in a certain range by integrating the probability density function over that range.

In other words, you can not evaluate the Maxwell-Boltzmann distribution function for v = 2.0 m/s and get the probability of a molecule travelling at that speed. What you can do is determine the probability that a molecule's speed is between 1.9 m/s and 2.1 m/s by integrating the Maxwell-Boltzmann distribution function using 1.9 m/s and 2.1 m/s as the limits.

However, you can calculate expected values for v and v^2, which you can use to calculate the average speed and average kinetic energy of a molecule, respectively.

The basic properties of probability density functions (pdfs), and the definition of expected value can be found in any probability textbook, such as *Introduction to Probability* by Bertsekas and Tsitsiklis, or *A First Course in Probability* by Sheldon Ross.

First, the value of the integral of the pdf over all possibilities must be one.

$$\int_{-\infty}^{+\infty} \text{pdf}(x)\,dx = 1$$

In the case of the Maxwell-Boltzmann distribution, $f(v) = 0$ for v less than zero, because speed is never negative. Our integrals over all possible speeds will be from zero to infinity. Also, the expected value of a given function of x is the integral of that function weighted by the probability density function:

$$\langle g(x) \rangle = \int_{-\infty}^{+\infty} g(x)\,\text{pdf}(x)\,dx$$

The mean value, μ, is the expected value of the integration variable:

$$\mu = \langle x \rangle = \int_{-\infty}^{+\infty} x \cdot \text{pdf}(x)\,dx$$

The variance is the expected value of $(x-\mu)^2$:

$$\sigma^2 = \langle (x-\mu)^2 \rangle = \int_{-\infty}^{+\infty} (x-\mu)^2 \cdot \text{pdf}(x)\,dx$$

We will be using the mean value equation, but not the variance equation. We will be finding the expected value of the square of the speed, which is *not* the same as the square of the expected value of the speed.

$$\langle v^2 \rangle \neq \langle v \rangle^2$$

The Maxwell-Boltzmann distribution is:

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

First, let's check to see if it normalized.

$$\int_0^\infty f(v)dv = 4\pi\int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv$$

There are many ways to perform this integration. One way commonly used in statistical mechanics applications is detailed below.

A substitution will be used that changes the integration variable to one that is dimensionless:

$$u = v\sqrt{\frac{m}{2kT}}$$

The integration becomes:

$$\int_0^\infty f(v)dv = \frac{4}{\sqrt{\pi}}\int_0^\infty \frac{m}{2kT} v^2 e^{-mv^2/2kT}\sqrt{\frac{m}{2kT}}dv$$

$$\int_0^\infty f(v)dv = \frac{4}{\sqrt{\pi}}\int_0^\infty u^2 e^{-u^2}\,du$$

$$\int_0^\infty f(v)dv = \frac{4}{\sqrt{\pi}}\frac{\sqrt{\pi}}{4}$$

$$\int_0^\infty f(v)dv = 1$$

By choosing a variable that simplifies the argument of the exponential, the overall integral is simplified.

Also, by choosing a dimensionless integration variable, any dimensioned quantities can be factored out of the integral. Before the integration in terms of *u* was even performed, the factor outside of it was found to be a dimensionless constant. Since the value of the integral was supposed to be the dimensionless constant 1, we have preliminary confirmation that the distribution function has the correct dimensions. In other words, all the "physics" was factored out first, and the integral was just a dimensionless factor.

Evaluation of this integral:

$$\int_0^\infty u^2 e^{-u^2}\,du = \frac{\sqrt{\pi}}{4}$$

is covered later.

Before finding $v_{\text{av}} = \langle v \rangle$ and $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$, we will find the most probable speed, v_{mp}.

The most probable speed is found by finding the maximum of $f(v)$:

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

$$4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left(2ve^{-mv^2/2kT} + v^2 \left(-\frac{2mv}{2kT} \right) e^{-mv^2/2kT} \right) = 0$$

$$2v - \frac{m}{kT} v^3 = 0$$

The solution set for this equation is:

$$v \in \left\{ 0, \sqrt{\frac{2kT}{m}}, -\sqrt{\frac{2kT}{m}} \right\}$$

Since $-\sqrt{\frac{2kT}{m}}$ is outside the domain, we exclude it. The minimum value of $f(v)$ is zero, and since $f(0) = 0$, we will exclude $v = 0$. Since the function is zero at the zero end of its domain, approaches zero as v goes to infinity, and is positive-valued for all non-zero v, we can safely assume that $v = \sqrt{\frac{2kT}{m}}$ corresponds to a maximum value for $f(v)$. We will forego the second derivative test. Therefore:

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

To find the expected value of v, $\langle v \rangle$:

$$\langle v \rangle = \int_0^\infty v f(v) dv$$

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

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

Again, letting $u = v\sqrt{\frac{m}{2kT}}$:

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

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

$$\langle v \rangle = \frac{4}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} \int_0^\infty \left(\left(\frac{m}{2kT}\right)^{1/2} v\right)^3 e^{-mv^2/2kT} \sqrt{\frac{m}{2kT}} dv$$

$$\langle v \rangle = 4\sqrt{\frac{2kT}{\pi m}} \int_0^\infty u^3 e^{-u^2} du$$

$$\langle v \rangle = 4\sqrt{\frac{2kT}{\pi m}} \left(\frac{1}{2}\right)$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

The fact that $\int_0^\infty u^3 e^{-u^2} du = \frac{1}{2}$ will be shown later.

To find v_{rms}, we need to find $\langle v^2 \rangle$:

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv$$

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

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

Again, letting $u = v\sqrt{\frac{m}{2kT}}$:

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

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

$$\left\langle v^2 \right\rangle = \frac{4}{\sqrt{\pi}} \left(\frac{2kT}{m} \right) \int_0^\infty \left(\frac{m}{2kT} \right)^{1/2} \left(\frac{m}{2kT} \right)^{3/2} v^4 e^{-mv^2/2kT} \sqrt{\frac{m}{2kT}} dv$$

$$\left\langle v^2 \right\rangle = \frac{4}{\sqrt{\pi}} \left(\frac{2kT}{m} \right) \int_0^\infty \left(\left(\frac{m}{2kT} \right)^{1/2} v \right)^4 e^{-mv^2/2kT} \sqrt{\frac{m}{2kT}} dv$$

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

$$\left\langle v^2 \right\rangle = \frac{4}{\sqrt{\pi}} \left(\frac{2kT}{m} \right) \left(\frac{3}{8} \sqrt{\pi} \right)$$

$$\left\langle v^2 \right\rangle = \frac{3kT}{m}$$

$$v_{\text{rms}} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3kT}{m}}$$

The fact that $\int_0^\infty u^4 e^{-u^2} du = \frac{3}{8}\sqrt{\pi}$ will be shown in the next section.

In summary:

$$v_{\text{mp}} = \sqrt{\frac{2kT}{m}}, \; v_{\text{av}} = \sqrt{\frac{8kT}{\pi m}}, \; v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

Note that:

$$v_{\text{mp}} < v_{\text{av}} < v_{\text{rms}}$$

Evaluation of improper integrals involving e^{-x^2}

Since we need to evaluate more than one improper integral containing the term e^{-x^2}, let's start with a general integral of this form and see if we can save some time.

Let I_k represent the integral from zero to infinity with x^k in the integrand:

$$I_\text{k} = \int_0^\infty x^k e^{-x^2}\,dx$$

To evaluate this integral, we will integrate by parts. We will assume that k is non-negative.

Letting $u = e^{-x^2}$ and $dv = x^k\,dx$, we also have $du = -2xe^{-x^2}\,dx$ and $v = \dfrac{1}{k+1}x^{k+1}$:

$$I_\text{k} = \int_0^\infty x^k e^{-x^2}\,dx$$

$$I_\text{k} = \left[\frac{1}{k+1}x^{k+1}e^{-x^2}\right]_0^\infty - \frac{1}{k+1}\int_0^\infty x^{k+1}\left(-2xe^{-x^2}\,dx\right)$$

$$I_\text{k} = \frac{1}{k+1}\left[0-0\right] + \frac{2}{k+1}\int_0^\infty x^{k+2}e^{-x^2}\,dx$$

$$I_\text{k} = \frac{2}{k+1}I_{\text{k}+2}$$

Assuming that k is non-negative is important when evaluating the uv term at $x = 0$, and for avoiding division by zero at $k = -1$. This restriction does not conflict with our purposes. This does not give us the value of any integral, but it does give us something very valuable. The relation derived here is a *recurrence relation*. If we know *any* I_k, then we can quickly evaluate the corresponding $I_{\text{k}+2}$, if k is non-negative.

Actually, we are going to use this recurrence relation in a different form by substituting $k = n - 2$.

$$I_\text{k} = \frac{2}{k+1}I_{\text{k}+2}$$

$$I_{\text{n-2}} = \frac{2}{n-2+1}I_\text{n}$$

$$I_{\text{n-2}} = \frac{2}{n-1}I_\text{n}$$

$$I_\text{n} = \frac{n-1}{2}I_{\text{n-2}}$$

With our recurrence relation, we need only to evaluate the integral for two non-negative consecutive integer values of n, and we can easily find evaluate the integral for any such n. Of course, we will have to use methods other than integration by parts, since that method did not give us direct answers.

We will evaluate I_0 and I_1, and use our recurrence relation to get the values through I_4.

To evaluate I_0, we will use a common trick:

$$I_0 = \int_0^{\infty} e^{-x^2} dx$$

$$I_0{}^2 = \int_0^{\infty} e^{-x^2} dx \int_0^{\infty} e^{-y^2} dy$$

$$I_0{}^2 = \int_0^{\infty}\int_0^{\infty} e^{-\left(x^2+y^2\right)} dxdy$$

$$I_0{}^2 = \int_0^{\pi/2}\int_0^{\infty} e^{-r^2} rdrd\theta$$

$$I_0{}^2 = \frac{\pi}{2}\int_0^{\infty} e^{-r^2} rdr$$

From here, we simply use the substitution: $u = -r^2 \Rightarrow du = -2rdr \Rightarrow -\frac{1}{2}du = rdr$

$$I_0{}^2 = \frac{\pi}{2}\int_0^{\infty} e^{-r^2} rdr$$

$$I_0{}^2 = \frac{\pi}{2}\left(-\frac{1}{2}\right)\int_{r=0}^{r=\infty} e^{u} du$$

$$I_0{}^2 = -\frac{\pi}{4}\left[e^{u}\right]_{r=0}^{r=\infty}$$

$$I_0{}^2 = -\frac{\pi}{4}\left[e^{-r^2}\right]_0^{\infty}$$

$$I_0{}^2 = -\frac{\pi}{4}\left[0-1\right] = \frac{\pi}{4}$$

$$I_0 = \frac{1}{2}\sqrt{\pi}$$

Evaluating I_1 is straightforward:

$$I_1 = \int_0^\infty x e^{-x^2}\, dx$$

Let $u = -x^2 \Rightarrow du = -2xdx \Rightarrow -\frac{1}{2}du = xdx$

$$I_1 = \int_0^\infty x e^{-x^2}\, dx$$

$$I_1 = \left(-\frac{1}{2}\right)\int_{x=0}^{x=\infty} e^u du$$

$$I_1 = \left(-\frac{1}{2}\right)\left[e^u\right]_{x=0}^{x=\infty} = \left(-\frac{1}{2}\right)\left[e^{-x^2}\right]_0^\infty$$

$$I_1 = \left(-\frac{1}{2}\right)\left[0-1\right] = \frac{1}{2}$$

With the two values $I_0 = \frac{1}{2}\sqrt{\pi}$ and $I_1 = \frac{1}{2}$, we can use our recurrence relation $I_n = \frac{n-1}{2} I_{n-2}$ to determine the required values.

$$I_0 = \int_0^\infty e^{-x^2}\, dx = \frac{1}{2}\sqrt{\pi}$$

$$I_1 = \int_0^\infty x e^{-x^2}\, dx = \frac{1}{2}$$

$$I_2 = \int_0^\infty x^2 e^{-x^2}\, dx = \left(\frac{2-1}{2}\right)\left(\frac{1}{2}\sqrt{\pi}\right) = \frac{1}{4}\sqrt{\pi}$$

$$I_3 = \int_0^\infty x^3 e^{-x^2}\, dx = \left(\frac{3-1}{2}\right)\left(\frac{1}{2}\right) = \frac{1}{2}$$

$$I_4 = \int_0^\infty x^4 e^{-x^2}\, dx = \left(\frac{4-1}{2}\right)\frac{1}{4}\sqrt{\pi} = \frac{3}{8}\sqrt{\pi}$$

Values of I_n for integer values of n greater than four can be found in a straightforward manner if desired.