Maxwell Distribution of Particle Velocities

Given a set of particles, N, with a temperature, T, then according to the Boltzmann distribution, the number of particles, N_i, with a kinetic energy, E_i, is

$$\frac{N_i}{N} = \frac{g_i \exp\left(-\frac{E_i}{k_B T}\right)}{\sum_j g_j \exp\left(-\frac{E_j}{k_B T}\right)} \tag{1}$$

where g_i is the degeneracy, that is, the number of states having the same energy, E_i. The kinetic energy of a particle is

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) \tag{2}$$

In considering a large number of particles, we can generalize the degeneracy concept as follows. In 3-dimensional velocity space (v_x, v_y and v_z), the velocity vectors that correspond to a given speed, $|v|$, lie on the surface of a sphere with radius $|v|$. The larger $|v|$ is, the bigger the sphere is, and the more possible velocity vectors there are. So the number of possible velocity vectors for a given speed scales with the surface area of a sphere of radius $|v|$. Therefore the probability density of the speed is

$$f\left(|\vec{v}|\right) = c\ 4\pi v^2 \exp\left(-\frac{m\left(v_x^2 + v_y^2 + v_z^2\right)}{2k_B T}\right) = c\ 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{3}$$

where $\int f\left(|v|\right)dv = 1$, that is the integral over all probability density must integrate to 1. We use this to determine the constant, c, in (3) so that (3) is properly normalized.

$$\int_0^\infty f\left(|\vec{v}|\right)dv = 1 = \int_0^\infty c\ 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)dv = c\ 4\pi \int_0^\infty v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)dv \tag{4}$$

We use the definite integral

$$\int_0^\infty x^2 e^{-ax^2}dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \tag{5}$$

with $a = m/(2\ k_B T)$ to get

$$\int_0^\infty f\left(|\vec{v}|\right)dv = 1 = c\ 4\pi \int_0^\infty v^2 \exp\left(-av^2\right)dv = \frac{c\ 4\pi}{4}\sqrt{\frac{\pi}{a^3}} = c\left(\frac{2\pi k_B T}{m}\right)^{3/2} \tag{6}$$

Therefore the normalization constant, c, is given by

$$c = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \tag{7}$$

and the probability density of the particle thermal or kinetic speed is

$$f\left(\left|\vec{v}\right|\right) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{m\left(v_x^2 + v_y^2 + v_z^2\right)}{2k_B T}\right) \tag{8}$$

The ***expected or mean value of* |v|** is therefore

$$\overline{\left|v\right|} = \int_0^\infty v f\left(\left|\vec{v}\right|\right) dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \tag{9}$$

Combining (9) with the definite integral

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} \tag{10}$$

and defining $a = m/(2\ k_B T)$ yields the mean of the kinetic speed

$$\overline{\left|v\right|} = \int_0^\infty v f\left(\left|\vec{v}\right|\right) dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{4\pi}{2} \left(\frac{2k_B T}{m}\right)^2 = \left(\frac{8k_B T}{\pi m}\right)^{1/2} \tag{11}$$

The ***most probable value*** of |v| is when f(|v|) reaches a maximum where d{ f(|v|)}/d|v| = 0

$$\frac{df\left(\left|\vec{v}\right|\right)}{dv} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi \left\{2v \exp\left(-\frac{mv^2}{2k_B T}\right) + v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)\left[-\frac{mv}{k_B T}\right]\right\} = 0 \tag{12}$$

$$2v = v^2 \left[\frac{mv}{k_B T}\right] \tag{13}$$

$$v = \sqrt{\frac{2k_B T}{m}} \tag{14}$$

The square root of the mean square or ***rms velocity*** is

$$\overline{v^2} = \int_0^\infty v^2 f\left(\left|\vec{v}\right|\right) dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \tag{15}$$

Combining (15) with the definite integral

$$\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{2^3} \frac{\sqrt{\pi}}{a^{5/2}} \tag{16}$$

with $a = m/(2\ k_B T)$ yields

$$\overline{v^2} = \int_0^\infty v^2 f\left(\left|\vec{v}\right|\right) dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{m}\right)^{5/2} = \frac{3k_B T}{m} \tag{17}$$

$$v_{rms} = \left(\overline{v^2}\right)^{1/2} = \sqrt{\frac{3k_B T}{m}} \tag{18}$$