27.2: The Gaussian Distribution of One Component of the Molecular Velocity

As was shown in section 27.1, the pressure of an ideal gas is given as the total force exerted per unit area

$$P = \frac{F_{tot}}{A} = N_{tot}\left(\frac{mv_x^2}{V}\right) = \frac{N_{tot}m}{V}v_x^2$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replaced (v_x^2) with the squared average of velocity in the x direction $\langle v_x \rangle^2$.

$$P = \frac{N_{tot}m}{V}\langle v_x \rangle^2$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}} \tag{27.2.1}$$

This function has two parts: a **normalization constant** and an exponential term. The normalization constant is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 \tag{27.2.2}$$

Normalizing the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution has to be normalized because it is a continuous probability distribution. As such, the sum of the probabilities for all possible values of v_x **must** be unity. And since v_x can take any value between -∞ and ∞, then Equation 27.2.2must be true. So if the form of $f(v_x)$ is assumed to be

$$f(v_x) = N\exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

The normalization constant N can be found from

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} N\exp\left(\frac{-mv_x^2}{2k_B T}\right)dv_x = 1$$

The expression can be simplified by letting $\alpha = m/2k_B T$:

$$N\int_{-\infty}^{\infty} \exp(-\alpha v_x^2)dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

So

$$N\sqrt{\frac{\pi}{\alpha}} = 1$$

Thus,

$$N = \sqrt{\frac{\alpha}{\pi}} = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \tag{27.2.3}$$

Calculating an Average from a Probability Distribution

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^{N} x_i P_i$$

where P_i is the probability of measuring the value x_i. This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability is of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int x P(x) dx$$

where $P(x)$ is the function describing the probability distribution, and with the integration taking place across all possible values that x can take.

Calculating the average velocity in the x direction

A value that is useful (and will be used in further developments) is the average velocity in the x direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of v_x is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the +x direction, and half in the –x direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of v_x, which gives the speed in the x direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes

$$\langle |v_x| \rangle = 2\int_{0}^{\infty} v_x f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N \exp(-\alpha v_x^2)$$

where

$$N = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

and

$$\alpha = \frac{m}{2k_B T}.$$

A table of definite integrals shows

$$\int_0^\infty xe^{-ax^2}\,dx = \frac{1}{2a}$$

so

$$\langle v_x\rangle = 2N\left(\frac{1}{2\alpha}\right) = \frac{N}{\alpha}$$

Substituting our definitions for N and α produces

$$\langle v_x\rangle = \left(\frac{m}{2\pi k_B T}\right)^{1/2}\left(\frac{2k_BT}{m}\right) = \left(\frac{2k_BT}{\pi m}\right)^{1/2}$$

This expression indicates the average speed for motion in one direction.

It is important to note that equation 27.2.1 describes the distribution function for one component of the molecular ***velocity***. Because a molecule is able to move in a positive or a negative direction, the range of one component of the molecular velocity (v_x in this case) is $-\infty$ to ∞. This distribution of velocities is a Gaussian distribution of velocities, as shown in Figure 27.2.1 .

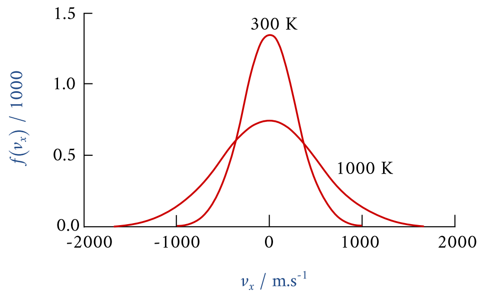

Figure 27.2.1 : Distribution of the x component of the velocity of a nitrogen molecule at 300 K and 1000 K. (CC BY-NC; Ümit Kaya via LibreTexts)

We will find in section 27.3 that the distribution of molecular ***speeds*** is not a Gaussian distribution.

Contributors and Attributions

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