10.3: Average and RMS Velocities

Now that we have the Maxwell-Boltzmann distribution as a function of net velocity we can calculate the average and second moment. The average velocity <v> is determined via:

$$\langle v\rangle=\int_0^\infty 4\pi\cdot v^2\cdot v\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

To simplify matters, we will call all the constants "Q" = $4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}}$, leaving us to solve a less-scary expression: $Q\cdot\int_0^\infty v^3\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$. We can do this using an integral identity as shown in the Example box. However, to improve our math skills we will solve it here the long way using integration by parts:

$$\int_a^b f(x)\cdot\frac{\partial g(x)}{\partial x}\cdot\partial x=f(x)\cdot g(x)]_a^b-\int_a^b\frac{\partial f(x)}{\partial x}\cdot g(x)\cdot\partial x$$

We have to conform the formula above to the Maxwell-Boltzmann distribution. First, we define $f(x)$, whereby $x=v$, a = 0 m/s and b = ∞ m/s. It is tempting to make $f(v)=v^3$, however, the "trick" is to leave one velocity term out which means $f(v)=v^2$ and $\frac{\partial f(v)}{\partial v}=2\cdot v$ The remaining terms define $\frac{\partial g(v)}{\partial v}=v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$, and thus $g(v)=\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$. As a result, the integration by parts gives an average velocity of:

$$\langle v\rangle=Q\cdot f(v)\cdot g(v)]_0^\infty-Q\cdot\int_0^\infty\frac{\partial f(v)}{\partial v}\cdot g(v)\cdot\partial v$$

The first term:

$$Q\cdot f(v)\cdot g(v)]_0^\infty=Q\cdot v^2\cdot\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\Big|_0^\infty=0$$

since the limits are evaluated as: $\infty^2 e^{-\infty}\to 0$ and: $0^2 e^{-0}\to 0$.

The second term is:

$$-Q\cdot\int_0^\infty\frac{\partial f(v)}{\partial v}\cdot g(v)\cdot\partial v=2\cdot Q\cdot\frac{k_B\cdot T}{m}\int_0^\infty v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

Oddly, we have already evaluated the above because it is basically the same as $\frac{\partial g(v)}{\partial v}$, the integration of which is g(v). Thus:

$$2\cdot Q\cdot\frac{k_B\cdot T}{m}\int_0^\infty v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v=2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)\cdot\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\Big|_0^\infty=-2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)^2\cdot\left(e^{-\infty}-e^0\right)$$
$$=2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)^2$$

Work through the constants (Q is defined above) to simplify them and you see:

$$\langle v\rangle=\int_0^\infty v\cdot 4\cdot\pi\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot v^2\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v=\left(\frac{8\cdot k_B\cdot T}{\pi\cdot m}\right)^{\frac{1}{2}}$$

10.2.1 Average square velocity. Let's work out the second moment, i.e. the average squared velocity of a gas $\langle v^2\rangle$, by integration of the Maxwell-Boltzmann distribution. The second moment of velocity is found via:

$$\langle v^2\rangle=\int_0^\infty 4\pi\cdot v^2\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

Again we will remove all the constants by calling them Q = $4\cdot\pi\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}$ and we will us integration by parts to solve $Q\cdot\int_0^\infty v^4\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\partial v$. Like before we use the "trick" of partitioning an odd factor of velocity for: $f(v)=v^3$, which makes

$\frac{\partial f(v)}{\partial v} = 3 \cdot v^2$. This leaves a factor of velocity for: $\frac{\partial g(v)}{\partial v} = v \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v$, the integration of which gives: $g(v) = \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}}$.

Now the integration by parts fomula is:

$$\langle v^2 \rangle = Q \cdot f(v) \cdot g(v)]_0^\infty - Q \cdot \int_0^\infty \frac{\partial f(v)}{\partial v} \cdot g(v) \cdot \partial v$$

The first term is:

$$Q \cdot f(v) \cdot g(v) = Q \cdot v^3 \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \Big|_0^\infty = 0$$

since $\infty^3 e^{-\infty} \to 0$ and $0^3 e^{-0} \to 0$. The second term is:

$$-Q \cdot \int_0^\infty \frac{\partial f(v)}{\partial v} \cdot g(v) \cdot \partial v = -Q \cdot \int_0^\infty 3 \cdot v^2 \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v =$$

$$Q \cdot \int_0^\infty 3 \cdot v^2 \cdot \left(\frac{k_B \cdot T}{m}\right) \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v$$

which means we must do another integration by parts. We will define g(v) and $\frac{\partial g(v)}{\partial v}$ as above and now: $f(v) = v$ and $\frac{\partial f(v)}{\partial v} = 1$. Next, we factor out the constants:

$$3 \cdot Q \cdot \frac{k_B \cdot T}{m} \cdot \int_0^\infty v \cdot v \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v$$

$$= 3 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right) \cdot v \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \Big|_0^\infty - 3 \cdot Q \cdot \frac{k_B \cdot T}{m} \cdot \int_0^\infty \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v$$

The first term is 0 like in the other examples. The second term is solved using a standard Gaussian integral similar to the one that was introduced earlier: $\int_0^\infty e^{-a \cdot v^2} \cdot \partial v = \frac{1}{2}\sqrt{\frac{\pi}{a}}$. This allows us to demonstrate:

$$\langle v^2 \rangle = \int_0^\infty v^2 \cdot 4 \cdot \pi \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot v^2 \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v = 3 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right)^2 \cdot \frac{1}{2} \cdot \left(\frac{2 \cdot \pi \cdot k_B \cdot T}{m}\right)^{\frac{1}{2}}$$

Work through it (remember Q is defined above) and you find:

$$\langle v^2 \rangle = \frac{3 \cdot k_B \cdot T}{m}$$

Often we express the above as the root-mean-squre, or rms velocity $\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 \cdot k_B \cdot T}{m}}$. This is because it has the same units as average velocity and is thus comparable.

10.2.2 Pressure-volume and the perfect gas equation. We hope that it is interesting that humanity has evolved to the point where we can derive such knowledge of nature without resorting to actually making measurements, which is the end goal of Physical Chemistry. There are a few interesting points that can be made with the derivations thus far. For example, we remind you that the Boltzmann constant is related to the gas constant R via Avogadro's number. As a result, algebraic manipulation of the average square velocity reveals:

$$langlev^2 \rangle = \frac{3 \cdot k_B \cdot T}{m} \cdot \frac{N_A}{N_A} = \frac{3 \cdot R \cdot T}{M}$$

where M is the mass in kg per mole. Since all these derivations were performed on a perfect gas, we know that for 1 mole: $P \cdot V = R \cdot T$ and as a result:

$$P = \frac{M \cdot \langle v^2 \rangle}{V \cdot 3}$$

Now we can make a simple measurement of the pressure of a gas and know how fast the individual molecules are moving. Score!

10.2.3 Most probable velocity. Here we locate the top of the Maxwell-Boltzmann distribution by first determining the derivative: $\frac{\partial\left(4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\right)}{\partial v}=$

$$8\pi\cdot v\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}+4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot\left(\frac{-m\cdot v}{k_B\cdot T}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$$

The two terms can be set across the equal sign once we set the expression to 0 s/m, and the velocity terms in the derivative become the most probable because there is only one velocity that maximizes the distribution:

$$8\pi\cdot v_{mp}\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v_{mp}^2}{2\cdot k_B\cdot T}}=4\pi\cdot v_{mp}^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot\left(\frac{m\cdot v_{mp}}{k_B\cdot T}\right)\cdot e^{\frac{-m\cdot v_{mp}^2}{2\cdot k_B\cdot T}}$$

Several simplifications can me made: $2=v_{mp}\cdot\left(\frac{m\cdot v_{mp}}{k_B\cdot T}\right)$ from which we solve:

$$v_{mp}=\sqrt{\frac{2\cdot k_B\cdot T}{m}}$$

10.2.4 Flux. One of the more interesting things that Maxwell-Boltzmann calculations can be used for is to model the flux of molecules hitting a surface. A flux is the collision rate of gas molecule striking an area per unit time. We express the flux as per unit area so that the data can be applied to different systems. To determine the flux we will use a phenomenological model shown in Figure 10.6. Here we see that a gas molecule is moving to the right, and in Δt time it will strike the wall of area A. It has to travel some distance to do so; this distance is specifically the molecule's speed in the "right-moving" direction times the time (Δt) it takes to reach the wall. We can easily calculate the average speed in the x- (or y- or z-) direction by solving: $\langle v_x\rangle=\int_{-\infty}^{\infty}v_x\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$, but hopefully you realize that this is 0 m/s. It also isn't what is being asked- we want to know the average speed of a molecule under the condition that it is only moving to the right, or in other words with a positive velocity. This is:

$$\langle v_x\rangle^+=\int_0^{\infty}v_x\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$$

(see the change in the lower limit?) This is solved with the identity$int_0^{\infty}x\cdot e^{-a\cdot x^2}\cdot\partial x=\frac{1}{2a}$:

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

Now that we have the length that the red gas molecule is travelling to hit the wall, we now have the volume that the molecule resides in: $\Delta t\cdot\langle v_x\rangle^+\cdot A$. If we simply multiply this volume by the number density (number of molecules per volume in the container), we just calculated how many molecules are going to strike the wall in time Δt. The number density is $\frac{N}{V}$, and thus:

$$\#collisions=A\cdot\Delta t\cdot\langle v_x\rangle^+\cdot\frac{N}{V}=A\cdot\Delta t\cdot\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}$$

Last, recall that the flux is the number of collisions per unit area per unit time. Consequently:

$$Flux=\frac{A\cdot\Delta t\cdot\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}}{A\cdot\Delta t}=\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}$$

Using the perfect gas law \(PV=nRT)can be expressed using the number of molecules N with Avogadro's number: $PV=\frac{N}{N_A}RT$, and since $\frac{R}{N_A}=k_B$ we have:$fracPk_B\cdot T=\frac{N}{V}$. When we use this in the expression above we determine that:

\[Flux={\left(\frac{k_B\cdot T}{2\pi \cdot m}\right)}^{\frac{1}{2}}\cdot \frac{P}{k_B\cdot T}=\frac{P}{\sqrt

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\nonumber \]

Again, we demonstrate how simple measurements like pressure yield information about the individual molecules themselves when you understand their statistical behavior.