10.4: Average relative velocity and collision frequency

Another interesting use of the Maxwell-Boltzmann distribution is to examine how gas molecules interact with each other, and to do so we have to consider our observational frame of reference. By this we mean that, in all the derivations above, we are outsiders looking into a vacuum chamber containing a moderate pressure of gas. However, our observations may change if we are strapped to be back of a gas molecule and riding it around in the same chamber.

How do we observe other molecules if we are one of them? In other words, we go from the laboratory to the molecular frame. To do so, the transformation is that all the velocities are now relative to our own. Let's say we are molecule "a" moving at speed v_a and we see molecule "b" with speed v_b. If "b" is going in same direction at the same speed, it appears not be moving at all. If heading straight towards us, "b" appears to be scarily moving fast. Mathematically we are observing not the absolute velocity but the relative velocity:

$$V_{rel} = v_a - v_b$$

Perhaps we can now perform Maxwell-Boltzmann calculations on relative velocity? Not quite, which is because originally we had a 2-dimensional system of two "a" and "b" velocity vectors. As a result, we still have to perform a 2-dimensional calculation, or we have arbitrarily lost information and our analyses will be wrong (recall this was a problem we encountered when transforming $\partial v_x \cdot \partial v_y \cdot \partial v_z \rightarrow \partial v$).Therefore we define the second orthogonal velocity to V_{rel}, which is the center of mass velocity G shown in the figure above:

$$G = \frac{m_a v_a + m_b v_b}{m_a + m_b}$$

To proceed, we need to be able to write the vectors v_a and v_b in terms of G and V_{rel}. Its just an exercise in algebra and the results are:

$$v_a = G + \frac{m_b}{m_a + m_b} V_{rel}$$
$$v_b = G - \frac{m_a}{m_a + m_b} V_{rel}$$

What do we do with their Maxwell-Boltzmann distributions such that the velocities or "a" and "b" are analyzed together? Let's rather start with this question- what is the probability that "a" is moving forward? Why, its 0.5 or 50%! What about "b"? The same, 50%. Now what is the likelihood that both "a" and "b" are moving forwards? Clearly that's 0.25 = 25%, which is the product of the individual probabilities (like heads-heads in a coin flip).

Now we can answer the question- how do we analyze the velocity distributions for two particles simultaneously? We simply use the product of the individual Maxwell-Boltzmann distributions:

$$MB(v_a) \cdot MB(v_b) = \left(\frac{1}{2\pi k_B T}\right)^3 \cdot (m_a m_b)^{\frac{3}{2}} \cdot e^{-\frac{m_b {v_b}^2 + m_a {v_a}^2}{2k_B T}}$$

The above is just the standard velocity probability distribution using two different masses (m_a and m_b) as well as velocities (v_a and v_b). Notice that the usual Maxwell-Boltzmann factor: $\left(\frac{1}{2\pi k_B T}\right)^{\frac{3}{2}}$ is squared in the equation above. However, the masses are not because the mass for particle "a" and "b" may be different.

Moving forward, the clever thing is to redefine: $m_b v_a^2 + m_a v_a^2$ that appears in the exponential in terms of V$_{rel}$ and G. We expressed v_a and v_b above, and now we square them and do some algebra. There is a cross term $\mathbf{G \cdot V_{rel}}$ that has been made bold for emphasis:

$$m_b v_b^2 + m_a v_a^2$$

$$= m_b \left[G^2 + \frac{m_a^2}{(m_a + m_b)^2} V_{rel}^2 - \frac{2m_a}{m_a + m_b} G \cdot V_{rel}\right] + m_a \left[G^2 + \frac{m_b^2}{(m_a + m_b)^2} V_{rel}^2 + \frac{2m_b}{m_a + m_b} G \cdot V_{rel}\right]$$

$$= (m_a + m_b) G^2 + \left[\frac{m_b \cdot m_a^2 + m_a \cdot m_b^2}{(m_a + m_b)^2}\right] V_{rel}^2$$

$$=(m_a+m_b)\,G^2+\frac{m_a\cdot m_b}{(m_a+m_b)}V_{rel}^2$$

Notice how above that the $\mathbf{G\cdot V_{rel}}$ cross terms in the second step cancel? This simplifies the remaining derivation because we can now separate the G and V_{rel}. as shown here:

\[MB\left(G\right)\cdot MB\left(V_{rel}\right)={\left(\frac

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{2\pi k_BT}\right)}^3

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\nonumber \]

Now we are almost ready to integrate the expression, but just like last time we have to be careful with partials. As we started with the expression $MB(v_a)\cdot MB(v_b)$, of course it uses partials of $\partial v_a\cdot\partial v_b$. When transforming: $\partial v_a\cdot\partial v_b\rightarrow\partial G\cdot\partial V_{rel}$, the geometry factor (also known as the "Jacobian") is 1.0; see the Appendix. This means:

$$MB\left(v_a\right)\cdot MB\left(v_b\right)\cdot\partial v_a\cdot\partial v_b=MB\left(G\right)\cdot MB\left(V_{rel}\right)\cdot\partial G\cdot\partial V_{rel}$$

However, we still need to remember that we live in three dimensions. Consequently the expression is:

\[{\left(\frac

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{2\pi k_BT}\right)}^3{e^-}^{\frac{(m_a+m_b)({G_x}^2+{G_y}^2+{G_z}^2)}{2k_BT}}{e^-}^{\frac{\frac{m_am_b}{m_a+m_b}V^2_{rel}}{2k_BT}}\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}\partial G_x\partial G_y\partial G_z \nonumber \]

Ultimately, we want $\langle V_{rel}\rangle$, so we want to remove all the reduced mass velocities (the G's). To do so we integrate them out from -∞<$G_{x,y,z}$<∞:

\[\int^{\infty }_{-\infty }{}\int^{\infty }_{-\infty }{}\int^{\infty }_{-\infty }{}{\left(\frac

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{2\pi k_BT}\right)}^3{e^-}^{\frac{(m_a+m_b)({G_x}^2+{G_y}^2+{G_z}^2)}{2k_BT}}\partial G_x\partial G_y\partial G_z={\left(\frac{\left(m_am_b\right)}{2\pi k_BT(m_a+m_b)}\right)}^{\frac{3}{2}} \nonumber \]

This was solved using a standard Gaussian integral; it's actually nearly identical to our derivation of the normalization factor in the velocity Maxwell-Boltzmann distribution. The remaining part of the distribution is only in terms of the relative velocities:

$$\left(\frac{(m_am_b)}{2\pi k_BT(m_a+m_b)}\right)^{\frac{3}{2}}e^{-\frac{(m_am_b)V_{rel}^2}{2k_BT(m_a+m_b)}}\cdot\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}$$

From here, you transform $\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}\rightarrow 4\pi\cdot V_{rel}^2\cdot\partial V_{rel}$ as before and we will also substitute in "μ", called the reduced mass, for $\frac{(m_am_b)}{(m_a+m_b)}$. We can work the average relative velocity expression:

\[\langle V_{rel}\rangle =\int^{\infty }_0{}4\pi {\cdot V_{rel}}^3\cdot {\left(\frac{\mu }{2\pi k_BT}\right)}^{\frac{3}{2}}

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\cdot \partial V_{rel}={\left(\frac{8\cdot k_B\cdot T}{\pi \cdot \mu }\right)}^{\frac{1}{2}} \nonumber \]

The only difference between the average velocity $\langle v\rangle = \left(\frac{8\cdot k_B\cdot T}{\pi\cdot m}\right)^{\frac{1}{2}}$ and the average relative velocity above is just an alternate definition of the mass! Notice that the relative velocity is bigger (by $\sqrt{2}$) than the vs. laboratory velocity if the masses are equal ($m_a = m_b$).

10.4.1 Collision frequency and mean free path. Here we present an interesting use of the relative velocity, which is the collision frequency and mean free path among gas particles. To calculate the collision frequency, we have to use the phenomenological model shown in Figure 10.8. The purpose is to derive an expression for what is called a "collision volume". This is a space that, if occupied by two molecules, then they must have collided because there isn't enough room for them not to do so. As we see in Figure 10.8, the gas molecule has a diameter d that creates a collisional cross-sectional area of $A = \pi d^2$. In Δt amount of time the gas moves over a distance $\Delta t\cdot\langle V_{rel}\rangle$, which allows us to define the collision volume:

$$\Delta t\cdot\langle V_{rel}\rangle\cdot A = \Delta t\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$$

If we simply multiply this volume by the number density $\frac{N}{V}$ then we know how many collisions occur between gas molecules over a timescale. The collision frequency, usually abbreviated Z, is thus the number of collisions per unit time: $Z = \frac{N}{V}\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$. As we showed in the calculation of flux: $fracNV = fracPk_B\cdot T$ so the above can be expressed as:

$$Z = \frac{P}{k_B\cdot T}\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$$

From this we see that larger molecules will hit each other more often, although larger molecules may weigh more which will also slow down the collision frequency. Gases under higher pressure collide more. Finally, we can also use collision frequency to determine how far a gas can travel before it hits another. This is the mean free path, called λ, which is $\lambda = \frac{\langle v\rangle}{Z} = \frac{\langle v\rangle}{\frac{P}{k_B\cdot T}\cdot\langle V_{rel}\rangle\cdot\pi d^2}$. You may recall that $\frac{\langle v\rangle}{\langle V_{rel}\rangle} = \frac{1}{\sqrt{2}}$ for a homogeneous gas, which makes:

$$\lambda = \frac{k_B\cdot T}{\sqrt{2}\cdot\pi d^2\cdot P}$$

Given the 0.346 nm diameter of oxygen, the collision frequency for O_2 at room temperature and pressure is 5.8 $\times 10^9$ s^{-1}, which makes it's mean free path 76 nm. This is relatively far compared to the size of the molecule, which is why the "perfect" non-interacting description of gas molecules is fairly accurate.