

Molecular Collisions

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Molecular Visualization of the Diffusion Process

In analyzing the gas so far, we've ignored collisions between molecules, and in fact for air at ordinary temperatures the relationship between pressure, volume and temperature came out correctly. Furthermore, Maxwell's speed distribution can be used to find what fraction of the molecules in a planet's atmosphere are moving at above escape velocity, so we can predict what gases will remain surrounding a planet, given the gravitational force near the surface, and the temperature.

But there are other phenomena for which an understanding of collisions is all-important. For example, if two different gases, say oxygen and nitrogen, in a container at the same pressure and temperature are separated by a partition, how quickly will they mix once the partition is removed? Assuming room temperature, the molecules will be moving at hundreds of meters per second, so one might imagine the mixing will be over in hundredths of a second. But *that is not the case at all*—observationally, it might take an hour, for a box holding a few liters. This surprisingly slow penetration of one gas by another is called *diffusion*. (We're assuming the temperature is kept constant so that convection currents don't arise—such currents could reduce the time substantially.)

The reason it takes the gases so long to mix becomes evident on tracking one molecule as it enters the other gas. Think of an oxygen molecule moving into nitrogen. We'll take O_2 and N_2 to be little spheres of diameter d . (You're used to seeing them pictured like dumbbells and that's true of the two nuclei, but the surrounding electron cloud is in fact close to spherical.) So now visualize the little O_2 sphere shooting into this space where all these other spheres are moving around. *Temporarily, for ease of visualization, let's imagine all the other spheres to be at rest.*

How far can we expect the O_2 to get before it hits an N_2 ? The *average* distance before a collision is called the *mean free path*. Let's try to picture how much room there is to fly between these fixed N_2 spheres. We do know that if it were *liquid* nitrogen, there would be *very little* room: liquids are just about incompressible, so the molecules must be touching. Roughly speaking, a molecule of diameter d will occupy a cubical volume of about d^3 (there has to be some space left over—we can pack cubes to fill space, but not spheres.)

We also know that liquid nitrogen weighs about 800 kg per cubic meter, whereas N_2 gas at room temperature (and pressure) weighs about 1.2 kg per cubic meter, a ratio of 670. This means that *on average each molecule in the gas has 670 times more room*—that is, it has a space 670 times the volume d^3 we gave it in the liquid. So in the gas, the average center-to-center separation of the molecules will be the cube root of 670, which is about $8.75d$. So the picture is a gas of spheres of diameter d , placed at random, but separated on average by distances of order $10d$. It's clear that shooting an oxygen molecule into this it will get quite a way.

We now try to estimate just how far an O_2 will get, on average, as it shoots into this forest of spheres. Picture the motion of the center of the oxygen molecule. Before any collision, it will be

moving on a straight-line path. Just how close does the O₂ center have to get to an N₂ center for a hit? Taking both O₂, N₂ to be spheres of diameter d , if an N₂ center lies within d of the O₂ center's path, there will be a hit. So we can think of the O₂ as sweeping out a volume, a cylinder of *radius* d centered on its path, hitting and deflecting if it encounters an N₂ *centered within that cylinder*. So how far will it get, on average, before a hit? In traveling a distance x , it sweeps out a volume $\pi d^2 x$. Now picture it going through the gas for some considerable length of time, so there are many collisions. The volume swept out will look like a stovepipe, long straight cylindrical sections connected by elbows at the collisions. The total volume of this stovepipe (ignoring tiny corrections from the elbows) will be just $\pi d^2 L$, L being the total length, that is, the total distance the molecule traveled.

If the density of the nitrogen is n molecules per cubic meter, the number of N₂'s in this stovepipe volume will be $\pi d^2 L n$, in other words, this will be the number of collisions. Therefore, the average distance *between* collisions, the mean free path l , is given by:

$$\text{mean free path } l = \frac{\text{total distance traveled}}{\text{number of collisions}} = \frac{L}{\pi d^2 L n} = \frac{1}{\pi d^2 n}$$

So what is n ? We estimated above that each molecule has space $670d^3$ to itself, so n is just how many of those volumes there are in one cubic meter, that is, $n = 1/670d^3$.

Therefore, the mean free path is given by

$$l = \frac{1}{\pi d^2 n} = \frac{670d^3}{\pi d^2} \approx 200d.$$

(We can see from this that the average length of stovepipe sections between elbows is 200 times the pipe radius, so neglecting any volume corrections from the elbows was an excellent approximation.)

Notice that this derivation of the mean free path *in terms of the molecular diameter* depends *only* on knowing the *ratio of the gas density to the liquid density*—it *does not depend on the actual size of the molecules!* But it *does* mean that if we can somehow measure the mean free path, by measuring how fast one gas diffuses into another, for example, we can deduce the size of the molecules, and historically this was one of the first ways the size of molecules was determined, and so Avogadro's number was found.

Let us now put in some numbers to find this mean free path: for O₂, N₂, $d \approx 0.3$ nm, so the mean free path $l \approx 60$ nm, or 6×10^{-8} m. The speed of the molecules at room temperature v is approximately 500 meters per sec., so the molecule has of order 10^{10} collisions per second!

Actually, there is one further correction we should make. We took the N₂ molecules to be at rest, whereas in fact they're moving as fast as the oxygen molecule, approximately. This means that even if the O₂ is temporarily at rest, it can undergo a collision as an N₂ comes towards it. Clearly, what really counts in the collision rate is the *relative* velocity of the molecules.

Defining the average velocity as the root mean square velocity, if the O₂ has velocity \vec{v}_1 and the N₂ \vec{v}_2 , then the square of the relative velocity $\overline{(\vec{v}_1 - \vec{v}_2)^2} = \overline{v_1^2} - 2\overline{\vec{v}_1 \cdot \vec{v}_2} + \overline{v_2^2} = \overline{v_1^2} + \overline{v_2^2}$, since $\overline{\vec{v}_1 \cdot \vec{v}_2}$ must average to zero, the relative directions being random. So the average *square* of the relative velocity is twice the average square of the velocity, and therefore the average root-mean-square velocity is up by a factor $\sqrt{2}$, and the collision rate is increased by this factor. Consequently, the mean free path is *decreased* by a factor of $\sqrt{2}$ when we take into account that *all* the molecules are moving.

Our final result, then, is that the mean free path

$$l = \frac{1}{\sqrt{2}\pi d^2 n}.$$

Finding the mean free path is—literally—the first step in figuring out how rapidly the oxygen atoms will diffuse into the nitrogen gas, and of course vice versa.

What we really want to know is just how much we can expect the gases to have intermingled after a given period of time. We'll just follow the one molecule, and estimate how far it gets. To begin with, let's assume for simplicity that it takes steps all of the same length l , but after each collision it bounces off in a random direction. So after N steps, it will have moved to a point

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots + \vec{l}_N,$$

where each vector \vec{l}_j has length l , but the vectors all point in random different directions.

If we now imagine many of the oxygen molecules following random paths like this, how far on average can we expect them to have drifted after N steps? (note that they could with equal likelihood be going backwards!) The appropriate measure is the root-mean-square distance,

$$\overline{L^2} = \overline{(\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots + \vec{l}_N)^2} = Nl^2 + \sum_{i,j} \overline{\vec{l}_i \cdot \vec{l}_j}$$

Since the direction after each collision is completely random, $\overline{\vec{l}_i \cdot \vec{l}_j} = 0$, and the root-mean-square distance

$$\sqrt{\overline{L^2}} = \sqrt{N} l.$$

If we allow steps of different lengths, the same argument works, but now l is the root-mean-square path length.

The important factor here is the \sqrt{N} . Recall from above that $l \approx 60$ nm, or 6×10^{-8} m., and there are of order 10^{10} collisions per second. This means that the average distance diffused in

one second is $\sqrt{10^{10}} l = 10^5 l$, say half a centimeter. The average distance in one hour would be only 60 times this, or 30 cm., one foot, and in a day about five feet—the average distance traveled is only increasing as the *square root* of the time elapsed!

This is a very general result. For example, suppose we have a gas in which the mean free path is l and the average speed of the molecules is v . Then the average time between collisions $\tau = l/v$. The number of collisions in time t will be t/τ , so the average distance a molecule moves in time t will be $r = l\sqrt{t/\tau}$.

Why did Newton get the Speed of Sound Wrong?

A famous mystery cleared up by arguments like this was that Newton predicted the speed of sound would be given by $c^2 = B/\rho$, as we discussed earlier in the course, with B the bulk modulus. But when B was measured carefully by slowly compressing air, the result was in error by about 30%! The speed of sound predicted a higher (stiffer) bulk modulus.

The explanation turned out to be that in a slow measurement of the bulk modulus, the gas stays at the same temperature—the heating caused by slow compression leaks away. But if the compression is rapid, the gas heats up and so the pressure goes up more than if it had stayed at the same temperature. So the question is whether the compression and decompression as a sound wave passes through is so rapid that the heated-up gas doesn't have time to spread to the cooled regions. For sound at say 1000Hz, the wavelength is 34 cm. If compression heats gas locally, the hot molecules will diffuse away in a similar manner to that discussed above. They will be slightly faster than the average molecules. In 1/1000 th of a second, they will have 10^7 collisions, so will travel about $\sqrt{10^7} l \approx 3000l \approx 0.2 \text{ mm}$. This tiny distance compared with the wavelength of the sound wave means that during the compression/decompression cycles as the wave passes through, the heat has no chance to dissipate—so, effectively, it's like compressing a gas in an insulated container, it's harder to compress than it would be if the heat generated could flow away, and the bulk modulus is higher by an amount (around 30%) we shall work out in a forthcoming lecture.