PHY 171
Lecture 14
(February 16, 2012)

In the last lecture, we looked at a quantitative connection between macroscopic and microscopic quantities by deriving an expression for pressure based on the assumptions of the kinetic theory of gases. We found that

$$PV = \frac{1}{3} Nm \langle v^2 \rangle$$

In this form, the macroscopic quantities, pressure P and volume V are on the left, whereas the microscopic quantities — number of molecules N, mass of a molecule m, and average speed (squared) of all molecules $\langle v^2 \rangle$, are on the right. By comparing this equation to the Ideal Gas Law, we were able to show that the average kinetic energy $\langle K \rangle$ is equal to

$$\langle K \rangle = \frac{3}{2} k_{\mathrm{B}} T$$

where k_{B} is the Boltzmann constant, and T is the absolute temperature (in Kelvins). We interpreted this equation to mean that the higher the temperature, the faster the molecules are moving on the average.

We will now calculate the root mean square (rms) speed, which gives us an idea of how fast the gas molecules are moving on average.

Root mean square speed

Let us put back $\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle$ into the equation for $\langle K \rangle$ above, which then becomes

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_{\mathrm{B}} T$$

Rearranging terms, we get

$$\langle v^2 \rangle = \frac{3 k_{\mathrm{B}} T}{m}$$

Look carefully at the left hand side. We have the square of the velocity, and then we have written its mean (average) value. The square root of this quantity is called the root mean square (rms) speed, v_{rms}. That is,

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle}$$

It gives one way to characterize the typical speeds of gas molecules; we will look at two other ways below. Therefore, we find that the root mean square velocity v_{rms} is given by

$$v_{\mathrm{rms}} = \sqrt{\frac{3 k_{\mathrm{B}} T}{m}} \tag{L14.1}$$

In eq. (L14.1) above, T is the absolute temperature (in K), m is the mass of a single molecule, and k_{B} is the Boltzmann constant.

Example Calculation:

Let us calculate the rms speed for oxygen molecules at room temperature, usually taken to be 27°C, so that we get a rounded number for the Kelvin temperature of 300 K. Of course, 27°C (or 81°F) is a little higher than you'd want your room to be, but the rounded number of 300 K is too good to sacrifice for some imaginary discomfort!

It is a case of straightforward substitution in equation (L14.1), of course, but be careful about writing the mass m in the denominator. The easiest way is to multiply the atomic mass of oxygen by 2, and then by the mass of a proton to get m in kg. So

$$m = \Big(16 \times 2\Big)\Big(1.67 \times 10^{-27}\,\mathrm{kg}\Big)$$

This will give us:

$$v_{\mathrm{rms}} = \sqrt{\frac{3\left(1.38 \times 10^{-23}\,\mathrm{J/K}\right)300\,\mathrm{K}}{32\left(1.67 \times 10^{-27}\,\mathrm{kg}\right)}} = 482\,\mathrm{m/s}$$

This value is quite large, about 1100 miles per hr. One may well ask — if the molecules are moving so fast, why does it take so long to smell a perfume opened across the room (i.e., why doesn't the scent travel instantaneously across the room)? The answer is that this is due to collisions. Collisions between perfume molecules and air molecules do not allow molecules to move straight through the room. The perfume molecules suffer many collisions before reaching the person's nose at the other end of the room.

In fact, you read in the warm-up assignment how one can define a *mean free path* λ as the average distance between such collisions. If a molecule undergoes N_{coll} collisions as it travels distance L, then the average distance between collisions is given by the mean free path:

$$\lambda = \frac{L}{N_{\mathrm{coll}}} \tag{L14.2}$$

Page 543 of your text shows how N_{coll} can be determined from a simple model of two colliding spheres.

Note that the rms speed only tells us how fast the gas molecules are moving on average. Some molecules will be moving faster, others will be slower. In fact, even if you start out with all molecules having the same speed v, collisions will quickly change this state of affairs. We will demonstrate this below.

In reality, the speeds of molecules are distributed according to well known laws. Their distribution was worked out by Maxwell and Boltzmann.

Distribution of Speeds: Maxwell-Boltzmann Distribution

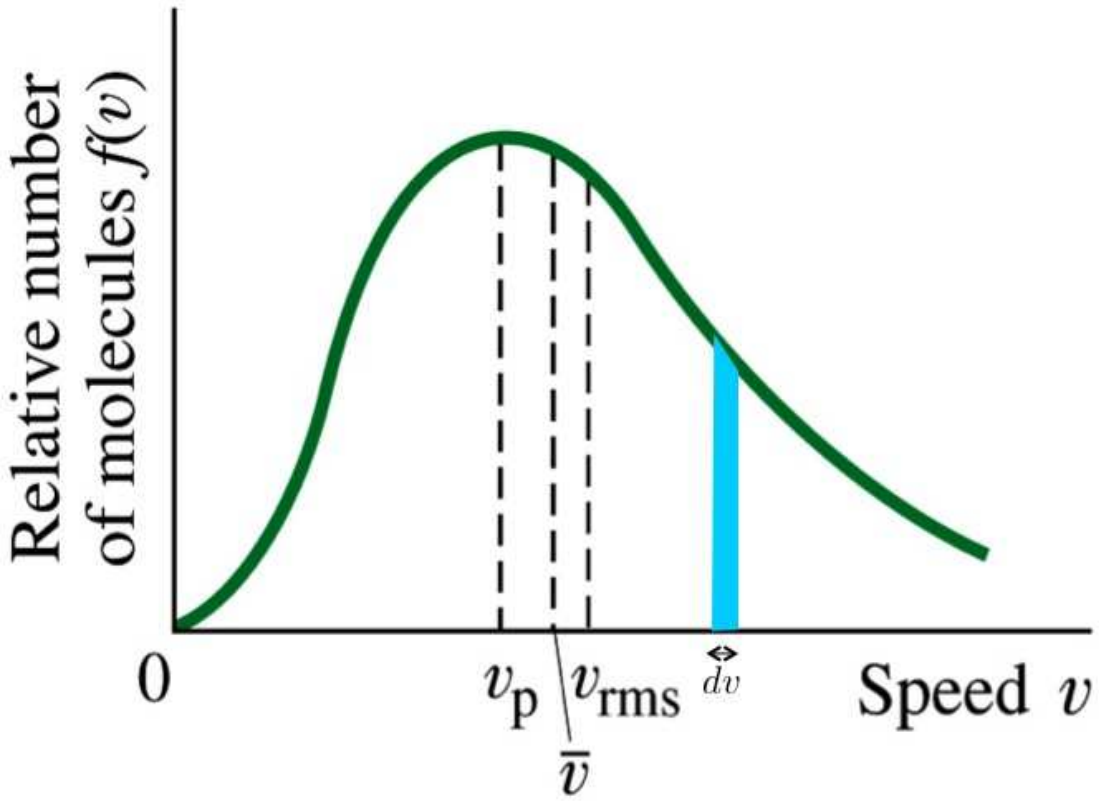
Think of the Maxwell-Boltzmann distribution as a probability distribution of the speeds of molecules in a gas. That is, if we pick a velocity v, the Maxwell-Boltzmann distribution tells us what fraction of molecules has velocity between v and $(v + dv)$.

The distribution function looks complicated, but we will write it down because it reveals one very important feature. The Maxwell-Boltzmann distribution of the velocities of gas molecules looks like:

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left[\frac{-mv^2}{2k_B T}\right] \tag{L14.3}$$

It is clear from eq. (L14.3) above that, for a given gas (i.e., once we have fixed the mass m), the Maxwell-Boltzmann distribution *depends only on the absolute temperature of the gas.*

A plot of the distribution in eq. (L14.3) is shown below. The distribution function $f(v)$ is plotted along the vertical axis, whereas the speed v is plotted along the horizontal axis.



What does the distribution function tell us? If we look at the blue rectangle of width dv, then its area $f(v)dv$ gives the fraction of molecules whose speeds lie in the interval v to $(v + dv)$.

Another way to think of $f(v)$ is to say that it is equal to $N(v)/N$, where N is the total number of molecules, and $N(v)$ is the number of molecules with speed v.

Based on our discussion above, we find that the fraction of molecules with speeds between v_1 and v_2 is

$$\int_{v_1}^{v_2} f(v)\,dv \tag{L14.4}$$

Since all molecules must have speeds between 0 and infinity, summing up the fraction $f(v)$ over this entire range of possible velocities must be equal to 1. That is

$$\int_0^{\infty} f(v)\,dv = 1 \tag{L14.5}$$

If we write $f(v) = \dfrac{N(v)}{N}$ as stated above, then another way of thinking about eq. (L14.5) is to say that

$$\int_0^{\infty} N(v)\,dv = N$$

where N is the total number of molecules.

Looking again at the plot of $f(v)$ *vs.* v, note how the distribution has very low tails on both sides. This makes sense: the distribution of velocities is established by collisions, and we do not expect too many molecules to have speeds much greater or much less than v_{rms}, because that would require an unlikely series of preferential collisions.

As stated above, if all the molecules of the gas had the same speed v, this situation would not last very long due to collisions. For a demonstration, look at the applet at

`comp.uark.edu/~jgeabana/mol_dyn`

— enter 300 in the top square and click `Set`, then click `Run` in the lower left corner — notice how the molecules quickly settle into the Maxwell-Boltzmann distribution, even when you start with an ordered distribution of particles.

Average speed, Most Probable speed, and RMS speed

In addition to the rms speed, two other speeds are used to characterize the velocity distribution of molecules in a gas. They are the average speed, and the most probable speed.

The ***most probable speed*** v_{p} is the speed at which $f(v)$ is a maximum. In other words, at any given temperature the number of molecules in a given speed interval increases with increasing speed up to a maximum given by v_{p}, then decreases asymptotically toward zero. Recall from calculus that such a maximum value is found by setting $df/dv = 0$, and then solving for v. If we do this, we will get

$$v_{\text{p}} = \sqrt{\frac{2k_{\text{B}}T}{m}} \tag{L14.6}$$

The most probable speed v_{p} is marked on the plot of the Maxwell-Boltzmann distribution shown above. Note that the distribution is not symmetrical about v_{p}. Why? It is because the lowest speed must be zero, but there is no classical limit to the upper speed a molecule can attain.

The ***average speed*** $\langle v \rangle$ is found by multiply v by the distribution $f(v)$, and integrating over all velocities; that is

$$\langle v \rangle = \int_0^\infty v\, f(v)\, dv \tag{L14.7}$$

If we substitute eq. (L14.3) and integrate, we will find for the average speed that

$$\langle v \rangle = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}} \tag{L14.8}$$

Clearly, the average speed (L14.8) is greater than the most probable speed (L14.6); see the plot of the Maxwell-Boltzmann distribution above where both velocities are marked. This is because the distribution is not symmetrical about the most probable speed, as we noted above. There are more molecules with speeds greater than the most probable speed, so the average shifts to a higher value than v_p.

We have already defined the rms speed v_rms above. Another way to think of it is to define it via the integral over v^2, namely

$$v_\mathrm{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^\infty v^2\, f(v)\, dv} \tag{L14.9}$$

As we have seen above, this gives us the expression

$$v_\mathrm{rms} = \sqrt{\frac{3k_\mathrm{B}T}{m}} \tag{L14.10}$$

Since it is based on the average of the squares of the speeds, v_rms will be greater than $\langle v \rangle$. Putting it all together

$$v_\mathrm{p} < \langle v \rangle < v_\mathrm{rms}$$

This is shown on the plot of the Maxwell-Boltzmann distribution above.

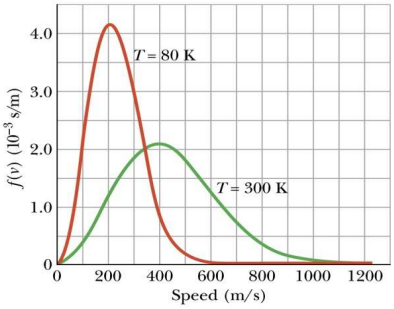
Maxwell-Boltzmann Distribution: Effect of Temperature Increase

We will now examine the effect of increase in temperature on the Maxwell-Boltzmann distribution.

As the temperature increases, the rms speed increases (as do the mean speed, and the most probable speed), as indicated by its formula above.

From the figure above, it is clear that the number of molecules that have speeds greater than some given speed increases as the temperature increases. This explains many phenomena, such as the rates of chemical reactions with rising temperature.

The range of typical speeds is now greater, so the distribution broadens. Since the area under the distribution curve gives the total number of molecules in the sample, it must remain the same. Therefore, the distribution must also flatten as the temperature rises. All of this is shown in the figure on the right. The brown curve is for $T = 80$ K, whereas the green curve is for a higher $T = 300$ K.



The distribution of speeds of molecules in liquids also resembles the M-B distribution. This explains evaporation, in which some molecules in a liquid can escape through the surface even when the temperature is very much below the boiling point. The molecules that are escaping are the fast ones at the high-velocity tail of the distribution. Since the molecules with high kinetic energy have escaped, the average kinetic energy of the remaining molecules drops, meaning that there is a drop in the temperature of the liquid. This explains the cooling effect of evaporation. (Note that if the surface area exposed is small, this cooling effect is often offset by the liquid absorbing heat energy from its surroundings to warm back up again). The authors present a discussion of this in explaining rain. They also present a discussion of the proton-proton chain in the Sun that causes nuclear reactions. Usually protons would repel each other, since they have the same (positive) charge; but high velocity protons in the tail are able to come together and cause the reaction.

Notice also in the M-B speed distribution formula that there is a mass dependence. The smaller the mass, the larger the proportion of high-speed molecules at a given temperature. You can also realize this by calculating rms speed — it is much greater for hydrogen than for oxygen. This explains why the Earth's atmosphere has little hydrogen in it, although the primordial Earth must have had quite a bit of it.

Internal Energy

Recall that we learned that temperature (in K) is a measure of the *average* kinetic energy of individual molecules. Below, we will see that the *total* energy of all the molecules in the object is called the **internal energy**.

Internal Energy of an Ideal Gas

Consider an ideal monatomic gas. The internal energy E_{int} of the gas is the sum of the translational kinetic energy of all the atoms. But this is just equal to the average kinetic energy per molecule times the total number of molecules N.

$$E_{\text{int}} = N\left[\frac{1}{2}m\left\langle v^2\right\rangle\right]$$

Now, recall that we have obtained previously:

$$\frac{1}{2}\,m\left\langle v^2\right\rangle = \langle K\rangle = \frac{3}{2}\,k_{\rm B}T$$

Therefore

$$E_{\rm int} = \frac{3}{2}\,Nk_{\rm B}T \qquad \text{or} \qquad E_{\rm int} = \frac{3}{2}\,nRT$$

where, as you should know from earlier discussions,

$\longrightarrow$ N is the number of molecules

$\longrightarrow$ $k_{\rm B}$ is the Boltzmann constant

$\longrightarrow$ n is the number of moles

$\longrightarrow$ R is the Universal Gas Constant

$\longrightarrow$ T is the absolute temperature in kelvin (K).

Therefore

- Internal energy of an ideal gas depends only on temperature and the number of moles of gas.
- If gas molecules contain more than one atom, we need to take into account rotational and vibrational energies also — then $E_{\rm int}$ will be greater at a given T than for a monatomic gas, but it will still be a function of temperature for an ideal gas.
- Likewise for real gases, but when they deviate from ideal gas behavior, $E_{\rm int}$ also depends somewhat on P and V.
- Things get more complicated for solids and liquids, becayse $E_{\rm int}$ must include electrical potential energy associated with the forces (or chemical bonds) between atoms and molecules.

Some parts of this lecture were delivered on Wednesday (Feb 15), but are written in these notes for continuity. The lecture today was shorter because a significant amount of class time was spent on the worksheet with concept questions.