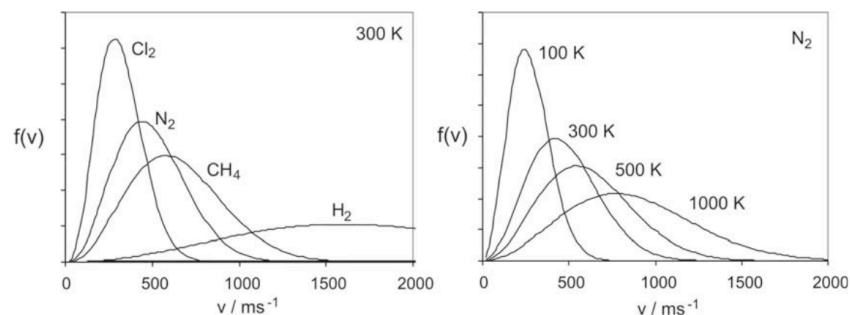


## The Distribution Of Molecular Speeds

In the previous section on the **kinetic theory of gases** we used the average velocity of the particles in a gas to derive the ideal gas equation. However, in a gas the particles do not all have the same velocity, rather they exhibit a distribution of molecular speeds. The distribution of molecular speeds  $f(v)$  in an ideal gas at thermal equilibrium is given by the Maxwell-Boltzmann distribution.

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

The distribution depends on the ratio  $m/T$ , where  $m$  is the mass of a gas particle and  $T$  is the temperature. The plots below show the Maxwell-Boltzmann speed distributions for a number of different gases at two different temperatures. As we can see, average molecular speeds for common gases at room temperature (300 K) are generally a few hundred metres per second.



We can make two observations:<sup>5</sup>

1. Increasing the temperature broadens the distribution and shifts the peak to higher velocities.

<sup>5</sup> A good java applet demonstrating these ideas can be found at:  
<http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm>

2. Decreasing the mass of the gas particles has the same effect as increasing the temperature (i.e. heavier particles have a slower, narrower distribution of speeds than lighter particles).

## The Maxwell-Boltzmann Distribution

To understand why the distribution of molecular speeds has this form, we must understand how this distribution is constructed. In the following version of the derivation much of the hard work is done by means of symmetry arguments.

### Maxwell's Symmetry Argument

First, we need a function that describes the likelihood of a particular particle in a gas having a particular speed.

A **probability distribution function** is an equation that links an outcome of an experiment with its probability of occurring. In our case, the probability that a gas particle has a velocity component  $v_x$  in the range  $v_x$  to  $v_x + dv_x$  is  $P(v_x)dv_x$ , where  $P(v_x)$  is an appropriate (and currently unknown) probability distribution function. If we can determine the functional form of  $P(v)$  in all three dimensions, we can work out the form of the distribution of molecular speeds.

As each velocity component may be treated independently, the total probability of finding a particle with components  $v_x$ ,  $v_y$ ,  $v_z$  in the range  $dv_x$ ,  $dv_y$ ,  $dv_z$  is the product of the probabilities for each component.

$$P(v_x, v_y, v_z)dv_x dv_y dv_z = P(v_x)dv_x P(v_y)dv_y P(v_z)dv_z$$

Since all directions within the gas are equivalent, we can argue that an alternative to the above distribution function is one in which the distribution function depends only on the total speed of the particle (i.e.  $P(v)$ ) not on each independent velocity component (i.e.  $P(v_x, v_y, v_z)$ ).

So, we need to figure out how to convert the above distribution function into one in terms of  $P(v)$ . An expression for the overall velocity is  $v^2 = v_x^2 + v_y^2 + v_z^2$  so we might construct a probability distribution function as  $P(v_x^2 + v_y^2 + v_z^2)$ , rather than  $P(v_x, v_y, v_z)$ .

Now, for any given speed these two functions must return the same probability, so we can conclude that

$$P(v_x^2 + v_y^2 + v_z^2) = P(v_x)P(v_y)P(v_z)$$

Notice that the sum of the variables on the left is related to the product of the functions on the right.

So what type of function would satisfy this equation? A **Gaussian** function satisfies this relationship (using the fact that  $e^{x+y+z} = e^x e^y e^z$ ). Thus, a suitable solution is:

$$P(v_x) = Ae^{-Bv_x^2}$$

The argument in the exponential is negative because in our model, the probability of finding a particle must decrease as we go to higher particle speeds.

Since  $P(v_x)$  is a probability distribution function, it must be normalised (i.e. the total probability must add up to one).

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x$$

and so

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2} dv_x$$

This definite integral is of a standard form

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

it is therefore straightforward to show

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2} dv_x = A\sqrt{\frac{\pi}{B}}$$

and hence,

$$A = \sqrt{\frac{B}{\pi}}$$

We obviously need another relation between  $A$  and  $B$  to complete our expression for  $P(v_x)$ .

We can also use our probability distribution function to calculate the mean squared speed in the  $x$  direction,  $\langle v_x^2 \rangle$

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 P(v_x) dv_x = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{\infty} v_x^2 e^{-Bv_x^2} dv_x$$

This integral also has a standard form

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

so we can solve, giving

$$\langle v_x^2 \rangle = \frac{1}{2B}$$

We can then use our result from the kinetic theory of gases to write an alternative expression for  $\langle v_x^2 \rangle$  and hence determine  $B$ .

Using classical equipartition again, for the single degree of freedom we are considering in  $x$ , we have

$$\frac{1}{2}k_B T = \frac{1}{2}m \langle v_x^2 \rangle$$

Therefore

$$B = \frac{m}{2k_B T}$$

Finally (!), we can write out our probability distribution function as

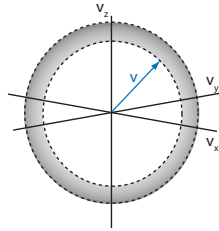
$$P(v_x) dv_x = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \exp \left( -\frac{mv_x^2}{2k_B T} \right) dv_x$$

This is the distribution only for one dimension, as we saw at the beginning of this section for three dimensions, we must multiply three identical distributions.

$$\begin{aligned}
 P(v_x, v_y, v_z) dv_x dv_y dv_z &= P(v_x)^3 dv_x dv_y dv_z \\
 &= \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp - \frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} dv_x dv_y dv_z \\
 &= \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp - \frac{mv^2}{2k_B T} dv_x dv_y dv_z
 \end{aligned}$$

The above expression gives the probability of the speed distribution having components  $v_x, v_y, v_z$ , whereas what we would really like to know is the probability  $P(v)dv$  that the molecular speed lies in the range  $v$  to  $v+dv$ .

This is simply the sum of the probabilities that a particle's velocity lies in range in the range  $v$  to  $v+dv$ . Imagine a 3D plot of  $v_x, v_y, v_z$  components. The range  $v$  to  $v+dv$  is a spherical shell in this plot of volume  $dv_x dv_y dv_z$ . This shell has a radius  $v$  and thickness  $dv$ .



The appropriate volume element for the distribution is therefore the volume of this shell, which is  $4\pi v^2 dv$ . We substitute this for the volume element  $dv_x dv_y dv_z$  in the above expression to give the final form for the Maxwell-Boltzmann distribution of molecular speeds.

$$P(v)dv = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp - \frac{mv^2}{2k_B T} dv$$

#### An Alternative Derivation of the Maxwell-Boltzmann Distribution

You will not cover **Statistical Thermodynamics** until your second year, when you will learn how the Boltzmann distribution describes how energy is distributed between identical but distinguishable particles.

$$f(E) = Ae^{-E/k_B T}$$

This expression can be used as the starting point to derive the Maxwell-Boltzmann distribution of molecular speeds without resorting to lengthy symmetry arguments.

Although **not formally a part of this course**, the derivation is included here for reference next year.

Considering the motion of gas particles as purely elastic collisions. For one-dimensional motion, the Boltzmann distribution is

$$f(v_x) = Ae^{-mv_x^2/2k_B T}$$

We must again normalise this distribution as the total probability of finding a particle must be equal to unity. We can make use of the definite integral

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

where we can substitute

$$x = \sqrt{\frac{m}{2k_B T}} v_x$$

to give

$$A \sqrt{\frac{2k_B T}{m}} \int_{-\infty}^{\infty} e^{-mv_x^2/k_B T} \sqrt{\frac{m}{2k_B T}} dv_x = 1$$

so

$$A = \sqrt{\frac{m}{2\pi k_B T}}$$

The one-dimensional distribution is thus

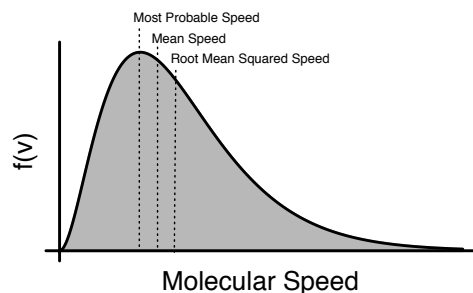
$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp - \frac{mv_x^2}{2k_B T}$$

Again, we must multiply three identical probability distribution functions and account for the density of velocity states available to particles (by multiplying by  $4\pi v^2$ ) to give the Maxwell-Boltzmann distribution of molecular speeds.

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

### Mean Speed, Most Probable Speed and Root-Mean-Square Speed

We can use the Maxwell Boltzmann distribution to determine the mean speed and the most probable speed of the particles in the gas.



Since the probability distribution is normalised, the mean speed is determined from the following integral:

$$\begin{aligned}\langle v \rangle &= \int_0^\infty v f(v) dv \\ &= \left( \frac{8k_B T}{\pi m} \right)^{1/2}\end{aligned}$$

We can find the most probable speed by maximising the distribution with respect to  $v$

$$\langle v_{\text{mode}} \rangle = \left( \frac{2k_B T}{m} \right)^{1/2}$$

For completeness, we can also quote again the root-mean-square speed we found in the previous section when we derived the kinetic theory of gases.

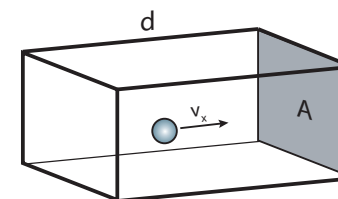
$$\langle v_{\text{rms}} \rangle = \left( \frac{3k_B T}{m} \right)^{1/2}$$

### Collision frequency

Collisions are one of the most fundamental processes in chemistry, and provide the mechanism by which both chemical reactions and energy transfer occur in a gas. The rate at which collisions occur determines the time scale of these events. The rate of collisions is usually expressed as a **collision frequency**, defined as the number of collisions a particle undergoes per unit time. We will use kinetic theory to calculate collision frequencies for two cases: collisions with the container walls; and intermolecular collisions.

#### Collisions With The Container Walls

We have already done much of the work required to calculate the frequency of collisions with the container walls. For a wall of area  $A$ , all particles in a volume  $A v_x \Delta t$  with positive velocities will collide with the wall in the time interval  $\Delta t$ . We can use our probability distribution  $P(v_x)$  to determine the average value  $\langle V \rangle$  of this volume



$$\begin{aligned}\langle V \rangle &= \int_0^\infty V P(v_x) dv_x \\ &= A \Delta t \int_0^\infty v_x \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-m v_x^2}{2k_B T}\right) dv_x\end{aligned}$$

We can solve this using the standard integral

$$\int_0^\infty x e^{-x^2} dx = \frac{1}{2}$$

yielding

$$\langle V \rangle = A \Delta t \left( \frac{k_B T}{2\pi m} \right)^{1/2}$$

Multiplying the result by the number density of particles,  $N/V = p/k_B T$ , yields the number of collisions occurring in the time interval  $\Delta t$ . For unit time and unit area ( $A = 1 \text{ m}^2$ ,  $\Delta t = 1 \text{ s}$ ), this yields a collision frequency,  $z_{\text{wall}}$

$$z_{\text{wall}} = \frac{p}{k_B T} \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{p}{(2\pi m k_B T)^{1/2}}$$

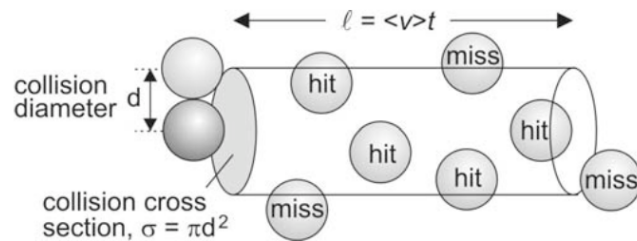
#### An Example, Your Desk

Calculate the number of collisions for air (i.e.  $\text{N}_2$  molecules) at 1 bar pressure and 298 K on a  $1 \text{ m}^2$  area (like your desk). [about  $2.9 \times 10^{27}$  collisions every second!]

#### Collisions Between Particles

To determine the number of collisions a particle undergoes with other particles per unit time, we need to introduce the concept of the **collision cross section**,  $\sigma$ . This is defined as the cross sectional area that the centres of two particles must lie within if they are to collide.

In our kinetic model, the particles act like hard spheres (there are no intermolecular forces) and a collision only occurs when the centres of two particles are separated by a distance equal to the particle diameter,  $d$ .



Imagine that we have 'frozen' the motion of all of the particles except one. We can see that this particle will only collide with particles whose centres are within the cross sectional area  $\sigma = \pi d^2$ . In a time interval  $\Delta t$ , this particle will move a distance  $\langle v \rangle \Delta t$ , represented by the length of the cylinder.

The number of collisions the particle undergoes in the time interval  $\Delta t$  will therefore be equal to the number density of particles in the gas,  $N/V = p/k_B T$ , multiplied by the volume  $\sigma \langle v \rangle \Delta t$  of the 'collision cylinder' the particle has sampled.

We want to know the number of collisions per unit time, so set  $\Delta t = 1 \text{ s}$ . Since the particles are not really stationary, we need to replace  $\langle v \rangle$ , the average speed of one particle in the gas, by  $\langle v_{\text{rel}} \rangle$ , the mean relative velocity of the gas particles.

The collision frequency is therefore:

$$z = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V} = \sigma \langle v_{\text{rel}} \rangle \frac{p}{k_B T}$$

This collision frequency,  $z$ , is the number of collisions made by a single particle per second. Usually what we would like to know is the total collision frequency, or collision density,  $Z$ ; the total number of collisions occurring in the gas per unit volume, so we must multiply by  $N/V$

$$Z = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V} = \sigma \langle v_{\text{rel}} \rangle \frac{p}{k_B T}$$

To progress we substitute the expression for the mean relative speed,  $\langle v_{\text{rel}} \rangle = \sqrt{2} \langle v \rangle$  that we derived earlier when considering the mean relative speed.

$$\begin{aligned} \langle v \rangle &= \int_0^\infty v f(v) dv \\ &= \left( \frac{8k_B T}{\pi m} \right)^{1/2} \end{aligned}$$

so the collision frequency is

$$Z = \frac{1}{2} \sigma \sqrt{2} \sqrt{\frac{8k_B T}{\pi m}} \left( \frac{N}{V} \right)^2$$

The additional factor of  $\frac{1}{2}$  in this expression ensures that we avoid double counting of each collision, so the collision of particle X with particle X' is counted as the same collision as that of X' with X.

Using the fact that we can relate concentrations  $[X]$  and number densities using  $[X]N_A = N/V$ , we can write this equation as

$$Z_{XX} = \sigma \left( \frac{4k_B T}{\pi m} \right)^{1/2} N_A^2 [X]^2$$

Collision densities can be enormous. As an example, for  $N_2$  gas under standard conditions, with a collision diameter of 0.28 nm,  $Z_{XX} = 5 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3}$ .

## Mean Free Path

The average distance a particle travels between collisions is called the mean free path,  $\lambda$ .

The time between collisions is just the inverse of the collision frequency ( $1/z$ ). If the particle is travelling at a mean speed  $\langle v \rangle$ , then (since distance = velocity x time) the mean free path is

$$\lambda = \frac{\langle v \rangle}{z}$$

At standard pressure and temperature, the mean free path is generally of the order of a few tens of nanometres. This is an order of magnitude larger than the average molecular separation, you can check this. Since  $z$  is proportional to pressure,  $\lambda$  is inversely proportional to pressure, e.g. doubling the pressure will halve the mean free path.

