8. KINETIC THEORY

We have spent the whole of this course considering equilibrium states and the thermodynamics of such states. At the very beginning we derived the relationship between pressure, volume and internal energy for a monatomic gas, $U = \frac{3}{2}PV$ using simple concepts from kinetic theory, that is by considering the collision and consequent momentum change of a gas molecule with the wall of its container as the source of the pressure of the gas. We also went on to consider energy exchange between the walls of the container and the gas and demonstrated that there is a net flow of energy from gas to container walls only when the gas was at a higher temperature than the container walls and not in equilibrium with the container. This was done through an argument due to Jeans. While considering the behavior of the microscopic components that make up the gas in these exercises and recognizing that any description of the microscopic behavior would need to recognize that the gas atoms were all possessing different velocities, it was the case that in these simple considerations the average velocity was the required quantity and no knowledge of the distribution was needed to obtain physical descriptions of how the atomistic behavior influenced the macroscopic state and its variables P and V. The thermodynamic equilibrium described by these state functions, that neither varied with time or position, is of course hiding a much more transient behavior at the microscopic level by virtue of the vast number of particles involved in the macrostate. If we could place ourselves at the atomic level all around us our world would be in flux with every atom rushing around doing its own thing sometimes in concert with a neighbour with whom it collides. As the equilibrium of the macrostate suggests, over time and in space the distribution of particle positions does not change. Neither does the distribution of speeds and velocities. But any ***individual*** particle is constantly changing position and velocity (momentum) as it collides with the others. It is this description of a system in flux that kinetic theory aims to open up to scrutiny.

8.1 Velocity & Speed Distributions

Maxwell-Boltzmann velocity distribution.

While the velocities of individual particles are continuously changing with time we expect the distribution of velocities to remain constant with fewer high speeds than lower and there being equal numbers of molecules moving in any given direction in the absence of potential fields and inhomogeneous particle distributions. If there are equal numbers of cars to north and south of Newport Pagnell on the M1 and no more reason to travel to London than Manchester then we expect the cars to be traveling with a speed distribution (more slow than fast and tending to zero at very high speeds or at zero speed the law notwithstanding) but the velocity is equally likely to be northbound as southbound!

To describe this complex situation requires some subtle arguments perhaps more complex than any we have so far undertaken.

We begin by introducing distribution functions for each component of the particle velocity as well as for the velocity vectors. These functions are $\boldsymbol{f_1(v_x)}$, $\boldsymbol{f_2(v_y)}$, $\boldsymbol{f_3(v_z)}$ and $\boldsymbol{f(\underline{v})}$ which are defined as follows;

$f_1(v_x)dv_x$ = The probability of finding the particle with an x component of velocity lying between $v_x \; and \; v_x + dv_x$ or in the velocity interval $(v_x, v_x + dv_x)$

$f_2(v_y)dv_y$ = The probability of finding the particle with a y component of velocity lying between $v_y \; and \; v_y + dv_y$ or in the velocity interval $(v_y, v_y + dv_y)$.

$f_3(v_z)dv_z$ = The probability of finding the particle with a z component of velocity lying between $v_z \; and \; v_z + dv_z$ or in the velocity interval $(v_z, v_z + dv_z)$

The distribution of velocity vectors is defined through

$f(\vec{v})dv_x dv_y dv_z = f(\vec{v})d^3\vec{v}$ = The probability of finding the particle with a velocity lying in the cell of volume $d^3\underline{\mathbf{v}} = dv_x dv_y dv_z$ containing $\underline{\mathbf{v}}$.

We have allowed for the possibility that the distributions are different for different directions.

By probability we mean the frequency of occurrence of the particular value of velocity if the same measurement is performed many times thus if we measure the *x* component of velocity of each of a large number of gas particles then $f_1(v_x)dv_x$ is to be understood as the fraction of those particles that had the value of *x* component of velocity lying between v_x *and* $v_x + dv_x$. The *f* would be smooth functions provided the interval $(v_x, v_x + dv_x)$ is large enough for the measurement to contain many molecules within that velocity range. There is a further requirement that the velocity component has some value over the range allowed and that then the *f* must add to one, this is the normalization condition and may be written formally as

$$\int_{-\infty}^{+\infty} f_1(v_x)dv_x = 1$$

$$\int_{-\infty}^{+\infty} f_2(v_y)dv_y = 1$$

$$\int_{-\infty}^{+\infty} f_3(v_z)dv_z = 1$$

and

$$\int f(\vec{v})d^3v = \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z f(\vec{v}) = 1$$

The function $f(\vec{v})$ depends on all three components , $f(\vec{v}) = f(v_x, v_y, v_z)$.

Because the molecules are continually in collision with the walls and with each other in an uncorrelated (random) manner we expect the overall probability of having components v_x , v_y and v_z to be simply the product of the three independent probabilities;

$$f(\vec{v}) = f_1(v_x)f_2(v_y)f_3(v_z)$$

We know that a gas is isotropic, it looks the same in all directions thus the distribution of positive x components of velocity must be the same as the distribution for negative x components ie.

$$f_1(+v_x) = f_1(-v_x)$$

$$f_1(+v_y) = f_1(-v_y)$$

$$f_1(+v_z) = f_1(-v_z)$$

That is they are all even functions and further our choice of the x, y and z axes was completely arbitrary and therefore f_1 , f_2 and f_3 must be identical functional forms.

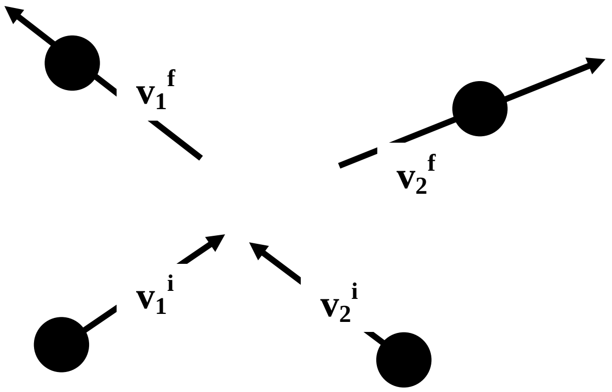
We can also say that because of the isotropic nature of a gas the function $f(\underline{\mathbf{v}})$ cannot depend on direction and that $f(\underline{\mathbf{v}}) = f(v)$ where $v = |\vec{v}| = \sqrt{\vec{v} \bullet \vec{v}}$.

Boltzmann gave an argument that allowed the detailed form of $f(\underline{\mathbf{v}})$ to be brought out, a result also known and derived independently by Maxwell. We begin by noting the fact that $f(v)$ is constant in time. This means that although every time a molecule collides it will change velocity from velocity v and bin $dv_x dv_y dv_z$ to velocity $v^{\prime}$ and bin $dv^{\prime}_x dv^{\prime}_y dv^{\prime}_z$ nevertheless in order that the distribution function remains unaltered there must be another molecule taking its place in the vacated bin. In other words as many molecules enter the bin $dv_x dv_y dv_z$ per unit time as leave it. This is quite a simple but subtle idea and is simply an article of book keeping. It will prove to be one of the most useful ideas in this derivation and is known as ***detailed balance***.

To understand the molecular collision we have the four conservation laws given to us by physics;

(i) Conservation of mass
(ii) Conservation of energy
(iii) Conservation of linear momentum
(iv) Conservation of angular momentum

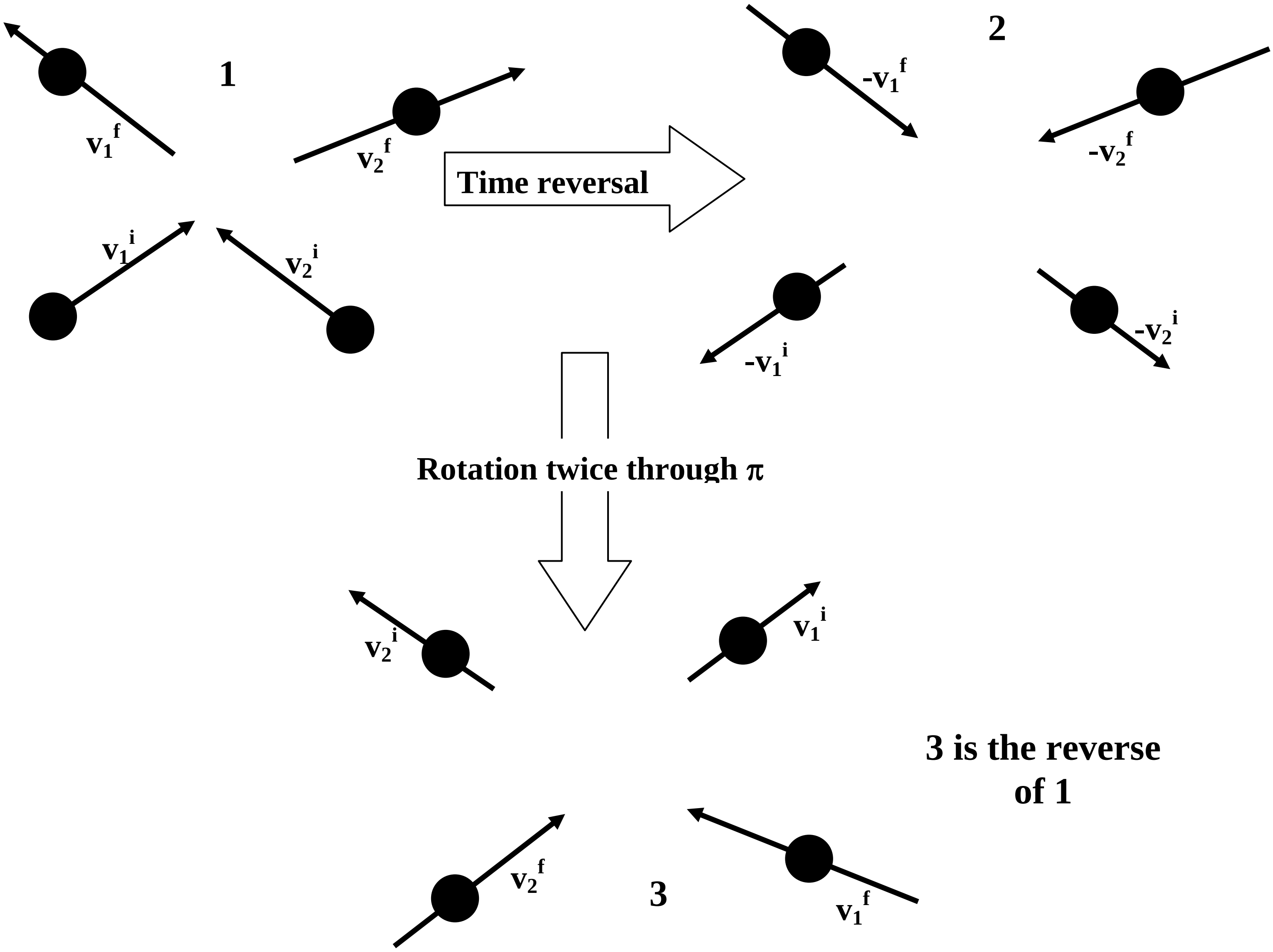
We can use the hard sphere approximation for our molecule, hard implying no potential interaction until just before and just after the collision, this allows us to express the conservation of energy in terms of kinetic energies before and after the collision. We consider a two body collision



The conservation of kinetic energy then requires

$$\frac{1}{2}mv_1^{i\,2}+\frac{1}{2}mv_2^{i\,2}=\frac{1}{2}mv_1^{f\,2}+\frac{1}{2}mv_2^{f\,2}$$

Kinetic energy is also conserved if the molecule collides with a wall. While linear momentum and angular momentum are conserved in all molecule-molecule collisions they are not conserved in molecule – wall collisions. Mass conservation is trivial in that it tells us that *m* = *m*. The only non-trivial conservation law that applies to collisions with both wall and other molecules is the kinetic energy conservation. Newtons laws also hold under time reversal and so any collision $\left\{v_1^i,v_2^i\right\}\Rightarrow\left\{v_1^f,v_2^f\right\}$ holds the possibility of the reverse collision $\left\{v_1^f,v_2^f\right\}\Rightarrow\left\{v_1^i,v_2^i\right\}$. We may see this by running the original collision backwards in time and then rotating it through π radians about their centre of mass in the plane of the collision as shown below.



***In dynamic equilibrium detailed balance demands equal probability of both the collision* 1 *and the reverse collision* 3.** There is no reason why nature should favour one over the other given the laws of physics that we know about. If they occur with equal probability this allows the loss of particles with velocities v_1^i and v_2^i in **collision 1** to be replaced by those final velocities in **collision 3** and also the gain of particles with velocities v_1^f and v_2^f in **collision 1** is offset by their loss in **collision 3** thus maintaining a strict detailed balance. We now need to make sure that **collision 1** and **collision 3** which are both allowed by Newtonian mechanics occur with equal probability

In order for collision **1,** $\left\{v_1^i, v_2^i\right\} \Rightarrow \left\{v_1^f, v_2^f\right\}$, to occur we of course require the molecules with these initial velocities and the number of pairs of molecules with these velocities is proportional to the product of the individual probabilities of finding each one separately (they are independent probabilities) ie.it is proportional to;

$$f\left(v_1^i\right)f\left(v_2^i\right)$$

and the number of reverse collisions, **3**, $\left\{v_1^f, v_2^f\right\} \Rightarrow \left\{v_1^i, v_2^i\right\}$, is proportional to;

$$f\left(v_1^f\right)f\left(v_2^f\right)$$

And the requirement for detailed balance is thus embodied in the equation

$$f\left(v_1^i\right)f\left(v_2^i\right) = f\left(v_1^f\right)f\left(v_2^f\right)$$

This ensures that as many molecules pass from v_1^i due to collision **1** as pass back into it due to collision **3 and detailed balance is maintained.**

We may take the log of each side to re-write the condition as

$$ln\ f\left(v_1^i\right) + ln\ f\left(v_2^i\right) = ln\ f\left(v_1^f\right) + ln\ f\left(v_2^f\right)$$

This appears to be an additive conservation law for the collision!

But we know that the only additively conserved quantities in these collisions is mass which is constant and kinetic energy (velocity dependent). This allows us to conclude that the correct form for ln$f(v)$ must be

$$ln\ f(v) = a - b\left(\frac{1}{2}mv^2\right)$$

where a and b are constants. A little thought shows this form to have the property demanded. The constant a must be kept for the time being as we have not yet formally precluded it. We can re-write this form for $f(v)$ by exponentiation to obtain

$$f(v) = A\,exp\left[-\frac{b}{2}mv^2\right]$$

We require the probability of very large velocities to be small, otherwise normalization would never be possible, and can therefore conclude that *b* is positive to obtain a negative or decreasing exponential. We can also see that the condition $f(v) = f(v_x)f(v_y)f(v_z)$ is satisfied by the above

$$f(v) = Ae^{-bmv^2/2} = Ae^{-bm(v_x^2+v_y^2+v_z^2)/2}$$

$$f(v) = \left(A^{1/3}e^{-bmv_x^2/2}\right)\left(A^{1/3}e^{-bmv_y^2/2}\right)\left(A^{1/3}e^{-bmv_z^2/2}\right) = f(v_x)f(v_y)f(v_z)$$

We may use the normalization condition to find *A*

$$\int f(\vec{v})d^3v = \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z\, f(v) = 1$$

$$\int f(\vec{v})d^3v = A\int_{-\infty}^{+\infty} e^{-bmv_x^2/2}\, dv_x \int_{-\infty}^{+\infty} e^{-bmv_y^2/2}\, dv_y \int_{-\infty}^{+\infty} e^{-bmv_z^2/2}\, dv_z = 1$$

Each of the above three integrals on the right hand side have the same form and are known as Gaussian integrals whose value we may look up and find

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

Using this in the triple integral we note

$$\alpha = \frac{bm}{2}$$

And using this in the given solution for the Gaussian integral we straightforwardly obtain

$$A\left(\sqrt{\frac{2\pi}{bm}}\right)^{3}=1$$

Re-arranging with *A* as the subject

$$A=\left(\frac{mb}{2\pi}\right)^{3/2}$$

Finally we need to find the unknown constant *b*.

We can do this by using the knowledge we have previously gained telling us that the average kinetic energy in a gas is related to its temperature as follows,

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}k_BT \ ,$$

We are able to calculate the average kinetic energy in terms of *f*(*v*) using the properties of a probability distribution function,

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \iiint \frac{1}{2}mv^2 f(v)dv_xdv_ydv_z = \frac{3}{2}k_BT$$

$$\left\langle \frac{1}{2}mv^2 \right\rangle = A\int_{-\infty}^{+\infty} \frac{1}{2}mv^2 e^{-bmv^2/2}\, d^3v = \frac{3}{2}k_BT$$

Looking at the structure of the integrand we note that it is possible to re-write each component of the triple integral as follows

$$I_x = A^{1/3}\int_{-\infty}^{+\infty} \frac{1}{2}mv_x^2 e^{-bmv_x^2/2}\, dv_x$$

The above is the component of the kinetic energy due to translational motion in the x direction.

By use of the observation

$$\frac{\partial}{\partial b} e^{-bmv_x^2/2} = -\frac{1}{2} m v_x^2 e^{-bmv_x^2/2}$$

we may rewrite the integral of interest as

$$I_x = -A^{1/3} \frac{\partial}{\partial b} \int_{-\infty}^{+\infty} e^{-bmv_x^2/2} \, dv_x$$

The integral is again, the Gaussian integral whose solution we know

$$I_x = -A^{1/3} \frac{\partial}{\partial b} \left(\frac{2\pi}{mb} \right)^{1/2}$$

$$I_x = \frac{1}{2} A^{1/3} \left(\frac{2\pi}{m} \right)^{1/2} b^{-3/2}$$

The entire integral is the sum of three of these (one for each translational degree of freedom, $I = I_x + I_y + I_z$

$$\frac{3}{2} A^{1/3} \left(\frac{2\pi}{m} \right)^{1/2} b^{-3/2} = \frac{3}{2} k_B T$$

We know *A* already in terms of *b* and use this next to obtain

$$\frac{3}{2} \left(\frac{mb}{2\pi} \right)^{1/2} \left(\frac{2\pi}{m} \right)^{1/2} b^{-3/2} = \frac{3}{2} b^{-1} = \frac{3}{2} k_B T$$

giving for *b*

$$b = \frac{1}{k_B T}$$

We are now in a position to bring everything together to get the velocity distribution function

$$f(v) = A\,exp\left[-\frac{b}{2}mv^2\right] = \left(\frac{m}{2\pi k_B T}\right)^{3/2} exp\left[-\frac{mv^2}{2k_B T}\right]$$

The Maxwell-Boltzmann Velocity Distribution

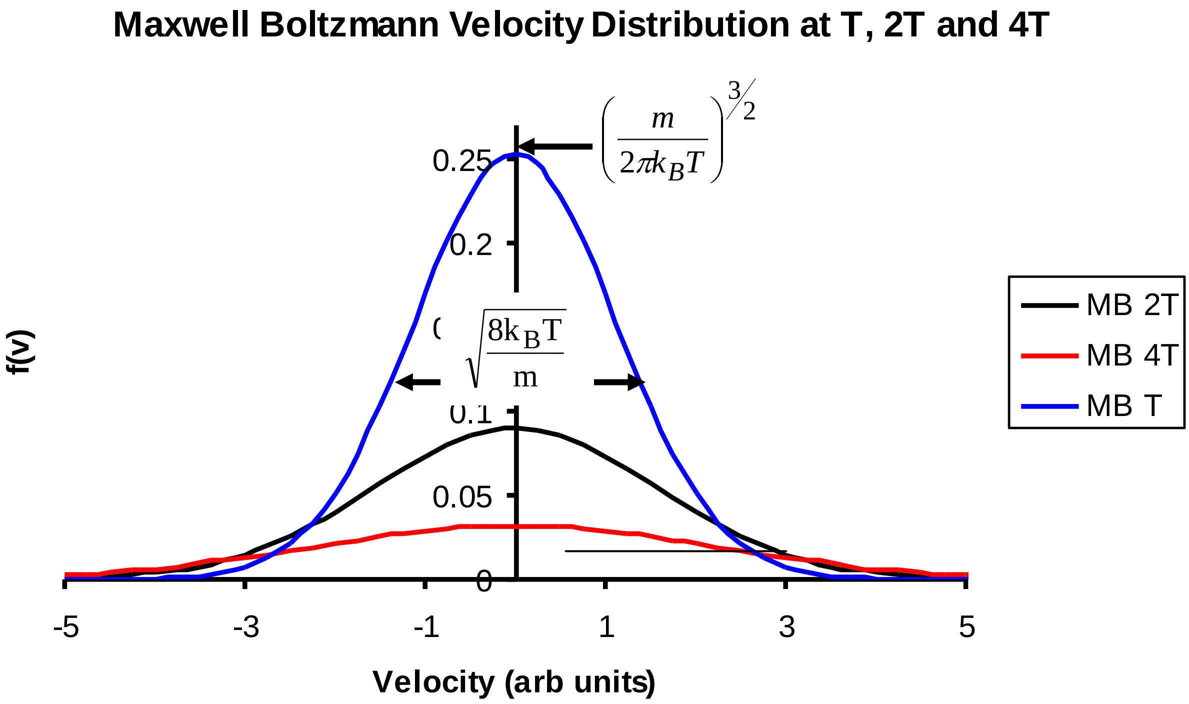
We obtained this velocity distribution by using the following physics;

(i) A simple application of detailed balance
(ii) The conservation laws, specifically conservation of energy
(iii) Time reversal and rotational symmetry of Newton's laws.

The dilute gas has zero potential interaction and therefore, for a particular molecule the kinetic energy is its total energy, *E*, $\frac{1}{2}mv^2 = E$ and we may see the Maxwell-Boltzmann distribution in terms of the probability that a molecule has an energy, *E*

$$P(E) \propto exp\left(-\frac{E}{k_B T}\right)$$

The exponential factor is known as the **Boltzmann factor or the Boltzmann-Gibbs factor** and it appears throughout all strands of physics (and physical chemistry). We note that its appearance here was arrived at in a very general way. It will be found in classical systems and in quantum systems as a description of the probability that in equilibrium at temperature *T* the system has energy *E*. Indeed we have already seen it in our discussions on paramagnets and the energy of alignment in external magnetic fields.



The Maxwell-Boltzmann velocity distribution is a Gaussian function of the type $y = A exp\left(-\frac{(x-x_0)^2}{\sigma^2}\right)$ as shown above. The Gaussian function as written in this general form has three basic parameters describing it as follows;

- (i) A is the maximum value at the peak of the distribution,
- (ii) 2σ, is a measure of its width where the value of the Gaussian has fallen to $\frac{1}{e}$ of the peak value when $(x - x_0) = \sigma$. and
- (iii) x_0 is where the maximum occurs.

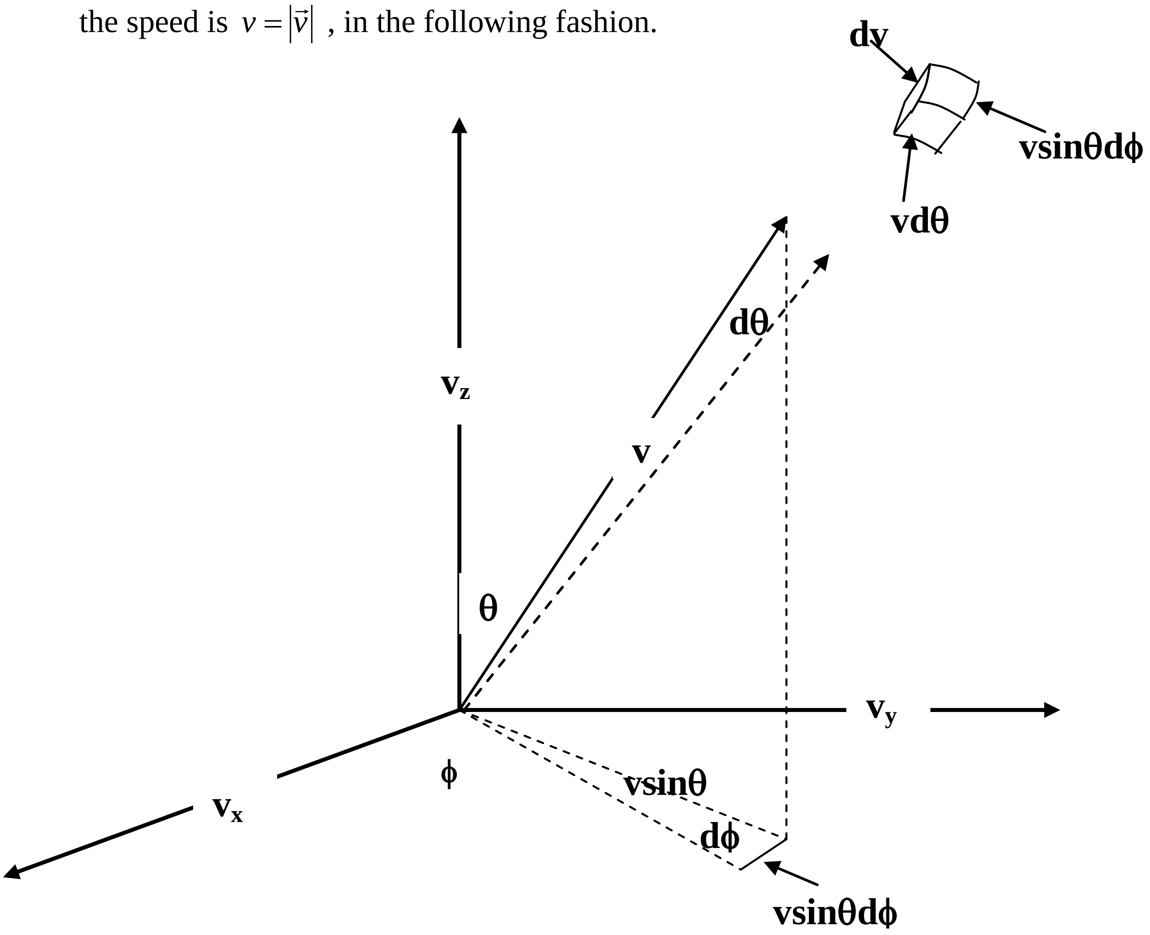
In the case of the Maxwell Boltzmann distribution it is worth noting that the maximum value of the distribution function appears at $v = 0$ ie. $v = 0$ is the most likely value for the velocity!

The width of the distribution function is $\Delta v = \sqrt{\frac{8k_BT}{m}}$.

For values of v beyond $v = \sqrt{\frac{2k_BT}{m}}$ the probability $f(v)$ falls very rapidly to zero.

The speed distribution.

We may want to know something quite different however. For many physical problems we will want the most probable speed and it is important to realize that this is not zero. To find the most probable speed, where we are not interested in the direction at all, requires a further tweaking of the Maxwell-Boltzmann velocity distribution function. $f(v)\mathrm{d}^3v$ gives us the probability that the velocity vector lies in a cell at v with volume $\mathrm{d}v_x dv_y dv_z$ and we now use this to find the probability $P(v)$ that the speed is $v = |\vec{v}|$, in the following fashion.



In Cartesians the element volume is $\mathrm{d}^3v = dv_x dv_y dv_z$ and in spherical polar coordinates with the angles defined in the diagram above, this becomes

$$d^3v = v^2 dv \sin\theta d\theta d\phi$$

We recall that $f(v)\mathrm{d}^3v$ gives the probability that the velocity lies within that cell. Now we don't care in which direction the velocity arrow in the above diagram is pointing as long as it has length v, so keeping this length (v) fixed we can vary the angles θ

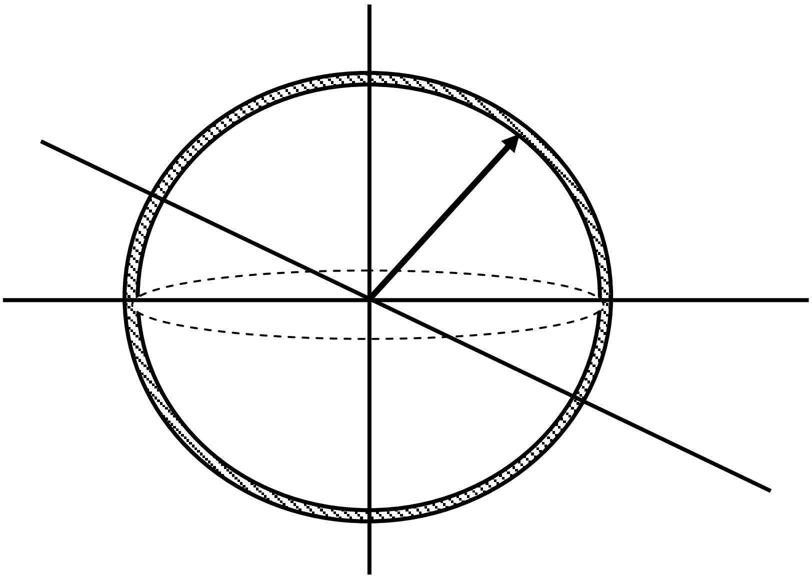
and ϕ and carry out an integration over the appropriate limits to find the probability to be in any volume element that lies at a distance (speed) v from the origin

$$P(v)dv = f(v)v^2 dv \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$\int_0^{\pi} \sin\theta d\theta = (-\cos\theta)_0^{\pi} = 2 \qquad \int_0^{2\pi} d\phi = 2\pi$$

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

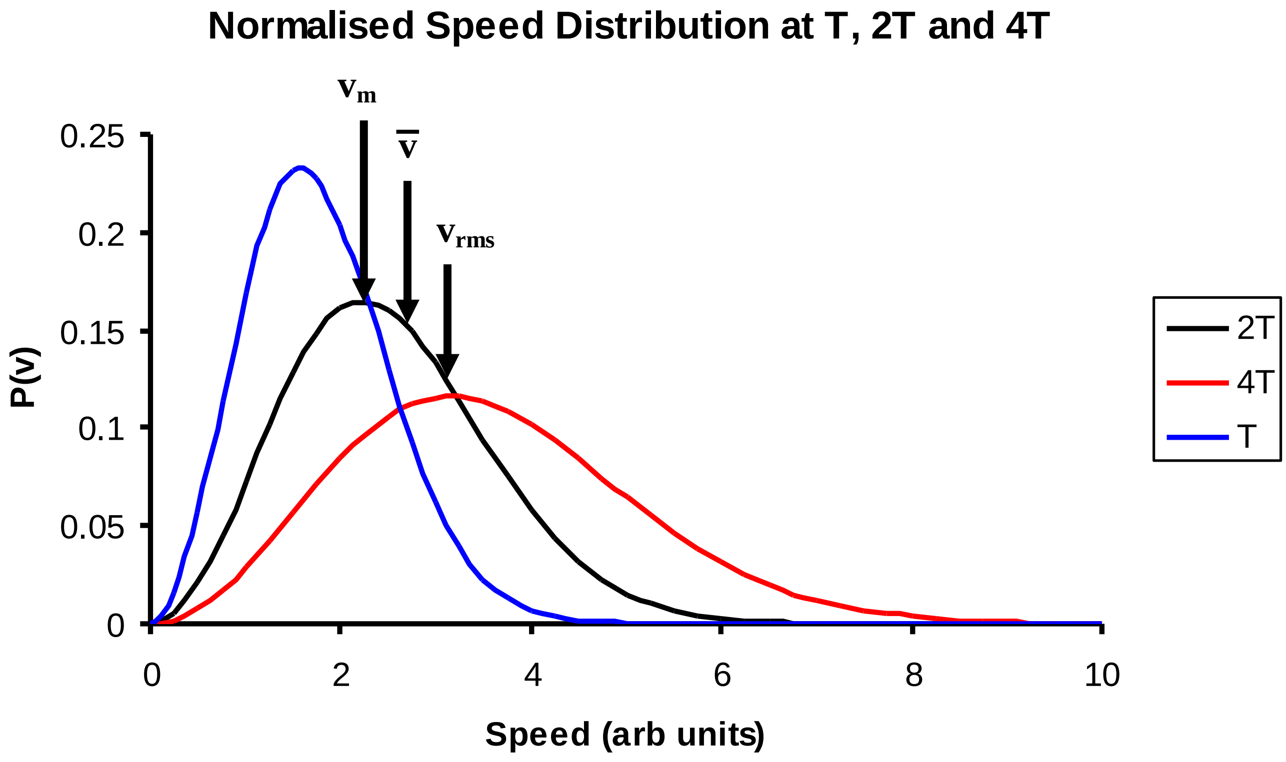
The Speed Probability Distribution.



The above diagram indicates in a geometric argument how the expression for $P(v)$ comes about in terms of $f(v)$. Consider the sphere and its associated shell lying with velocity (radius)between v and $v + dv$. The velocity distribution, $f(v)$ gives the probability that the arrow pointing in a particular direction lies in a velocity volume element $dv_x dv_y dv_z$. For the speed distribution we only care that the arrow has a length v and ends somewhere within the volume defined by the shell whose volume is

$4\pi v^2$dv. Hence the relationship between $P(v)$ and $f(v)$, $P(v)=4\pi v^2 f(v)$. The speed probability distribution $P(v)$ still has the Gaussian function in it but it is this time moderated by the v^2 factor that gives the distribution an entirely different shape.

The major difference between the velocity distribution and the speed distribution is the fact that while the velocity distribution has a most probable velocity of zero, the probability of having a speed of zero is zero. The v^2 factor in the speed distribution makes sure that this is the case. We can see why it should happen by considering how the speed distribution comes about. In terms of the volume of our spherical shell between $v \text{ and } v+dv = 4\pi v^2 dv$ containing the gas molecules whose speed is v. As v tends to zero the volume of this shell goes to zero even while the probability that a molecule has a velocity component at zero tends to a maximum.



We can ask "what is the velocity of a typical gas molecule in a gas at a particular temperature". There are several possible answers we might give to this question as follows;

(i) The ***root mean square velocity*** might be given, v_{rms}. This we have seen previously when obtaining the relation between temperature, kinetic energy and internal energy.

$$v_{rms} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3k_BT}{m}} = 1.73\sqrt{\frac{k_BT}{m}}$$

We may check this directly from the speed distribution function by finding the mean square speed and taking the square root as follows;

$$\left\langle v^2 \right\rangle = \int_0^\infty v^2 P(v)dv$$

$$\left\langle v^2 \right\rangle = 4\pi\left[\frac{m}{2\pi k_BT}\right]^{3/2}\int_0^\infty v^4\, exp\left(-\frac{mv^2}{2k_BT}\right)dv$$

The integral may be found using the results for the standard integral;

$$I_j = \int_0^\infty x^j\, exp\left(-\alpha x^2\right)dx$$

with the standard results

$$I_0 = \sqrt{\frac{\pi}{4\alpha}}, \quad I_1 = \frac{1}{2\alpha}, \qquad I_{2n} = \frac{2n-1}{2\alpha}I_{2n-2}, \quad I_{2n+1} = \frac{n}{\alpha}I_{2n-1}$$

From these results we have

$$I_4 = \frac{4-1}{2\alpha}I_2 = \frac{4-1}{2\alpha}\frac{1}{2\alpha}\sqrt{\frac{\pi}{4\alpha}} = \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}}$$

Writing

$$\alpha = \frac{m}{2k_BT}$$

$$\left\langle v^2 \right\rangle = 4\pi\left[\frac{m}{2\pi k_BT}\right]^{3/2}\frac{3}{8}\left[\frac{\pi(2k_BT)^5}{m^5}\right]^{1/2}$$

$$\left\langle v^2 \right\rangle = \frac{3}{2}\left[\frac{m}{2k_BT}\right]^{3/2}\left[\frac{2k_BT}{m}\right]^{5/2} = \frac{3}{2}\left[\frac{2k_BT}{m}\right]$$

$$v_{rms} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3k_BT}{m}} \qquad \textbf{\textit{QED}}$$

(ii) We might also give the ***mean speed*** $\bar{v}$ defined as

$$\bar{v} = \int_0^\infty vP(v)dv = \sqrt{\frac{8k_BT}{\pi m}} = 1.59\sqrt{\frac{k_BT}{m}}$$

To carry out the above integral in order to find $\bar{v}$ we make substitutions as follows;

$$\bar{v} = 4\pi\left[\frac{m}{2\pi k_BT}\right]^{3/2}\int_0^\infty v^3\, exp\left(-\frac{mv^2}{2k_BT}\right)dv$$

Making the substitution $v^2 \to x$, dv = $\frac{dx}{2v}$ and writing $a = \frac{m}{2k_BT}$

$$\bar{v} = 4\pi\left[\frac{a}{\pi}\right]^{3/2}\frac{1}{2}\int_0^\infty x\, exp(-ax)dx = 2\pi\left[\frac{a}{\pi}\right]^{3/2}\int_0^\infty x\, exp(-ax)dx$$

We can find this integral by integrating by parts; $\int udv = uv - \int vdu$

$$u = x \qquad dv = e^{-ax}$$

$$du = dx \qquad v = -\frac{1}{a}e^{-ax}$$

$$\int udv = \int xe^{-ax} = -\frac{x}{a}e^{-ax} - \int -\frac{1}{a}e^{-ax}dx$$

$$\int_0^\infty xe^{-ax}dx = \left[-\frac{x}{a}e^{-ax} - \frac{1}{a^2}e^{-ax}\right]_0^\infty = \frac{1}{a^2}$$

$$\bar{v} = 2\pi\left[\frac{a}{\pi}\right]^{3/2}\frac{1}{a^2} = \sqrt{\frac{4}{\pi a}} = \sqrt{\frac{8k_BT}{\pi m}}$$

Alternatively we could use the standard integrals given earlier when finding v_{rms} and using a similar method write

$$\bar{v} = \int_0^\infty vP(v)dv$$

$$\bar{v} = 4\pi\left[\frac{m}{2\pi k_BT}\right]^{3/2}\int_0^\infty v^3\, exp\left(-\frac{mv^2}{2k_BT}\right)dv$$

The integral we recognize as I_3 with $\alpha = \dfrac{m}{2k_BT}$ and using $I_3 = I_{2n+1}$ for n = 1 and the standard integral

$$I_{2n+1} = \frac{n}{\alpha}I_{2n-1} = \frac{1}{\alpha}I_1 = \frac{1}{2\alpha^2} = \frac{1}{2}\left(\frac{2k_BT}{m}\right)^2$$

giving

$$\bar{v} = 4\pi\left[\frac{m}{2\pi k_BT}\right]^{3/2}\frac{1}{2}\left[\frac{2k_BT}{m}\right]^2 = 2\left[\frac{2k_BT}{\pi m}\right]^{1/2} = \left[\frac{8k_BT}{\pi m}\right]^{1/2} \qquad \textit{\textbf{QED}}$$

(iii) Finally we could offer ***<u>the most probable or mode speed</u>***, v_m , which is the value of *v* at which *P*(*v*) has its maximum.

$$v_m = \sqrt{\frac{2k_BT}{m}} = 1.4\sqrt{\frac{k_BT}{m}}$$

This may be demonstrated by differentiating *P*(*v*) wrt *v* and finding the maximum.

$$\frac{dP(v)}{dv} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\frac{d}{dv}\left(v^2\, exp\left(\frac{-mv^2}{2k_BT}\right)\right)$$

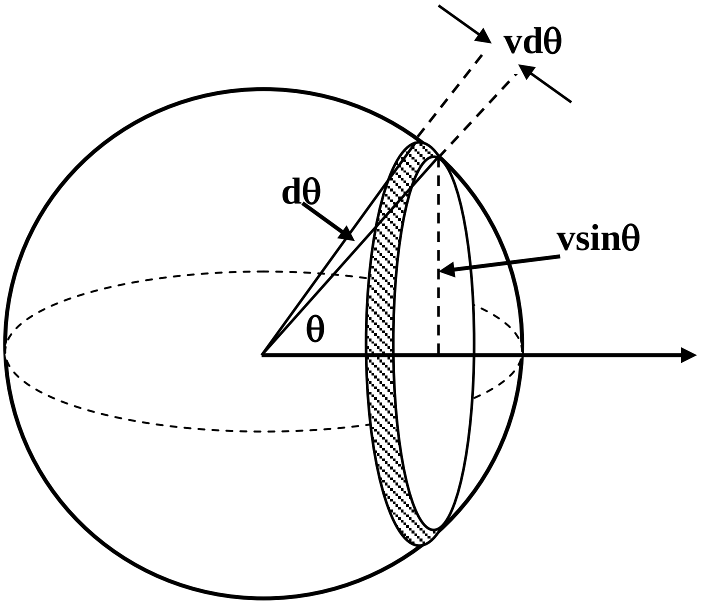
$$\frac{dP(v)}{dv} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\left[2v\, exp\left(\frac{-mv^2}{2k_BT}\right) - v^2\frac{m}{2k_BT}2v\, exp\left(\frac{-mv^2}{2k_BT}\right)\right] = 0$$

$$1 = \frac{mv_m^2}{2k_BT}$$

$$v_m = \sqrt{\frac{2k_BT}{m}}$$

8.2 Bouncing off the walls.

We have already seen how the constant collision of molecules of a gas in equilibrium with the walls of the container confining them provides the pressure which pushes outwards against the walls. We need to know for a number of purposes about the flux of particles onto a surface, that is the number of particles hitting a unit area of that surface per unit time. Now that we have the speed distribution function we can obtain a precise estimate of this flux which we now proceed to do.



Consider the sphere shown above in velocity space with a radius *v*. An annulus representing an area of the sphere at an angle between θ and $\theta + \mathrm{d}\theta$ wrt a direction of interest (the arrow) is shown. This has an area

$$A_{annulus} = 2\pi v \sin\theta v d\theta = 2\pi v^2 \sin\theta d\theta$$

Whereas the whole of the sphere representing the molecules traveling in all directions has an area

$$A_{sphere} = 4\pi v^2$$

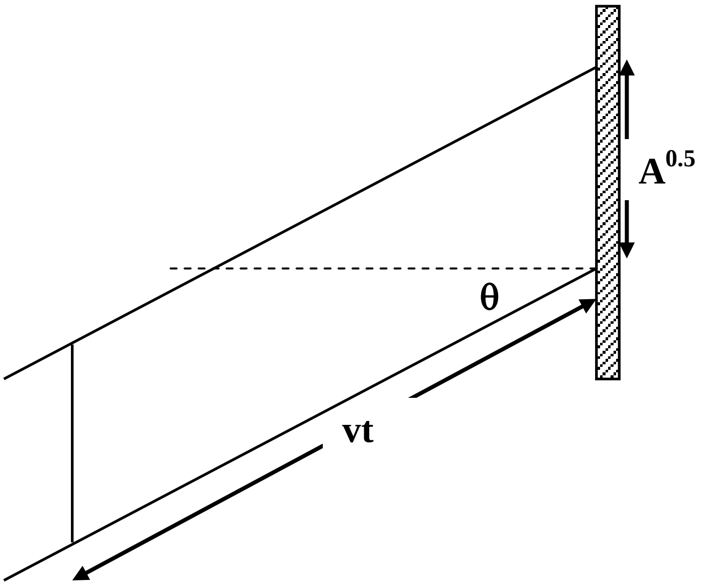
Considering that the gas is isotropic and the molecule is equally likely to be traveling in any direction there is therefore a fraction *F* of molecules traveling at a particular angle between θ *and* $\theta + d\theta$ with speed, *v*, given by

$$F = \frac{1}{2} \sin\theta d\theta$$

The number of molecules per unit volume with speed between v *and* $v + dv$ is simply found from the speed distribution function as $n(v) = nP(v)$. The number of these, $n(v,\ \theta)$, traveling between θ *and* $\theta + d\theta$ is then

$$n(v,\theta) = nP(v)dv \frac{1}{2} \sin\theta d\theta$$

where *n* is the total number of molecules per unit volume at all velocities.



We may now specify the direction of interest by asking for the molecules to travel at an angle θ to the normal to the wall with a velocity *v*, intercepting the wall in an area *A*. The above diagram shows the situation in 2D. The volume of the oblique cylinder swept out by the set of molecules traveling at speed *v* in time *t* , is

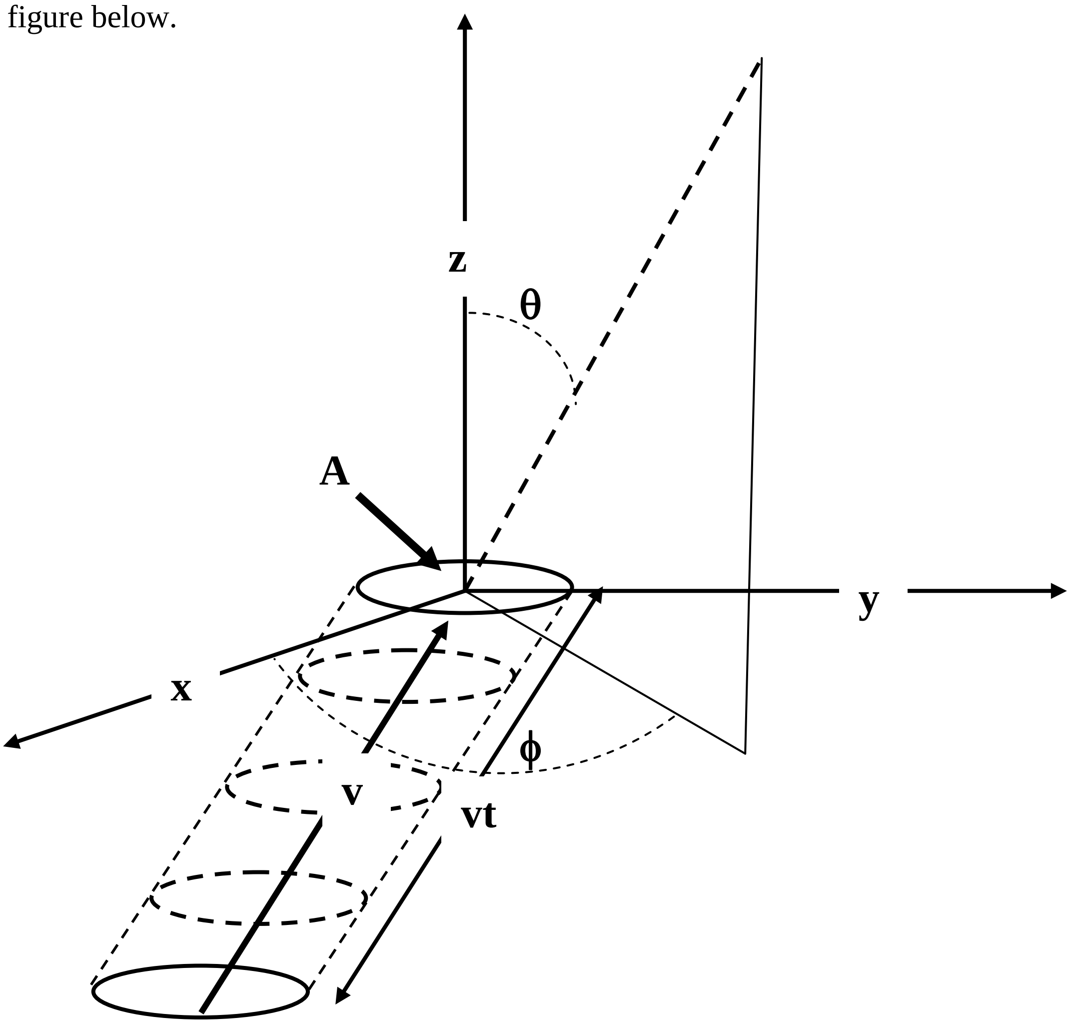
$$V = Avt\cos\theta$$

Where $A\cos\theta$ is the cross section area of the cylinder perpendicular to the axis
The number of molecules traveling in this volume at angle θ to the wall with velocity *v* and bouncing off the wall is then given by

$$N(v,\theta) = VnP(v)dvF$$

$$N(v,\theta) = Avt\cos\theta nP(v)dv\frac{1}{2}\sin\theta d\theta$$

We can picture this situation in 3D, choosing our coordinate system such that the wall lies in the *x*-*y* plane with the gas lying below the wall, *z* , 0. This situation is depicted in the figure below.



We are looking for the flux, Φ , of molecules colliding with the wall (number of molecules per unit time per unit area). This will require an integral over all possible speeds and all possible angles.

$$\Phi = \int \frac{N(v,\theta)}{At} = \frac{n}{2}\int_0^\infty vP(v)dv \int_0^{\pi/2} \cos\theta \sin\theta d\theta$$

To understand the limits on the integrals refer to the earlier diagram of the annulus and note that we need only consider θ from 0 to $\pi/2$ ***<u>to include all forward directions</u>*.** We begin to evaluate the integral by noting and using the definition of the mean velocity, $\bar{v} = \int_0^\infty vP(v)dv$

The integral over angles can be achieved by the substitution $u \Rightarrow \cos\theta$ and $\frac{du}{d\theta} \Rightarrow -\sin\theta$

This allows us to write the integral as

$$\int_0^{\pi/2} \cos\theta \sin\theta d\theta = -\int u \sin\theta \frac{du}{\sin\theta} = -\frac{u^2}{2} = -\frac{\cos^2\theta}{2}\Bigg|_0^{\pi/2} = \frac{1}{2}$$

We now have the flux as desired

$$\Phi = \frac{1}{4} n\bar{v}$$

We can use the expression for the mean speed of a molecule in a gas at temperature T to get the flux bouncing off the wall in terms of temperature

$$\Phi = \frac{1}{4} n\bar{v} = \frac{1}{4} n\sqrt{\frac{8k_B T}{\pi m}}$$

If the gas is an ideal gas with the usual equation of state, $PV = Nk_BT$ ($nR = Nk_B$) then

$$n = \frac{N}{V} = \frac{P}{k_B T}$$

$$\Phi = \frac{1}{4} n \sqrt{\frac{8k_BT}{\pi m}} = \frac{P}{\sqrt{2\pi m k_B T}}$$

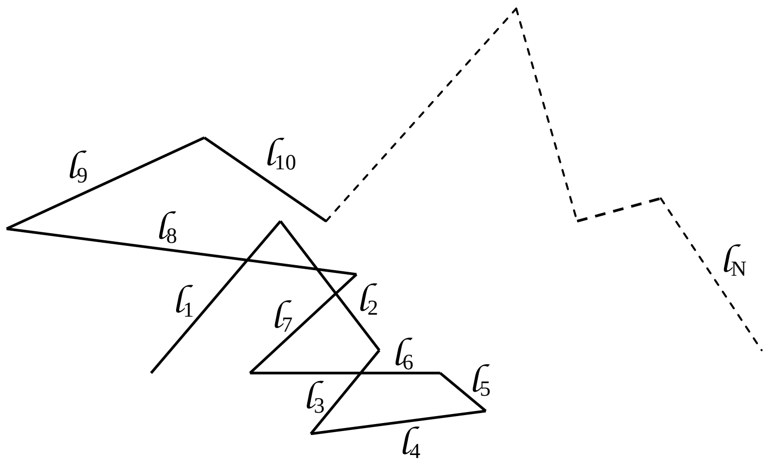
NB we have two n's in the last simplification, the n as representing the number of moles of gas in the ideal gas equation of state briefly made an appearance in brackets and n that represents the number density of molecules, the one that matters for this and subsequent discussion.

8.3 Colliding with other molecules (the mean free path).

We can now look at the frequent collisions that must occur even in a dilute gas in order that we can speak of mean velocities or distributions or equilibrium.

These collisions are essential for mass, momentum and energy transport within the gas. These microscopic transport processes are closely related to macroscopic processes such as diffusion, viscosity and thermal conductivity. If there were no collisions the transport of mass, momentum and energy would occur at speeds typical of the mean molecular velocity $\bar{v}$. They are in fact very much slowed due to intermolecular collisions and the speed at which they occur is closely related to the frequency of inter molecular collision, something which is defined by a property called the ***mean free path.***

The trajectory of a particular molecule in a dilute gas may look something like the schematic trajectory shown below.

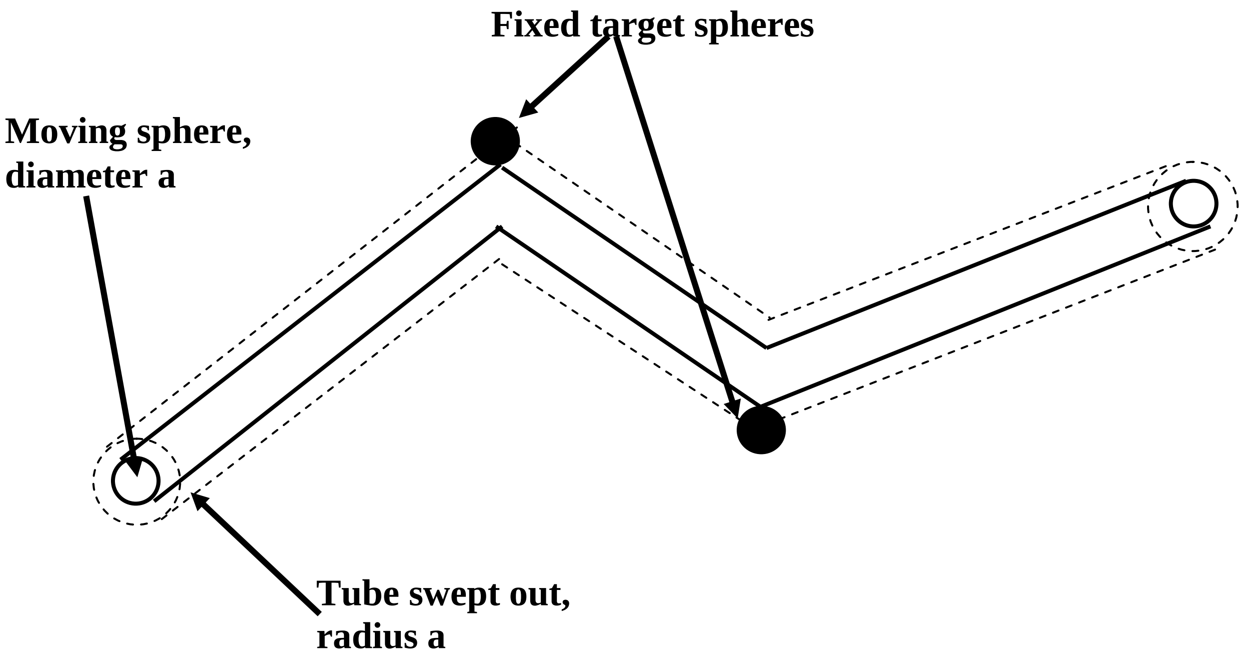


The trajectory is made up of a series of straight line segments interrupted after some length, ℓ by collision, resulting in change of direction. The actual distance traveled, $\mathcal{L} = \sum_i \ell$ is considerably greater than the actual distance traversed in real space due to this frequent change of direction hence the reduced speed of transport processes. We can look at this more closely by defining an average distance traveled between collisions, λ, called the mean free path defined as

$$\lambda = \frac{\sum_i^N \ell_i}{N}$$

where N is the number of segments and ℓ_i is the length of free flight on segment i. To get a reproducible value for λ under given conditions, of eg temperature and pressure, a large number of segments would be taken.

The value of λ depends on the size of the molecules or on the range of the forces between them, ie they present an area to other molecules within which, if the other molecule trespasses it can be deemed to have collided with (felt the influence of) the other molecule. We assume the molecules to be hard spheres with a disc of area σ fixed to them so that as they travel on their trajectories they etch out a series of parallelepipeds as shown below



The diagram shows a **molecule represented as a sphere of diameter a sweeping out a series of cylinders of radius a.**

Any other sphere **whose centre lies within the volume** swept out will suffer collision. We need to find the number of such collisions with this molecule per unit time. To do this, imagine straightening out the tube to estimate its volume. The cylinder so obtained has a geometric cross section area,

$$\sigma_G = \pi a^2.$$

The tube length will be approximately $\bar{v}t$ giving a total volume

$$V = \sigma_G \bar{v} t$$

Inside a volume V we will encounter nV other molecules where n is the number density of molecules giving a number of collisions

$$N_C = n\sigma_G \bar{v} t$$

for a distance $\bar{v}t$ traveled. The number of collisions per distance traveled is then

$$\frac{N_C}{\bar{v}t} = n\sigma_G$$

The distance traveled between collisions is the mean free path, λ, and is equal to the inverse of this

$$\lambda = \frac{1}{n\sigma_G}$$

There have been some simplifications made here in order to arrive at a simple characterization. These simplifications are;

(i) The target spheres themselves are stationary when of course they are moving.

(ii) The hard spheres only collide on contact whereas the forces between spheres will have some extent.

If we use the velocity distribution function to take some account of the motion of the target spheres then we can get a more precise estimate of the mean free path;

$$\lambda = \frac{1}{\sqrt{2}n\sigma_G}$$

To account for the second simplification we use a collision cross section, σ_C in place of σ_G . Values of σ_C may be obtained experimentally in molecular scattering experiments and can be looked up in tables of properties of atoms.

We may also speak of the collision frequency, ν_C , as an alternative description of the collision process where ν_C is the number of collisions suffered per second

$$\nu_C = \frac{\bar{v}}{\lambda} = \sqrt{2}n\sigma_C\bar{v}$$

or a scattering time τ_S where

$$\tau_S = \frac{1}{\nu_C} = \frac{\lambda}{\bar{v}} = \frac{1}{\sqrt{2}n\sigma_C\bar{v}}$$

We now have a simple language in which we may describe and discuss molecular collisions with mean free path, λ, scattering cross section, σ_C , collision frequency ν_C and scattering time, τ_S.

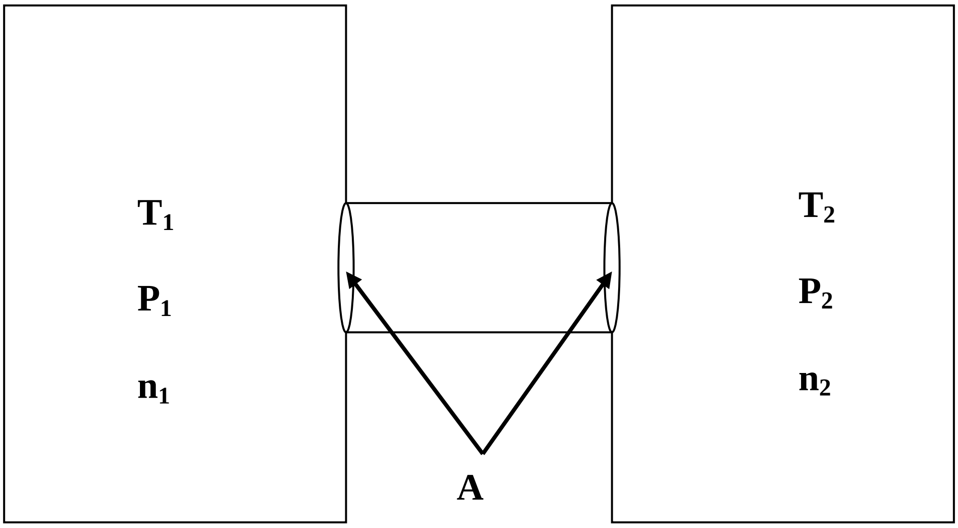
Molecular Effusion

In general, the exertion of forces by gas particles on one another via the collisions just examined ***are essential for the ability of a gas to flow in response to macroscopic pressure differences***, that is, ***gas molecules in one region are able to exert influence over those molecules in an adjacent region via the intermolecular collisions.***

The model we have just developed involving the concept of mean free path may however break down in circumstances where the gas is restricted to movement in structures whose characteristic dimensions are smaller than the mean free path. An example of one such restrictive structure may be eg. a narrow pipe. To deal with such situations it will be necessary to drop the concept of mean behaviours such as the mean free path and develop other microscopic models. Such a regime is called the **Knudsen regime.** Such a regime may occur in certain common circumstances where it is the mean free path that is unusually large rather than a structure that is particularly small eg.

(i) We note that λ increases as the number density decreases and therefore a high vacuum system will always go through a Knudsen regime when the vacuum is good enough.

(ii) The mean free path will also become very large as temperature and consequently mean velocity are greatly reduced and systems such as those involving liquid Helium and its vapour will pass through a Knudsen regime.



We investigate the difference between normal and Knudsen behaviour by consideration of two chambers connected by a narrow pipe as shown above.

The thermodynamic criteria for thermal equilibrium between the two chambers is that temperatures and pressures must be equal, $T_1 = T_2$ and $P_1 = P_2$. If there were a pressure difference between the two chambers the gas in the pipe would undergo molecular collisions more frequently from the high pressure side than the low pressure side and a resultant force would exist on the gas in the pipe leading to a pressure driven flow from high to low pressure tending to equalize the pressures. We now consider this arrangement but such that the diameter of the pipe is less than or equal to the mean free path in the gas. A molecule will pass into the pipe or not according to the prescripts of kinetic theory and if the molecule is within distance λ of the pipe entrance it will not (on average) be hit by another molecule before it has either entered the pipe or missed the entrance altogether. Equilibrium will now be determined by the equality of molecular flux onto either end of the pipe. In other words we may use our expressions for the flux to find

$$\frac{1}{4}n_1\bar{v}_1 A = \frac{1}{4}n_2\bar{v}_2 A$$

We may substitute into the equation to find the equilibrium condition in terms of pressures and temperatures; For example

$$\frac{n_1}{n_2} = \frac{\bar{v}_2}{\bar{v}_1} = \sqrt{\frac{T_2}{T_1}}$$

or use the fact that

$$P = \frac{Nk_B T}{V} = nk_B T$$

whence

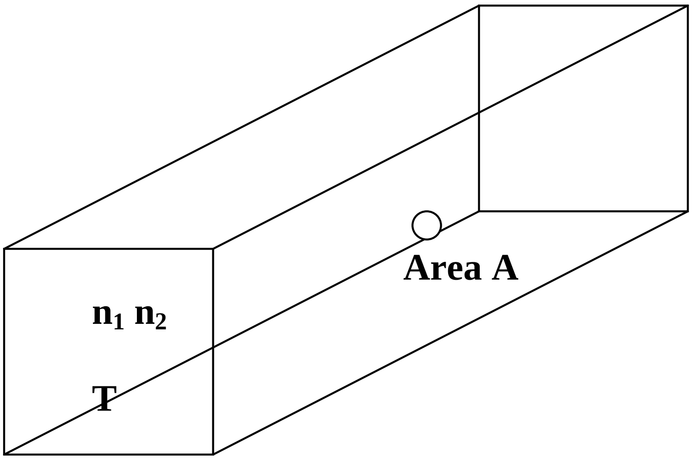
$$\frac{n_1 T_1}{n_2 T_2} = \frac{P_1}{P_2}$$

and

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}$$

The chambers in these circumstances can be at different temperatures and pressures and the pressure difference in this situation is called the **thermomolecular pressure** difference. This may become a problem when trying to measure the pressure of a low temperature gas via a thin pipe connected to a pressure gauge elsewhere.

The entrance or exit of a gas molecule through a hole smaller than the mean free path is called effusion in order to distinguish it from macroscopic flow and effusion is a useful technique for separating isotopes of atoms with slightly different masses. To see how this works we can consider a chamber containing a mixture of two types of gas, n_1 and n_2 at temperature T with a small pinhole exit in the chamber.



We can write an expression for the number of molecules of species i that impinge on the hole from inside the box and escape through the hole in a time, t using our previously derived expression

$$N_i^e = \Phi_i \times A \times t = \frac{1}{4} n_i \bar{v}_i t A$$

We use the expression for the mean speed, $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$ to find the ratio of two types of molecule that have escaped in time t as

$$\frac{N_1^e}{N_2^e} = \frac{n_1}{n_2}\sqrt{\frac{m_2}{m_1}}$$

We find the fraction of each species that have escaped as

$$\frac{N_1^e}{n_1} = f_1 = \frac{N_2^e}{n_2}\sqrt{\frac{m_2}{m_1}} = f_2\sqrt{\frac{m_2}{m_1}}$$

And

$$f_1 \big/ f_2 = \sqrt{\frac{m_2}{m_1}}$$

We have assumed negligible depletion of the molecular densities inside the chamber ie. n_i does not change substantially with time.

If molecular species 1 is lighter than molecular species 2 then clearly

$$\frac{f_1}{f_2} > 1$$

ie. the escaped gas is enriched in species 1 or the gas left behind is enriched in the heavier species.

(NB this does not imply that there is a greater amount of one kind of gas compared to the other as this would depend on the starting condition).

This effect was used by Lord Rayleigh and Ramsay in 1895 to isolate Argon from the atmosphere for whose discovery they shared the Nobel prize. The most well known use of effusion separation was to separate the light fissionable isotope of Uranium, U_{235} from the more common and heavier isotope, U_{238} and the process was carried out on industrial scale during the Second World War to produce nuclear fuel for the atom bomb programme and later for civil energy use. Nowadays the more effective centrifugation process is used which was previously unavailable.

8.5 Free Path Distributions

In an earlier discussion on mean free path we saw that during their travels, gas molecules would suffer trajectory altering collisions after a variety of free flight distances the mean of these being λ, the mean free path. There is however a distribution of free paths contributing to the mean and we now need to investigate and establish this distribution of free paths.

We may imagine having a collection of N_0 particles which have each just suffered a collision and we then follow their subsequent history through a function of distance, $N(\ell)$, which is **the number of this group of particles having traveled a distance ℓ without suffering a further collision**.

It then follows from this definition that the difference $N(\ell)-N(\ell+d\ell)$ is **the number of this group of particles which suffer a further collision in the interval (ℓ, ℓ+ dℓ).**

We can make two simple assumptions;

(i) $N(\ell)-N(\ell+d\ell)$ is proportional to the distance dℓ.

(ii) $N(\ell)-N(\ell+d\ell)$ is proportional to $N(\ell)$, the number of particles that started in the interval $(\ell,\ell+d\ell)$.

We may express these two assumptions mathematically as

$$N(\ell)-N(\ell+d\ell)=CN(\ell)d\ell \qquad C = \text{constant}$$

Dividing through by dℓ we obtain a simple differential equation;

$$\frac{N(\ell+d\ell)-N(\ell)}{d\ell}=\frac{dN(\ell)}{d\ell}=-CN(\ell)$$

Rearrangement gives

$$\frac{dN(\ell)}{N(\ell)}=-Cd\ell$$

With boundary condition $N(\ell) = N_0$ at $\ell = 0$ this has a simple solution

$$N(\ell) = N_0\, exp(-C\ell)$$

We can see that $N(\ell)/N_0$ is simply **the fraction of particles which have a free path greater than or equal to ℓ.**

Or alternatively that $N(\ell)/N_0 = exp(-C\ell)$ is **the probability that a particle which has just undergone a collision will survive a free flight of at least distance ℓ**

We may now introduce a related probability density, $P(\ell)$ by identifying $P(\ell)d\ell$ as **the proportion of sample particles starting at $\ell = 0$ which suffer their first collision between ℓ and ℓ + dℓ**

Alternatively $P(\ell)d\ell$ is the probability that a particle which has just suffered a collision will have its next collision between ℓ *and* $\ell + d\ell$

Mathematically this probability may simply be written as

$$P(\ell)d\ell = \frac{N(\ell) - N(\ell + d\ell)}{N_0} = C\frac{N(\ell)d\ell}{N_0}$$

Hence the probability distribution is simply

$$P(\ell) = Ce^{-C\ell}$$

To determine the constant C we note that the mean free path, λ, is the average free path and therefore

$$\lambda = C\int_0^\infty \ell e^{-C\ell} d\ell$$

We need to integrate by parts to evaluate the above integral;

$$u = \ell \qquad dv = e^{-C\ell} d\ell$$

$$du = d\ell \qquad v = -\frac{e^{-C\ell}}{\mathrm{C}}$$

Using the integration by parts formula

$$\lambda = C\int_0^\infty \ell e^{-C\ell} = C\int_0^\infty u dv = C\left[uv - \int_0^\infty v du\right]$$

$$\lambda = C\int_0^\infty \ell e^{-C\ell} = -C\left[\frac{\ell e^{-C\ell}}{C}\right]_0^\infty - C\int_0^\infty -\frac{e^{-C\ell}}{C} d\ell = 0 - C\left[\frac{e^{-C\ell}}{C^2}\right]_0^\infty = \frac{1}{C}$$

C is just the inverse mean free path.

In summary

(i) $P(\ell) = \frac{1}{\lambda} e^{-\ell/\lambda}$

$P(\ell)d\ell$ is the probability that a particle that has just undergone a collision will have its next collision after traveling a free flight distance between ℓ *and* $\ell + d\ell$

(ii) $\frac{N(\ell)}{N_0} = e^{-\ell/\lambda}$

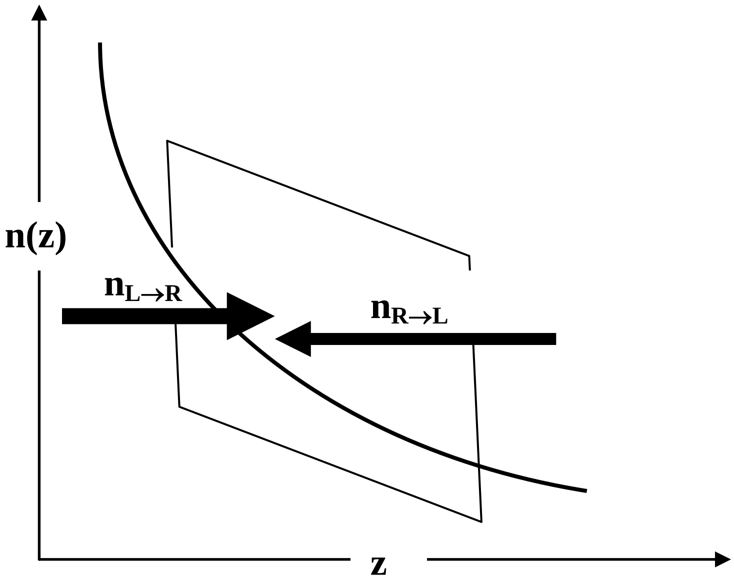
$N(\ell)/N_0$ is the probability that a particle having just undergone a collision will have a subsequent free path equal to or greater than ℓ.

Diffusion.

Diffusion is a process whereby particles (or energy as heat etc.) move from a high concentration region to that of lower concentration due to an imbalance in the flux at an interface from two opposite directions. We have the flux impinging on a surface as

$$J = \frac{1}{4} n\bar{v}$$

As derived earlier the flux was incident on the inside wall of a container and there is nothing coming from the other direction. We could now imagine a virtual wall inside a box of gas molecules (or other particles) and if there is a concentration gradient across the wall (as shown) with the concentration diminishing towards the right



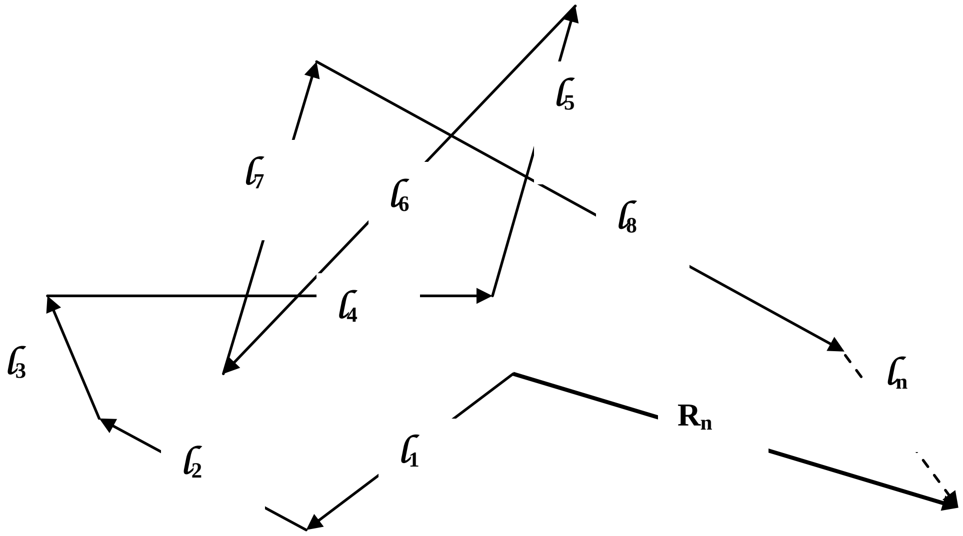
then n will be greater one side than the other with $n_{L\to R} > n_{R\to L}$ in the above example. This will lead to a net flux traveling left to right across the virtual wall and the concentration gradient will gradually diminish as a result of this net left → right flow. In similar fashion if the temperature varies from point to point then this will be eventually evened out by the transport of energy from a region of high temperature (high mean velocity, $\bar{v}$) to one of low temperature (low mean velocity, $\bar{v}$) The high velocity particles will impact on our virtual wall from the high temperature side more frequently than the lower velocity particles on the low temperature side. Furthermore the high mean velocity particles traveling L → R will carry with them more energy from the LH region to the RH region than vica versa. Both these facts lead to a gradual smoothing out of the temperature variation as the RHS warms and the LHS cools. We can analyse this process in a more rigorous fashion using what we have already discovered.

1. Inhomogeneities in density, *n*(*z*) and diffusion of material particles/mass.

A gas or fluid is said to be in **local equilibrium** if properties such as density (particle number), pressure, temperature, velocity distributions are well defined quantities over very small but macroscopic volumes (many thousands of molecules so a volume of a few cubic microns say) and if these properties relate to one another via an equation of state whereas over larger distances (eg. millimeters) they are allowed to vary slowly. These non local inhomogeneities will eventually even out if the different parts of the system are in thermal contact with one another and particles are allowed to redistribute themselves freely. As we saw above in the example of density variation the particles will move from the high concentration region to the low concentration region and in the case of temperature variation the faster particles will move into the low velocity/temperature region more easily than the slower particles can into the high velocity/temperature region. As long as these inhomogeneities are not too large then we are able to derive some macroscopic laws describing the transport of mass or energy. If we are too far from equilibrium then we are unable to use the tools recently developed describing statistical average properties and life becomes far more complicated with the tools of computer simulation coming to the fore. To consider how the particle density evens out through diffusion we need to first develop some tools for our understanding of the random walk process.

Random walk of individual particles

Let us then consider the diffusion process by following a particular molecule and in particular following the details of the random walk it will undergo due to the many collisions suffered. We have been here recently when we defined the mean free path, λ of such a multiply colliding particle that moves freely in between collisions at a mean speed $\bar{v}$.



We need to find out two things concerning this random walk;

- **(i)** How rapidly does an individual molecule move through the gas?
- **(ii)** How do we relate this to the gradual homogenization of the gas?

For an individual molecule, after *n* collisions there will be a net displacement

$$\vec{R}_n = \vec{\ell}_1 + \vec{\ell}_2 + \vec{\ell}_3 + \vec{\ell}_4 + ... + \vec{\ell}_n$$

Now, it is clear that the direction of the vector displacement is equally likely in any direction and so we can expect $\overline{R_n} = 0$. It is not however the case that the scalar magnitude averages to zero

$$\left\langle \left|R_n\right|^2 \right\rangle = \left\langle R_n \cdot R_n \right\rangle = \Big\langle \Big(\ell_1 + \ell_2 + \ell_3 ... + \ell_n\Big) \cdot \Big(\ell_1 + \ell_2 + \ell_3 ... + \ell_n \Big\rangle$$

$$\left\langle |R_n|^2 \right\rangle = \left\langle |\ell_1|^2 \right\rangle + \left\langle |\ell_2|^2 \right\rangle + ... + \left\langle |\ell_n|^2 \right\rangle + 2\left\langle \ell_1 \cdot \ell_2 \right\rangle + 2\left\langle \ell_1 \cdot \ell_3 \right\rangle + ... + 2\left\langle \ell_{n-1} \cdot \ell_n \right\rangle$$

We can note that in the above summation;

(i) In a random series of collisions there is no correlation between the direction taken by a molecule after a collision and the direction taken after the previous collision and therefore on average

$$\left\langle \ell_i \cdot \ell_j \right\rangle = \left\langle \ell_i \ell_j \cos\theta \right\rangle = 0 \qquad\qquad i \neq j$$

ie. the angle θ between the original and scattered direction is random and averages to zero and all of the cross terms vanish.

(ii) The ℓ_i are statistically identical, ie. the average value of all ℓ_i must be equal therefore

$$\left\langle |R_n|^2 \right\rangle = \left\langle |\ell_1|^2 + |\ell_2|^2 + |\ell_3|^2 + ... + |\ell_n|^2 \right\rangle = n\left\langle |\ell|^2 \right\rangle$$

The average of the square of the free path length is calculated using the probability distribution previously derived

$$\left\langle |\ell|^2 \right\rangle = \left\langle \ell^2 \right\rangle = \int_0^\infty \ell^2 P(\ell)\, d\ell = \frac{1}{\lambda}\int \ell^2 e^{-\ell/\lambda} d\ell$$

We can perform the integration by ***(several)*** parts as follows;

Part 1.

$$u = \ell^2 \qquad\qquad dv = e^{-\ell/\lambda}\, \mathrm{d}\ell$$

$$du = 2\ell d\ell \qquad\qquad v = -\lambda e^{-\ell/\lambda}$$

$$\frac{1}{\lambda}\int u\,dv = \frac{1}{\lambda}\int \ell^{2} e^{-\ell/\lambda} d\ell = \frac{1}{\lambda}\left\{\left[-\ell^{2}\lambda e^{-\ell/\lambda}\right]_{0}^{\infty} + 2\lambda\int \ell e^{-\ell/\lambda} d\ell\right\}$$

$$\left\langle \ell^{2}\right\rangle = \frac{1}{\lambda}\int_{0}^{\infty} \ell^{2} e^{-\ell/\lambda} d\ell = 2\int_{0}^{\infty} \ell e^{-\ell/\lambda} d\ell$$

Part 2. We need a second integration by parts to evaluate the new integral

$$u = \ell \qquad\qquad dv = e^{-\ell/\lambda} d\ell$$

$$du = d\ell \qquad\qquad v = -\lambda e^{-\ell/\lambda}$$

$$\frac{1}{\lambda}\int_{0}^{\infty} \ell^{2} e^{-\ell/\lambda} d\ell = 2\int_{0}^{\infty} \ell e^{-\ell/\lambda} d\ell = 2\left[-\lambda \ell e^{-\ell/\lambda}\right]_{0}^{\infty} - 2\int_{0}^{\infty} -\lambda e^{-\ell/\lambda} d\ell$$

$$\frac{1}{\lambda}\int_{0}^{\infty} \ell^{2} e^{-\ell/\lambda} d\ell = 2\lambda\int_{0}^{\infty} e^{-\ell/\lambda} d\ell = \left[-2\lambda^{2} e^{-\ell/\lambda}\right]_{0}^{\infty} = 2\lambda^{2}$$

We then arrive at

$$\left\langle |\ell|^{2}\right\rangle = \left\langle \ell^{2}\right\rangle = \int_{0}^{\infty} \ell^{2} P(\ell)\, d\ell = 2\lambda^{2}$$

The **mean square displacement** is then

$$\left\langle |R_{n}|^{2}\right\rangle = 2n\lambda^{2}$$

We can convert the number of collisions, n , to the more useful parameter, the time elapsed, *t*, since the last collision, in the above equation where

$$n \approx \frac{t}{\tau_S}$$

with $\tau_S = \frac{\lambda}{\bar{v}}$, the **scattering time** being the time between collisions.

Thus, $n \approx \frac{\bar{v}t}{\lambda}$ and we may write the mean square displacement as

$$\left\langle |R_n|^2 \right\rangle = 2n\lambda^2 = 2\bar{v}\lambda t \equiv 6Dt$$

where the **diffusion coefficient** D is defined as

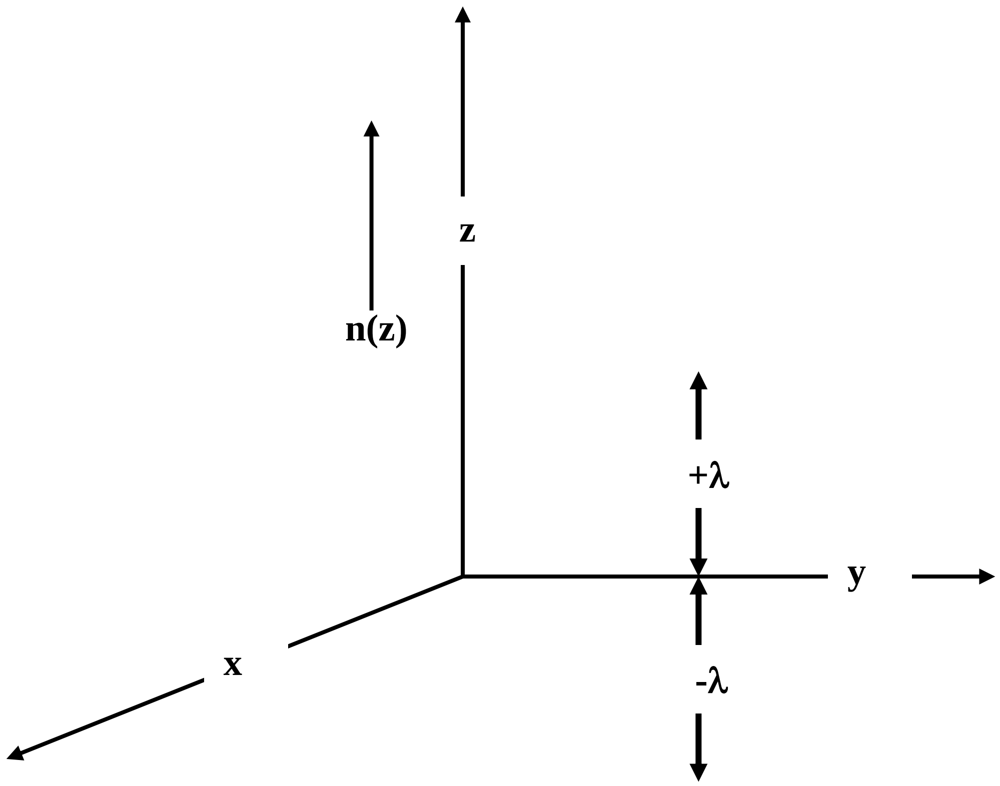
$$D = \frac{1}{3}\bar{v}\lambda$$

We note that the **root mean square displacement** increases as the square root of time whereas in free flight it increases linearly with time thus diffusion becomes a very slow process for individual molecules.

We may now develop a macroscopic diffusion law.

The diffusion law (Ficks Law)

We have already noted that a concentration gradient of particles will tend to disappear as the particles diffuse simple because more particles will impinge on a virtual wall from one side than the other if the wall is oriented perpendicular to the concentration gradient. Diffusion governs how this movement comes about and it is true for “tagged” particles in a gas (eg isotopically different) , for electrons (or holes) in a doped semiconductor , for the dopants that put them there or for solids or fluids introduced into other solvents eg. sugar in tea or dye solutions into a bucket of water. Having looked at how we may describe the history of an individual particle we now wish to describe how variations in density vary in space and time. There exists an **empirical law of diffusion** named after Fick, the scientist who developed it. In simple terms it states that the particle flux (number per second per unit area) due to diffusion is proportional to the density gradient and flows in the direction in which the gradient is most negative (from high to low concentrations). Fick's constant of proportionality is the diffusion coefficient, *D*. We can now derive Fick's law using the tools already established. Let us stick with a gas (although many other systems will be analyzable in these terms) and assume that there is a majority molecular type pervading the volume with some particular tagged particles with a varying density in which we are interested. The majority gas merely acts as the carrier gas or background medium against which the tagged particles move. Let the density of those gas particles vary with *z* and assume that *n*(*z*) is a slowly varying function of *z*.



The simple model, illustrated above, assumes that molecules from within a distance λ (the mean free path) of this plane cross without scattering and also that the density varies slowly over one mean free path.

This allows us to approximate the number density in the vicinity of the plane ($z = 0$) by a Maclaurin expansion

$$n(z) = n(0) + \left.\frac{\partial n}{\partial z}\right|_{z=0} dz + ...$$

The flux traversing the *xy* plane at $z = 0$ is made up of those coming from below and those coming from above and we may use our previously derived formula for the flux to give

$$\text{Flux from above} \qquad = \frac{1}{4} n(\lambda)\bar{v} = \frac{1}{4}\left(n(0) + \left.\frac{\partial n}{\partial z}\right|_{z=0} \lambda \right)\bar{v}$$

$$\text{Flux from below} \qquad = \frac{1}{4} n(-\lambda)\bar{v} = \frac{1}{4}\left(n(0) - \left.\frac{\partial n}{\partial z}\right|_{z=0} \lambda \right)\bar{v}$$

The net flux in the positive *z* direction is the difference between the second and the first of these

$$J_z = -\left(\frac{1}{2}\bar{v}\lambda\right)\left.\frac{\partial n}{\partial z}\right|_{z=0} = -D\frac{\partial n}{\partial z}$$

This is known as Fick's law.

In our simplified model the relation between $\bar{v}$, λ and D is slightly different the correct form having been given previously.

$$D = \frac{1}{2}\bar{v}\lambda$$

Whereas previously we had the correct form,

$$D = \frac{1}{3}\bar{v}\lambda$$

To obtain agreement we need to;

(i) Allow the particles to make their last collision before crossing, at any distance ℓ.

(ii) Allow the particles to cross the $z = 0$ plane at a range of angles instead of at normal incidence.

We note that we may generalize Fick's Law to three dimensions by the simple expedient of replacing the operator $\frac{\partial}{\partial z}$ with the grad operator, ∇, and to treat J_z as a vector, $\vec{J}$.

$$\vec{J} = -D\nabla n$$

The magnitude of the vector $\vec{J}$ is now the number of particles passing per unit time per unit area through an area perpendicular to the direction of $\vec{J}$.

Having obtained a derivation of Fick's Law we may now derive the full differential equation known as the **Diffusion Equation** which in its one dimensional form is

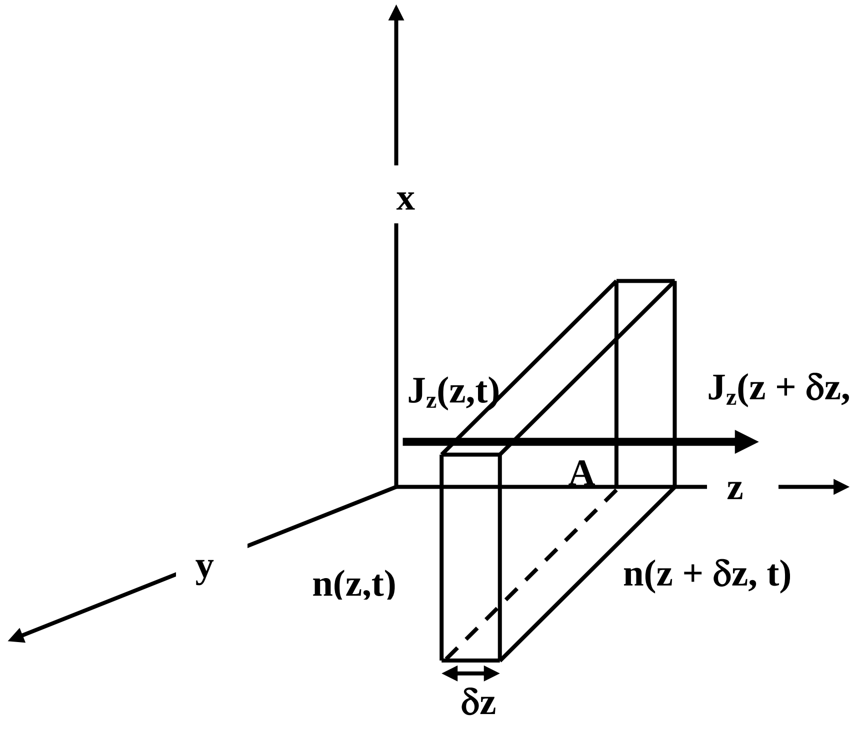
$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial z^2}$$

Using two concepts;

(i) Fick's Law of diffusion.

(ii) The conservation of particle number.

We may derive the diffusion equation by considering the diagram below.



The particle flux flows in at z and flows out at $z + \delta z$ through an area A and we shall let δN be the change in the number of particles inside the volume $A\delta z$ in a time δt. The change, δN can be related to the change in density inside the volume

$$\delta N = A\delta z\delta n$$

We also require that the total number of particles is conserved and therefore δN must be equal to the number of particles that flow in at z minus the number of particles that flow out at $z + \delta z$ which we may express in terms of the particle flux, J_z.as described by Fick's law

$$\delta N = A\delta t J_z(z,t) - A\delta t J_z(z+\delta z,t)$$

rearranged

$$\delta N = -A\delta t\left(J_z(z+\delta z,t) - J_z(z,t)\right)$$

We obtain this with the RHS expressed as a differential

$$\delta N \approx -A\delta t\frac{\partial J_z}{\partial z}\delta z$$

The two expressions for δN must be equal and so

$$A\delta z\delta n = -A\delta t\frac{\partial J_z}{\partial z}\delta z$$

This can be re-arranged

$$\frac{\delta n}{\delta t} = -\frac{\partial J_z}{\partial z}$$

And we can take the limit $\delta t \to 0$ to give a differential equation

$$\frac{\partial n}{\partial t} = -\frac{\partial J_z}{\partial z}$$

Finally by substituting the Fick's law expression for J_z ,

$$J_z = -D\frac{\partial n}{\partial z},$$

we obtain

$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial z^2}$$

This is the diffusion equation in one dimension that we saw earlier.

A similar derivation can be carried out for the 3D problem to give

$$\frac{\partial n(x,y,z,t)}{\partial t} = -\nabla \cdot J = D\nabla^2 n(x,y,z,t)$$

The above equation, $\frac{\partial n(x,y,z,t)}{\partial t} = -\nabla \cdot J$, is in fact a general way of writing a conservation law and is known as the continuity equation that in the present case expresses the conservation of particle number. If we were considering electrically charged particles such as electrons then with J as the current density, $J = \frac{i}{A}$ and ρ the charge density with e the charge on the electron, the continuity equation would read

$$\frac{\partial n(x,y,z,t)}{\partial t} = -\frac{\nabla \cdot J}{e} \qquad \frac{\partial \rho(x,y,z,t)}{\partial t} = -\nabla \cdot J$$

In general the 1D and 3D equations are difficult to solve except in simple cases of high symmetry. In the 1D case, with simple boundary conditions the differential equation may be solved by using the separation of variables (z and t) technique.

8.7 Heat Conduction.

We have so far related the diffusion equation to a particle concentration gradient but there are other ways in which local equilibrium may be disturbed and an important way is by having a spatial variation of temperature (or energy density) throughout the sample. The diffusion equation can be used to examine this situation with minor adjustments.

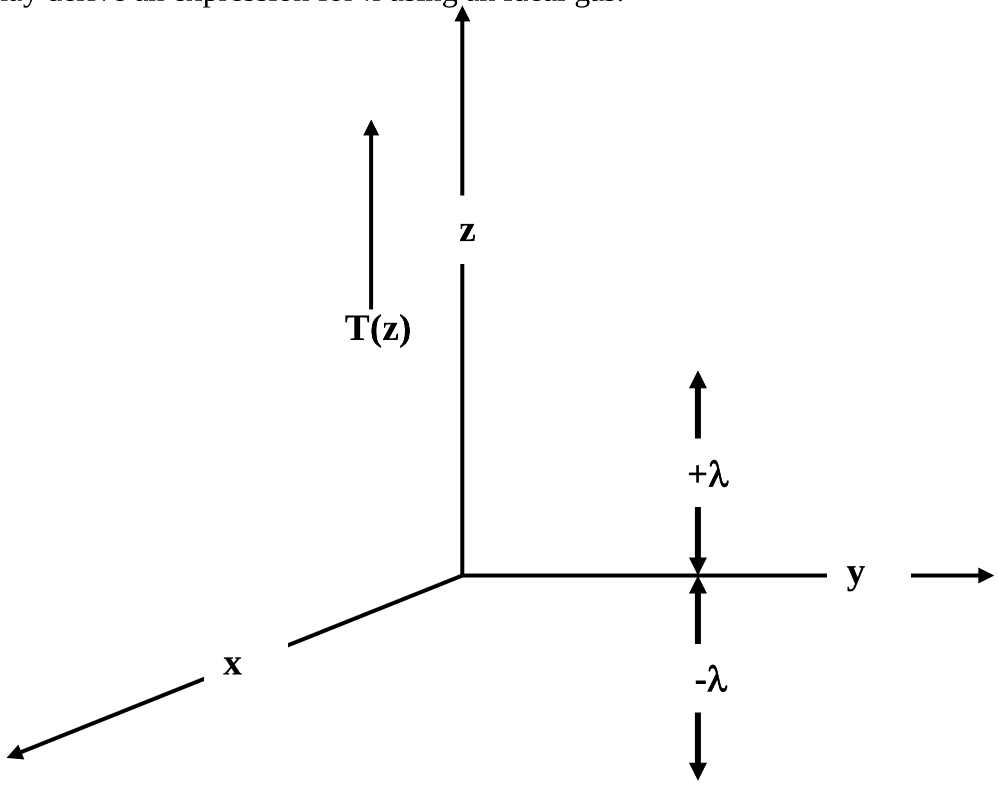
The macroscopic law of heat conduction known as **Fouriers law** can be stated as follows in one dimension

$$J_z(z,t) = -\kappa \frac{\partial T(z,t)}{\partial z}$$

Where J_z is now the heat flow through unit area per second (J $m^{-2}s^{-1}$) and κ is the thermal conductivity coefficient. This equation may be written in 3D as follows

$$\vec{J} = -\kappa \nabla T$$

Fouriers law is equivalent to Fick's law for diffusion of material particles with κ, the thermal conductivity coefficient being analogous to D, the diffusion coefficient and we may derive an expression for κ using an ideal gas.



In analogy to our previous derivation of *D* we consider the temperature, *T*(*z*) to increase in the positive *z* direction (rather than *n*(*z*) in the previous analysis). We know that the mean kinetic energy of a molecule is proportional to the temperature and that therefore a molecule at a position λ above the *z* = 0 plane will have a kinetic energy $\varepsilon = \frac{3}{2}k_B T(\lambda)$ and a molecule below the *z* = 0 plane at position -λ will have a lower kinetic energy, $\varepsilon = \frac{3}{2}k_B T(-\lambda)$. Each molecule will have a heat capacity

$$c_m = \frac{\partial \varepsilon}{\partial T} = \frac{3}{2}k_B$$

We have already calculated the net flux of molecules traveling in the plus *z* direction from below the *z* = 0 plane and those traveling in the negative *z* direction from above the plane *z* = 0 with the latter carrying greater energy on average (coming from a region of higher temperature). There will then be a net flow of energy from plus *z* to minus *z* through the *z* = 0 plane or from higher to lower temperature. We may in this fashion obtain Fouriers law and the microscopic expression for κ.
The argument is made as follows;

Consider the molecules traveling in the *z* direction with a speed *v*, at an angle θ to the *z* axis and crossing a plane of constant *z*. They travel a distance λ between collisions and so travel a distance $\lambda\cos\theta$ in the *z* direction between collisions taking with them an energy and contributing to an energy deficit in the region they leave.

$$\Delta\varepsilon = c_m \times \Delta T = -c_m \times \frac{\partial T}{\partial z}\lambda\cos\theta$$

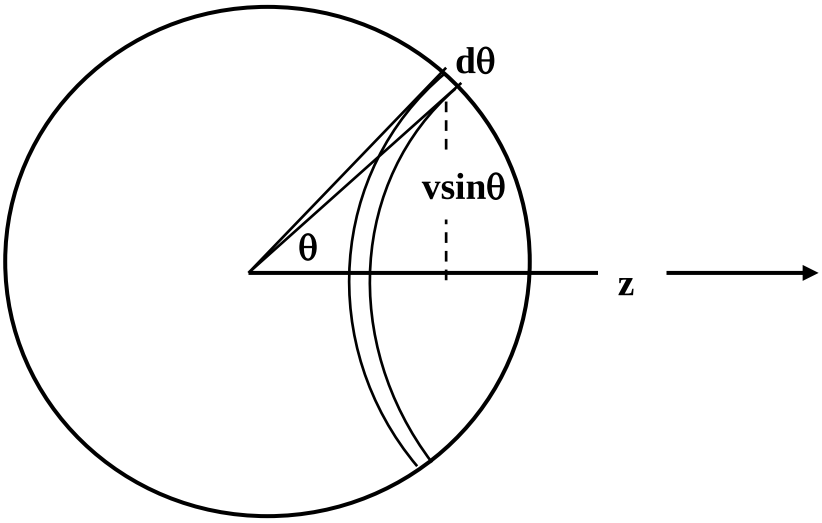
where c_m **is the heat capacity of a single molecule**.

If the molecule has velocity, *v* then this crossing occurs in a time $t = \frac{\lambda\cos\theta}{v}$ and the molecules occupy a sub-volume $V = \lambda A$ of the entire sample therefore involving $n_v \times \lambda A$ molecules with n_v the number of molecules per unit volume with velocity *v*.

We only want to include (for now) the ones traveling at an angle θ to the z axis

The number of such molecules is easily found. In fact we have done this before when finding the flux of molecules colliding with a wall.

Consider the diagram in velocity space shown below



A sphere of radius v is shown with the z direction indicated and an annulus representing the molecules traveling between θ and $\theta + \mathrm{d}\theta$.

This annulus has an area $A_{annulus} = 2\pi v \times v d\theta$ thus representing a fraction

$$F = \frac{2\pi v^2 \sin\theta d\theta}{4\pi v^2} = \frac{1}{2}\sin\theta d\theta$$

$$n_v = n \times f(v)dv \times F = n\frac{1}{2}f(v)\sin\theta dv$$

This is the subset of molecules traveling with speed v and at angle θ.

Finally we obtain the total number of such molecules traveling in the volume $A\lambda\cos\theta$ adjacent to the xy plane at z = 0.

$$N = n_v A\lambda\cos\theta$$

They transport an energy

$$\Delta E = N\Delta\varepsilon = n_v A\lambda \cos\theta \times \Delta\varepsilon$$

$$\Delta E = -n_v A\lambda \cos\theta \times c_m \frac{\partial T}{\partial z}\lambda \cos\theta$$

They then contribute to the total heat flux an amount

$$j_z(v,\theta) = \frac{\Delta E}{At} = \frac{\Delta E_{Tot} v}{A\lambda} = -n_v v \cos\theta \times c_m \frac{\partial T}{\partial z}\lambda \cos\theta$$

$$j_z(v,\theta) = -nvf(v)\frac{1}{2}\sin\theta\cos\theta \times c_m \cos\theta\frac{\partial T}{\partial z}$$

We need to sum over all the velocities in the positive z direction using the Maxwell speed distribution and to average over all θ between 0 and π. The total thermal energy transported across unit area in unit time is then

$$J_z = \int_0^\infty dv\int_0^\pi\left(-nc_m \times \frac{\partial T}{\partial z}\lambda\cos\theta\right)v\cos\theta f(v)\frac{1}{2}\sin\theta d\theta$$

$$J_z = -\frac{1}{2}nc_m\lambda\frac{\partial T}{\partial z}\int_0^\infty vf(v)dv\int_0^\pi \cos^2\theta\sin\theta d\theta$$

The first integral gives the mean speed $\bar{v}$

$$\int_0^\infty vf(v)dv = \bar{v}$$

the second averaging over all directions (angles θ)

$$\int_0^\pi \cos^2\theta\sin\theta d\theta$$

Substitution of U for $cos\theta$ gives

$$\frac{dU}{d\theta} = -sin\,\theta \qquad d\theta = -\frac{dU}{sin\,\theta}$$

allows us to write the integral

$$\int_0^{\pi} cos^2\,\theta\,sin\,\theta d\theta = -\int U^2\,sin\,\theta\frac{dU}{sin\,\theta} = -\frac{U^3}{3} = -\frac{cos^3\,\theta}{3}$$

$$\int_0^{\pi} cos^2\,\theta\,sin\,\theta d\theta = -\left[\frac{-cos^3\,\theta}{3}\right]_0^{\pi} = \frac{2}{3}$$

giving a factor $\frac{2}{3}$.

Finally we have

$$J_z = -\frac{1}{3}nc_m\lambda\bar{v}\frac{\partial T}{\partial z}$$

We write $c_m = \frac{3}{2}k_B$ $\qquad$ $\frac{5}{2}k_B$ or $\frac{7}{2}k_B$ for diatomic gases.

$$J_z = -\frac{1}{3}n\bar{v}\lambda\left(\frac{3}{2}k_B\right)\frac{\partial T}{\partial z}$$

Thus deriving Fouriers law and giving the advertised result for κ.

We may now use the previously derived expression for the mean velocity to find how κ depends on temperature

$$\kappa = \frac{1}{3}n\bar{v}\lambda\left(\frac{3}{2}k_B\right) = \frac{1}{2}n\lambda\sqrt{\frac{8k_BT}{\pi m}}k_B = n\lambda\sqrt{\frac{2T}{\pi m}}k_B^{3/2}$$

Showing that κ is proportional to the square root of the temperature. We will also find it instructive to compare heat diffusion with particle diffusion by writing the mean free path in terms of the diffusion coefficient D as previously derived to find the relation between κ and D

$$\kappa = \frac{1}{3}n\bar{v}\lambda\left(\frac{3}{2}k_B\right) = \frac{1}{3}n\bar{v}\left(\frac{3D}{\bar{v}}\right)\left(\frac{3}{2}k_B\right) = \frac{3}{2}nDk_B$$

Or

$$\frac{\kappa}{D} = \frac{3}{2}nk_B \qquad\qquad \frac{5}{2}nk_B \; or \; \frac{7}{2}nk_B \text{ for diatomic gases.}$$

Having established the Fourier law (equivalent to Fick's law) we may now turn to the heat equation (equivalent to the diffusion equation).

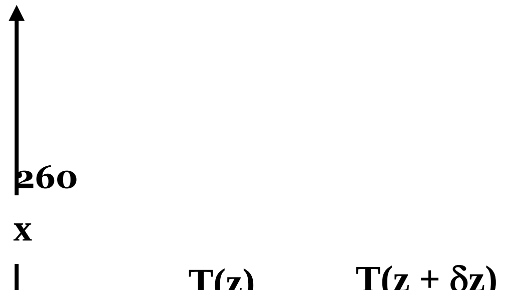
The Heat Equation.

As for the diffusion equation, to establish the heat equation we need two equivalent physical principles;

(iii) Fouriers's Law of heat conduction.

(iv) The conservation of energy.

The derivation of the heat equation proceeds from these two in an exactly analogous way to the diffusion equation with an extra step in order to relate temperature to the conservation of energy. We restrict ourselves to a one dimensional analysis ie. the temperature varies in the z direction only. The diagram below, illustrates the situation which we are analyzing. The parallelepiped has faces of area A, through which heat flows, lying normal to the z direction, separated by a distance, δz. This is the only way by which heat enters or leaves the volume and we apply the conservation law to this small volume over a small period of time, δt. To substitute temperature for energy in the conservation law we need the mass density, ρ, and the specific heat capacity, c_P , at constant pressure for the substance being considered.



The only way energy can be added to or subtracted from the volume is through the walls of area *A* and we will denote δQ as the heat gained per unit time by the substance in this volume requiring the net heat flow into the volume

$$\delta Q = heat \;\; flow \;\; in - heat \;\; flow \;\; out$$

If we write the heat flux in the *z* direction (heat energy passing unit area in unit time) as J_z then we have

$$\delta Q = A\delta t J_z(z,t) - A\delta t J_z(z+\delta z,t)$$

Rearranging

$$\delta Q = -A\delta t\left(J_z(z+\delta z,t) - J_z(z,t)\right)$$

$$\delta Q \approx -A\delta t \frac{\partial J_z}{\partial z}\delta z$$

We can also write δQ in terms of the change in temperature, δT

$$\delta Q = \rho(A\delta z) \times c_P \times \delta T$$

We may introduce this into the previous equation

$$\rho A\delta z c_P \delta T \approx -A\delta t \frac{\partial J_z}{\partial z}\delta z$$

This reduces to

$$\frac{\delta T}{\delta t} = -\frac{1}{\rho c_P}\frac{\partial J_z}{\partial z}$$

We can turn the left hand side into a partial differential by taking the limit $\delta t \to 0$ and substitute the form of J_z given by Fouriers law on the right hand side to obtain the heat equation as

$$\frac{\partial T(z,t)}{\partial t} = \frac{\kappa}{\rho c_P}\frac{\partial^2 T(z,t)}{\partial z^2}$$

This is sometimes written in terms of the heat diffusivity, $D^h = \frac{\kappa}{\rho c_p}$

$$\frac{\partial T(z,t)}{\partial t} = D^h \frac{\partial^2 T(z,t)}{\partial z^2}$$

Mathematically the heat equation and the diffusion equation are identical differing only in the physical properties being represented.

In 3D the heat equation may be written as

$$\frac{\partial T(x,y,z,t)}{\partial t} = \frac{\kappa}{\rho c_P}\nabla^2 T(x,y,z,t)$$