Maxwell's Distribution Law for the distribution of molecular speeds

This law gives the fraction of gas molecules at different speeds.

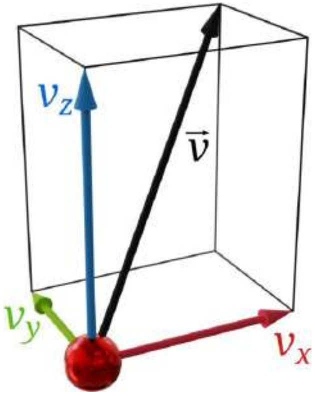
In 1859, Maxwell derived this law just from the premise that a sample of gas is isotropic (i.e. its properties are the same in all directions). Here, we will do the derivation of this law on the basis Boltzmann distribution law and the classical formula for the translational energies of gas molecules.

What is speed? It's the rate of change of distance with time. It has only magnitude. So it is a scalar quantity.

What is velocity? It's the rate of change of displacement with time. It has both magnitude and direction. So it is a vector quantity.

The velocity vector

Generally, gas molecules have velocity components in all three directions (v_x, v_y and v_z). The velocity vector $\vec{v}$ of a gas particle can be represented by these three components:



For the magnitude of the velocity vector $|\vec{v}|$ or, for the square $|\vec{v}|^2$ applies:

$$|\vec{v}| = (v_x^2+v_y^2+v_z^2)^{1/2}$$

$$|\vec{v}|^2 = v_x^2+v_y^2+v_z^2$$

Note that when squaring the magnitude of an vector, the vertical bars that indicate the magnitude can be omitted. This actually leads to the same result i.e.

$$\vec{v}^2 = v_x^2+v_y^2+v_z^2 = |\vec{v}|^2$$

The square of a vector is therefore a scalar. We can conclude from this that by squaring a vector the information about the direction is lost. This fact will become important later!

Molecular Speeds in One Dimension

The x-component of the translational kinetic energy, E_x , of a particle is related to its velocity in that direction , v_x, by

$E_x = ½\, m v_x^2$…………………(1)

Suppose, E_x is quantized. So, v_x is also, i.e., only a particular set of velocity, $v_{x,i}$ values are allowed.

Therefore, the fraction of molecules with velocity, $v_{x,i}$, can be written using Boltzmann distribution law as

$f(v_{x,i}) = \exp(-m\, v_{x,i}^2/2k_BT) \,/\, \Sigma \exp(-m\, v_{x,i}^2/2k_BT)$ …………………(2)

Since distribution may be discrete and continuous and there is an infinite set of possible values in a continuous distribution, the number of molecules having any one particular velocity may be zero. Hence we can talk about the fraction of molecules between two velocity limits, which can be infinitesimally close. Let $f(v_x)\, dv_x$ be the fraction of molecules between v_x and $(v_x + dv_x)$. It will be given by

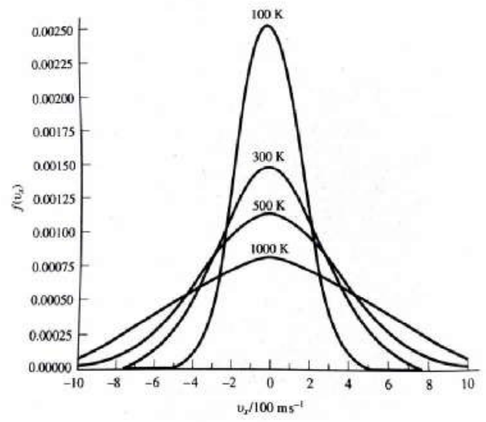
$f(v_x)\, dv_x = \exp(-m\, v_{x,i}^2/2k_BT)\, dv_x \,/ \int_{-\infty}^{\infty} \exp(-m\, v_{x,i}^2/2k_BT)\, dv_x = (m/2\pi\, k_BT) \exp(-m\, v_x^2/2k_BT)\, dv_x$ ………………(3)

since the integral in the denominator, $\int_{-\infty}^{\infty} \exp(-m\, v_{x,i}^2/2k_BT)\, dv_x = (2\pi\, k_BT/m)½$

as $\int_{-\infty}^{\infty} \exp(-ax^2)\, dx = 2\int_0^{\infty} \exp(-ax^2)\, dx = 2 \times ½ \times (\pi/a)½ = (\pi/a)½$, here, $a = m/2k_BT$ = constant.

This function $f(v_x)$ is the velocity distribution function in one dimension. It is also called the probability density function. Note that it has dimension of velocity^{-1}.

One dimensional distribution function for different temperatures has been illustrated in the figure given below:



Here, as the temperature increases, a larger fraction of molecules acquire a higher velocity. However, the average velocity remains zero since +ve and –ve values for any particular velocity are equally probable.

Molecular Speeds in Three Dimensions

Since the total kinetic energy is the sum of three terms: $E = E_x + E_y + E_z = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2)$ ………………(4)

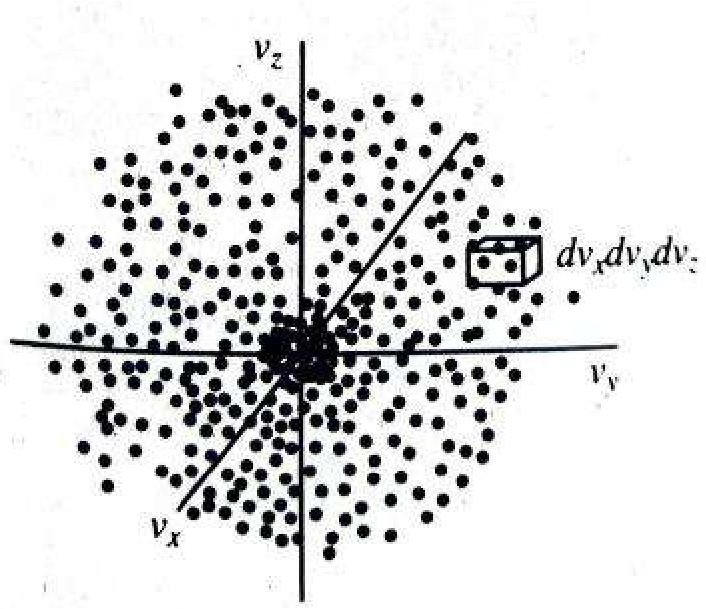
The fraction of molecules with velocities between v_x and $(v_x + dv_x)$, v_y and $(v_y + dv_y)$, and v_z and $(v_z + dv_z)$ is given by

$f(v_x\, v_y\, v_z)\, dv_x\, dv_y\, dv_z = (m/2\pi k_BT)^{3/2} \exp(-mv^2/2k_BT)\, dv_x\, dv_y\, dv_z$ …………………(5)

This expression is referred as the Maxwell-Boltzmann distribution law for velocities.

Distribution of Speeds

Let us consider a velocity space in which 3 axes V_X, V_z and V_z are the three components of velocity (Figure given below).



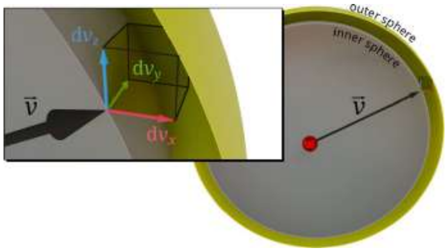
Each point in this space corresponds to a particular set of values for the velocity components.

At any given moment the velocity of each molecule is represented by a dot.

The velocity distribution function (Equation 5) gives the number of points in a given volume element (dv_x dv_y dv_z) in the velocity space.

Since the molecular velocities change with time because of frequent collisions, some molecules move out of a region of the velocity space, while an equal number of other molecules, on the average, enter the region. So, at equilibrium, the number of points in any given volume element (dv_x dv_y dv_z) in the velocity space remains constant with time.

The fraction of molecules with speeds between v and $(v + dv)$ is given by the volume of a spherical shell of thickness dv at radius v (Figure given below).



(Due to the infinitesimal distance between the two spheres, the volume of the sphere (*volume* in a velocity space!) can be determined from the product of the area of the sphere $4\pi v^2$ and the distance dv between the spherical shells and becomes equal to $4\pi v^2 \cdot dv$)
(ref: https://www.tec-science.com/thermodynamics/kinetic-theory-of-gases/derivation-of-the-maxwell-boltzmann-distribution-function/)

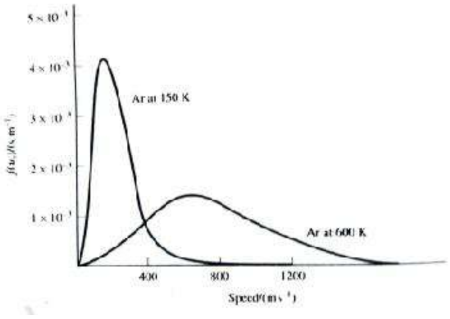
This is obtained by transforming the Cartesian coordinates to polar coordinates and integrating over the angles.

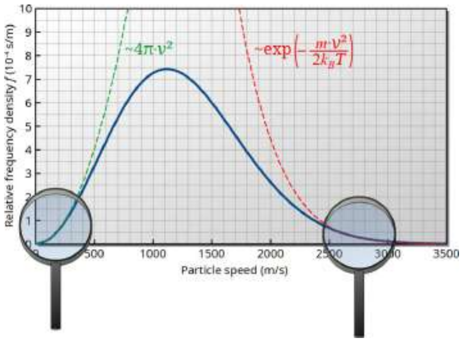
Since the procedure is identical to the one followed in obtaining the radial distribution function for the the electron in a hydrogen atom, I will just state the result. The fraction of molecules between speeds v and $(v + dv)$ is given by

$$f(v)dv = 4\pi\,(m/2\pi k_BT)^{3/2}\, v^2 \exp(-mv^2/2k_BT)\, dv = 4\pi\,(M/2\pi RT)^{3/2}\, v^2 \exp(-Mv^2/2RT)\, dv \quad \text{......................(6)}$$

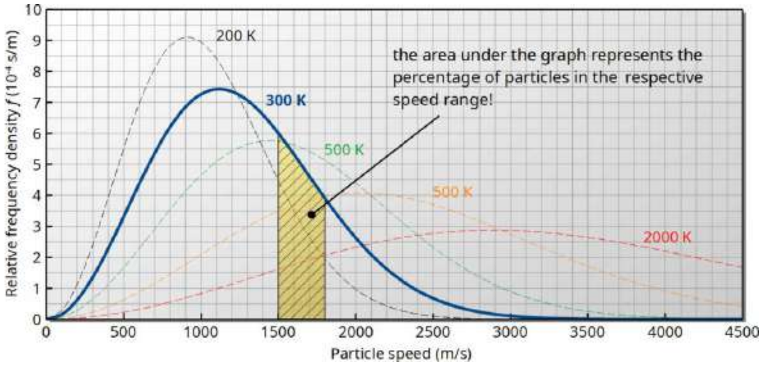
This is the famous Maxwell distribution of speeds.

The following figure illustrates the distribution for two different temperatures. As temperature increases, the number of molecules above a given speed increases. The number of molecules in the neighborhood of zero velocity is vanishingly small since the volume element $4\pi v^2\, dv$ goes to zero as v approaches zero. Near the origin, curves are parabolic because of the dominance of the v^2 term in the equation. But at higher speed the exponential term is more important. It is to be noted that the curve becomes much flatten as the temperature is raised.





Features of Maxwell distribution of speeds



(ref. https://www.tec-science.com/thermodynamics/kinetic-theory-of-gases/derivation-of-the-maxwell-boltzmann-distribution-function/)

1. With respect to exp($-Mv^2/2RT$) term: (a) fraction of molecules with very high speeds will be very small because when $Mv^2/2RT$ is large; (b) when the molar mass M is large, the exponential factor goes most rapidly towards zero since $Mv^2/2RT$ will be large. That means, heavy molecules are unlikely to be found with very high speeds. (c) when T is high, $Mv^2/2RT$ will be small, the exponential term falls towards zero relatively slowly as v increases. That means a greater fraction of molecules can be expected to have high speeds at high temperatures than at low temperatures.
2. With respect to v^2 term, $f(v)$ goes to zero as v goes to zero. So, the fraction of molecules with very low speeds will also be very small.
3. The remaining terms simply ensure that when we add together fractions over the entire range of speeds from zero to infinity then we get 1.

Most Probable Speeds (v_{mp})

-the speed of the largest number of molecules

- it corresponds to the peak of the Maxwell distribution function.

At the maximum, $df(v)/dv = 0$ …………………(7)

From this eqn and eqn. 6, we have

$4\pi (m/2\pi k_BT)^{3/2}$ — $[v^2 \exp(-mv^2/2k_BT)]=0$

Or, $4\pi (m/2\pi k_BT)^{3/2} [2v.\exp(-mv^2/2k_BT) + v^2.\exp(-mv^2/2k_BT).(-m.2v/2k_BT] = 0$

Or, $[1 - (mv^2/2k_BT)].2v.\exp(-mv^2/2k_BT) = 0$ …………………(8)

Three obvious possibilities:

(i) v = 0. When v ----> 0, f(v)---> 0,. This condition is corresponding to a minimum of the curve.

(ii) exp($-mv^2/2k_BT$) = 0. When v ----> ∞, f(v)---> 0,. This condition is also corresponding to a minimum of the curve.

(iii) 1 – ($mv^2/2k_BT$) = 0. This condition is corresponding to the maximum of the curve.

Then, most probable velocity, $v_{mp} = (2k_BT/m)^{1/2} = (2RT/M)^{1/2}$…………………(9)

$= 1.41(k_BT/m)^{1/2}$

Average Speed (<v>, or, v_{av})

By definition, average value of a property *q*, <q>, is the sum of all possible values (q_i) of that property weighted by the fraction (f_i) of times each value appears: $\langle q\rangle = \Sigma f_i q_i$

For a continuous distribution, one replaces summation with integration.

So, average speed, $\langle v\rangle = \sum f_i v_i$

$= \int_0^\infty f(v)\, v\, dv$

$= 4\pi (m/2\pi k_BT)^{3/2} \int_0^\infty v^3 \exp(-mv^2/2k_BT)]dv$

$= 4\pi (m/2\pi k_BT)^{3/2}. (2k_B{}^2 T^2/m^2)$

$= (8k_BT/\pi m)^{1/2} = (8RT/\pi M)^{1/2}$…………………(10)

$= 1.60(k_BT/m)^{1/2}$

Since $\int_0^\infty x^{2n+1} \exp(-ax^2)\, dx = n! / (2\, a^{n+1})$

$= 1! / [2\, .\, (m/2k_BT)^{1+1}]$ [here, n = 1, and a = $m/2k_BT$]

$= 4k_B{}^2 T^2/2m^2 = 2k_B{}^2 T^2/m^2$

Root Mean Square Speed (v_{rms})

Average of the square of the speed, $\langle v^2\rangle = \sum f_i v_i^2$

$= \int_0^\infty f(v)\, v^2\, dv$

$= 4\pi (m/2\pi k_BT)^{3/2} \int_0^\infty v^4 \exp(-mv^2/2k_BT)]dv$

$= 4\pi (m/2\pi k_BT)^{3/2}. (3/8).\ \pi^{1/.2} (2k_BT/m)^{5/2}$

$= 3k_BT/m$ …………………(11)

Since $\int_0^\infty x^{2n} \exp(-ax^2)\, dx = 1\, .\, 3\, .\, 5$……………(2n-1).$(\pi / a^{2n+1})^{1/2} / (2^{n+1})$

$$= 1 \,.\, 3 \,.\, [\pi / (m/2k_BT)^{(2\,.\,2+1)}]^{1/2} / (2^{2+1}) \text{ [here, n = 2, and a = } m/2k_BT]$$

$$= (3/8).\ \pi^{1/.2}\ (2k_BT/m)^{5/2}$$

So, root mean square speed, $v_{rms} = (3k_BT/m)^{1/2} = (3RT/M)^{1/2}$…………………(12)

$$= 1.73(k_BT/m)^{1/2}$$

Therefore, the translational kinetic energy of a particle, $E = ½\ mv_{rms}^2 = ½\ m\ .\ (3k_BT/m) = 3k_BT/2$ and its specific heat at constant volume, $C_v = d(E)/dT = 3k_B/2$

Please note that $\boldsymbol{v_{rms} > v_{av} > v_{mp}}$ and $\boldsymbol{v_{mp} : v_{av} : v_{rms} = 1 : 1.135 : 1.227}$

Maxwell-Boltzmann Distribution Law for the distribution of molecular energies

Here, we will consider the translational kinetic energy (E) as molecular energy.

The translational kinetic energy of a particle, $E = ½\ mv_{rms}^2$

So, $d(E)/dv = ½\ m.\ 2\ v_{rms} = mv_{rms} = m.\ (2E/m)^{1/2} = (2Em)^{1/2}$

$\Rightarrow dv = (2Em)^{-1/2}dE$

We know from eqn. 6 that the fraction of molecules having speeds between v and $(v + dv)$ is given by

$$f(v)dv = 4\pi\,(m/2\pi k_BT)^{3/2}\ v^2 \exp(-mv^2/2k_BT)\ dv$$

Similarly, the fraction of molecules having energies between E and $(E + dE)$ is given by

$f(E)dE = 4\pi\,(m/2\pi k_BT)^{3/2}\ (2E/m) \exp(-E/k_BT)\ (2Em)^{-1/2}dE$ (via substitution v in terms of E)

$$= [2\pi/(\pi k_BT)^{3/2}]\ \exp(-E/k_BT)\ (E)^{1/2}dE$$

$$= 2(E/\pi)^{1/2}(k_BT)^{-3/2} \exp(-E/k_BT)dE \text{ …………………(13)}$$

This expression is known as Maxwell-Boltzmann distribution law for kinetic energy.

Average Kinetic Energy (<*E*>)

So, average kinetic energy, $<E> = \sum \quad f_i E_i$

$$= (½)m \sum \quad f_i v_i^2$$

$$= (½)m \int_0^\infty f(v)\, v^2\, dv \qquad \text{(using eqn. 11)}$$

$$= (½)m\ .\ (3k_BT/m)$$

$$= 3k_BT/2 \text{ …………………(14)}$$