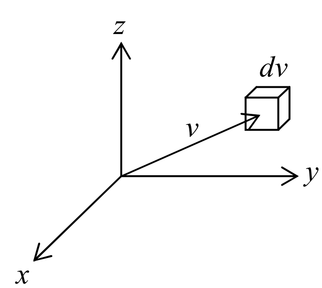
Kinetic Theory of Gases

4. Maxwell-Boltzmann Distribution Law:

Distribution of Molecular velocity in perfect gas.

Maxwell-Boltzmann distribution law is applicable for Ideal gas where molecules have no vibrational or rotational energies.

In the equilibrium state of the molecules have complete random motion and probability that a molecule has a given velocity component is independent of other two components.



In given figure dv is volume element in velocity space for a molecule at velocity $\vec{v} \equiv (v_x, v_y, v_z)$.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

We need to calculate number of molecules simultaneously having component in the range v_x to $v_x + dv_x, v_y$ to $v_y + dv_y$ and v_z to $v_z + dv_z$

It is assumptions in Maxwell-Boltzmann distribution law is that probability that molecule selected at random has velocities in a given range is a function purely at the magnitude of velocity and the width of the interval.

So fraction of molecule having velocity component in the range v_x to $v_x + dv_x, v_y$ to $v_y + dv_y$ and v_z to $v_z + dv_z$ is $f(v_x)dv_x, f(v_y)dv_y$ and $f(v_z)dv_z$ respectively.

$$\frac{dN}{N} = f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z$$

where dN is number of molecule having between velocity v to $v + dv$ and N is total number of molecules.

$$dN = N\, f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z$$

Number of molecule having velocity v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ is same as number of molecule having velocity v to $v + dv$.

So $$N\, f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z = N\, F(v^2)dv_x dv_y dv_z$$

F is some function of v^2 (magnitude of velocity) and for fixed value of $\vec{v}$, $F(v^2)$ is constant.

So $dF(v^2) = 0$ is equivalent to $d[f(v_x)f(v_y)f(v_z)] = 0$

$$f'(v_x)dv_x f(v_y)f(v_z) + f'(v_y)dv_y f(v_x)f(v_z) + f'(v_z)dv_z\, f(v_x)f(v_y) = 0$$

Dividing both side with $f(v_x)\, f(v_y)\, f(v_z)$

$$\frac{f'(v_x)}{f(v_x)}dv_x + \frac{f'(v_y)}{f(v_y)}dv_y + \frac{f'(v_z)}{f(v_z)}dv_z = 0 \qquad \text{(i)}$$

v^2 = constant $v_x^2 + v_y^2 + v_z^2 = v^2$

$$v_x dv_x + v_y dv_y + v_z dv_z = 0 \qquad \text{(ii)}$$

by method of Lagrange's method of undetermined multiplies multiply by 2β in equation (ii) and add in equation (i)

$$\left(\frac{f'(v_x)}{f(v_x)} + 2\beta v_x\right)dv_x + \left(\frac{f'(v_y)}{f(v_y)} + 2\beta v_y\right)dv_y + \left(\frac{f'(v_z)}{f(v_z)} + 2\beta v_z\right)dv_z = 0$$

hence v_x, v_y and v_z are independent

$$\frac{f'(v_x)}{f(v_x)}+2\beta v_x=0 \Rightarrow \frac{f'(v_y)}{f(v_y)}+2\beta v_y=0 \Rightarrow \frac{f'(v_z)}{f(v_z)}+2\beta v_z=0$$

$$f(v_x)=A_x e^{-\beta v_x^2} \qquad f(v_y)=A_y e^{-\beta v_y^2} \qquad f(v_z)=A_z e^{-\beta v_z^2}$$

$f(v_x), f(v_y), f(v_z)$ are probability density, so

$$\int_{-\infty}^{\infty} f(v_x)dv_x=1, \qquad \int_{-\infty}^{\infty} f(v_y)dv_y=1, \qquad \int_{-\infty}^{\infty} f(v_z)dv_z=1,$$

Use the integration

$$\int_0^{\infty} e^{-\beta v^2} v^n dv=\frac{1}{2\beta^{\left(\frac{n+1}{2}\right)}}\left\lceil \frac{n+1}{2}\right.$$

$$A_x\int_{-\infty}^{\infty} e^{-\beta v_x^2}dv_x=1 \;= A_x \quad 2\cdot\int_0^{\infty} e^{-\beta v_x^2}dv_x=1$$

$A_x=\left(\frac{\beta}{\pi}\right)^{1/2}$ Similarly, $A_y=\left(\frac{\beta}{\pi}\right)^{1/2}$ $A_z=\left(\frac{\beta}{\pi}\right)^{1/2}$

$$f(v_x)=\left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_x^2}, \quad f(v_y)=\left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_y^2}, \quad f(v_z)=\left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_z^2}$$

$$\frac{dN}{N}=\left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta\left(v_x^2+v_y^2+v_z^2\right)}dv_x dv_y dv_z$$

where $-\infty<v_x<\infty$, $\qquad -\infty<v_y<\infty$, $\qquad -\infty<v_z<\infty$

The Distribution in Term of Magnitude

$v^2=v_x^2+v_y^2+v_z^2$ which is equation of sphere and $dv_x dv_y dv_z$ can be replace by $4\pi v^2 dv$

$$f(v)dv=\frac{dN}{N}=\left(\frac{\beta}{\pi}\right)^{3/2} 4\pi e^{-\beta v^2} v^2 dv \qquad 0<v<\infty$$

To Determine Value of *β* in Term of Temperature *T*.

Mean square velocity $\left(\langle v^2\rangle\right)$ can be calculated by

$$\int_0^{\infty} v^2 f(v^2)dv$$

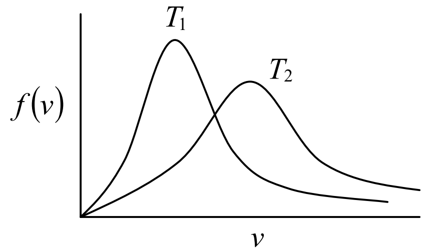
$$4\pi\left(\frac{\beta}{\pi}\right)^{3/2}\int_0^{\infty} v^4 e^{-\beta v^2}\,dv \qquad \Rightarrow \qquad 4\pi\left(\frac{\beta}{\pi}\right)^{3/2}\frac{1}{2\beta^{5/2}}\left\lceil 5/2\right.$$

$$4\pi\left(\frac{\beta}{\pi}\right)^{3/2}\frac{1}{2\beta^{5/2}}\frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi} \quad\Rightarrow\quad \langle v^2\rangle = \frac{3}{2}\cdot\frac{1}{\beta}$$

Now average energy of temperature T equivalent to

$$\frac{3}{2}k_BT = \frac{1}{2}m\langle v^2\rangle$$

$$\frac{3}{2}k_BT = \frac{1}{2}m\ \frac{3}{2}\frac{1}{\beta}\ = \beta = \frac{m}{2k_BT}$$



$T_1 < T_1$

So, $$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}}dv_x dv_y dv_z$$

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

Average Velocity

$$\langle v\rangle = \int_0^\infty vf(v)dv \qquad = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int e^{-\frac{mv^2}{2k_BT}}v^3dv \ = \sqrt{\frac{8k_BT}{\pi m}}$$

Root Mean Square Velocity

$$\left[\langle v^2\rangle\right]^{1/2} = \left[\int_0^\infty v^2 f(v)dv\right]^{1/2}$$

$$= \left[4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\right]^{1/2}\left[\int_0^\infty e^{-\frac{mv^2}{2k_BT}}v^2dv\right]^{1/2} = \sqrt{\frac{3k_BT}{m}}$$

Most Probable Velocity v_p : $\dfrac{df}{dv} = 0 \Rightarrow v_p = \sqrt{\dfrac{2k_BT}{m}}$

Example: For Maxwellian gas find the $\langle v\rangle \times \left\langle \frac{1}{v}\right\rangle$

Solution: $\langle v\rangle = \sqrt{\dfrac{8k_BT}{\pi m}} \Rightarrow \left\langle\dfrac{1}{v}\right\rangle = 4\pi\left(\dfrac{m}{2\pi k_BT}\right)^{3/2}\displaystyle\int_0^\infty \frac{1}{v}f(v)\ dv = \left(\frac{2m}{\pi k_BT}\right)^{1/2}$

$$\Rightarrow \langle v\rangle \times \left\langle\frac{1}{v}\right\rangle = \frac{4}{\pi}$$

Example: If V_x and V_y are x and y component of velocity then find the average value of $(av_x + bv_y)^2$

Solution: $\left\langle (av_x + bv_y)^2 \right\rangle = a^2 \left\langle v_x^2 \right\rangle + b^2 \left\langle v_y^2 \right\rangle + 2ab \left\langle v_x \cdot v_y \right\rangle$

$= a^2 \langle v_x^2 \rangle + b^2 \langle v_y^2 \rangle + 2ab \langle v_x \rangle \langle v_y \rangle$

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}} dv_x dv_y dv_z = 0$$

$$\langle v_x^2 \rangle = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x^2 e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}} dv_x dv_y dv_z = \frac{k_BT}{m}$$

Similarly, $\langle v_y \rangle = 0 \qquad \langle v_y^2 \rangle = \frac{k_BT}{m}$

$$\left\langle (av_x + bv_y)^2 \right\rangle = a^2 \langle v_x^2 \rangle + b^2 \langle v_y^2 \rangle + 2ab \langle v_x \rangle \langle v_y \rangle$$

$$= a^2 \frac{k_BT}{m} + b^2 \frac{k_BT}{m} + 0 = \frac{k_BT}{m}\left(a^2 + b^2\right)$$

Example: Write down expression of energy distribution function for Maxwellian gas between E and $E + dE$. Hence find $\langle E \rangle$ down $\langle E^2 \rangle$.

Solution: $E = \frac{1}{2} mv^2$, $dv = \frac{dE}{(2mE)^{1/2}}$

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_BT}} v^2 dv$$ put value of *v* and *dv*

$$f(E)dE = \frac{2}{\sqrt{\pi}} \frac{1}{(k_BT)^{3/2}} e^{-\frac{E}{k_BT}} E^{1/2} dE \qquad 0 < E < \infty$$

$$\langle E \rangle = \int_0^\infty Ef(E)dE \quad \langle E \rangle = \frac{3}{2} k_BT$$

$$\langle E^2 \rangle = \int_0^\infty E^2 f(E) \; dE,$$

$$\langle E^2 \rangle = \int_0^\infty E^2 \frac{2}{\sqrt{\pi}} \frac{1}{(k_BT)^{3/2}} e^{-\frac{E}{k_BT}} E^{1/2} dE = \frac{2}{\sqrt{\pi}}.(k_BT)^2.\frac{5}{2}.\frac{3}{2}\sqrt{\pi} = \frac{15}{2}.(k_BT)^2$$

Example: Write down expression of energy distribution function for Maxwellian gas between E and $E+dE$ in two dimensional system. Hence find $\langle E \rangle$.

Solution: $E = \frac{1}{2}mv^2$, $dv = \frac{dE}{(2mE)^{1/2}}$

$$f(v)dv = 2\pi\left(\frac{m}{2\pi k_B T}\right)^{2/2} e^{-\frac{mv^2}{2k_B T}} v dv$$ put value of *v* and *dv*

$$f(E)dE = \frac{1}{(k_B T)} e^{-\frac{E}{K_B T}} dE \qquad 0 < E < \infty$$

$$\langle E \rangle = \int_0^\infty E f(E) dE \Rightarrow \langle E \rangle = k_B T$$

Example: Using the Maxwell distribution function, calculate the mean velocity projection $\langle v_x \rangle$ the mean value of the modulus of the modulus of this projection $\langle |v_x| \rangle$ if the mass of each molecule is equal to m and the gas temperature is T.

Solution: We know Mean Velocity

$$= \langle v_x \rangle = \int_{-\infty}^{\infty} \frac{v_x dN}{N} = \frac{\int_{-\infty}^{\infty} v_x N \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m}{2k_B T}v_x^2} dv_x}{N} = 0$$

Mean speed $$\langle |v_x| \rangle = \frac{\int_{-\infty}^{\infty} |v_x| N \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m}{2k_B T}v_x^2} dv_x}{N}$$

$$\langle |v_x| \rangle = \frac{2\int_0^{\infty} v_x N \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m}{2k_B T}v_x^2} dv_x}{N} \Rightarrow \langle |v_x| \rangle = \sqrt{\frac{2k_B T}{\pi m}}$$