Velocity component distribution

What is the number of molecules within velocity u & $u+du$ but any value in $\hat{y}$ or $\hat{z}$ direction.

$$dN_{u,v,w} = N\left(\frac{m}{2\pi K_B T}\right)^{3/2} e^{-\frac{m}{2K_BT}(u^2+v^2+w^2)}\, du\, dv\, dw.$$

$$\therefore \quad dN_u = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dN_{u,v,w}$$

$$= N\left(\frac{m}{2\pi K_B T}\right)^{3/2} du \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv \int_{-\infty}^{\infty} e^{-\frac{mw^2}{2K_BT}} dw \times e^{-\frac{mu^2}{2K_BT}}$$

$$\left[\text{Now} \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv = 2\int_{0}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv \right.$$

$\left[\text{put } z = \frac{mv^2}{2K_BT}.\right.$

$dz = \frac{mv\,dv}{K_BT}$

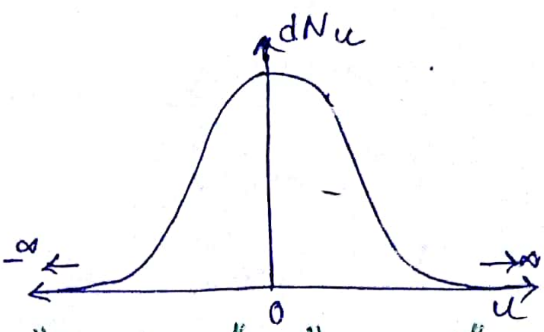
$\left.dv = \frac{K_BT\,dz\,\sqrt{m}}{m\sqrt{2K_BT}\sqrt{z}}\right]$

$$= \frac{2\sqrt{K_BT}}{\sqrt{2}\sqrt{m}} \int_{0}^{\infty} e^{-z} z^{-1/2} dz$$

$$\left.= \sqrt{\frac{2K_BT}{m}} \times \sqrt{\pi} = \sqrt{\frac{2\pi K_BT}{m}}\right]$$

$$\therefore \quad dN_u = N\left(\frac{m}{2\pi K_BT}\right)^{3/2}\left(\frac{2\pi K_BT}{m}\right)^{2/2} e^{-\frac{mu^2}{2K_BT}} du$$

$$dN_u = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{mu^2}{2K_BT}} du$$



"Gaussian" or "Normal" distribution

Similarly, $dN_v = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{mv^2}{2K_BT}} dv$

$$dN_w = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{mw^2}{2K_BT}} dw.$$

Average velocity, RMS velocity, Most probable velocity

Avg. velocity $\langle c \rangle = \frac{N_1c_1 + N_2c_2 + \cdots}{N_1 + N_2 + \cdots} = \frac{\sum N_i c_i}{\sum N_i}$

$$= \int_0^\infty c\,dN_c / N$$

remember,

$A = \left(\frac{m}{2\pi k_BT}\right)^{1/2}$

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

$$= 4\pi \left(\frac{m}{2\pi k_BT}\right)^{3/2} \int_0^\infty c \cdot c^2 e^{-\frac{mc^2}{2k_BT}} dc$$

$$= 4\pi A^3 \int_0^\infty c^3 e^{-bc^2} dc$$

put $bc^2 = z$

$2bc\,dc = dz$

$$= 4\pi A^3 \int \frac{z}{b} e^{-z} \frac{dz}{2b} = \frac{4\pi A^3}{2b^2} \int e^{-z} z\,dz$$

$$= \frac{4\pi A^3}{2b^2}\Gamma(2) = \frac{4\pi A^3}{2b^2} = 4\pi \frac{m}{2\pi k_BT}\left(\frac{m}{2\pi k_BT}\right)^{1/2} \times \frac{4k_B^2T^2}{2m^2}$$

$\Gamma(2) = 1$

$$= \left(\frac{8k_BT}{m\pi}\right)^{1/2}$$

$$\therefore \boxed{\langle c \rangle = \sqrt{\frac{8k_BT}{m\pi}}}$$

RMS velocity $c_{rms}^2 = \frac{\sum N_i c_i^2}{\sum N_i} = \frac{1}{N}\int_0^\infty c^2 dN_c$

$$= 4\pi A^3 \int_0^\infty c^4 e^{-bc^2} dc$$

put, $bc^2 = z$

$2bc\,dc = dz$

$dc = \frac{dz\sqrt{b}}{2b\sqrt{z}}$

$$= 4\pi A^3 \int_0^\infty \frac{z^2}{b^2} e^{-z} \frac{dz\sqrt{b}}{2b\sqrt{z}}$$

$$= \frac{4\pi A^3}{2b^{5/2}} \int_0^\infty e^{-z} z^{3/2} dz = \frac{4\pi A^3}{2b^{5/2}} \Gamma(5/2)$$

$$= \frac{4\pi A^3}{2b^{5/2}} \frac{3}{2} \times \frac{1}{2} \times \sqrt{\pi} = \frac{3\pi^{3/2}}{2}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2k_B T}{m}\right)^{5/2}$$

$$= \frac{3k_B T}{m}$$

$$\therefore \boxed{c_{rms} = \sqrt{\frac{3k_B T}{m}}}$$

Most probable velocity c_m is $\left.\frac{dF_c}{dc}\right|_{c=c_m} = 0$.

$$\therefore \left.\frac{d}{dc}\left\{4\pi A^3 c^2 e^{-bc^2}\right\}\right|_{c=c_m} = 0$$

$$\text{or } \frac{d}{dc}\left\{c^2 e^{-bc^2}\right\}_{c=c_m} = 0$$

$$\text{or } \left\{2c\,e^{-bc^2} - c^2\, 2bc\, e^{-bc^2}\right\}_{c=c_m} = 0.$$

$$\text{or } \left\{2c\,e^{-bc^2}(1-bc^2)\right\}_{c=c_m} = 0.$$

This can be true if $c \to \infty$ (unphysical) or $\{1-bc^2\}_{c=c_m} = 0$

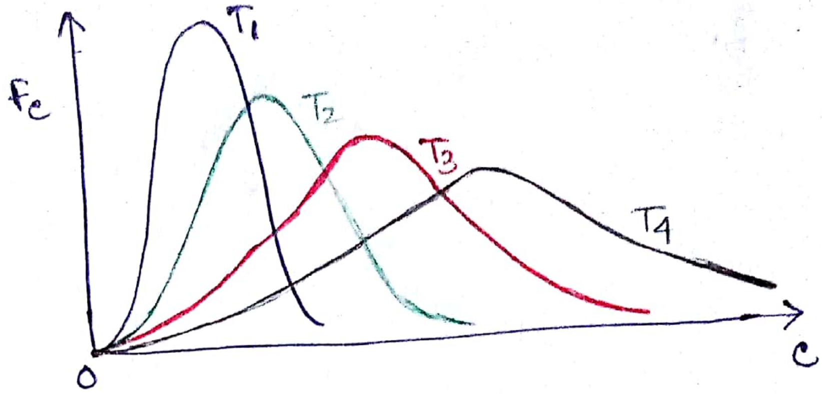
$$\therefore bc_m^2 = 1 \quad \text{or} \quad c_m = \frac{1}{\sqrt{b}} = \sqrt{\frac{2k_B T}{m}}$$

$$\text{or } \boxed{c_m = \sqrt{\frac{2k_B T}{m}}}$$

Note $c_{rms} > \langle c \rangle > c_m$

Corollary $\int_0^\infty f_c\, dc = 1$

$T_4 > T_3 > T_2 > T_1$



Also, no. of molecules colliding per unit area per unit time

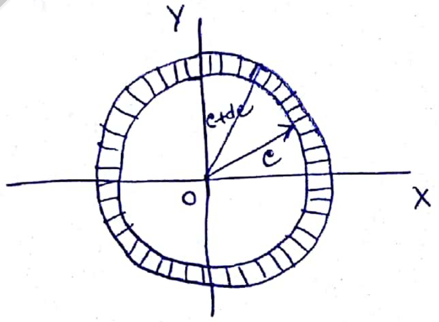
$$dn = \frac{1}{4} n \bar{c} = \frac{1}{4} n \sqrt{\frac{8K_BT}{m\pi}} = \frac{1}{4}\frac{P}{K_BT}\sqrt{\frac{8K_BT}{m\pi}} \quad (\text{as } P = nk_BT)$$

$$\boxed{dn = \frac{P}{\sqrt{2m\pi K_BT}}}$$

CW 1. The velocity distribution in two dimension is

$$dn_{u,v} = n\left(\frac{m}{2\pi K_BT}\right) e^{-\frac{m(u^2+v^2)}{2K_BT}}\, du\,dv.$$ From this, find the distribution of molecular speed. Using that, find c_m, $\bar{c}$, c^2_{rms}.

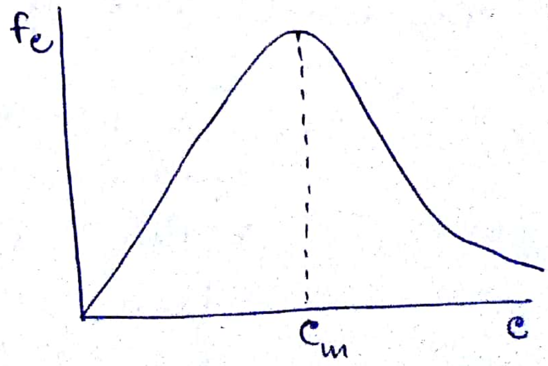
$c^2 = u^2 + v^2$.



Take two concentric circles between velocity c & $c+dc$, area

$$du\,dv = \pi(c+dc)^2 - \pi c^2 = 2\pi c\,dc.$$

$$\therefore\ dn_c = n\left(\frac{m}{2\pi K_BT}\right) e^{-\frac{mc^2}{2K_BT}}\, 2\pi c\,dc = f_c\,dc.$$



$$\left.\frac{df_c}{dc}\right|_{c=c_m} = 0$$

$$\text{or } \frac{d}{dc}\left(c\,e^{-mc^2/2K_BT}\right) = 0$$

$$\text{or } 1 - c_m^2\frac{m}{K_BT} = 0 \quad \text{or } c_m = \sqrt{\frac{K_BT}{m}}$$

please also calculate $\frac{1}{n}\int_0^\infty c\,dn_c$ & $\frac{1}{n}\int_0^\infty c^2\,dn_c$.

Convince yourself that $c_{rms} = \sqrt{\frac{2K_BT}{m}}$ and $\bar{c} = \sqrt{\frac{\pi K_BT}{2m}}$.

2. Using Maxwell velocity distribution, calculate the probability that the velocity of O_2 molecule lies between 100 m/s & 101 m/s at $-73^\circ C$.

$$dN_c = 4\pi N\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{mc^2}{2K_BT}} c^2 dc.$$

$$\therefore \text{ Probability } P = \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-mc^2/2K_BT} c^2 dc. \quad \text{— (1)}$$

$$\text{Now } m = \frac{M}{N} = \frac{32\ gm}{6.023\times10^{23}} = 5.31\times10^{-26}\ kg.$$

$$T = -73^\circ c = 200K, \quad c = 100\ m/s, \quad dc = 101-100 = 1\ m/s.$$

$$\therefore P = 4\pi\left[\frac{5.31\times10^{-26}}{2\pi\times1.38\times10^{-23}\times200}\right]^{3/2} \times \exp\left[-\frac{5.31\times10^{-26}\times10^4}{2\times1.38\times10^{-23}\times200}\right] \times 10^4\times1$$

$$= 4\pi\times5.36\times10^{-9}\times0.9\times10^4 = 6.06\times10^{-4}. = 0.06\%$$

3. Compute the fraction of molecules of a gas possessing speeds within 1% of the most probable speed.

$$C_m = \sqrt{\frac{2K_BT}{m}}$$

fraction = probability P in equation (1) above. with $c = C_m$

$$P = 4\pi\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\cancel{\frac{m}{2K_BT}}\cancel{\frac{2K_BT}{m}}} \frac{2K_BT}{m} dc_M$$

~~dcm is 1% of Cm~~ ~~As Cm~~

As c varies within 1% of $C_m \Rightarrow [0.99C_m, 1.01C_m]$.

$$\therefore dC_m = (1.01-0.99)C_m = 0.02\times\sqrt{\frac{2K_BT}{m}}.$$

$$\therefore P = \frac{4}{\sqrt{\pi}}\cancel{\left(\frac{m}{2K_BT}\right)^{3/2}} e^{-1} \cancel{\frac{2K_BT}{m}} \cancel{\sqrt{\frac{2K_BT}{m}}} \times 0.02$$

$$= 0.016 = 1.6\%.$$

HW

1. At what value of speed c will the Maxwell's distribution F_c yield same magnitude for a mixture of hydrogen & helium gases at $27°c$?

2. Find $\langle c^{-1} \rangle$ using F_c.

3. Molecular mass of an ideal gas of O_2 is 32. Calculate c_m, $\bar{c}$, c_{rms} of the gas at $27°c$. (Given $R = 8.3\ J/°c/mol$)

4. Convince yourself that $\frac{RT}{M} = \frac{P}{\rho}$. Using that, calculate $c_m, \bar{c}, c_{rms}$ of the molecules of gas at density 1.293×10^{-3} gm/cc at 76 cm of Hg pressure.

5. The quantity $(c-\bar{c})^2 = c^2 - 2c\bar{c} + \bar{c}^2$ is squared deviation of atomic speed from average speed. Calculate the average value of this using Maxwell distribution & obtain the rms deviation.

Maxwell's distribution in reduced format

$$dN_c = 4\pi N \left(\frac{m}{2\pi K_B T}\right)^{3/2} e^{-mc^2/2K_BT} c^2 dc$$

with respect to $C_m = \sqrt{\frac{2K_BT}{m}}$, non dimensionalized velocity $U = \frac{c}{C_m}$

Substitute $c = \sqrt{\frac{2K_BT}{m}}\, U$,

$$dN_c = 4\pi N \left(\frac{m}{2\pi K_B T}\right)^{3/2} \frac{2K_BT}{m} U^2 \sqrt{\frac{2K_BT}{m}}\, dU\, e^{-\frac{m}{2K_BT}\frac{2K_BT}{m}U^2}$$

$$dN_U = \frac{4N}{\sqrt{\pi}} U^2 e^{-U^2} dU.$$

This distribution is <u>independent of temperature</u>.

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