

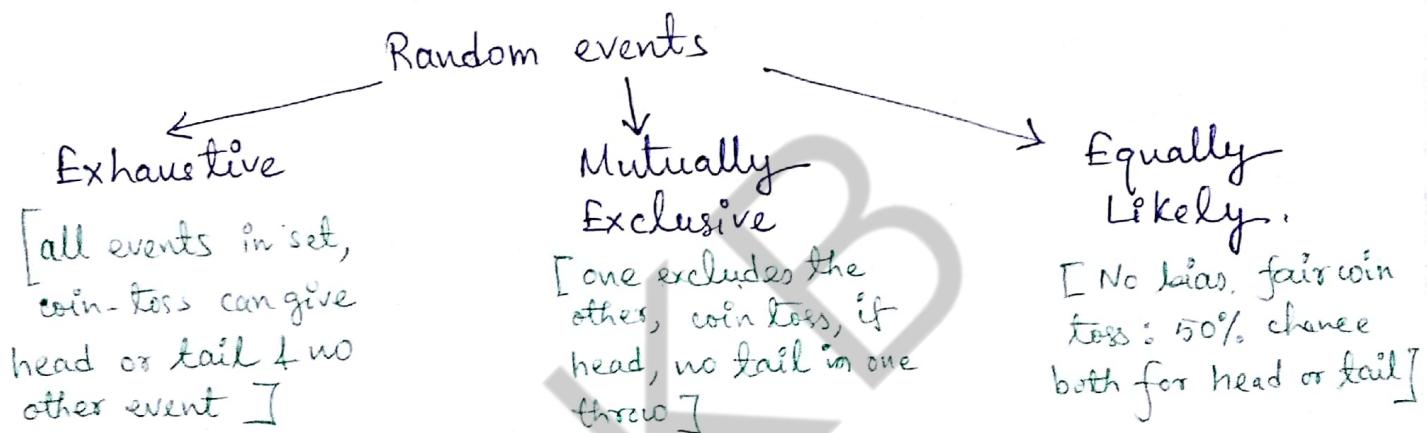
## Maxwell-Boltzmann law of distribution of velocity

The question is what is  $dn_c$ ? Physically  $dn_c$  is no. of atoms per unit volume within velocity  $c$  &  $c+dc$ .

Can we calculate  $dn_c$ ?  $dn_c \stackrel{?}{=} f(P, T)$ .

J.C. Maxwell computed it in 1859.

Let's digress & an excursion to random events & what we mean by "probability".



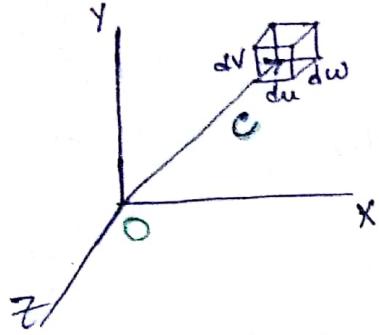
If there are  $N$  number of exhaustive, mutually exclusive and equally likely events of which  $M$  number are favourable to event A, then

$$P(A) = \frac{M}{N}$$

If two events A & B mutually exclusive, then total probability of either of them to happen in a trial is  $P(A) + P(B)$

If two events A & B happen independently, then total probability of both events happening simultaneously in a trial is  $P(A) P(B)$ .

If  $x$  is random variable defined by a function  $f(x)$ ,  
 then  $f(x)dx = \text{probability of a variate falling within}$   
 $x \& x+dx.$



- Assumptions :
- (a) density is uniform & velocity in all direction is equal.
  - (b) isotropy  $\rightarrow$  results independent of coordinate system.
  - (c) velocities in any 3 coordinates is independent

If a molecule at  $0$  has velocity  $\vec{c} = (u\hat{i}, v\hat{j}, w\hat{k})$   
 then  $c^2 = u^2 + v^2 + w^2$ . Components  $u, v, w$  can change as  
 $\vec{c}$  changes direction but magnitude of  $c = \text{constant}$ .

$$\therefore dc^2 = 0 = 2udu + 2vdv + 2wdw$$

$$\text{So } udu + vdv + wdw = 0 \quad \text{--- (1)}$$

This means  $du, dv$  &  $dw$  are not independent.

Probability that an atom has  $x$  component of velocity  
 $u$  &  $u+du$  is  $f(u)du$ , mathematically,  $P_u = \frac{dn_u}{n} = f(u)du$ .  
 $n = \text{number density}$ .

Similarly, between  $v$  &  $v+dv$  is  $P_v = \frac{dn_v}{n} = f(v)dv$

" "  $w$  &  $w+dw$  is  $P_w = \frac{dn_w}{n} = f(w)dw$ .

As they're independent\*, the total probability is

$$P_{u,v,w} = \frac{dn_{u,v,w}}{n} = f(u)f(v)f(w) du dv dw$$

$dn_{u,v,w} = n f(u)f(v)f(w) du dv dw$ , also means

$$dN_{u,v,w} = N f(u)f(v)f(w) du dv dw$$

So in  $N$  number of molecules,  $dN_{u,v,w}$  means this many of them are between  $u \& u+du$ ,  $v \& v+dv$ ,  $w \& w+dw$ .

$$\therefore \text{Molecular density } \rho = \frac{dN_{u,v,w}}{du dv dw} = N f(u) f(v) f(w)$$

& as this is uniform,  $d\rho = 0$

$$= f'(u) f(v) f(w) du + f(u) f'(v) f(w) dv + f(u) f(v) f'(w) dw$$

$$\text{Divide by } \frac{1}{f(u) f(v) f(w)} \Rightarrow \frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} dw = 0 \quad \text{--- (2)}$$

when ① & ② both are true, we invoke Lagrange's undetermined multiplier  $\lambda$  do ①  $\times \lambda +$  ②,

$$\left[ \frac{f'(u)}{f(u)} + \lambda u \right] du + \left[ \frac{f'(v)}{f(v)} + \lambda v \right] dv + \left[ \frac{f'(w)}{f(w)} + \lambda w \right] dw = 0$$

If we say,  $du$  is dependent, then we choose  $\lambda$  such that

$$\frac{f'(u)}{f(u)} + \lambda u = 0$$

& because  $dv$  &  $dw$  is dependent, so

$$\frac{f'(v)}{f(v)} + \lambda v = 0, \quad \frac{f'(w)}{f(w)} + \lambda w = 0.$$

$$\therefore \frac{df(u)}{f(u)} = -\lambda u du.$$

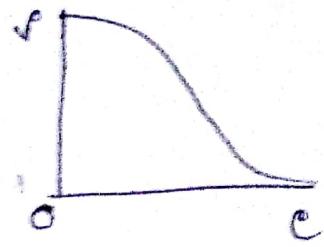
$$\text{Integrating, } \ln f(u) = -\frac{\lambda}{2} u^2 + \ln A$$

$$\text{or } f(u) = A e^{-\frac{\lambda u^2}{2}} = A e^{-\frac{b u^2}{2}} \quad \left\{ b = \frac{\lambda}{2} \right\}$$

$$\text{Similarly, } f(v) = A e^{-\frac{b v^2}{2}}, \quad f(w) = A e^{-\frac{b w^2}{2}}$$

$$\text{So } f = N A^3 e^{-b(u^2+v^2+w^2)} = N A^3 e^{-bc^2}$$

$$dN_{u,v,w} = N A^3 e^{-b(u^2+v^2+w^2)} du dv dw$$



What is remaining now is to find out

constants A & b.

$$\iiint_{-\infty}^{\infty} dN_{u,v,w} = N$$

$$\text{or } NA^3 \int_{-\infty}^{\infty} e^{-bu^2} du \int_{-\infty}^{\infty} e^{-bv^2} dv \int_{-\infty}^{\infty} e^{-bw^2} dw = N$$

$$\left[ \text{Now } \int_{-\infty}^{\infty} e^{-bu^2} du \right]$$

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

$$= \frac{1}{2\sqrt{b}} \int_0^{\infty} e^{-z} z^{-1/2} dz = \frac{\Gamma(1/2)}{\sqrt{b}} = \frac{\sqrt{\pi}}{\sqrt{b}}$$

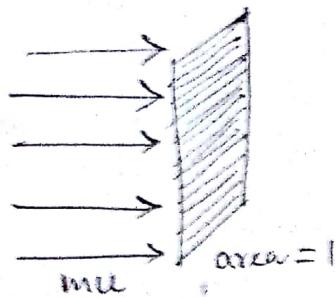
$$A^3 \left(\frac{\pi}{b}\right)^{1/2} = 1 \Rightarrow A = \sqrt{\frac{b}{\pi}}$$

Evaluate b

Collisions per second

= area  $\times$  velocity  $\times$  number density at that

$$= 1 \times u \times n_u$$



Change in momentum =  $2mu$ .

So pressure = rate of change of momentum per unit area.

$$P_u = \sum_{u=0}^{\infty} u n_u \times 2mu = 2m \sum_{u=0}^{\infty} n_u u^2 = 2m \int_0^{\infty} n_u u^2 f(u) du$$

$$= 2m n_u \int_0^{\infty} A e^{-bu^2} u^2 du$$

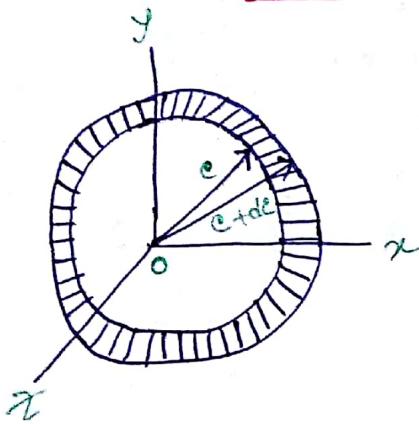
$$\begin{aligned}\therefore P_u &= 2mn_u A \int_0^\infty e^{-\frac{z^2}{b}} \frac{z}{b} \frac{dz}{2b\sqrt{z}} \quad [\text{put } bu^2 = z] \\ &= \frac{mn_u A}{2b^{3/2}} \Gamma\left(\frac{1}{2}\right) \\ &= \frac{mn_u}{2b^{3/2}} \frac{b^{1/2}}{\pi^{1/2}} \cdot \cancel{\pi^{1/2}} = \frac{mn_u}{2b} = n_u K_B T.\end{aligned}$$

$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right)$

[from Clapeyron's equation]

$$\therefore b = \frac{m}{2K_B T} \quad A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi K_B T}}$$

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

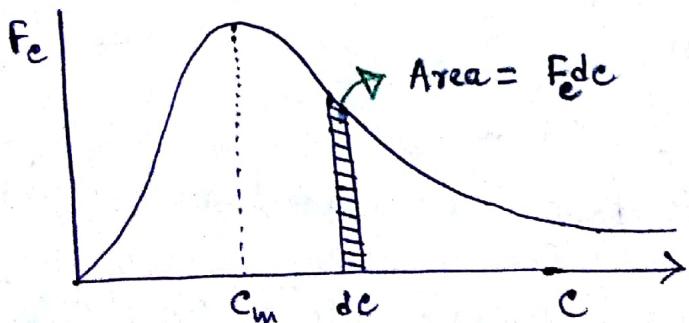


volume between  $c$  &  $c+dc$  is

$$\begin{aligned}&\frac{4}{3}\pi(c+dc)^3 - \frac{4}{3}\pi c^3 \\&= \frac{4}{3}\pi c^3 + \frac{4}{3}\pi 3c^2 dc + \frac{4}{3}\pi 3c(dc)^2 + \frac{4}{3}\pi (dc)^3 \\&= 4\pi c^2 dc.\end{aligned}$$

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

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



Remarks : (a)  $c \rightarrow 0, F_c \rightarrow 0$

(b)  $c \rightarrow \infty, F_c \rightarrow 0$

$$c_m = F_c^{\text{maximum}}$$

= most probable velocity

= maximum no. of atoms  
will possess this velocity

## Velocity component distribution

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

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

$$\begin{aligned} \therefore dN_u &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dN_{u,v,w} \\ &= N \left( \frac{m}{2\pi k_B T} \right)^{3/2} du \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv \int_{-\infty}^{\infty} e^{-\frac{mw^2}{2k_B T}} dw \times e^{-\frac{mu^2}{2k_B T}} \end{aligned}$$

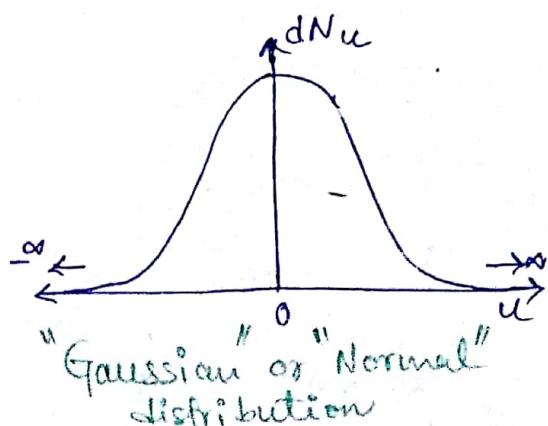
$$\begin{aligned} \left[ \text{Now } \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv \right] &= 2 \int_0^{\infty} e^{-\frac{mv^2}{2k_B T}} dv \\ &= \frac{2\sqrt{k_B T}}{\sqrt{2\pi m}} \int_0^{\infty} e^{-z^2} z^{-1/2} dz \\ &= \sqrt{\frac{2k_B T}{m}} \times \sqrt{\pi} = \sqrt{\frac{2\pi k_B T}{m}}. \end{aligned}$$

$$\therefore dN_u = N \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left( \frac{2\pi k_B T}{m} \right)^{1/2} e^{-\frac{mu^2}{2k_B T}} du$$

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

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

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



Average velocity, RMS velocity, Most probable velocity

$$\text{Avg. velocity } \langle c \rangle = \frac{N_1 c_1 + N_2 c_2 + \dots}{N_1 + N_2 + \dots} = \frac{\sum N_i c_i}{\sum N_i}$$

$$= \int_0^\infty c dN_c / N$$
$$= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty c \cdot c^2 e^{-\frac{mc^2}{2k_B T}} dc$$
$$= 4\pi A^3 \int_0^\infty c^3 e^{-bc^2} dc$$

remember,

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

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

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

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

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

put  $be^2 = 2$   
 $2bcdc = dz$

$$\Gamma(2) = 1$$

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

$$\begin{aligned}
 \text{RMS velocity } C_{\text{rms}}^2 &= \frac{\sum N_i c_i^2}{\sum N_i} = \frac{1}{N} \int_0^\infty c^2 dN_c \\
 &= 4\pi A \int_0^\infty c^4 e^{-bc^2} dc \\
 &= 4\pi A \int_0^\infty \frac{z^2}{b^2} e^{-z^2} \frac{dz \sqrt{b}}{2b\sqrt{z}} \\
 &= \frac{4\pi A^3}{2b^{5/2}} \int_0^\infty e^{-z^2} z^{3/2} dz = \frac{4\pi A^3}{2b^{5/2}} \Gamma(5/2) \\
 &= \frac{A\pi A^3}{2b^{5/2}} \frac{3}{2} \times \frac{1}{2} \times \sqrt{\pi} = \frac{3\pi^{3/2}}{2} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(\frac{2k_B T}{m}\right)^{5/2} \\
 &= \frac{3k_B T}{m} \quad \therefore C_{\text{rms}} = \boxed{\sqrt{\frac{3k_B T}{m}}}
 \end{aligned}$$

put,  $bc^2 = z$

$$2bc dc = dz$$

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

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

$$\begin{aligned}
 \therefore \frac{d}{dc} \left\{ 4\pi A c^3 e^{-bc^2} \right\} \Big|_{c=c_m} &= 0 \\
 \text{or } \frac{d}{dc} \left\{ c^2 e^{-bc^2} \right\} \Big|_{c=c_m} &= 0 \\
 \text{or } \left\{ 2ce^{-bc^2} - c^2 2bc e^{-bc^2} \right\} \Big|_{c=c_m} &= 0 \\
 \text{or } \left\{ 2ce^{-bc^2} (1 - bc^2) \right\} \Big|_{c=c_m} &= 0.
 \end{aligned}$$

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

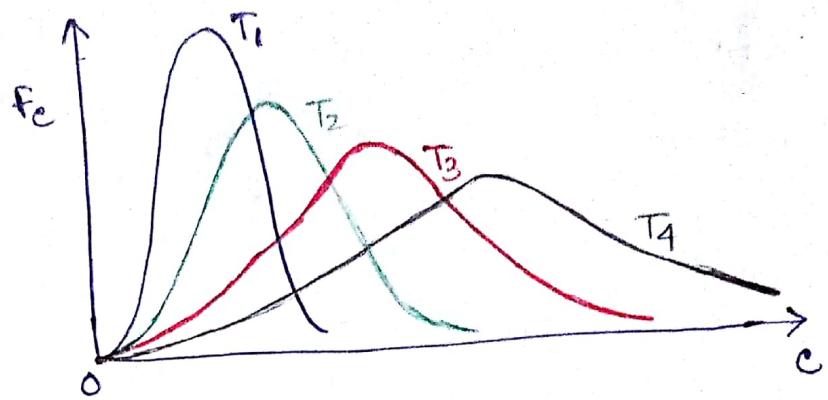
$$\therefore bc_m^2 = 1 \quad \text{or} \quad c_m = \frac{1}{\sqrt{b}} = \sqrt{\frac{2k_B T}{m}}$$

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

Note  $C_{\text{rms}} > \langle c \rangle > C_m$

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

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

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

CW 1. The velocity distribution in two dimension is

$$d^2n_{u,v} = n \left( \frac{m}{2\pi k_B T} \right) e^{-\frac{m(u^2+v^2)}{2k_B T}} du dv.$$

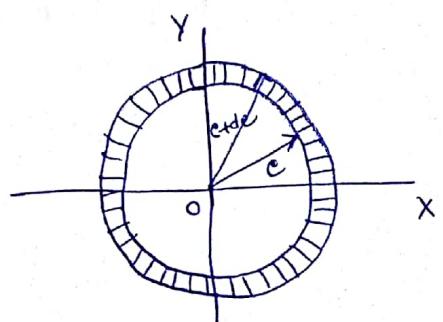
Find the distribution of molecular speed. Using that, find  $c_m, \bar{c}, c_{rms}$ .

$$\bar{c}^2 = u^2 + v^2.$$

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

$$dudv = \pi(c+dc)^2 - \pi c^2 = 2\pi c dc.$$

$$\therefore d^2n_c = n \left( \frac{m}{2\pi k_B T} \right) e^{-\frac{mc^2}{2k_B T}} 2\pi c dc = f_c dc.$$

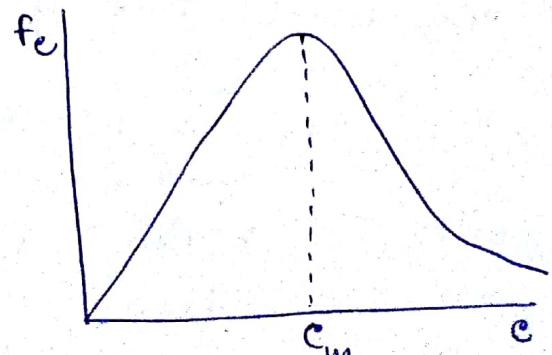


$$\frac{df_c}{dc} \Big|_{c=c_m} = 0$$

$$\therefore \frac{d}{dc} \left( c e^{-\frac{mc^2}{2k_B T}} \right) = 0$$

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

Please also calculate  $\frac{1}{n} \int_0^\infty c^2 dc$  &  $\frac{1}{n} \int_0^\infty c^2 dc$ .



convince yourself that  $c_{rms} = \sqrt{\frac{2k_B T}{m}}$  and  $\bar{c} = \sqrt{\frac{k_B T}{2m}}$ .

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

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

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

$$\text{Now } m = \frac{M}{N} = \frac{32 \text{ gm}}{6.023 \times 10^{23}} = 5.31 \times 10^{-26} \text{ kg.}$$

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

$$\therefore P = 4\pi \left[ \frac{5.31 \times 10^{-26}}{2\pi \times 1.38 \times 10^{-23} \times 200} \right]^{3/2} \times \exp \left[ -\frac{5.31 \times 10^{-26} \times 10^4}{2 \times 1.38 \times 10^{-23} \times 200} \right] \times 10^4 \times 1 \\ = 4\pi \times 5.36 \times 10^{-9} \times 0.9 \times 10^4 = 6.06 \times 10^{-4} = 0.06\%$$

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

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

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

$$P = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m}{2k_B T} \frac{2k_B T}{m}} \frac{2k_B T}{m} dc_m$$

~~$dc_m$  is  $\pm 1\%$  of  $c_m$~~  As  $dc_m$

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

$$\therefore dc_m = (1.01 - 0.99)c_m = 0.02 \times \sqrt{\frac{2k_B T}{m}}.$$

$$\therefore P = \frac{1}{\sqrt{\pi}} \left( \frac{m}{2k_B T} \right)^{3/2} e^{-\frac{1}{\frac{2k_B T}{m}}} \sqrt{\frac{2k_B T}{m}} \times 0.02 \\ = 0.016 = 1.6\%.$$

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  $27^\circ\text{C}$ ?
2. Find  $\langle c \rangle$  using  $F_c$ .
3. Molecular mass of an ideal gas of  $\text{O}_2$  is 32. Calculate  $c_m, \bar{c}, c_{rms}$  of the gas at  $27^\circ\text{C}$ . (Given  $R = 8.3 \text{ J}/\text{K}\cdot\text{mol}$ )
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  $1.293 \times 10^{-3} \text{ gm/cc}$  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

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

with respect to  $c_m = \sqrt{\frac{2k_B T}{m}}$ , non dimensionalized  $U = \frac{c}{c_m}$  velocity

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

$$-\frac{m}{2k_B T} \frac{2k_B T}{m} U^2$$

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

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

This distribution is independent of temperature.

## Energy distribution of the gaseous atoms

What we are after is to find the no. of atoms having K.E. between  $E$  &  $E + dE$ . As they don't have P.E.

$$E = \frac{1}{2}mc^2 \quad \text{or} \quad dE = mcdc.$$

$$\text{or} \quad dc = \frac{dE}{m\sqrt{\frac{2E}{m}}} = \frac{dE}{\sqrt{2mE}}$$

From Maxwell's velocity distribution, we have

$$dn_c = 4\pi n c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc^2/2k_B T} dc.$$

$$\therefore dn_E = 4\pi n \frac{2E}{m} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-E/k_B T} \frac{dE}{\sqrt{2mE}}$$

$$dn_E = 2n \sqrt{\frac{E}{\pi}} (k_B T)^{-3/2} e^{-E/k_B T} dE$$

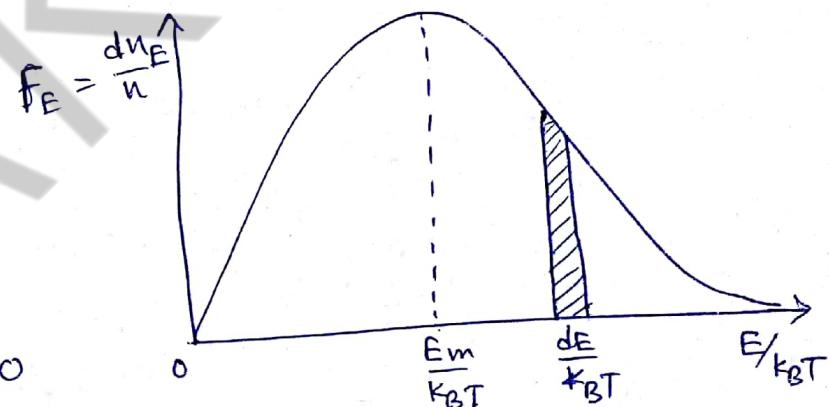
(remember if  $V$  is cancelled  $dN_E \sim N$ )

$$\text{fraction of atoms } \frac{dn_E}{n} \text{ or } \frac{dN_E}{N} = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T} dE = f_E dE$$

$$f_E = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T}$$

$$\text{at } E = E_m, \frac{df_E}{dE} = 0$$

$$\frac{d}{dE} \left\{ \sqrt{E} e^{-E/k_B T} \right\}_{E=E_m} = 0$$



$$\therefore \frac{1}{2\sqrt{E_m}} e^{-E_m/k_B T} - \frac{\sqrt{E_m}}{k_B T} e^{-E_m/k_B T} = 0$$

$$\therefore \frac{1}{2\sqrt{E_m}} = \frac{\sqrt{E_m}}{k_B T} \quad \text{or} \quad E_m = \frac{k_B T}{2}$$

Compare result with  $C_m = \sqrt{\frac{2k_B T}{m}}$ . Notice that

$$E_m \neq \frac{1}{2}mc_m^2 = \frac{1}{2}m \frac{2k_B T}{m} = k_B T.$$

## Momentum distribution of the gaseous atoms

No. of molecules in a range of momentum  $p$  to  $p+dp$ .

$$p = mc \quad \& \quad dp = mdc.$$

Again, start from Maxwell's distribution

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

$$\therefore dN_p = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} \frac{p^2}{m^2} e^{-\frac{p^2}{2k_B T m}} \frac{dp}{m}$$

$$= N \sqrt{\frac{2}{\pi}} (m k_B T)^{-3/2} p^2 e^{-\frac{p^2}{2m k_B T}} dp = f_p dp.$$

at  $p = p_m$  (most probable momentum), maximum no. of molecules

lie  $\frac{df_p}{dp} \Big|_{p=p_m} = 0 \quad \text{or} \quad \frac{d}{dp} \left( p^2 e^{-\frac{p^2}{2m k_B T}} \right) \Big|_{p=p_m} = 0$

$$\text{or} \quad \frac{d}{dp} \left( p^2 e^{-bp^2} \right) \Big|_{p=p_m} = 0$$

$$\text{or} \quad \left( 2p e^{-bp^2} - p^2 \cdot 2bp e^{-bp^2} \right) \Big|_{p=p_m} = 0$$

$$\text{or} \quad \left[ 2p e^{-bp^2} (1 - bp^2) \right] \Big|_{p=p_m} = 0 \quad \Rightarrow \quad p_m = \frac{1}{\sqrt{b}} = \sqrt{2m k_B T}$$

$$\text{put } b = \frac{1}{2m k_B T}$$

$$\text{Again, } c_m = \sqrt{\frac{2k_B T}{m}}$$

$$\text{So } mc_m = \sqrt{2m k_B T} = p_m.$$

So most of the atoms have velocity  $c_m$  are also having the momentum  $mc_m$ , but ~~most~~ most of them do not have  $\frac{1}{2}mc_m^2$  energy, rather most of the atoms have energy half of that.

If P.E. included in gravitational field  $dN_c = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} \times e^{-(mgh + \frac{1}{2}mc^2)/k_B T} c^2 dc$

Maxwell-Boltzmann distribution.

14

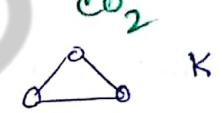
Degrees of freedom

1D motion  $\rightarrow$  1 d.o.f.  
 2D (unconstrained) motion  $\rightarrow$  2 d.o.f.  
 3D (unconstrained) motion  $\rightarrow$  3 d.o.f.

constraint reduce no. of independent variables necessary to designate the configuration of a dynamical system.

N particles in 3D coordinates  $(x_1, y_1, z_1), (x_2, y_2, z_2) \dots (x_N, y_N, z_N)$   
 with constraint  $F_j(x_1, y_1, z_1, \dots, x_N, y_N, z_N) = 0, j=1, 2, 3, \dots, m.$

$$\therefore K = 3N - m = \text{d.o.f.}$$

- Example
- (1) Monoatomic atom :  $K = 3$  for one atom.
  - (2) Diatomic molecule :  $K = 2 \times 3 - 1 = 5$  for one molecule.
  - (3) Triatomic molecule :
    - (a) linear   
 $\text{CO}_2$   $K = 3 \times 3 - 2 = 7$
    - (b) Nonlinear   
 $\text{H}_2\text{O}, \text{O}_3$   $K = 3 \times 3 - 3 = 6$

So trivial case,  $m = 3N \rightarrow$  only one configuration.

$m > 3N$  not feasible, more constraint equation than unknowns.  
 $m < 3N$  is only feasible.

### Generalized position & velocity coordinates

If a system has N d.o.f. then we can choose a set of N elements  $q_1, q_2, q_3, \dots, q_N$  that correspond to configuration &  $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_N$  which is velocity vector at that configuration. These are generalized coordinates.

### Law of equipartition of energy

Energy of a dynamical system in thermal equilibrium is equally divided amongst its d.o.f. & the value is  $\frac{1}{2}kT$  for each d.o.f.

Suppose a system of free atoms has  $f$  d.o.f.

Every d.o.f. gets  $\frac{1}{2}k_B T$  energy, then the energy per gm molecule

$$\therefore \Theta = \frac{1}{2}Nf k_B T = \frac{1}{2}RfT \quad [k_B = \frac{R}{N}]$$

$$\therefore C_V = \left(\frac{d\Theta}{dT}\right)_V = Rf/2.$$

From  $C_P - C_V = R$ , we have  $C_P = R + \frac{Rf}{2}$ .

$$\therefore \frac{C_P}{C_V} = \frac{R + \frac{Rf}{2}}{Rf/2} = \frac{2}{f} + 1 \quad \Rightarrow \quad \gamma = 1 + \frac{2}{f}$$

for monoatomic gas,  $K=3$ ,  $\gamma = 1 + \frac{2}{3} = 1.66$ .

for diatomic gas,  $K=5$ ,  $\gamma = 1 + \frac{2}{5} = 1.4$

for triatomic linear gas,  $K=7$ ,  $\gamma = 1 + \frac{2}{7} = 1.28$

for triatomic not collinear gas,  $K=6$ ,  $\gamma = 1 + \frac{2}{6} = 1.33$ .

### Dulong & Petit's law

1819 Experimental investigation  $\Rightarrow$  product of atomic weight & specific heat of almost all solid substances are nearly equal to 6 calories.

Consider 1 mole of a solid with each atom/molecule have 3 translational d.o.f. & 2 rotational d.o.f. & 3 vibrational d.o.f. (vibration about mean equilibrium configuration). Rotation isn't allowed in crystal, as they're rigidly fixed.

$\therefore$  Number of d.o.f. of 1 mole solid is  $6N$ .

Every d.o.f. gets  $\frac{1}{2}k_B T$  energy from Equipartition theorem.

$\therefore$  Total energy  $= U = 6N \frac{1}{2}k_B T = 3Nk_B T = 3RT$

$\therefore C_V = \left(\frac{dU}{dT}\right)_V = 3R = 3 \times 1.98 \text{ cal} \approx 6 \text{ cal.}$

Sometimes "atomicity" is also equivalent to d.o.f,  $f = \frac{2}{\gamma - 1}$ .

### Variation of $\gamma$ with temperature

High T, translation + rotation + vibration,

$$f(\text{diatomic molecule}) = 7, \gamma = 1 + \frac{2}{7} = 1.29.$$

like  $H_2 > 5000^\circ C$   $C_V = \frac{7}{2}R$

Medium T, translation + rotation

$$f(\text{diatomic molecule}) = 5, \gamma = 1 + \frac{2}{5} = 1.4.$$

like  $H_2 \approx 250K$   $C_V = \frac{5}{2}R$ .

Low T, translation

$$f(\text{diatomic molecule}) = 3, \gamma = 1 + \frac{2}{3} = 1.66$$

like  $H_2 \approx 70K$   $C_V = \frac{3}{2}R$ .

CW 1. What is the atomicity of a gas with heat capacity ratio 1.33? Given,  $R = 8.31 \text{ J/mol/K}$ . Calculate  $C_p, C_V$  values also.

$$C_p - C_V = R \quad \text{or} \quad C_V \left( \frac{C_p}{C_V} - 1 \right) = R \quad \text{or} \quad C_V (\gamma - 1) = R.$$

$$\therefore C_V = \frac{R}{\gamma - 1} = \frac{8.31}{1.33 - 1} = 25.18 \text{ J/mol/K}.$$

$$C_p = \gamma C_V = 33.49 \text{ J/mol/K}.$$

$\therefore$  Atomicity  $f = \frac{2}{\gamma - 1} = \frac{2}{0.33} = 6$ . (not monoatomic gas).

2. Calculate (a) K.E. of translation of  $O_2$  molecule, (b) total

K.E. and (c) total K.E. of a gram molecule at  $27^\circ C$ . Given

$$k_B = 1.37 \times 10^{-23} \text{ J/K} \quad N = 6.02 \times 10^{23}$$

$O_2 = 3 \text{ translation} + 2 \text{ rotation } (\theta, \phi), f = 5.$   
( $x, y, z$ )

$$(a) \text{ K.E. of translation} = \frac{3}{2} k_B T = \frac{3}{2} \times 1.37 \times 10^{-23} \times 300$$
$$= 6.17 \times 10^{-21} \text{ J.}$$

$$(b) \text{ K.E. of total} = \frac{5}{2} k_B T = 10.275 \times 10^{-21} \text{ J}$$

$$(c) \text{ of 1 gram molecule} = \frac{5}{2} k_B T \times N = 10.275 \times 10^{-21} \times 6.02 \times 10^{23}$$
$$= 6185.55 \text{ J.}$$

## $\gamma$ for a mixture of ideal gases

At temperature  $T$ ,  $N_1$  moles of ideal gas with  $f_1$  d.o.f.  
 $N_2$  moles of ideal gas with  $f_2$  d.o.f.  
 $N_3$  moles of ideal gas with  $f_3$  d.o.f.  
 $\dots$   
 $N_N$  moles of ideal gas with  $f_N$  d.o.f.

$$\text{Total internal energy } U = \frac{1}{2} k_B T N_1 f_1 + \frac{1}{2} k_B T N_2 f_2 + \dots + \frac{1}{2} k_B T N_N f_N$$

$$\therefore C_V = \left( \frac{dU}{dT} \right)_V = \frac{1}{2} k_B N (N_1 f_1 + N_2 f_2 + \dots + N_N f_N)$$

$$\text{Also } C_P - C_V = (N_1 + N_2 + \dots + N_N) k_B T \quad [R/N = k_B]$$

$$\begin{aligned} \therefore C_P &= (N_1 + N_2 + \dots + N_N) k_B T + \frac{1}{2} (N_1 f_1 + N_2 f_2 + \dots + N_N f_N) k_B N \\ &= \frac{(2+f_1)N_1 + (2+f_2)N_2 + \dots + (2+f_N)N_N}{2} k_B N \end{aligned}$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{(2+f_1)N_1 + (2+f_2)N_2 + \dots + (2+f_N)N_N}{f_1 N_1 + f_2 N_2 + \dots + f_N N_N}$$

### Example

$$1 \text{ mole of monoatomic gas } (f=3) \text{ & } 1 \text{ mole of diatomic gas } (f=5), \quad \gamma = \frac{(2+f_1)N_1 + (2+f_2)N_2}{f_1 N_1 + f_2 N_2} = \frac{5+7}{3+5} = 1.5$$

$$1 \leq \gamma \leq 1.67$$