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 ? $dn_c \overset{?}{=} f(P,T)$.

J.C. Maxwell computed it in 1859.

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

Random events

Exhaustive
[all events in set, coin-toss can give head or tail & no other event]

Mutually Exclusive
[one excludes the other, coin toss, if head, no tail in one throw]

Equally Likely.
[No bias, fair coin toss: 50% chance both for head or tail]

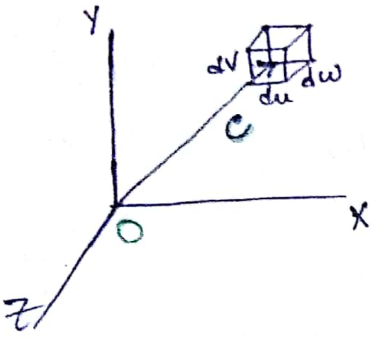
If there are N number of exhaustive, mutually exclusive and equally likely events of which M number are favourable to event A, then

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

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 $f(x)\,dx$ = probability of a variate falling within x & $x+dx$.



Assumptions : (a) density is uniform & velocity in all direction is equal.

(b) isotropy → results independent of coordinate system.

(c) velocities in any 3 coordinates is independent

If a molecule at O 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 = constant.

$$\therefore \; dc^2 = 0 = 2u\,du + 2v\,dv + 2w\,dw$$

$$\text{So} \quad u\,du + v\,dv + w\,dw = 0 \quad \text{——— (1)}$$

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 = 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 & $w+dw$.

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

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

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

Divide by $\dfrac{1}{f(u)f(v)f(w)}$ $\Rightarrow$ $\dfrac{f'(u)}{f(u)}du + \dfrac{f'(v)}{f(v)}dv + \dfrac{f'(w)}{f(w)}dw = 0$ — (2)

When (1) & (2) both are true, we invoke Lagrange's undetermined multiplier & do (1) $\times \alpha$ + (2),

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

If we say, du is dependent, then we choose α such that

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

& because dv & dw is dependent, so

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

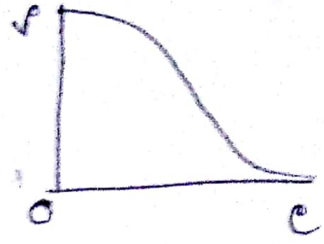
$$\therefore \frac{df(u)}{f(u)} = -\alpha u\,du.$$

Integrating, $\ln f(u) = -\dfrac{\alpha}{2}u^2 + \ln A$

or $f(u) = Ae^{-\alpha u^2/2} = Ae^{-bu^2}$ $\{b = \alpha/2\}$

Similarly, $f(v) = Ae^{-bv^2}$, $f(w) = Ae^{-bw^2}$

So $f = NA^3 e^{-b(u^2+v^2+w^2)} = NA^3 e^{-bc^2}$



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

What is remaining now is to find out constants $\underline{A \ \& \ b}$.

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

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

[Now $\int_{-\infty}^{\infty} e^{-bu^2} du$

Let $bu^2 = z$

$2bu\,du = dz$

or $du = \dfrac{dz\sqrt{b}}{2b\sqrt{z}}$

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

$$= \frac{1}{\cancel{2}\sqrt{b}} \cancel{2}\int_{0}^{\infty} e^{-z} z^{-1/2} dz = \frac{\Gamma(1/2)}{\sqrt{b}} = \sqrt{\frac{\pi}{b}}. \ ]$$

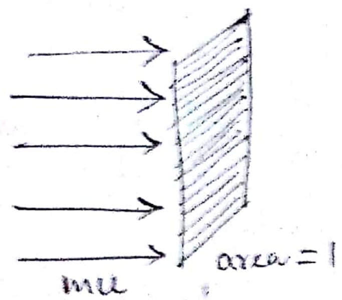
$$A^3\left(\frac{\pi}{b}\right)^{3/2} = 1 \quad \text{or} \quad A = \sqrt{\frac{b}{\pi}}$$

<u>Evaluate b</u>

Collisions per second

= area × velocity × number density at that . n_u

$= 1 \times u \times n_u$



Change in momentum = 2mu.

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

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

$$= 2m n_u \int_{0}^{\infty} A e^{-bu^2} u^2 du$$

$$\therefore \; P_u = 2mn_u A \int_0^\infty e^{-z}\,\frac{z}{b}\,\frac{dz\sqrt{b}}{2b\sqrt{z}} \qquad [\text{put } bu^2 = z]$$

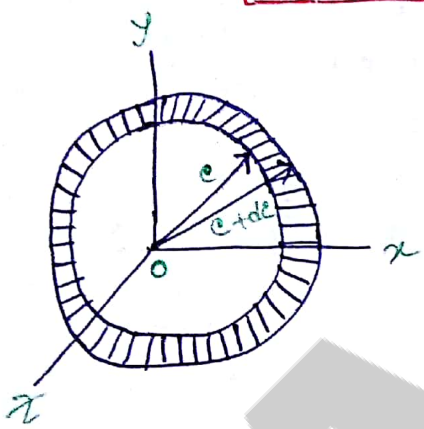
$$= \frac{mn_u A}{2b^{3/2}}\,\Gamma\left(\tfrac{1}{2}\right) \qquad \Gamma\left(\tfrac{3}{2}\right) = \tfrac{1}{2}\Gamma\left(\tfrac{1}{2}\right)$$

$$= \frac{mn_u}{2b^{3/2}}\,\frac{b^{1/2}}{\cancel{\pi^{1/2}}}\,\cancel{\pi^{1/2}} = \frac{mn_u}{2b} = n_u k_B T.$$

[from Clapeyron's equation]

$$\therefore \; b = \frac{m}{2k_B T}, \quad A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi k_B T}}$$

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



volume between c & $c+dc$ is

$$\tfrac{4}{3}\pi(c+dc)^3 - \tfrac{4}{3}\pi c^3$$

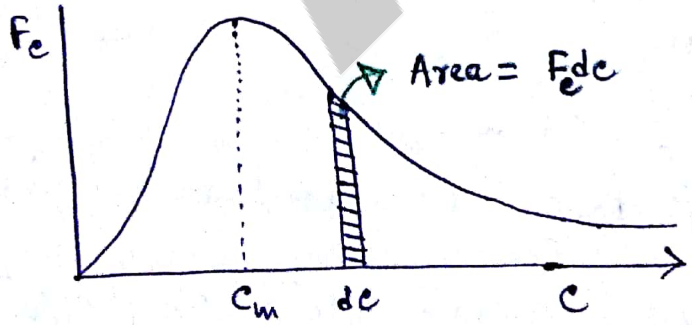
$$= \cancel{\tfrac{4}{3}\pi c^3} + \tfrac{4}{\cancel{3}}\pi\,\cancel{3}c^2 dc + \cancel{\tfrac{4}{3}\pi\,3c(dc)^2} + \cancel{\tfrac{4}{3}\pi(dc)^3}$$

$$- \cancel{\tfrac{4}{3}\pi c^3}$$

$$= 4\pi c^2 dc.$$

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

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



<u>Remarks</u>: (a) $c \to 0$, $F_c \to 0$

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

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

= most probable velocity

= maximum no. of atoms will possess this velocity