Application D : Maxwell Distribution of Molecular Speeds

D. Maxwell Distribution of Molecular Speeds in a Gas

[This is a by-product of Eq. (C4) (general gas) and Eq. (C5) (ideal gas)]

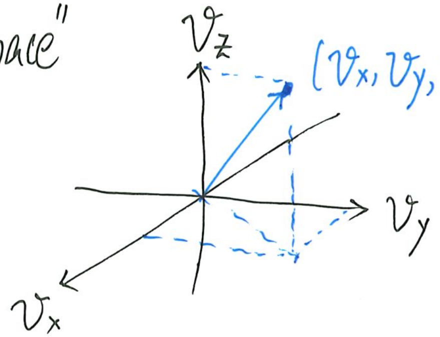
See $e^{-\frac{p_x^2+p_y^2+p_z^2}{2mkT}}$ due to kinetic energy $K.E. = \frac{p_x^2+p_y^2+p_z^2}{2m} = \frac{1}{2}m\underbrace{(v_x^2+v_y^2+v_z^2)}$

$\vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$

- Prob. of particle with $\vec{v} = (v_x, v_y, v_z)$ [velocity (NOT speed)] is:

$$P(v_x, v_y, v_z) \propto e^{-\frac{1}{kT}\left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2\right)} \propto e^{-\frac{mv_x^2}{2kT}} \cdot e^{-\frac{mv_y^2}{2kT}} \cdot e^{-\frac{mv_z^2}{2kT}} \qquad (D1)$$

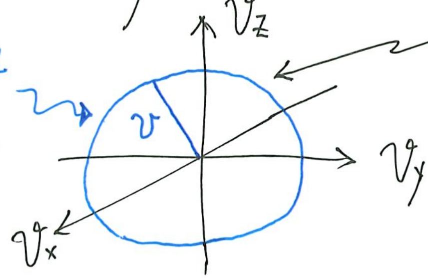
"velocity space"



(v_x, v_y, v_z) ← asking about a particular velocity

Practically, more interested in asking the SPEED

Surface of sphere



All points on surface defined by $v_x^2 + v_y^2 + v_z^2 = v^2 = (\text{speed})^2$ have the SAME SPEED

Prob. of finding a molecule in a gas to have <u>a SPEED v to $v+dv$</u>

$$\propto \left(\begin{array}{c}\text{how many ways that} \\ \text{speeds are in } v \to v+dv\end{array}\right) \cdot e^{-\frac{1}{2}\frac{mv^2}{kT}} \propto \underbrace{4\pi v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv} \qquad \text{(D2)}$$

[regardless of direction]

[Note: m, T, v are all in]

<u>Consider a gas of N molecules</u>

a "normalization" constant

$$n(v)\,dv = \#\text{ molecules with speeds in } v \to v+dv = [\quad]\, v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv$$

Require $\int_0^\infty n(v)\,dv = N \Rightarrow$ constant found!

$$\boxed{n(v)\,dv = N \frac{4\pi m^3}{(2\pi mkT)^{3/2}} \cdot v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv} \qquad \text{(D3)}$$

$\frac{n(v)}{N}$ = Prob. of a particle having speed v

This is the Maxwell ~~distribution~~ distribution of Molecular Speeds (~1859).
[Found before Statistical Mechanics was established]

Standard Consequences

- Mean Speed $\langle v \rangle = \int_0^\infty \frac{4\pi m^3}{(2\pi m k T)^{3/2}} \cdot v \cdot v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv$

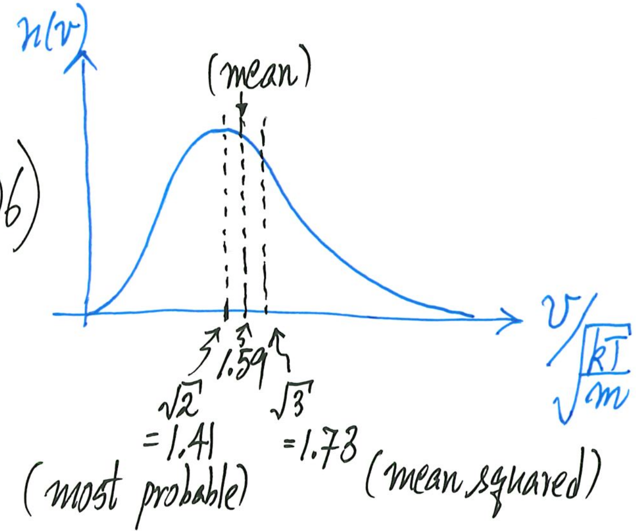
$$= 2 \cdot \sqrt{\frac{2}{\pi}} \sqrt{\frac{kT}{m}} = 1.59 \sqrt{\frac{kT}{m}} \qquad \text{(D4)} \quad \text{(Ex.)}$$

- Mean square speed $\langle v^2 \rangle = \int_0^\infty \frac{4\pi m^3}{(2\pi m k T)^{3/2}} \cdot v^2 \cdot v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv = 3\frac{kT}{m}$

$$\sqrt{\langle v^2 \rangle} = 1.73 \sqrt{\frac{kT}{m}} \quad \text{(D5)} \quad \text{OR} \quad \boxed{\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT} \quad \text{(D5)}$$

- Most Probable Speed, i.e. where $n(v)$ peaks

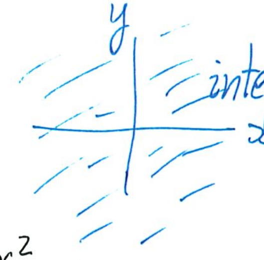
$$\left.\frac{dn(v)}{dv}\right|_{v=v_{mp}} = 0 \Rightarrow \boxed{v_{mp} = \sqrt{2}\sqrt{\frac{kT}{m}} = 1.41\sqrt{\frac{kT}{m}}} \quad \text{(D6)}$$



Aside: Gaussian Integrals

$$I=\int_{-\infty}^{\infty} e^{-x^2}\,dx$$ often encountered in stat. mech. calculations $\left[\text{e.g. } \int_{-\infty}^{\infty} e^{-\beta\frac{p^2}{2m}}\,dp\right]$

$$I^2=\int_{-\infty}^{\infty} e^{-x^2}dx\int_{-\infty}^{\infty} e^{-y^2}dy=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(x^2+y^2)}\,dx\,dy$$



integrate over all 2D space

$$=\int_0^{\infty}\int_0^{2\pi} e^{-r^2}\,r\,d\theta\,dr = 2\pi\int_0^{\infty} e^{-r^2}\,r\,dr$$

$$=\pi\int_0^{\infty} e^{-r^2}\,d(r^2) = \pi\int_0^{\infty} e^{-x}\,dx = \pi\left[-e^{-x}\right]_0^{\infty} = \pi$$

$$\therefore \boxed{I=\int_{-\infty}^{\infty} e^{-x^2}\,dx=\sqrt{\pi}} \quad \text{OR} \quad \boxed{\int_{-\infty}^{\infty} e^{-ax^2}\,dx=\sqrt{\frac{\pi}{a}}} \quad \text{(GI1)}$$

Also useful are:

$$\boxed{\int_0^{\infty} e^{-x^2}\,dx=\frac{\sqrt{\pi}}{2}} \quad \text{OR} \quad \boxed{\int_0^{\infty} e^{-ax^2}\,dx=\frac{1}{2}\sqrt{\frac{\pi}{a}}} \quad \text{(GI2)}$$

note low limit

note lower limit

Knowing $I(a) \equiv \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$, what is $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx$?

$$\frac{dI(a)}{da} = -\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{d}{da}\left(\sqrt{\frac{\pi}{a}}\right) = -\frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

$$\therefore \boxed{\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}} \qquad (GI3)$$

But $\int_{0}^{\infty} x\, e^{-ax^2} dx$ or $\int_{0}^{\infty} x^3 e^{-ax^2} dx$ is more troublesome!

(i) use table or web

(ii) learn Γ-functions $\Gamma(x) \equiv \int_{0}^{\infty} z^{x-1} e^{-z} dz$

You have used (GI1) and (GI3) in the Quantum Mechanical Harmonic Oscillator Problem.