

Kinetic Theory of gases & Maxwell Boltzmann Distribution

Assumptions of KTG:

- ① large no of molecules in a small volume of a gas.
- ② gas made up of ~~small~~ ^{identical} molecules
- ③ molecules continuously move about in random directions; all are equally probable
- ④ size of molecule \ll average distance between them.
- ⑤ molecules of gas exert no forces on each other except when they collide i.e. no intermolecular forces.
- ⑥ collisions b/w molecules and b/w molecules and walls are perfectly elastic
- ⑦ uniform distribution of molecules in the absence of an external field
- ⑧ molecules move with all speeds ranging from 0 to ∞ .
- ⑨ time of collision \ll time b/w collisions.

Pressure exerted by a gas

Suppose there are n molecules per cubic ~~cm~~ m^3 ; each of mass m ,

we can divide the molecules into j groups each containing

n_i ($i=1, 2, \dots, j$) no. of molecules per m^3 with velocity v_i

They will be moving in all possible directions. To begin with,

let us consider the molecules with v_i velocity which can be resolved into 3 mutually orthogonal components u_{ix}, u_{iy}, u_{iz} parallel to the sides of the cube.

$$u_i^2 = u_{ix}^2 + u_{iy}^2 + u_{iz}^2$$

The molecule moving in z direction will have a momentum $+mv_{iz}$ ~~and~~ ^{normal} to the $y-z$ face of cube, which after collision with other face at $x=L$, will have the momentum $-mv_{iz}$. \therefore for each collision, the value of momentum added is given by $2mv_{iz}$. Time ~~has~~ elapsed b/w 2 collisions is:

$$t = 2L/u_{iz} \Rightarrow \text{molecules make } u_{iz}/2L \text{ collisions per sec.}$$

\therefore The momentum transferred per second per molecule will be equal to

$$\frac{2mv_{iz}}{dt} = \frac{mv_{iz}^2}{L}$$

\therefore Total momentum transferred per sec. by all molecules of this group to the wall at $x=L$ will be equal to $\frac{n_i m v_{iz}^2}{L}$.

\therefore rate of change of momentum = force; we have force exerted by all the molecules of this group moving along x -direction is:

$$f_{ix} = \frac{n_i m u_{ix}^2}{L}$$

Pressure = force / area, and the above force is exerted on an area L^2 .

$$P_{ix} = \frac{n_i m v_{ix}^2}{L^3}$$

Similarly, for all other molecules, we can write

$$P_{iz} = \frac{n_i m v_{iz}^2}{L^3}$$

∴ Total pressure exerted by all molecules is -

$$p_x = \sum F_{ix} = \frac{m}{L^3} \sum n_i v_{ix}^2$$

Average value of v_x^2 can be defined as:

$$\bar{v}_x^2 = \frac{\sum n_i v_{ix}^2}{N}$$

∴ we can write $p_x = \frac{m}{L^3} \sum n_i v_{ix}^2$
 or $p_x = \frac{m}{L^3} N \bar{v}_x^2$

Since all the molecules are identical and all directions are equally probable, we get,

$$p_x = p_y = p_z = \bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{1}{3} \bar{v}^2 \quad \leftarrow \text{mean squared velocity.}$$

$$p = p_x = \frac{1}{3} \frac{m}{L^3} N \bar{v}^2$$

$$\text{or } \boxed{pV = \frac{1}{3} m N \bar{v}^2}$$

- For, 1 mole of gas, we can write
 or $pV = \frac{1}{3} M \bar{v}^2$

M: molecular mass of gas

- Also, $p = \frac{1}{3} m n \bar{v}^2 = \frac{1}{3} \rho \bar{v}^2$ where n : no. density and ρ : density of gas.

$$\text{or } \boxed{p = \frac{1}{3} m n v_{rms}^2} \quad \text{where } \boxed{v_{rms} = \sqrt{\bar{v}^2}}$$

Kinetic interpretation of Temp.

$$E = \frac{1}{2} m \bar{v}^2$$

$$\text{also } p = \frac{1}{3} m n \bar{v}^2$$

$$= \frac{2}{3} n \left(\frac{1}{2} m \bar{v}^2 \right)$$

$$= \frac{2}{3} n E$$

we know that, $pV = nRT$ where $n = \frac{N}{N_A}$: no. of kilomoles of gas.

$$\frac{2}{3} n N A E = nRT$$

$$\text{or } E = \frac{3}{2} \frac{R}{N_A} \theta T$$

$$\Rightarrow \boxed{E = \frac{3}{2} k_B T}$$

$$\text{where } k_B = \frac{R}{N_A}$$

RMS speed

$$v_{rms} = \left(\frac{3pV}{M} \right)^{1/2} \text{ or } \boxed{v_{rms} = \sqrt{\frac{3RT}{M}}}$$

Deductions from KTG:

- ① $pV = \frac{2}{3} n E$; for T fixed, n fixed $\Rightarrow pV = \text{const.}$ Boyle's law
- ② $V \propto T$ = Charles law at a constant P
- ③ Avogadro's law: At const. temp and pressure, equal volume of gas contains equal no. of molecules.

$$p = \frac{1}{3} n_1 m_1 \bar{v}_1^2 = \frac{1}{3} n_2 m_2 \bar{v}_2^2$$

② same temp. $E_1 = E_2 : \frac{1}{2} m_1 \bar{v}_1^2 = \frac{1}{2} m_2 \bar{v}_2^2$

$$\therefore \boxed{\gamma_1 = \gamma_2}$$

→ No. of degree of freedom of a system can be written as

$$f = 3p - c \quad (c < 3p)$$

↓ ↙ constraints
no. of particles

$$C_v = \frac{1}{2} Rf, \quad (p = R(\frac{f}{2} + 1))$$

$$\therefore \boxed{\gamma = 1 + \frac{2}{f}}$$

★

see some
reference
not clear

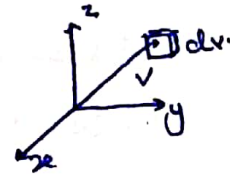
→ $E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{pot}$

↳ for polyatomic

Maxwell Boltzmann Distribution

Assumptions:

1. In Eqm state, molecules have complete randomness of direction & velocity.
2. no mass motion or convection currents.
3. probability that a molecule has a given velocity component is independent of other 2 components.
4. The probability that a molecule selected at random has velocity in a given range is purely a function of the magnitude of the velocity and the width of the interval.
5. molecules have no vibrational or rotational energies.



For a molecule with velocity \vec{v} , can be written as

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

No. of velocity vectors ending in volume dv . can be written as $= dv_x dv_y dv_z$ gives

the no. of molecules with velocity b/w \vec{v} and $\vec{v} + d\vec{v}$.

∴ our problem to find the no. of molecules simultaneously having velocity components in the range $v_x + dv_x, v_y + dv_y, v_z + dv_z$.

From assumption (4), we can write the fraction of molecules in the velocity range v_x and $v_x + dv_x$ can be written as:

$$\frac{dN_{v_x}}{N} = f(v_x) dv_x$$

where dN_{v_x} : total no. of molecules having velocity in the range $v_x + dv_x$, N : total no. of molecules.

Mathematically, $\frac{dN_{v_x}}{N} \rightarrow$ probability of finding a molecule with x -component of velocity in the range v_x to $v_x + dv_x$.

$$P_1 = f(v_x) dv_x$$

Similarly, probabilities of finding a molecule having velocity components v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$ is written as:

$$P_2 = f(v_y) dv_y, P_3 = f(v_z) dv_z$$

Using the law of prob, the prob. that a molecule will simultaneously have all 3 velocity components will be:

$$\frac{d^3 N_{v_x v_y v_z}}{N} = P_1 P_2 P_3 = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

The no of molecules - - - :

$$d^3 N_{v_x v_y v_z} = N f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

\vec{v} is the velocity of the molecules, the nos. must also be a fun. of \vec{v} and the interval $dv_x dv_y dv_z$.

$$\therefore N f(v_x) \dots dv_z = N F(\vec{v}) dv_x \dots = N f(v^2) dv_x dv_y dv_z$$

→ After a large no of collisions, the distribution will be isotropic and depend upon v^2 only.

For a fixed value of \vec{v} , $f(v^2)$ will be a constant and hence $d[f(v^2)] = 0$

$$\Rightarrow d[f(v_x) f(v_y) f(v_z)] = 0$$

$$(f'(v_x) dv_x) f(v_y) f(v_z) + \dots = 0$$

$$\propto \frac{f'(v_x)}{f(v_x)} dv_x + \frac{f'(v_y)}{f(v_y)} dv_y + \frac{f'(v_z)}{f(v_z)} dv_z = 0 \quad \text{--- (1)}$$

Also, $v^2 = \text{constant}$:

$$v_x dv_x + v_y dv_y + v_z dv_z = 0 \quad \text{--- (2)}$$

We use Lagrange's method of undetermined multiplier to solve these.

Multiplying (2) with $2B$ and adding to (1):

$$\left(\frac{f'(v_x)}{f(v_x)} + 2Bv_x \right) dv_x + \dots = 0$$

Let us choose B such that,

$$\frac{f'(v_x)}{f(v_x)} + 2Bv_x = 0$$

$$\frac{f'(v_y)}{f(v_y)} + 2Bv_y = 0$$

$$\frac{f'(v_z)}{f(v_z)} + 2Bv_z = 0$$

This gives us:

$$f(v_x) = A e^{-Bv_x^2}$$

$$f(v_y) = A e^{-Bv_y^2}$$

$$f(v_z) = A e^{-Bv_z^2}$$

\therefore we finally get:

$$d^3 N_{v_x v_y v_z} = N A^3 e^{-(v_x^2 + v_y^2 + v_z^2) B} dv_x dv_y dv_z$$

The quantity $N A^3 e^{-B u^2}$ represents the no. density, n , to know as the Maxwell's velocity distribution function.



Distribution of molecular speeds

Generally, we are interested in knowing the no. of molecules having speeds in a certain range, say u to $u+du$. To do this, we assume a sphere of radius u & another of $u+du$. The no. of velocity vectors ending in such a spherical shell gives the required number.

$$\text{Volume of shell} = 4\pi u^2 du.$$

$$\text{Then } dN_u = 4\pi N A^3 e^{-B u^2} du.$$

The ratio $\frac{dN_u}{N} \rightarrow$ Maxwellian distribution function.

Determination of constant

$$N = \int dN_u = 4\pi N A^3 \int_0^{\infty} e^{-B u^2} u^2 du.$$

$$\int_0^{\infty} e^{-\beta u^2} u^2 du = \frac{1}{2\beta^{3/2}} \Gamma\left(\frac{3}{2}\right)$$

$$\therefore N = 4\pi N A^3 \cdot \frac{1}{2\beta^{3/2}} \sqrt{\pi}$$

$$\Rightarrow A = \sqrt{\beta/\pi}$$

We can find

$$\bar{u}^2 = \frac{\int u^2 dN_u}{\int dN_u} = \frac{\int u^4 e^{-B u^2} du}{\int u^2 e^{-B u^2} du}$$

$$= \frac{\frac{3}{2} \frac{1}{2} \sqrt{\pi} \cdot \frac{1}{B^{5/2}}}{\frac{\sqrt{\pi}}{2} \frac{1}{B^{3/2}}}$$

$$\bar{u}^2 = \frac{3}{2B}$$

We also know that $\frac{1}{2} m \bar{u}^2 = \frac{3}{2} k_B T$.

$$\therefore \boxed{B = \frac{m}{2k_B T}} \quad \therefore A = \sqrt{\frac{m}{2\pi k_B T}}$$

\therefore we can write no. of molecules in the range u and $u+du$ can be written as

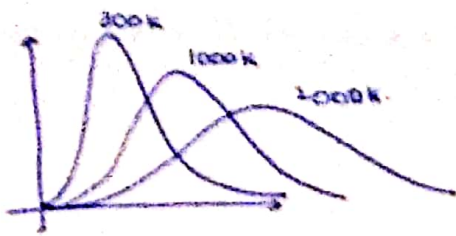
$$dN_u = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m u^2}{2k_B T}} u^2 du.$$

This function plot:

① $f_v = \frac{dN_u}{du} \rightarrow 0$ as $v \rightarrow 0$ or ∞ .

② B for smaller u , f is prop. to u^2 , for large exponential terms come into picture.

③ $\therefore f_v \uparrow$, takes a max and then \downarrow .



\bar{U} , U_{rms} , U_p

$$\begin{aligned} \textcircled{1} \quad \bar{U} &= \frac{\int U dN_u}{\int dN_u} = \frac{\int U e^{-\beta U} du}{\int e^{-\beta U} du N} \\ &= \frac{\frac{6}{\beta^2} \frac{4\pi^2 N^2}{\sqrt{\pi}} \int U^3 e^{-\beta U} du}{\frac{6}{\beta^2} \frac{4\pi^2 N^2}{\sqrt{\pi}} \int e^{-\beta U} du} \\ &= 4\pi^2 N^2 \times \frac{\sqrt{\pi}}{2} \frac{1}{\beta^2} \\ &= 4\pi^2 \times \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{\sqrt{\pi}}{2} \left(\frac{2k_B T}{m}\right) \end{aligned}$$

$$\therefore \boxed{\bar{U} = \sqrt{\frac{8k_B T}{\pi m}}}$$

$$\textcircled{2} \quad U_{rms} = \sqrt{\bar{U}^2}$$

$$\bar{U}^2 = \frac{\int U^2 e^{-\beta U} du}{\int e^{-\beta U} du} = \sqrt{\frac{3k_B T}{m}}$$

$\textcircled{3}$ Most Probable:

$$\begin{aligned} \frac{df_u}{du} &= 0 \\ \Rightarrow U_p &= \sqrt{\frac{2k_B T}{m}} \end{aligned}$$

$$\therefore U_p : \bar{U} : U_{rms} :: 1 : 1.128 : 1.224$$

$$\therefore U_{rms} > \bar{U} > U_p$$

Ex: 1.3 For a monatomic gas: $\bar{U} \times \left(\frac{1}{\sigma}\right) = \frac{4}{\pi}$

$$\Rightarrow \bar{U} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\frac{1}{\sigma} = \frac{\int \bar{U} e^{-\beta U} du}{\frac{\sqrt{\pi}}{2} \times \beta^{3/2}} = \frac{1}{\sigma} = \frac{2\sqrt{\pi}}{\sqrt{\pi}} = 2\sqrt{\frac{\pi}{\pi}}$$

$$= 2\sqrt{\frac{3k_B T}{\pi m}} \cdot 2\sqrt{\frac{m}{2k_B T}} = \sqrt{\frac{2m}{\pi k_B T}}$$

$$\therefore \boxed{\bar{U} \times \frac{1}{\sigma} = \frac{4}{\pi}}$$

Energy distribution function

$$E = \frac{1}{2} m v^2$$

$$dE = m v dv$$

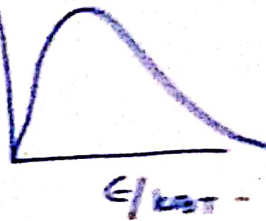
$$dv = \frac{dE}{m v} = \frac{dE}{(2Em)^{1/2}}$$

$$dN_E = dN_v$$

$$= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-E/k_B T} \left(\frac{2E}{m} \right)^{1/2} \times (2mE)^{-1/2} dE$$

$$\therefore \boxed{dN_E = \frac{2N}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} e^{-E/k_B T} \sqrt{E} dE}$$

$$\frac{dN_E}{dE}$$



Ex. Find mean energy & most probable energy.

$$1) \bar{E} = \frac{\int E dN_E}{\int dN_E} = \frac{\int E^{3/2} e^{-E/k_B T} dE}{\int E^{1/2} e^{-E/k_B T} dE}$$

$$= \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} \int_0^{\infty} E^{3/2} e^{-E/k_B T} dE$$

$$= \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} \cdot (k_B T)^{5/2} \int_0^{\infty} x^{3/2} e^{-x} dx \quad x = E/k_B T$$

$$\text{or } \boxed{\bar{E} = \frac{3}{2} k_B T}$$

$$2) \frac{d}{dE} = 0$$

$$\Rightarrow \boxed{E_p = \frac{k_B T}{2}}$$