Thermal Physics - I

Development of Kinetic Theory:

Anonymous theory: 1761 J. Black: observed same temperature for ice & water & conjectured about "latent" heat.

1797 J. Watt: converted heat → work as steam engine

1797 B. Thompson, C. Rumford: work → heat

Caloric fluid theory: 1783 A. Lavoisier: conjectured heat as invisible fluid.

1824 S. Carnot: Carnot engine → Thermochemistry.

Kinetic theory:

1738 D. Bernoulli: molecular theory of fluid.

1847 J.P. Joule, J. von Mayer, H. von Helmholtz: heat & work equivalent form of energy.

1850 R. Clausius: (a) showed that "caloric fluid theory" is reconciled in "kinetic theory", (b) First law of Thermodynamics, (c) defined "entropy".

1854 Thomson or Lord Kelvin → Thermodynamics

18th century

19th century

Experimental gas laws:

1662 Boyle's law: $P \propto V^{-1}$

1802 Charle's law: $V \propto T$

1802 Gay-Lussac's law:

International scale of temperature

Lord Kelvin introduced lowest temperature independent of property of substance

absolute zero	$-273^\circ C$ or 0K	Sulphur point	$444.6^\circ C$
ice point	$0^\circ C$ or 273K	Antimony point	$630.5^\circ C$
steam point	$100^\circ C$ or 373K	Silver point	$960.8^\circ C$
		Gold point	$1063.8^\circ C$

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Human body temperature $98.4^\circ F \Leftrightarrow 36.9^\circ C$ (remember, least count is $0.1^\circ C$)

relation between C, F, R (Reumer scale)

$$\frac{C}{5} = \frac{F-32}{9} = \frac{R}{4}.$$

Basics of Thermometry

a) Liquid Thermometer: Hg in glass, 6's max-min, Beckmann, Index

b) Gas Thermometer: Callendar's Air, Hydrogen

c) Metal Thermometer: Platinum resistance,

d) Thermoelectric Thermometer: thermocouple generates e.m.f. $e = at + bt^2$

e) Radiation Thermometer:

principle of thermometry: let A = thermometric property

For uniform variation of A with temperature T

$$A_T = A_0(1+\alpha T), \quad A_0 = \text{value of } A \text{ at } 0^\circ C$$

A_{100} = value of A at $100^\circ C$.

$$A_{100} = A_0(1+100\alpha)$$

$$\therefore \quad \boxed{T = 100\,\frac{A_T - A_0}{A_{100} - A_0}}$$

What is A? If you take simple Hg-in glass thermometer then A = length of Hg column. For Pt-resistance thermometer A = resistance R of Pt. For constant volume gas thermometer A = pressure of air.

Hg in glass thermometer

pros (a) liquid range $[-38.87^\circ C, 356^\circ C]$

(b) low thermal capacity & high conductivity

(c) uniform expansion, (d) shining liquid (easy to see).

cons (a) high specific gravity (less sensitive)

(b) high surface tension (motion is jerkey)

unsuitable for low T.

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Alcohol thermometer

pros (a) liquid range [$-112^\circ C$, $78^\circ C$]
(b) high coefficient of expansion (more sensitive)
(c) low surface tension (motion is smooth)

cons unsuitable for high temperature.

Gas thermometer

(a) Very high coefficient of expansion (more sensitive
(b) low thermal capacity, low specific gravity
(c) constant volume / constant pressure thermometer.

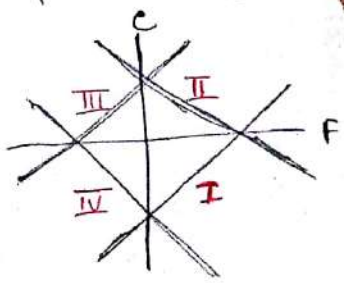
Platinum Resistance thermometer :

Resistance smooth in range [$-200^\circ C$, $1200^\circ C$]
least count = $0.01^\circ C$ $\quad R_t = R_0(1+\alpha T)$

Low temperature Thermometry	High temperature thermometry
$0^\circ C$ to $630^\circ C$ → all	$630^\circ C$ to $1000^\circ C$ → liquid, gas, resistance, thermocouple.
$-20^\circ C$ to $0^\circ C$ → liquid, gas, resistance, thermocouple, vapour pressure.	$1000^\circ C$ to $1600^\circ C$ → gas, thermocouple.
$-272^\circ C$ to $-20^\circ C$ → resistance, vapour pressure, magnetic	$1600^\circ C$ to $3000^\circ C$ → thermocouple, pyrometer.
below $-272^\circ C$ → magnetic	

HW

1. At what temperature do the Fahrenheit & Celsius scale give the same reading ?



2. In figure beside, which line represents $C/5 = \frac{F-32}{9}$?

3. In a constant volume gas thermometer, pressure of air at $0^\circ C$ is 80 cm & at $100^\circ C$ is 109.3 cm. Calculate the temperature of a hot bath, in which when the thermometer is immersed shows a pressure 100 cm.

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Calorimetry Definition of Calorie (heat) ⇒ quantity of heat needed to raise temperature of 1 gm of water by 1°C. But heat 5°C → 6°C ≠ 80°C → 81°C.

Mean calorie heat [0°C → 100°C]/100.

15°C Calorie heat 14.5°C → 15.5°C

B.Th.U. quantity of heat needed to raise temperature of 1 lb of water by 1°F.

1 B.Th.U. = 252 cals

1 C.H.U. = 453.6 cals.
(centigrad heat unit)

$$\underset{\text{heat}}{H} = \underset{\text{mass of substance}}{m}\ \underset{\text{specific heat}}{s}\ \overset{\text{temperature}}{T} = \underset{\text{thermal capacity}}{C}\ T$$

Basic principle of Calorimetry conservation of heat energy or sum total of (body + heat bath) is conserved.

Specific heat of solid: Method of mixture, Copper block calorimeter, Electrical method (Lindemann calorimeter), Latent heat (Bunsen ice calorimeter).

Specific heat of liquid: Method of mixture, Bunsen ice calorimeter, Method of cooling, Nernst calorimeter, continuous flow calorimeter.

Specific heat of gas: # why constant pressure or volume?

$C = \frac{dQ}{dT}$ → suppose system expands → temperature falls to prevent, dQ heat added, so $dT = 0$.

$C = \frac{dQ}{0} \rightarrow \infty$

→ suppose system compresses → temperature rise dT without the need of dQ ∴ $dQ = 0$

$C = \frac{0}{dT} = 0$.

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$\therefore \quad C_p = \left(\frac{dQ}{dT}\right)_p, \quad C_v = \left(\frac{dQ}{dT}\right)_v$

definition: at P = constant, increase temperature of 1 gm of gas through 1°c. If 1 gm molecule of gas is taken → molar specific heat. $C_p = \mu c_p$

$C_p > C_v$? # heat transfer at V = constant, $dV = 0$. $dW = PdV = 0$
no work done by the gas.
So heat supplied transformed to thermal energy

$C_p - C_v = \frac{R}{J}$ (heat unit)

$\boxed{C_p - C_v = R}$

heat transfer at P = constant, $dW = PdV \neq 0$.
So heat supplied → thermal energy + external work.

Isothermal transformation : T = constant $\boxed{PV = RT = \text{constant}}$

Adiabatic transformation : Q = constant, $dQ = C_v dT + PdV$ — ①

Now from $PV = RT$, $PdV + VdP = RdT = (C_p - C_v)dT$

put dT in ① : $dQ = C_v \frac{PdV + VdP}{C_p - C_v} + PdV = 0$ (as Q = constant)

$\therefore \quad C_v VdP + C_p PdV = 0$

or $\frac{C_p}{C_v}\frac{dV}{V} = -\frac{dP}{P}$, (put $\gamma = \frac{C_p}{C_v}$)

Integrating both sides, $\gamma \ln V = -\ln P + \ln C$.

$\boxed{PV^{\gamma} = \text{constant}}$

Corollary: PT relation : put $PV = RT$, $P\left(\frac{RT}{P}\right)^{\gamma} = C \Rightarrow P^{1-\gamma} T^{\gamma} = \text{constant}$

VT relation: put $PV = RT$, $\frac{RT}{V} V^{\gamma} = C \Rightarrow V^{\gamma-1} T = \text{constant}$

CW Suppose dry air is enclosed in a cylinder fitted with piston. Initial temperature of air is 30°c. Find the change in temperature if the gas is compressed (a) slowly, (b) suddenly to one-half of its volume? What'll be the pressure?

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(a) piston moves inwards → gas compresses

↓

temperature rises → heat goes to surrounding by conducting wall slowly → no change in temperature (isothermal)

$T = 30^\circ C$

(b) Temperature rise rate >>> heat diffusion rate to surrounding

adiabatic process → no Q transfer.

So $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ & given $V_2 = \frac{V_1}{2}$

$\therefore P_2 = 2^{\gamma} P_1 = 2^{1.4} P_1 = 2.6 P_1 = 2.6$ atm when $P_1 = 1$ atm.

Compare with isothermal, $P_2 = 2P_1 = 2$ atm.

Again from TV relation, $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$\therefore T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 2^{0.4} T_1 = 1.319 \times (273+30)K$

$= 399.7K = (399.7 - 273)^\circ C = 127^\circ C.$

HW 4. Air in a Wilson's cloud chamber at $20^\circ C$ is abruptly expanded to 1.4 times its initial volume. Calculate the final temperature. Given $\gamma = 1.4$.

5. At 10^6 dynes/cm^2 pressure, a gas ($\gamma = 1.4$) expands isothermally until its volume is double of the initial volume. Then it adiabatically expands until its volume is redoubled. Calculate the final pressure of the gas.

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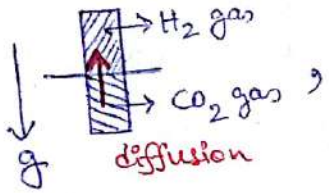
Kinetic Theory of Gases (K.T.)

Rule of thumb: Every material (solid, liquid, gas, plasma, intermedial phases) are made of atoms. They "may" attract or repel & form molecules of liquid or be restricted in definite shape of solid by huge cohesive force.

Experimental hints in favour of K.T.

1. Diffusion and Solution:



when slowly poured Alcohol over water, it spreads throughout.

2. Expansion of substance with heat. : atoms tend to move away.
3. Phenomena of evaporation & vapour pressure.
4. Brownian motion. 1827 R. Brown + incessant motion of polens on water.

Basic assumptions & postulates of K.T.

1. A gas consists of large number of identical atoms, which are rigid, elastic & equal mass objects.
2. Atoms are in chaos → motion is fully irregular & spans in all three directions.
3. Inevitably the gas molecules collide with each other & surface of container (wall, sphere, cylinder). Total K.E. remains constant, but velocity of each atom continuously changes both in magnitude & direction. In evolving state (intermediate) density in a volume element will change but in steady state, collisions do not affect the density.
4. In between two successive collisions, molecules move in straight line following Newton's law.
5. Collisions are perfectly elastic i.e. no force of attraction/repulsion (P.E. = 0), energy is fully kinetic.

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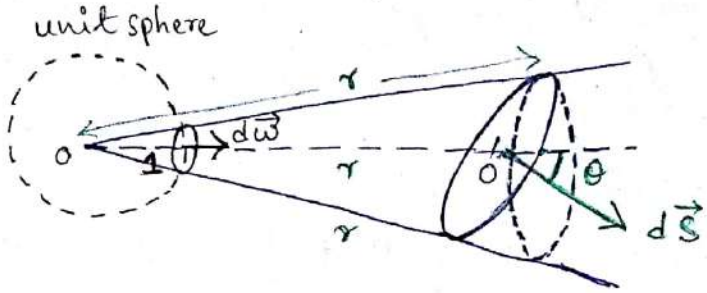
6. Atoms are "point" mass, meaning, their total volume <<<< volume of the container.

Concept of solid angle



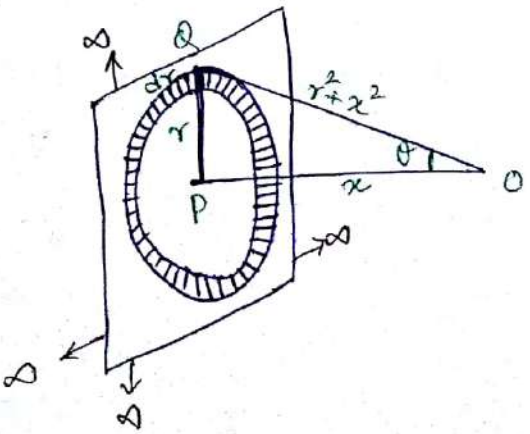
Solid angle subtended by an area at a point is defined as the area intercepted by the cone on a unit sphere (radius = 1) with its centre at the apex of the cone.

If dS is an area that makes a solid angle dω at origin O at a distance $OO' = r$, then from similar figures

$$\frac{d\omega}{1^2} = \frac{dS\cos\theta}{r^2} \quad \therefore \quad d\omega = \frac{dS\cos\theta}{r^2}$$

unit of solid angle = steradian.

CW 1. Calculate the solid angle (a) subtended by an infinite plain at a point in front of it, (b) hemisphere and (c) full sphere at its center.



Consider the annular ring, r distance apart from P & thick dr.

Area of this ring $= \pi(r+dr)^2 - \pi r^2$

$= 2\pi r\,dr$

(N.B. we throw $O(dr^2)$ term in limit $dr \to 0$)

So solid angle subtended by that circular annulus

$$d\omega = \frac{dS\cos\theta}{OQ^2} = \frac{2\pi r\,dr\cos\theta}{r^2+x^2}$$

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Infinite plain meaning θ going from 0 to $\pi/2$.

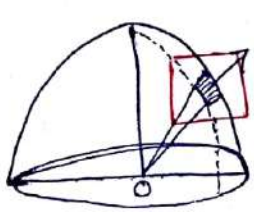
$$\therefore \quad \omega = \int_{\theta=0}^{\pi/2} \frac{2\pi r\, dr \cos\theta}{r^2 + x^2}$$

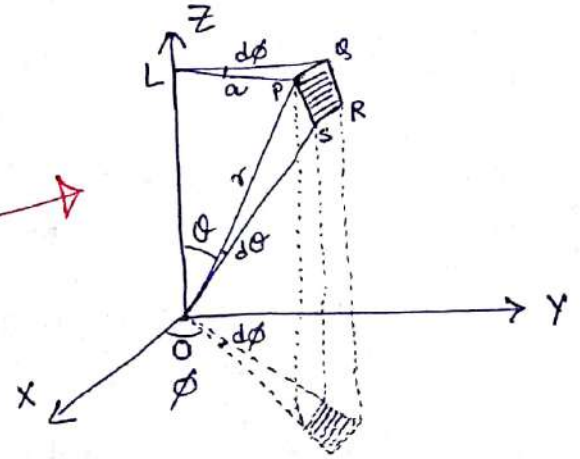
$$= 2\pi \int_{\theta=0}^{\pi/2} \frac{x \tan\theta \; x \sec^2\theta \, d\theta \cos\theta}{x^2 \sec^2\theta}$$

$$= 2\pi \int_0^{\pi/2} \sin\theta \, d\theta = \underline{2\pi}.$$

[$r = x \tan\theta$
$dr = x \sec^2\theta \, d\theta$
& $x^2 + r^2 = x^2 \sec^2\theta$]

Hemisphere





$LP = a$
$OP = r$

$$\frac{a}{r} = \sin\theta$$

$PQ = a\,d\phi$
$PS = r\,d\theta$

$\therefore dS =$ area $PQRS = a\,d\phi \times r\,d\theta = r^2 \sin\theta \, d\theta \, d\phi.$

So $d\omega$ at point O $= \dfrac{r^2 \sin\theta \, d\theta \, d\phi}{r^2} \times \cos 0 = \sin\theta \, d\theta \, d\phi.$

So solid angle subtended $= \int d\omega = \displaystyle\int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \sin\theta \, d\theta \, d\phi = \underline{2\pi}.$

Full sphere

solid angle subtended $= \displaystyle\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \sin\theta \, d\theta \, d\phi = \underline{4\pi}.$

We will find out now pressure exerted by a perfect gas from K.T. (a) collisionless atoms in a box moving in 3 directions, (b) collisionless atoms coming from all directions.

collision will be dealt in "mean free path".

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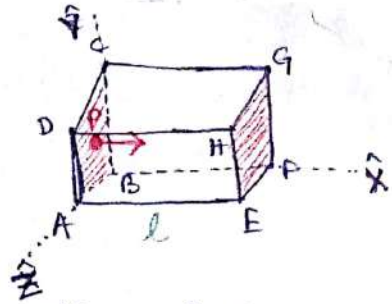
Method 1 $\quad AB = AD = AE = l$



The gas is confined within this cube of volume l^3. P (say) is a gas atom with velocity "c" whose components in 3-direction is (u, v, w).

N = total no. of atoms or molecules.

So each of them have different velocity $c_1, c_2, c_3, c_4, \dots$ etc so different components $(u_1, v_1, w_1), (u_2, v_2, w_2), (u_3, v_3, w_3), \dots$

Mean square average $\overline{c^2} = \dfrac{c_1^2 + c_2^2 + c_3^2 + \cdots}{N} = \dfrac{u_1^2 + u_2^2 + u_3^2 + \cdots}{N}$

$$+ \frac{v_1^2 + v_2^2 + v_3^2 + \cdots}{N} + \frac{w_1^2 + w_2^2 + w_3^2 + \cdots}{N}$$

$$= \overline{u^2} + \overline{v^2} + \overline{w^2} \quad \text{— (1)}$$

mean square velocity in x-direction $\quad$ y-direction $\quad$ z-direction.

Consider particle P with mass m, velocity $\vec{c} = (\vec{u}, \vec{v}, \vec{w})$.

It travels from ABCD to EFGH, makes collision to exert pressure, rebounds elastically, momentum gets changed, comes back to ABCD to make another collission.

Total distance traveled with velocity u is $2l$.

$\therefore$ Time between collission $= \dfrac{2l}{u}$, meaning number of collission per second $= \dfrac{u}{2l}$.

Momentum imparted in $+x$ direction ~~of~~ on EFGH $= mu$.

Momentum obtained in $-x$ direction after collission $= -mu$.

$\therefore$ change of momentum $= mu - (-mu) = 2mu$.

Rate of change of momentum for one atom in x direction

$$= 2mu \times \frac{u}{2l} = \frac{mu^2}{l}.$$

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Similarly in Y and Z direction, rate of change of momentum is $\frac{mv^2}{l}$ & $\frac{mw^2}{l}$ for one atom

∴ Total rate of change of momentum for all atoms per unit area along X direction is

$$P_x = \frac{m(u_1^2+u_2^2+u_3^2+\cdots)}{l} \times \frac{1}{l^2} = m\overline{u^2}\frac{N}{l^3} = mn\overline{u^2}$$

(see eqn. ①)

Similarly $P_y = mn\overline{v^2}$, $P_z = mn\overline{w^2}$.

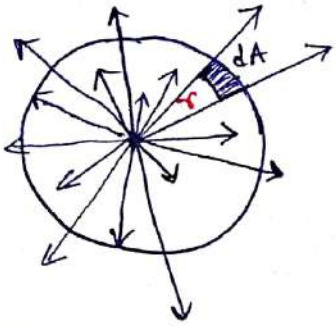
In steady state, molecules move in all directions, so no preference, meaning $\overline{u^2} = \overline{v^2} = \overline{w^2}$, & $P_x = P_y = P_z$.

Meaning $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$ (see eqn. ①)

Collecting all pieces together,

$$P_x = P_y = P_z = \frac{1}{3}mn\overline{c^2} \quad \text{or} \quad \boxed{P = \frac{1}{3}mn\overline{c^2}}$$

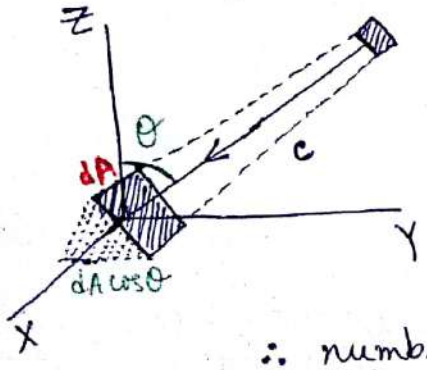
Method 2



N no. of molecules moving in all directions with all possible velocity. How many collide with vessel & insert pressure?

number of vectors per unit area $= \frac{N}{4\pi r^2}$

∴ number of molecules at dA is $\frac{N\,dA}{4\pi r^2}$



We already learned that $dA = r^2 \sin\theta\, d\theta\, d\phi$

$$\frac{N\,dA}{4\pi r^2} = \frac{N}{4\pi}\sin\theta\, d\theta\, d\phi$$

∴ number of molecules per unit volume within velocity range c & $c+dc$ $[dn_c]$, within direction θ & $\theta+d\theta$ & ϕ & $\phi+d\phi$ $[d\omega = \sin\theta\, d\theta\, d\phi]$

$$dn_{c,\theta,\phi} = \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi$$

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Let's find now, how many of them strike dA of the wall of container. Geometrically, this is the number of molecules within the slanted prism of length $c\,dt$ with edges in the direction θ & ϕ $= \frac{dn_c}{4\pi} \sin\theta\, d\theta\, d\phi \times c\,dA \cos\theta\, dt$

$\therefore$ Total number of collisions at dA per unit time

$$\int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi} \sin\theta\, d\theta\, d\phi \times c\,dA \cos\theta$$

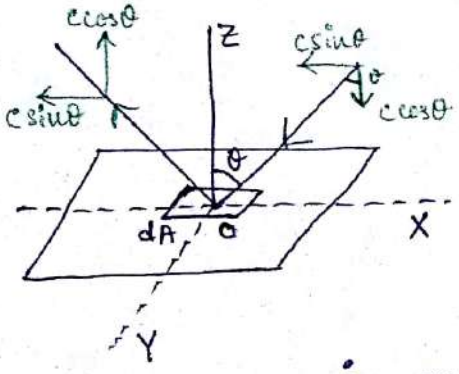
$$= \frac{dA}{4\pi} \int_0^{\infty} c\,dn_c \underbrace{\int_0^{\pi/2} \sin\theta \cos\theta\, d\theta}_{1/2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = \frac{dA}{4} \int_0^{\infty} c\,dn_c .$$

If n_1 atoms per unit volume moves with velocity c_1,
n_2 " " " " " c_2,
n_3 " " " " " $c_3, \ldots$

average velocity $\bar{c} = \dfrac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \cdots}{n_1 + n_2 + n_3 + \cdots}$

$$= \frac{\sum n_i c_i}{\sum n_i} = \frac{1}{n} \int_0^{\infty} c\,dn_c$$

$\therefore$ Number of molecules colliding at dA of the container per unit time $= \boxed{\frac{dA}{4}\, n\bar{c}}$



Now let's compute change in momentum by molecules striking area dA in unit time.

normal component of incident momentum is $mc\cos\theta$ & reflected momentum $-mc\cos\theta$.

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So each atom had a change in momentum $2mc\cos\theta$.

$\therefore$ Total change of momentum experienced by all gas atoms/molecules colliding to area dA, per unit time is

$$\int_{c=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA\cos\theta \times 2mc\cos\theta$$

$$= \frac{m\,dA}{2\pi}\int_{c=0}^{\infty} c^2 dn_c \underbrace{\int_{\theta=0}^{\pi/2}\cos^2\theta\sin\theta\, d\theta}_{=1/3}\underbrace{\int_{\phi=0}^{2\pi} d\phi}_{2\pi} = \frac{1}{3}m\,dA\int_{c=0}^{\infty} c^2 dn_c$$

$$c_{rms}^2 = \bar{c}^2 = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \cdots}{n_1+n_2+n_3+\cdots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

$$= \int_0^{\infty}\frac{c^2 dn_c}{n}$$

$\therefore$ Force exerted by gas atoms on dA is

$$F = \frac{1}{3}m\,dA\, n\bar{c}^2$$

Thus, pressure exerted $\boxed{p = \frac{F}{dA} = \frac{1}{3}mn\bar{c}^2}$

<u>Corollary</u> From above, $p = \frac{1}{3}\rho\bar{c}^2 \Rightarrow \bar{c} = \sqrt{\frac{3p}{\rho}}$

For Hydrogen $\rho = 8.9\times10^{-5}$ gm/cc.

1 atm pressure $P = h\rho g = 76\times13.6\times981$ dynes/cm^2

$$\therefore \bar{c} = \sqrt{\frac{3\times76\times13.6\times981}{8.9\times10^{-5}}} = \underline{1.85\times10^5}\ \text{cm/sec.}$$

$c_l = 3\times10^8$ m/s, $c_s = 300$ m/s

$= \underline{3\times10^{10}}$ cm/s, $c = \underline{3\times10^4}$ cm/s.

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Kinetic interpretation of temperature

From K.T. $p = \frac{1}{3} mn\bar{c}^2 = \frac{1}{3} m \frac{N}{V} \bar{c}^2$

But we assume!!

$\therefore PV = \frac{1}{3} mN\bar{c}^2 = RT$ [Boyle's law]

$\bar{c} = \sqrt{\frac{3RT}{mN}} = \sqrt{\frac{3RT}{M}}$ where M = molecular weight

$\therefore \bar{c} \propto \sqrt{T}$ RMS velocity of gas atom is proportional to square root of absolute temperature.

As from $T = 0$, $\bar{c} = 0$ ie. absolute zero temperature is where molecule cease to move.

Now $\bar{c}^2 = \frac{3RT}{M} \Rightarrow \frac{1}{2} M\bar{c}^2 = \frac{3}{2} RT$

divide by N, $\underbrace{\frac{1}{2} m\bar{c}^2}_{\text{mean K.E.}} = \frac{3}{2} k_B \underset{\text{abs. temp.}}{T}$, k_B = Boltzmann's constant.

for a given T, there is always a K.E. & molecular collision lead to uniform T.

Boyle's law from K.T.

$PV = \frac{1}{3} M\bar{c}^2$ & because $\bar{c}^2 \propto T$.

So if T is fixed $\bar{c}^2$ is constant so PV = constant.

Charle's law from K.T.

Again $\bar{c}^2 \propto T$, so $PV \propto T$.

i.e. $V \propto T$ when p = constant.

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Avogadro's law from K.T.

For same T & P, equal V of gases contain equal number of atoms.

$\boxed{P, V, N_1}$ 1 $\quad$ $\boxed{P, V, N_2}$ 2

$$P = \frac{1}{3} m_1 \frac{N_1}{V} \bar{c}_1^2$$
$$P = \frac{1}{3} m_2 \frac{N_2}{V} \bar{c}_2^2$$
$$\therefore m_1 N_1 \bar{c}_1^2 = m_2 N_2 \bar{c}_2^2$$

But T is equal, so K.E. is equal.

$$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2 \Rightarrow m_1 \bar{c}_1^2 = m_2 \bar{c}_2^2$$

$$\therefore N_1 = N_2$$

Clapeyron's equation from K.T.

$$P = \frac{1}{3} m n \bar{c}^2 = \frac{1}{3} \frac{n}{N} m N \bar{c}^2 = \frac{n}{N} \times \frac{1}{3} M \bar{c}^2$$

$$= \frac{n}{N} RT = n K_B T. \qquad \left[K_B = \frac{R}{N}\right]$$

$N = 6.023 \times 10^{23}$ atoms/mole.

Universal gas constant R

$PV = RT.$

$$\therefore R = \frac{PV}{T} = \frac{(76 \times 13.6 \times 981) \times 22.4 \times 10^3}{273}$$

$= 8.31 \times 10^7$ dynes-cm/°K/mole or erg/degK/mole.

in heat units, $= \dfrac{8.31 \times 10^7}{4.18 \times 10^7} = 2$ cal/degK/mole

& $K_B = \dfrac{R}{N} = \dfrac{8.31 \times 10^7}{6.023 \times 10^{23}} = 1.38 \times 10^{-16}$ ergs/degK/mole

Dalton's law of partial pressure

N no. of gases with density ρ_1, ρ_2, ρ_3 with rms velocities $\bar{c}_1, \bar{c}_2, \bar{c}_3$ etc, $P = \frac{1}{3}\rho_1 \bar{c}_1^2 + \frac{1}{3}\rho_2 \bar{c}_2^2 + \frac{1}{3}\rho_3 \bar{c}_3^2 = P_1 + P_2 + P_3 + \cdots$

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Relation between pressure & K.E.

$$P = \frac{1}{3}\rho\bar{c}^2 = \frac{2}{3}\frac{1}{2}\rho\bar{c}^2 = \frac{2}{3}E$$

So pressure of a gas is 2/3 the translational K.E. of the atoms per unit volume.

CW Compute the r.m.s. velocity of oxygen (O_2) & ~~hydrogen~~ CO_2 atoms at 27°c. Given, density of oxygen at N.T.P. = 1.43 kg/m³ & molecular weight of CO_2 = 44 gm, (molecular weight of O_2 = 32 gm).

at N.T.P. ($T_0 = 273K$) for O_2, $\rho_0 = 1.43$ kg/m³.

[If not this supplied, then molecular weight = 32 gm = 0.032 kg

at N.T.P. gram molecular volume = 22.4 litre
= 22.4×10^{-3} m³
= 0.0224 m³.

Density $\rho_0 = \frac{0.032}{0.0224} = 1.43$ kg/m³]

Similarly for CO_2, density $\rho_0 = \frac{0.044}{0.0224} = 1.96$ kg/m³ at N.T.P.

Using K.T. we have $\rho_0 T_0 = \rho T$.

$$\therefore \rho_{27^\circ} = \frac{\rho_0 T_0}{T} = \frac{1.43 \times 273}{(27+273)} = 1.3 \text{ kg/m}^3 \text{ for } O_2$$

$$\rho_{27^\circ} = \frac{\rho_0 T_0}{T} = \frac{1.96 \times 273}{(27+273)} = 1.79 \text{ kg/m}^3 \text{ for } CO_2$$

pressure $P = 0.76 \times 13.6 \times 10^3 \times 9.8 = 1.013 \times 10^5$ N/m².

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from K.T. $P = \frac{1}{3}\rho \bar{c}^2$

So r.m.s. velocity $\bar{c}_{O_2} = \sqrt{\frac{3P}{\rho_{O_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.3}}$

$= 4.835 \times 10^2$ m/s.

$\bar{c}_{CO_2} = \sqrt{\frac{3P}{\rho_{CO_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.79}}$

$= 4.12 \times 10^2$ m/s.

HW

1. Calculate the number of molecules/cc of an ideal gas at 27°C & at pressure of 20 mm of mercury. Density of mercury = 13.6 gm/cc & mean KE of a molecule at 27°C is 4×10^{-21} Joules.

2. At what temperature will the r.m.s. velocity of a gas will become half its value at 0°C?

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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".

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 <u>mutually exclusive</u>, then total probability of either of them to happen in a trial is $\underline{p(A) + p(B)}$

If two events A & B happen <u>independently</u>, then total probability of both events happening simultaneously in a trial is $\underline{p(A)\,p(B)}$.

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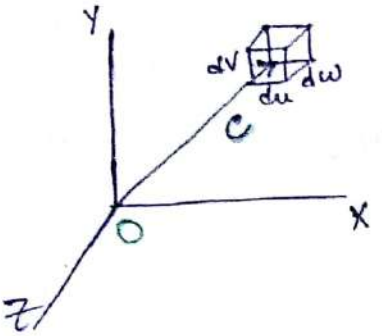
If x is random variable defined by a function $f(x)$, then $f(x)\,dx$ = probability of a variate falling within x & $x+dx$.



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.

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

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

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

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

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

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

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

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

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

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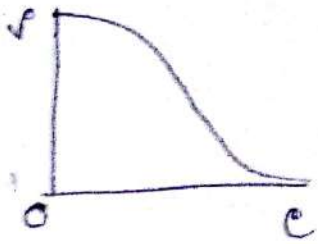
So $\rho = NA^3 e^{-b(u^2+v^2+w^2)} = NA^3 e^{-bc^2}$



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

What is remaining now is to find out constants <u>A & b.</u>

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

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

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

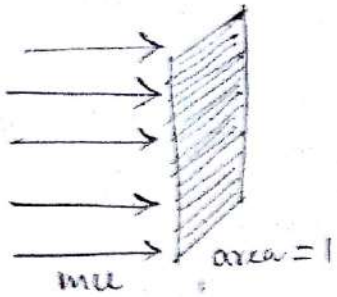
$$= \frac{1}{\cancel{2}\sqrt{b}} \cancel{2}\int_{0}^{\infty} e^{-z} z^{-1/2} dz = \frac{\Gamma(1/2)}{\sqrt{b}} = \sqrt{\frac{\pi}{b}}. \quad]$$

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

<u>Evaluate b</u> Collisions per second

= area × velocity × number density at that

= $1 \times u \times n_u$



Change in momentum = $2mu$.

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

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

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

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

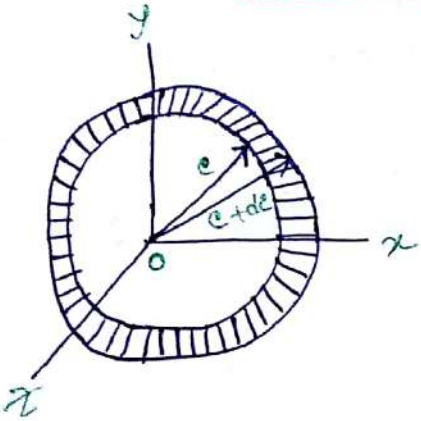
$$= \frac{mn_u A}{2b^{3/2}} \Gamma\left(\tfrac{1}{2}\right) \qquad \Gamma\left(\tfrac{3}{2}\right) = \tfrac{1}{2}\Gamma\left(\tfrac{1}{2}\right)$$

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

[from Clapeyron's equation]

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

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



volume between c & $c+dc$ is

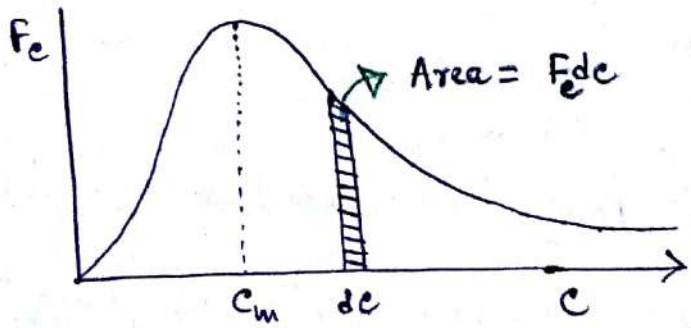
$$\frac{4}{3}\pi(c+dc)^3 - \frac{4}{3}\pi c^3$$

$$= \cancel{\frac{4}{3}\pi c^3} + \frac{4}{3}\pi\, 3c^2 dc + \frac{4}{3}\pi\, 3c\,\cancel{(dc)^2}^{\,0} + \cancel{\frac{4}{3}\pi (dc)^3}^{\,0} - \cancel{\frac{4}{3}\pi c^3}$$

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

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

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



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

(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

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Velocity component distribution

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

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

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

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

$$\left[\text{Now } \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv = 2\int_0^{\infty} e^{-\frac{mv^2}{2K_BT}} dv \right.$$

$$\left[\text{put } z = \frac{mv^2}{2K_BT}.\quad dz = \frac{mv\,dv}{K_BT}\quad dv = \frac{K_BT\,dz\sqrt{m}}{m\sqrt{2K_BT}\sqrt{z}}\right]$$

$$= \frac{2\sqrt{K_BT}}{\sqrt{2}\sqrt{m}}\int_0^{\infty} e^{-z} z^{-1/2} dz$$

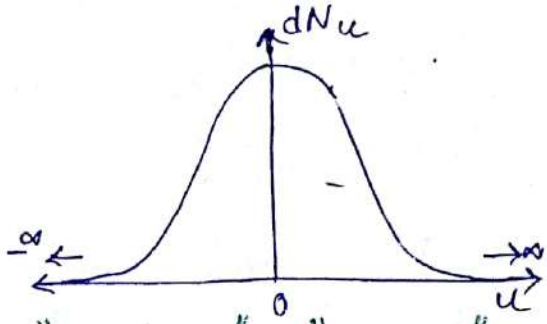
$$\left. = \sqrt{\frac{2K_BT}{m}} \times \sqrt{\pi} = \sqrt{\frac{2\pi K_BT}{m}}\right]$$

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

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

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

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



"Gaussian" or "Normal" distribution

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Average velocity, RMS velocity, Most probable velocity

Avg. velocity $\langle c \rangle = \dfrac{N_1 c_1 + N_2 c_2 + \cdots}{N_1 + N_2 + \cdots} = \dfrac{\sum N_i c_i}{\sum N_i}$

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

remember,

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

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

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

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

put $bc^2 = z$

$2bc\,dc = dz$

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

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

$\Gamma(2) = 1$

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

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

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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, $bc^2 = z$

$2bcdc = dz$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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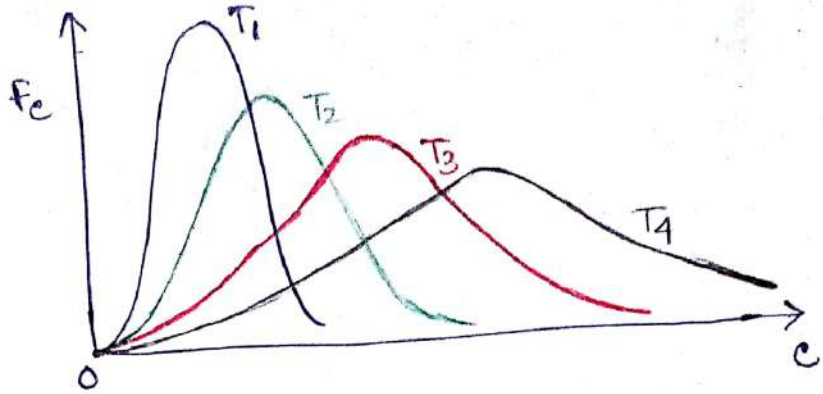
Corollary $\int_0^\infty F_c \, dc = 1$

$T_4 > T_3 > T_2 > T_1$



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

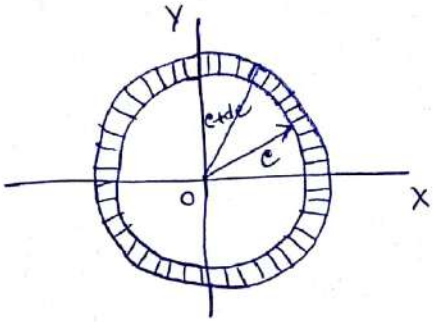
$$dn = \frac{1}{4} n \bar{c} = \frac{1}{4} n \sqrt{\frac{8 k_B T}{m\pi}} = \frac{1}{4} \frac{P}{k_B T} \sqrt{\frac{8 k_B T}{m\pi}} \quad (\text{as } P = n k_B T)$$

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

CW 1. The velocity distribution in two dimension is

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

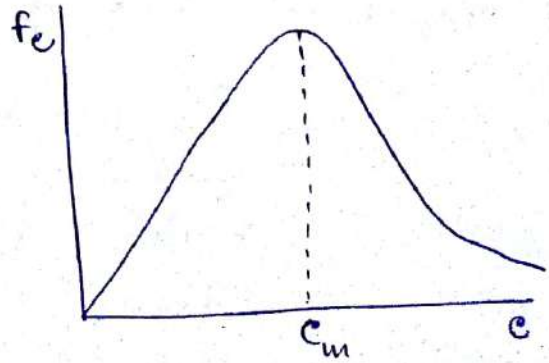
$$du\,dv = \pi(c+dc)^2 - \pi c^2 = 2\pi c\,dc.$$

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

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

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

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



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

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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 $-73^\circ C$.

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

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

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

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

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

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

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 $c = c_m$

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

~~dc_m is 1% of c_m~~ ~~As c_m~~

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

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

$$\therefore P = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2K_BT}\right)^{3/2} e^{-1}\frac{2K_BT}{m}\sqrt{\frac{2K_BT}{m}}\times0.02$$

$$= 0.016 = 1.6\%.$$

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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 $27^\circ c$?

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 $27^\circ c$. (Given $R = 8.3\ J/^\circ c/mol$)

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.

<u>Maxwell's distribution in reduced format</u>

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

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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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.

$$E = \frac{1}{2} m c^2 \quad \text{or} \quad dE = mc\,dc.$$

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

From Maxwell's velocity distribution, we have

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

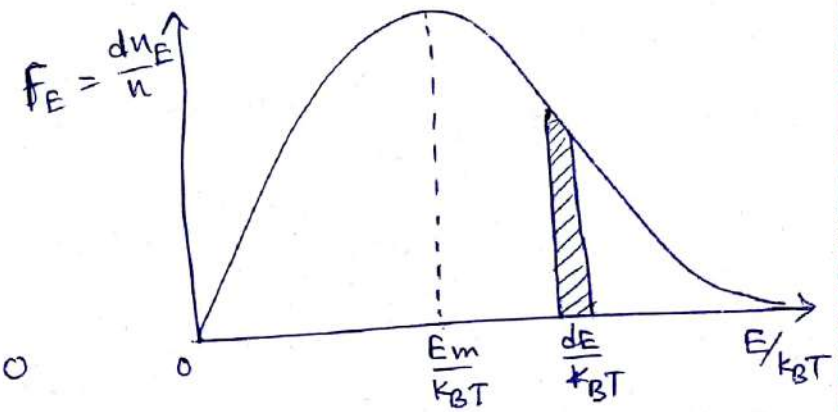
$$\therefore \quad dn_E = 4\pi n \frac{2E}{m}\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-E/k_BT} \frac{dE}{\sqrt{2mE}}$$

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

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

Fraction of atoms $\frac{dn_E}{n}$ or $\frac{dN_E}{N} = \frac{2}{\sqrt{\pi}}(k_BT)^{-3/2}\sqrt{E}\, e^{-E/k_BT}\, dE = f_E\, dE$

$$F_E = \frac{2}{\sqrt{\pi}}(k_BT)^{-3/2}\sqrt{E}\, e^{-E/k_BT}$$



at $E = E_m$, $\frac{dF_E}{dE} = 0$.

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

$$\text{or} \quad \frac{1}{2\sqrt{E_m}} e^{-E_m/k_BT} - \frac{\sqrt{E_m}}{k_BT} e^{-E_m/k_BT} = 0.$$

$$\therefore \quad \frac{1}{2\sqrt{E_m}} = \frac{\sqrt{E_m}}{k_BT} \quad \text{or} \quad E_m = \frac{k_BT}{2}.$$

Compare result with $c_m = \sqrt{\frac{2k_BT}{m}}$. Notice that

$$E_m \neq \frac{1}{2} m c_m^2 = \frac{1}{2} m \frac{2k_BT}{m} = k_BT.$$

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Momentum distribution of the gaseous atoms

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

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

Again, start from Maxwell's distribution

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

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

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

at $p = p_m$ (most probable momentum), maximum no. of molecules lie $\left.\frac{df_p}{dp}\right|_{p=p_m} = 0$. or $\frac{d}{dp}\left(p^2 e^{-p^2/2mk_BT}\right)_{p=p_m} = 0$

put $b = \frac{1}{2mk_BT}$

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

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

or $\left[2p\, e^{-bp^2}(1 - bp^2)\right]_{p=p_m} = 0 \Rightarrow p_m = \frac{1}{\sqrt{b}} = \sqrt{2mk_BT}$

Again, $c_m = \sqrt{\frac{2k_BT}{m}}$

So $mc_m = \sqrt{2mk_BT} = p_m$.

So most of the atoms have velocity c_m are also having the momentum mc_m, but ~~to~~ 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 $dN_c = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \times e^{-(mgh + \frac{1}{2}mc^2)/k_BT} c^2 dc$

Maxwell-Boltzmann distribution.

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Degrees of freedom

1D motion → 1 d.o.f.

2D (unconstrained) motion → 2 d.o.f

3D (unconstrained) motion → 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 $f_j(x_1, y_1, z_1, \dots, x_N, y_N, z_N) = 0$, $j = 1, 2, 3, \dots, m$.

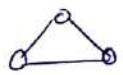
$\therefore$ $K = 3N - m$ = d.o.f.

Example (1) Monoatomic atom : $K = 3$ for one atom.

(2) Diatomic ~~atom~~ molecule : $K = 2 \times 3 - 1 = 5$ for one molecule.

(3) Triatomic molecule : (a) linear $K = 3 \times 3 - 2 = 7$

CO_2

(b) Nonlinear  $K = 3 \times 3 - 3 = 6$

H_2O, O_3

So trivial case, $m = 3N$ → 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 to 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 $\frac{1}{2} k_B T$ for each d.o.f.

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

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

is $U = \frac{1}{2}Nf K_BT = \frac{1}{2}RfT$ $\quad [\because K_B = \frac{R}{N}]$

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

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

$\therefore \frac{C_p}{C_V} = \frac{R + Rf/2}{Rf/2} = \frac{2}{f} + 1$ or $\boxed{\gamma = 1 + \frac{2}{f}}$

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 colinear 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 $\frac{1}{2}K_BT$ energy from Equipartition theorem.

$\therefore$ Total energy $= U = 6N\frac{1}{2}K_BT = 3NK_BT = 3RT$

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

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

Variation of γ with temperature

High T, translation + rotation + vibration,

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

like $H_2 > 5000°C$ $\quad C_V = \frac{7}{2}R$

Medium T, translation + rotation

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

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

low T, translation

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

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

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

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

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

$C_p = \gamma C_V = 33.49$ 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°C. Given $k_B = 1.37 \times 10^{-23}$ J/K & $N = 6.02 \times 10^{23}$.

O_2 = 3 translation + 2 rotation (θ, ϕ), $f = 5$.
(x, y, z)

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

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

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

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γ 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.
.....
N_N moles of ideal gas with f_N d.o.f.

Total internal energy $U = \frac{1}{2}k_BTN_1f_1N + \frac{1}{2}k_BTN_2f_2N + \cdots + \frac{1}{2}k_BTN_Nf_NN$

$$\therefore C_V = \left(\frac{dU}{dT}\right)_V = \frac{1}{2}k_BN(N_1f_1 + N_2f_2 + \cdots + N_Nf_N)$$

Also $C_p - C_V = (N_1 + N_2 + \cdots + N_n)k_BN$ $\quad [R/N = k_B]$

$$\therefore C_p = (N_1 + N_2 + \cdots + N_n)k_BN + \frac{1}{2}(N_1f_1 + N_2f_2 + \cdots + N_Nf_N)k_BN$$

$$= \frac{(2+f_1)N_1 + (2+f_2)N_2 + \cdots + (2+f_N)N_N}{2}k_BN$$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{(2+f_1)N_1 + (2+f_2)N_2 + \cdots + (2+f_N)N_N}{f_1N_1 + f_2N_2 + \cdots + f_NN_N}$$

Example 1 mole of monoatomic gas $(f=3)$ & 1 mole of diatomic gas $(f=5)$, $\gamma = \frac{(2+f_1)N_1 + (2+f_2)N_2}{f_1N_1 + f_2N_2} = \frac{5+7}{3+5} = 1.5$

$$\boxed{1 \leq \gamma \leq 1.67}$$

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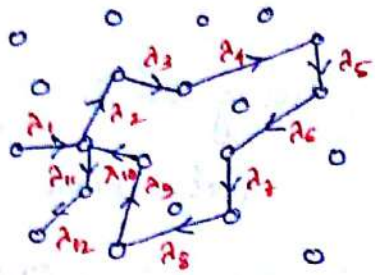
Mean free path

We calculated that K.T. gives ~ 1 Km/S velocity for molecular movement. But we see clouds suspended in air holds together for hours. So there must be some factors that prevent the free escape of atoms.

Clausius showed that such discrepancy goes away if we take small & finite volume for atoms & they change velocity & direction of motion in the process of collission, zigzag path (discrete)

In between two successive collission, the traversed path is free path $(\lambda_1, \lambda_2, \dots, \lambda_n)$.



$$\text{Mean free path} = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{\text{Number of collision}}$$

Collision probability

Suppose collision rate is P, average velocity of an atom is $\bar{c}$ & in time t, distance covered $= \bar{c}t$ & number of collisions suffered is Pt. then $\lambda_{\bar{c}} = \frac{\bar{c}t}{Pt} = \frac{\bar{c}}{P}$.

Before we calculate "λ", let's compute the distribution of λ, meaning probability of an atom moving a distance x without collision, say $f(x)$. This means that $f(x+dx)$ is the probability that atom traverses $x+dx$ length without collision.

If P is collission probability per unit time, then for N atoms number of collisions in time $t = \frac{1}{2}NPt$. ($\frac{1}{2}$ because each collission between 2 atoms is counted twice).

Probability that after traversing x, an atom will suffer a collission within dx in time $dt = Pdt = P\frac{dx}{c} = \frac{dx}{\lambda}$

where $\lambda = \frac{c}{P}$ is the free path for atoms with velocity c.

$\therefore$ As total probability $= 1$, probability of no collision in distance $dx = \left(1 - \frac{dx}{\lambda}\right)$.

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As successive collisions are independent, therefore the joint probability of no collision at $x+dx$ is $f(x) \times (1-\frac{dx}{\lambda})$

$$\therefore \; f(x+dx) = f(x)(1-\frac{dx}{\lambda}).$$

Expand LHS using Taylor's theorem.

$$f(x) + f'(x)\,dx + \frac{1}{2} f''(x)\cancel{(dx)^2}^{\to 0} + \cdots = f(x)(1-\frac{dx}{\lambda}) \quad [\lim_{dx\to 0}]$$

$$\text{or } f'(x) = -f(x)/\lambda. \quad \text{or} \quad \frac{f'(x)}{f(x)} = -\frac{1}{\lambda}.$$

Integrating, $\ln f(x) = -\frac{x}{\lambda} + \ln c \Rightarrow f(x) = c e^{-x/\lambda}$.

note that when $x=0$, $f(x)=1$. $\therefore c=1$.

$$\therefore f(x) = e^{-x/\lambda}. \Longrightarrow \text{law of distribution of free paths}$$

<u>Method 2</u> Let, out of N atoms, N' atoms cross x without collision. & after that in dx distance, dN' atoms are throw out due to collision. Then $dN' \propto N'$, $\propto dx$ or $dN' = -pN'dx$ (−ive for decrease)

$$\text{or } \frac{dN'}{N'} = -p\,dx$$

Integrating $\ln N' = -px + \ln c$

or $N' = ce^{-px}$. Now put boundary condition at $x=0$, $N'=N$.

$\therefore c = N$. $\therefore N' = Ne^{-px}$

thrown out molecules are $dN' = +pNe^{-px}dx$ (+ive number)

$$\lambda = \frac{x_1 dN_1' + x_2 dN_2' + \cdots}{N} = \frac{1}{N}\int_0^\infty x\,dN'$$

$$= \frac{1}{N}\int_0^\infty x p N e^{-px} dx = p\int_0^\infty e^{-px} x\,dx$$

put $px = z$, $p\,dx = dz$

$$= p\frac{1}{p^2}\int_0^\infty e^{-z} z\,dz = \frac{1}{p}\Gamma(2) = \frac{1}{p}.$$

$$\therefore \boxed{N' = Ne^{-x/\lambda}} \quad \text{or} \quad f(x) = e^{-x/\lambda}$$

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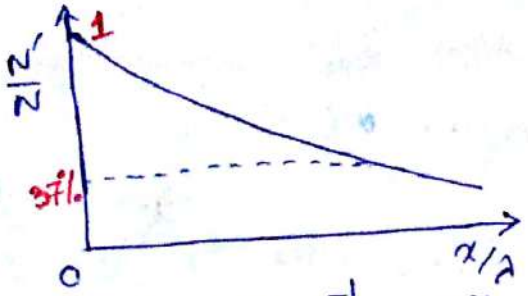
This is the "survival equation".

$$dN' = \frac{N}{\lambda} e^{-x/\lambda} dx \quad \text{or} \quad \boxed{\frac{dN'}{dx} = \frac{N}{\lambda} e^{-x/\lambda}}$$



Number $> \lambda$ is $e^{-1} \sim 37\%$

$< \lambda$ is $1 - 37\% = 63\%$

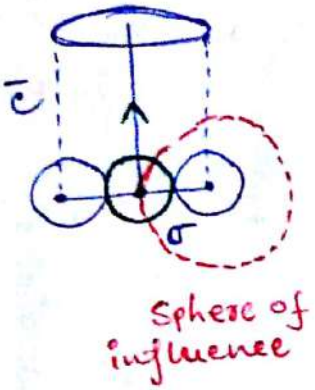
(a) $P \propto 1/\lambda \Rightarrow$ collision probability is reciprocal of free path.

(b) Intensity of atomic beam $\propto$ number of atoms. $\therefore I' = I e^{-x/\lambda}$.

I' → final intensity.

I → initial intensity

Calculation of λ



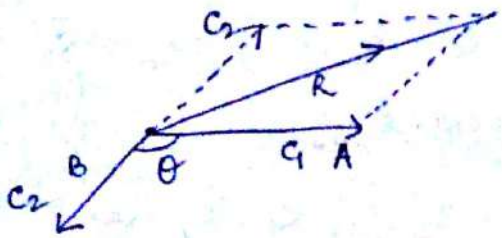
Suppose all atoms are rest but only one moves with velocity $\bar{c}$. Rigid spherical shape with diameter σ. It can only collide when they touch. & can reach distance $\bar{c}$, so it collides with $\pi\sigma^2\bar{c}n$ many atoms. This is also number of collisions per second.

$$\therefore \text{Mean free path } \lambda = \frac{\bar{c}}{\pi\sigma^2\bar{c}n} = \frac{1}{n\pi\sigma^2}$$

This is approximate & Clausius did the first correction followed by Maxwell - Tait.

Clausius correction

Introduction of relative velocity as all atoms are in motion.



Consider A & B atom moves with velocity C_1 & C_2 & angle θ. Making atom B observer (meaning applying equal & opposite velocity C_2 to B), B is in rest & relative to that A moves with relative velocity

$$R = \sqrt{C_1^2 + C_2^2 - 2C_1C_2\cos\theta}$$

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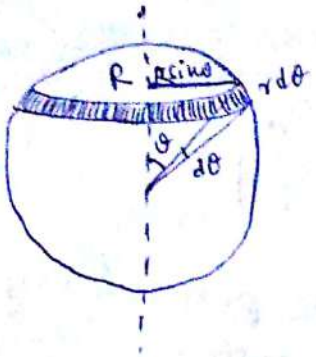

Now we have to find mean relative velocity of atom A with respect to all others. If $dN_{\theta,\phi}$ is the number of atoms moving between θ & $\theta+d\theta$, ϕ & $\phi+d\phi$ then

$$dN_{\theta,\phi} = \frac{N}{4\pi R^2} R^2 \sin\theta\, d\theta\, d\phi = \frac{N \sin\theta\, d\theta\, d\phi}{4\pi}$$

and
$$\bar{R} = \frac{\int R\, du_{\theta,\phi}}{\int du_{\theta,\phi}} = \frac{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sqrt{c_1^2+c_2^2-2c_1c_2\cos\theta}\, \frac{N\sin\theta\, d\theta\, d\phi}{4\pi}}{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \frac{N\sin\theta\, d\theta\, d\phi}{4\pi}}$$

$$= \cancel{\frac{N}{4\pi}}\, \cancel{2\pi} \int_{\theta=0}^{\pi} \sqrt{c_1^2+c_2^2-2c_1c_2\cos\theta}\, \sin\theta\, d\theta \Big/ \cancel{\frac{N}{4\pi}}\, \cancel{4\pi}^{\,2}$$

substitute $c_1^2+c_2^2-2c_1c_2\cos\theta = z$ or $2c_1c_2\sin\theta\, d\theta = dz$

$$\int z^{1/2} \frac{1}{2c_1c_2} dz = \frac{1}{2c_1c_2}\int_{(c_1-c_2)^2}^{(c_1+c_2)^2} \sqrt{z}\, dz = \frac{1}{2c_1c_2}\left[\frac{z^{3/2}}{3/2}\right]_{(c_1-c_2)^2}^{(c_1+c_2)^2}$$

$$= \frac{1}{3c_1c_2}\left[(c_1+c_2)^3 - (c_1-c_2)^3\right]$$

$$\therefore \bar{R} = \frac{1}{6c_1c_2}\left[(c_1+c_2)^3 - (c_1-c_2)^3\right].$$

According to Clausius's assumption $c_1 = c_2 = \bar{c}$

$$\therefore \bar{R} = \frac{1}{6\bar{c}^2} 8\bar{c}^3 = \frac{4}{3}\bar{c},$$ meaning in traveling a distance $\bar{c}$, number of collision by molecule A with relative velocity $\bar{R}$ is $\pi\sigma^2\bar{R}n$ & therefore $\lambda_{cl} = \frac{\bar{c}}{\pi\sigma^2 n\bar{R}} = \frac{3}{4}\frac{1}{n\pi\sigma^2}$.

Maxwell's correction

Clausius took $c_1 = c_2 = \dots = c_N = \bar{c}$ but they're Maxwellian distributed in reality!

Maxwell corrected by considering both $c_1 > c_2$ & $c_1 < c_2$ case with $dN_{c_2} = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc_2^2/2k_BT} c_2^2\, dc_2$

to obtain $\bar{R} = \sqrt{2}\,\bar{c}$ (see AB Gupta § 2.21.2 for derivation)

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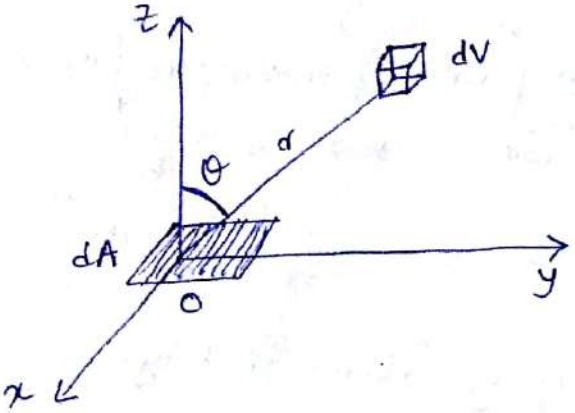
$$\therefore \lambda_{Maxwell} = \frac{\bar{c}}{\sqrt{2}\pi\sigma^2 n \bar{c}} = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

Pressure of a gas using mean free path



Once again, we want to compute atoms within volume dV at distance r with inclination θ to a surface dA at origin that reach dA after collision with other atoms, using survival equation.

Number of molecules between c & c+dc in volume dV is $dn_c dV$.

If λ is mean free path of the gas atoms then number of collision suffered by one atom per unit time $= \frac{c}{\lambda}$.

As $1 \to 2$ & $2 \to 1$ collision is counted twice, so the number of collisions suffered by $dn_c dV$ number of atoms in unit time is $\frac{1}{2}\frac{c}{\lambda} dn_c dV$. But each collision results to two new paths along which atoms travel.

∴ The number of new paths or number of atoms emanating from dV per unit time $= \frac{1}{2}\frac{c}{\lambda} dn_c dV \times 2$ & fraction that are pointed towards the area dA is the solid angle subtended by dA at dV $= \frac{dA\cos\theta/r^2}{4\pi}$ (4π = all molecules contained)

∴ That exit from dV pointing to dA, that number is

$$N_0 = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2} \quad \text{(per unit time)}.$$

In N_0, only those atoms with $\lambda \geq r$ can reach dA, which is

$$N = N_0 e^{-r/\lambda} = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2} e^{-r/\lambda}$$

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$$= \frac{c\,du_c\,dA\cos\theta\,\cancel{r^2}\sin\theta\,d\theta\,d\phi\,dr\;e^{-r/\lambda}}{\lambda\,4\pi\cancel{r^2}} \qquad (dV = r^2\sin\theta\,d\theta\,d\phi\,dr)$$

$$= \frac{dA}{\cancel{\phi}} \times \frac{c\,du_c\,\sin\theta\cos\theta\,d\theta\,d\phi}{4\pi} \times \frac{e^{-r/\lambda}}{\lambda}\,dr$$

$\therefore$ No. of atoms striking dA $\therefore$ $= \frac{dA}{4\pi}\int_{c=0}^{\infty} c\,du_c \int_{\theta=0}^{\pi/2} \sin\theta\cos\theta\,d\theta \int_{\phi=0}^{2\pi} d\phi \times \int_{r=0}^{\infty} e^{-r/\lambda}/\lambda\,dr$

$$= \frac{dA}{4\pi}\,n\bar{c}\,\frac{1}{2}\,2\pi \times 1 = \frac{dA}{4}\,n\bar{c}$$

So per unit area per unit time, number of atoms striking

$\therefore$ $\boxed{\frac{n\bar{c}}{4}}$.

Again, we know one colliding atom suffers momentum change $= 2mc\cos\theta$

So change of momentum for all atom are

$$\frac{dA}{4\pi}\int_{c=0}^{\infty} 2mc^2\,du_c \int_{\theta=0}^{\pi/2} \sin\theta\cos^2\theta\,d\theta \int_{\phi=0}^{2\pi} d\phi \int_{r=0}^{\infty} e^{-r/\lambda}\,d(r/\lambda).$$

$$dF = \frac{m\,dA}{2\pi}\,n\bar{c}^2_{rms}\,\frac{1}{3}\,2\pi = \frac{1}{3}\,mn\bar{c}^2_{rms}\,dA. \qquad \left[\bar{c}^2_{rms} = \frac{1}{n}\int_{c=0}^{\infty} c^2\,du_c\right]$$

$$\therefore\; p = \frac{dF}{dA} = \boxed{\frac{1}{3}\,mn\,\bar{c}^2_{rms}}$$

<u>Mean free path of a mixture of a gas</u>

If we consider two different molecule with diameter σ_1, σ_2 then, σ_1 diameter molecule will collide with all molecule that are $\frac{\sigma_1+\sigma_2}{2}$ distance apart from σ_1 molecule. Hence λ will be $1/n\pi\sigma_a^2$ where $\sigma_a = \frac{\sigma_1+\sigma_2}{2}$ & n = number of molecules per unit volume of σ_2 type. But σ_2 molecules are not in rest then if σ_1 type moves with $\bar{c}_1$ & σ_2 type moves with $\bar{c}_2$ & if the molecules of σ_2 move perpendicular to σ_1 then

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relative velocity $R = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$ & therefore $\frac{R}{\bar{c}_1} = \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}$

So λ_1 of σ_1 type of molecules within σ_2 type molecules are

$$\lambda_1 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}}.$$ Similarly, λ_2 of σ_2 type of molecules within σ_1 type molecules are $$\lambda_2 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_2}}.$$ The perpendicular directionality assumption gives Maxwell's distribution with relative velocity R, & if we had assumed $\bar{c}_1 = \bar{c}_2$ & then we could get back Maxwell's expression of free path.

If we now consider n_1 molecule of σ_1 type with $\bar{c}_1$ & n_2 molecule of σ_2 type with $\bar{c}_2$ avg. velocity then no. of impact/sec by σ_1 molecules

$$\Gamma_1 = \underbrace{\sqrt{2}\,\bar{c}_1 n_1 \pi \sigma_1^2 \left(= \frac{\bar{c}_1}{\lambda_{11}}\right)}_{\sigma_1 \text{ with } \sigma_1} + \underbrace{n_2 \pi \sigma_a^2 \cancel{\bar{c}_1} \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\cancel{\bar{c}_1}} \left(= \frac{\bar{c}_1}{\lambda_{12}}\right)}_{\sigma_1 \text{ with } \sigma_2}$$

∴ Mean free path of σ_1 type molecules in the gas mixture

$$\lambda_1 = \frac{\bar{c}_1}{\Gamma_1} = \frac{\bar{c}_1}{\sqrt{2}\pi n_1 \bar{c}_1 \sigma_1^2 + \pi\sigma_a^2 n_2 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$ & Mean free path for the other

$$\lambda_2 = \frac{\bar{c}_2}{\Gamma_2} = \frac{\bar{c}_2}{\sqrt{2}\pi n_2 \bar{c}_2 \sigma_2^2 + \pi\sigma_a^2 n_1 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$

HW 1. Estimate the size of a He atom, assuming its mean free path is 28.5×10^{-6} cm at N.T.P. & density is 0.178 gm/litre at N.T.P. & the mass of He atom is 6×10^{-24} gm.

2. The diameter of a gas molecule is 3×10^{-8} cm. Calculate the mean free path at N.T.P. Given $K_B = 1.38 \times 10^{-16}$ ergs/°c.

3. Find the diameter of a molecule of Benzene if its mean-free path is 2.2×10^{-8} m & the number of Benzene molecules/unit volume is 2.79×10^{25} molecules/m^3.

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(Nonequilibrium) Transport Phenomena in Gases

(i) **Viscosity :** velocity varies from layer to layer & momentum is transferred from layer to layer leading to kinetic interpretation of viscosity in gases. In 1860, Maxwell interpreted that if two layer have relative velocity, viscous force acts along the surface of contact retarding the faster moving layer & making the slower moving layer to move faster. Retarding force is proportional to area of contact & velocity gradient.

$$F \propto A \quad \text{or} \quad F = \eta A \frac{dv}{dz} \quad \text{or} \quad \sigma = \eta \dot{\gamma} \longrightarrow \text{strain rate}$$

$$\propto \frac{dv}{dz}$$

σ → stress, η → coeff^n of viscosity

$\boxed{\text{Newton's law of viscosity}}$

(ii) **Thermal conductivity :** Taken a solid rod & heated in one end, after sufficiently long time when measured temperature at different distances then amount of heat conducted (rate) is proportional to temperature gradient, area of face of slab.

$$Q \propto A \quad \text{or} \quad Q = KA \frac{dT}{dz}$$

$$\propto \frac{dT}{dz}$$

K → thermal conductivity

$\boxed{\text{Fourier's law of heat conduction}}$

(iii) **Diffusion :** Whenever there is difference in concentration, mass transfer results to an equilibrium distribution of concentration. In monodisperse system, diffusion to concentration gradient is called self-diffusion & if two gases diffuse into each other, called inter-diffusion. Number of molecules crossing is proportional to

$$N \propto \frac{dn}{dz} \quad \text{or} \quad N = DA \frac{dn}{dz}$$

$$\propto A$$

$\boxed{\text{Fick's law of diffusion}}$

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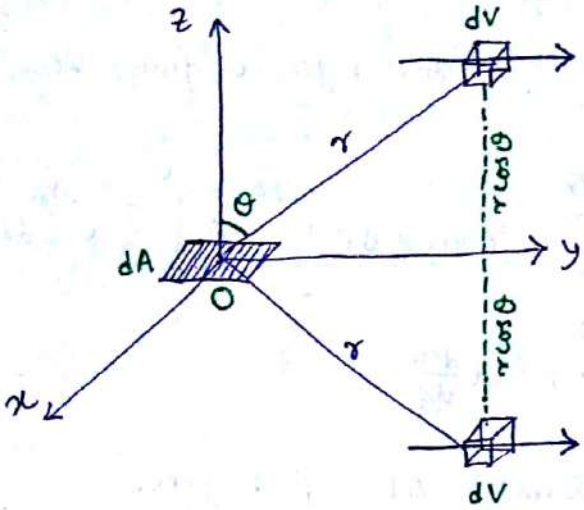
General method for obtaining coefficient of viscosity & conduction



In a reference frame, consider an elementary volume dV at coordinate (r, θ). The layer that contains dV is at a vertical height $r\cos\theta$ from XY plane at origin O. If the physical entity has a value $\mathcal{H}$ (energy, momentum etc) on the XY plane at origin, then the value at the upper layer is $\mathcal{H} + r\cos\theta \frac{d\mathcal{H}}{dz}$. For an identical layer beneath at same distance, the value is $\mathcal{H} - r\cos\theta \frac{d\mathcal{H}}{dz}$

The number of molecules within c & c+dc in dV is $dn_c dV$. If A is the mean free path, then the number of collison suffered in unit time is $\frac{c}{\lambda} \frac{1}{2} dn_c dV$. Factor ½ is because collision between two molecules are identical & counted twice. But each collision results in 2 paths. So the number of molecule coming out of dV in all possible direction is $2 \times \frac{1}{2} \frac{c}{\lambda} dn_c dV$.

Number of molecules which are headed towards area dA at origin is $\frac{dA\cos\theta}{4\pi r^2} \frac{c}{\lambda} dn_c dV$. Due to collisions some of them cannot reach dA & the number that reaches dA in unit time is

$$\frac{dA\cos\theta}{4\pi r^2} \frac{c}{\lambda} dn_c dV \, e^{-r/\lambda} = \frac{dA\cos\theta}{4\pi r^2} \frac{c}{\lambda} dn_c \, r^2 \sin\theta \, d\theta \, d\phi \, dr \, e^{-r/\lambda}$$

If the molecule carry the physical entity characteristic of the layer when they last suffered collisions then the transport of physical entity downwards through area dA per unit time is

$$L\downarrow = \frac{dA}{4\pi} \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} c \, dn_c \sin\theta \cos\theta \, d\theta \, d\phi \, e^{-r/\lambda} \frac{dr}{\lambda} \left(\mathcal{H} + r\cos\theta \frac{d\mathcal{H}}{dz}\right)$$

Considering an identical volume below the reference frame, the transport of physical entity upwards is

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$$L\uparrow = \frac{dA}{4\pi}\int_{c=0}^{\infty}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} c\,dn_c \sin\theta\cos\theta\, d\theta\, d\phi\; e^{-r/\lambda}\frac{dr}{\lambda}\left(\mathcal{H} - r\cos\theta\frac{d\mathcal{H}}{dz}\right)$$

$\therefore$ The net transfer of physical entity to the reference frame via area dA in unit time is

$$\Delta L = L\downarrow - L\uparrow = \frac{2\,dA}{4\pi}\frac{d\mathcal{H}}{dz}\int_0^{\infty} c\,dn_c \int_0^{\pi/2}\cos^2\theta\sin\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty}\frac{r}{\lambda}e^{-r/\lambda}dr$$

$$= dA\frac{d\mathcal{H}}{dz}\,\frac{1}{3}\lambda\int_0^{\infty} c\,dn_c = \frac{1}{3}n\bar{c}\lambda\, dA\frac{d\mathcal{H}}{dz}$$

(i) <u>Viscosity</u>: $\mathcal{H} = mv$ = momentum, $\Delta L = F$ = force

$$\therefore F = \frac{1}{3}n\bar{c}\lambda\, dA\; m\frac{dv}{dz} = \eta\, dA\frac{dv}{dz}$$

$$\therefore \boxed{\eta = \frac{1}{3}mn\bar{c}\lambda = \frac{1}{3}\rho\bar{c}\lambda}$$

(ii) <u>Thermal conductivity</u>: $\mathcal{H} = E$ = thermal energy, $\Delta L = Q$ = heat

$$\therefore Q = \frac{1}{3}n\bar{c}\lambda\, dA\frac{dE}{dz} = \frac{1}{3}n\bar{c}\lambda\, dA\frac{dE}{dT}\frac{dT}{dz} = K\, dA\frac{dT}{dz}$$

$$\therefore K = \frac{1}{3}n\bar{c}\lambda\frac{dE}{dT}$$

If C_V = specific heat of molecules, $E = mC_V T \Rightarrow \frac{dE}{dT} = mC_V$

$$\therefore \boxed{K = \frac{1}{3}n\bar{c}\lambda m C_V = \eta C_V}$$

<u>Variation of $K/\eta C_V$ with the atomicity of molecules</u>

$K/\eta C_V = 1$ was not matching with experiments, because many factors are omitted to reach the expression. In general $K/\eta C_V = \epsilon = [1, 2.5]$

For a polyatomic molecule, the energy transfer is not only translational but also internal energy (rotational, vibrational etc) In rigorous calculation, Chapman found total energy transferred per unit time is $\frac{1}{3}n\bar{c}\lambda\, dA\left(\frac{5}{2}\frac{dE_T}{dz} + \frac{dE_R}{dz}\right)$ E_T = Translational energy & E_R = Rotational energy.

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$$\therefore \quad K\,dA\,\frac{dT}{dz} = \frac{1}{3} n\bar{c}\lambda\, dA \frac{dT}{dz}\left\{\frac{5}{2}\frac{dE_T}{dT} + \frac{dE_R}{dT}\right\}$$

$$\text{or} \quad K = \frac{\eta}{m}\left(\frac{5}{2}\frac{dE_T}{dT} + \frac{dE_R}{dT}\right) \quad \text{— (1)}$$

From the principle of equipartition of energy, total energy associated with 1 gm molecule of gas is $\frac{3+\beta}{2}RT$, β = # of d.o.f. for rotational motion. $\therefore$ Molar specific heat $C_V = \frac{dE}{dT} = \frac{3+\beta}{2}R$.

Using $C_p - C_V = R$, $C_p = \frac{5+\beta}{2}R$

$$\text{or} \quad \gamma = C_p/C_V = \frac{5+\beta}{3+\beta} = 1 + \frac{2}{3+\beta} \quad \text{— (2)} \quad \text{or} \quad \beta = \frac{2}{\gamma-1} - 3$$

But $E_T = \frac{3}{2}K_BT$, $E_R = \frac{\beta}{2}K_BT$ or $\frac{dE_T}{dT} = \frac{3}{2}K_B$, $\frac{dE_R}{dT} = \frac{\beta}{2}K_B$

putting in (1), $K = \frac{\eta}{m}\left(\frac{15K_B}{4} + \frac{\beta K_B}{2}\right)$

But $C_v = \frac{3+\beta}{2}\frac{K_B}{m}$ (molecular specific heat)

$$= \frac{K_B}{m(\gamma-1)} \quad [\text{using (2)}] \quad \text{or} \quad K_B = m(\gamma-1)C_v$$

$$\therefore K = \frac{\eta}{m} m(\gamma-1)C_v\left(\frac{15+2\beta}{4}\right) = \eta C_V(\gamma-1)\left(\frac{15}{4} + \frac{\beta}{2}\right)$$

$$= \eta C_V(\gamma-1)\left[\frac{15}{4} + \frac{1}{\gamma-1} - \frac{3}{2}\right] = \eta C_V(\gamma-1)\left(\frac{9}{4} + \frac{1}{\gamma-1}\right)$$

$$= \eta C_V\left(\frac{9\gamma-5}{4}\right). \qquad \therefore \epsilon = \frac{9\gamma-5}{4}$$

monoatomic gas $\gamma = 1.66$, $\epsilon = 2.5$
diatomic gas $\gamma = 1.4$, $\epsilon = 1.9$

Variation of η with temperature & pressure

$$\eta = \frac{1}{3} m n \bar{c}\lambda = \frac{1}{3} m \cancel{n} \bar{c} \frac{1}{\sqrt{2}\pi\sigma^2 \cancel{n}} = \frac{1}{3}\frac{m\bar{c}}{\sqrt{2}\pi\sigma^2}$$

η is independent of concentration, that Maxwell found at moderate pressure. At very high pressure, η increases & at low pressure, η decreases with pressure. At very high pressure, mean free path of molecules are comparable to the molecular dimension. Hence $\eta \propto p$ as λ = constant. At low pressure, mean free path is comparable to the dimension of the container

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& again is constant. So reducing pressure n decreases & hence η.

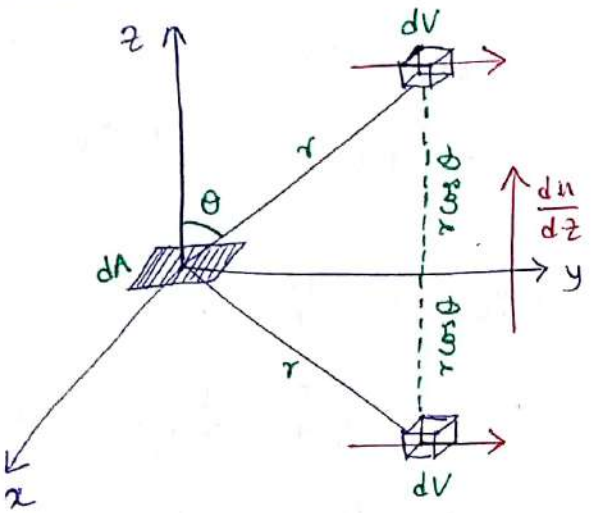
as $\bar{c} = \sqrt{\frac{8K_BT}{m\pi}}$, so $\eta \propto \sqrt{T}$ but in reality η varies more rapidly.

This is because in K.T. molecular interaction is not taken care of.

The molecular force field in K.T. is zero but in reality increase in temperature impinges the molecules to penetrate into each other & thus effective size of molecule decreases or increase in η.

Sutherland found that $\eta = \frac{A\sqrt{T}}{1+b/T}$ holds for hydrogen, helium, argon etc.

General Method for obtaining Diffusivity



If there is a concentration gradient $\frac{dn}{dz}$ along z-direction, then the number of molecules that flows through dA per unit time is $N = DdA\frac{dn}{dz}$

Let the concentration in XY plane is n & concentration gradient increases in z direction,

No. of molecules within c & $c+dc$ contained at dV located at (r, θ) is $4\pi A^3 e^{-bc^2} c^2 dc \left(n + r\cos\theta \frac{dn}{dz}\right) dV$, $A = \sqrt{\frac{m}{2\pi K_BT}}$, $b = \frac{m}{2K_BT}$

Due to collision, number of new paths emanating in unit time is $2 \times \frac{1}{2} \frac{c}{\lambda} \left(n + r\cos\theta \frac{dn}{dz}\right) 4\pi A^3 e^{-bc^2} c^2 dc\, dV$ & out of them, the number that will head towards dA is

$$\frac{dA\cos\theta}{\cancel{4\pi r^2}} \frac{c}{\lambda} \left(n + r\cos\theta \frac{dn}{dz}\right) \cancel{4\pi} A^3 e^{-bc^2} c^2 dc\, dV \left(= \cancel{r^2} \sin\theta\, d\theta\, d\phi\right)$$

Taking collision into account, total number of molecules crossing area dA in downward direction

$$N\downarrow = A^3 dA \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \left(n + r\cos\theta \frac{dn}{dz}\right) \cos\theta \sin\theta\, d\theta\, d\phi\, dr \frac{e^{-r/\lambda}}{\lambda} c^3 e^{-bc^2} dc$$

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Similarly the number of molecules crossing dA in upward direction

$$N\uparrow = A^3 dA \int_{c=0}^{\infty}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \left(n - r\cos\theta \frac{du}{dz}\right) \sin\theta \cos\theta \, d\theta \, d\phi \, dr \, \frac{e^{-r/\lambda}}{\lambda} c^3 e^{-bc^2} dc$$

∴ Net number of molecules moving through dA in unit time

$$\Delta N = N\downarrow - N\uparrow = 2A^3 dA \int_0^{\infty} c^3 e^{-bc^2} dc \int_0^{\infty} r e^{-r/\lambda} dr/\lambda \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta \times$$

$$\int_0^{2\pi} d\phi \times \frac{du}{dz}$$

$$= \frac{2\pi}{3} \lambda \, dA \frac{du}{dz} \, A^3/b^2 = \frac{1}{3} dA \, \lambda \frac{du}{dz} \sqrt{\frac{8KT}{m\pi}} = \frac{1}{3} \lambda \bar{c} \, dA \frac{du}{dz}$$

From Fick's law, $\Delta N = D \, dA \frac{du}{dz}$

$$\therefore \boxed{D = \frac{1}{3} \lambda \bar{c} = \frac{\eta}{\rho}}$$

$$= \frac{1}{3} \frac{1}{\sqrt{2}\pi\sigma^2 n} \sqrt{\frac{8KT}{m\pi}} \qquad \therefore D \propto \frac{1}{n} \propto \frac{T^{3/2}}{P}$$

$$\propto \frac{1}{\sqrt{m}} \quad \text{(Graham's law)}$$

Brownian motion

First observed by R. Brown in 1827 on suspended polen grains on water. Perpetual, random motion of big solute particle in solvent is the Brownian motion.

Features: (i) Motion of Brownian particle is completely irregular. No two particle execute the same motion.

(ii) Motion ~~of~~ is continuous & based on discrete collisional steps.

(iii) Smaller particles are more agitated than larger particles, but motion is independent of the nature of suspended particles. Two particles of same weight & size move equally fast at same temperature

(iv) The motion is vigorous with increasing temperature, & in lower viscosity

(v) Motion is not modified due to shaking of container.

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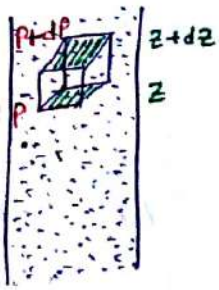
Basis fluctuation + dissipation

Law of Atmosphere



Brownian particles form a gas in equilibrium under the gravitational force. Consider a vertical cylinder of unit cross-section in a gas having end face at z & $z+dz$ & corresponding pressure P & $P+dP$ then

Force of gravity in layer vertically downward $= 1 \times dz \times \rho g = \rho g dz$

As cylinder is in equilibrium, net force on layer $= 0$.

$$(P+dP) - P + \rho g dz = 0$$

$$\text{or } dP = -\rho g dz \quad \text{— (1)}$$ (−ive sign means P decreases with z)

m = mass of single molecule, n = average number of molecules per unit volume.

$\rho = mn$.

Using Clapeyron's equation $P = nK_BT$, $dP = dnK_BT$. — (2)

Equating (1) & (2), $dnK_BT = -mngdz$

$$\text{or } \frac{dn}{n} = -\frac{mg}{K_BT}dz = -\frac{mgN}{RT}dz \qquad \left(K_B = \frac{R}{N}\right)$$

Integrating $\ln n = -\frac{mgN}{RT}z + \ln C$

at $z = z_0$, $n = n_0$ $\qquad \ln n_0 = -\frac{mgN}{RT}z_0 + \ln C$

$$\text{or } \ln n = -\frac{mgN}{RT}z + \ln n_0 + \frac{mgN}{RT}z_0$$

$$\text{or } \ln\frac{n}{n_0} = -\frac{mgN}{RT}(z - z_0)$$

$$\text{or } \boxed{n = n_0 e^{-\frac{mgN}{RT}(z-z_0)}}$$

Exponential decrease of no. density of Brownian particles with height.

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For colloidal solution, particles have downward force due to gravity & upward force due to the buoyancy of liquid. If ρ' is the density of particle then effective mass of particle $m = \frac{4}{3}\pi r^3(\rho' - \rho)$

$$\therefore \ln \frac{n}{n_0} = -\frac{4\pi r^3(\rho'-\rho)gN}{3RT}(z-z_0)$$

$$\text{or} \quad N = \frac{3RT}{4\pi r^3(\rho'-\rho)g(z-z_0)} \ln \frac{n_0}{n}$$

Thus Avogadro number can be calculated if r, ρ' are known.

Langevin equation of Brownian motion

Equation of motion $\quad m\frac{d\vec{v}}{dt} = \underbrace{-\vec{F}_v}_{\text{viscous}} + \underbrace{\vec{F}_B(t)}_{\text{Brownian}}$

Time average over sufficiently long time $t >> \tau$, $m\frac{d\langle\vec{v}\rangle}{dt} = \langle\vec{F}_v\rangle$

For colloidal fluid $\quad m\frac{dv}{dt} = -\alpha v + F_B(t)$

From hydrodynamics, Stokes calculated that $\alpha = 6\pi\eta a$ for a spherical object of size a moving at velocity v through a liquid with viscosity η. This is known as Stokes law.

Clearly $\langle x\rangle = 0$ but $\langle x^2\rangle \neq 0$. $\langle F_B(t)\rangle = 0$

Magnitude of fluctuations

$$m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + f_B(t)$$

$$\text{or} \quad m\,x\frac{d^2x}{dt^2} = -\alpha x\frac{dx}{dt} + x f_B(t)$$

$$\text{or} \quad m\left[\frac{d}{dt}(x\dot{x}) - \dot{x}^2\right] = -\alpha x\frac{dx}{dt} + x f_B(t)$$

Now $\langle x F_B(t)\rangle = \langle x\rangle\langle F_B(t)\rangle = 0$ "statistical independence"

and from equipartition theorem, $\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_BT$

$$\therefore m\left\langle\frac{d}{dt}(x\dot{x})\right\rangle = m\langle\dot{x}^2\rangle - \alpha\left\langle x\frac{dx}{dt}\right\rangle + \cancel{\langle x F_B(t)\rangle}^{\,0}$$

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or $m \frac{d}{dt} \langle x\dot{x} \rangle = k_B T - \alpha \langle x\dot{x} \rangle$

or $\frac{d\langle x\dot{x}\rangle}{dt} + \frac{\alpha}{m} \langle x\dot{x} \rangle = \frac{k_B T}{m}$

integrating factor $= e^{+\alpha/m\, t}$

particular integral $= e^{-\alpha/m\, t} \int e^{\alpha/m\, t'} \frac{k_B T}{m} dt'$

$= e^{-\alpha/m\, t} \frac{k_B T}{m} \left(\frac{m}{\alpha} e^{\alpha/m\, t} + c' \right)$

$\langle x\dot{x} \rangle = \frac{k_B T}{\alpha} + c\, e^{-\alpha/m\, t}$

at $t=0$, $\langle x\dot{x} \rangle = \langle x \rangle \langle \dot{x} \rangle = 0$ $\therefore$ $c + \frac{k_B T}{\alpha} = 0$

$\therefore \langle x\dot{x} \rangle = \frac{k_B T}{\alpha} (1 - e^{-\alpha/m\, t})$

or $\frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = \frac{k_B T}{\alpha} (1 - e^{-\alpha/m\, t})$

or $\boxed{\langle x^2 \rangle = \frac{2 k_B T}{\alpha} \left[t - \frac{m}{\alpha} (1 - e^{-\alpha/m\, t}) \right]}$

<u>Case I</u> $\frac{m}{\alpha} >> t$, $e^{-\alpha/m\, t} \simeq 1 - \frac{\alpha}{m} t + \frac{1}{2} \frac{\alpha^2}{m^2} t^2 - \cdots$

$\therefore \langle x^2 \rangle = \frac{k_B T}{m} t^2$. Therefore for a short time interval the particle moves ballistically with constant velocity $v = \sqrt{\frac{k_B T}{m}}$

<u>Case II</u> $\frac{m}{\alpha} << t$, $e^{-\alpha/m\, t} \simeq 0$, $t - \frac{m}{\alpha} >> 0$. $\simeq t$

$\langle x^2 \rangle = \frac{2 k_B T}{\alpha} t$. Therefore the Brownian particle diffuses

as $\langle x^2 \rangle = 2Dt = \frac{2 k_B T}{\alpha} t = \frac{k_B T}{3\pi\eta a} t = \frac{RT}{3\pi N \eta a} t$

or $\boxed{D = \frac{RT}{6\pi N \eta a}}$ $D \propto \frac{1}{a}$ but <u>independent of mass</u>.

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Einstein's argument

τ = time interval << observation time scale
>> large enough than individual collision

that two consecutive intervals of τ are mutually independent.

For N solute (Brownian) particle in time interval τ, x coordinate increase by Δ (both $\pm$ive) due to thermal motion, no. of solute particles that are between Δ & $\Delta + d\Delta$ is

$$dN = N\phi(\Delta)\,d\Delta \quad \text{with the property} \quad \phi(\Delta) = \phi(-\Delta) \;\&$$

$$\int_{-\infty}^{\infty} \phi(\Delta)\,d\Delta = 1. \quad \text{(normalized)}$$

If $f(x,t)$ is the no. of particles at time t at position x

Then $$f(x, t+\tau)\,dx = dx \int_{-\infty}^{\infty} f(x+\Delta; t)\,\phi(\Delta)\,d\Delta$$

Kramers - Moyal Expansion: $$f(x+\Delta, t) = f(x,t) + \Delta \frac{\partial f(x,t)}{\partial x} + \frac{\Delta^2}{2}\frac{\partial^2 f(x,t)}{\partial x^2} + \cdots$$

$$f(x, t+\tau) = f(x,t) + \tau \frac{\partial f(x,t)}{\partial t} \quad \text{as } \tau \text{ is short.}$$

$$\therefore \; f + \tau\frac{\partial f}{\partial t} = f\underbrace{\int_{-\infty}^{\infty}\phi(\Delta)\,d\Delta}_{=1} + \frac{\partial f}{\partial x}\underbrace{\int_{-\infty}^{\infty}\Delta\phi(\Delta)\,d\Delta}_{\text{odd function}\;\to\;0} + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)\,d\Delta + \cdots$$

Equating $$\frac{\partial f}{\partial t} = \frac{1}{\tau}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)\,d\Delta\;\frac{\partial^2 f}{\partial x^2} = D\frac{\partial^2 f}{\partial x^2}$$

So $$\boxed{D = \frac{1}{\tau}\int_{-\infty}^{\infty}\Delta^2/2\;\phi(\Delta)\,d\Delta}$$

$$\boxed{\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2}}$$ Diffusion equation

CW Observation on Brownian movement in water showed that the horizontal displacement for a test particle in 11 successive intervals of 33 secs were $[0, 5.6, -1.7, -10.8, 6.6, -9.8, -11.2, -4.0, 15.0, 19.1, 16.0]\times 10^{-1}$ cm $T = 20^\circ C$ & $\eta_{water} = 0.01$ cgs unit, radius of particle 1.15×10^{-5} cm & $R = 8.32\times 10^{7}$ ergs/deg/mole. Obtain N.

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$$\langle x^2 \rangle = \frac{RT}{N} \frac{1}{3\pi\eta a} t$$

$$\langle x^2 \rangle = \frac{x_1^2 + x_2^2 + x_3^2 + \cdots + x_{11}^2}{11} = 1.18 \times 10^{-6} \text{ cm}^2$$

$$\therefore \quad N = \frac{RTt}{\langle x^2 \rangle 3\pi\eta a} = \frac{8.32 \times 10^7 \times 293 \times 30}{1.18 \times 10^{-6} \times 3 \times 3.14 \times 0.01 \times 1.15 \times 10^{-5}}$$

$$= 5.72 \times 10^{23}.$$

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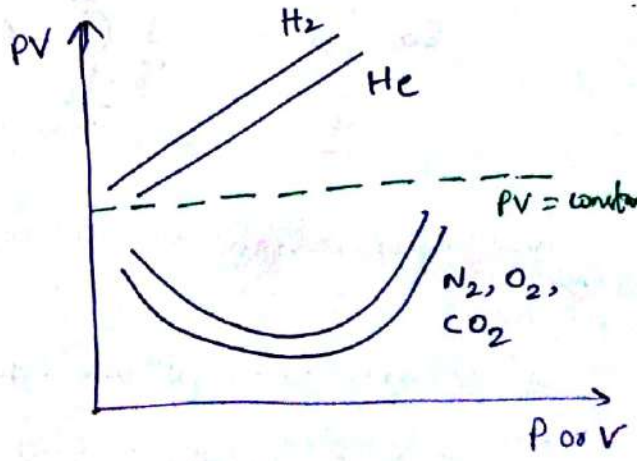
Equation of State for Real Gases

To define the state of a gaseous system completely, we need to know three parameters P, V & T. By equation of state we mean the mathematical relation that express functional form of P, V, T as $f(P, V, T) = 0$. The equation of state of a perfect gas $PV = RT$ is the most simple form of equation of state.

Insufficiency of the perfect gas equation

Boyle found that that the perfect gas equation $PV = RT$ does not fit the experimental results and works only at ideal condition i.e. at very high temperature & very low pressure. In indicator diagram (P vs. V) one can obtain isothermals. Experiment by Regnault showed that no gas obeys PV = constant but either increases with pressure or they decrease & increase with pressure. So modification of perfect gas laws is necessitated.



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To explain the gradual increment of PV with P for H_2, He etc consider the modified equation $P(V-b)$ = constant or PV = constant + Pb. which increases with P. On the other hand to explain the initial drop of curves for O_2, N_2, CO_2 we take $(P+P_i)V$ = constant.

∴ In combined form $(P+P_i)(V-b)$ = constant was noted in 1860.

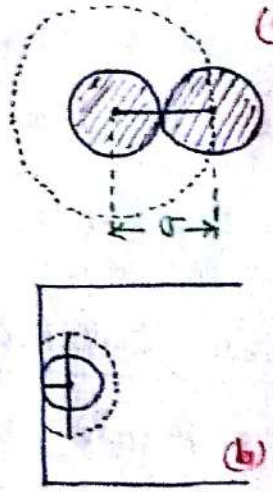
Semiderivation of Vanderwaal's equation

To obtain heuristically an expression for real gas, in 1909, Vanderwaal made a few simplifying assumptions that

(i) The molecules are rigid spherical objects of diameter σ

(ii) They attract each other with a weak force that depends only on the intermolecular distance & independent of the orientation of the molecules. To derive, first he considered the effect of finite size of molecules & then considered the weak attractive force & then superposed them which cannot be rigorously justified.

Volume Correction



We know that $\frac{4}{3}\pi\sigma^3$ is the sphere of influence of a molecule, so that center of no other molecule can penetrate it. So if the total space contains N molecules then $(N-1)\frac{4}{3}\pi\sigma^3$ is excluded from the center of others.

∴ The actual free volume is $V-(N-1)\frac{4}{3}\pi\sigma^3$

$\simeq V-\frac{4}{3}\pi N\sigma^3$ as $N \sim 10^{23} >> 1$.

∴ The actual number density is $n_r = \frac{N}{V-2b}$ where $b = \frac{2}{3}\pi N\sigma^3$.

As in figure (b), if we consider the gas to be enclosed in a vessel, then the molecule may approach only to a distance $\sigma/2$ from the wall, as then the surface of the molecule will touch the wall. But since the sphere of influence is of radius σ meaning when a

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molecule is at a distance σ, its sphere of influence extends to the wall & therefore the center of no other molecule can lie within the hemisphere $\frac{2}{3}\pi\sigma^3$.

∴ If we consider an elementary volume dV in the neighbourhood of the wall, then $\frac{2}{3}\pi n_r \sigma^3$ is the fraction of volume unavailable for the center of other molecules. So if dV_a is the amount of dV existing as free space, then

$$dV_a = dV - \frac{2}{3}\pi\sigma^3 n_r\, dV = dV\left(1 - \frac{2/3\,\pi N\sigma^3}{V-2b}\right) = dV\left(1 - \frac{b}{V-2b}\right)$$

The actual number of molecules in dV is $n_r\, dV_a$

$$= \frac{N}{V-2b}\left(1 - \frac{b}{V-2b}\right)dV = \frac{N\,dV}{V-2b}\,\frac{\left(1-\frac{b}{V-2b}\right)\left(1+\frac{b}{V-2b}\right)}{\left(1+\frac{b}{V-2b}\right)}$$

$$= \frac{N\,dV}{V-2b}\,\frac{1}{1+\frac{b}{V-2b}} \qquad \left(\text{as } \frac{b^2}{(V-2b)^2} << 1\right)$$

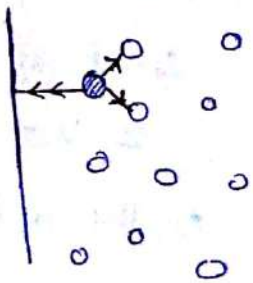
$$= \frac{N\,dV}{V-b}$$

If we would've considered the molecules as geometrical point mass objects, then the number of molecules in dV would be $\frac{N}{V}dV$

So finite size correction is V−b and ~~the~~ volume correction is

$$b = \frac{2}{3}\pi\sigma^3 N = 4\times\frac{4}{3}\pi N\left(\frac{\sigma}{2}\right)^3 = 4\times \text{Total volume of all molecules.}$$

Pressure Correction



The molecule attract with a cohesive force that varies inversely as some power of the distance between them, which is negligible at long distance. On average, molecule get zero force due to isotropicity except near a surface. Parallel to surface forces will still balance but not pependicular to it, so uncompensated inward force ⊥r to boundary.

Force on single molecule ∝ number of attracting molecule / cc

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Also force acting / unit area of surface $\propto$ number of molecules in that area of surface. Hence cohesive force / unit area of the surface is $\propto n^2 = \left(\frac{N}{V}\right)^2$ where N is the total number of molecules & V is the total volume. $\therefore P_1 \propto \frac{1}{V^2} = \frac{a}{V^2}$. This cohesive pressure is called internal pressure or intrinsic pressure & acts only in the boundary layer of any solid or fluid giving rise to surface tension in liquids & tensile force in solids. It opposes the kinetic pressure but assists the external pressure in keeping the substance together. So it opposes the outward motion & decreases the momentum & hence the pressure. So P is replaced by $P + \frac{a}{V^2}$ as if the external pressure is increased.

$\therefore$ for one mole gas $\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT}$ Vanderwaals equation of state.

Constant volume method of finding "a" and "b"

From ~~the~~ VW equation, $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$ or $\boxed{b = V - \frac{R}{\left(\frac{\partial P}{\partial T}\right)_V}}$

$\boxed{a = V^2\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}}$

Therefore "a" and "b" can be obtained by observing the rate of increase of pressure with temperature as in constant volume gas thermometer very accurately. But they vary with temperature.

At N.T.P.

Gas	a in atm cm^6 ($\times 10^{-5}$)	b in cc ($\times 10^{-5}$)
He	6.8	106
Ar	268.0	143
O_2	273.0	143
N_2	272.0	173
CO_2	717.0	191
NH_3	833.0	168

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Vander Waal's equation from Clausius virial theorem

In an entirely different approach, Clausius deduced rigorously the equation for a real gas, using Newtonian concept of classical dynamics. If x, y, z denote the coordinate of a molecule in an arbitrary reference frame and f_x, f_y, f_z denote the force components, then

$$m\frac{d^2x}{dt^2} = f_x, \quad m\frac{d^2y}{dt^2} = f_y, \quad m\frac{d^2z}{dt^2} = f_z$$

as $\frac{d^2}{dt^2}(x^2) = 2\frac{d}{dt}\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2}$

$\therefore\ x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2$, similarly for y and z.

$\therefore\ m x\frac{d^2x}{dt^2} = f_x x \Rightarrow m\left\{\frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2\right\} = f_x x$

or $\frac{m}{2}\left(\frac{dx}{dt}\right)^2 = \frac{m}{4}\frac{d^2}{dt^2}(x^2) - \frac{1}{2}f_x x$, similarly for y and z.

Adding all components, we get the K.E. of a molecule. $\frac{1}{2}m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\} = \frac{m}{4}\frac{d^2}{dt^2}(x^2+y^2+z^2) - \frac{1}{2}(xf_x + yf_y + zf_z)$

Summing over all molecule and taking average over sufficiently long interval τ, we get

$$\frac{1}{2}\overline{\sum_i mv^2}^{\tau} = \frac{m}{4}\overline{\sum_i \frac{d^2}{dt^2}(r^2)}^{\tau} - \frac{1}{2}\overline{\sum_i xf_x + yf_y + zf_z}^{\tau} \qquad \left[\overline{X}^{\tau} = \frac{1}{\tau}\int_0^{\tau} X\,dt\right]$$

In steady state, $\frac{1}{2}\overline{\sum_i mv^2}^{\tau}$ and $\frac{1}{2}\overline{\sum_i \vec{r}\cdot\vec{F}}^{\tau}$ are approximately constant throughout the motion. But $\frac{m}{4}\frac{1}{\tau}\int_0^{\tau}\sum_i \frac{d^2}{dt^2}(r^2)\,dt = \frac{m}{4\tau}\int_0^{\tau}\sum_i \frac{d}{dt}\left(2r\cdot\frac{dr}{dt}\right)dt$

$= \frac{m}{2\tau}\sum_i \vec{r}\cdot\frac{d\vec{r}}{dt}\Big|_0^{\tau} = 0$ as $\vec{v} = \frac{d\vec{r}}{dt}$ fluctuates irregularly with time and using the Brownian motion concept, $\overline{r\cdot\frac{dr}{dt}}^{\tau} = \overline{r}^{\tau}\cdot\overline{\frac{dr}{dt}}^{\tau} = 0$. Remember in Einstein's theory (Langevin equation)

$$\underset{\text{inertial}}{m\frac{dv}{dt}} = \underset{\text{Viscous}}{-\alpha v} + \underset{\text{Brownian}}{f_B(t)}, \qquad \overline{x f_B}^{\tau} = 0 \quad \text{(Markovian)}$$

$$\overline{v f_B}^{\tau} \neq 0 = \alpha k_B T \quad \text{(non-Markovian)}$$

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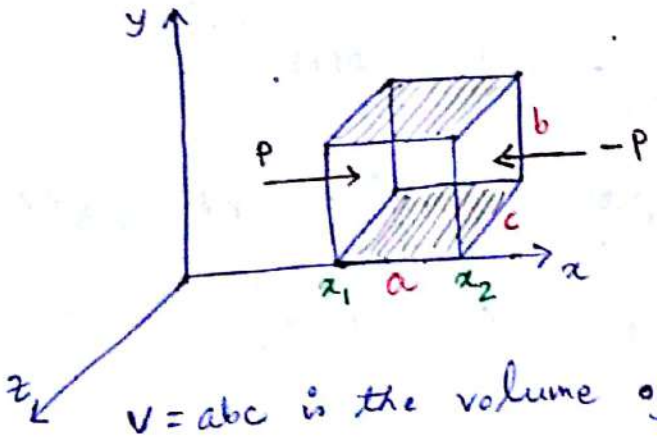
$$\therefore \boxed{\underbrace{\frac{1}{2}\overline{\sum_i^n mv^2}}_{KE} = \underbrace{-\frac{1}{2}\overline{\sum_i^n \vec{r}\cdot\vec{F}}}_{virial}}$$

Virial theorem states that average kinetic energy of translation of the molecules of a gas in the steady state is equal to its virial.

Now, F_x, F_y and F_z include all the forces that act on the molecule. These forces can be broadly categorized as.

1. The force of impact on the molecule due to collision with the walls of the vessel.
2. The force due to collision between two molecules.
3. The force of attraction between molecules within some distance.

We consider the contribution of 1 to the virial. Imagine the gas confined in a box of dimension a, b, and c with faces cutting x axes at x_1 & x_2. If the pressure exerted by the gas is P, then



$\sum F_x$ at $x_1 = Pbc$

$\sum F_x$ at $x_2 = -Pbc$.

$$\therefore -\frac{1}{2}\sum F_x x = \frac{1}{2}Pbc(x_2 - x_1)$$

$$= \frac{1}{2}Pabc = \frac{1}{2}PV. \text{ where}$$

$V = abc$ is the volume of the box. Similarly $-\frac{1}{2}\sum F_y y = \frac{1}{2}PV$ and $-\frac{1}{2}\sum F_z z = \frac{1}{2}PV$ for two other faces. $\therefore$ Total contribution by the forces acting on the wall is $\frac{3}{2}PV$.

For an ideal gas, contribution form 2 and 3 is neglected, because there is no cohesive force, nor they've a finite size, then,

$$\frac{1}{2}mN\bar{c}^2 = \frac{3}{2}PV = \frac{3}{2}RT \quad \text{(using Virial theorem)}$$

$$\text{or } \boxed{P = \frac{1}{3}mn\bar{c}^2}$$

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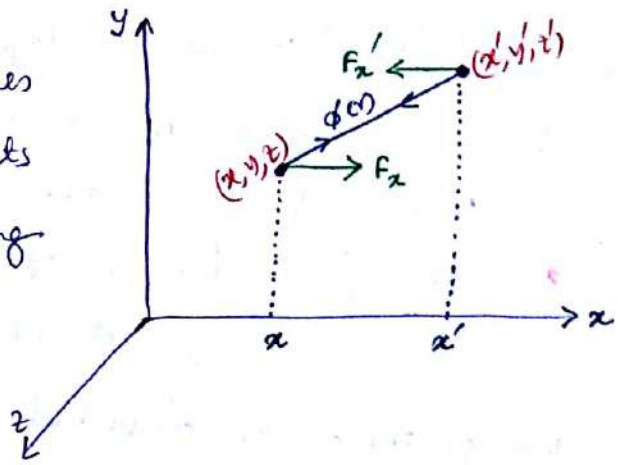
Equation of state for real gases

Now we incorporate point 2 and 3 but we do not know the nature of forces. For simplicity, let's assume isotropicity so that the force is fully radial, say $\phi(r)$, with $\phi(r) = -\frac{dE}{dr}$ where E is the P.E. due to intermolecular force. Let the coordinates of the center of two molecules be (x,y,z) and (x',y',z'). Then the components (F_x, F_y, F_z) and (F_x', F_y', F_z') of the forces acting are



$$F_x = \phi(r)\left(\frac{x-x'}{r}\right)$$

$$F_x' = \phi(r)\left(\frac{x'-x}{r}\right).$$ Therefore the contribution to $\sum F_x x$ by these forces is $F_x x + F_{x'} x' = \frac{\phi(r)}{r}(x-x')^2$

similarly for the y and z components. So the total contribution is

$$-\frac{1}{2}\sum \frac{\phi(r)}{r}\Big[\underbrace{(x-x')^2+(y-y')^2+(z-z')^2}_{r^2}\Big] = -\frac{1}{2}\sum r\phi(r).$$

Hence from the virial theorem, we get $\frac{1}{2}mN\bar{c}^2 = \frac{3}{2}PV - \frac{1}{2}\sum r\phi(r)$

But $\frac{1}{2}m\bar{c}^2 = \frac{3}{2}k_BT$, $\therefore$ $\boxed{PV = Nk_BT + \frac{1}{3}\sum r\phi(r)}$

Evaluation of $\sum r\phi(r)$

According to MB distribution with P.E. we know

$$N_c = N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2} 4\pi c^2 e^{-(\frac{1}{2}mc^2+E)/k_BT}\, dc.$$

$\hookrightarrow$ no. of molecules when P.E. = 0. $\simeq N_0 e^{-E/k_BT}$

Let us calculate the contribution of one molecule to the virial. Average number of other molecules lying within r and $r+dr$ from this molecule is $4\pi r^2 dr\, n$ & the force exerted by them is $\phi(r)$. So the contribution of one molecule to $r\phi(r)$ is

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$\int_0^\infty 4\pi r^3 n_0 e^{-E/k_BT} \phi(r)\, dr$ and so the contribution of N molecules is $\frac{N}{2}\int_0^\infty 4\pi r^3 n_0 \phi(r) e^{-E/k_BT} dr$ where division by 2 is to avoid the double-counting. Substituting $n_0 = \frac{N}{V}$ and $\phi(r) = -\frac{\partial E}{\partial r}$ we have

contribution of N molecules $= \frac{2\pi N^2}{V}\int_0^\infty r^3 e^{-E/k_BT} dr\, \phi(r)$

Now $\int e^{-E/k_BT}\phi(r)\, dr = -\int e^{-E/k_BT}\frac{\partial E}{\partial r} dr = -k_BT\int e^{-E/k_BT} d(E/k_BT)$

$= k_BT e^{-E/k_BT} + \text{Constant}$, (constant $= -k_BT$)

$\therefore$ Integrating by parts $\left[\int u\,dv = uv - \int v\,du\right]$

$$\frac{2\pi N^2}{V}\left[\left\{r^3(k_BT e^{-E/k_BT} + \text{constant})\right\}_0^\infty - \int_0^\infty 3r^2(k_BT e^{-E/k_BT} + \text{constant})dr\right]$$

$$= \frac{2\pi N^2}{V} 3k_BT\int_0^\infty r^2(1 - e^{-E/k_BT})dr = \sum r\phi(r).$$

Substituting this to real gas equation of state, we obtain

$$PV = Nk_BT + \frac{2\pi N^2}{V}k_BT\int_0^\infty r^2(1 - e^{-E/k_BT})dr.$$

To evaluate the integral, we assume that molecules are rigid spheres of diameter σ, so $E = \infty$ for $r < \sigma$

$= \text{small for } r > \sigma$

$$\therefore \int_0^\sigma r^2 dr + \int_0^\infty r^2(1 - e^{-E/k_BT})dr = \frac{1}{3}\sigma^3 + \int_0^\infty \frac{r^2 E\, dr}{k_BT}$$

$$\therefore \boxed{PV = RT + \frac{RT}{V}\left(b - \frac{a}{RT}\right)} \quad \text{with} \quad \boxed{\begin{aligned} b &= \frac{2}{3}N\pi\sigma^3 \\ a &= -2\pi N^2\int_0^\infty E r^2 dr. \end{aligned}}$$

Note that "b" is identical to VW constant and "a" is positive (as E is negative). Thus the second virial coefficient obtained from virial theorem is $\frac{RT}{V}\left(b - \frac{a}{RT}\right)$

from VW equation $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ we have

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

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$$\therefore \boxed{PV = RT + \frac{RT}{V}\left(b - \frac{a}{RT}\right) + RT\left(\frac{b}{V}\right)^2 + \cdots}$$

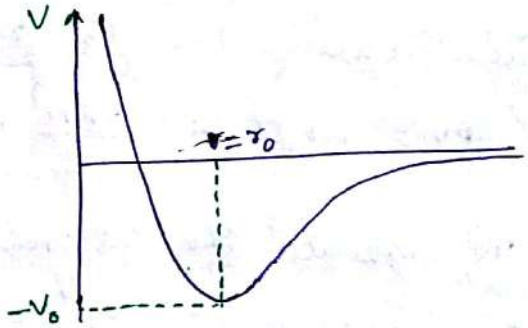
This equation agrees with the earlier obtained expression (using virial theorem) upto second virial coefficient. Third virial coefficient isn't correct & do not agree with Clausius's virial theorem. So VW equation is theoretically correct upto $\frac{1}{V}$ term & no further.

Nature of molecular force

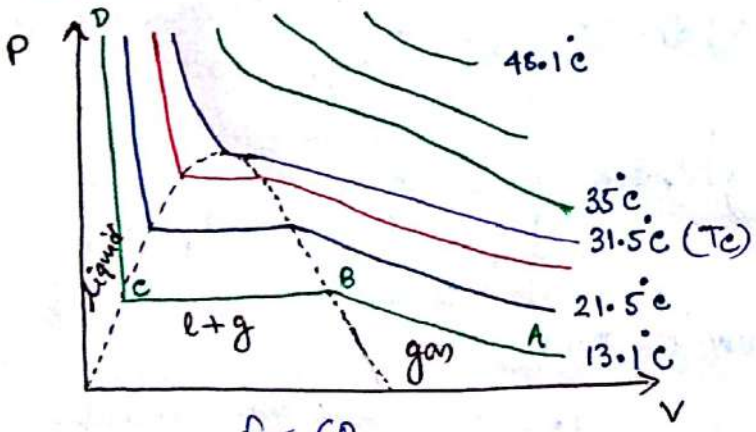
The force of interaction between the molecules of a gas is a very complicated phenomena. It is found that the force is attractive when the molecules are far apart & strongly repulsive when they are closeby. Lennard & Jones showed by taking fluctuating dipole-dipole interaction that the P.E. without any charge is

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

where r is intermolecular distance and A & B are constants.



Andreco's Experiments & inferences



for CO_2

Isothermals:

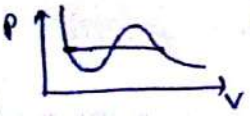
AB → P increases, V decreases

BC → V decreases without P changing (Lever rule)

CD → almost negligible change of V, P shoots up

"Critical Opalescence" 1910 Einstein's final theoretical investigation on Brownian motion.

liquifaction of gas. Vanderwaal's equation gives a curve as



Thomson hypothesized but Maxwell's construction was

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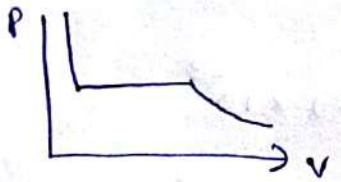
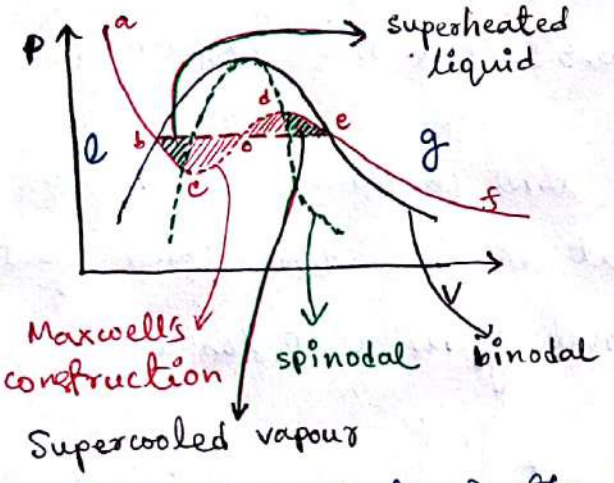
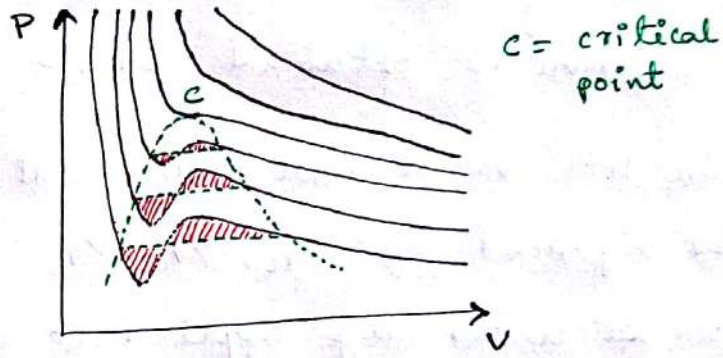


So that ambiguity can be removed, $\frac{\partial P}{\partial V} > 0$.

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{or } \frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \quad \frac{\partial^2 P}{\partial V^2} = -\frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$





Critical constants & the law of corresponding states

From pictures above we find that there are three points b, o, e where P is same for three values of V which becomes one at point C. So the temperature at which maximum & minimum coalesce is the critical temperature & corresponding pressure & volume is the critical pressure & critical volume. To evaluate P_c, V_c, T_c we see that at C, $\frac{\partial P}{\partial V} = 0$

Equation for the points of maxima-minima (dotted graph) is

$$\frac{RT}{(V-b)^2} = \frac{2a}{V^3} \quad \text{or} \quad T = \frac{2a(V-b)^2}{RV^3} \quad \text{— (1)}$$

$$\therefore P = \frac{R}{V-b}\,\frac{2a(V-b)^2}{RV^3} - \frac{a}{V^2} = \frac{2a(V-b)}{V^3} - \frac{a}{V^2} \quad \text{— (2)}$$

At the critical point, $\left.\frac{dP}{dV}\right|_{V=V_c} = 0 = \frac{2a}{V_c^3} - \frac{6a(V_c-b)}{V_c^4} + \frac{2a}{V_c^3}$

or, $2aV_c - 6aV_c + 6ab + 2aV_c = 0$ or $\boxed{V_c = 3b}$

from (1), $T_c = \frac{2a \cdot 4b^2}{R \times 27b^3} = \frac{8a}{27Rb}$, or $\boxed{T_c = \frac{8a}{27Rb}}$

from (2), $P_c = \frac{2a \times 2b}{27b^3} - \frac{a}{9b^2} = \frac{a}{27b^2}$, or $\boxed{P_c = \frac{a}{27b^2}}$

At 1 cc at STP, $a = 0.00874$ atm-cm^6, $b = 0.0023$ cc for CO_2 ($T = 273K$), $P = 1$atm, $V = 1$cc.

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Using VW equation $\left(P + \frac{a}{V^2}\right)(V-b) = RT$,

$$\left(1 + \frac{0.00874}{1^2}\right)(1-0.0023) = 273R, \quad \therefore R = 3.687 \times 10^{-3}$$

$$\therefore T_c = \frac{8a}{27Rb} = \frac{8 \times 0.00874}{27 \times 3.687 \times 10^{-3} \times 0.0023} = 305.5^\circ K = 32.5^\circ C.$$

Experiments obtained $31.1^\circ C$ & $30.9^\circ C$ (Andrews experiment).

In 1881, van der Waal found that the three constants a, b, R can be replaced by P/P_c, V/V_c, T/T_c so that the non-dimensional equation can be universally applied to all real gases that has an indicator diagram of VW.

If $P/P_c = P^*$, $V/V_c = V^*$, $T/T_c = T^*$ are reduced (P, V, T) then

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \Rightarrow \left(P^* P_c + \frac{a}{V^{*2} V_c^2}\right)(V^* V_c - b) = R T_c T^*$$

Substituting P_c, V_c, T_c, $\left(\frac{a}{27b^2} P^* + \frac{a}{9b^2 V^{*2}}\right)(3bV^* - b) = RT^* \frac{8a}{27Rb}$

$$\therefore \boxed{\left(P^* + \frac{3}{V^{*2}}\right)\left(V^* - \frac{1}{3}\right) = \frac{8}{3} T^*}$$

The states of two substances for which their values of (P^*, V^*, T^*) are equal are called "corresponding states." Clearly critical states of all bodies are their corresponding states. If two reduced parameters of any two substances are same, then the third reduced parameter must be identical for them. This is called the "law of corresponding states."

$$(P^*)_{CO_2} = (P^*)_{SO_2} \;\&\; (V^*)_{CO_2} = (V^*)_{SO_2} \text{ then } (T^*)_{CO_2} = (T^*)_{SO_2}$$

HW 1. Calculate VW constants "a" and "b" for a gm-mole of He gas using $T_c = 5.3$ K, $P_c = 2.25$ atm & $R = (273)^{-1}$ litre atmosphere $/^\circ$.

2. Calculate P_c & T_c of He gas using $a = 6.15 \times 10^{-5}$ atm-cm^6, $b = 9.95 \times 10^{-}$ cc per gm-molecule, where pressure is 1 atm & volume is volume of gas at S.T.P.

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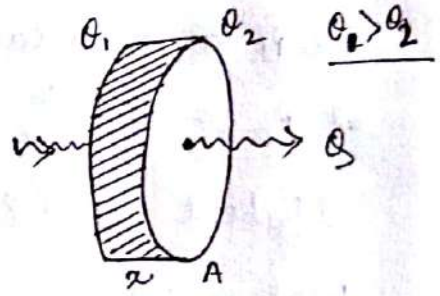
Conduction

Transmission of Heat : CONDUCTION, CONVECTION, RADIATION

In conduction, heat is transmitted from one point to other through the substance without actual motion of particles. Air or vacuum is poor conductor of heat, hence wooden fabric keeps us warm or thermos flask keeps thing isolated. In convection, heat is transmitted by the actual motion of particles. Hot water circulation in heated kettle. Heat radiation is transmitted directly without any intervening medium. Like sun radiation into earth by EM spectrum.

Coefficient of Thermal Conductivity



If we have a plane slab of area A, thickness x having temperature θ_1 & θ_2 at its two faces then if Q amount of heat is transmitted in time t, then,

$$Q \propto A$$
$$\propto (\theta_1 - \theta_2)$$
$$\propto 1/x$$
$$\propto t$$

$$\therefore \boxed{Q = \frac{KA(\theta_1 - \theta_2)t}{x}}$$

K = coeff^n of thermal conductivity

$$\therefore \underset{\text{heat current}}{q} = \frac{Q}{t} = \frac{KA(\theta_1 - \theta_2)}{x} = \frac{\theta_1 - \theta_2}{x/KA} = \frac{\theta_1 - \theta_2}{\underset{\text{thermal resistance}}{R_{Th}}}.$$

This equation is similar to Ohm's law $I = \frac{V}{R}$, redefined in terms of thermal resistance & heat current. We know $R = \rho \frac{l}{A} = \frac{l}{\sigma A}$ where $\sigma = \frac{1}{\rho}$ is the electrical conductivity. Comparing with $R_{Th} = \frac{x}{KA}$ we can define the proportionality constant as coeff^n of thermal conductivity.

Dimension of $[Q] = [ML^2T^{-2}]$, $[x] = [L]$, $[A] = [L^2]$, $[\theta] = [\theta]$,
$[t] = [T]$

$$\therefore [K] = [MLT^{-3}\theta^{-1}]$$

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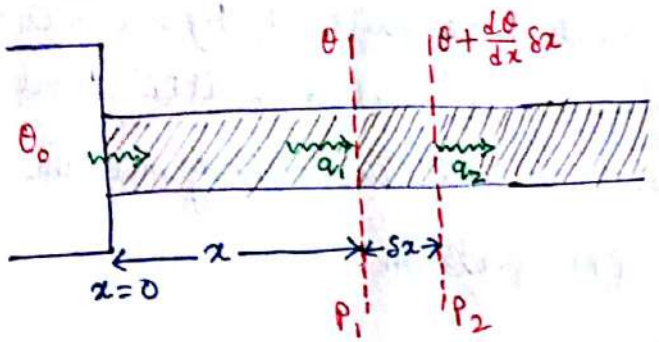
Thermal diffusivity is defined as the ratio of thermal conductivity to thermal capacity per unit volume. If ρ = density & S = specific heat then $h = \frac{K}{\frac{mS}{V}} = \frac{K}{\rho S}$ = "Thermometric conductivity"

Rectilinear Propagation of heat along a bar



Consider a bar of uniform area of cross-section A contact with an oven at temperature θ_0 at $x=0$. If θ is the excess temperature above the surroundings of the bar at P_1 at a distance x from the point of contact, then excess temperature at $P_2 = \theta + \frac{d\theta}{dx}\delta x$.

If heat flowing through P_1 in one second $q_1 = -KA\frac{d\theta}{dx}$ &

heat flowing through P_2 in one second $q_2 = -KA\frac{d}{dx}(\theta + \frac{d\theta}{dx}\delta x)$

$\therefore$ Heat gained per second by the rod between P_1 & P_2

$$Q = Q_1 - Q_2 = -KA\frac{d\theta}{dx} + KA\frac{d}{dx}(\theta + \frac{d\theta}{dx}\delta x)$$

$$= KA\frac{d^2\theta}{dx^2}\delta x$$

This amount of heat is used in two ways before steady state is reached. (1) A part will increase the temperature, (2) Rest part is lost due to radiation from the exposed surface of the slab.

If rate of rise of temperature is $\frac{d\theta}{dt}$ then heat used per second

$= \underbrace{(A\delta x)\rho}_{\text{mass}} \times \underbrace{S}_{\text{specific heat}} \times \frac{d\theta}{dt}$ & heat lost per second due to radiation

$= EP\delta x\theta$ where E = emissive power of surface, p = perimeter & θ = average excess of temperature within P_1 & P_2.

$$\therefore q = A\delta x\rho S\frac{d\theta}{dt} + EP\delta x\theta = KA\frac{d^2\theta}{dx^2}\delta x$$

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$$\boxed{\frac{K}{\rho S}\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \frac{PE}{A\rho S}\theta}$$ Fourier's differential equation

Special Cases 1: when heat lost by radiation is negligible:

When rod is covered by insulating materials, heat lost $EP\delta x\theta = 0$ & total heat gained by rod is to raise the temperature, using

$$\frac{K}{\rho S}\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} \quad \text{or} \quad h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt}$$

Special Cases 2: after the steady state is reached:

$$\frac{d\theta}{dt} = 0 \quad \text{and} \quad \frac{d^2\theta}{dx^2} = \frac{PE}{KA}\theta = \mu^2\theta$$

This is a second order homogeneous linear differential equation

If $\theta = e^{mx}$ is the trial solution then $m^2 = \mu^2$ or $m = \pm\mu$

$$\therefore \theta = \underbrace{A_1 e^{\mu x} + A_2 e^{-\mu x}}_{\text{Boundary conditions}}$$

If the bar is sufficiently long, we can assume that under steady state no heat is lost from free end of the bar, as whole of the heat is lost from ~~free end~~ sides as radiation & free end will be at the temperature of the surroundings.

(a) when bar is of infinite length:

Boundary condition, $x = 0,\ \theta = \theta_0$ (Dirichlet B.C.)

$x = \infty,\ \theta = 0$

we see that $\theta = A_1 e^{\infty}$ can be true only if $A_1 = 0$. and

$\theta_0 = A_2$. $\therefore \boxed{\theta = \theta_0 e^{-\mu x}}$

Thus after steady state is reached, temperature is exponentially distributed. This is useful in Ingen-Hausz experiment.

(b) When bar is of finite length: $x = 0,\ \theta = \theta_0$

$x = L,\ \frac{d\theta}{dx} = 0$ (Neumann B.C.)

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In this case $A_1 = \dfrac{\theta_0}{1+e^{2\mu L}}$, $A_2 = \dfrac{\theta_0}{1+e^{-2\mu L}}$

$\therefore$ Solution $\boxed{\theta = \theta_0 \left[\dfrac{e^{\mu x}}{1+e^{2\mu L}} + \dfrac{e^{-\mu x}}{1+e^{-2\mu L}} \right]}$

<u>Special Cases I at steady state</u> Ideal case when there is no loss of heat by radiation i.e. rod is thermally lagged & in steady state

$$h \frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} = 0 \quad \text{or} \quad \frac{d^2\theta}{dx^2} = 0 \quad (\text{as } h \neq 0)$$ [Laplace equation in electrostatics]

Solving $\dfrac{d}{dx}\left(\dfrac{d\theta}{dx}\right) = 0$ or $\dfrac{d\theta}{dx} = \text{constant} = A$

or $\theta = Ax + B$.

Find A & B using B.C. that $x = 0,\ \theta = \theta_0$

$x = l,\ \theta = \theta_m$ (say)

at unknown distance l, the temperature is θ_m.

$\theta_0 = B$. and then $\theta_m = Al + \theta_0$ or $A = \dfrac{\theta_m - \theta_0}{l}$

$\therefore \boxed{\theta = \theta_0 - \dfrac{\theta_0 - \theta_m}{l} x}$

The decrement is linear, as "solution of Laplace equation is always a straight line".

<u>In steady state length upto which wax melts in wax coated bar</u>

From $\theta = \theta_0 e^{-\mu x}$, $\ln \dfrac{\theta}{\theta_0} = -\mu x$ we see that if we have number of bars with conductivities $K_1, K_2, K_3, \ldots$ etc & wax melts upto length $l_1, l_2, l_3, \ldots$ etc then at these length the temperature would be melting point of wax (say θ_m).

$$\therefore \ln \frac{\theta_m}{\theta_0} = -\mu_1 l_1 = -\mu_2 l_2 = -\mu_3 l_3 = \cdots$$

$$\therefore \sqrt{\frac{PE}{K_1 A}}\, l_1 = \sqrt{\frac{PE}{K_2 A}}\, l_2 = \sqrt{\frac{PE}{K_3 A}}\, l_3 = \cdots$$

or $l/\sqrt{K} = \text{constant}$ or $l \propto \sqrt{K}$

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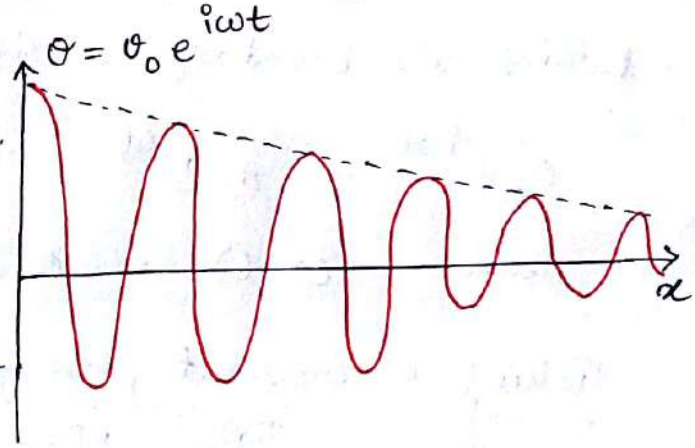
Hence in a steady state the length upto which the wax melts along a wax coated bar is proportional to the square root of the coefficient of thermal conductivity of the material.

Periodic flow of heat : Propagation of heat wave in an insulated rod with one end heated sinusoidally.



Consider a system of infinite length, well insulated (no loss due to radiation) whose one end is connected to an heat source from where heat is supplied not continuously but periodically. with θ_0 amplitude and ω being the angular frequency.

Using Fourier's equation $h\dfrac{d^2\theta}{dx^2} = \dfrac{d\theta}{dt} + \cancel{\dfrac{PE}{A\rho S}\theta}^{\,0}$ without radiation loss, the unidirectional heat equation is $h\dfrac{d^2\theta}{dx^2} = \dfrac{d\theta}{dt}$, $h = \dfrac{K}{\rho S}$ is the thermal diffusivity of the rod.

Let $\theta = u(x) + v(x,t)$ is a trial solution. then separating the variables, $\dfrac{d^2u}{dx^2} = 0$, $h\dfrac{d^2v}{dx^2} = \dfrac{dv}{dt}$

The solution of v-equation can be $v = F(x)e^{i\beta t}$

$\therefore\ hF''(x) = i\beta F(x)$ or $F''(x) = \dfrac{i\beta}{h}F(x) = \left(\sqrt{\dfrac{i\beta}{h}}\right)^2 F(x)$.

Taking the trial solution as $F(x) = Ae^{mx}$ we obtain,

$m^2 = \dfrac{i\beta}{h}$ or $m = \pm\sqrt{\dfrac{i\beta}{h}}$ $\therefore\ F(x) = A_1 e^{\sqrt{i\beta/h}\,x} + A_2 e^{-\sqrt{i\beta/h}\,x}$

As $x \to \infty$ yields $F(x) \to \infty$ (unphysical), so $A_1 = 0$.

$\therefore\ F(x) = A_2 e^{-\sqrt{\frac{i\beta}{h}}\,x}$

Now $(1+i)^2 = 2i$ or $i = \frac{1}{2}(1+i)^2$ or $\sqrt{i} = \pm\frac{1}{\sqrt{2}}(1+i)$

$\therefore\ F(x) = A_2 e^{-(1+i)\sqrt{\frac{\beta}{2h}}\,x} + A_3 e^{(1+i)\sqrt{\frac{\beta}{2h}}\,x}$

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$$\therefore v = f(x)\, e^{i\beta t} = \left[A_2 e^{-\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t - \sqrt{\frac{\beta}{2h}}x)} + A_3 e^{\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t + \sqrt{\frac{\beta}{2h}}x)} \right]$$

Here also, as $x \to \infty$, $v \to \infty$ (unphysical), hence $A_3 = 0$.

$$\therefore v(x,t) = A_2 e^{-\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t - \sqrt{\frac{\beta}{2h}}x)}$$

Putting the boundary condition for $\theta = \theta_0 e^{i\omega t}$ at $x = 0$, we see

$$\theta_0 e^{i\omega t} = A_2 e^{i\beta t} \qquad \therefore A_2 = \theta_0,\ \beta = \omega.$$

Hence $v(x,t) = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} e^{i(\omega t - \sqrt{\frac{\omega}{2h}}x)}$

Taking a constant phase factor ϕ from the solution of u, we have

$$\boxed{\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} e^{i[\omega t - \sqrt{\frac{\omega}{2h}}x - \phi]}}$$

This represents a progressive wave traveling with velocity

$$v = \frac{\omega}{K} = \frac{\omega}{\sqrt{\frac{\omega}{2h}}} = \sqrt{2\omega h} = \sqrt{\frac{2\omega K}{\rho S}} = \sqrt{\frac{2K}{\rho S}\frac{2\pi}{T}} = \sqrt{\frac{4\pi K}{T\rho S}}$$

damping factor $= \sqrt{\frac{\omega}{2h}}$

As $\frac{\lambda}{T} = v = \sqrt{\frac{4\pi K}{T\rho S}}$ or $K = \frac{\lambda^2 \rho S}{4\pi T}$

<u>CW</u> In a periodic flow of heat along an iron bar, the periodic time is 4 minute. If the temperature travels maximum 6 cm in 1 minute, calculate the thermal conductivity of iron. Density of iron = 7.8 gm/cm^3, specific heat of iron = 0.11 cal/gm °C.

$$v = \sqrt{2\omega h} = \sqrt{\frac{4\pi K}{T\rho S}} \quad \text{or} \quad v^2 = \frac{4\pi K}{T\rho S}$$

Here $v = 6$ cm/min $= 0.1$ cm/sec, $T = 4$ min $= 4 \times 60 = 240$ sec

$S = 0.11$ cal/gm °C, $\rho = 7.8$ gm/cm^3

$$\therefore K = \frac{v^2 T \rho S}{4\pi} = \frac{0.1^2 \times 240 \times 7.8 \times 0.11}{4 \times 3.14} = 0.1639 \text{ cal cm}^{-1}\text{sec}^{-1}\,°\text{C}^{-1}$$

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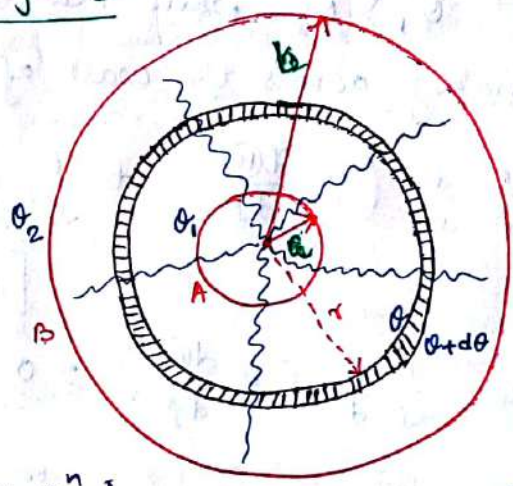
Heat flow in three dimensions

We have learned Fourier's law in one dimension,

$$h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \mu^2 h\theta .$$ In three dimensions, we have

$$h\nabla^2\theta = \frac{d\theta}{dt} + \mu^2 h\theta .$$ In steady state, $\frac{d\theta}{dt} = 0$ and without radiation loss, $\mu^2 = 0$ yields $\boxed{\nabla^2\theta = 0}$ This is called "Laplace equation" of heat flow. Compare with Electrostatics, Laplace equation

(a) Spherical shell Method (Radial flow)



Consider a spherical shell of inner radius a and outer radius b. Let θ_1 & θ_2 are the temperature at inside & outside the sphere. We want to find out temperature at $a<r<b$.

In ~~sphe~~ spherical polar coordinates, Laplace eqn is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \Theta}{\partial r}\right) + \cancelto{0}{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)} + \cancelto{0}{\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Theta}{\partial\phi^2}} = 0$$

$$[\text{as } \Theta \neq \Theta(\theta,\phi)]$$

or $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Theta}{\partial r}\right) = 0$$

or $$r^2\frac{d\Theta}{dr} = \text{constant} = C_1 \text{ (say)}$$

or $$d\Theta = \frac{C_1}{r^2}dr \quad \text{or} \quad \Theta = -\frac{C_1}{r} + C_2$$

Now we use Dirichlet Boundary condition $\Theta = \theta_1$ at $r=a$
$\Theta = \theta_2$ at $r=b$.

$$\therefore \quad \theta_1 = -\frac{C_1}{a} + C_2$$
$$\theta_2 = -\frac{C_1}{b} + C_2$$

or $$(\theta_1 - \theta_2) = C_1\left(\frac{1}{b} - \frac{1}{a}\right)$$

or $$C_1 = \frac{ab(\theta_1 - \theta_2)}{a-b}$$

$$\therefore C_2 = \theta_1 + \frac{C_1}{a} = \theta_1 + \frac{(\theta_1-\theta_2)b}{a-b} = \frac{a\theta_1 - b\theta_2}{a-b}.$$

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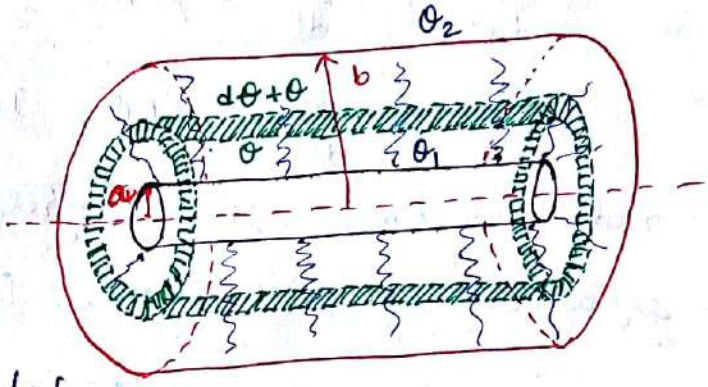
$\therefore$ The temperature at any distance r is

$$\Theta = \left[\frac{ab(\theta_1-\theta_2)}{b-a}\right]\frac{1}{r} + \frac{a\theta_1 - b\theta_2}{a-b}$$

(b) Cylindrical flow of heat



Consider a cylindrical tube of length l, inner radius a & outer radius b with temperature of inner surface θ_1 & outer surface θ_2 with $\theta_1 > \theta_2$ where heat is conducted radially across the wall of the tube. Laplace eqn becomes

$$\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{\partial\Theta}{\partial\rho}\right) + \frac{1}{\rho^2}\cancel{\frac{\partial^2\Theta}{\partial\theta^2}}^{\,0} + \cancel{\frac{\partial^2\Theta}{\partial\phi^2}}^{\,0} = 0$$

$$[\Theta \neq \Theta(\theta,\phi)]$$

$$\text{or } \frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{d\Theta}{d\rho}\right) = 0 \quad \text{or } \rho\frac{d\Theta}{d\rho} = \text{constant} = C_1$$

$$\text{or } d\Theta = \frac{C_1}{\rho}d\rho \quad \text{or } \Theta = C_1\ln\rho + C_2$$

We use Dirichlet boundary condition, $\Theta = \theta_1$ at $\rho = a$

$\Theta = \theta_2$ at $\rho = b$.

$$\therefore \theta_1 = C_1\ln a + C_2 \qquad \text{or } \theta_1 - \theta_2 = C_1\ln a/b.$$

$$\theta_2 = C_1\ln b + C_2 \qquad \text{or } C_1 = \frac{\theta_1-\theta_2}{\ln a/b}.$$

$$\therefore C_2 = \theta_1 - C_1\ln a = \theta_1 - \frac{(\theta_1-\theta_2)}{\ln a/b}\ln a = \frac{\theta_1(\ln a - \ln b) - (\theta_1-\theta_2)\ln a}{\ln a/b}$$

$$= \frac{\theta_2\ln a - \theta_1\ln b}{\ln a/b}.$$ So the temperature at any distance r is,

$$\Theta = \frac{\theta_1-\theta_2}{\ln a/b}\ln\rho + \frac{\theta_2\ln a - \theta_1\ln b}{\ln a/b}$$

Using Fourier's law at unit time, $Q = K\,2\pi r l\,\frac{d\theta}{dr}$

$$\text{or } Q\int_a^b \frac{dr}{r} = 2\pi K l\int_{\theta_1}^{\theta_2} d\theta = 2\pi K l(\theta_2-\theta_1).$$

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$\Rightarrow Q_1 \ln \frac{b}{a} = 2\pi K l (\theta_2 - \theta_1) \quad \Rightarrow \quad Q_1 = \frac{2\pi K l (\theta_1 - \theta_2)}{\ln a/b}$

$\Rightarrow K = \frac{Q_1 \ln a/b}{2\pi l (\theta_1 - \theta_2)}$

<u>Wiedemann-Franz law</u> The law states that ratio of thermal and electrical conductivities for all metals is directly proportion to the absolute temperature of the body.

$$\frac{K}{\sigma} \propto T \quad \text{or} \quad \frac{K}{\sigma T} = \text{constant} = 2\sqrt{\frac{6}{\pi}}\frac{k_B^2}{e^2} = L \text{ (Lorentz number)}$$

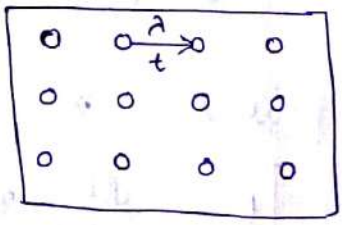
Physically this means that substances which are good conductor of heat are also good conductor of electricity.

Drude's theory of electrical conduction

Drude in 1900 introduced the concept of free electron gas model of metals, & obtained the electric conductivity of the metal. All metals (conductors) contain a huge number of nearly free electrons that behave as gas atoms in Kinetic theory. If m is mass of electron & v is velocity at temperature T,

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T \quad \Rightarrow \quad v_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

If we apply an electric field E & then electron will experience a force eE and accelarate with $\frac{eE}{m}$. Now as the electron moves to hit an atom or ion, if λ is the mean interatomic distance that is gone in time t then average drift velocity of the electron



$$\Rightarrow v_d = \frac{eE}{2m} t = \frac{eE}{2m}\frac{\lambda}{v}$$

$\therefore$ The current density $J = nev_d = \frac{ne^2\lambda}{2mv_{rms}} E = \sigma E$

and Thermal conductivity $K = \frac{1}{3} n \bar{c} \lambda \frac{dE}{dT}$ & for only translational energy case, $E = \frac{3}{2} k_B T$, $K = \frac{1}{3} n \bar{c} \lambda \frac{3}{2} k_B = \frac{1}{2} n \bar{c} \lambda k_B$

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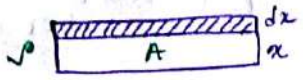
$$\therefore \frac{K}{\sigma} = \frac{\frac{1}{2} n \bar{c} \lambda k_B}{ne^2 \lambda} 2m \sqrt{\frac{3k_B T}{m}}$$

$$= 2\sqrt{\frac{8k_B T}{\cancel{m}\pi}} \frac{\cancel{n}\cancel{\lambda} k_B}{2\cancel{n}e^2\cancel{\lambda}} \cancel{m}\sqrt{\frac{3k_B T}{\cancel{m}}} = 2\sqrt{\frac{6}{\pi}} \frac{k_B^2}{e^2} T.$$

$$\therefore \frac{K}{\sigma T} = \text{constant} = \text{Lorelz number } L.$$

Heat conduction through a slab of varying thickness



To form ice, 80 cals of heat are given out at 0°c when some thick ice layer has formed, heat given out has to conduct through this thickness. Let us find out the time required to increase the icelayer from x_1 to x_2. If at t, ice formed is x then within time dt, dx thickness of ice is formed, then the heat liberated is $Q = A\,dx\,\rho L$. This heat flows in dt from 0°c to outside temperature $-\theta$°c. $\therefore Q = \frac{KA[0-(-\theta)]dt}{x} = \frac{KA\theta}{x} dt$

$$\therefore A\,dx\,\rho L = \frac{KA\theta}{x} dt \quad \text{or} \quad x\,dx = \frac{K\theta}{\rho L} dt$$

Integrating, $\frac{1}{2}x^2 = \frac{K\theta}{\rho L} t + c$

Now at $t=0$, $x = x_1$, $t = t_2$, $x = x_2$

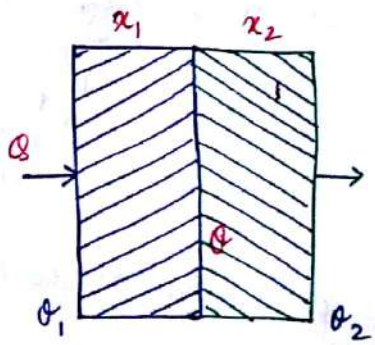
$$\therefore \frac{1}{2}x_1^2 = c \quad \& \quad \frac{1}{2}x_2^2 = \frac{K\theta}{\rho L} t_2 + \frac{1}{2}x_1^2$$

$$\text{or } t_2 = \frac{\rho L}{2K\theta}(x_2^2 - x_1^2)$$

If at $t=0$, $x=0$ then time required to form a layer of thickness x is

$$\boxed{t = \frac{\rho L}{2K\theta} x^2}$$

Heat conduction through a composite slab



Consider a slab made of two materials of thickness x_1 and x_2 and conductivities K_1 and K_2. At steady state, heat enters at θ_1

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crossing interface at θ & leaves out of the second face θ_2.

$$Q = \frac{K_1 A(\theta_1 - \theta)}{x_1} = \frac{K_2 A(\theta - \theta_2)}{x_2}$$

$$\text{or } Q = \frac{A(\theta_1 - \theta)}{\frac{x_1}{K_1}} = \frac{A(\theta - \theta_2)}{\frac{x_2}{K_2}} = \frac{A(\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2}}$$

If the composite slab can be replaced by a single slab of thickness $x_1 + x_2$ such that it will conduct in unit time heat Q under temperature difference $\theta_1 - \theta_2$, then the equivalent conductivity be K, then

$$Q = \frac{KA(\theta_1 - \theta_2)}{x_1 + x_2} = \frac{A(\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2}} \quad \therefore \frac{x_1 + x_2}{K} = \frac{x_1}{K_1} + \frac{x_2}{K_2}$$

If we have $n \geq 2$ slabs then $\frac{x_1 + x_2 + x_3 + \cdots}{K} = \frac{x_1}{K_1} + \frac{x_2}{K_2} + \frac{x_3}{K_3} + \cdots$

$$\text{or } \sum_{i=1}^{N} x_i \frac{1}{K} = \sum_{i=1}^{N} \frac{x_i}{K_i} \quad \therefore \boxed{K = \frac{\sum_{i=1}^{N} x_i}{\sum_{i=1}^{N} \frac{x_i}{K_i}}}$$

HW ① One end of a metal rod is in contact with a source of heat at 100°C. In the steady state the temperature at a point 10 cm from the source is 60°C. Find the temperature at a point 20 cm from the source.

② Suppose 10 cm of ice has already formed on a pond so that the air outside is at −5°C. How long will it take for the next milimeter to form? Given for ice $L = 80$ cal/gm, $\rho = 0.917$ gm/cc & $K = 0.005$ cgs unit.

③ A lake is covered with ice 2 cm thick. Temperature of air is −15°C. Find the rate of thickening of ice in cm/hour. For ice given $K = 0.004$ cgs unit, $\rho = 0.9$ gm/cc, $L = 80$ cal/gm.

④ Two equal bars of copper & aluminium are welded end to end and lagged. If the free ends of the copper & aluminium are maintained at 100°C and 0°C respectively. Find the temperature of welded surface. K of Cu & Al are 0.92 and 0.5 cgs unit respectively.

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Radiation

According to Maxwell, thermal radiation is defined as the transfer of heat from hot to cold body without any heating of the intervening medium. Thermal radiation, e.g. heat, has the same nature as light with properties:

(i) Electromagnetic wave nature to travel in Ether/vacuum at velocity of light.

(ii) travels in a straight line like light & exhibit reflection, refraction, interference, diffraction & polarisation.

These are not visible radiation but usually in UV, X ray or γ-ray. These can be detected using Thermopiles, Bolometer etc.

Blackbody radiation If heat is transferred through matter, a fraction of incident radiation is absorbed (say a), a fraction reflected (say b) and rest transmitted (say c) then $a+b+c=1$ and if $b=c=0$ then the body appears black because nothing is reflected or transmitted. When heated, such blackbody radiates energy of all wavelengths. These principles are used for instance

(a) white clothes are trendy in summer but dark coloured clothes in winter, as white clothes reflect maximum light & is least warm. Converse is true with dark shades. (b) Utensils are polished atop & blackened bottom so that maximum heat is absorbed & minimal heat flows out from above, (c) Hot water pipes are painted black inside room & white outside to provide heating to room in winter & prevent radiation at outside. (d) thermocouple junctions that has to be heated is painted black and so on.

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Spectral Emissive Power e_λ : It is the radiant energy emitted normally from unit area of the blackbody surface per unit time in unit solid angle within a unit wavelength range.

If spectral energy density is u_λ then $u_\lambda d\lambda$ is radiated energy from area dS in solid angle $d\omega$ in time dt, then

$$e_\lambda d\lambda = \frac{u_\lambda d\lambda}{dS\, d\omega\, dt} \longrightarrow [\lambda, \lambda + d\lambda]$$

Absorptive power a_λ : It is the fraction of incident to absorbed radiation, so if Q_λ is incident & Q_λ' is absorbed then

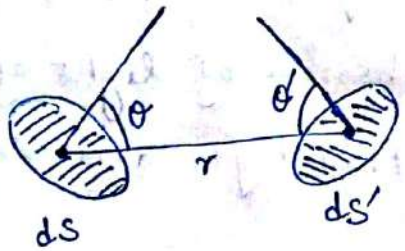
$$a_\lambda = \frac{Q_\lambda'}{Q_\lambda} \quad \text{and total heat absorbed by all } \lambda = \int_0^\infty a_\lambda Q_\lambda\, d\lambda.$$

Total Emission from dS

$$dQ_\lambda = \frac{u_\lambda d\lambda}{dt} = e_\lambda d\lambda\, dS\, d\omega.$$ So the total emission on one side $= \int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} e_\lambda d\lambda\, dS\, d\omega \cos\theta$

$$= e_\lambda d\lambda\, dS \int_0^{\pi/2} \sin\theta\cos\theta\, d\theta \int_0^{2\pi} d\phi = \pi e_\lambda d\lambda\, dS.$$

Mutual radiation between two surfaces



The solid angle subtended by dS' at dS is $d\omega' = \frac{dS'\cos\theta'}{r^2}$. So the amount of radiation incident on dS is $e_\lambda d\lambda\, dS \cos\theta\, d\omega'$

$$= e_\lambda d\lambda\, dS \cos\theta \frac{dS'\cos\theta'}{r^2}$$ and the energy absorbed

is $a_\lambda e_\lambda d\lambda\, dS \cos\theta \frac{dS'\cos\theta'}{r^2}$ and energy reflected will be

$$(1 - a_\lambda) e_\lambda d\lambda\, dS \cos\theta \frac{dS'\cos\theta'}{r^2}.$$

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Kirchhoff's law Ratio of emissive to absorptive power for a given wavelength at a given temperature for all bodies is same & equal to the emissive power of a perfect black body.

By definition, a_λ = absorptive power of a body, if dQ heat is incident on unit area in unit time within λ & $\lambda + d\lambda$, then heat absorbed $= a_\lambda dQ$ and $dQ - a_\lambda dQ$ will be transmitted or reflected. If e_λ = emissive power then $e_\lambda d\lambda$ is the energy emitted per unit area per unit time within λ & $\lambda + d\lambda$.

$\therefore$ Total emitted energy $= (1 - a_\lambda) dQ + e_\lambda d\lambda$ and in equilibrium, $\cancel{dQ} = (\cancel{1} - a_\lambda) dQ + e_\lambda d\lambda \Rightarrow a_\lambda \underline{\underline{dQ}} = e_\lambda d\lambda$.

For a perfect blackbody $e_\lambda = E_\lambda$ (notation) & $a_\lambda = 1$.

$\therefore \underline{\underline{dQ}} = E_\lambda d\lambda$. $\quad \therefore a_\lambda E_\lambda d\lambda = e_\lambda d\lambda$

$$\therefore \boxed{E_\lambda = \frac{e_\lambda}{a_\lambda}}$$ Kirchhoff's law

It also means not only radiation is independent on the shape or nature of wall of a hollow radiator & good absorbers are also good emitters. Na vapour that emit yellow D_1 & D_2 lines of λ 5890 Å & 5896 Å is also a good absorber of light of these two wavelengths. This explains the Fraunhofer dark lines in Sun's spectrum.

Pressure of diffuse radiation

When radiation falls normally to a surface then the radiation pressure is the sum of incident & reflected waves energy density. Larmor calculated it using Kepler's observation of radiation pressure of

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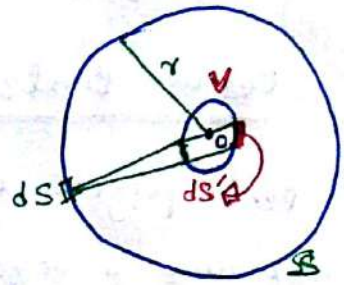
tail of comets rotating around so as to be always opposite to sun. Inside a heated container such radiation is diffuse.



Consider volume V at a very large distance from container wall so that radiation through V is the radiation coming from surface of sphere of radius r. As by construction $ds << V$, we can divide solid angle subtended by V at dS into many cones of solid angle $d\omega$ with area ds', so that $d\omega = \frac{ds'}{r^2}$.

If the volume V intersects infinitesimal cone of length l then time taken by radiation to travel is $dt = \frac{l}{c}$. If K is specific intensity or radiation emitted per unit area per unit time per unit solid angle then energy coming from $dS = K\,dS\,d\omega\,dt$

$$= K\,dS\,\frac{ds'}{r^2}\,\frac{l}{c}$$

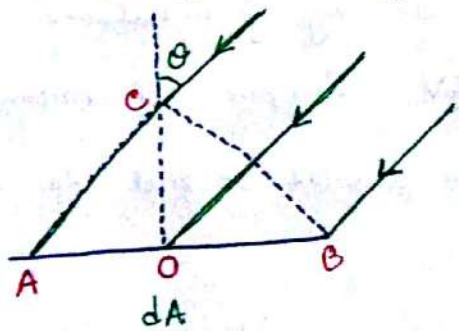
So the radiation contained in $V = \sum_V K\,ds\,\frac{ds'}{r^2}\,\frac{l}{c} = \frac{K\,ds}{cr^2}\sum_V l\,ds'$

$$= \frac{K\,ds}{cr^2}\,V$$

$\therefore$ Total radiation in V from the whole surface is $= \sum_S \frac{K\,ds}{cr^2}\,V$

$$= \frac{KV}{cr^2}\sum_S ds = \frac{KV}{cr^2}\,4\pi r^2 = \frac{4\pi K}{c}\,V, \quad E = \frac{4\pi K}{c}$$

or energy density of diffuse radiation is $\frac{4\pi K}{c}$. Suppose a parallel beam of radiation is incident on dA at angle θ so that, pressure on BC is



$$P = \frac{\text{intensity of radiation}}{\text{speed of radiation}} = \frac{K}{c}\sin\theta\,d\theta\,d\phi$$

Force due to radiation on BC $= \frac{K}{c}\sin\theta\,d\theta\,d\phi\,BC$ & the normal component is $= \frac{K}{c}\sin\theta\,d\theta\,d\phi\,BC\cos\theta = \frac{K}{c}\sin\theta\,d\theta\,d\phi\,AB\cos^2\theta$

$\therefore$ Total radiation pressure on AB $= 2\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi}\frac{K}{c}\sin\theta\,d\theta\,d\phi\,\cos^2\theta$

also reaction pressure

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$$= \frac{2K}{c}\int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta \int_{\phi=0}^{2\pi} d\phi = \frac{1}{3}\frac{4\pi K}{c} = \frac{1}{3}E.$$

$$\therefore \boxed{P = \frac{1}{3}E}$$

Stefan - Boltzmann law

For a perfect blackbody, the rate of emission of radiant energy by unit area is proportional to the fourth power of its absolute temperature.

$$E = \sigma T^4, \quad \sigma = \text{Stefan's constant} = 5.67 \times 10^{-8}\ W m^{-2} K^{-4}$$

In other words, if a blackbody at absolute temperature T is surrounded by another blackbody at absolute temperature T_0 then the net rate of loss of heat energy per unit area of the surface per unit time is $E = \sigma(T^4 - T_0^4)$.

Note that this is in accordance with "Prevost's theory of heat exchange" that states, "the net loss of heat is the difference in the heat radiated by the hot body and the heat absorbed by it from its surroundings." Stefan's law refers to the emission of heat radiation only by the blackbody and not to the net loss of heat by the blackbody after heat exchange with its surroundings.

In 1884, Boltzmann theoretically proved Stefan's law using Thermodynamics. Suppose an encloser of volume V is filled with radiation at uniform temperature T. E is the energy density of radiation so that total internal energy is $U = EV$. Suppose dQ amount of heat is flowed into the enclosure from outside so that the volume changed to $V + dV$.

Using first law of T.D. $dQ = dU + PdV$ and Maxwell's thermodynamic relation $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$ we have

$$\left(\frac{\partial U + PdV}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

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or $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

Using $P = \frac{1}{3}E$ and $U = EV$, we have $\left(\frac{\partial U}{\partial V}\right)_T = E$, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\left(\frac{\partial E}{\partial T}\right)_V$

$\therefore\ E = \frac{T}{3}\frac{dE}{dT} - \frac{E}{3}$ or $\frac{4E}{\cancel{3}} = \frac{T}{\cancel{3}}\frac{dE}{dT}$

or $\int \frac{dE}{E} = 4\int \frac{dT}{T} + \text{constant}$ or $\ln E = 4\ln T + \ln\sigma$

or $E = \sigma T^4$

Newton's law of cooling

Stefan's law is applicable for all temperatures but Newton's law is applicable when temperature difference between blackbody & surrounding is small. If T_1 is hotbody's temperature which is placed in an enclosure at T_2 then from Stefan's law

$$E = \sigma(T_1^4 - T_2^4) = \sigma(T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3).$$

While $(T_1 - T_2)$ is small, $T_1 \approx T_2$ so that $T_1^2T_2 \sim T_2^3$ & so on

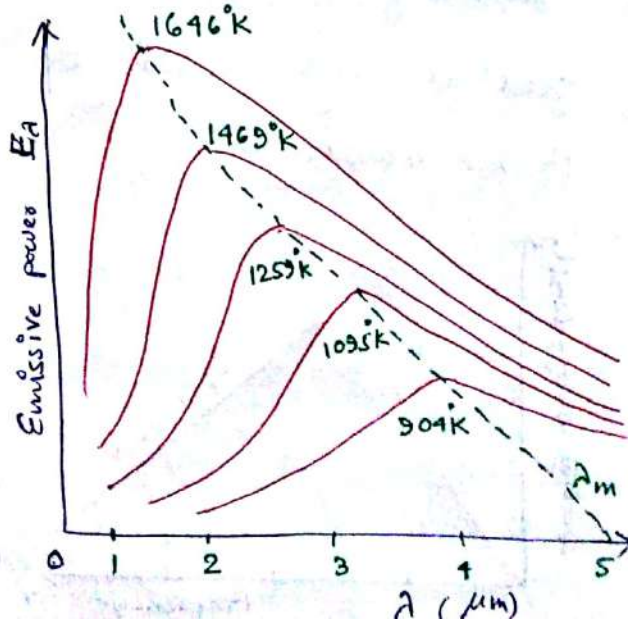
$$\therefore\ E = \sigma(T_1 - T_2)(T_2^3 + T_2^3 + T_2^3 + T_2^3)$$

$$= \underbrace{4\sigma T_2^3}_{K}(T_1 - T_2). = K(T_1 - T_2).$$

$\therefore\ E \propto (T_1 - T_2)$

Distribution of Energy in Blackbody Spectrum

Energy is not uniformly distributed for isothermals, and exhibits a maxima at a particular wavelength. If λ_m is the wavelength for which the emitted energy is maximum, then Wien's displacement law states that $\lambda_m T$ = constant.



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for all wavelengths, increase in temperature leads to increase in energy emission. Area under each curve represents total energy emitted & is found to be directly proportional to T^4, or $E \propto T^4$ which is the Stefan-Boltzmann's law.

Wien's Displacement law

When an electric wire is heated, at 500°C it is dull red, at 900°C its cherry red, at 1100°C its orange red, at 1250°C its yellow and at > 1600°C becomes white. So as the temperature is raised, the maximum intensity of emission is displaced towards the shorter wavelength. Wien's law is $\lambda_m T$ = constant = 0.2892 cmK

$$E_m \propto T^5 \quad \text{or} \quad E_m T^{-5} = \text{constant}$$

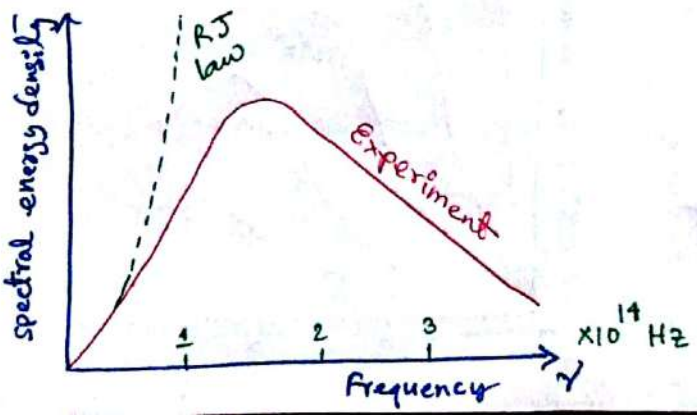
This can be combined with Stefan's law in one form as

$$E_\lambda = C \lambda^{-5} f(\lambda T)$$

Wien derived that $E_\lambda d\lambda = K \lambda^{-5} e^{-a/\lambda T} d\lambda$. This law holds good only at shorter wavelength & lower temperature, but do not hold good at longer wavelengths & higher temperature.

Rayleigh - Jeans law & the UV Catastrophe :

According to RJ law, $E_\lambda d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$. This law holds good at longer wavelengths at higher temperatures and not good at shorter wavelengths.



Writing $\lambda = \frac{c}{\nu}$ or $d\lambda = \frac{c}{\nu^2} d\nu$

using RJ law we can write

$$dE = E_\lambda d\lambda = \frac{8\pi k_B T}{c^4} \nu^4 \frac{c}{\nu^2} d\nu$$

$$= \frac{8\pi \nu^2 k_B T}{c^3} d\nu$$

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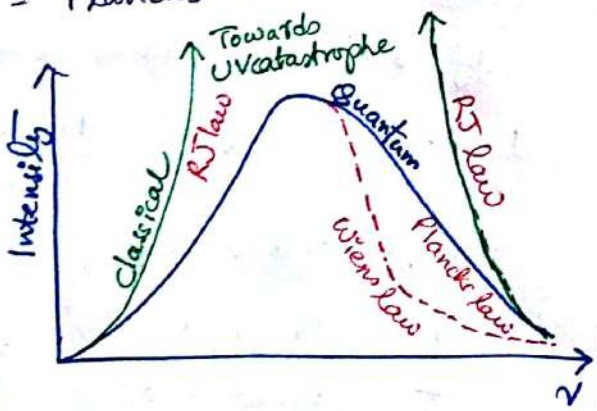
for $\nu \to \infty$, $dE \to \infty$ is a direct contradiction to experimental observations $\to$ "ultraviolet Catastrophe". Again,

$$E = \int_0^\infty \frac{8\pi\nu^2 k_B T \, d\nu}{c^3} \to \infty$$ which is contradiction to Stefan's law.

Thus before 1900, UV catastrophe was the biggest failure of classical physics until Max Planck, who used quantum mechanics idea to treat radiation as emitted quanta of energy $h\nu$. According to his treatment

$$\boxed{\begin{aligned} E_\nu \, d\nu &= \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \\ E_\lambda \, d\lambda &= \frac{8\pi h c}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1} \end{aligned}}$$

, $h = 6.626 \times 10^{-34}$ Js = Planck's constant.



This is called Planck's radiation law, that agrees perfectly with experiments.

Planck's quantum postulates say that

(a) A radiation enclosure can be imagined as a collection of resonators (simple harmonic oscillators) that can vibrate at all frequencies. (b) Resonators cannot radiate/absorb energy continuously but in the form of quanta-packets (photons). Each photon has energy $h\nu$ so that energy emitted/absorbed is $0, h\nu, 2h\nu, \ldots, nh\nu$ or "quantum".

① $\lambda \ll$ (short wavelengths) Planck's Radiation law

$$E_\lambda \, d\lambda = \frac{8\pi h c}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1} \simeq \frac{8\pi h c}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T}}$$

$$= \frac{8\pi h c}{\lambda^5} e^{-hc/\lambda k_B T} d\lambda \Rightarrow \text{"Wien's displacement law."}$$

② $\lambda \gg$ (larger wavelengths) $e^{hc/\lambda k_B T} \simeq 1 + \frac{hc}{\lambda k_B T}$

Planck's radiation law $E_\lambda d\lambda = \frac{8\pi h c}{\lambda^5} \frac{d\lambda}{1 + \frac{hc}{\lambda k_B T} - 1} = \frac{8\pi k_B T}{\lambda^4} d\lambda$

$\Rightarrow$ "Rayleigh-Jeans law."

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Solar Constant

It is the amount of radiation absorbed per unit time per unit area of a black body placed at a mean distance between sun & earth in the absence of atmosphere with the surface held normal to the sun rays.

If mean distance between sun & earth = R, solar constant = S

∴ Total amount of radiation received by the sphere in 1 minute $= 4\pi R^2 S$.

If r = sun's radius then radiation by 1 square cm surface in 1 minute $E = \frac{4\pi R^2 S}{4\pi r^2}$

$r = 6.928 \times 10^5$ Km, $R = 148.48 \times 10^7$ Km, $S = 1.94$ cals/cm²/minute

$$E = \frac{(148.48 \times 10^7)^2}{(6.928 \times 10^5)^2} \times \frac{1.94}{60} \text{ cals/second.}$$

But from Stefan's law $E = \sigma T^4 = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} T^4$ as

$\sigma = 5.75 \times 10^{-5}$ Ergs/cm²/deg⁴ $= \frac{5.75 \times 10^{-5}}{4.2 \times 10^7}$ cals/cm²/deg⁴

Equating, $\frac{(148.48 \times 10^7)^2}{(6.928 \times 10^5)^2} \frac{1.94}{60} = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} T^4$

or $T = 5730$ K.

The photosphere of sun (outer surface) is approximately 6000K. Calculated value yields the effective temperature when sun acts as a blackbody radiator.

This can also be calculated from Wien's displacement law

$\lambda_m T = 0.2892$. $\lambda_m = 4900 \times 10^{-8}$ cm (maximum in spectrum)

or $T = 5902$ K.

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CW 1. (a) Two large closely spaced concentric spheres (blackbody radiator) are kept at temperature 200K & 300K & the in between space is vacuum. Calculate the net rate of energy transfer between the two spheres. (b) Calculate the radiant emittance of a blackbody at temperatures 400K & 4000K. Given $\sigma = 5.672 \times 10^{-8}$ M.K.S. units.

(a) $T_1 = 300K$, $T_2 = 200K$ ∴ from Stefan's law, net rate of energy transfer $E = \sigma(T_1^4 - T_2^4)$

$= 5.672 \times 10^{-8} (300^4 - 200^4) = 368.68$ watts/m^2

(b) for $T = 400K$, $E = 5.672 \times 10^{-8} \times 400^4 = 1452$ watts/m^2

for $T = 4000K$, $E = 5.672 \times 10^{-8} \times 4000^4 = 1452 \times 10^4$ watts/m^2

$= 14520$ Kilowatts/m^2.

2. An aluminium foil is placed between two concentric spheres (blackbody radiators) at temperatures 300K & 200K. Calculate the temperature of the foil in the steady state. Also calculate the rate of energy transfer between one of the spheres and the foil.

If x is the temperature of foil in steady state then we have using Stefan's law, $\sigma(T_1^4 - x^4) = \sigma(x^4 - T_2^4)$

here $T_1 = 300K$, $T_2 = 200K$. or $300^4 - x^4 = x^4 - 200^4$

or $x = 263.8$ K.

∴ Rate of energy transfer $E = \sigma(T_1^4 - x^4)$

$= 5.672 \times 10^{-8} (300^4 - 263.8^4)$

$= 185$ watts/m^2.

[N.B. If relative emittance is mentioned (say $e = 0.1$) then $E = e\sigma(T_1^4 - x^4) = 18.5$ watts/m^2]

3. Obtain the number of modes of vibration per unit volume in the wavelength range 1990 Å to 5010 Å for a cubic shaped cavity of a blackbody.

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Number of modes / volume within λ & $\lambda + d\lambda$

$$n = \frac{E_\lambda d\lambda}{k_B T} = \frac{8\pi d\lambda}{\lambda^4}$$ using Rayleigh-Jean's law.

$\lambda = 5000\,\mathring{A} = 5000 \times 10^{-8}$ cm, $d\lambda = (5010 - 4990) = 20\mathring{A} = 20 \times 10^{-8}$ cm

$$\therefore n = \frac{8 \times 3.14 \times 20 \times 10^{-8}}{(5000 \times 10^{-8})^4} = 8.038 \times 10^{11} \text{ /cc.}$$

[Same thing, if asked frequency range say 4×10^{14} & 4.01×10^{14} sec^{-1} for a chamber of volume 50 cc, then $n = \frac{8\pi \nu^2 d\nu}{c^3} = 1.5 \times 10^{11}$ /cc and total number of modes in $V = 50$ cc is $= 1.5 \times 10^{11} \times 50$
$= 7.5 \times 10^{12}$]

HW 1. If a black body at a temperature 6174 K emits 4700 Å with maximum energy, calculate the temperature at which it will emit a wavelength of 1.4×10^{-5} m with maximum energy.

2. Using Stefan's law, calculate the total radiant energy emitted by Sun / second. Also calculate the rate at which energy is reaching the top of earth's atmosphere. Given radius of sun $= 7 \times 10^8$ m & distance of earth's atmosphere from sun $= 1.5 \times 10^{11}$ m and sun (blackbody) temperature $= 5800$ K.

3. The order of magnitude of the energy received from sun at earth's surface is 10^{-1} Joule / cm^2 sec. Calculate the order of magnitude of the total force due to solar radiation on the earth (perfectly absorbing). Given earth's diameter $= 10^7$ metre, & radiation pressure $P = \frac{E}{c}$.

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