

LECTURE - I

LECTURE - II

- Topics:-
- ① Mathematical modelling
 - ② Classical mechanics
 - ③ Thermodynamics
 - ④ Statistical Mechanics
 - ⑤ Quantum Mechanics

- Reference books:-
- 1) Concepts of Modern Physics - Arthur Compton & Philip Morrison
 - 2) Feynman Lectures on Physics
 - 3) Physical Chemistry - Atkins
 - 4) Fundamentals of Statistical and Thermal Physics - F. Reif
 - 5) Classical Mechanics - Goldstein
 - 6) Mechanics - L.D. Landau & Lifschitz
 - 7) Quantum Chemistry - I.M. Levine
 - 8) Quantum mechanics - Griffiths

grading :- Mid I - 20% at end of semester - 1st

Mid II - 20% at end of semester - 2nd

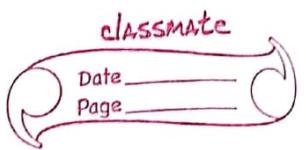
End Sem 40% final mark

Assignments & Quizzes - 20% throughout

Final Exam
1-6 = 100 marks

Introduction to modern physics - X

$$\frac{N!}{N^{N/2} \cdot \left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} p^{N/2} \cdot q^{N/2}$$



LECTURE-III

Diffusion or Brownian Motion

The model we use is random walk.

⇒ One-Dimensional Random Walk

→ Axioms :-

- 1.) It is one dimensional
- 2.) A particle starts from $x=0$.
- 3.) Each step ~~he/she takes~~ it takes is of equal length (l).
- 4.) The direction of each step is completely independent of the preceding step (i.e. it is random).
- 5.) At each time, the probability of a step to be to the right is p , while the probability for step to be to the left is q .

→ Question:- After N ~~a second~~ ^{steps}, what is the probability of it being at some x ?

→ ~~geo~~ Analysis

n_1 - number of steps to the right

n_2 - number of steps to the left

$$\therefore n_1 + n_2 = N \quad \underline{\text{P} = II} \quad \underline{n_1 = \frac{N+m}{2}, n_2 = \frac{N-m}{2}}$$

Taking l as a unit,

Net Displacement $= m = (n_1 - n_2)$

We need to find ~~P~~ the probability ~~of~~ of taking

~~P~~ $m \geq n_1$ steps to the right, out of N steps. (W. $\omega_N(n_1)$)

Simple Case :-

$$N = 3, n_1 = 2, n_2 = 1$$

$\therefore \rightarrow \rightarrow \leftarrow, \rightarrow \leftarrow \rightarrow, \leftarrow \rightarrow \rightarrow \Rightarrow 3$ possibilities

$X \rightarrow$ number of experiments

$\frac{p(x=x)}{A}$

$$v = \sqrt{\frac{3RT}{2m}} = \sqrt{\frac{3RT}{n}} \Rightarrow \sqrt{\frac{3X}{2 \times 10}}$$

$$p^n q^{(N-n)}$$

$$\frac{N!}{n!} \left(\frac{1}{2}\right)^{N/2}$$

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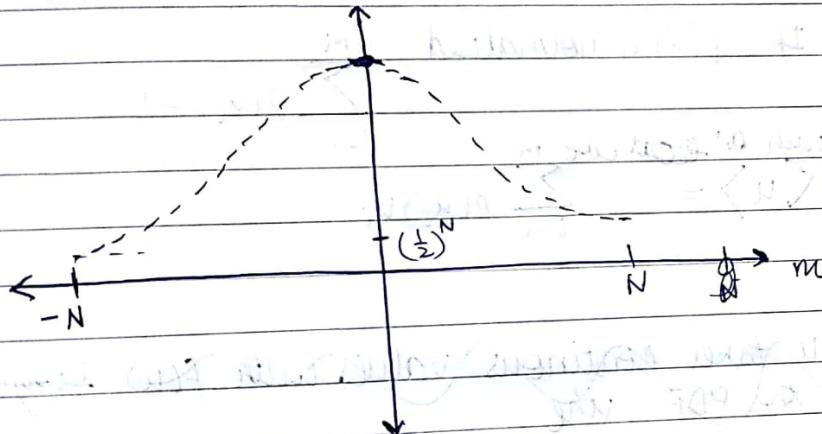
In general

$$W_N(n) = \frac{n!}{n_1! n_2!} \cdot p^{n_1} \cdot q^{n_2}$$

: Probability for net displacement to be N m after N steps, is

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{\left(\frac{(N+m)/2}{2}\right)} q^{\left(\frac{(N-m)/2}{2}\right)}$$

for unbiased random walk, $p = q = \frac{1}{2}$



Statistics =

we find $\langle n \rangle$ & $\text{mean of } m$

$\langle n_i \rangle$ - mean value of n_i

$\langle n_i - \langle n_i \rangle \rangle$ - mean deviation in n_i
(average of deviation)

$\langle (n_i - \langle n_i \rangle)^2 \rangle$ - fluctuation or second moment
(average of deviation squared)
& mean-squared deviation

$\langle m \rangle, \langle m - \langle m \rangle \rangle, \langle (m - \langle m \rangle)^2 \rangle$

General statistics :-

If u is variable that can take M discrete values.

u_1, u_2, \dots, u_M with respective probabilities

$p(u_1), p(u_2), \dots, p(u_M)$.

Then,

$$\langle u \rangle = \sum_{i=1}^M p(u_i) u_i$$

$$\sum_{i=1}^M p(u_i) = 1$$

If $p(u)$ is normalised,

$$\sum_{i=1}^M p(u_i) = 1$$

In such a case,

$$\langle u \rangle = \sum_{i=1}^M p(u_i) u_i$$

If u takes continuous values with $f(u)$ being probability density function, then

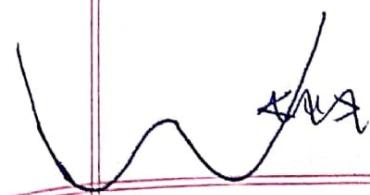
If $f(u)$ is any function of u , then

$$\langle f(u) \rangle = \sum_{i=1}^M p(u_i) f(u_i)$$

$$\sum_{i=1}^M p(u_i)$$

If, $\Delta u = u - \langle u \rangle$, where Δu is deviation, then

$$\langle \Delta u \rangle = \langle u - \langle u \rangle \rangle = \langle u \rangle - \langle u \rangle = 0$$



$$\langle (\Delta u)^2 \rangle = \langle u^2 \rangle + \langle u \rangle^2 - 2u\langle u \rangle \langle u - \langle u \rangle \rangle^2$$

$$= \langle u^2 \rangle + \cancel{\langle u \rangle^2} - \langle u \rangle^2 - 2u\langle u \rangle$$

$$= \langle u^2 \rangle + \langle u \rangle^2 - 2\langle u \rangle^2$$

~~$$= \langle u^2 \rangle - \langle u \rangle^2$$~~

$$\langle (\Delta u)^2 \rangle = \langle u^2 \rangle - \langle u \rangle^2$$

Note that

$$\langle u \rangle^2 \geq 0 \Rightarrow \langle u^2 \rangle \geq \langle u \rangle^2$$

nth moment of the Probability Distribution =

$$\langle (\Delta u)^n \rangle = \langle (u - \langle u \rangle)^n \rangle = \langle u^n \rangle$$

For our random walker,

$$\langle n_1 \rangle = \sum_{n_1=0}^N P(n_1) n_1$$

$$= \sum_{n_1=0}^N \left(\frac{N!}{(n_1)(N-n_1)!} \cdot p^{n_1} q^{N-n_1} \right) n_1$$

$$= \sum_{n_1=0}^N \left(\frac{N!}{n_1!(N-n_1)!} \cdot p^{n_1} q^{N-n_1} \right) n_1$$

$$\text{classmate} \sum_{n=0}^N {}^N C_{n_1} \cdot p^{n_1} q^{N-n_1} n_1! = (p+q)^N$$

$$f(p) = \sum_{n=0}^N {}^N C_{n_1} \cdot p^{n_1} q^{N-n_1} n_1! = (p+q)^N$$

$$\langle n_1 \rangle = pN(p+q)^{N-1}$$

Note that

$$p \cdot \frac{\partial(p^n)}{\partial p} = n p^{n-1}$$

$$\therefore \langle n_1 \rangle = \sum_{n_1=0}^N \frac{N!}{n_1!(N-n_1)!} q^{N-n_1} \cdot p \cdot \frac{\partial(p^{n_1})}{\partial p} =$$

$$\Rightarrow \langle n_1 \rangle = p \frac{\partial}{\partial p} \left[\sum_{n_1=0}^N \frac{N!}{n_1!(N-n_1)!} q^{N-n_1} p^{n_1} \right] = p \frac{\partial}{\partial p} [(p+q)^N] =$$

$$= p \frac{\partial}{\partial p} [(p+q)^N] = N(p+q)^{N-1}$$

$$\therefore \langle n_1 \rangle = p \cdot N \cdot (p+q)^{N-1}$$

$$\Rightarrow \langle n_1 \rangle = pN(p+q)^{N-1} = \langle n_1 \rangle$$

If $p+q=1$, then e.g. unbiased walk, then

$$\langle n_1 \rangle = pN$$

Similarly, $\langle n_2 \rangle = qN$

$$\langle n_2 \rangle = qN$$

$$P = \sum_{n=0}^N C_n p^n q^{N-n}$$

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LECTURE - IV

$$\Delta n_i \equiv l_i - \langle n_i \rangle$$

We need to find

$$\langle \Delta n_1 \rangle, \langle \Delta n_2 \rangle, \langle \Delta m \rangle \text{ & } \langle m \rangle$$

$$\langle (\Delta n_1)^2 \rangle, \langle (\Delta n_2)^2 \rangle, \langle (\Delta m)^2 \rangle$$

This quantity can be measured experimentally for any solute in a solvent.

$$W_N(n_1) = \frac{N!}{(n_1!) (n_2!) p^{n_1} q^{n_2}} = \frac{N!}{n_1! n_2!} p^{n_1} q^{N-n_1}$$

$$\langle n_1 \rangle = pN, \langle n_2 \rangle = qN$$

$$(\quad = \sum_{n_1=0}^N n_1 W_N(n_1))$$

$$\langle m \rangle = \langle n_1 - n_2 \rangle = \langle n_1 \rangle - \langle n_2 \rangle = pN - qN$$

$$\Rightarrow \langle m \rangle = (p-q)N$$

e.g. for unbiased random walk, $\langle m \rangle = 0$

Now, $\langle (\Delta n)^2 \rangle = \langle (n_1 - \langle n_1 \rangle)^2 \rangle$

$$\langle (\Delta n)^2 \rangle = \langle n_1^2 \rangle - \langle n_1 \rangle^2$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^N n_1^2 \cdot W_N(n_1) = \sum_{n_1=0}^N C_{n_1} p^{n_1} q^{N-n_1} n_1^2$$

$$\frac{\partial^2 p^{n_1}}{\partial p^2} = n_1(n_1-1)p^{n_1-2} \quad |_{n_1 p^{n_1}}$$

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$$\langle n_1^2 \rangle = \sum_{n=0}^N n_1^2 \cdot {}^N C_{n_1} p^{n_1} q^{n_2}$$

$$\textcircled{1} \quad n_1 p \frac{\partial}{\partial p} p^{n_1} = n_1^2 p^{n_1} \quad \textcircled{2} \quad = p \frac{\partial^2}{\partial p^2} p^{n_1}$$

$$p \frac{\partial}{\partial p} \left(p \frac{\partial}{\partial p} p^{n_1} \right) = n_1^2 p^{n_1}$$

$$= \sqrt{p} \sum_{n_1=0}^N {}^N C_{n_1} \cdot n_1 \cdot p \frac{\partial}{\partial p} p^{n_1} \cdot p^{n_1} \cdot q^{n_2}$$

$$= \sqrt{p} \frac{\partial}{\partial p} \left[\sum_{n_1=0}^N {}^N C_{n_1} p^{n_1} q^{N-n_1} \cdot n_1 \right]$$

$$= p \frac{\partial}{\partial p} \left(\sum_{n_1=0}^N n_1^2 p^{n_1} \right) = n_1^2 p^{n_1}$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^N n_1^2 \cdot {}^N C_{n_1} p^{n_1} q^{N-n_1}$$

$$n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}$$

$$n_1^2 p^{n_1} = p \frac{\partial}{\partial p} \left(p \frac{\partial}{\partial p} p^{n_1} \right) = p \left[p \frac{\partial^2}{\partial p^2} p^{n_1} + \frac{\partial}{\partial p} p^{n_1} \right]$$

$$= p \frac{\partial}{\partial p} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1}$$

$$= p^2 \frac{\partial^2}{\partial p^2} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1}$$

$$p^2 \frac{\partial}{\partial p} p^{n_1}$$

$$p^{n_1}$$

$$n_1(n_1-1) \frac{\partial^2}{\partial p^2}$$

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$$\langle n_1^2 \rangle = \sum_{n_1=0}^N {}^N C_{n_1} \cdot q^{N-n_1} \left(p^2 \frac{\partial^2}{\partial p^2} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1} \right)$$

$$= p^2 \frac{\partial^2}{\partial p^2} \left[\sum_{n_1=0}^N {}^N C_{n_1} q^{N-n_1} \cdot p^{n_1} \right] + p \frac{\partial}{\partial p} \left[\sum_{n_1=0}^N {}^N C_{n_1} p^{n_1} q^{N-n_1} \right]$$

$$= p^2 \frac{\partial^2}{\partial p^2} [(p+q)^N] + p \frac{\partial}{\partial p} [(p+q)^N]$$

$$= p^2 [N(N-1)(p+q)^{N-2}] + pN(p+q)^{N-1}$$

$$\langle n_1^2 \rangle = p^2 [N^2 - N] + pN$$

$$= p^2 N^2 - Np^2 + pN$$

$$= p^2 N^2 + pN(1-p)$$

$$\langle n_1^2 \rangle = (pN)^2 + pqN$$

$$\therefore \langle (\Delta n_1)^2 \rangle = \langle n_1^2 \rangle - (\langle n_1 \rangle)^2$$

$$= (pN)^2 + pqN - (pN)^2$$

$$\boxed{\langle (\Delta n_1)^2 \rangle = pqN}$$

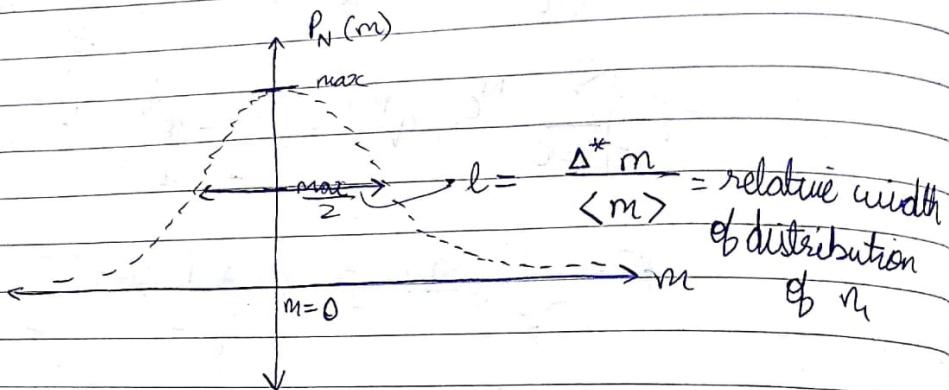
\therefore Root mean square deviation of $n_1 = \sqrt{\langle (\Delta n_1)^2 \rangle} = \Delta^* n_1$

$$\Rightarrow \Delta^* n_1 = \sqrt{\langle (\Delta n_1)^2 \rangle} = \sqrt{Npq}$$

$$\langle (\Delta n_2)^2 \rangle = pqN$$

$$\therefore \Delta^* n_2 = \sqrt{pqN}$$

The relative width of the distribution of $n_1 \equiv \frac{\Delta^* n_1}{\langle n_1 \rangle}$



For n_1 , relative width of distribution = $\sqrt{pq/N}$

$$= \sqrt{\frac{q}{pN}}$$

∴ For unbiased case,

$$\text{relative width} = \sqrt{\frac{1}{N}}$$

Width measured the spread of data and is, in some sense, the error in measurement.

So here, error decreases with number of measurements.

$$\langle (\Delta m)^2 \rangle = \langle m_2 \rangle - (\langle m_1 \rangle)^2 = 4 \langle (\Delta n)^2 \rangle$$

as

$$m = n_1 - n_2 = 2n_1 - N$$

$$\Delta m = m - \langle m \rangle$$

$$= 2n_1 - N - \langle 2n_1 \rangle + N$$

$$= 2[n_1 - \langle n_1 \rangle] = 2\Delta n$$

$$\Rightarrow (\Delta m)^2 = 4(\Delta n)^2$$

$$\therefore \langle (\Delta m)^2 \rangle = 4 \langle (\Delta n)^2 \rangle$$

$$\langle (\Delta m)^2 \rangle = 4pqN$$

$$\Delta^* m = 2\sqrt{pqN}$$

e.g. for unbiased case,

$$\Delta^* m = \sqrt{N}$$

Also, in general,

$$\langle (\Delta m)^2 \rangle \propto N$$

$$\langle (\Delta m)^2 \rangle = \langle m^2 + m^2 - 2m \Delta m \rangle = \langle m^2 \rangle + \langle m \rangle^2 - 2\langle m \rangle \langle \Delta m \rangle$$

since $\Delta m = 0$ for unbiased random walker,

$$\therefore \langle m^2 \rangle \propto N$$

mean square displacement

Mean square displacement of random walker increases linearly with time.

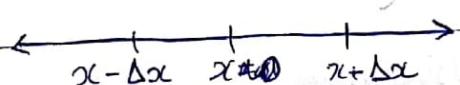
LECTURE-II

For random distribution diffusion, ①

$$\langle x^2 \rangle \propto \text{time}$$

random diffusion

→ Derivation of the Diffusion Equation from the random walk model
(one dimensional)



$\Delta x \rightarrow$ step length of random walker

$$\frac{d^2 f(t)}{dt^2} = \lim_{h_1 \rightarrow 0} \lim_{h_2 \rightarrow 0} \frac{f(x_0 + h_1 + h_2) - f(x_0 + h_1) - f(x_0 + h_2) + f(x_0)}{h_1 h_2}$$

$$= \lim_{h \rightarrow 0} \frac{f(x+2h) - 2f(x+h) + f(x)}{h}$$

$P(x,t)$ → probability of that random walker is at x at time t .

We try to find $P(x, t + \Delta t)$

$$P(x, t + \Delta t) = ?$$

Δt - the timestep

In fact

$$P(x, t + \Delta t) = P(x, t) \prod$$

$$= P(x + \Delta x, t) \prod (x + \Delta x \rightarrow x)$$

$$+ P(x - \Delta x, t) \prod (x - \Delta x \rightarrow x) \xrightarrow{\text{transitional probability}}$$

$$- P(x, t) \prod (x \rightarrow x + \Delta x) \quad \text{i.e. probability to move}$$

$$- P(x, t) \prod (x \rightarrow x - \Delta x) \quad \text{from } x + \Delta x \rightarrow x$$

For an unbiased random walker,

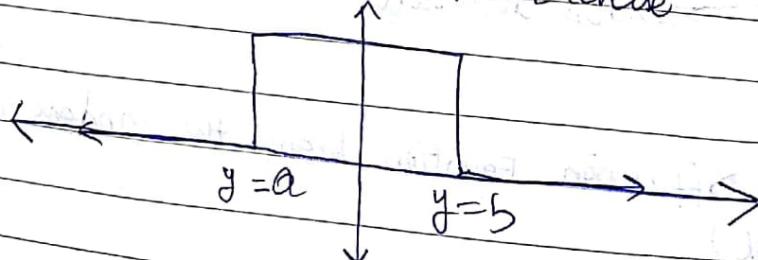
$$\prod (x \rightarrow x + \Delta x) = \prod (x \rightarrow x - \Delta x) = \frac{1}{2}$$

i.e. all transitional probabilities ~~now~~ is equal to 0.5

$$P(x, t + \Delta t) = P(x, t) = \frac{1}{2} [P(x + \Delta x, t) - 2P(x, t) + P(x - \Delta x, t)]$$

Computational Exercise

①



Uniform distribution.

$$P(y) = \begin{cases} 0 & y \notin [a, b] \\ \frac{1}{b-a} & y \in [a, b] \end{cases}$$

Range: $y \in [0,1]$ i.e $a=0, b=1$

If $y < \frac{1}{2}$, x moves left else it moves right

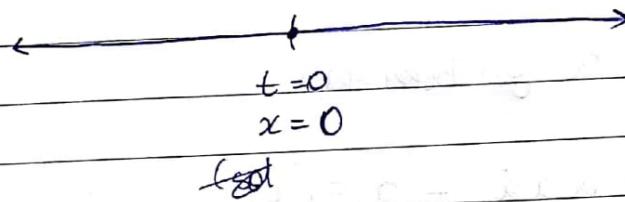
LECTURE - VI

23 August 2018

Langevin Dynamics

Mathematical model for dissolution of solute in a solvent.

One dimensional case:-



Solute, at $x=0$, at $t=0$, in a solvent

Two forces - viscous force, which resists motion of particle, and a random force, which acts on the particle randomly.

$m \rightarrow$ mass of particle

$x(t) \rightarrow$ position of particle at time t

Equation of motion -

$$m \frac{d\dot{x}}{dt} = -\alpha \dot{x} + F(t) \quad \text{--- (1)}$$

↓ ↓ ↓
 damping random
 force force

($\alpha > 0$ is friction coefficient)

(fluctuates randomly with t)

$\uparrow F(t)$

$$\langle F \rangle = 0$$

What is $\langle x^2 \rangle$ of the solute?

For a random walk, $\langle x^2 \rangle \propto t$

$$\langle x^2 \rangle$$

$$t \langle x \rangle$$

$$m \frac{d\dot{x}}{dt} = -\alpha \dot{x} + F(t)$$

Multiplying with α on both sides,

$$m \alpha \frac{d\dot{x}}{dt} = -\alpha \alpha \dot{x} + \alpha F(t)$$

$$\Rightarrow m \left[\frac{d}{dt} (\alpha \dot{x}) - (\dot{x})^2 \right] = -\alpha \alpha \dot{x} + \alpha F(t)$$

Taking average on both sides,

$$m \left[\left\langle \frac{d}{dt} (\alpha \dot{x}) \right\rangle - \left\langle (\dot{x})^2 \right\rangle \right] = -\alpha \left\langle \alpha \dot{x} \right\rangle + \left\langle \alpha F(t) \right\rangle$$

$$= -\alpha \left\langle \alpha \dot{x} \right\rangle + \underbrace{\left\langle \alpha \right\rangle \left\langle F(t) \right\rangle}_{\downarrow}$$

as $\alpha, F(t)$ are uncorrelated i.e. independence.

Q. Since $\langle F(t) \rangle = 0$

$$m \left[\left\langle \frac{d(x\dot{x})}{dt} \right\rangle - \left\langle \dot{x}^2 \right\rangle \right] = -\alpha \left\langle x\dot{x} \right\rangle - \textcircled{2}$$

We know that, mean K.E $\langle \text{K} \rangle$ is

$$\langle \text{K} \rangle = \frac{1}{2} k_B T = \frac{1}{2} m \langle \dot{x}^2 \rangle$$

k_B = Boltzmann Constant
 T = temperature

From $\textcircled{2}$,

$$m \left[\left\langle \frac{d(x\dot{x})}{dt} \right\rangle - \frac{k_B T}{m} \right] = -\alpha \left\langle x\dot{x} \right\rangle$$

$$\Rightarrow m \left\langle \frac{d(x\dot{x})}{dt} \right\rangle = \alpha k_B T - \alpha \left\langle x\dot{x} \right\rangle$$

$$\text{Also, } \left\langle \frac{du}{dt} \right\rangle = -\frac{d}{dt} \langle u \rangle$$

$$\therefore m \frac{d}{dt} \langle x\dot{x} \rangle = k_B T - \alpha \left\langle x\dot{x} \right\rangle - \textcircled{3}$$

This is an 1^{st} order linear differential equation in $\langle x\dot{x} \rangle$.

\therefore Solution is

$$\langle x\dot{x} \rangle = \cancel{ce^{st}} + \frac{k_B T}{\alpha} + ce^{-st} - \textcircled{4}$$

Here, c is the constant of integration.

$$\cancel{ce^{st}} = \frac{\alpha}{m}$$

Note at $t=0$,

Note that,

$$\langle x_{ji} \rangle = \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle$$

Equation 4 implies

$$\frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = ce^{-\alpha t} + \frac{k_B T}{\alpha}$$

According to initial condition, at $t=0$, $x=0$

$$\therefore c = -\frac{k_B T}{\alpha} \quad (\text{at } t=0, \langle x^2 \rangle = 0)$$

\therefore (4) becomes

$$\frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = \frac{k_B T}{\alpha} (1 - e^{-\alpha t}) \quad (5)$$

Integrating

Integrating from $t=0$ to $t=t$,

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

$$\Rightarrow \boxed{\langle x^2 \rangle = \frac{2 k_B T}{\alpha} \left[t - \left(1 - e^{-\alpha t} \right) \right]} \quad (6)$$



$$+ \frac{e^{-\alpha t}}{\alpha} \Big|_0 \quad \frac{d}{dt} \langle x^2 \rangle = \langle \frac{d}{dt} (x^2) \rangle$$

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Limiting cases :-

i) When $t \ll \frac{1}{\alpha} \Rightarrow 0 < \alpha t \ll 1$ (short time diffusion)

$$\therefore p \approx 0 \\ e^{-\alpha t} \approx 1$$

$$\therefore \langle x^2 \rangle = 2k_B T \cancel{\sqrt{t}} = 0$$

$$\therefore e^{-\alpha t} = 1 - \alpha t + \frac{\alpha^2 t^2}{2} + \dots$$

(neglecting higher powers)

$$e^{-\alpha t} = 1 - \alpha t + \frac{1}{2} \alpha^2 t^2$$

$$\langle x^2 \rangle = 2k_B T \cancel{(t - \frac{1}{2} \alpha t)} = 0$$

$$\therefore \langle x^2 \rangle = \frac{2k_B T}{\alpha} \left[t - \frac{1}{2} \left(1 - (1 - \alpha t + \frac{1}{2} \alpha^2 t^2) \right) \right]$$

$$= \frac{2k_B T}{\alpha} \left[t - \frac{1}{2} (\alpha t - \frac{1}{2} \alpha^2 t^2) \right]$$

$$\langle x^2 \rangle = \frac{2k_B T}{\alpha} \alpha t^2 = \left(\frac{k_B T}{m} \right) t^2$$

This is similar to a free particle with no force as

$$\frac{dx}{dt} = 0 \Rightarrow x \propto t \Rightarrow x^2 \propto t^2 \Rightarrow \langle x^2 \rangle \propto t^2$$

\therefore Solute behaves like a free particle for a short period of time

$$\sum_{n_1=0}^{\infty} w_N^2(n_1) = \sum_{n_1=0}^{\infty} \left[\frac{(N!)^2}{(n_1)!(N-n_1)!} \left(\frac{1}{2}\right)^N \right]^2$$

2. Long time limit i.e.

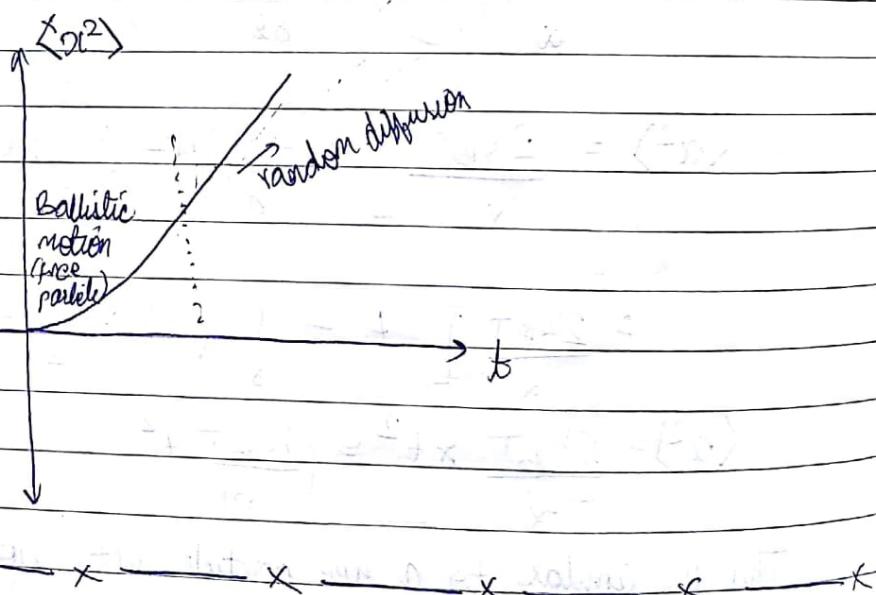
$$t \gg \frac{1}{\gamma} \Rightarrow \gamma t \gg 1$$

$$\therefore e^{-\gamma t} \approx 0$$

Now:

$$\begin{aligned} \langle x^2 \rangle &= \frac{2k_B T}{\alpha} \left(t - \left(1 - \frac{e^{-\gamma t}}{\gamma} \right) \right) \\ &= \frac{2k_B T}{\alpha} \left(t - \frac{1}{\gamma} \right) \end{aligned}$$

After a very long time it tends to linear time dependence
i.e. it tends to a random walk.

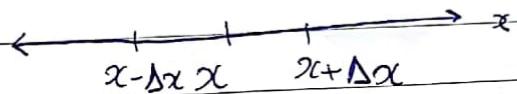


Class Assignment :-

Two drunks start out at the origin, each having equal probabilities of making a step to the left or right along the x-axis. Find the probability that they meet again after N steps. It is to be understood that the men take their steps simultaneously.

LECTURE - VII

Derivation of the differential diffusion equation from random walk Model (one-dimensional case) -



$\Delta x \rightarrow$ step length in a given time step Δt
It is an unbiased random walker.

Transition Probabilities =

$$\pi(x + \Delta x \rightarrow x) = \frac{1}{2}$$

$$\pi(x - \Delta x \rightarrow x) = b_2$$

$$\pi(x \rightarrow x + \Delta x) = b_2$$

$$\pi(x \rightarrow x - \Delta x) = \frac{1}{2}$$

$P(x, t) \Rightarrow$ probability of finding the random walker at x at time t .

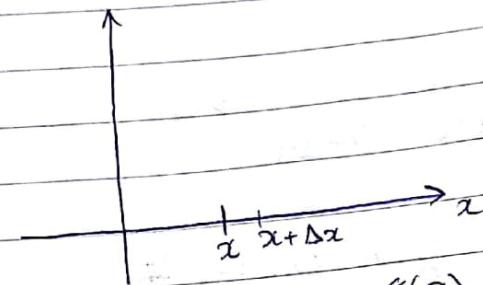
The change in probability can be written as

$$\begin{aligned} P(x, t + \Delta t) &= P(x, t) - P(x, t) \\ &= -\pi(x \rightarrow x + \Delta x) \cdot P(x, t) \\ &\quad - \pi(x \rightarrow x - \Delta x) \cdot P(x, t) \\ &\quad + \pi(x \rightarrow x + \Delta x \rightarrow x) \cdot P(x + \Delta x, t) \\ &\quad + \pi(x - \Delta x \rightarrow x) \cdot P(x - \Delta x, t) \end{aligned}$$

$$\begin{aligned} P(x, t + \Delta t) &= P(x + \Delta x, t) \pi(x + \Delta x \rightarrow x) \\ &\quad + P(x - \Delta x, t) \pi(x - \Delta x \rightarrow x) \end{aligned}$$

$$P(x, t + \Delta t) - P(x, t) = \frac{1}{2} [P(x + \Delta x, t) - 2P(x, t) + P(x - \Delta x, t)] \quad (1)$$

Taylor's Series expansion:-



We know $f(x), f'(x), f''(x), f'''(x)$ at x
i.e. we know

$$f(x), \left. \frac{df}{dx} \right|_x, \left. \frac{d^2 f}{dx^2} \right|_x, \dots, \left. \frac{d^n f}{dx^n} \right|_x$$

Then, for sufficiently small Δx ,

$$f(x + \Delta x) \approx$$

$$\begin{aligned} f(x + \Delta x) &= \cancel{f(x)} + \cancel{\left. \frac{df}{dx} \right|_x \Delta x} + \cancel{\frac{1}{2!} \left. \frac{d^2 f}{dx^2} \right|_x (\Delta x)^2} \\ &\quad + \dots + \cancel{\frac{1}{n!} \left. \frac{d^n f}{dx^n} \right|_x (\Delta x)^n} \end{aligned}$$

$$\therefore P(x + \Delta x, t) = P(x, t) + \frac{1}{2} P(x, t) \cdot \Delta x$$

$$+ \frac{1}{2!} \frac{\partial^2 P(x, t)}{\partial x^2} (\Delta x)^2 + \dots$$

similarly >

$$P(x - \Delta x, t) = P(x, t) - \frac{1}{2} P(x, t) \Delta x + \frac{1}{2!} \frac{\partial^2 P(x, t)}{\partial x^2} (\Delta x)^2$$

For sufficiently small $\Delta x \rightarrow 0$, we ignore $(\Delta x)^n$ for $n > 2$.

\therefore For $\Delta x \rightarrow 0$,

$$P(x+\Delta x, t) + P(x-\Delta x, t) = 2P(x, t) + \frac{\partial^2}{\partial x^2} P(x, t) (\Delta x)^2$$

$$\Rightarrow P(x+\Delta x, t) - 2P(x, t) + P(x-\Delta x, t) = \left[\frac{\partial^2}{\partial x^2} P(x, t) \right] (\Delta x)^2$$

②

Putting in ①,

$$\therefore P(x, t+\Delta t) - P(x, t) = \frac{1}{2} \left[\frac{\partial^2}{\partial x^2} P(x, t) \right] (\Delta x)^2$$

Note:-

② can also be defined in the following way

$$g(x) = \frac{d}{dx} f(x) = \lim_{\Delta x \rightarrow 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

$$h(x) = \frac{d}{dx} g(x) = \frac{d^2}{dx^2} f(x) = \lim_{\Delta x \rightarrow 0} \frac{g(x+\Delta x) - g(x)}{\Delta x}$$

$$= \lim_{\Delta x \rightarrow 0} \frac{\lim_{\Delta x \rightarrow 0} \frac{f(x+2\Delta x) - 2f(x) + f(x+\Delta x)}{(\Delta x)^2}}{(\Delta x)^2}$$

$$= \lim_{\Delta x \rightarrow 0} \frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{(\Delta x)^2}$$

\therefore For small Δx ,

$$f(x+\Delta x) - 2f(x) + f(x-\Delta x) = (\Delta x)^2 \cdot \frac{d^2}{dx^2} f(x)$$

$$BC e^{\alpha x + \beta t} = D \alpha^2 e^{\alpha x + \beta t}$$

$$BC = \alpha^2 D$$

\therefore for $\Delta x \rightarrow 0$

$$P(x+\Delta x, t+\Delta t) - P(x, t) = \frac{1}{2} \left(\frac{\partial^2 P(x, t)}{\partial x^2} \right) (\Delta x)^2$$

$$\Rightarrow P(x, t+\Delta t) - P(x, t) = \frac{1}{\Delta t} \left(\frac{\partial^2 P(x, t)}{\partial x^2} \right) \cdot \frac{(\Delta x)^2}{\Delta t}$$

Now, for $\Delta t \rightarrow 0$,

$$\frac{\partial P(x, t)}{\partial t} = \frac{1}{2} \frac{(\Delta x)^2}{\Delta t} \cdot \frac{\partial^2 P(x, t)}{\partial x^2}$$

\downarrow
time derivative

\downarrow
spatial derivative

$$\text{Let } D = \frac{(\Delta x)^2}{2 \Delta t}$$

D is called the diffusion constant or diffusion coefficient.

$$\boxed{\frac{\partial P(x, t)}{\partial t} = D \cdot \frac{\partial^2 P(x, t)}{\partial x^2}}$$

Diffusion equation

In general, if we solve the diffusion equation, we can determine $P(x, t)$ (given the initial conditions).

For 3-D, the diffusion equation is, given that $\vec{r} = [x \ y \ z]$

$$\boxed{\frac{\partial P}{\partial t} = D \nabla^2 P}$$

$$\frac{\partial^2 f(x,y)}{\partial x^2} = 0$$

$$\Rightarrow \frac{\partial}{\partial x} f(x,y) = g(y) \Rightarrow f(x,y) = \alpha x + g(y)$$

$$\frac{\partial^2 f(x,y)}{\partial y^2} = 0$$

$$\Rightarrow f(x,y) = g(y)$$

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$$\frac{\partial P(\vec{r}, t)}{\partial t} = D_x \frac{\partial^2 P(\vec{r}, t)}{\partial x^2} + D_y \frac{\partial^2 P(\vec{r}, t)}{\partial y^2} + D_z \frac{\partial^2 P(\vec{r}, t)}{\partial z^2}$$

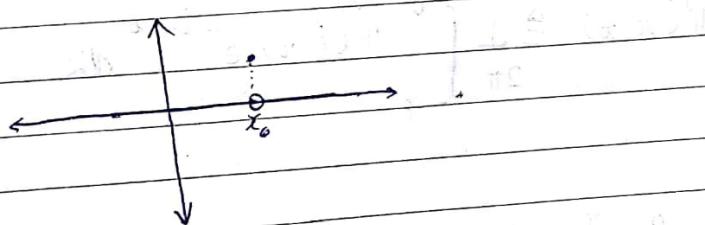
D_x, D_y, D_z - diffusion coefficient along the 3 axes.
 ⚡ for a homogenous medium

$$D_x = D_y = D_z = D$$

→ Solving the diffusion equation (1-D)

Initial condition :- $P(x, t=0) = S(x-x_0)$, where

$S(x)$ is a function 0 everywhere but $x_0 = 0$



For our case, take $x_0 = 0$
 $\therefore P(x, 0) = S(x)$

LECTURE VIII

Diffusion equation :-

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2}$$

Initial condition :-

$$P(x, 0) = S(x)$$

$$\int_{-\infty}^{\infty} u dx = \int_{-\infty}^{\infty} f(x) dx - \int_{-\infty}^{\infty} \frac{d}{dx} \left(\int_0^\infty e^{ikx} P(x, \tau) d\tau \right) dx$$

We use Fourier Transformation technique to solve the problem.

Fourier Transformation :-

$$\tilde{P}(k, t) \stackrel{\text{defn as}}{=} \int_{-\infty}^{\infty} P(x, t) e^{-ikx} dx$$

k = element in inverse space of x -space angular
e.g. we can move from time domain t to frequency ($\frac{2\pi}{t}$)

space.

Here we move from ~~real~~ space to inverse space.

Laplace Transform: Similar to Fourier transform, but we use e^{-kx} kernel

Inverse Fourier Transform:-

$$P(x, t) \stackrel{\text{defn}}{=} \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{P}(k, t) e^{ikx} dk$$

Now

We calculate the Fourier transform of $\frac{\partial P(x, t)}{\partial t}$ and $\frac{\partial^2 P(x, t)}{\partial t^2}$

$$\frac{\partial \tilde{P}(k, t)}{\partial t} = \int_{-\infty}^{\infty} \frac{\partial P(x, t)}{\partial t} e^{ikx} dx$$

top

$$\frac{\partial P(x, t)}{\partial t} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{P}(k, t) e^{ikx} dk$$

$$\frac{\partial \tilde{P}(k, t)}{\partial t} = \frac{1}{2\pi} \frac{\partial \tilde{P}(k, t)}{\partial t} - ①$$

$$vdx = V \int vdx - \int \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} R(x,t) e^{ikx} dx \right) e^{-ikx} dk$$

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$$\frac{\partial}{\partial x} P(k,t) = \int_{-\infty}^{\infty} \frac{\partial}{\partial x} P(x,t) e^{ikx} dx$$

By now by integration by parts,

$$= \left[e^{ikx} \cdot P(x,t) \right]_{-\infty}^{\infty} - ik \int_{-\infty}^{\infty} P(x,t) e^{ikx} dx$$

$$+ ik \int_{-\infty}^{\infty} P(x,t) e^{ikx} dx$$

For $x \rightarrow \pm\infty$, and finite t , $P(x,t) \rightarrow 0$, $\frac{\partial}{\partial x} P(x,t) \rightarrow 0$

$$\therefore \frac{\partial}{\partial x} P(k,t) = -ik \cdot P(k,t) \quad \text{--- (1)}$$

$$\text{Now, } \frac{\partial^2}{\partial x^2} P(k,t) = \int_{-\infty}^{\infty} \frac{\partial^2}{\partial x^2} P(x,t) e^{ikx} dx$$

$$= \left[e^{ikx} \cdot \frac{\partial}{\partial x} P(x,t) \right]_{-\infty}^{\infty} - e^{ikx} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} P(x,t) e^{ikx} dx$$

As $\frac{\partial}{\partial x} P(x,t) \rightarrow 0$ as $x \rightarrow \pm\infty$,

$$\frac{\partial^2}{\partial x^2} P(x,t) = -ik \frac{\partial}{\partial x} P(x,t) = -ik(-ik \tilde{P}(k,t))$$

c (from (1))

$$\Rightarrow \frac{\partial^2}{\partial x^2} P(k,t) = -k^2 P(k,t)$$

\therefore In ~~the~~ ~~in phase space~~ k -space, diffusion equation becomes

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}$$

Taking Fourier transform on both sides, and simplifying,

$$\frac{\partial}{\partial t} (\hat{P}(k, t)) = D \cdot (-k^2) \hat{P}(k, t)$$

$$\frac{\partial \hat{P}(k, t)}{\partial t} = -Dk^2 \hat{P}(k, t)$$

First order D.E.

Solving this, we get

$$\hat{P}(k, t) = C \cdot e^{-Dk^2 t}$$

From initial condition

$$P(x, 0) = \delta(x) = \int_{-\infty}^{\infty} \delta(x-x') e^{ikx'} dx' \quad \text{discussed}$$

$$P(x=0, t=0) = 1$$

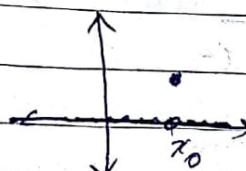
$$P(x, 0) = \underbrace{\delta(x)}$$

Dirac Delta function at $x=0$

$$\therefore \hat{P}(k, 0) = \int_{-\infty}^{\infty} \delta(x) \cdot C e^{ikx} dx = C$$

$$\Rightarrow C = \int_{-\infty}^0 \delta(x_0) \cdot C e^{ikx} dx, x_0 = 0$$

$$\delta(x-x_0)$$



$$\frac{\partial f(k,t)}{\partial t} = -D k^2 f(k,t)$$

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$$c = e^{ik_0 x_0} \quad (\text{this is because } \delta(x) \text{ is limit of Gaussian as width} \rightarrow 0)$$

since $x_0 = 0$, $c = 1$

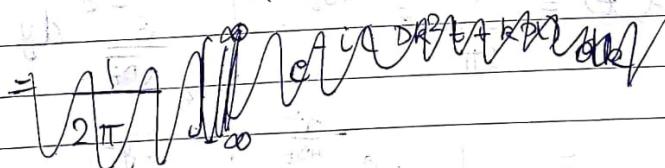
$$\therefore \tilde{P}(k,t) = e^{-Dk^2 t}$$

To calculate integration
we integrate Gaussian and then take the limit.

Now, we apply the inverse Fourier transform.

$$\therefore P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{P}(k,t) \cdot e^{-ikx} dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} e^{-Dk^2 t} dk$$



$$\Rightarrow P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sqrt{a^2 + Dk^2} e^{-ikx}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(Dk^2 t + ikx)} dk$$

$$\text{Let } a^2 = Dk^2 t, \quad 2ab = ikx$$

$$\Rightarrow b = \frac{ikx}{2\sqrt{Dt}}$$

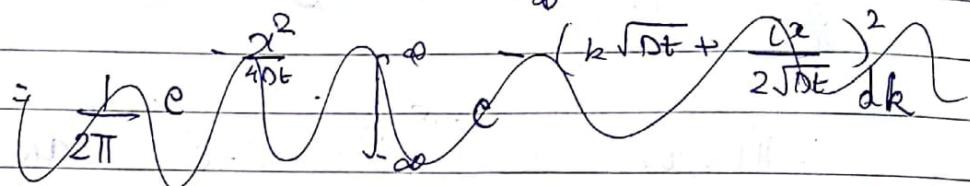
Adding and subtracting b^2 in exponent,

Q.

$$P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-[Dk^2 t + ikx + \left(\frac{ix}{2\sqrt{Dt}}\right)^2] + \left(\frac{ix}{2\sqrt{Dt}}\right)^2} dk$$

$$= \frac{1}{2\pi} e^{-(\frac{ix}{2\sqrt{Dt}})^2} \cdot \int_{-\infty}^{\infty} e^{-(a+b)^2} dk$$

$$\Rightarrow P(x,t) = \frac{1}{2\pi} e^{-\frac{x^2}{4Dt}} \cdot \int_{-\infty}^{\infty} e^{-(a+b)^2} dk$$



$$\text{Let } y = a+b = k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}$$

$$\Rightarrow dy = \sqrt{Dt} dk$$

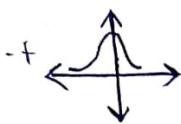
$$\therefore P(x,t) = \frac{1}{2\pi} e^{-\frac{x^2}{4Dt}} \cdot \int_{-\infty}^{\infty} \frac{e^{-y^2}}{\sqrt{Dt}} dy$$

$$= \frac{1}{2\pi\sqrt{Dt}} e^{-\frac{x^2}{4Dt}} \int_{-\infty}^{\infty} e^{-y^2} dy$$

Gaussian

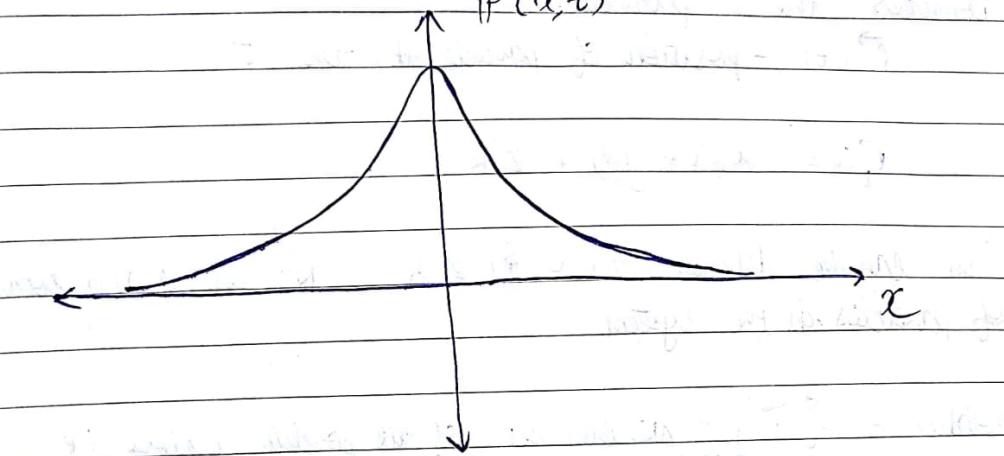
$$\int_{-\infty}^{\infty} y e^{-y^2} dy = \sqrt{\pi}$$

$$\therefore P(x,t) = \boxed{\frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}}$$



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$$P(x, t)$$



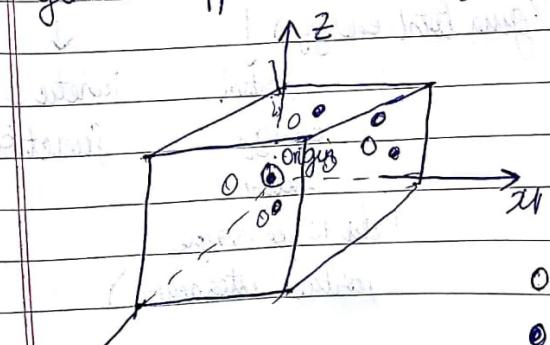
For the 3-D case, solving equation yields

$$\frac{(x^2 + y^2 + z^2)}{4Dt}$$

$$P(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \cdot c$$

LECTURE IX

general approach to study dynamics At a microscopic level



We wish to study dynamics of the entire system.

$\circ \Rightarrow$ solvent | water

$\circ \Rightarrow$ solute | protein or jet etc

Measurements done relative to origin

comes

Consider the i^{th} particle.

$\vec{r}_i(t)$:- position of particle at time t

$$\vec{r}_i(t) = x_i \hat{i} + y_i \hat{j} + z_i \hat{k}$$

This can be defined $\forall i \in \{1, 2, 3, \dots, N\}$, where N is total no. of particles in the system

Notation :- $\{\vec{r}_i\}$ = denotes set of all position vectors i.e
 $\{\vec{r}_i\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
set of position

Similarly, define a set of momenta as

$$\{\vec{p}\} = (\vec{p}_1(t), \vec{p}_2(t), \dots, \vec{p}_N(t))$$

Fact - If you know $\vec{r}_i, \vec{p}_i \forall i$, then you know everything about the system.

$$H(\{\vec{r}_i(t)\}, \{\vec{p}_i(t)\}) = U(\{\vec{r}_i\}) + K(\{\vec{p}_i\})$$

Hamiltonian of a system (gives total energy)

↓ ↓
potential energy kinetic energy function

(due to, for example, particle interaction)

We try to calculate

$$\frac{dH}{dt}$$
 ie variation of total energy with time.

Example:-

1-Dimensional case of a single particle :-

$$\therefore H(x, p) = U(x) + K(p)$$

$$\frac{dH}{dt} = \frac{dU(x)}{dt} + \frac{dK(p)}{dt}$$

$$= \underbrace{\frac{dU}{dx} \left(\frac{dx}{dt} \right)}_{\text{Acceleration}} + \underbrace{\frac{dK}{dp} \left(\frac{dp}{dt} \right)}_{\text{Force}}$$

If the system is isolated, then

For an isolated system, total energy is conserved.

$$\therefore H(x, p) = C \Rightarrow \frac{dH}{dt} = 0$$

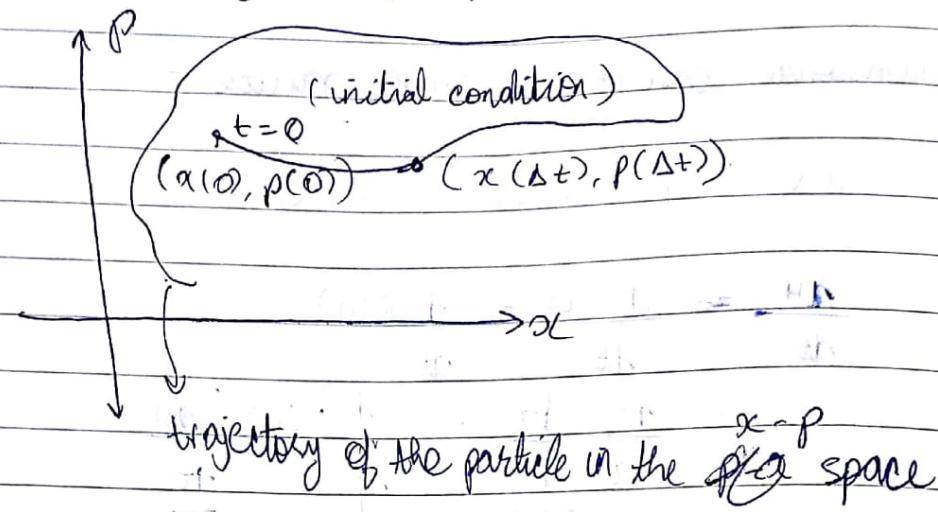
$$\Rightarrow \frac{dU}{dx} \left(\frac{dx}{dt} \right) = - \frac{dK}{dp} \cdot \left(\frac{dp}{dt} \right)$$

Hamilton's equations of motion :-

$$\begin{aligned} \frac{dp}{dt} &= - \frac{dU}{dx} \\ \frac{dx}{dt} &= \frac{dK}{dp} \end{aligned}$$

($= F$) \Rightarrow negative gradient of P.E is equal to the force on the particle

Dynamics = Finding x, p as functions of time.



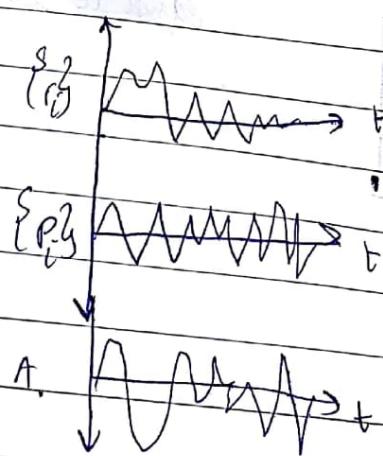
The x - p space is called the phase space.

For N particle in 3-D space, we have $3N$ dimension of x and $3N$ dimension of $p \Rightarrow 6N$ total dimensions.

General statement :- Any arbitrary property of a system can be found if it is a function of the position and momenta i.e.

$$A(x_i, p_i)$$

\downarrow
arbitrary property.



If we have $\langle A \rangle$ as a function of time,

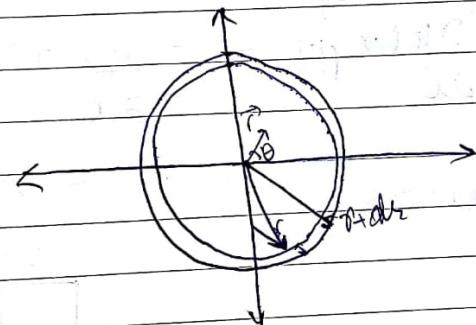
$$\langle A \rangle = \frac{1}{t_{\text{max}}} \sum_{i=0}^{t_{\text{max}}} A_i, \text{ where } A_i \text{'s are sample values of } A \text{ at certain times.}$$

$\langle A \rangle$ can be determined using experimentally found.



Computational Exercise - II

2-D Diffusion equation



Polar coordinates =
 $\vec{r} = x\hat{i} + y\hat{j}$
 $|\vec{r}| = r$

$N \Rightarrow$ number of random walkers (i.e. number of molecules).

Initial condition \Rightarrow starting from the origin
 Call two random numbers θ - one for r and one for θ , for each random walker.

After n steps, we would \rightarrow will find number of walkers lying

between r , $r\theta$ and $r + dr$,

Then, we find $P_N(r)$

Now, $P_N(r)$ should be

$$P_N(r) \propto$$

LECTURE - X

STATISTICAL PHYSICS

for one particle in one dimension,

$$H(x, p) = U(x) + K(p)$$

↓

Hamiltonian (total energy) function

Hamilton's equations of motion:-

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{\partial K}{\partial p}$$

$$\frac{dp}{dt} = -\frac{\partial H(x, p)}{\partial x} = -\frac{\partial U(x)}{\partial x}$$

for N particles in 3-dimensions,

$$H(S)$$

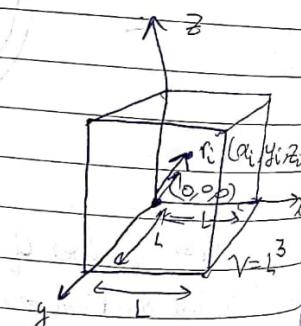
 $U(S)$ → potential energy function

 $K(S)$ → kinetic energy function

⇒ Hamilton's equations of motion :-

$$\frac{d\vec{r}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i}$$

$$\Rightarrow \begin{bmatrix} \frac{d x_i}{dt} \\ \frac{d y_i}{dt} \\ \frac{d z_i}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial H}{\partial p_{x,i}} \\ \frac{\partial H}{\partial p_{y,i}} \\ \frac{\partial H}{\partial p_{z,i}} \end{bmatrix}$$



Q 12-1

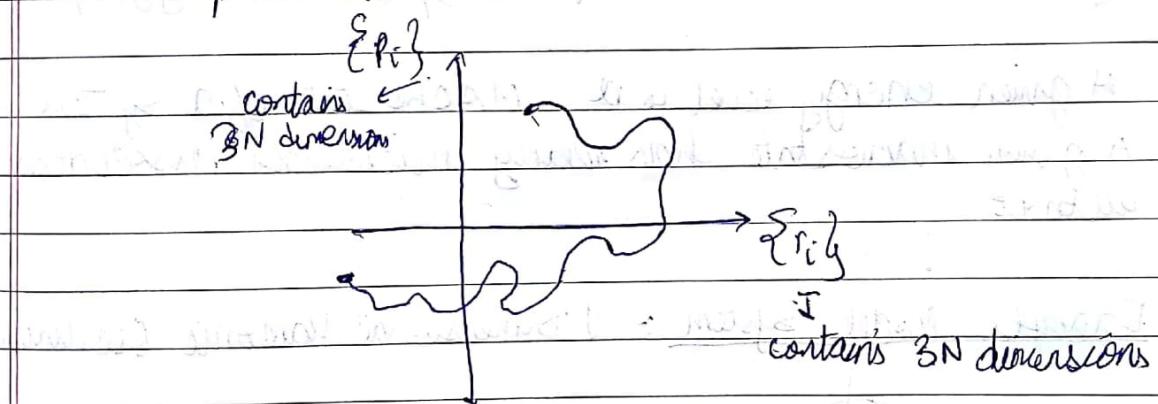
Microstate :-

$$\frac{d\vec{p}_i}{dt} = \cancel{\vec{F}} - \frac{\partial H}{\partial \vec{r}_i}$$

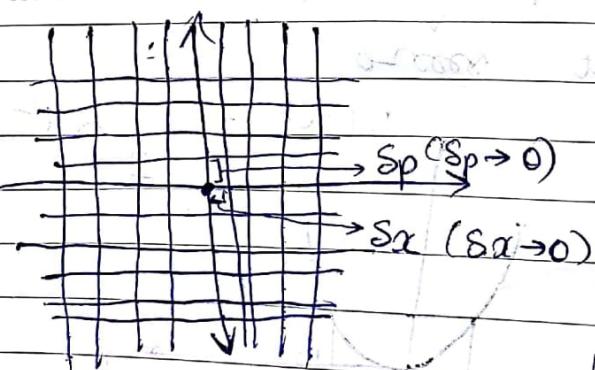
$$\Rightarrow \begin{bmatrix} \frac{dp_{x,i}}{dt} \\ \frac{dp_{y,i}}{dt} \\ \frac{dp_{z,i}}{dt} \end{bmatrix} = \begin{bmatrix} -\frac{\partial H}{\partial x_i} \\ -\frac{\partial H}{\partial y_i} \\ -\frac{\partial H}{\partial z_i} \end{bmatrix}$$

∴ For an N -particle system, we would have $6N$ equations.
we would

Phase space has $6N$ dimensions.



∴ If we return to 1-Dimensional case.

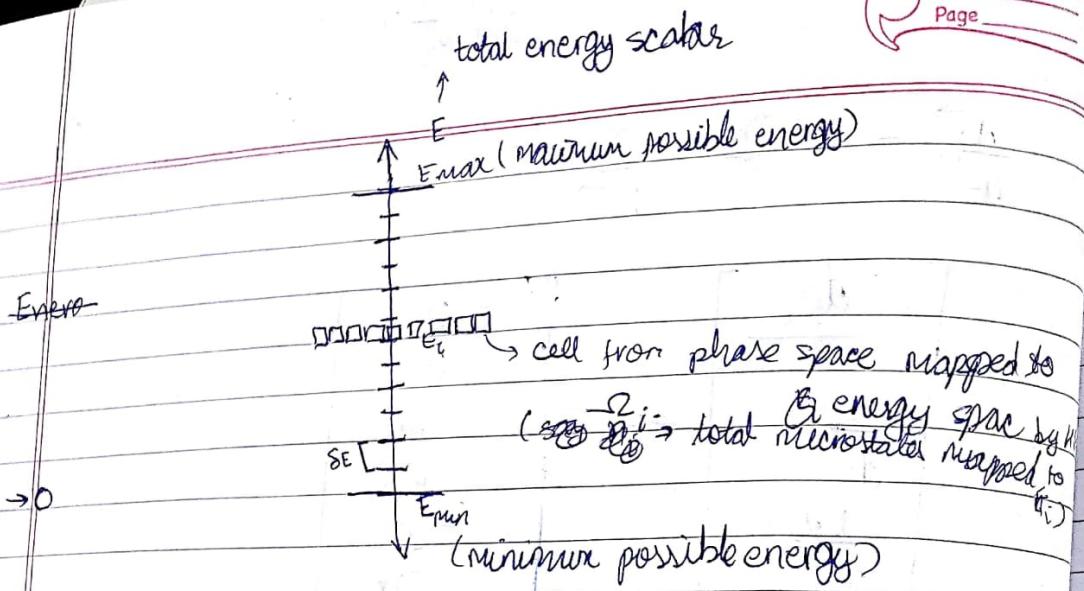


$$\text{Area of a cell} = S_x \cdot S_p = \frac{h}{2\pi}$$

Unit of angular momentum

Here, h is the Planck's constant
(has order 10^{-34})

Microstate:- Each cell in the phase space i.e. a point in the phase space.
(α_m)

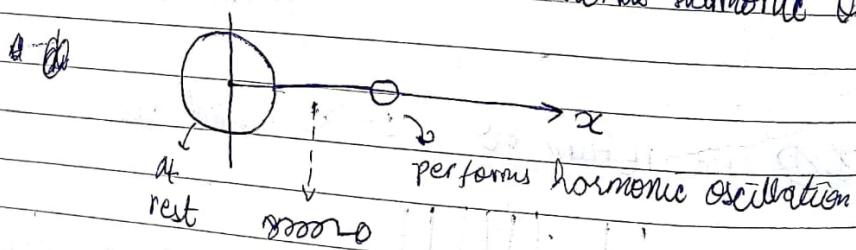


Energy Level Diagram

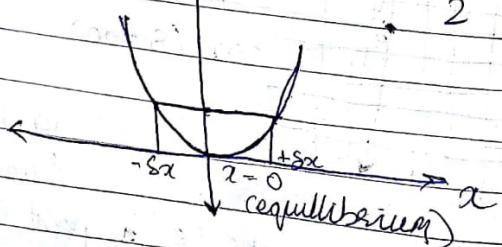
$n(x, p)$: Function from phase space to energy space

A given energy level is a MACRO state of a system.
A given macrostate has many microstates associated with it.

Example Model System - 1 Dimensional Harmonic Oscillator



$$U(x) = \frac{1}{2} k x^2, k \text{ is called the spring constant}$$



$$\begin{aligned} & \text{if } C^{-1}AC - \lambda I \\ & = C^{-1}AC - \lambda C^{-1}CI \end{aligned}$$

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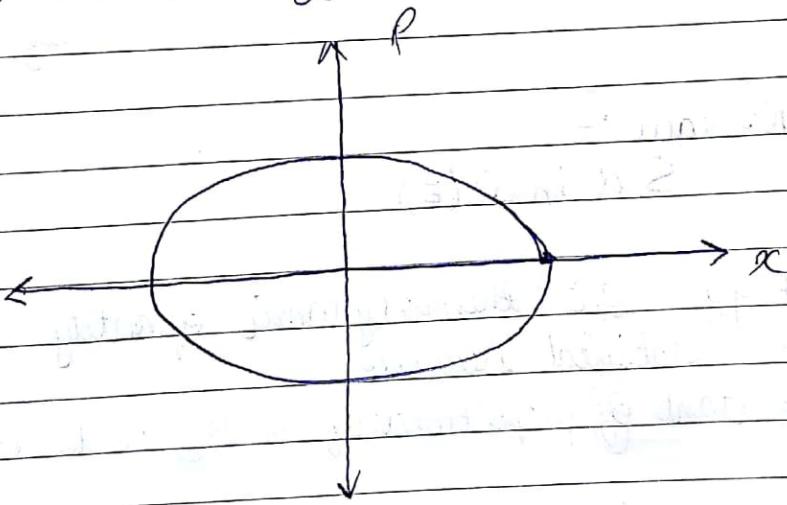
For this system,

$$\begin{aligned} H(x, p) &= U(x) + K(p) \\ &= \frac{1}{2} kx^2 + \frac{p^2}{2m} = E \text{ (constant), as isolated system} \end{aligned}$$

$$\Rightarrow \boxed{\frac{x^2}{(\sqrt{\frac{2E}{k}})^2} + \frac{p^2}{(\sqrt{\frac{2mE}{k}})^2} = 1}$$

ellipse

\therefore Trajectory in phase space is an ellipse. Particle visits only those microstates with energy E .



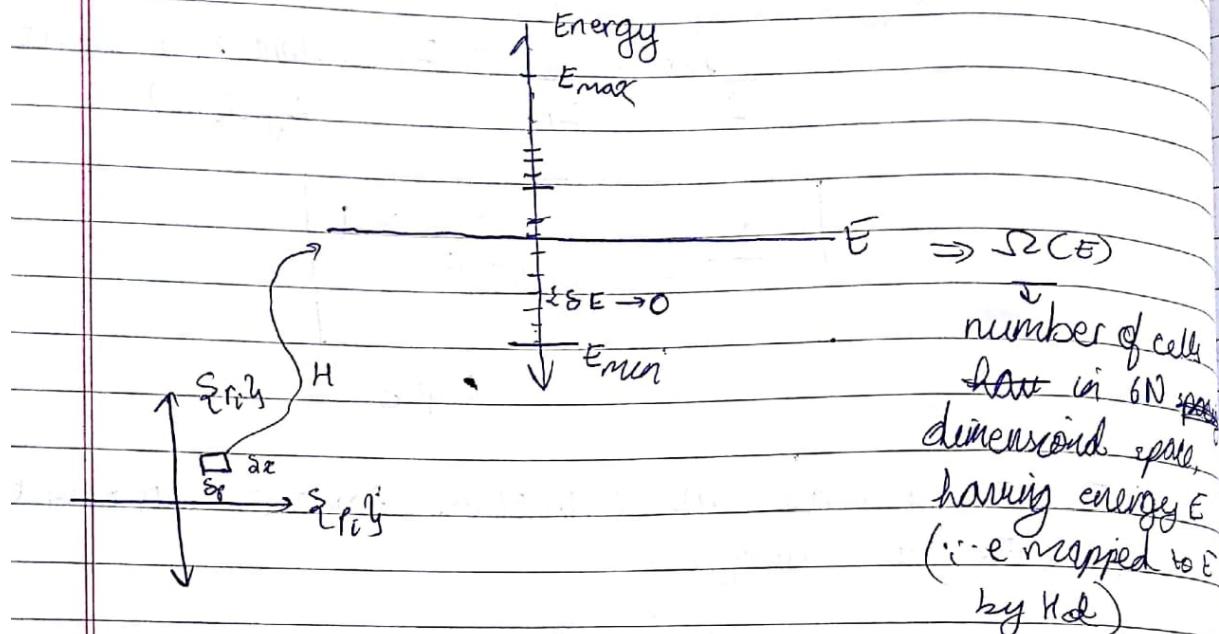
LECTURE - ~~XI~~ XII

for an N -particle system,

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N), K(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$$

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) = U + K$$

We move from $6N$ dimensions to 1 dimension of energy with H acting as the map.



Boltzmann's Law :-

$$S \propto \ln \Omega(E)$$

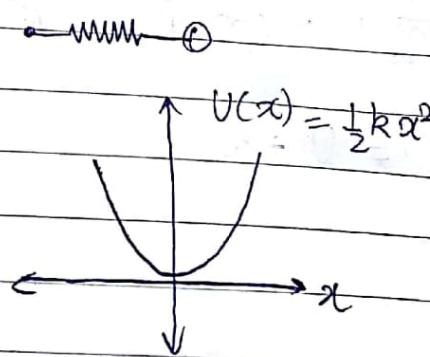
S:- entropy, ~~size~~ (thermodynamic quantity).

$\Omega(E)$:- statistical measure.

The constant of proportionality is k_B i.e. the Boltzmann ^{const}.

$$\therefore S = k_B \ln (\Omega(E))$$

↳ Example Model :- 1-D Harmonic Oscillator



k → measure of 'strength'

of spring

$$\text{B} k = \frac{d^2 U(x)}{dx^2}$$

$$H(x, p) = \frac{1}{2} k x^2 + \frac{p^2}{2m} = E \quad (\text{initial energy, constant})$$

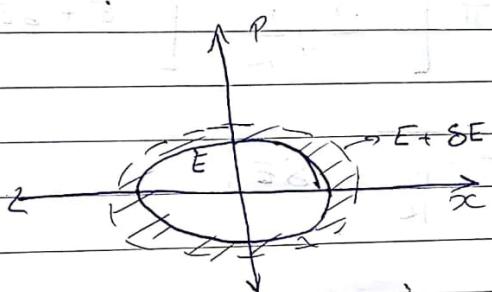
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$$\left(\frac{p^2}{2mE}\right)^2 + \frac{kx^2}{2E} = 1$$

(1)

→ ellipse

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \quad a = \sqrt{\frac{2E}{k}}, \quad b = \sqrt{2mE}$$



Now, we wish to find $\Omega(E)$. i.e.

Hypothesis - All states of the system have equal probabilities
i.e. are equally likely at a given time -

$\therefore P = \frac{1}{\Omega(E)}$ for each system state ($\Omega(E)$ total states for energy E)

We find the area of elliptical ring b/w ellipse of E and ellipse of $E + SE$. Then

Taking $\lim_{SE \rightarrow 0}$, we find the number of microstates corresponding to E . (rather $\Omega(E) \propto$ difference of areas $(SE \rightarrow 0)$)

i.e. $\Omega(E) \propto$ circumference of an ellipse.

$$A(E+SE) - A(E) = \pi \left[\sqrt{\frac{2E+SE}{k}} + \sqrt{2m(E+SE)} - \sqrt{\frac{2E}{k}} - \sqrt{2mE} \right]$$

$$= \pi \left[\frac{2}{k} \left(\sqrt{E+SE} - \sqrt{E} \right) + \sqrt{2m} \left(\sqrt{E+SE} - \sqrt{E} \right) \right]$$

$$A(E+SE) - A(E) = \pi \left[\sqrt{\frac{2}{k}} (\sqrt{E+SE} - \sqrt{E}) \right]$$

$$= \pi \left[\left(\sqrt{\frac{2}{k}} + \sqrt{2m} \right) (\sqrt{E+SE} - \sqrt{E}) \right]$$

$$A(E+SE) - A(E) = \pi \left[\sqrt{2m(E+SE)} - \frac{\sqrt{2(E+SE)}}{k} - \pi \sqrt{2mE} \right]$$

$$= \pi \left[2 \sqrt{\frac{m}{k}} [E+SE - E] \right]$$

$$= 2\pi \sqrt{\frac{m}{k}} \cdot (SE)$$

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$\Omega(E) \propto$ circumference of ellipse

$$\Omega(E) \propto \sqrt{E}$$

i.e. number of accessible microstates increases with E.

S increases with E. (as $S \propto \ln \Omega(E)$)

∴ ~~when~~ $\Omega(E) = 1$ (i.e. only one state), S=0 (occurs in crystals). As energy is added, S increases (as E and $\Omega(E)$ increases).

When gas is released it expands rather than compresses as it tends to increase $\Omega(E)$.

ʃ

Information entropy -

$$S = - \sum_i p_i \ln(p_i) \quad \text{↑}$$

the probability for system to be in
ith state.

For an isolated system with $\Omega(E)$ states,

$$\pi \sqrt{2ME} \cdot \sqrt{\frac{2\pi}{k}}$$

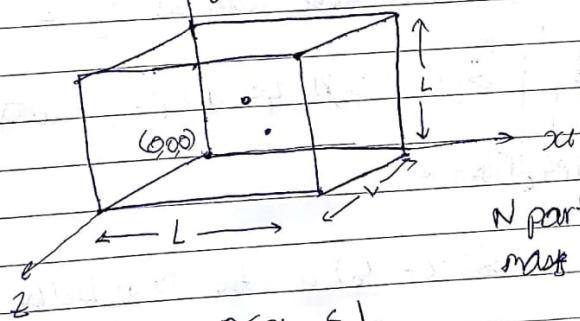
$$p_i = \frac{1}{\Omega(E)}$$

(definition of entropy?!)

$$\therefore S = -k_B \sum_i \frac{1}{\Omega^2} \ln\left(\frac{1}{\Omega^2}\right) \quad \begin{matrix} \text{(entropy (thermodynamic)} \\ = k_B \cdot \text{info-entropy} \end{matrix}$$

$$\Rightarrow S = k_B \ln(\Omega(E))$$

↳ Example model - II :- Gas cylinder



N particles, identical with mass m .

$$0 \leq x_i \leq L$$

$$0 \leq y_i \leq L$$

$$0 \leq z_i \leq L$$

$$H(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^N \frac{\vec{p}_i \cdot \vec{p}_i}{2m} + U(\vec{r}_i)$$

$$= U(\vec{r}_i) + \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2$$

C occurs
as (as E increases)

reverses as it

According to our model, assume that particles don't interact
(ideal gas model).

$$\therefore U(\vec{q}_1, \vec{q}_2) = 0$$

$$H(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2) = \frac{1}{2m} \sum_{i=1}^{3N} (p_x^{i2} + p_y^{i2} + p_z^{i2}) = E$$

$$\Rightarrow E = \sum_{i=1}^{3N} (p_x^{i2} + p_y^{i2} + p_z^{i2}) = (\sqrt{2mE})^2$$

This equation represents a
3N dimensional hypersphere, with radius $\sqrt{2mE}$.

All microstates falling on this sphere map to E.

We find $\Omega(E)$

To do this, we must visit all possible states in phase space, and sum over those with energy E.

$$\text{i.e. } \Omega(E) \propto \int_{-\infty}^{\infty} S(H(\vec{q}_1, \vec{p}_1) - E) d\vec{q}_1 d\vec{p}_1$$

or proportional, $\vec{p}_1 = \{p_i\} = -\infty$

as difference in
dimensionality

$S(x - x_0)$ is the Dirac Delta function

Integration over entire cube, over all momenta, and we integrate only those points for which $\delta(S(x_0) - 0) = 0$ i.e.

$$\therefore H(\vec{q}_1, \vec{p}_1) = E$$

Since $H(\vec{q}_1, \vec{p}_1) = K(\vec{q}_1)$, we have

$$\Omega(E) \propto \int_{\vec{q}_1=0}^L d\vec{q}_1 \cdot \int_{\vec{p}_1=-\infty}^{\infty} S(K(\vec{q}_1) - E) d\vec{p}_1$$

EN.

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S(\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - E) dx dp = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S(x - \sqrt{\frac{2mE}{k}}) dx dp$$

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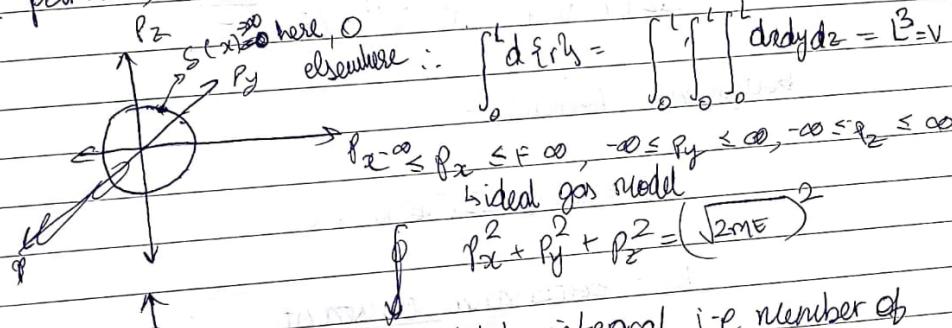
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$$\Rightarrow \Omega(E) \propto \int_0^L d\vec{r} \cdot \int_{-\infty}^{\infty} S\left(\sum_{i=1}^N p_i^2 - E\right) dp$$

this is itself a triple integral multiple integral with

$$\Rightarrow \Omega(E) \propto \frac{L^{3N}}{V^N} \int_{-\infty}^{\infty} S\left(\sum_{i=1}^N p_i^2 - E\right) dp$$

. for 1 particle, $0 \leq x \leq L, 0 \leq y \leq L, 0 \leq z \leq L$



Now, the total integral i.e number of microstates with energy E, is proportional to surface area of the sphere.

Now, surface area of an N-dimensional sphere of radius $r \propto r^{N-1}$

$$\int_{-\infty}^{\infty} S\left(\frac{1}{2m} \left(\sum_{i=1}^N p_i^2 - E\right)\right) dp \propto \text{surface area of } 3N- \text{dimensional sphere of radius } \alpha \left(\frac{2mE}{k}\right)^{\frac{3N-1}{2}}$$

$$\therefore \Omega(E) \propto \sqrt{N} \cdot \pi^{\frac{3N-1}{2}} (2mE)^{\frac{3N-1}{2}}$$

LECTURE - XI C

Statistical Mechanics

$\Omega(N, V, E)$ = number of accessible microstates for N particles, in volume V , with energy E .

For an ideal gas of N particles in volume V , isolated with constant energy E ,

$$\Omega(N, V, E) \propto V^N \cdot (E)^{\frac{3N-1}{2}}$$

Boltzmann formula:-

$$S = k_B \ln \Omega(N, V, E)$$

k_B = Boltzmann constant

or microcanonical ensemble

NVE ensemble = systems with constant N, V, E (identical systems, in some sense). In thermodynamics, such a system is called an isolated system.

Now,

$$dS(N, V, E) = \left(\frac{\partial S}{\partial E}\right)_{N, V} dE + \left(\frac{\partial S}{\partial V}\right)_{N, E} dV + \left(\frac{\partial S}{\partial N}\right)_{V, E} dN$$

L0

$$\left(\frac{\partial S}{\partial E}\right)_{N, V} = k_B \cdot \frac{1}{\Omega(N, V, E)} \quad \frac{\partial \Omega(N, V, E)}{\partial E} = k_B \left(\frac{2 \ln \Omega}{\partial E}\right)$$

$$\left(\frac{\partial S}{\partial V}\right)_{N, E} = k_B \cdot \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N, E}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V, E} = k_B \cdot \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V, E}$$

From conventional thermodynamics

$$TdS = dE + PdV - \mu dN$$

(first law of thermodynamics)

($dQ = dU + dW$, μdN factor for change to account for change in N. μ is called chemical potential)

$$\Rightarrow dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN \quad \text{--- (2)}$$

Comparing (1) and (2),

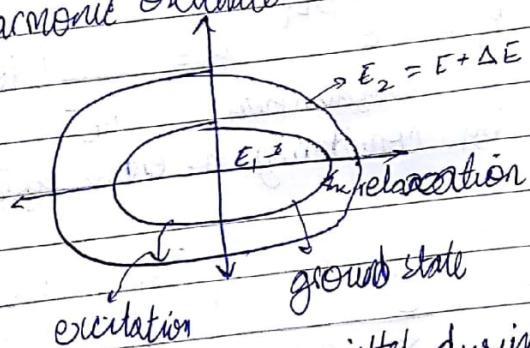
$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T} \Rightarrow \frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V}$$

$$\left(\frac{\partial S}{\partial V} \right)_{N,E} = \frac{P}{T} \Rightarrow \frac{P}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial V} \right)_{N,E}$$

$$\left(\frac{\partial S}{\partial N} \right)_{V,E} = -\mu \Rightarrow -\frac{\mu}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial N} \right)_{V,E}$$

\therefore we found a relationship between Ω , and a statistical quantity, and the general thermodynamic quantities.

for 1-D Harmonic oscillator

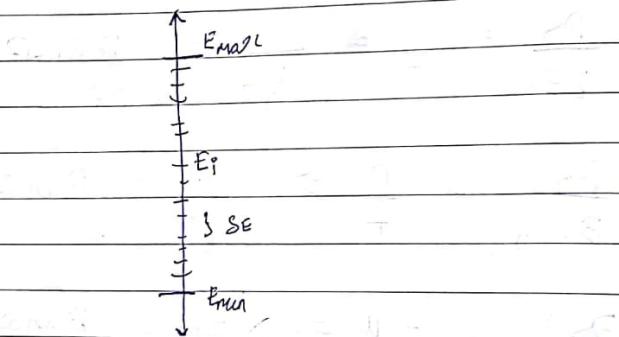
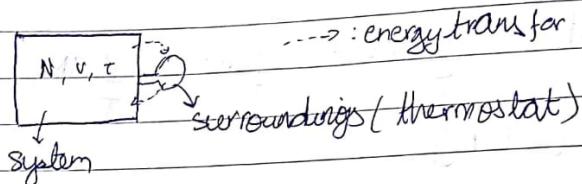


we can measure energy emitted during relaxation, in

CLOSED SYSTEM SYSTEM :- system can exchange ~~part~~
energy, NOT particles from the surroundings

: N → fixed, V → fixed, E = will vary, T → fixed

: This is an NVT ensemble or canonical ensemble in S.



Case

Here system visits different energy levels.

What is the probability that the system is in state with energy E_i ?

Boltzmann derived the following :-

$$P_i \propto e^{-\beta E_i}, \quad \beta = \frac{1}{k_B T} \quad (\text{for discrete energy levels})$$

can be derived by considering the entire system, and applying
procedure.

Since $\sum_i P_i = 1$,

$$\therefore P_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

introduced for dimension
no account for classical systems
 \hbar is an arbitrary width for quantum systems

\hbar is Planck's constant

For continuous systems

$$P_i = P(E_{\text{r},j}, p_{\text{r},j}) \cdot c$$

each point in phase space has a probability

a probability

PC

DR

ln

⇒ -

⇒

$$P_i =$$

$$\frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

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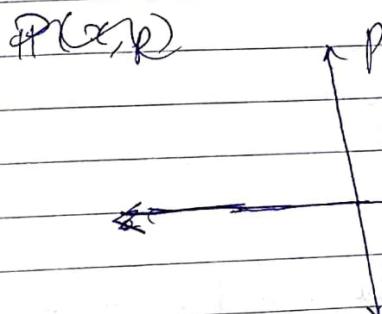
we define

$$Z = \sum_i e^{-\beta E_i}$$

as the partition function
(for discrete).

Case - I - 1 D Harmonic oscillator, with variable energy.
(closed)

$$H(x, p) = \frac{1}{2} kx^2 + \frac{p^2}{2m}$$



$$P(x, p) \propto e^{-\beta H(x, p)} \propto e^{-\beta \left[\frac{1}{2} kx^2 + \frac{p^2}{2m} \right]}$$

∴ As we move away from origin $P(x, p)$ decreases.

$$Z = \sum_i e^{-\beta E_i}$$

$$\ln(Z) = \ln \left(\sum_i e^{-\beta E_i} \right)$$

$$\Rightarrow -\frac{\partial \ln(Z)}{\partial \beta} = \frac{1}{\sum_i e^{-\beta E_i}} \cdot \sum_i E_i \cdot e^{-\beta E_i}$$

$$\Rightarrow -\frac{\partial \ln(Z)}{\partial \beta} = \sum_i E_i \cdot P_i = \boxed{\langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta}}$$

$$\frac{\partial^2 x}{\partial}$$

$\langle E \rangle$ is the internal energy of the system - the average energy of the closed system.

TUTORIAL-I

FOURIER TRANSFORM

$$\text{FORWARD} \rightarrow F(k) = \int_{-\infty}^{\infty} f(x) e^{i 2 \pi k x} dx$$

$$f(x) = \int_{-\infty}^{\infty} F(k) e^{-i 2 \pi k x} dk$$

Phenomenon

If $P(x, t)$ is a PDF

$$(i) \quad \frac{\partial (\tilde{P})}{\partial t} \Rightarrow \frac{\partial \tilde{P}}{\partial t} = \frac{\partial (\tilde{P})}{\partial t}$$

$$\frac{\partial \tilde{P}}{\partial t} = \int_{-\infty}^{\infty} \frac{\partial P}{\partial t} e^{i k x} dx = \frac{\partial}{\partial t} \left[\int_{-\infty}^{\infty} P(x, t) e^{i k x} dx \right] + 0$$

$$= \int_{-\infty}^{\infty} \left(\frac{\partial P}{\partial t} \right) e^{i k x} dx + \int_{-\infty}^{\infty} P(x, t) \cdot \left(\frac{\partial}{\partial t} (e^{i k x}) \right) dx$$

$$= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} (P e^{i k x}) dx$$

$$= \frac{1}{2t} \int_{-\infty}^{\infty} P e^{i k x} dx$$

$$\frac{\partial \tilde{P}}{\partial t} = \frac{1}{2t} (\tilde{P})$$

$$\frac{\partial}{\partial x} \left(\frac{\partial \tilde{P}}{\partial x} \right) = -k \frac{\partial \tilde{P}}{\partial x}$$

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i) $\frac{\partial \tilde{P}}{\partial x} = -ik \tilde{P}$

$$\frac{\partial \tilde{P}}{\partial x} = \int_{-\infty}^{\infty} \frac{\partial P}{\partial x} e^{ikx} dx *$$

$$= \int_{-\infty}^{\infty} \frac{\partial P}{\partial x} e^{ikx} dx + ik \int_{-\infty}^{\infty} P e^{ikx} dx - ik \int_{-\infty}^{\infty} P e^{ikx} dx$$

$$= \int_{-\infty}^{\infty} \left(\frac{\partial P}{\partial x} e^{ikx} \right) dx + \int_{-\infty}^{\infty} P \frac{\partial (e^{ikx})}{\partial x} dx$$

$$- ik \frac{\partial \tilde{P}}{\partial x}$$

$$= \int_{-\infty}^{\infty} \frac{\partial [P(e^{ikx})]}{\partial x} dx - ik \tilde{P}$$

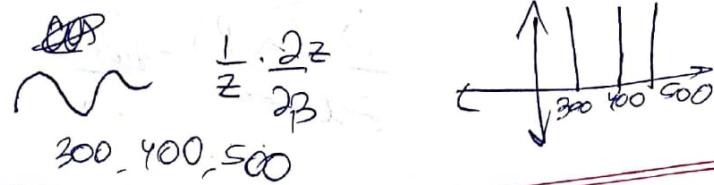
$$\hookrightarrow [P e^{ikx}]_{-\infty}^{\infty} = 0$$

$$\frac{\partial \tilde{P}}{\partial x} = -ik \tilde{P}$$

iii) $\frac{\partial^2 \tilde{P}}{\partial x^2} = (-ik)^2 \cdot \tilde{P} = -k^2 \tilde{P}$

$$\frac{\partial \tilde{P}}{\partial x} = \frac{\partial F}{\partial x}, F = \frac{\partial \tilde{P}}{\partial x} \Rightarrow F = -ik \frac{\partial \tilde{P}}{\partial x}$$

$$= -ik F = (-ik)^2 \tilde{P}$$



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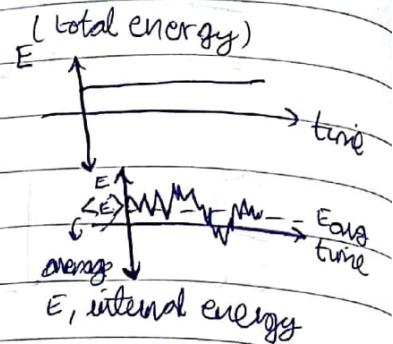
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LECTURE - XIII

Systems :-

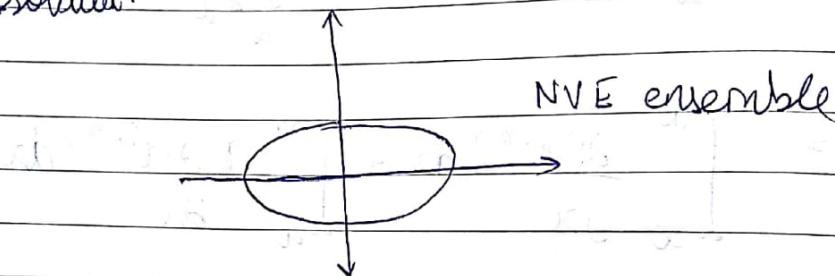
Isolated :- Constant energy; $\frac{dH}{dt} = 0$

Closed :- energy exchange; $\frac{dH}{dt} \neq 0$

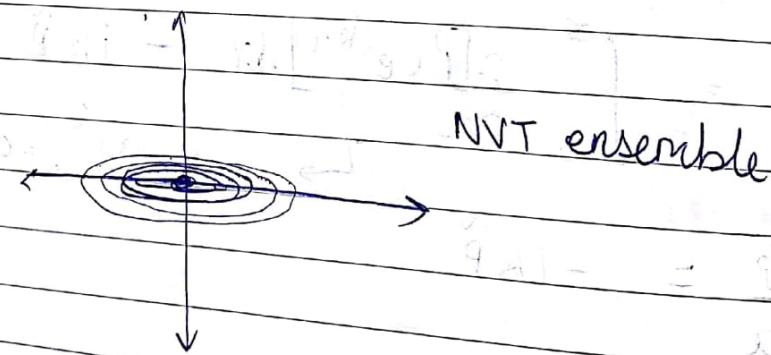


1-D Harmonic oscillator

Isolated :-



Closed :-



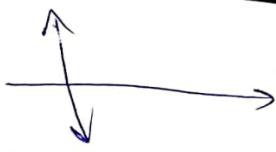
$$P_j \propto e^{-\beta E_j}$$

(probability P_j of finding at j^{th} state at energy E_j)

$$\Rightarrow P_j = e^{-\beta E_j}$$

where

$$Z = \sum_j e^{-\beta E_j}$$



For continuous systems

$$P(x, p) \propto e^{-\beta H(x, p)} = e^{-\beta \left(\frac{1}{2} kx^2 + \frac{p^2}{2m} \right)}$$

Z :- similar to the wavefunction of particle-in Q.M.

For N-dimensions,

$$P(\{r_i\}, \{p_i\}) \propto e^{-\beta H(\{r_i\}, \{p_i\})}$$

Here Z ,

$$Z = \frac{1}{h^{3N}} \iiint e^{-\beta H(\{r_i\}, \{p_i\})} dr_1 dp_1$$

to account for dimensions.

We consider states with discrete energy states.

We attempt to describe all macro-properties using the partition function Z .

(i) Internal energy

$$Z = \sum_j e^{-\beta E_j} \rightarrow \ln(Z) = -\ln \left(\sum_j e^{-\beta E_j} \right)$$

$$\Rightarrow -\frac{\partial \ln(Z)}{\partial \beta} = \sum_j E_j \left(\frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}} \right) = \sum_j E_j P(E_j)$$

$$\Rightarrow -\frac{\partial \ln(Z)}{\partial \beta} = \langle E \rangle$$

∴ $\boxed{\langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta}}$

(ii) Heat capacity

Consider

$$\Rightarrow \sum_j E_j \frac{e^{-\beta E_j}}{\sum e^{-\beta E_j}} = -\frac{\partial \ln(z)}{\partial \beta}$$

$\sum e^{-\beta E_j} \leftarrow z$

$$\Rightarrow \sum_j E_j \cdot e^{-\beta E_j} = -z \frac{\partial \ln(z)}{\partial \beta}$$

Differentiating,

$$\sum_j E_j^2 \cdot (e^{-\beta E_j}) = + \left[z \frac{\partial^2 \ln(z)}{\partial \beta^2} + \frac{1}{2} \frac{\partial z}{\partial \beta} \frac{\partial \ln(z)}{\partial \beta} \right]$$

$$\Rightarrow \frac{1}{z} \sum_j E_j^2 \left(\frac{e^{-\beta E_j}}{z} \right) = \frac{\partial^2 \ln(z)}{\partial \beta^2} + \frac{1}{z} \frac{\partial z}{\partial \beta} \frac{\partial \ln(z)}{\partial \beta}$$

$$\sum_j E_j^2 \cdot p(E_j) = \frac{\partial^2 \ln(z)}{\partial \beta^2} + \frac{1}{z} \frac{\partial z}{\partial \beta} \frac{\partial \ln(z)}{\partial \beta}$$

$$\therefore \langle E^2 \rangle = \frac{\partial^2 \ln(z)}{\partial \beta^2} + \frac{1}{z} \frac{\partial z}{\partial \beta} \frac{\partial \ln(z)}{\partial \beta} \quad \text{using } \frac{\partial z}{\partial \beta} = \frac{1}{2} \frac{\partial \ln(z)}{\partial \beta} \quad (2)$$

$$\therefore \langle E^2 \rangle = \frac{\partial^2 \ln(z)}{\partial \beta^2} + \left(\frac{\partial \ln(z)}{\partial \beta} \right)^2$$

$$\therefore \langle E^2 \rangle = \frac{\partial^2 \ln(z)}{\partial \beta^2} + \langle E \rangle^2 \quad [\text{as } \langle E \rangle = -\frac{\partial \ln(z)}{\partial \beta}]$$

$$\therefore \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln(z)}{\partial \beta^2}$$

$$\therefore \langle (\Delta E)^2 \rangle = \frac{\partial^2 \ln(z)}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{\partial \ln(z)}{\partial \beta} \right)$$

$$= -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$\text{Also, } \beta = \frac{1}{k_B T} \Rightarrow \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\Rightarrow \frac{\partial \langle E \rangle}{\partial T} = -\frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = -\frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{1}{k_B T^2}$$

$$\langle (\Delta E)^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = -\frac{\partial \langle E \rangle}{\partial T} \cdot \frac{1}{k_B T^2}$$

$$\Rightarrow \langle (\Delta E)^2 \rangle = \frac{1}{k_B \cdot T^2} \cdot 2 \langle E \rangle = \frac{2 k_B \langle E \rangle}{T}$$

$$\boxed{\langle (\Delta E)^2 \rangle = \frac{k_B T^2}{2T} \cdot 2 \langle E \rangle}$$

Note that $\frac{\partial \langle E \rangle}{\partial T} = C_V$ i.e. heat capacity at constant volume.

\therefore we can calculate C_V from $\langle (\Delta E)^2 \rangle$ at a given temperature.

Also note that, since $\langle (\Delta E)^2 \rangle \geq 0$

$$\Rightarrow \frac{\partial \langle E \rangle}{\partial T} \geq 0$$

CxKy

(iii) The Entropy and Free Energy

$$S = -k_B \sum_j P_j \ln(P_j)$$

$$P_j = \frac{e^{-\beta E_j}}{Z}$$

$$\therefore S = -k_B \sum_j \frac{\beta e^{-\beta E_j}}{Z} \cdot \ln\left(\frac{e^{-\beta E_j}}{Z}\right)$$

$$= k_B \left[\beta \sum_j e^{-\beta E_j} E_j P_j + \ln(Z) \right]$$

$$= k_B [\beta \cdot \langle E \rangle + \ln(Z)]$$

$$k_B \beta = \frac{1}{k_B T}$$

$$\therefore S = \frac{\langle E \rangle}{T} + k_B \ln(Z)$$

$$\Rightarrow TS = \langle E \rangle + k_B T \ln(Z)$$

$$\Rightarrow \boxed{\langle E \rangle - TS = -k_B T \ln(Z)}$$

Remember that, the ~~Gibbs~~ Helmholtz Free Energy (F),

$$F = \langle E \rangle - TS$$

$$\therefore \boxed{F = -k_B T \ln(Z)}$$

PP

(iv) Pressure

Microscopically, we can define pressure as

$$P_j = - \frac{\partial H(S, r^3, S_p^3)}{\partial V}$$

$$\therefore \langle P_j \rangle = \sum_j P_j \cdot P(E_j) \quad \text{macroscopic pressure}$$

$$= - \sum_j \frac{\partial E_j}{\partial V} \cdot \frac{e^{-\beta E_j}}{Z}$$

$$\text{Also, } \frac{\partial \ln(Z)}{\partial V} = \sum_j \frac{\partial Z}{\partial V} = \sum_j e^{-\beta E_j} \cdot \frac{\partial}{\partial V} e^{-\beta E_j}$$

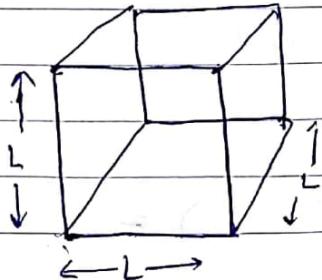
$$= -\beta \cdot \sum_j \frac{\partial E_j}{\partial V} \cdot \frac{e^{-\beta E_j}}{Z}$$

$$\therefore \langle P \rangle = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial V}$$

$$\Rightarrow \boxed{\langle P \rangle = k_B T \frac{\partial \ln(Z)}{\partial V}}$$

IDEAL-GAS SYSTEM

N atoms, confined in a volume V , in a closed system.



Since this is an ideal gas,

$$U(\xi_{r^3}, \xi_{p^3}) = 0$$

$$H(\xi_{r^3}, \xi_{p^3}) = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i$$

$$Z = \frac{1}{h^{3N}} \prod_{\{r^3\} \{p^3\}} e^{-\frac{\beta}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i} d\xi_{p^3} d\xi_{r^3}$$

$$\text{since } K(\xi_{r^3}, \xi_{p^3}) = K(\xi_{p^3})$$

$$Z = \cancel{\int_{r^3} h^{3N}} Z_r \cdot Z_p$$

$$Z_r = \int_{\{r^3\}} d\xi_{r^3} = V^N$$

$$Z_p = \int_{\{p^3\}} e^{-\frac{\beta}{2m} \left(\sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i \right)} \cdot d\xi_{p^3}$$

$$= \int_{\{p^3\}} e^{-\frac{\beta}{2m} \left(\sum_{i=1}^N p_x^{i2} + p_y^{i2} + p_z^{i2} \right)} d\xi_{p^3}$$

These are $3N$ integrals, all of which are Gaussian's with the same value.

$$Z_p = \left[\int_{x=-\infty}^{\infty} \left(e^{-\frac{\beta}{2m} x^2} \right)^{3N} dx \right] = e^{-\frac{\beta}{2m} \sum_{i=1}^{3N} p_i^2} = \frac{N}{\prod_{i=1}^{3N}} e^{-\frac{\beta}{2m} (p_x^2 + p_y^2 + p_z^2)}$$

$$Z_p = \left(\frac{\sqrt{2\pi T}}{\beta} \right)^{3N}$$

$$\Rightarrow Z_p = \left(\frac{2\pi T}{\beta} \right)^{\frac{3N}{2}} = \left(2\pi k_B T \right)^{\frac{3N}{2}}$$

$$\boxed{Z = \frac{1}{h^{3N}} \cdot V^N \cdot \left(2\pi \frac{k_B T}{\beta} \right)^{\frac{3N}{2}}}$$

Since we know Z , we can find all macroscopic properties.

$$\langle P \rangle = \frac{1}{P_0} \cdot \frac{\partial \ln(Z)}{\partial V}$$

$$= \frac{1}{P_0} \frac{\partial}{\partial V} [N \ln(V)] \quad (\text{using } Z = V^N \left(2\pi k_B T \right)^{\frac{3N}{2}})$$

$$= \frac{N}{P_0 V} \Rightarrow \langle P \rangle = \frac{k_B N T}{V}$$

$$\Rightarrow \frac{\partial \ln Z}{\partial V} = \frac{\partial \ln V}{\partial V}$$

$$\Rightarrow \langle P \rangle V = k_B N T \quad \text{Ideal gas equation}$$

LECTURE - XIV

If
The

Calculating Z for simple case - $N=1$ ~~and~~, in 2-D box.

$$Z = \frac{1}{h^2} \int_0^L \int_0^L dx dy \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{p_x^2 + p_y^2}{2m}} dp_x dp_y$$

$$= \frac{L^2}{h^2} \cdot \int_{-\infty}^{\infty} e^{-\frac{p_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\frac{p_x^2}{2m}} dp_x = \frac{L^2}{h^2} \left(\int_{-\infty}^{\infty} e^{-\frac{p_y^2}{2m}} dp_y \right)^2$$

$$= \frac{L^2}{h^2} \left(\frac{\sqrt{2\pi T}}{B} \right)^2 = \frac{L^2}{h^2} \left(\sqrt{2m k_B T \pi} \right)^2$$

$$= \frac{2\pi}{h^2} \frac{L^2}{m k_B T}$$

In general, for N -particles in 3 dimensions,

$$Z = \frac{1}{h^{3N}} V^N \left(\frac{2\pi m k_B T}{B} \right)^{3N/2}$$

$$= V^N \sigma \quad (- \text{ does not depend on } V)$$

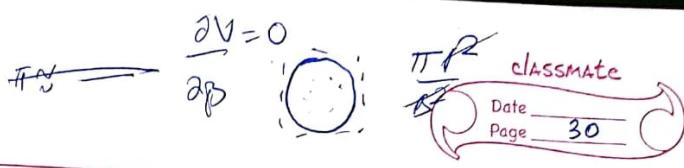
$$\Rightarrow \ln Z = \ln(\sigma) + N \ln V$$

$$\Rightarrow \langle P \rangle = \frac{1}{V} \frac{\partial \ln(Z)}{\partial V} = \frac{1}{V} \cdot \frac{\partial}{\partial V} (N \ln V)$$

$$= \frac{N}{V} \cdot \frac{1}{B}$$

This is the ideal gas equation i.e. the equation of state of an ideal gas

For most



If N is fixed, three parameters determine the state - P, V, T .
The equation linking all three is called the equation of state.

* For ideal gas,

$$\langle E \rangle = -\frac{\partial \ln(\sigma)}{\partial \beta} = -\frac{\partial}{\partial \beta} [\ln(\sigma) + N \ln V]$$

$$\sigma = (2\pi m k_B T)^{\frac{3N}{2}} = \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$\ln(\sigma) = \frac{3N}{2} [\ln(2\pi m) - \ln(\beta)]$$

Assuming $\frac{\partial \ln}{\partial \beta} = 0$,

$$\therefore \langle E \rangle = \frac{3N}{2} \cdot \frac{\partial \ln(\beta)}{\partial \beta} = \frac{3N k_B T}{2}$$

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

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{3N k_B}{2} \therefore \text{Dulong-Petit's law}$$

Note that C_V is independent of temperature.
For most materials,

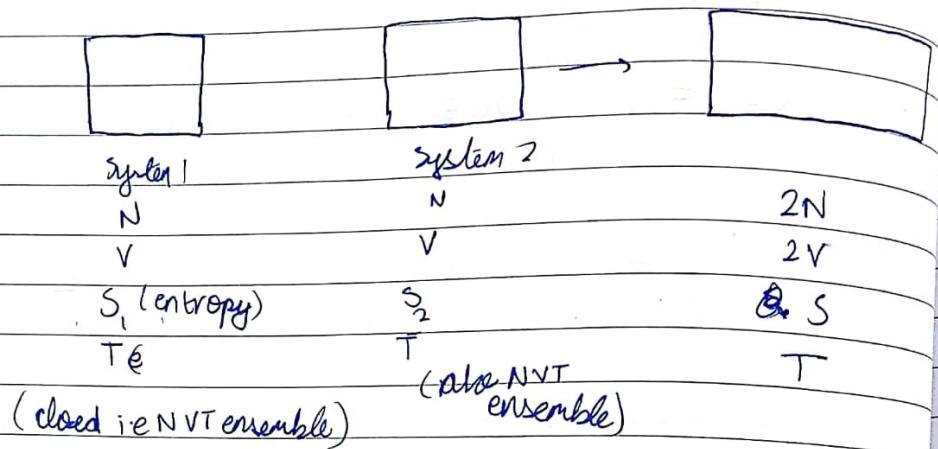
C_V plays
important role | U_{int} is not relevant
 $\frac{3N k_B}{2}$ (ideal)

experimental (for real gases)

T

ENTROPY

→ Entropy is an extensive property i.e. it depends on system size.
As size (V) increases, entropy increases.



Now, Helmholtz free energy

$$F = -k_B T \ln(z)$$

$\beta =$

$$S = + k_B \sum_j p_j \ln(p_j)$$

$$S = + k_B [\ln(z) + \beta \langle E \rangle]$$

$$\therefore S = -k_B [\ln(z) + \ln]$$

$$z = \frac{1}{h^{3N}} V^N \left(\frac{2\pi m k_B T}{h} \right)^{3N/2}$$

$$\ln(z) = N \ln V + \frac{3N}{2} \ln(2\pi m k_B T)$$

$$S_1 = +k_B [N \ln V + \frac{3N}{2} \ln(2\pi m k_B T)] + \frac{\beta_{3N} k_B T}{2} = S_2$$

$$S = + k_B \left\{ 2N \ln(2V) + \frac{3 \cdot 2N}{2} \ln(2 + m k_B T) + 3 \cdot \frac{3 \cdot 2N k_B T}{2} \right\}$$

$$= -k_B N \left[-k_B \left(\ln(2V) + \frac{3N}{2} \ln(2\pi m k_B T) \right) + \frac{3N k_B T}{2} \right]$$

\Rightarrow In general,

$$S_1 = \sigma + N k_B \left[\ln(V) + \frac{3}{2} \ln(T) + \lambda \right],$$

$$\lambda = \frac{3}{2} \ln \left(\frac{2 + m k_B T}{h^2} \right) + \frac{3}{2}$$

$$S_2 = S_1$$

$$S = -2N k_B \left[\ln(2V) + \frac{3}{2} \ln T + \lambda \right]$$

Now,

$$S - (S_1 + S_2) = 2N k_B \ln(2)$$

But, according to thermodynamics, entropy is extensive i.e

$$S - (S_1 + S_2) = 0$$

This is called Gibbs Paradox

The error occurred because we made an error in counting number of accessible microstates - we assumed two particles (indistinguishable) at (ϕ_1, x_1) at (ϕ_2, x_2) is different when first is at ϕ_1 , second at ϕ_2 , and when first is at ϕ_2 , second at ϕ_1 . This resulted in overcounting.

∴ To account for changes,

$$\frac{Z_{\text{correct}}}{Z} = \frac{Z}{N!} \quad (\text{as } N! \text{ permutations were overcounted})$$

With this Z ,

$$S_1 = k_B (\ln Z + \beta \langle E \rangle)$$

$$S_1 = Nk_B \left[\ln V + \frac{3}{2} \ln T + \beta \epsilon - \ln(N!) \right]$$

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m}{hB} \right)^{3N/2}$$

$$\ln Z = \beta N \ln V + \frac{3N}{2} \ln \left(\frac{2\pi m}{hB} \right) - \ln(N!)$$

Now, By Sterling's app

$$S_1 = k_B \left[N \ln V + \frac{3N}{2} \ln \left(\frac{2\pi m}{hB} \right) - \ln(N!) + \frac{3N}{2} \right]$$

$$S = k_B \left[2N \ln 2V + \frac{3N}{2} \ln \left(\frac{2\pi m}{hB} \right) - \ln((2N)!) + 3N \right]$$

$$S - (S_1 + S_2) = k_B \left[2N \ln 2V - 2N \ln V - \ln((2N)!) + \ln(N!) \right]$$

$$= k_B \left[2N \ln 2 - \ln \left(\frac{(N!)^2}{(2N)!} \right) \right]$$

Applying Sterling's approximation (or without \approx)

$$\ln(N!) \approx N \ln N - N$$

$$\therefore S_a = S_1 + S_2$$

→ Thermodynamic Limit :- Systems in which $N \rightarrow \infty$, $V \rightarrow \infty$, but $\frac{N}{V}$ is finite. When comparing experimentally, we should always take this limit.

4*

LECTURE - XV

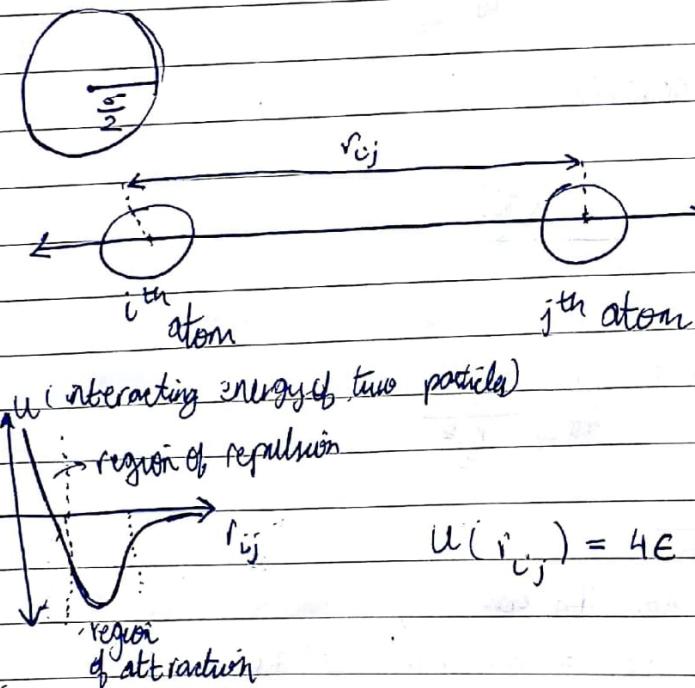
Analysis of non-ideal i.e Real gases :-

$$V(\Sigma r_i^3) \neq 0$$

N particles in volume V at temperature T .

In ideal gas, the particles are point particles i.e have zero size.

Real gases are particles with diameter σ .



$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^2 - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

potential for uncharged particles or inert gases.

ϵ :- width of the attraction region.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

For our system, $\sigma_{ij} = \sigma$

For this region, point of minima is

$$\frac{du}{dr_{ij}} = 0 \Rightarrow 4\epsilon \left[2 \cdot \frac{42}{r_{ij}^2} \left(\frac{\sigma}{r_{ij}} \right)^{12} + \frac{6}{r_{ij}^2} \left(\frac{\sigma}{r_{ij}} \right)^5 \right] = 0$$

$$\Rightarrow 6 \left(\frac{\sigma}{r_{ij}} \right)^5 = -2 \left(\frac{\sigma}{r_{ij}} \right)^{12}$$

$$\Rightarrow r_{ij} = 2^{\frac{1}{6}} \sigma$$

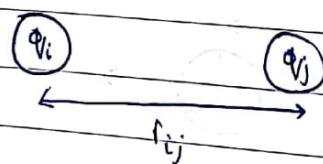
Also, point where

$$u(r_{ij}) = 0$$

$$\Rightarrow \left(\frac{\sigma}{r_{ij}} \right)^{12} = \left(\frac{\sigma}{r_{ij}} \right)^6$$

$$\Rightarrow \sigma r_{ij} = \sigma$$

For charged particles,



$$u(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

For non-ideal

Now, for this non-ideal gas

$$H(s_{rx}, s_{py}) = K(s_{px}^2) + U(s_{rx})$$

$$= \frac{1}{2m} \sum_{i=1}^N p_i^2 s_{xi} + U(s_{rx})$$

$$\frac{12}{R} \left(\frac{\sigma}{r_{ij}} \right)^6 = 6 \left(\frac{\sigma}{r_{ij}} \right)^5$$

r_{ij}

classmate

Date _____

Page _____

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Now,

$$U(\{r_i\}) = u_{12} + u_{13} + \dots + u_{N-1,N} \\ + u_{23} + u_{22} + \dots - \\ + \dots -$$

$$= \frac{1}{2} \sum_{j=1}^N \sum_{\substack{k=1 \\ j \neq k}}^N u_{jk}$$

Now,

$$Z = \frac{1}{h^{3N} N!} \iint_{\{r_i\} \{p_j\}} e^{-\beta U(\{r_i\}, \{p_j\})} dr_i dp_j$$

~~where~~ $= z_u z_p z_R$, where

$$z_R = \int_{\{r_i\}} e^{-\beta U(\{r_i\})} dr_i, \quad z_p = \int_{\{p_j\}} e^{-\beta K_i p_j} dp_j$$

↓ same as in ideal gas case

$$\therefore z_p = \frac{1}{h^{3N} N!} \cdot \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \cdot z_{\text{ideal}}$$

$$z_u = \int_{\{r_i\}} e^{-\beta U(\{r_i\})} dr_i$$

For an ideal gas $U(\{r_i\}) = 0 \Rightarrow z_u = V^N$

But now, $U(\{r_i\}) \neq 0$

$$\langle U \rangle = \frac{\int_{\{r_i\}} e^{-\beta U(\{r_i\})} U(\{r_i\}) dr_i}{\int_{\{r_i\}} e^{-\beta U(\{r_i\})} dr_i} = - \frac{2 \ln(z_u)}{\beta}$$

$$\frac{\partial \ln(z_u)}{\partial \beta} = -\langle u \rangle$$

We know, that when $\beta \rightarrow 0$ i.e. $\frac{1}{k_B T} \rightarrow 0$, $T \rightarrow +\infty$ i.e. it behaves like an ideal gas. i.e.

$$z_u(\beta \rightarrow 0) = V^N$$

$$\int_{\beta=0}^{\beta} \frac{\partial \ln(z_u)}{\partial \beta} d\beta = - \int_0^{\beta} \langle u \rangle d\beta$$

$$\ln(z_u(\beta)) - \ln(z_u(0)) = - \int_0^{\beta} \langle u \rangle d\beta$$

$$\ln(z_u(\beta)) = N \ln V - \int_0^{\beta} \langle u \rangle d\beta$$

There are $\frac{N(N-1)}{2}$ atom pairs in a system of N particles

$\therefore \langle u \rangle = \frac{N(N-1)}{2} \langle u \rangle$, where $\langle u \rangle$ is average energy per pair

We are using the thermodynamic limit i.e. $N \rightarrow \infty$ and $V \rightarrow \infty$.

$$\therefore \langle u \rangle \approx \frac{1}{2} N^2 \langle u \rangle \text{ i.e. } N-1 \approx N.$$

Now,

$$\langle u \rangle = \frac{\int_{R_{ij}} e^{-\beta U(r)} u(r) d\vec{r}}{\int_{R_{ij}} e^{-\beta U(r)} d\vec{r}}$$



$$\Rightarrow \langle u \rangle = \int_{\vec{R}} e^{-\beta U(\vec{R})} - \frac{\partial}{\partial \beta} \left[\ln \left(\int_{\vec{R}} e^{-\beta U(\vec{R})} d\vec{R} \right) \right]$$

consider

$$\int_{\vec{R}} e^{-\beta U(\vec{R})} d\vec{R} = \int_{\vec{R}} [1 + e^{-\beta U(\vec{R})} - 1] d\vec{R}$$

↳ integral over 3-D space

$$= \int_{\vec{R}} d\vec{R} + \int_{\vec{R}} (e^{-\beta U(\vec{R})} - 1) d\vec{R}$$

$$= V + I(\beta)$$

$$I(\beta) = \int_{\vec{R}} (e^{-\beta U(\vec{R})} - 1) d\vec{R}$$

In \Rightarrow Polar coordinates

$$I(\beta) = 4\pi \int_{\vec{R}} R^2 (e^{-\beta u} - 1) dR$$

due

to angle

angular integration

(u is not dependent on angle, only on R)

$$\therefore \langle u \rangle = - \frac{\partial}{\partial \beta} \ln \left[V \left(1 + \frac{I}{V} \right) \right]$$

Now, since $V \rightarrow \infty$, $I \ll V$ (dilute gas)

$$\therefore \langle u \rangle = - \frac{\partial}{\partial \beta} \ln(V)$$

$$\therefore \langle u \rangle = -\frac{\partial \ln(V)}{\partial \beta} - \frac{\partial \ln(I+V)}{\partial \beta}$$

↓

Since V is fixed, this is 0

$$\therefore \ln\left(\frac{I+V}{V}\right) \approx \frac{I}{V} + \dots$$

$$\therefore \langle u \rangle = -\frac{\partial \left(\frac{I}{V}\right)}{\partial \beta} = -\frac{1}{V} \frac{\partial I}{\partial \beta}$$

$$\langle v \rangle = \frac{-1}{2} \frac{N^2}{V} \frac{\partial I}{\partial \beta}$$

$$\therefore \ln(z_u(\beta)) = N \ln V + \int \frac{1}{2} \frac{N^2}{V} \frac{\partial I}{\partial \beta} d\beta$$

$$\boxed{\ln(z_u(\beta)) = N \ln V + \frac{1}{2} \frac{N^2}{V} I(\beta)}$$

To get the analogue of ideal gas equation, we find pressure as

$$\langle p \rangle = \frac{1}{\beta} \frac{\partial \ln(z)}{\partial V}$$

$$= \frac{1}{\beta} \frac{2 \ln(z_R) + \ln(z_u)}{2V} \quad \text{Q } z \text{ is not function of } V$$

$$\Rightarrow \langle p \rangle = \frac{1}{\beta} \frac{2 \ln(z_u)}{2V}$$

$$\Rightarrow \langle P \rangle = \frac{1}{B} \left[\frac{2}{\partial V} \left(N k_B T + \frac{1}{2} \frac{N^2}{V} I(B) \right) \right]$$

$$\underset{\text{ideal gas part}}{\frac{1}{B} \frac{N k_B T}{V}} = \underset{\text{interaction part}}{\frac{1}{2} \frac{N^2}{V^2} I(B)}$$

$$\frac{N}{V} = \text{density} = \rho$$

$$\therefore \frac{\langle P \rangle}{k_B T} = f - \frac{1}{2} f^2 I(B)$$

~~TOP~~ In general,

$$\frac{\langle P \rangle}{k_B T} = f + B_2(f) f^2 + B_3(f) f^3 + \dots$$

↓

Virial Equation

LECTURE - XVI

CLASS - ASSIGNMENT

- Q1.) There is a closed system consisting of N independent particles. Each particle can have only one of two energy levels $-E_0$ and $+E_0$. Calculate the thermodynamic properties of the system.

- Q2.) N monomeric units are arranged along a straight line to form a chain molecule. Each monomeric unit is assumed to be capable of being either in an α -state or a β -state. In former state the length is a and energy is E_α , and in β -state, they are b and E_β . Derive relation b/w length L of the chain molecule

and the tension γ applied by both ends of the molecule (closed system). Also calculate thermodynamic properties of the system.

A1) Since there are two energy states ϵ_0 and $-\epsilon_0$,

$$Z = \sum_i e^{-\beta E_i}, \quad \beta = k_B T$$

$$\begin{aligned} Z &= e^{-\beta \epsilon_0} + e^{\beta \epsilon_0} \\ Z &= \frac{1 + e^{2\beta \epsilon_0}}{e^{\beta \epsilon_0}} \end{aligned}$$

$$\Rightarrow \ln(Z) = \ln(1 + e^{2\beta \epsilon_0}) - \beta \epsilon_0$$

Internal energy:

$$\langle E \rangle = - \frac{\partial \ln(Z)}{\partial \beta}$$

Total ~~pos~~ energy = $\sum_{i=1}^N E_i$, $E_i = -\epsilon_0$ or ϵ_0 , where E_i is energy of i^{th} particle.

$$Z = \prod_i e^{-\beta E_i}$$

\therefore Total 2^N possible energy states, from

$$-N\epsilon_0, -(N-2)\epsilon_0, -(N-4)\epsilon_0, \dots, 0, 2\epsilon_0, 4\epsilon_0, \dots, N\epsilon_0$$

$$\therefore \Omega Z = \sum_i e^{-\beta E_i} = e^{N\epsilon_0} + e^{(N-2)\epsilon_0} + \dots + e^0 + e^{2\epsilon_0} + e^{4\epsilon_0} + \dots + e^{-N\epsilon_0}$$

$$\Rightarrow Z = e^{N\epsilon_0} \left(1 - e^{-2\epsilon_0} \right)^N$$

$$\Rightarrow Z = e^{\beta N E_0} \cdot \frac{(1 - e^{2\beta E_0})}{1 - e^{2\beta E_0}}$$

$$\ln(Z) = -N E_0 + \ln(1 - e^{2\beta E_0}) + \underline{\underline{\underline{\quad}}}$$

$$\therefore \langle E \rangle = -2\ln(Z)$$

$$\begin{aligned} &= \frac{\partial}{\partial \beta} (N E_0) - \frac{\partial}{\partial \beta} (\ln(1 - e^{\beta E_0})) \\ &= N E_0 + \frac{\beta 2 N E_0 + e^{\beta E_0}}{1 - e^{\beta E_0}} \times \end{aligned}$$

$$\Rightarrow \langle E \rangle = N E_0 - \frac{2 N E_0}{e^{1 - e^{-2\beta E_0}}}$$

~~for~~

A1) \rightarrow Let n particles be in $+E_0$ state. $\therefore n-r$ are in $-E_0$ state.

" C_n^n ways of forming this arrangement, and $E_{\text{tot}} = n E_0 + (n-r)(-E_0)$

$$\begin{aligned} &= n E_0 + (n-r)(-E_0) \\ &= (2n-r) E_0 \\ &= (2n-N) E_0 \end{aligned}$$

$$= C^{\beta N E_0} \sum_{n=0}^N N C_n e^{-2n\beta E_0}$$

LECTURE - XVII

THERMODYNAMICS

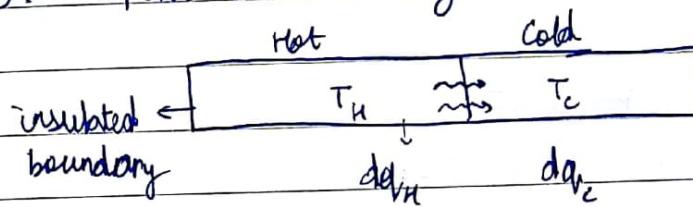
- 1.) Zeroth Law of Thermodynamics :- Thermal equilibrium \Rightarrow equality of temperatures.
 It defines temperature.
- 2.) First Law of Thermodynamics :- For an isolated system,
 $dU = dQ + dw$ (conservation of energy)
- dU :- change in internal energy
 dQ :- heat given to system ($dQ = Q_f - Q_i$) \Rightarrow +ve if heat is supplied
 dw :- work done on the system (dw -ve if work is done by the system).
- 3.) Second Law of Thermodynamics :-
 - a) Spontaneous processes are processes that do not require external work.
 - For any spontaneous process,
$$(ΔS)_{\text{total}} = (ΔS)_{\text{system}} + (ΔS)_{\text{surroundings}} \geq 0$$
 i.e total entropy increases for spontaneous processes.
- b) System-specific variant of the law =
 $(dS)_{\text{system}} \geq \frac{dQ}{T}$ [Clausius's inequality]
- dQ :- heat supplied to the system
- 4.) Third Law of Thermodynamics :- When $T \rightarrow 0$, $S \rightarrow 0$.
 S :- absolute value of entropy

Reversible Processes :- Processes that occur slowly i.e. quasi-statically.
For such processes, second law of thermodynamics becomes

$$ds = \frac{dq}{T}$$

EX EXAMPLE - SYSTEMS

→ Case ① :- Spontaneous cooling



$$|dq_H| = |dq_C|$$

Since process is spontaneous,

$$ds_H = \frac{dq_H}{T_H} ; ds_C = \frac{dq_C}{T_C}$$

Consider following possibilities :-

(a) Heat flows from cool to hot object

$$\therefore ds = ds_H + ds_C = -\frac{|dq_C|}{T_C} + \frac{|dq_H|}{T_H}$$

$$\Rightarrow ds = |dq_H| \left(\frac{1}{T_H} - \frac{1}{T_C} \right) < 0 \Rightarrow ds < 0$$

This contradicts the second-law.

(b) Heat flows from hot to cold object

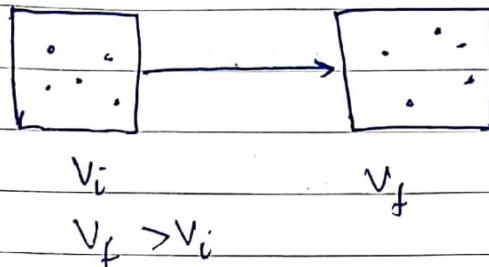
Here,

$$ds = |dq_H| \left(\frac{1}{T_C} - \frac{1}{T_H} \right) > 0$$

∴ Second law not violated.

Hence, case (b) is the only possible option.

Case (b): gas expansion (reversible, isothermal) of an ideal gas



Since gas is ideal,

$$PV = nRT$$

$$dU = 0 \text{ (as } dT = 0\text{)}$$

Also, for reversible process,

$$\Rightarrow dQ_{rev} = -dW_{rev} \Rightarrow Q = \Delta U - W$$

\hookrightarrow reversible work done by system.

$$\therefore \Delta S = \cancel{\Omega} \int_i^f dS = \frac{1}{T} \int_i^f dQ_{rev} = \frac{Q_{rev}}{T}$$

$$dW_{rev} = -PdV = -nRT \left(\frac{dV}{V} \right)$$

$$\therefore W_{rev} = \int_i^f (-nRT) \frac{dV}{V} = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$\therefore \Delta S = \frac{1}{T} Q_{rev} = \frac{-W_{rev}}{T} = nR \ln \left(\frac{V_f}{V_i} \right)$$

Case (a) $V_f < V_i$ (compression) $\Rightarrow \frac{V_f}{V_i} < 1$

$$\Rightarrow \Delta S < 0$$

\therefore Not a spontaneous process.

$$\text{Case (b)}: V_f > V_i \text{ (expansion)} \Rightarrow \frac{V_f}{V_i} > 1$$

$$\Rightarrow \Delta S > 0$$

\therefore spontaneous

→ THERMO & DYNAMIC POTENTIALS

From the second law of thermodynamics,

$$dS \geq \frac{dQ}{T}$$

Consider case (a) \Rightarrow Heat transfer at constant volume.

$$\therefore dW = 0$$

$$\text{then, } dQ = dU.$$

$$\Rightarrow dS \geq \frac{dU}{T}$$

$$\Rightarrow TdS - dU \geq 0$$

If process is a constant entropy process, $dS = 0 \Rightarrow dS = 0$

$$\therefore dU \leq 0$$

$$\Rightarrow (dU)_{S,V} \leq 0$$

\therefore For constant volume, constant entropy processes, $V(S,V)$ decreases.

But, it is difficult to maintain constant entropy.

(b) Define a new function, enthalpy, defined as

$$H = U + PV$$

$$\Rightarrow dH = dU + PdV + VdP$$

$$\Rightarrow dH = dQ - PdV + VdP + PdV$$

$$\Rightarrow dH = dQ + VdP$$

\therefore If P is constant, then

$$dH = dQ \Rightarrow \Delta H = \Delta Q$$

\therefore Enthalpy can be defined as heat supplied to the system at constant pressure.

For such a system, by second law, if volume is constant

$$TdS - dQ > 0$$

$$\Rightarrow TdS - dH \geq 0 \quad (\text{as } dQ = dH - TdS, \text{ so } dQ \leq dH)$$

$$\Rightarrow TdS \geq dH$$

\therefore If entropy is constant

$$dH \leq 0$$

$\Rightarrow H$ decreases.

Hence, if P and S are constant, then system evolves such that i.e. enthalpy is minimised.

But, even here, we cannot ~~not~~ control S .

(c) Constant T, P, V . (controllable parameters).

Define a new function A , called Helmholtz Free energy.

$$A = U - TS$$

$$\Rightarrow dA = dU - TdS - SdT$$

Since P, V are constant, $dP = 0 \Rightarrow dU = 0$

$$TdS - dQ \geq 0$$

$$\therefore dA = -PdV - SdT$$

At constant V, P , $dA \leq 0$

\therefore At such systems, A i.e. Helmholtz free energy is minimised.

(d)

constant P, T processes (most natural processes).

Here, a new function G , called Gibbs Free energy, defined as

$$G = U + PV - TS, \text{ is minimised.}$$

→ Maxwell's Relations

$$U = U(S, V) \quad \text{--- (1)}$$

$$H = U + PV = H(P, S)$$

$$A = U - TS = A(T, V)$$

$$G = G(T, P) = U + PV - TS$$

Now, for reversible processes,

$$dU = T dS - P dV \quad (\text{first and second laws})$$

Also, from (1)

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

It thus implies

$$\left(\frac{\partial U}{\partial V}\right)_S = -P, \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

Also, note that, for all thermodynamic processes,

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

Differentiating

$$\Rightarrow \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right) = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)$$

$$\Rightarrow \boxed{-\frac{\partial P}{\partial S} = \frac{\partial T}{\partial V}} \quad \text{--- (I)}$$

Similarly, we can derive other relations as

$$\text{From } H = H(P, S) \Rightarrow \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} \Rightarrow \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad \text{--- (II)}$$

$$\text{From } A = A(T, V) \Rightarrow \dots \rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad \text{--- (III)}$$

$$\text{From } G = G(T, P) \Rightarrow \dots \rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad \text{--- (IV)}$$

I, II, III, IV are very useful relations.

LECTURE XVIII

statistical mechanics
(microscopic approach)

Thermodynamics
(macroscopic approach)

$\{r_i\}, \{p_i\}$

P, V, T, n

$P = f(V, T, n)$:- Equation of state
(or $g(P, V, T, n) = 0$, in general)

→ Gibbs Free Energy = $G(P, T)$

By Maxwell's relations,

$$\frac{\partial S}{\partial T} = -\frac{\partial G}{\partial T}$$

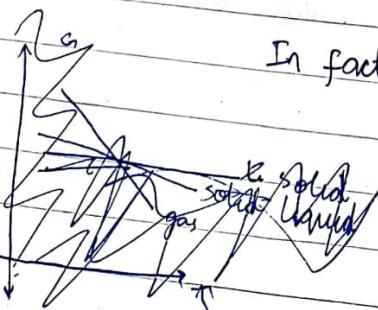
$$\frac{\partial G}{\partial P} = V$$

In all cases, $S > 0 \Rightarrow \frac{\partial G}{\partial T} < 0 \Rightarrow G$ must always decrease with increase in temperature

Also,

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

$\Rightarrow \frac{\partial G}{\partial T}$ is different for different phases.



In fact,

$$\left(\frac{\partial G}{\partial T}\right)_{\text{solid}} > \left(\frac{\partial G}{\partial T}\right)_{\text{liquid}} > \left(\frac{\partial G}{\partial T}\right)_{\text{gas}}$$

∴ response of G to T would be greatest for gases.

X 20

Now, $\frac{\partial G}{\partial P} = V \geq 0 \Rightarrow G$ must increase with increase in P

Also,

$$V_{\text{gas}} > V_{\text{liquid}} > V_{\text{solid}}$$

$$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_{\text{gas}} > \left(\frac{\partial G}{\partial P}\right)_{\text{liquid}} > \left(\frac{\partial G}{\partial P}\right)_{\text{solid}}$$

Gibb's - Helmholtz equation :-

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_V = -\text{we know also,}$$

$$H = U + PV$$

$$\therefore G = U + PV - TS$$

$$\Rightarrow G = H - TS$$

$$\Rightarrow S = \frac{H - G}{T}$$

$$\therefore \frac{\partial G}{\partial T} = Q - S = \frac{G - H}{T}$$

$$\frac{\partial G}{\partial T} - \frac{G}{T} = -\frac{H}{T}$$

Multiplying by $\frac{1}{T}$ on both sides,

$$\frac{1}{T} \frac{\partial G}{\partial T} - \frac{G}{T^2} = -\frac{H}{T^2}$$

$$\boxed{\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}}$$

Gibbs Helmholtz equation

H can be measured relatively easily (as compared to entropy).

Using G , we can determine the stability of a phase.

The phas-

At a given temperature and pressure, the ~~st~~ phase with the least energy and pressure G would be the most stable phase.

e.g.

$$G_{\text{water}} (T = 300\text{K}, P = 1\text{atm}) < G_{\text{ice}} (T = 300\text{K}, P = 1\text{atm})$$

like \rightarrow

\hookrightarrow for same n

* sometimes,

Instead of G , we use the chemical potential ($\frac{G}{n}$) to compare the

stability of two systems.

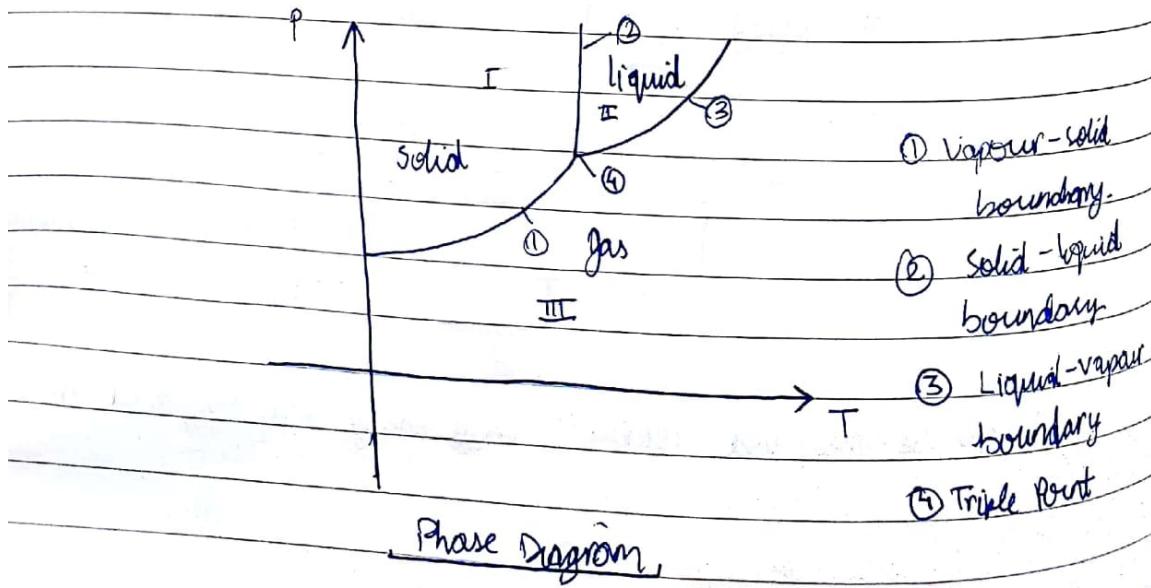
Chemical Potential :-

$$\mu(T, P) = \frac{G(T, P)}{n}$$

\therefore At $T_0 = 300\text{K}, P_0 = 1\text{atm}$,

$$\mu_{\text{water}}(T_0, P_0) < \mu_{\text{ice}}(T_0, P_0)$$

\therefore In a $P-T$ diagram, we can find μ at each point, for each phase, and assign the most stable phase to each point to find the phase at each point. such a diagram is called a phase diagram.



$$G = U + PV - TS$$

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The lines separating each point phase are called phase boundaries.
At these boundaries, μ for the two phases are equal e.g. at the vapour-solid boundary,

$$\mu_{\text{gas}}(T_0, P_0) = \mu_{\text{solid}}(T_0, P_0)$$

The triple-point is a point where μ of all phases are the same.

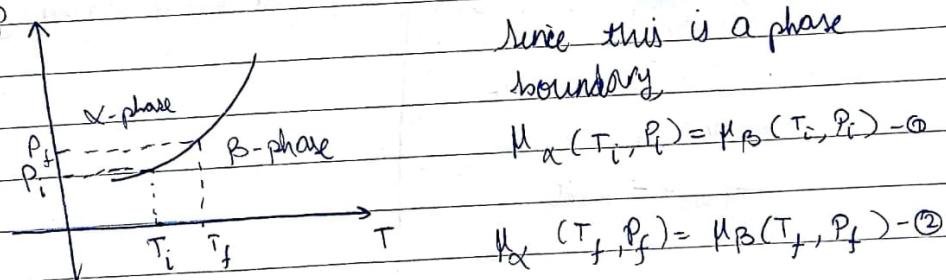
i.e.

$$\mu_{\text{gas}}(T_0, P_0) = \mu_{\text{liquid}}(T_0, P_0) = \mu_{\text{solid}}(T_0, P_0)$$

→ Phase Transitions,

Crossing the solid-liquid boundary from the solid phase \Rightarrow melting
Note, from the phase diagram, at higher pressure, higher temperature is needed for melting.

→ Equations of the Phase boundaries



Since the $\Rightarrow \mu_\alpha(T_f, P_f) - \mu_\alpha(T_i, P_i) = \mu_\beta(T_f, P_f) - \mu_\beta(T_i, P_i)$
For $T_f \rightarrow T_i$, $P_f \rightarrow P_i$,

$$d\mu_\alpha(T, P) = \delta E \mu_\beta(T, P) - ③$$

Now,

$$dG = -SdT + VdP$$

Dividing by n ,

$$\frac{d\mu}{n} = \frac{dG}{n} = -\frac{S_m dT}{n} + \frac{V_m dP}{n} \Rightarrow = -S_m dT + V_m dP, \text{ where } S_m, V_m \text{ are molar values.}$$

∴ Putting in ③ yields

$$-S_{m,\alpha} dT + V_{m,\alpha} dP = -S_{m,\beta} dT + V_{m,\beta} dP$$

$$(V_{m,\alpha} - V_{m,\beta}) dP = (S_{m,\alpha} - S_{m,\beta}) dT$$

$$\Rightarrow (V_{m,\beta} - V_{m,\alpha}) \frac{dP}{dT}$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta_{trans} S}{\Delta_{trans} V} \left(\frac{S_{m,\alpha} - S_{m,\beta}}{V_{m,\alpha} - V_{m,\beta}} \right)$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta_{trans} S}{\Delta_{trans} V}}$$

Clayperon equation gives slope of phase boundary.

$\Delta_{trans} S$ = change of S during transition.

$\Delta_{trans} V$ = change of V during transition

→ Solid-liquid boundary
(melting)

For such a transition, at constant pressure,

$$\Delta_{trans} S = \frac{\Delta H}{T}$$

→ Liquid-vapour boundary

ΔH = fusion enthalpy.

This equation occurs due to

a consequence of second law of Thermodynamics $-dS = \frac{dQ}{T}$

$$\therefore \frac{dP}{dT} = \frac{\Delta H}{T \cdot \Delta V_m}, \Delta H > 0, \Delta V > 0$$

$\Delta H > 0$ (Liquid entropy > solid)

$$\Rightarrow \int_{P_1}^P dP = \int_{T_1}^T \frac{\Delta H \cdot dT}{\Delta V \cdot T}$$

The integral appears if we assume ΔH and ΔV do not change much with T and P ,

$$P - P^* = \frac{\Delta H}{\Delta V} \ln\left(\frac{T}{T^*}\right)$$

P^*, T^* = transition pressure, temp.

$$\therefore P = P^* + \frac{\Delta H}{\Delta V} \ln\left(\frac{T}{T^*}\right)$$

If $T \rightarrow T^*$,

$$\ln\left(\frac{T}{T^*}\right) = \ln\left(1 + \frac{T-T^*}{T^*}\right)$$

$$\approx \frac{T-T^*}{T^*}$$

$$\therefore P = P^* + \left(\frac{\Delta H}{\Delta V}\right) \left(\frac{T-T^*}{T^*}\right)$$

This is an equation of a straight line.

LECTURE - XX

$G(T, P)$:- Gibbs Free Energy

$$\mu(T, P) = \frac{G(T, P)}{n}$$

n :- number of moles

Phase with the least $\mu(T, P)$ at a given T and P is the most stable phase.

Types of Phase Transitions:-

Ehrenfest phase transition classification -

- 1) First Order Phase Transition :-
- 2) Second Order Phase Transition

① First order Phase Transitions :- In such transitions,

$\frac{\partial \mu(T, P)}{\partial T}$ should be discontinuous i.e. at P^*, T^*

$\frac{\partial \mu(T, P)}{\partial P}$ should be discontinuous at P^*, T^* \rightarrow The

P^*, T^* :- transition temperature and pressure

$$\frac{\partial \mu(T, P)}{\partial T} = -\frac{S}{n}, \quad \frac{\partial \mu(T, P)}{\partial P} = \frac{V}{n}$$

i.e.

S, V are discontinuous during first order phase transitions.

② Second order Phase Transitions

$\frac{\partial \mu(T, P)}{\partial T}, \frac{\partial \mu(T, P)}{\partial P}$ should be continuous, but

$\frac{\partial^2 \mu(T, P)}{\partial T^2}, \frac{\partial^2 \mu(T, P)}{\partial P^2}$ should be discontinuous, at

transition point (T^*, P^*) .

→ Chemical Equilibrium :- Constant μ

Thermal equilibrium :- Constant T .

q.v. :- E

We path

Long time

K C

V o

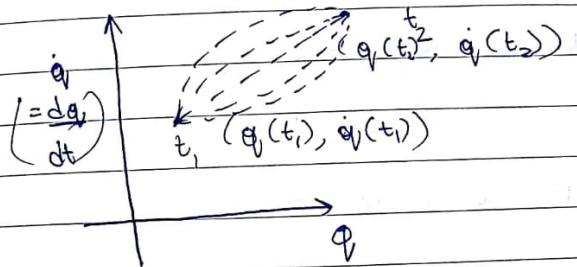
Action

Princip
is the

Classical Mechanics

P

→ The Principle of Least Action (or) Hamilton's Principle



q_i - generalised coordinate

We are given positions at two times, and wish to find the path taken by the particle.

~~Least~~ Lagrangian :- $L(q_i, \dot{q}_i, t)$; a function with implicit time dependence. (time dependence not explicit)

$$L(q_i, \dot{q}_i, t) = K(\dot{q}_i) - U(q_i)$$

$K(\dot{q})$ ← kinetic energy

$U(q)$ ← Potential energy

$$\text{Action } S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt$$

Principle of least action :- The path P with the minimum action is the most probable path of the system.

$$S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt = \int_{t_1}^{t_2} K(q_i) dt - \int_{t_1}^{t_2} U(q_i) dt$$

$$\therefore ds = K(q_i) dt - U(q_i) dt$$

Now $\int_{t_1}^{t_2} K(q_i) dt \propto$ mean KE

$\int_{t_1}^{t_2} U(q_i) dt \propto$ mean PE

$\therefore S$ is proportional to KE, PE : mean value of KE, PE.

Let $q_i(t), \dot{q}_i(t) \forall t_1 \leq t \leq t_2$ be the least action path for the system.

We create a neighbouring path which is arbitrarily close to the optimum path i.e. it is defined by

$$q_i(t) + \delta q_i(t), \dot{q}_i(t) + \delta \dot{q}_i(t) \forall t_1 \leq t \leq t_2$$

& At end points $\delta q_i(t_1) = 0, \delta q_i(t_2) = 0$

$\delta q_i(t_1) = 0, \delta q_i(t_2) = 0$ (or neighbouring path is also a possible path)

\therefore Difference in path action in the two paths is

$$\delta S = \int_{t_1}^{t_2} L(q_i + \delta q_i, \dot{q}_i + \delta \dot{q}_i, t) dt - \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt$$

$$\begin{aligned} \delta S &= \int_{t_1}^{t_2} L(q_i + \delta q_i, \dot{q}_i + \delta \dot{q}_i, t) dt - \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt \\ &= \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt \end{aligned}$$

$$\delta S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt = \int_{t_1}^{t_2}$$

Also,

$$\int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q_i} \cdot \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \right) dt$$

: Now, $\delta q_i = \frac{d(\delta q_i)}{dt}$

$$\therefore \delta S = \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_i} \cdot \delta q_i dt + \frac{\partial L}{\partial \dot{q}_i} \frac{d(\delta q_i)}{dt} dt \right]$$

Consider the second term.

$$\begin{aligned} \int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}_i} \frac{d(\delta q_i)}{dt} dt &= \left[\frac{\partial L}{\partial \dot{q}_i} \int \frac{d(\delta q_i)}{dt} dt \right]_{t_1}^{t_2} \\ &\quad - \int_{t_1}^{t_2} \left(\frac{\partial^2 L}{\partial \dot{q}_i^2} \right) \int \frac{d(\delta q_i)}{dt} dt dt \\ &= \left. \frac{\partial L}{\partial \dot{q}_i} \delta q_i(t) \right|_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{d(\partial L)}{dt} \frac{\delta q_i}{dt} dt \end{aligned}$$

Now, $\delta q_i(t_1) = \delta q_i(t_2) = 0$

$$\therefore \int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}_i} \frac{d(\delta q_i)}{dt} dt = - \int_{t_1}^{t_2} \frac{d(\partial L)}{dt} \frac{\delta q_i}{dt} dt$$

$$\therefore SS = \int_{t_1}^{t_2} \frac{\partial L}{\partial q_j} dq_j dt - \int_{t_1}^{t_2} dt \left(\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) \right) dq_j dt$$

$$SS = \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_j} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) \right] dq_j dt$$

Now, if $Sq(t) \rightarrow 0$, $SS \rightarrow 0$ i.e. if Sq tends to zero, then path becomes the optimum path and, for such a path, $SS = 0$.

Also, this must be true for any two arbitrary t_1 and t_2 .
 $\therefore SS$ however close they may be. Therefore, this must be zero for any least action path and hence, it must be true for each point.

$$\therefore SS = 0$$

$$\Rightarrow \boxed{\frac{\partial L}{\partial q_j} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = 0}$$

Lagrange's equation or
Euler-Lagrange equation

LECTURE - XXI

$$\frac{\partial L}{\partial q_j} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = 0$$

$$L = K(\dot{q}_j) - U(q_j)$$

$$\therefore \frac{\partial L}{\partial q_j} = \frac{\partial K(\dot{q}_j)}{\partial \dot{q}_j} \quad (= \frac{dK(\dot{q}_j)}{d\dot{q}_j})$$

$$K = \frac{1}{2} m \dot{q}_j^2 \Rightarrow \frac{\partial L}{\partial \dot{q}_j} = m \dot{q}_j$$

generalised
kinetic energy.
in Cartesian-like
coordinates only? \rightarrow in linear coordinates only??

$$\therefore \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = m \ddot{q}_j, \text{ where } \ddot{q}_j = \frac{d \dot{q}_j}{dt}$$

$$\Rightarrow \frac{d \dot{q}_j}{dt} = \frac{1}{m} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right)$$

$$L = K(\dot{q}) - V(q)$$

$$\Rightarrow \frac{\partial L}{\partial q_j} = - \frac{\partial V(q)}{\partial q_j}$$

From Lagrange's equation,

$$\boxed{\frac{\partial V(q)}{\partial q_j} = m \ddot{q}_j} \rightarrow \text{equation of motion, gives us how } \dot{q} \text{ evolves with time.}$$

$\therefore - \frac{\partial V(q)}{\partial q_j} \rightsquigarrow \text{force (along } q_j\text{).}$

$$\therefore \frac{d \dot{q}_j}{dt} = - \frac{1}{m} \frac{\partial V}{\partial q_j} = \frac{1}{m} \frac{\partial L}{\partial q_j}$$

$$\Rightarrow \frac{d \dot{q}_j}{dt} \text{ Also, } \frac{d q_j}{dt} = \frac{1}{m} \frac{\partial L}{\partial \dot{q}_j}$$

We can solve the equations to study evolution of the system in phase space.

Now,

$\frac{dL}{dt} \quad L(q, \dot{q}, t)$, q, \dot{q} is a vector of order n , where n is number of free degrees of freedom.

$$\therefore \frac{dL}{dt} = \sum_{i=1}^n \left(\frac{\partial L}{\partial q_i} \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i \right) \quad \left(\text{as } dL = \sum_{i=1}^n \frac{\partial L}{\partial q_i} dq_i + \sum_{i=1}^n \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i \right)$$

$$\Rightarrow \frac{dL}{dt} = \sum_{i=1}^n \frac{\partial L}{\partial q_i} dq_i + \sum_{i=1}^n \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

From Lagrange's equation, $\frac{\partial L}{\partial \dot{q}_i} = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right)$

$$= \sum_{i=1}^n \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \frac{d\dot{q}_i}{dt}$$

$$\therefore \frac{dL}{dt} = \sum_{i=1}^n \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right) = \frac{d}{dt} \sum_{i=1}^n \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right)$$

$$\Rightarrow \frac{d}{dt} \left(L - \sum_{i=1}^n \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right) = 0$$

$L - \sum_{i=1}^n \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i$ is a constant of motion.

Now,

$$L = K(\dot{q}) - V(q)$$

$$\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial K(\dot{q})}{\partial \dot{q}_i} = m \dot{q}_i$$

$$(K(\dot{q}) = \frac{1}{2} m \sum_{i=1}^n \dot{q}_i^2)$$

$$\Rightarrow \sum_{i=1}^n \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} = \sum_{i=1}^n m \dot{q}_i^2 = 2K$$

$$\therefore \sum_{i=1}^n \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = 2K - (K - V) = K + V \in \mathbb{R}$$

Q. This quantity is the Hamiltonian i.e. the total energy of the system. It is conserved through the motion.

$$\therefore H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$$

This represents a Legendre transform.

\therefore The Hamiltonian is the Legendre transform of the Lagrangian.

Legendre Transformation: Represents Transform function to other space.

Let $f = f(x, y)$ i.e function in xy space.
 $x \rightarrow x+dx, y \rightarrow y+dy, f \rightarrow f+df$, where

$$\therefore df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

$$df = u dx + v dy, u = \frac{\partial f}{\partial x}, v = \frac{\partial f}{\partial y}$$

$$\text{consider } d(vy) = y dy + v y dx + y dv + v dy - \textcircled{2}$$

$$\textcircled{1} - \textcircled{2} - \textcircled{1}$$

$$\Rightarrow df - d(vy - f) = y dv - u dx - \textcircled{3}$$

Let $g = g(x, v)$ & i.e a function in xv space. The transformation
from $x-y \rightarrow x-v$ space will be the Legendre transform.

$$dy \circ g(x, v) = \frac{\partial y}{\partial x} \frac{\partial g}{\partial x} dx = \frac{\partial y}{\partial v} dv - \textcircled{4}$$

Comparing $\textcircled{3}$ and $\textcircled{4}$,

$$g(x, v) = vy - f(x, y)$$

A similar transform is the ~~L~~ $L \rightarrow H$ transform

$$L(q, \dot{q}) \rightarrow H(q, mq = p)$$

\therefore Hamiltonian is a function of (q, p) .

$$L(q, \dot{q}, t) \rightarrow H(q, p, t)$$

$H(p, q, t)$:- Hamiltonian, also has time ~~only~~ independence ~~or~~ implicit (mostly).

$$\text{to} \quad H(p, q, t)$$

$$dH = \frac{\partial H}{\partial p} dp + \frac{\partial H}{\partial q} dq + \frac{\partial H}{\partial t} dt \quad \text{--- (1)}$$

→ only arises if time dependence is explicit.

$$H = pq - L$$

$$\Rightarrow dH = pdq + qdp - \frac{\partial L}{\partial q} dq$$

$$\Rightarrow dH = pdq + qdp - \frac{\partial L}{\partial q} dq - \frac{\partial L}{\partial q} dq - \frac{\partial L}{\partial t} dt$$

Using Lagrange's equations of motion,

$$+ \frac{\partial L}{\partial q} = + \dot{p}, \quad + \frac{\partial L}{\partial t} = \dot{q}$$

$$\therefore dH = pdq + qdp - pdq - \dot{p}\dot{q} - \frac{\partial L}{\partial t} dt$$

$$dH = qdp - \dot{p}dq - \frac{\partial L}{\partial t} dt \quad \text{--- (2)}$$

From (1) and (2), comparing,

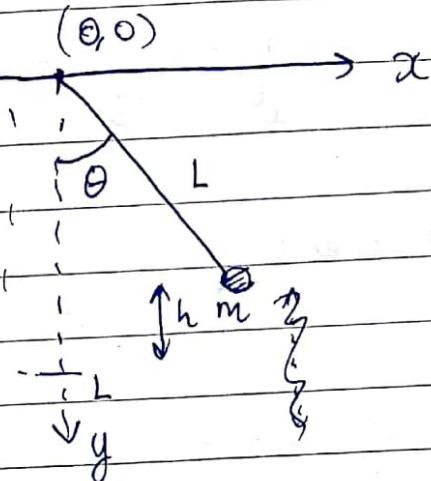
$$\frac{\partial H}{\partial p} = \dot{q}, \quad \frac{\partial H}{\partial q} = -\dot{p}, \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$$

$$\therefore \boxed{\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}} \rightarrow \text{Hamilton's equations of motion.}$$

$$\text{Also, } \frac{\partial L}{\partial t} = - \frac{\partial H}{\partial t}$$

If H is constant i.e total energy is conserved, then
 $\frac{\partial L}{\partial t} = 0 \Rightarrow L$ is also conserved.

→ Example I:- Simple Pendulum



No. of degrees of freedom = 1

We take θ as the generalized coordinate.

$$K(\dot{\theta}) =$$

(I) calculate the Lagrangian/Lagrange/Hamiltonian

$$x = L \sin \theta, \quad y = L \cos \theta$$

$$T = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2) \quad \therefore \dot{x} = L \cos \theta \dot{\theta}, \quad \dot{y} = -L \sin \theta \dot{\theta}$$

$$V = \omega L = L \dot{\theta}$$

$$K(\dot{\theta}) = \frac{1}{2} m v^2 = \frac{1}{2} m L^2 \dot{\theta}^2$$

$$\frac{1}{2} m (\dot{x}^2 + \dot{y}^2)$$

$$U(\theta) = 0 \quad (\text{as no fo})$$

$$U(\theta) = mgL \cos \theta \quad (= mgh)$$

$$U(\theta) = -mgL \cos \theta \quad (\text{taking } U=0 \text{ at } (0,0))$$

$$\therefore L(\theta, \dot{\theta}); t = \cancel{K} - V = \frac{1}{2} m L^2 \dot{\theta}^2 + mgL \cos \theta$$

$$H(\theta, p) = \frac{1}{2} m L^2 \dot{\theta}^2 - mgL \cos\theta =$$

$\bullet \quad \ddot{\theta} = \frac{\partial H}{\partial p}$

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$$L(\theta, \dot{\theta}) = \frac{1}{2} m L^2 \dot{\theta}^2 + mgL \cos\theta$$

Lagrange's equation:-

$$\frac{\partial L}{\partial q} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = 0$$

$$\bullet \quad \frac{\partial L}{\partial \theta} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = 0$$

$$\Rightarrow -mgL \sin\theta - \frac{d}{dt} \left(\frac{1}{2} m L^2 \dot{\theta}^2 \right) = 0$$

$$\Rightarrow +mgl \sin\theta + \frac{1}{2} m L^2 \ddot{\theta} = 0$$

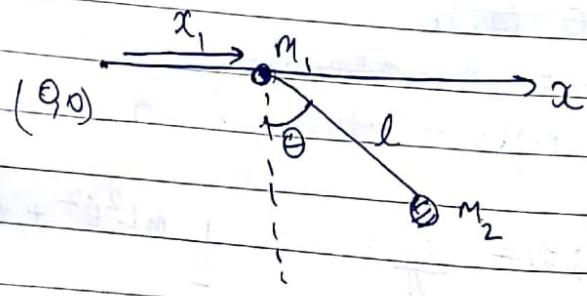
$$\Rightarrow \boxed{\ddot{\theta} + \frac{g \sin\theta}{l} = 0} \rightarrow \text{equation of motion of a pendulum.}$$

For very small θ , $\sin\theta \approx \theta$

$$\therefore \ddot{\theta} + \frac{g \theta}{l} = 0$$

$$\Rightarrow \theta = A \sin \left(\sqrt{\frac{g}{l}} t + \phi \right)$$

\rightarrow Example - II :- Sliding Pendulum



A simple pendulum of mass m_2 with a mass m_1 at the point of support, which constrains the mass to move on a horizontal line lying along the

No. of degrees of freedom - 2

Generalised coordinates :- x_1, θ

LECTURE - XVIII

→ Conservation Laws

(I) Homogeneity of time → L would not depend on time explicitly.
This is somewhat related to the convergence of conservation of energy.
At any point in phase space, L would be the same at different points in time.

(II) Homogeneity of space: L does not change by translation of the whole system. Related to conservation of linear momentum.

(III) Isotropy of space → L does not change by rotation of the whole system.
Related to conservation of angular momentum.

Proof :-

→ Conservation of momentum (cont.)

→ Homogeneity of space :- the mechanical properties of a closed system are unchanged by any parallel (rigid body) displacement of the entire system in space.

Are conservation of p and conservation of angular p just special cases of the conservation of generalised momentum?

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Displace every degree of freedom by ϵ .

$$q_i \rightarrow q_i + \epsilon \quad \text{if } q_i \text{ is unchanged}$$

$$\therefore SL = \sum_i \frac{\partial L}{\partial \dot{q}_i} \cdot \epsilon \ddot{q}_i$$

$$\Rightarrow SL = \epsilon \sum_i \frac{\partial L}{\partial \dot{q}_i}$$

Since system is homogenous in space, $SL=0$ due to displacement.

$$\therefore \sum_i \frac{\partial L}{\partial \dot{q}_i} = 0$$

$$\Rightarrow \sum_i \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) = 0 \quad - \text{from Euler-Lagrange equation}$$

$$\Rightarrow \frac{d}{dt} \left(\sum_i \frac{\partial L}{\partial \dot{q}_i} \right) = 0$$

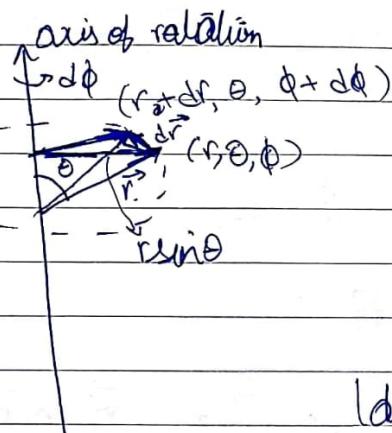
$$\text{Also, } \frac{\partial L}{\partial \dot{q}_i} = m \ddot{q}_i$$

$$\therefore \frac{d}{dt} \left(\sum_i m \ddot{q}_i \right) = 0$$

\therefore Total momentum $P = \sum_i m \dot{q}_i$ is a constant for the motion.

↳ Conservation of angular momentum

Isotropy of space :- Lagrangian is invariant under rotation of the whole system by an arbitrary angle?



$\theta \rightarrow$ does not change
(spherical coordinates)

$r \rightarrow$ may change if axis does

$$|dr|^2 = r \sin \theta d\phi^2$$

$$\rightarrow d\vec{r} = d\vec{\phi} \times$$

$$\therefore \vec{s} = \vec{s} \times \vec{r}$$

$$\therefore d\vec{r} = d\vec{\phi} \times \vec{r}, \quad \Rightarrow d\vec{v} = d\vec{\phi} \times \vec{v}$$

This can be done for all the points in the body.

$$L = L(\vec{r}_i, \vec{\theta}_i) \quad \dots$$

$$\Rightarrow \delta L = \sum_i \left(\frac{\partial L}{\partial \vec{r}_i} \cdot \delta \vec{r}_i + \frac{\partial L}{\partial \vec{\theta}_i} \cdot \delta \vec{\theta}_i \right)$$

$$\frac{\partial L}{\partial \vec{r}_i} = \begin{bmatrix} \frac{\partial L}{\partial x_i} \\ \frac{\partial L}{\partial y_i} \\ \frac{\partial L}{\partial z_i} \end{bmatrix}$$

$$= \sum_i \left(\vec{p}_i \cdot (d\vec{\phi} \times \vec{r}) + \vec{p}_i \cdot (d\vec{r} \times \vec{v}) \right)$$

Also, the scalar triple product STP is invariant under circulation
i.e. $[\vec{x} \vec{y} \vec{z}] = [\vec{y} \vec{z} \vec{x}] = [\vec{z} \vec{x} \vec{y}]$

$$\therefore SL = \sum_i \partial \vec{d\phi} \cdot (\vec{r}_i \times \vec{p}_i) + \vec{d\phi} \cdot (\vec{v}_i \times \vec{p}_i)$$

$$= \vec{d\phi} \cdot \left(\sum_i (\vec{r}_i \times \vec{p}_i) + (\vec{v}_i \times \vec{p}_i) \right)$$

Also, note that $\vec{v}_i \times \vec{p}_i = 0$

$$\therefore SL = \vec{d\phi} \cdot \sum_i \vec{r}_i \times \vec{p}_i$$

$$\text{Also, } \frac{d}{dt} (\vec{r}_i \times \vec{p}_i) = \vec{r}_i \times \dot{\vec{p}}_i + \vec{v}_i \times \vec{p}_i$$

$$\therefore SL = \vec{d\phi} \cdot \sum_i \frac{d}{dt} (\vec{r}_i \times \vec{p}_i)$$

$$= \vec{d\phi} \cdot \frac{d}{dt} \left(\sum_i \vec{r}_i \times \vec{p}_i \right)$$

Now, by isotropy of space,

$$SL = 0$$

Also, since $\vec{d\phi} \neq 0$, \therefore

$$\frac{d}{dt} \left(\sum_i \vec{r}_i \times \vec{p}_i \right) = 0$$

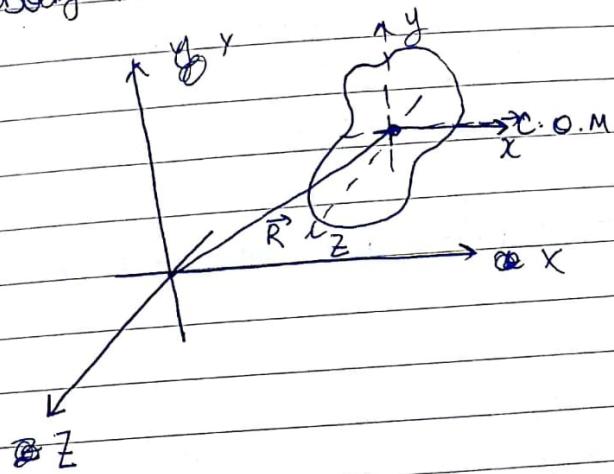
what if $\vec{d\phi}, \frac{d}{dt} \left(\sum_i \vec{r}_i \times \vec{p}_i \right)$
are perpendicular?

The total angular momentum of the system remains conserved.



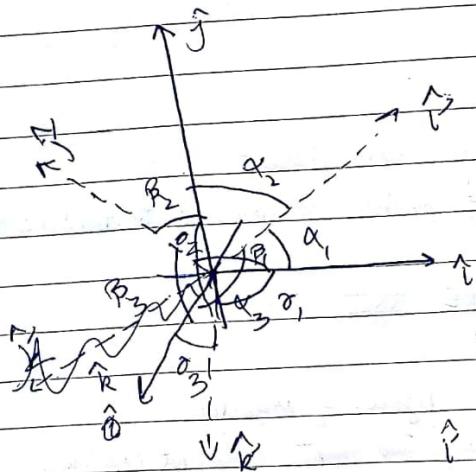
→ ROTATION MATRICES

Rigid body mechanics :-



∴ we can try study translation of C.O.M., and study the angles made by x, y, z with $\hat{x}, \hat{y}, \hat{z}$ to study rotational dynamics
(there are ~~two~~ such degrees of freedom, as $\hat{x} \times \hat{y} = \hat{z}$)

Rotational mechanics :-



$\hat{i}, \hat{j}, \hat{k} \rightarrow$ After rotation

We express \hat{i} in terms of $\hat{i}, \hat{j}, \hat{k}$.

$$\hat{i} = (\hat{i} \cdot \hat{i})\hat{i} + (\hat{i} \cdot \hat{j})\hat{j} + (\hat{i} \cdot \hat{k})\hat{k}$$

Similarly, we can find express \hat{j}', \hat{k}' .

$$\hat{j} = (\hat{j} \cdot \hat{i})\hat{i} + (\hat{j} \cdot \hat{j})\hat{j} + (\hat{j} \cdot \hat{k})\hat{k}$$

$$\hat{k} = (\hat{k} \cdot \hat{i})\hat{i} + (\hat{k} \cdot \hat{j})\hat{j} + (\hat{k} \cdot \hat{k})\hat{k}$$

$$K = \frac{1}{2} \sum m_i v_i^2$$

$$= \frac{1}{2} \sum m_i (v_i^2 + v_{cm}^2 + 2v_i \cdot \vec{v}_{cm})$$

$$\vec{r}_i = \vec{r} + \vec{R}$$

$$v_i = v + \vec{v}$$

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$$\therefore \begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix} = \begin{bmatrix} \hat{i} \cdot \hat{i} & \hat{i} \cdot \hat{j} & \hat{i} \cdot \hat{k} \\ \hat{j} \cdot \hat{i} & \hat{j} \cdot \hat{j} & \hat{j} \cdot \hat{k} \\ \hat{k} \cdot \hat{i} & \hat{k} \cdot \hat{j} & \hat{k} \cdot \hat{k} \end{bmatrix} \begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix}$$

rotation matrix \mathbf{R}

Note that, $\hat{i} \cdot \hat{i} = \cos \theta = \hat{i} \cdot \hat{i}$, where θ is angle b/w \hat{i}, \hat{i} .

$$\begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix} = \begin{bmatrix} \cos \alpha_1 & \cos \alpha_2 & \cos \alpha_3 \\ \cos \beta_1 & \cos \beta_2 & \cos \beta_3 \\ \cos \gamma_1 & \cos \gamma_2 & \cos \gamma_3 \end{bmatrix} \begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix}$$

Note that $\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3, \gamma_1, \gamma_2, \gamma_3$ are constrained.

$$\hat{i} \cdot \hat{j} = \hat{j} \cdot \hat{k} = \hat{k} \cdot \hat{i} = 0$$

$$\hat{i} \cdot \hat{i} = 1$$

$$\hat{j} \cdot \hat{j} = \hat{k} \cdot \hat{k} = 1$$

$\therefore 9 - 6 = 3$ degrees of freedom are present

\therefore only 3 angular degrees of freedom are required to describe rotation

LECTURE XXII

Rigid body dynamics:- Has 6 degrees of freedom

Rigid body:- Distance b/w any two points does not change.

can be broken into two parts - translation of C.O.M, and rotation about the C.O.M

$$\vec{r}, \vec{r} = c \Rightarrow \vec{r} \cdot \vec{r} = 0 \quad U = \sum m g k_e (h_{cm} + h)$$

$$\frac{d\vec{r}}{dt} \cdot \vec{r} = 0 \quad \text{Q} \frac{\vec{r} \cdot d\vec{r}}{dt} + \frac{d(\vec{r})}{dt} \cdot \vec{r} = 0 \quad = Mgh_{cm} +$$

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\therefore KE, PE of the C.O.M can be calculated.

Rotation matrix:-

$$\begin{bmatrix} i' \\ j' \\ k' \end{bmatrix} = \begin{bmatrix} \cos \alpha, \cos \beta, \cos \gamma \\ \cos \beta, \cos \gamma, \cos \alpha \\ \cos \gamma, \cos \alpha, \cos \beta \end{bmatrix} \begin{bmatrix} i \\ j \\ k \end{bmatrix}$$

$$i' \cdot j' = 0 \Rightarrow \cos \alpha, \cos \beta, + \cos \alpha_2 \cos \beta_2 + \cos \alpha_3 \cos \beta_3 = 0$$

After applying the 6 constraints we will get 5 more constraint equations.

$$\vec{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = x \hat{i} + y \hat{j} + z \hat{k} \quad (\text{i.e. space-fixed set of unit vectors})$$

To express \vec{r} in terms of i', j', k' ,

$$\vec{r} \cdot i' = x(i \cdot i') + y(j \cdot i') + z(k \cdot i') = x'$$

$$\vec{r} \cdot j' = x(i \cdot j') + y(j \cdot j') + z(k \cdot j') = y'$$

$$\vec{r} \cdot k' = x(i \cdot k') + y(j \cdot k') + z(k \cdot k') = z'$$

Now,

$$\vec{r} = x' i' + y' j' + z' k'$$

Also,

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos \alpha, \cos \beta, \cos \gamma \\ \cos \beta, \cos \gamma, \cos \alpha \\ \cos \gamma, \cos \alpha, \cos \beta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

\hookrightarrow since this maps a unit basis to another basis, this is distance preserving.

\therefore Applying this to a rigid body does not change distance b/w points.

$$(AB) \cdot (BA)^{-1}$$

$$= (AB) \cdot (\cancel{A}^{-1} \cancel{B})$$

$$= A(B \cdot A^{-1})B^{-1}$$

$$A \cdot A^T = I$$

$$B \cdot B^T = I$$

$$AB = BA$$

$$(AB) \cdot (BA)^{-1} = I$$

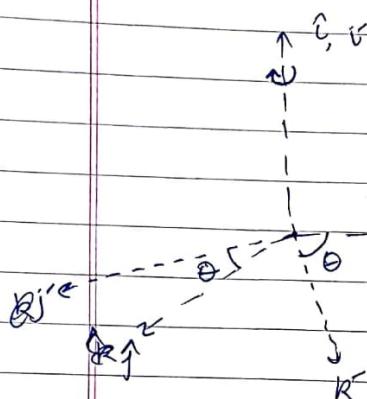
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$\Rightarrow A$.

Example : rotate a point, about x -axis by $\theta = 90^\circ$, clockwise



$$\alpha_1 = 0, \alpha_2 = \frac{\pi}{2}, \alpha_3 = \frac{\pi}{2}$$

$$\beta_1 = \frac{\theta\pi}{2}, \beta_2 = \theta, \beta_3 = \frac{\pi}{2} + \theta$$

$$\gamma_1 = \frac{\pi}{2}, \gamma_2 = \frac{\pi}{2} - \theta, \gamma_3 = \theta$$

$$\therefore \cos \alpha_1 = 1, \cos \alpha_2 = 0, \cos \alpha_3 = 0$$

$$\cos \beta_1 = 0, \cos \beta_2 = \cos \theta, \cos \beta_3 = -\sin \theta$$

$$\cos \gamma_1 = 1, \cos \gamma_2 = \sin \theta, \cos \gamma_3 = \cos \theta$$

\therefore Rotation matrix is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{bmatrix}$$

no change along x revolution about θ in y - z plane

for anti-clockwise rotation, matrix is

$$A \cdot R \cdot A^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix}$$

Note that $A \cdot A^T = I \Rightarrow A$ is an orthogonal matrix

Properties of a rotation matrix :-

$$A = \begin{bmatrix} \cos\alpha, \cos\beta, \cos\gamma \\ \cos\theta, \cos\phi, \cos\psi \\ \cos\varphi, \cos\theta, \cos\psi \end{bmatrix}$$

(A must be an orthogonal matrix).

→ successive rotations are just products of corresponding rotation matrices.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \xrightarrow{A_1} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \xrightarrow{A_2} \begin{bmatrix} x'' \\ y'' \\ z'' \end{bmatrix}$$

$A_2 A_1$

Note that $A_2 A_1 \neq A_1 A_2$)

→ Inverse rotation $\Rightarrow A^{-1}$

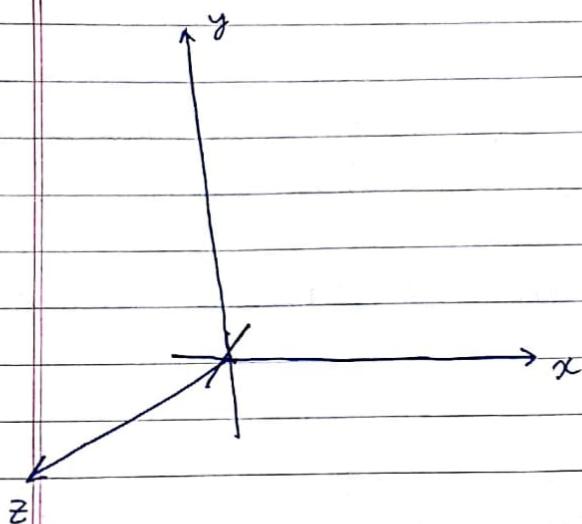
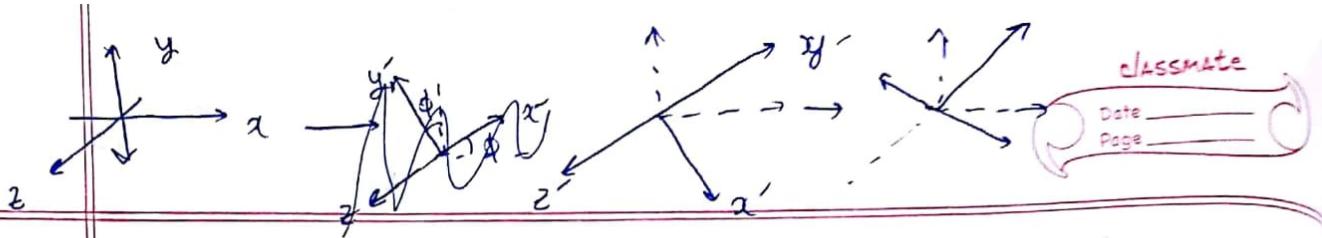
→ $A^T = A^{-1}$, for orthogonal (rotation) matrices.
 \downarrow
 $A \cdot A^T = I = A^T A$

→ Euler Angles :- can be used to describe any rotations about any arbitrary axis.

Any arbitrary axis rotation can be written as a composition of three rotations along x, y, z axes.

Any rotation can be described by successive rotations about three linearly independent axes

Euler angles :- θ, ϕ, ψ



→ start from x, y, z frame
of reference

→ → Rotate by ϕ counter-clockwise
about z -axis.

$$\therefore A_1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{bmatrix}$$

$$A_1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi + \sin\phi & 0 \\ 0 & -\sin\phi & \cos\phi \end{bmatrix}$$

→ start

→ final

→ frame of reference is now $x', y', z' (\in z)$

→ rotate by θ counter-clockwise about x' axis

$$A_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$$

→ frame of reference is now $x'', y'', z'' (x'' = x')$

→ rotate by ψ counter-clockwise about z'' axis.

$$A_3 = \begin{bmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = A_3 A_2 A_1 \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

CLASS ASSIGNMENT

LECTURE - XXIV

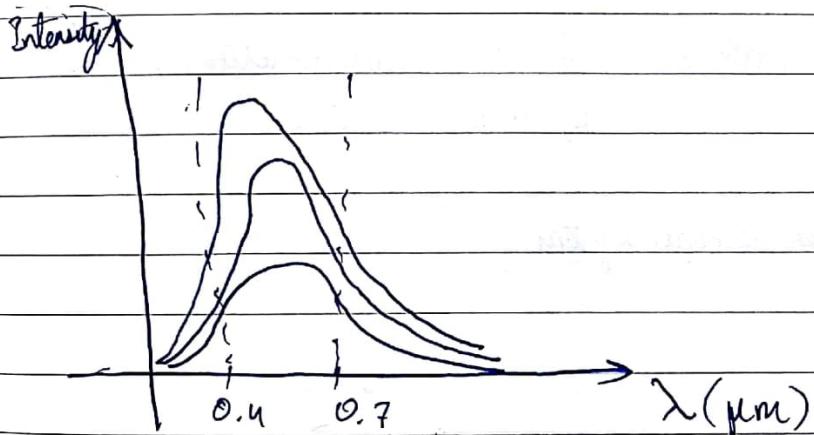
QUANTUM

MECHANICS

BLACK BODY RADIATION

Black body :- emits 100% of the light that falls on it.

Also, emits maximum possible radiation at given temperature.



→ Black body radiation curve changes with temp.

→ At a given temp, black body radiates at all wavelengths

→ As the temperature increases the peak wavelength emitted by the object decreases.

→ Total energy emitted (i.e. total area under the curve) increases with temperature.

Planck :- Only ~~or~~ ^{discrete} fixed packets of energy are released emitted called the smallest such energy unit being ~~the~~ ^h, where h is the Planck's constant.

Other experiments that pointed towards a quantum theory:-

- Double-slit experiment.
- Photoelectric effect
- Atomic spectra
- Stern-Gerlach experiment
- Heat capacity of solids
- Scattering of X-rays by solids (Compton effect)
- Diffraction of e^- by crystals.

→ Analysis of Quantum Systems

~~ψ~~ wave & Ψ = wavefunction, defines state of a quantum system.

For one-dimensional system,



$\hat{H}\Psi$

$\Psi(x, t)$, = wavefunction.

All the physical properties of a system can be expressed as operators

e.g.

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} \quad \text{- momentum operator, } \hbar = \frac{h}{2\pi}, h \text{ is the}$$

Planck's Constant

$$\hat{P}_x \Psi(x, t) = P \Psi(x, t) \quad (\text{Applying operator on wavefunction})$$

\hookrightarrow momentum

$$\hat{H} = i\hbar \frac{\partial}{\partial t} \quad \text{- Hamiltonian or energy operator.}$$

Schrodinger
System

$$\hat{H} \Psi(x, t) = E \Psi(x, t)$$

↓ total energy -

$$\hat{H} = \underbrace{\hat{T}}_{\text{K.E. operator}} + \underbrace{\hat{V}}_{\text{pot. PE operator}}$$

$$\hat{T} = \frac{\hat{P}_x^2}{2m}$$

$$\therefore \hat{V} = V(x)$$

$$\therefore \hat{H} = \frac{\hat{P}_x^2}{2m} + \hat{V}(x)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$$

$$\hat{H} \Psi(x, t) = \boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + \hat{V}(x) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}}$$

OR

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + \hat{V}(x) \Psi(x, t) = E \Psi(x, t)$$

Schroedinger equation is the equation of motion of quantum systems.