

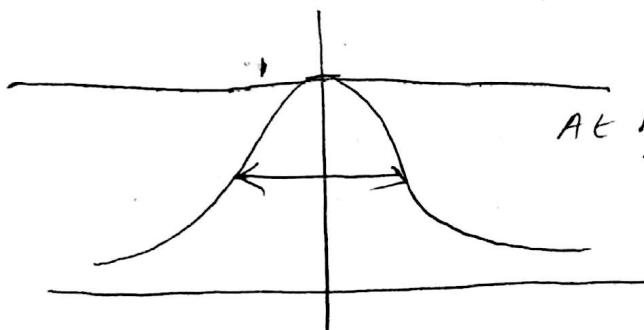
Quasistatic process - Process that happens slowly enough for the system to remain in internal equilibrium.

Any reversible process is quasi-static. However quasi-static processes involving entropy production is irreversible. (e.g. piston with friction present, but system is always in thermal equilibrium)

$F = \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{2}} dx$ gives width of Maxwell Boltzmann distribution

Maxwell Boltzmann equation & distribution :

Normal distribution is



$x = 0$ Kelvin
velocity
(temperature
is 0 Kelvin
 $\Rightarrow 0$ velocity)

At high temperature,
 $T \rightarrow \infty$, there is
non zero probability
for velocities
to be $-\infty$ to ∞
(flat distribution)

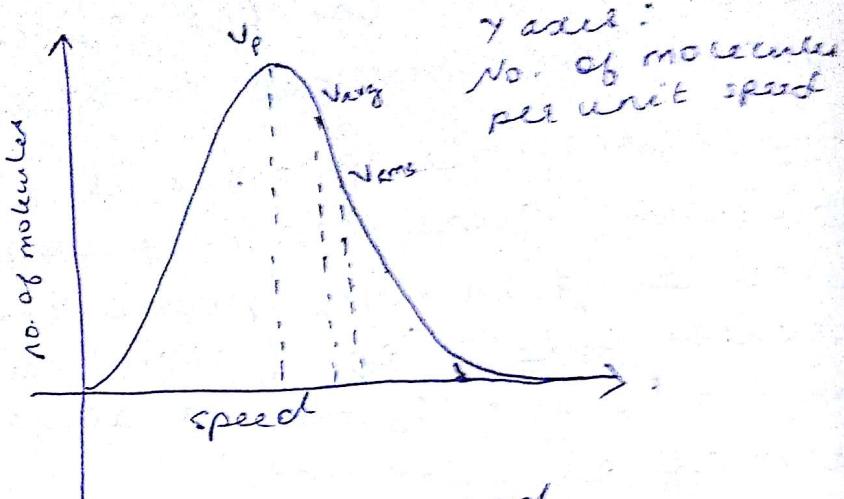
The width of the distribution represents temperature.

For ideal gas system,

$$\text{avg. K.E.} = \frac{3}{2} m k_B T$$

No particle can have velocity greater than light, so this distribution is wrong.

MAXWELL - BOLTZMAN DISTRIBUTION



v_p - most probable speed

v_{avg} - average speed (located to right of peak due to the longer tail)

v_{rms} - Square root of the mean of the squares of the velocities

$$v_{rms} = \sqrt{\frac{1}{N} (v_1^2 + v_2^2 + \dots)}$$

v_{rms} is required because velocity is a vector and can be negative or positive

Total area under the curve gives total no. of molecules in a gas. and is a constant.

As it is heated, peak of graph shifts to right (as speed increases) and height decreases to maintain total area.

TOPICS

- 1) mechanics
- 2) electric
- 3) thermo
- 4) SE astroph
- 5) Quant

BOOKS

- Concepts
Basics
Feynman
Physical
Fundamental
Thermal
classical
mechanics
Quantum
Quantum

GRADING

- Did 1
Did 2
Final
Assign

TOPICS

- 1) Mathematical modelling (Diffusion etc)
- 2) Classical mechanics
- 3) Thermodynamics
- 4) Statistical mechanics
- 5) Quantum mechanics

BOOKS

Concepts of modern physics - Arthur
Bass

Feynman lectures on physics

Physical chemistry - Atkins

Fundamentals of statistical &
thermal physics - F. Reif

Classical mechanics - H. Goldstein

Mechanics - L.D Landau & E.M Lifshitz

Quantum chemistry - J.N. Greene

Quantum mechanics - Y. Dvaidhae

GRADING

mid 1 - 20%

mid 2 - 20%

Final - 40%

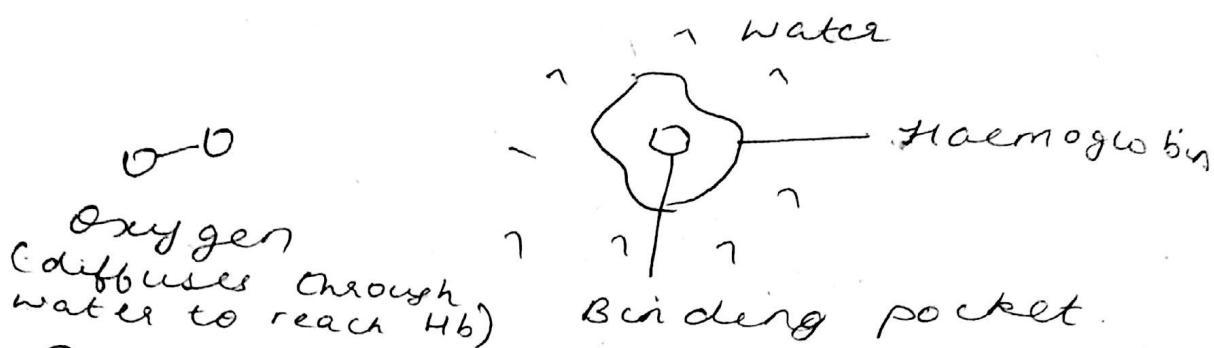
assignment / quizzes - 20%

(Q) most probable speed of N_2 at room temp. and atmospheric pressure,

10^{-18} s (atto)

10^{-15} s (femto)

DIFFUSION



O₂ looks for a gate to enter in Hb. It has to move inside the protein to find target

Model: one dimensional random walk

A drunkard starts from $x=0$. Each step is of equal length (ℓ). Direction of each step is completely independent of the preceding step (random). At each time, the probability of a step to being to the right is p while the probability to the left is q .

Question: After n steps, what is the probability that he/she is located at a given distance from the origin?

$n_1 \Rightarrow$ no. of steps to the right
 $n_2 \Rightarrow$ " left

$N = n_1 + n_2$ = total no. of steps
 net displacement $m = n_1 - n_2$
 one probability of taking n_1 steps to the right out of N steps.

simple cases :

$$(i) N=3, n_1=2, n_2=1$$

$\begin{array}{c} ++- \\ +-+ \\ -++ \end{array} \left. \begin{array}{c} \\ \\ \end{array} \right\} 3 \text{ possibilities}$

$$(ii) N=4, n_1=2, n_2=2$$

$\begin{array}{c} ++-- \\ +-+ - \\ +- - + \end{array}$	$\begin{array}{c} - - + + \\ - + - + \\ - + + - \end{array} \left. \begin{array}{c} \\ \\ \end{array} \right\} 6$
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Probability gives n_1 and n_2 .

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

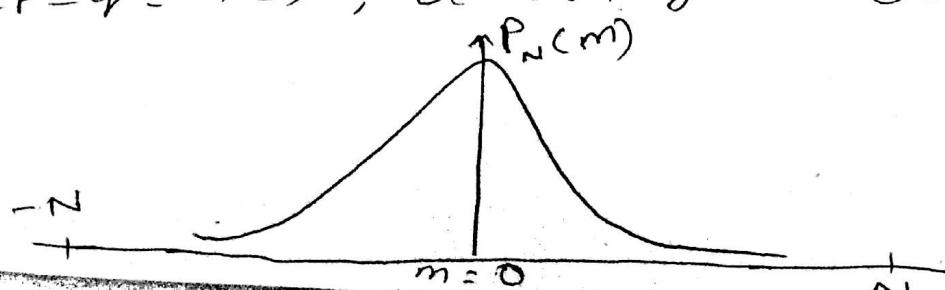
$$= {}^n C_{n_1} p^{n_1} q^{n_2}$$

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

$$\left\{ n_1 = \frac{N+m}{2}, n_2 = \frac{N-m}{2} \right\}$$

$$-N \leq m \leq N$$

In case of unbiased probability ($p=q=\frac{1}{2}$), it is symmetric



statistics : mean value of P_i ,
 $\langle n_i \rangle \Rightarrow$ mean value of experiments
 $\chi =$ no. of experiments
 $\langle (n_i - \langle n_i \rangle) \rangle =$ mean deviation in n_i

$\langle (n_i - \langle n_i \rangle)^2 \rangle =$ fluctuations
 $\text{(or)} \quad \text{second moment}$
 $\text{(or)} \quad \text{mean square deviation}$

\Rightarrow
 $u \Rightarrow$ a variable that can take
 m discrete values u_1, u_2, \dots, u_m
 with respective probabilities
 $p(u_1), p(u_2), \dots, p(u_m)$

mean value of u
 $\langle u \rangle = \frac{p(u_1)u_1 + p(u_2)u_2 + \dots + p(u_m)u_m}{p(u_1) + p(u_2) + \dots + p(u_m)}$

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

$$\sum_{i=1}^m p(u_i) = 1. \quad (\text{if } p(u) \text{ is normalised})$$

$f(u)$ is any function of u

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

Deviation :

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

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

$\langle u^2 \rangle$
 can equal
 n^{α} or
 distribution
 coming in
 walk

$$\langle n_i \rangle$$

cons

$$\langle n_i \rangle$$

sum

$$\begin{aligned}
 \langle (\Delta W)^2 \rangle &= \langle (u - \langle u \rangle)^2 \rangle \\
 &= \langle u^2 \rangle - 2\langle u \rangle \langle u \rangle + \langle u \rangle^2 \\
 &= \langle u^2 \rangle + \langle u \rangle^2 - 2\langle u \rangle^2 \\
 &= \langle u^2 \rangle - \langle u \rangle^2
 \end{aligned}$$

$\langle u^2 \rangle \geq \langle u \rangle^2$ since $\langle (\Delta u)^2 \rangle$ can only be greater than or equal to zero

n^{th} moment of the probability distribution is $\langle (u)^n \rangle$

coming back to the 1D random walk:

$$\begin{aligned}
 \langle n_i \rangle &= \frac{\sum_{n_i=0}^N w_N(n_i) n_i}{\sum_{n_i=0}^N w_N(n_i)} \\
 &= \frac{\sum_{n_i=0}^N w_N(n_i) n_i}{N} \quad \text{(since denominator = 1 (normalized))}
 \end{aligned}$$

$$= \frac{\sum_{n_i=0}^N w_N(n_i) n_i}{\sum_{n_i=0}^N w_N(n_i)} \quad \text{(since denominator = 1 (normalized))}$$

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

$$\text{Consider } p \frac{\partial}{\partial p} (p^{n_i}) = n_i p^{n_i}$$

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

sum of derivatives is derivative of sum.

$$\langle n_1 \rangle = \rho \frac{\partial}{\partial \rho} \left[\sum_{n_1=0}^N \frac{N!}{n_1!(N-n_1)!} \rho^{n_1} q^{N-n_1} \right] \quad \langle n_1^2 \rangle$$

$$\langle n_1 \rangle = \rho \frac{\partial}{\partial \rho} (\rho + q)^N \quad [\text{Binomial distribution}]$$

$$= \rho N (\rho + q)^{N-1}$$

$\langle (\Delta n)^2 \rangle \rightarrow$ this quantity can be measured experimentally for any source in a source.

$$\langle n_1 \rangle = \rho N \quad [\text{if } \rho = q = 1/2]$$

$$1/\text{ly} \quad \langle n_2 \rangle = Nq$$

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

$$= \langle n_1 \rangle - \langle n_2 \rangle$$

$$= N(\rho - q)$$

$$\text{For an unbiased case, } \rho = q = 1/2 \quad \langle \Delta n \rangle$$

$$\Rightarrow \langle m \rangle = 0$$

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

$$= \langle n_1^2 \rangle - \langle n_1 \rangle^2$$

$$\text{What is } \langle n_1^2 \rangle ?$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^N n_1^2 w_N(n_1)$$

$$= \sum_{n_1=0}^N \frac{N!}{n_1!(N-n_1)!} \rho^{n_1} q^{N-n_1} n_1^2$$

$$\rho^2 \frac{\partial \rho^n}{\partial \rho} = \rho \frac{\partial \rho^n}{\partial \rho} = \left(\rho^2 \frac{\partial^2 \rho^n}{\partial \rho^2} \right) \frac{\partial \rho^n}{\partial \rho}$$

$$\langle n_1^2 \rangle$$

over sum

one

mean

($\Delta^* n_1$)

$\Delta^* n_1$

of the

of n_1

$$\langle n_i^2 \rangle = \sum_{n=0}^{\infty} n_i^2 \frac{N!}{(n-n_i)!} \left(\rho + \frac{\partial \rho}{\partial n} \right)^n q^{n-n_i}$$

Once change the order of summation & differentiation

$$\langle n_i^2 \rangle = \left(\rho + \frac{\partial \rho}{\partial n} \right) \left[\sum_{n=0}^{\infty} \frac{N!}{n_i!(n-n_i)!} \rho^n q^{n-n_i} \right]$$

$$= \rho \cancel{\frac{\partial^2}{\partial n^2}} (\rho + q)^N \rightarrow \textcircled{*}$$

$$= \rho \left[N (\rho + q)^{N-1} + \rho N (\rho + q)^{N-2} \right]$$

$$= (N\rho)^2 + N\rho q \quad [\because \rho = q = \lambda]$$

$$= \langle n_i \rangle^2 + N\rho q$$

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

$$= N\rho q$$

mean square deviation of n_i

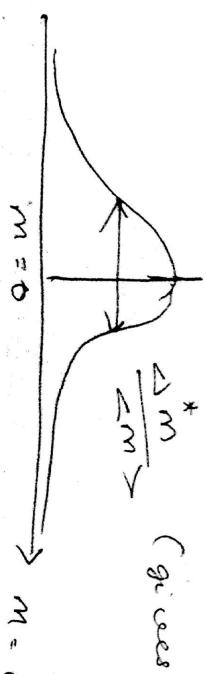
$$(\Delta^* n_i)$$

$$\Delta^* n_i = \sqrt{\langle (\Delta n_i)^2 \rangle}$$

$$\left. \begin{array}{l} \text{one requires which } \\ \text{of the distribution } \end{array} \right\} - \frac{\Delta^* n_i}{\langle n_i \rangle}$$

$$\text{of } n_i$$

$$\frac{\Delta m}{m} \quad (\text{gives error})$$



$$\frac{\Delta n_1}{\langle n_1 \rangle} = \sqrt{\frac{q_1}{p}} \sqrt{\frac{1}{N}}$$

Derivation

$$(*) \quad p \frac{\partial}{\partial p} \left(p \frac{\partial}{\partial p} (p+q)^N \right) \\ = p \frac{\partial}{\partial p} (p N(p+q)^{N-1}) \\ = p \{ N(p+q)^{N-1} + p N(N-1)(p+q)^{N-2} \}$$

$$\langle (\Delta n)^2 \rangle = 4 \langle (\Delta n_1)^2 \rangle$$

$$\begin{aligned} m &= n_1 - n_2 \\ &= 2n_1 - N \\ \Delta n &= m - \langle m \rangle = (2n_1 - N) - 2\langle n_1 \rangle + N \end{aligned}$$

$$= 2(n_1 - \langle n_1 \rangle)$$

$$\Rightarrow \langle (\Delta n)^2 \rangle = 4 \langle (\Delta n_1)^2 \rangle$$

$$= 4 N p q$$

\therefore For unbiased case, $\langle (\Delta n)^2 \rangle \propto 1$

$$\Delta^* n_1 = \langle (\Delta n_1)^2 \rangle^{1/2}$$

relative width of distribution of n

$$:= \frac{\Delta^* n_1}{\langle n_1 \rangle} = \frac{1}{\sqrt{N}}$$

constant

$$\frac{\Delta n_1}{\langle n_1 \rangle} = 0$$

mean square displacement of the random walks is increases linearly

Derivation
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$P(x)$

$P(x)$
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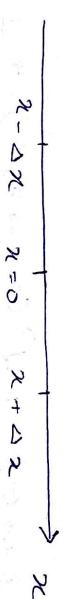
with
DERIVATION

with N

DERIVATION OF THE DIFFUSION EQUATION

Derivation from the random walk model
consider a 1D universe - ∞ to ∞
assume it starts from $x = 0$
and takes step length Δx

$$\rightarrow (P + q)^N \}$$

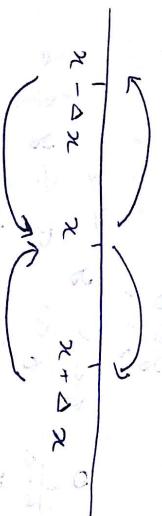


Probability of finding walker at a given x at some time t .

$P(x, t) \Rightarrow$ Probability walker is at x at time t .

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

where Δt is the time step branching probability



π denotes transition probability for him to go from one place to another.

$$P(x, t + \Delta t) = P(x + \Delta x, t) \pi_{(x+\Delta x \rightarrow x)} \\ - P(x, t)$$

$$\# P(x - \Delta x, t) \pi_{(x-\Delta x \rightarrow x)} \\ - P(x, t) \pi_{(x \rightarrow x + \Delta x)} \\ - P(x, t) \pi_{(x \rightarrow x - \Delta x)}$$

For an unbiased random walk

$$\begin{aligned} \Pi(x+\Delta x \rightarrow x) &= \Pi(x-\Delta x \rightarrow x) \\ &= \Pi(x \rightarrow x + \Delta x) \\ &= \Pi(x \rightarrow x - \Delta x) \\ &= 1/2 \end{aligned}$$

LANGEV

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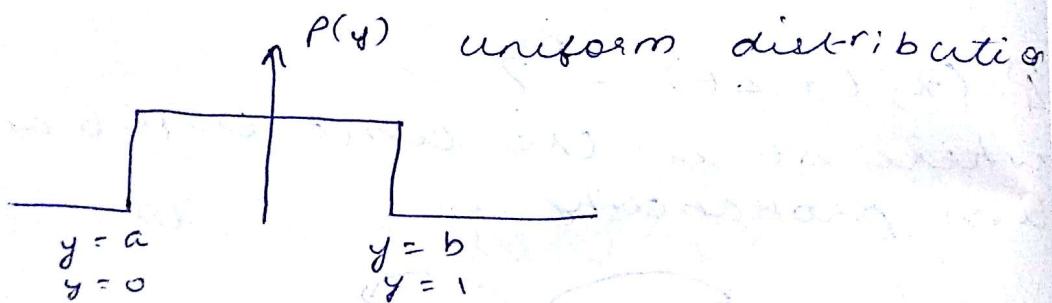
$x(t)$
time

let in

$\frac{d}{dt}$

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

COMPUTATIONAL TASK



$$P(y) = \begin{cases} 0 & \text{for } y < a \\ \frac{1}{b-a} & \text{for } a \leq y \leq b \\ 0 & \text{for } y > b \end{cases}$$

$\langle F \rangle =$

given

$\langle x^2 \rangle$

$\langle x^2 \rangle$

and

by

$m \kappa$

LANGEVIN DYNAMICS

consider 1 dimensional system
(for the sake of simplicity)



m = mass of solute

$x(t) \Rightarrow$ position of solution at time t

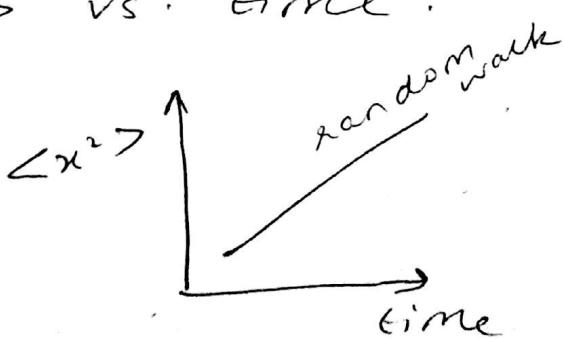
let $\dot{x} = \frac{dx}{dt}$

$$m \frac{d\dot{x}}{dt} = -\alpha \dot{x} + F(t) \quad \begin{matrix} \nearrow \text{random force} \\ \downarrow \\ \text{damping force} \end{matrix} \quad \rightarrow \textcircled{1}$$

α is a positive quantity
(friction coefficient)

$$\langle F \rangle = 0$$

Given this equation, what is $\langle x^2 \rangle$ of the solute? And plot $\langle x^2 \rangle$ vs. time.



multiplying both sides of $\textcircled{1}$
by x ,

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

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

Take average on both sides,

$$m \left[\langle \frac{d}{dt} \langle x \dot{x} \rangle \rangle - \langle \dot{x}^2 \rangle \right]$$

$$= -\alpha \langle x \dot{x} \rangle + \langle x F \rangle$$

$$= -\alpha \langle x \dot{x} \rangle + \langle x \rangle \langle F \rangle \quad [\text{avg. of products is product of avg.}]$$

$$= -\alpha \langle x \dot{x} \rangle + 0 \rightarrow ②$$

We know that, \rightarrow Temperature

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

\downarrow Boltzmann constant

② becomes

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

$$m \frac{d}{dt} \langle x \dot{x} \rangle = k_B T - \alpha \langle x \dot{x} \rangle \rightarrow ③$$

Solution of ③

$$\langle x \dot{x} \rangle = c e^{-\frac{\alpha t}{m}} + \frac{k_B T}{\alpha} \rightarrow ④$$

where c is constant of integration

$$t = \frac{\alpha}{m}$$

\rightarrow gamma

$$\text{Note } \langle x \dot{x} \rangle = \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle$$

$$④ \Rightarrow \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = c e^{-\frac{\alpha t}{m}} + \frac{k_B T}{\alpha}$$

Apply $t=0$
 $x=0$
 $\Rightarrow c =$

$$\therefore \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle$$

integrate
arbitrary
 $t=t$

$$\langle x^2 \rangle$$

This
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apply the initial condition at $t=0$

$$x = 0$$

$$\Rightarrow c = -\frac{K_B T}{\alpha}$$

$$\therefore \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = \frac{K_B T}{\alpha} [1 - e^{-\frac{t}{\tau}}] \rightarrow ⑤$$

integrating from $t=0$ to some arbitrary time of experiment

$$t = t$$

$$\langle x^2 \rangle = 2 \frac{K_B T}{\alpha} \left[t - \frac{(1 - e^{-\frac{t}{\tau}})}{\tau} \right] \rightarrow ⑥$$

This is exponentially proportional as compared to linear in case of random walk model which contradicts random walk model.

case when $t \ll \frac{1}{\tau}$

$$\tau t \ll 1$$

$$e^{-\tau t} = 1 - \tau t + \frac{1}{2} (\tau t)^2 + \dots$$

(Taylor series expansion)

higher powers can be neglected, since $\tau t \ll 1$

$$e^{-\tau t} \approx 1 - \tau t + \frac{1}{2} (\tau t)^2$$

substituting in ⑥

$$\langle x^2 \rangle \approx \frac{K_B T}{m} t^2 \quad (\tau = \frac{L}{m})$$

mean square displacement does not vary linearly with time

If force is zero,

$$m \cdot \frac{d\vec{x}}{dt} = 0$$

$$\frac{d\vec{x}}{dt} = 0$$

integrating,

$$\vec{x} \propto t$$

$$\langle x^2 \rangle \propto t^2$$

therefore when $t \ll \frac{1}{F}$

solute behaves like a free particle for a short period of time

Case 2.

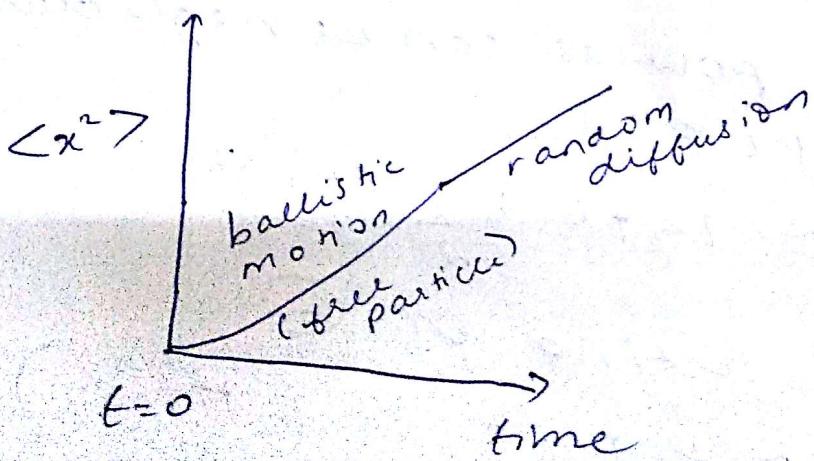
$$t \gg \frac{1}{F}$$

$$Ft \gg 1$$

$$\Rightarrow e^{-Ft} = 0$$

$$\textcircled{6} \Rightarrow \langle x^2 \rangle = 2 \frac{k_B T t}{\lambda}$$

so you get random behaviour at long time



CLASS ASSI

- 2 drunks each have of making eight steps
Find the meet again to be men take
eously
a) theor
b) comp

[soluti

Ans) Displa
get al

$P(m)$ =

for

for

$P(m)$

CLASS ASSIGNMENT

2 drunks start out at the origin each having equal probability of making a step to left or right ~~exist~~ along x axis.

Find the probability that they meet again after N steps. It is to be understood that the men takes their steps simultaneously.

a) Theoretical

b) Computational (Plot P_N vs. N)

$$[\text{solution: } \frac{(2N)!}{(N!)^2} \left(\frac{1}{2}\right)^{2N}]$$

ans) Displacement = 0

Total no. of steps = $2N$

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

for one drunk

For 2 drunks,

$$P(m) = \frac{(2N)!}{\left(\frac{2N}{2}\right)! \left(\frac{2N}{2}\right)!} p^N q^N$$

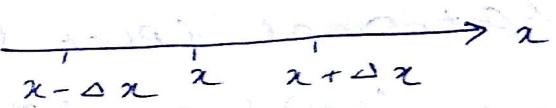
LANGEVIN DYNAMICS

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

where $\alpha = \frac{\alpha}{m}$

DERIVATION OF THE DIFFUSION EQUATION FROM THE RANDOM WALK MODEL

$\Delta x \Rightarrow$ step length
 $\Delta t \Rightarrow$ time step



transition probabilities

$$\pi(x + \Delta x \rightarrow x) = \gamma_2$$

$$\pi(x - \Delta x \rightarrow x) = \gamma_2$$

$$\pi(x \rightarrow x + \Delta x) = \gamma_2$$

$$\pi(x \rightarrow x - \Delta x) = \gamma_2$$

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

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

$$-P(x, t) - \pi(x \rightarrow x - \Delta x) P(x, t)$$

$$+ \pi(x + \Delta x \rightarrow x) P(x + \Delta x, t)$$

$$+ \pi(x - \Delta x \rightarrow x) P(x - \Delta x, t)$$

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

use Taylor
in $f(x)$
function
first, se
a value

$f(x), \frac{df}{dx}$

$f(x + \Delta x)$

$\therefore P(x + \Delta x, t)$

Δx ne

$P(x - \Delta x, t)$

$\Delta x -$

high

① + ②

use Taylor series expansion.

In Taylor series there is a function $f(x)$ and we know its first, second, ... derivatives at a value of x .

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

$$f(x + \Delta x) = f(x) + \frac{1}{1!} \frac{df}{dx}|_x \Delta x$$

$$+ \frac{1}{2!} \frac{d^2 f}{dx^2}|_x (\Delta x)^2 + \dots$$

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

Δx needs to be very very small.

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

$\Delta x \rightarrow 0$, so we can ignore higher terms

$$\textcircled{1} + \textcircled{2} \quad \frac{d^2 P}{dx^2} = P(x + \Delta x) + P(x - \Delta x) \\ - 2P(x) \\ \frac{(\Delta x)^2}{(\Delta x)^2}$$

$$\begin{aligned}
 \frac{d(g(x))}{dx} &= \frac{df(x)}{dx} \\
 &= \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} - \frac{\frac{df(x)}{dx}}{\Delta x} \\
 &= \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{(\Delta x)^2} \\
 &= \left[\frac{f(x + \Delta x) - f(x)}{\Delta x} \right] - \left[\frac{f(x) - f(x - \Delta x)}{\Delta x} \right]
 \end{aligned}$$

$$\begin{aligned}
 \rho(x, t + \Delta t) - \rho(x, t) &= \frac{1}{2} (\Delta x)^2 \frac{\partial^2 \rho(x, t)}{\partial x^2} \\
 &\div \text{ by } \Delta t \text{ on both sides}
 \end{aligned}$$

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

~~now~~ $\Delta x \rightarrow 0, \Delta t \rightarrow 0$

$$\frac{\partial \rho(x, t)}{\partial t} = \frac{(\Delta x)^2}{2 \Delta t} \frac{\partial^2 \rho(x, t)}{\partial x^2} \xrightarrow{\text{space}}$$

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

Diffusion coefficient / constant can be measured experimentally.

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

Diffusion equation
(same it)

$P(x, t) \rightarrow$ spatial and temporal evaluation of $P(x, t)$

For 3D: $\vec{x} = x \hat{i} + y \hat{j} + z \hat{k}$

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

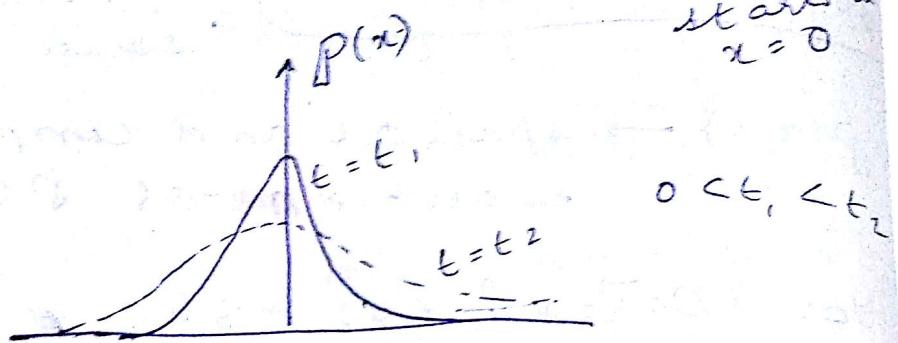
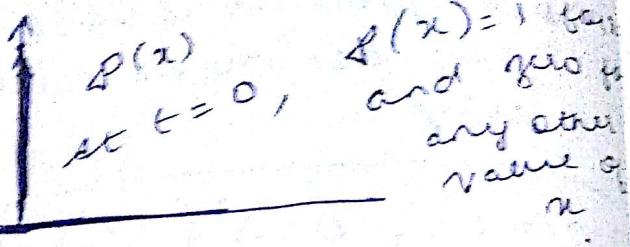
$D_x = D_y = D_z$ (for an isotropic, homogeneous medium)

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

initial condition $P(x, t=0) = \delta(x - x_0)$

$x_0 = 0$ except when $x_0 = x$ in which case $x_0 = 1$: the diffusing

particle starts from $x = 0$ (at $t = 0$)



it becomes uniform distribution after a while (homogeneous)
second derivative gives the curvature.

FOURIER TRANSFORMATION

$\tilde{P}(k, t) \xrightarrow{\sim}$ denotes fourier transform of function

reciprocal space

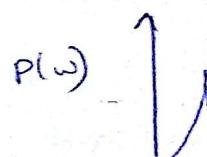
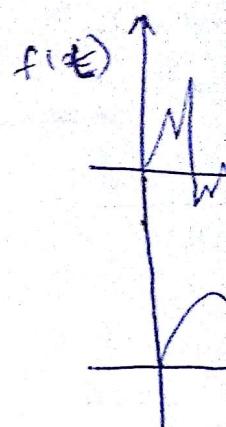
(inverse of length)

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

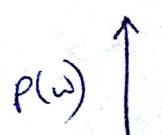
Partial fourier transform since we change only x to k .

Kernel shows how much is distributed to x .

consider
of lattice



sine
of or
vice
versa



Fourier

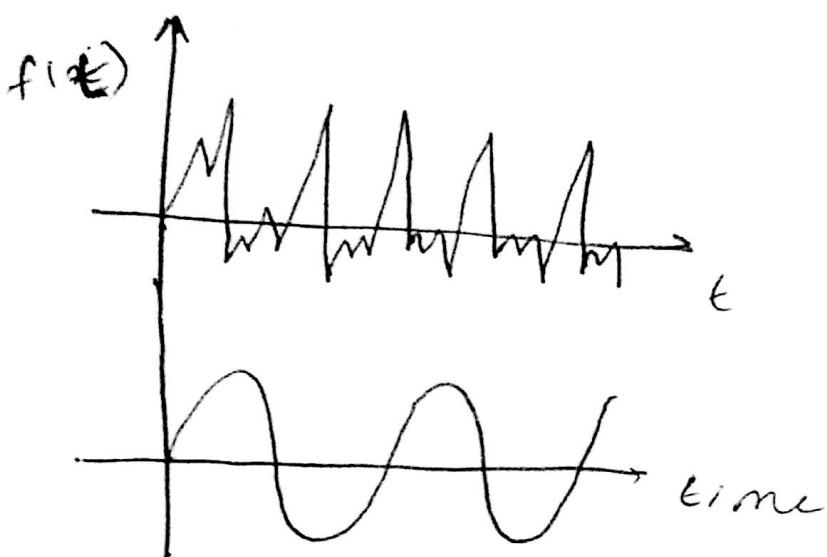
$\tilde{P}(k)$

Inverse

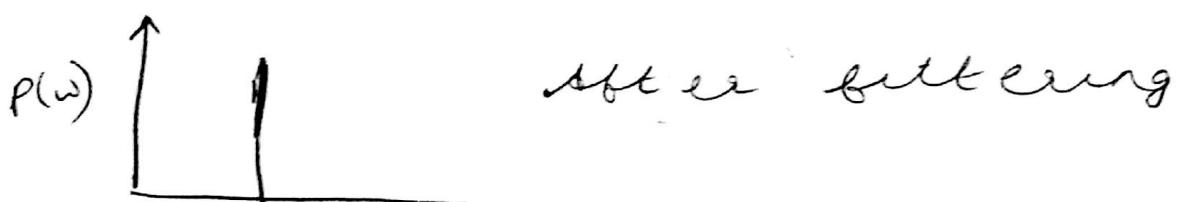
$P(x)$

w

of lattice is $\left(\frac{2\pi}{L}\right)$



Time to frequency using real
FFT or fourier transform.
Vice versa done using inverse
fast fourier transform



Fourier transform (forward)

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

Inverse fourier transform:

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

$$\omega = 2\pi \Delta t$$

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

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

$e^{ikx} \Rightarrow$ Laplace transform

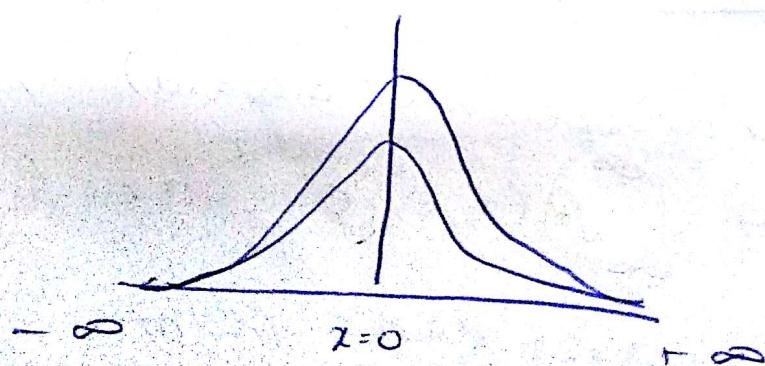
$$\frac{\partial \tilde{P}(k,t)}{\partial t} = \frac{\partial}{\partial t} \tilde{P}(k,t)$$

$$\frac{\partial \tilde{P}(k,t)}{\partial t} = \frac{\partial \tilde{P}(k,t)}{\partial t}$$

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

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

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



for $x \rightarrow \pm \infty$

$$\left[e^{ikx} P(x,t) \right]_{-\infty}^{\infty} = 0$$

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

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

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

$$\frac{\partial^2 \tilde{P}(k, t)}{\partial x^2} = \left[e^{ikx} \frac{\partial P(x, t)}{\partial x} \right]_{-\infty}^{\infty}$$

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

[when $x = \pm\infty$, gradient is 0.]

$$= f(k) (-ik \tilde{P}(k, t))$$

$$\frac{\partial^2 \tilde{P}(k, t)}{\partial x^2} = -k^2 \tilde{P}(k, t) \rightarrow \textcircled{1}$$

The diffusion equation in k-space

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

Take Fourier transformation on both sides.

$$\frac{\partial \tilde{P}(k, t)}{\partial t} = -D k^2 \tilde{P}(k, t) \quad [\text{from } \textcircled{1}]$$

Solution

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

const and integrated

$$P(x=0, t=0) = 1 \quad \text{Initial condition}$$

$$P(x, t=0) = \delta(x - x_0) \quad x_0 \geq 0$$

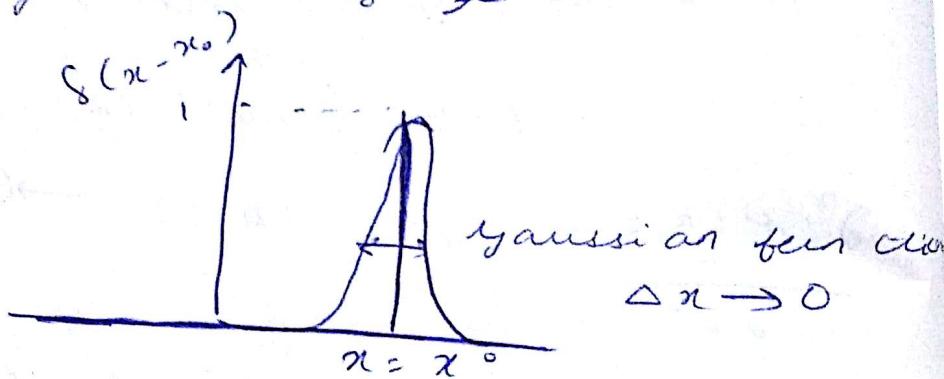
when $x=0$, it becomes 1.
→ calculate $\tilde{P}(k, t=0)$

at $t=0$

$$\tilde{P}(k, 0) = C$$

$$\tilde{P}(k, t=0) = \int_{-\infty}^{\infty} \delta(x - x_0) e^{ikx} dx$$

$\delta(x - x_0)$ takes non zero values
only when $x_0 = 0$



$$\tilde{P}(k, t=0) = e^{ikx_0}$$

since $x_0 = 0$,

$$\tilde{P}(k, t=0) = 1 = C$$

$$\tilde{P}(k, t) = e^{-0 k^2 t}$$

$P(x, t) = \text{Inverse Fourier of } \tilde{P}(k, t)$

$$P(x, t) = \frac{1}{2\pi} \int \tilde{P}(k, t) e^{-kx} dk$$

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

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

$$a^2 = Dk^2 t + i$$

$$2ab = ikx$$

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

$$b^2 = -\frac{x^2}{4Dt}$$

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

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

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

$$\text{set } y = k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}$$

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

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

$$= \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{4\pi Dt}} \cancel{\sqrt{\pi}}$$

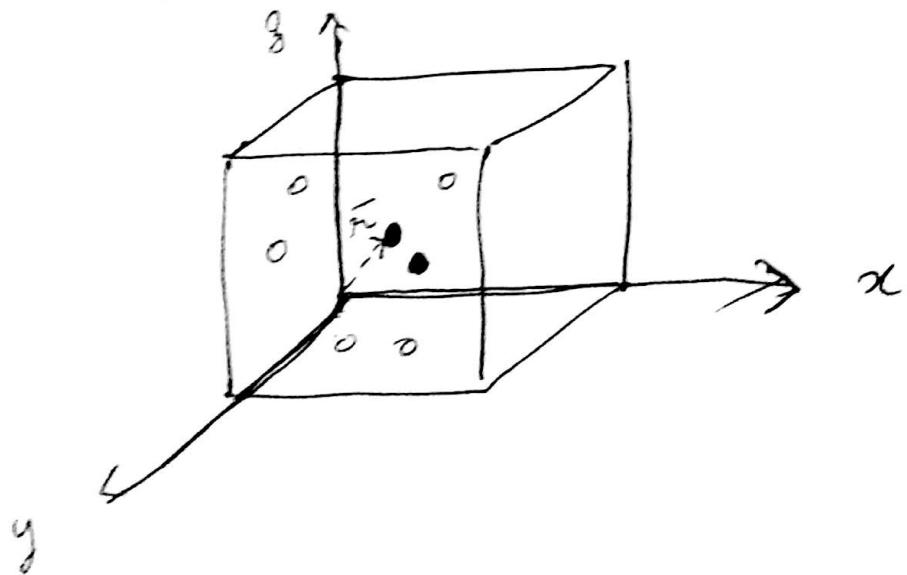
for three dimensions

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$P(\vec{r}, t) = \frac{1}{(4\pi D t)^{3/2}} e^{-\frac{(x^2 + y^2 + z^2)}{4Dt}}$$

GENERAL APPROACH TO STUDY
DYNAMICS AT A MACROSCOPIC LEVEL

- \rightarrow solute (eg. protein)
- \rightarrow solvent (eg. water)



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

(position of i^{th} atom)

$$\vec{r}(t) = x(t) \hat{i} + y(t) \hat{j} + z(t) \hat{k}$$

positions of particle changes with time

of which are N atoms in the system
 $\mathbf{x}_i, i=1, 2, 3, \dots, N$

$\{\vec{x}\}$ is the set of position of all atom

$$\{\vec{x}\} = (\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_n)$$

$$\{\vec{x}(t)\} = (\vec{x}_1(t), \vec{x}_2(t), \dots, \vec{x}_n(t))$$

set of momentum,

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

maxwell boltzman distribution gives velocity

$H \rightarrow$ hamiltonian of system
(total energy)

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

kinetic
energy
function

potential
energy
function

$$\frac{dH}{dt} = ?$$

$$H(x, p)$$

1 Dimension

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

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

$$= \frac{dU}{dx} \left(\frac{dx}{dt} \right) + \frac{dK(p)}{dp} \left(\frac{dp}{dt} \right)$$

velocity → force

If system is kept isolated, total energy remains constant.

$$H(x, p) = \text{constant}$$

$$\Rightarrow \frac{dH}{dt} = 0$$

$$-\frac{du}{dx} \frac{dx}{dt} = \frac{dk(p)}{dp} \frac{dp}{dt}$$

hamilton's equations

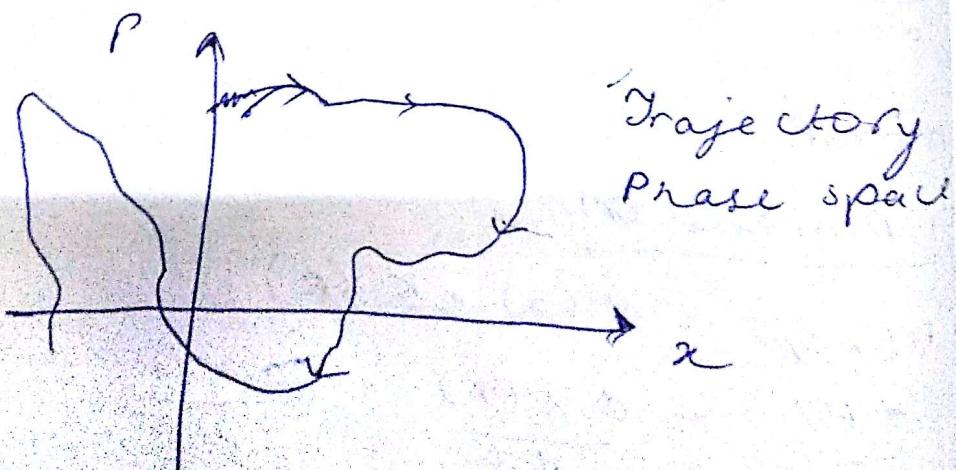
$$\frac{dp}{dt} = -\frac{du}{dx}$$

$$\frac{dx}{dt} = \frac{dk(p)}{dp}$$

} hamilton's
equations of
motion.

Negative gradient of potential energy is force on the particle.
velocity is the momentum gradie of K.E.

Dynamics : how x varies with time and how p varies with time



Initial conditions, $t=0$, $(x(0), p(0))$
Space formed by x and p is

called
for a
phase
space

A (Σ)
↓
arbitrary
prob
such a
square

Σ^2

Σ^3

Σ^4

Time



\leftarrow

$\langle A \rangle$

rec

Let
one

called phase space

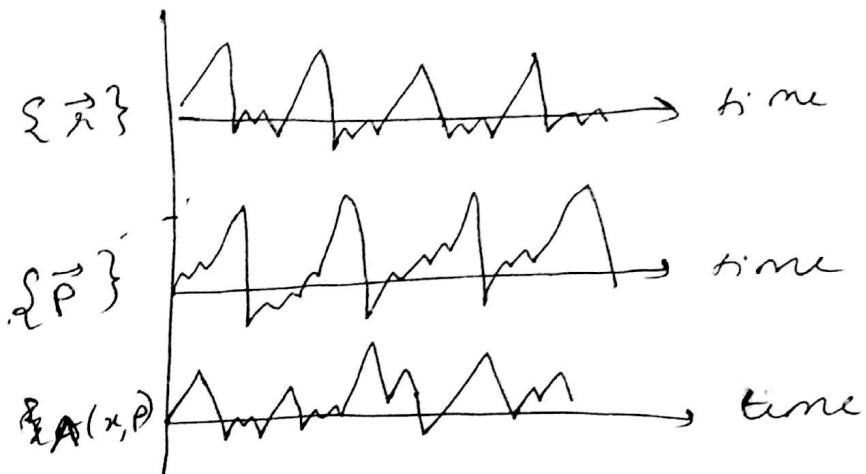
For a system of N particles,
phase space is $6N$ -dimensional

Phase space $(x_1, x_2, \dots, x_n, p_1, p_2, \dots, p_n)$

$$A(\{\vec{x}\}, \{\vec{p}\})$$



arbitrary
property
(such as mean
square displacement etc.)



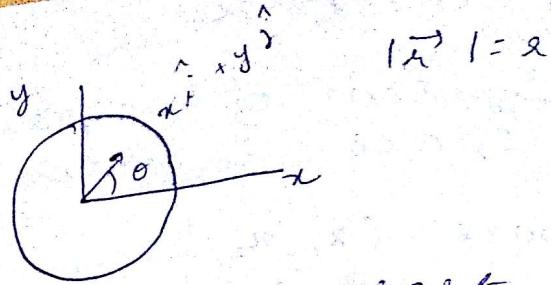
Time average of A (if we know
 x, p , we know
 $A(x, p)$)

$$\langle A \rangle_{\text{time}} = \frac{\sum_{i=0}^{\text{time}} A_i}{t_{\max}}$$

$\langle A \rangle$ is comparable to experimental
results

Let $N \rightarrow$ No. of random walkers
(no. of molecules)

2D:



$$|x| = r$$

initial condition \rightarrow start from
origin.

call random no. 1 (x)

call random no. 2 (θ)

$P_n(x)$ = probability of finding a
random walker at x after n steps

$$0 \leq \theta \leq 2\pi$$

$$0 \leq x \leq \infty$$

$$|x| = r$$

$H(x, P) =$
seamill

$$\frac{dx}{dt} =$$

$$\frac{dP}{dt} =$$

using
 $\alpha(t +$

$$P(t +$$

Phase
space
(1D)

Let
syst

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

hamilton's equations of motion

$$\frac{dx}{dt} = \cancel{\frac{\partial H(p)}{\partial p}} = \frac{\partial H}{\partial p}$$

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

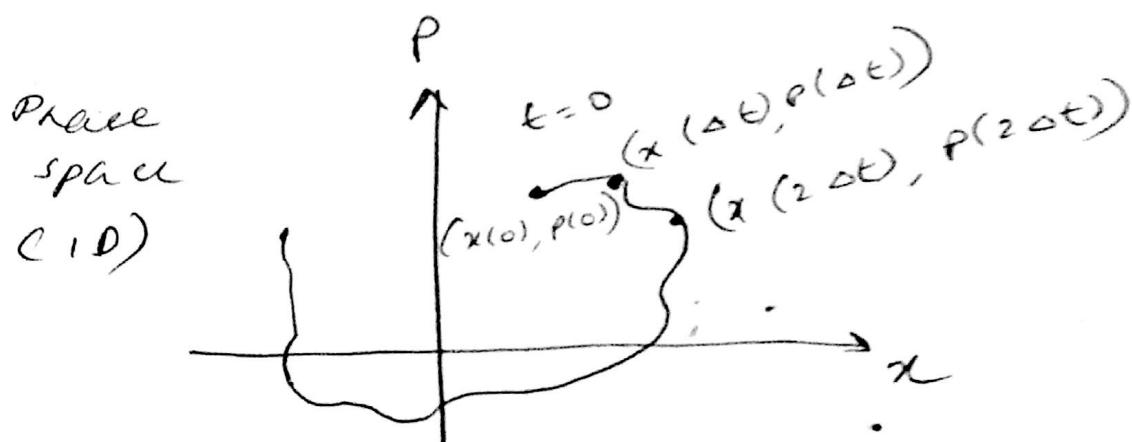
using Taylor series,

$$x(t+\Delta t) = x(t) + \frac{\partial x(t)}{\partial t} \Delta t$$

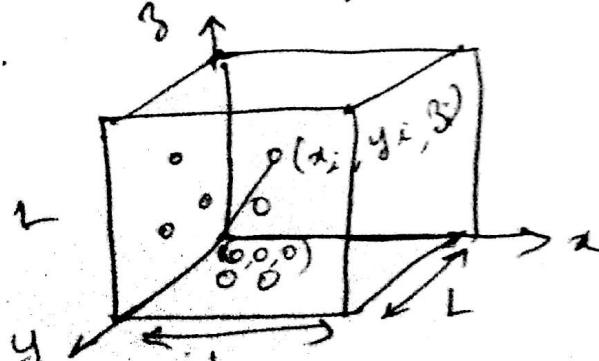
$$+ \frac{1}{2!} \frac{d^2 x}{dt^2} \Big|_t (\Delta t)^2 + \dots$$

$$p(t+\Delta t) = p(t) + \frac{\partial p(t)}{\partial t} \Delta t + \dots$$

↓
Force



Let there be n particles in a system.



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

$$\vec{p}_i = p_{x,i} \hat{i} + p_{y,i} \hat{j} + p_{z,i} \hat{k}$$

$U(\{\vec{r}_i\}) \rightarrow$ Potential energy function

$$\{\vec{r}_i\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$$

$$\{\vec{p}_i\} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_n)$$

$K(\{\vec{p}_i\}) \rightarrow$ Kinetic energy function

Equations of motion for n particle system.

~~$$\frac{d\vec{r}_i}{dt} = \frac{\partial H}{\partial \vec{p}_{x,i}}$$~~

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_{x,i}}$$

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

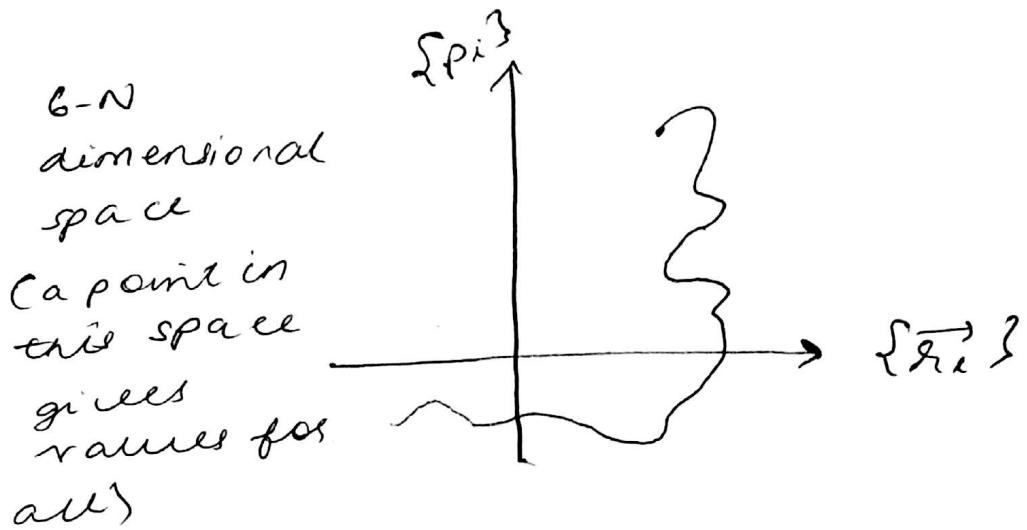
$$\Rightarrow \begin{bmatrix} \frac{dx_i}{dt} \\ \frac{dy_i}{dt} \\ \frac{dz_i}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial H}{\partial p_{x,i}} \\ \frac{\partial H}{\partial p_{y,i}} \\ \frac{\partial H}{\partial p_{z,i}} \end{bmatrix}$$

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

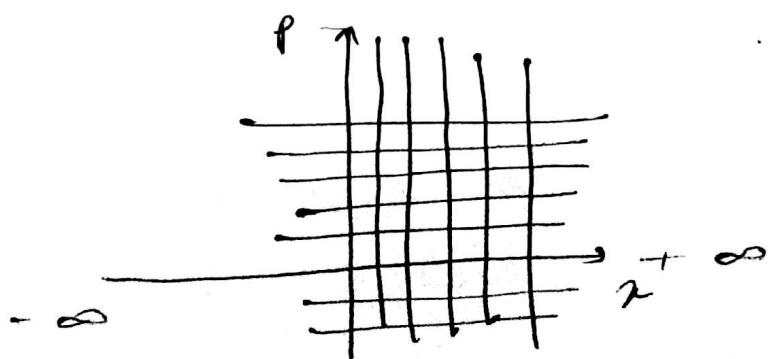
$$\begin{pmatrix} \frac{dP_{x,i}}{dt} \\ \frac{dP_{y,i}}{dt} \\ \frac{dP_{z,i}}{dt} \end{pmatrix} = \begin{pmatrix} -\frac{\partial H}{\partial x_i} \\ -\frac{\partial H}{\partial y_i} \\ -\frac{\partial H}{\partial z_i} \end{pmatrix}$$

There 6 differential equations.

\therefore For an N particle system,
we have $6N$ such equations.

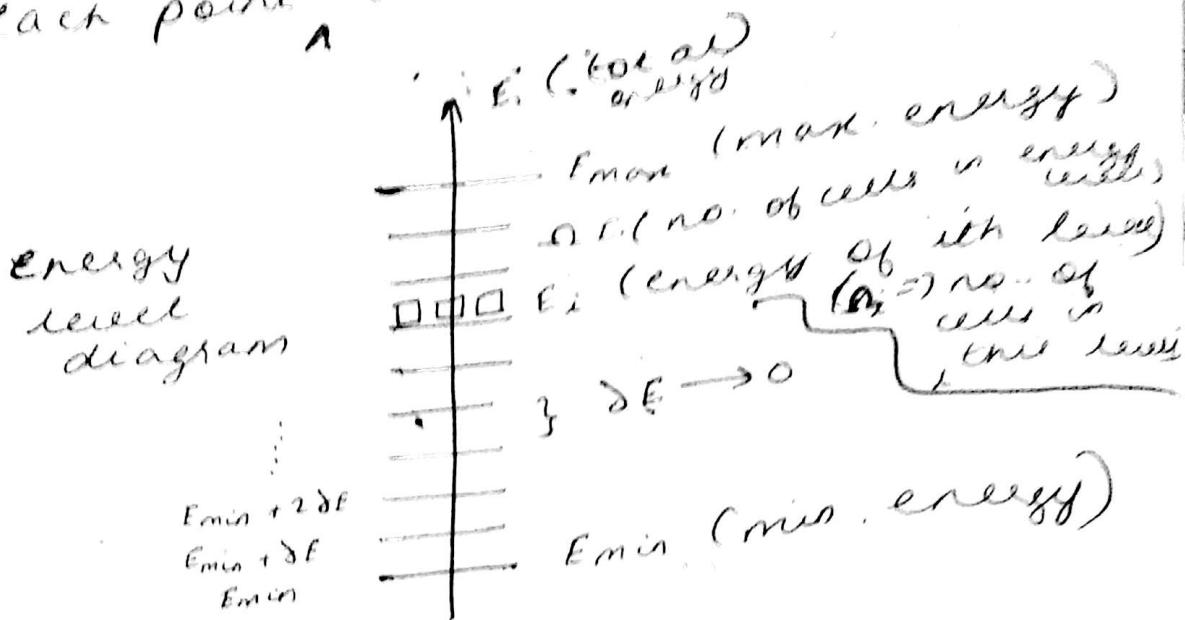


Divide it into several cells
(6 dimensions
cube)



$$\text{Area of a cell} = \delta x \delta p \quad (\delta x \rightarrow 0, \delta p \rightarrow 0) = \hbar = \frac{h}{2\pi} \quad \begin{cases} \text{Angular} \\ \text{momentum} \\ \text{unit} \end{cases}$$

\hbar is Planck's constant
or cell
each point is called a microstate



Take meter $H(x, p)$ and place it on every cell of the grid. That gives energy and based on energy value, stack it on the energy level diagram.

α_i denotes no. of microstates

is energy E_i

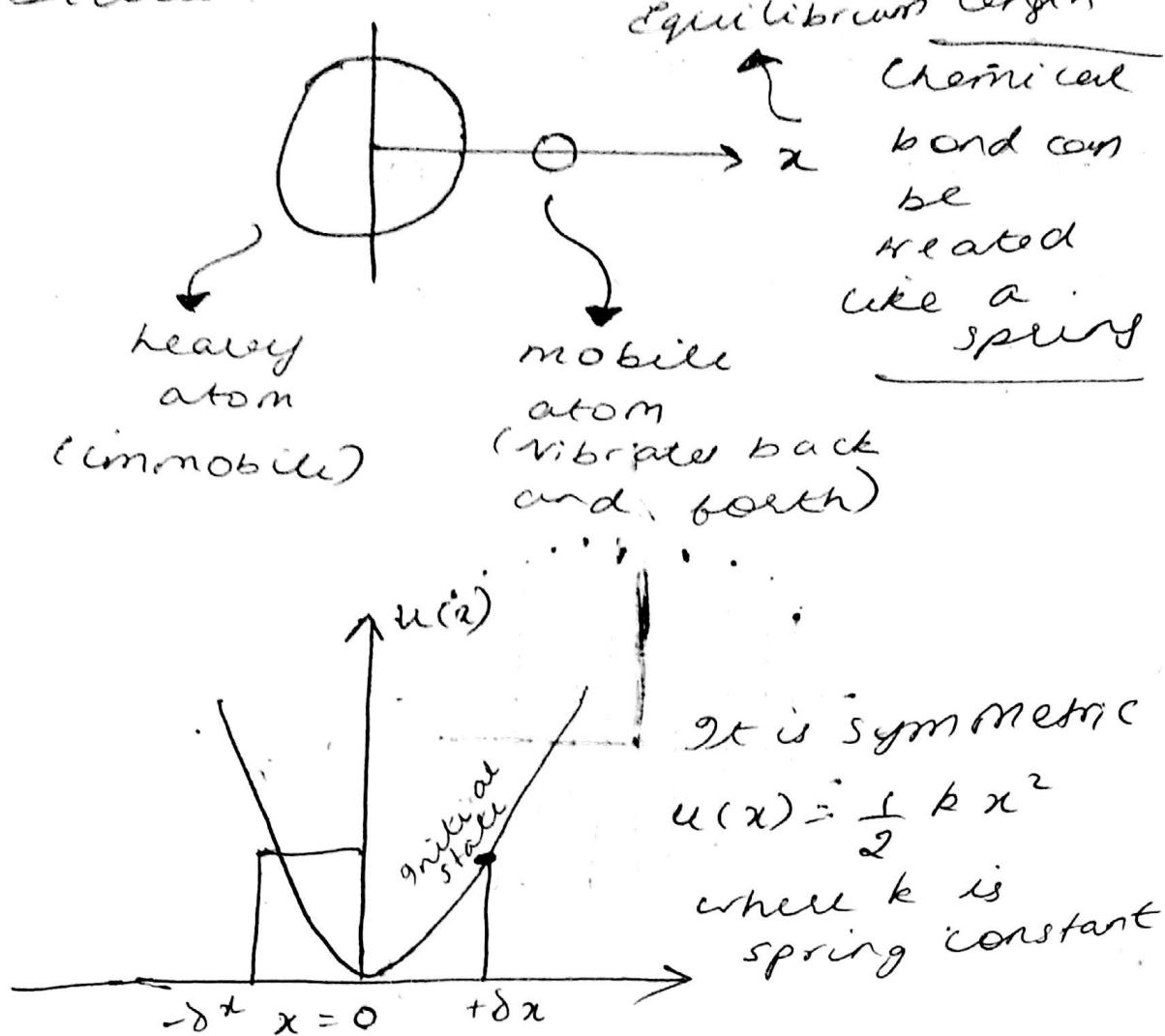
a given energy level is a macrostate of a system with many microstates.

e.g. simple model system

consider 1 dimensional harmonic oscillator

let there be a diatomic molecule - one translational

stationary and the other vibrates.



At initial state, let total energy be E

$$\frac{dH}{dt} = 0$$

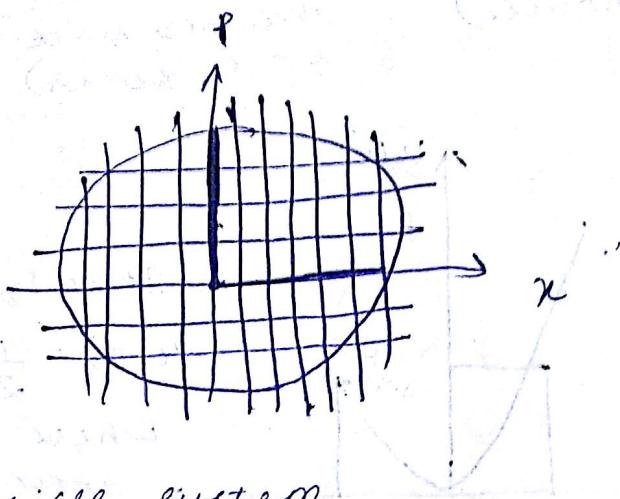
for an isolated system, since energy remains constant.

$$\begin{aligned}
H(x, p) &= u(x) + K(p) \\
&= \frac{1}{2} k x^2 + \frac{p^2}{2m} \xrightarrow{\text{mass of particle}} \\
&= E \quad (\text{critical fixed energy})
\end{aligned}$$

$$\frac{1}{2} k x^2 + \frac{p^2}{2m} = E \text{ which will be constant throughout}$$

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

is the equation of ellipse
path in the $x-p$ space is an ellipse.

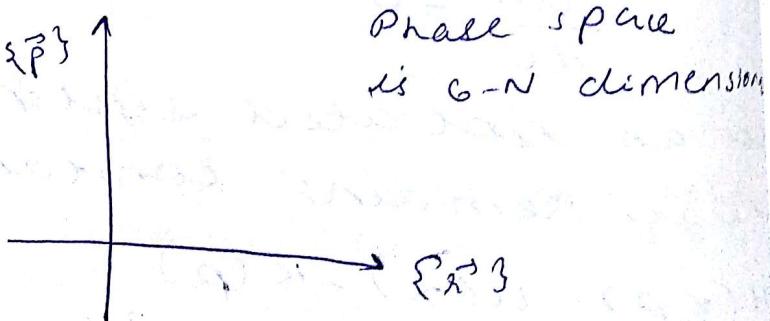


~~several~~
 n particle system

$$u(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n)$$

$$k(p_1, p_2, \dots, p_n)$$

$$H(\{\vec{x}\}, \{\vec{p}\}) = u(\{\vec{x}\}) + k(\{\vec{p}\})$$



go to one dimension

Boltzmann:

$$\text{Entropy } S \propto \ln(\Omega(E))$$

Entropy is proportional to $\ln(\Omega(E))$

where $\Omega(E)$
energy level
 $s = k_B \ln(\Omega)$
Boltzmann

case 1: 1 oscillator

For the energy is
harmonic
spring.

$$\frac{d^2 u(x)}{dx^2} =$$

$k = 0$ we

curve also
function

constant

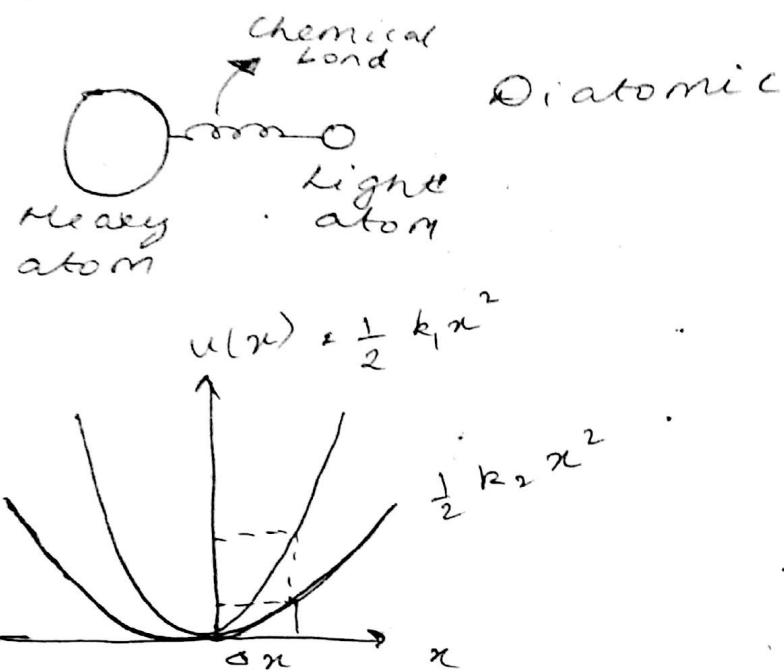
$$H(x, p) =$$

where $\Omega(E)$ is no. of cells in an energy level.

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

\rightarrow Boltzmann constant

Case 4: 1 dimensional harmonic oscillator



For the same value of o_n , more energy is required for k_1 than k_2 . Lower value of k , softer the spring.

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

$k=0$ would be a constant flat since curvature of potential energy function determines k .

Hamiltonian for this system:

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}kx^2 = E \quad (\text{energy of system})$$

$$\frac{P^2}{(\sqrt{2ME})^2} + \frac{x^2}{\left(\frac{\sqrt{2E}}{K}\right)^2} = 1$$

semi major axis : $\sqrt{\frac{2E}{K}}$

semi minor axis : $\sqrt{2ME}$

given this, we want to calculate $\Omega(E)$

all microstates would have energy, what is the probability that the system will visit a particular state?

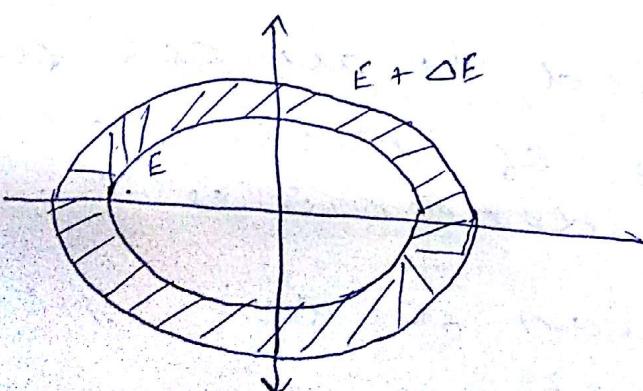
There are $\Omega(E)$ states.

Hypothesis: all states are equally likely

∴ Probability of a given state

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

Inject some energy ΔE to create a bigger ellipse



area of ellipse with $E + \Delta E$ energy will have larger area.

to find no. of microstates in the ring.

Find the area, and apply S = π A
and that gives no. of accessible microstates at energy E.

Area of ellipse with energy E

$$= \pi \left(\sqrt{\frac{2E}{K}} \right) \left(\sqrt{2mE} \right) \rightarrow (1)$$

Area of ellipse with energy $E + \Delta E$

$$= \pi \left(\sqrt{\frac{2(E + \Delta E)}{K}} \right) \left(\sqrt{2m(E + \Delta E)} \right) \rightarrow (2)$$

$$(2) - (1)$$

$$= \pi \left[\sqrt{\frac{4mE^2}{K}} + \sqrt{\frac{4m(E + \Delta E)^2}{K}} \right]$$

$$\pi \left[\sqrt{\frac{4m(E + \Delta E)^2}{K}} - \sqrt{\frac{4mE^2}{K}} \right]$$

$$= \frac{2\pi\sqrt{m}}{\sqrt{K}} (E + \Delta E - E)$$

$$= \frac{2\pi\Delta E\sqrt{m}}{\sqrt{K}}$$

No. of microstates \propto circumference
 $\Rightarrow n(E) \propto$ circumference of ellipse
with energy A

$$L \propto \sqrt{E}$$

The more the energy, the more microstates it resists. \Rightarrow it has

larger and larger entropy

$\Omega(E)$ is the no. of accessible microstates. It increases with E .

\Rightarrow Entropy's increase with E .

4) Entropy becomes zero when $\Omega(E)=1$, when temperature $\approx 0K$ and $K \cdot E = 0$

$$\rightarrow \boxed{\text{since } S = k_B \ln(\Omega(E))}$$

Information theory:

If a system can exist in n different states and you know the probabilities of each, then information theory ^{negative or} average of probability times its natural log with

$$S = - \sum_i P_i \ln P_i \quad (\text{Shannon})$$

$$S = -k_B \sum_i P_i \ln P_i$$

\rightarrow Thermodynamic entropy
information entropy

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

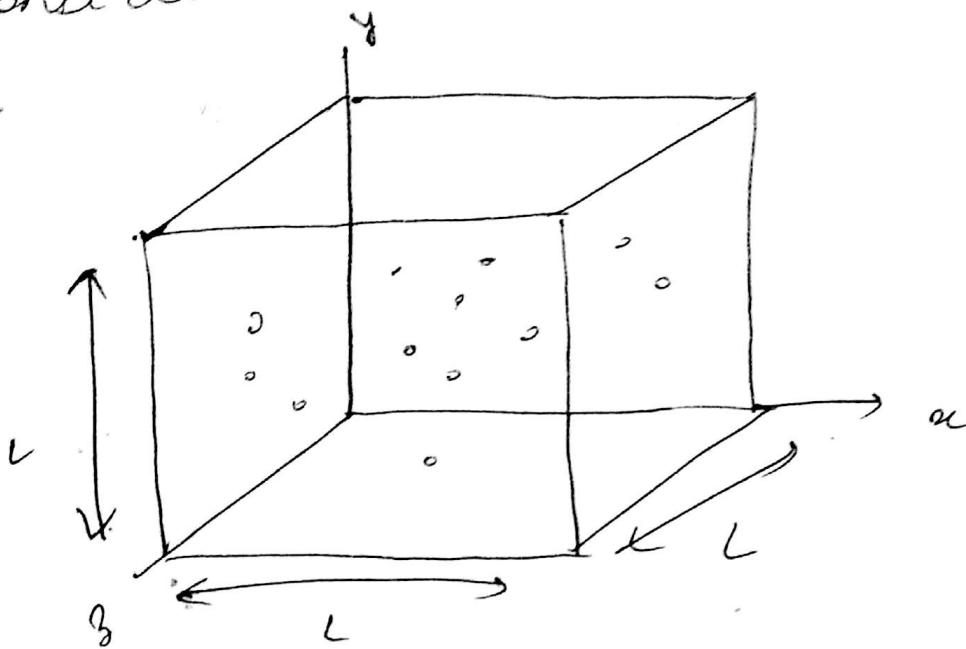
$$P_i = \frac{1}{\Omega(E)}$$

$$\Rightarrow S = -k_B \sum_i \frac{1}{\Omega(E)} \ln \left(\frac{1}{\Omega(E)} \right) = -k_B \ln \left(\frac{1}{\Omega(E)} \right)$$

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

case 2: gas cylinder

consider a cubic cylinder



volume $V = L^3$, $n = \text{no. of particles}$,
 m is mass of particle

$$0 \leq x_i \leq L$$

$$0 \leq y_i \leq L$$

$$0 \leq z_i \leq L$$

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

↓
momentum

In ideal gas system,

$u(\{\vec{r}\}) = 0$ and particles don't interact

$$\Rightarrow H(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{1}{2m} \sum_{i=1}^N \vec{p}_{x_i}^2 + \vec{p}_{y_i}^2 + \vec{p}_{z_i}^2$$

$$= E$$

$$\approx \sum_{i=1}^N \vec{p}_{x_i}^2 + \vec{p}_{y_i}^2 + \vec{p}_{z_i}^2 = (\sqrt{2mE})^2$$

equation of 3 n dimensional sphere

at radius r_{min}
 calculate $\Omega(r)$
 visit all possible states in
 phase space.

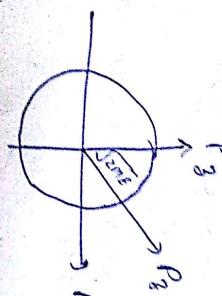
$$\Omega(r) = \int_{\text{min } r}^r S(E(r'), r') dr' \approx \frac{1}{2} \int_{\text{min } r}^r S(E) dr'$$

now give no. of accessible microstates with energy E .
 this hamiltonian function is
 not dependent on position, only
 momentum for ideal gas.

$$\therefore \Omega(E) = \int_{\text{min } r}^{\infty} S\left(\frac{1}{2m} \sum_{i=1}^N p_i^2 + E\right) dr$$

~~the first (r)~~

$$S(R) = \int_{\text{min } r}^{\infty} S\left(\frac{1}{2m} \sum_{i=1}^N p_i^2 + E - \epsilon\right) dr$$



are the points
on circumference
of this sphere

to move have

energy ϵ .

surface area of n dimensional
sphere $\propto r^n$.

surface area of 3^n dimensional ell
sphere satisfying this relation

One has
more

$$n = 3$$

case 2

$$S = k_B$$

\propto

$$S(N, V, P)$$

$$dS =$$

$$\sum_{i=1}^{\infty} \left(\overrightarrow{P_{xi}}^2 + \overrightarrow{P_{yi}}^2 + \overrightarrow{P_{zi}}^2 \right) = (\sqrt{2mE})^2$$

~~L \propto (radius)~~

$$L \propto (2mE)^{\frac{3m-1}{2}}$$

$$\therefore \Omega(E) \propto V^{(2mE)^{\frac{3m-1}{2}}}$$

The bigger the volume, the more the no. of microstates.

$$\Omega = f(N, V, E)$$

↓ ↓ ↓
 no. of volume total
 molec energy of system

case 1 : 1D oscillator

$$\Omega \propto \sqrt{E} \quad \Omega = \Omega(N, V, E)$$

case 2 : Ideal gas, N particles, V, E fixed

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

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

↓
Boltzmann constant.

$S(N, V, E)$. If we change each of the parameters, change in S?

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

→ ①

We change energy from E to $E + dE$
 V to $V + dV$
 N to $N + dN$

due to these $S \rightarrow S + dS$

$$\text{now, } \left(\frac{\partial S}{\partial E} \right)_{N,V} = K_B \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V}$$

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

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

From conventional thermodynamics

$$TdS = dE + PdV - \mu dN \rightarrow (2)$$

T = Temperature, μ = chemical potential

P = Pressure, V = Volume

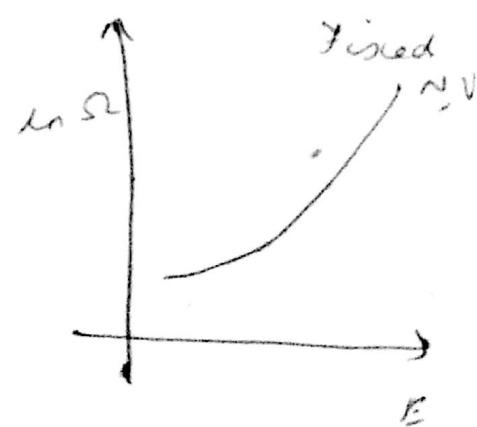
$$dS = \frac{dE}{T} + \frac{PdV}{T} - \frac{\mu dN}{k_B T} \rightarrow (2b)$$

From (1) and (2b)

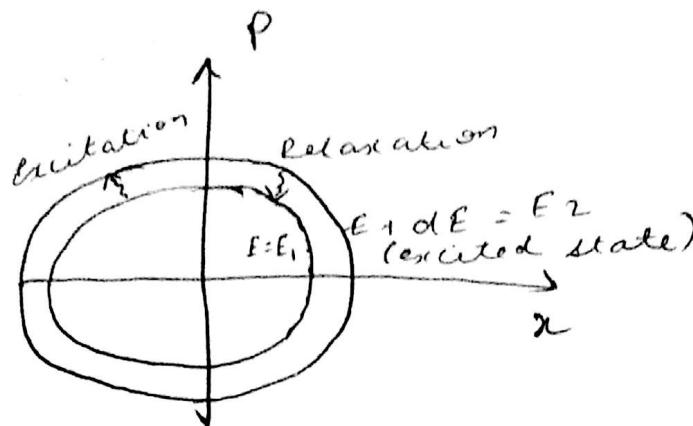
$$\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V,N}$$

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

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



Take 1D oscillator with energy E .
Let excite it to $E + dE$



Say E_1 is state of lowest energy.
Particle will return to ground state after excitation.
(relaxation)

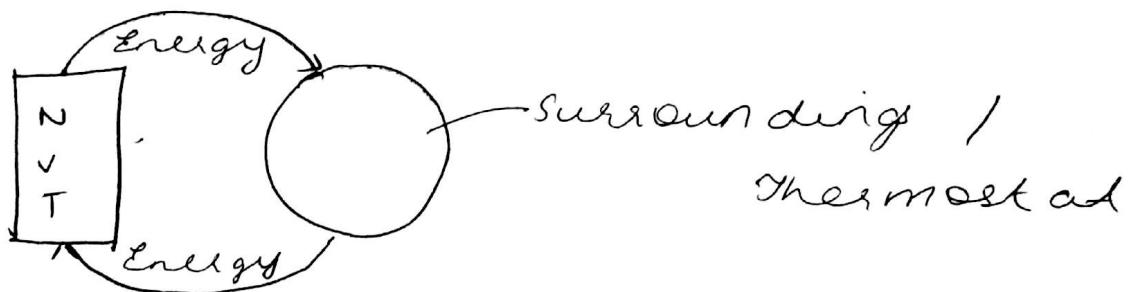
Closed system is a system where the system can exchange energy but not matter with surroundings

$N \rightarrow$ fixed $\Rightarrow NVT$ ensemble / canonical ensemble

$V \rightarrow$ fixed

$E \rightarrow$ Varies

$T \rightarrow$ Fixed



Due to energy exchanges, closed system would visit different energy levels.

Probability that system would visit energy level E_i ?

It turns out that $P_i \propto e^{-\beta E_i}$
(given by Boltzmann)

$e^{-\beta E_i}$ = Boltzmann factor

(The reason is by taking option
of convolutional net edge detection
and a softmax function's probability
will be increased)

θ = b

R_θ =



the θ will affect a distinguished feature
because every parameter has some
heights

$$P_i = e^{\theta t_i}$$

$$\sum P_i = 1$$

$$\sum e^{\theta t_i}$$

$$\sum e^{-\theta t_i}$$

2 : Partition function (the most
well known function in quantum field
theory)

$$\mu(n, \rho) = \prod_{i=1}^n \frac{1}{2} \rho^{t_i} + \rho^{1-t_i}$$

(If you know λ , you can find other
properties (like dual property))

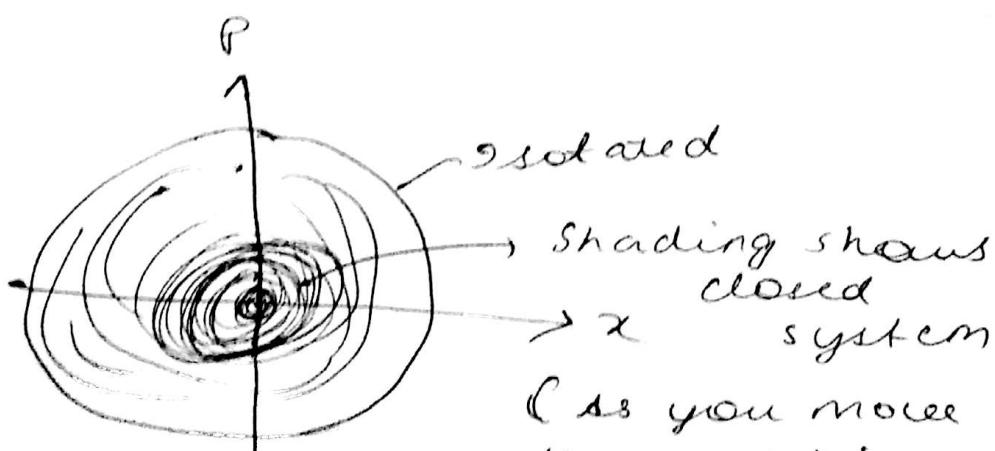
The old wave case,
 $\psi = e^{-\beta E_i}$
 $\psi = e^{-\beta E_i}$

For continuous
 $P(E_i, \bar{E}_i) = e^{-\mu H(E_i, \bar{E}_i)}$

$$\frac{1}{h^{3N}} \int \int \int e^{-\mu H(E_i, \bar{E}_i)} dE_i$$

- Planck's constant (for quantum system)
- arbitrary constant (for classical system)

$P(x, p) \propto e^{-\beta \left[\frac{1}{2} p^2 + \frac{p^2}{2m} \right]} \rightarrow$ Gaussian
 At $x=0, p=0$, we have highest probability

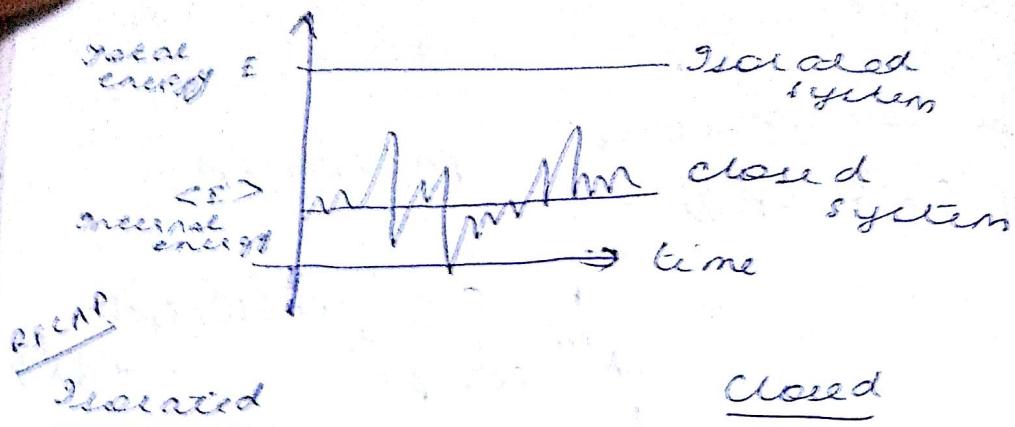


$$Z = \sum e^{-\beta E_i}$$

$$\ln Z = \ln \sum e^{-\beta E_i}$$

$$\frac{-\delta \ln Z}{\delta \beta} = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \sum E_i P_i$$

$\Rightarrow \langle E \rangle \rightarrow$ Definition of internal energy



(i) Constant energy

$$\frac{dH}{dt} = 0$$

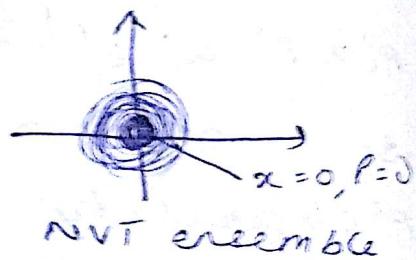
case (i) 1D harmonic oscillation



NVE ensemble

Closed

Energy exchange with surround.

$$\frac{dH}{dt} \neq 0$$


$$P_i \propto e^{-\beta E_i}$$

$$P_i = \frac{e^{-\beta E_i}}{Z}, \quad Z = \sum e^{-\beta E_i}$$

Partition function

FOURIER

$F(k)$

$f(x)$

(i)

$$\frac{\partial}{\partial t}$$

(ii)

$$\frac{\partial}{\partial x}$$

(iii)

$$\frac{\partial}{\partial P}$$

(iv)

FOURIER TRANSFORM

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

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

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

$$(ii) \quad \widetilde{\frac{\partial P}{\partial x}} = (-ik)\widetilde{P}$$

differentiation
by parts

$$\begin{aligned} (i) \quad \widetilde{\frac{\partial P}{\partial t}} &= -\int_{-\infty}^{\infty} \frac{\partial P(x,t)}{\partial t} e^{ikx} dx + 0 \\ &= -\int_{-\infty}^{\infty} \frac{\partial P}{\partial t} e^{ikx} dx + \int_{-\infty}^{\infty} P(x,t) \underbrace{\frac{\partial e^{ikx}}{\partial t} dx}_0 \end{aligned}$$

(since
independent
of t)

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

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

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

Since $\int v \frac{du}{dx} dx = uv - \int u \frac{dv}{dx} dx$

$$= -ik \int_{-\infty}^{\infty} P e^{ikx} dx$$

$$= (-ik) \widetilde{P}$$

$$(iii) \quad \widetilde{\frac{\partial^2 P}{\partial x^2}} = (-ik)^2 \widetilde{P}$$

$$\widetilde{\frac{\partial^2 P}{\partial x^2}} = \int_{-\infty}^{\infty} \frac{\partial^2 P}{\partial x^2} e^{ikx} dx$$

$$= \left[e^{ikx} \frac{\partial P}{\partial x} \right]_{-\infty}^{\infty} - ik \int_{-\infty}^{\infty} \frac{\partial P}{\partial x} e^{ikx} dx$$

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

$$\text{in a dimensional system, } P(\{\vec{r}\}, \{\vec{p}\}) = \frac{e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}}{Z}$$

$$Z = \prod_{j=1}^N \int_{\{\vec{r}_j\} \cup \{\vec{p}_j\}} e^{-\beta E_j} d\{\vec{r}_j\} d\{\vec{p}_j\}$$

you calculate Boltzmann factor for each point in space and then take total.

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

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

$$-\frac{\partial \ln Z}{\partial \beta} = \sum_j \frac{E_j (e^{-\beta E_j})}{\left(\sum_j e^{-\beta E_j} \right)} \xrightarrow{\substack{\text{Probability} \\ \rightarrow \textcircled{1}}} \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

$$\therefore \sum_j E_j P_j$$

$$= \langle E \rangle \Rightarrow \text{internal energy}$$

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

where $\langle E \rangle$ is internal energy.

If standard deviation is zero graph becomes horizontal and it is isolated system.

$$\text{Consider } \sum_j E_j e^{-\beta E_j} = -\frac{\partial \ln Z}{\partial \beta} \quad (\text{from \textcircled{1}})$$

Take $\frac{\partial}{\partial \beta}$ on both sides

$$\sum E_j^2 e^{-\beta E_j} = \left[z \frac{\partial^2 \ln z}{\partial \beta^2} + \frac{\partial \ln z}{\partial \beta} \frac{\partial z}{\partial \beta} \right]$$

Divide by z on both sides,

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

$$\langle E^2 \rangle = \sum_j E_j^2 \left(\frac{e^{-\beta E_j}}{z} \right) \quad \text{②}$$

$$\textcircled{2} \Rightarrow \langle E^2 \rangle = \frac{\partial^2 \ln z}{\partial \beta^2} + \langle E \rangle^2$$

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

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle \\ &= \langle E^2 \rangle - 2 \langle E \rangle^2 + \langle E \rangle^2 \end{aligned}$$

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

$$= \frac{\partial}{\partial \beta} \left(\frac{\partial \ln z}{\partial \beta} \right)$$

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

$$\beta = \frac{1}{k_B T} \rightarrow \text{Temperature}$$

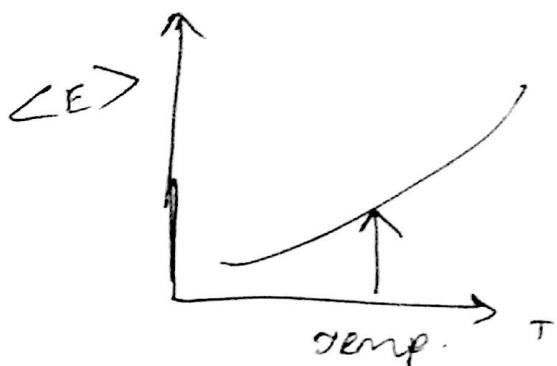
\downarrow Boltzmann factor

$$\Rightarrow \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial \langle E \rangle}{\partial T} \left(\frac{1}{\partial \beta / \partial T} \right)$$

$$\langle E^2 \rangle - \langle E \rangle^2 = + \frac{\partial \langle E \rangle}{\partial T} \left(\frac{K_B T^3}{K_F^2} \right) = \cancel{C_V}$$

↓
heat capacity at
constant volume (C_V)

Experimental measurement of C_V



In theoretical calculation, we've done only for one T

Theoretically, C_V is calculated from $\langle E^2 \rangle - \langle E \rangle^2$
(measured at a given temp.)

$\langle E^2 \rangle - \langle E \rangle^2$ is always +ve

$$\Rightarrow C_V \geq 0$$

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

$\Rightarrow \langle E \rangle$ increases with temp.

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

$$C_V \propto \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$S = -k_B \sum_i p_j \ln p_j \quad (S \text{ is entropy})$$

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

$$S = K_B [\beta \sum_j E_j P_j + \ln Z]$$

$$\therefore \frac{\langle E \rangle}{T} + \frac{k_B^2}{\beta} \cdot K_B \ln Z$$

$$TS = \langle E \rangle + K_B T \ln Z$$

$$\langle E \rangle - TS = -K_B T \ln Z$$

The helmholtz free energy (F)

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

$$F = -K_B T \ln Z$$

Pressure: $P_j = -\frac{\partial H(\tau, \vec{p})}{\partial V}$

compress the system and change in hamiltonian.

$$\langle P \rangle = \sum_j P_j \delta_j$$

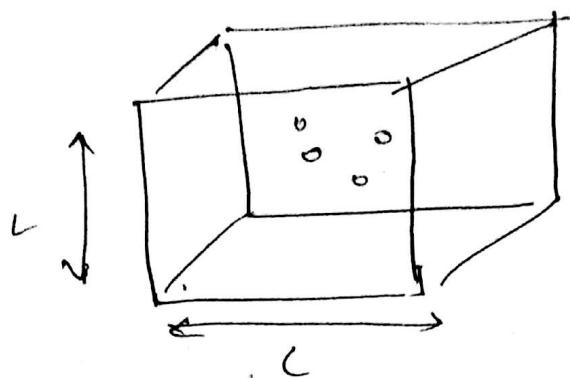
$$\langle P \rangle = - \sum_j \left(\frac{\partial E_j}{\partial V} \right) \delta_j$$

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

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

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

case 2 : ideal gas with N atoms confined in volume V



$$U(\{\vec{r}\}) = 0 \text{ (ideal gas)}$$

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

$$Z = \frac{1}{h^{3N}} \int \int_{\{\vec{r}\}} e^{-\beta \left(\sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i \right)} d\{\vec{r}\} d\{\vec{p}\}$$

$$Z = \frac{1}{h^{3N}} Z_p Z_r$$

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

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

$$Z_p = \left(\int_{\vec{r}} \left(e^{-\frac{\beta}{2m} r^2} \right)^{3N} d\vec{r} \right)$$

$$\sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i = p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2 + \dots + p_{x,N}^2$$

$$\sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i = p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + \dots + p_{x,N}^2 + p_{y,N}^2 + p_{z,N}^2$$

$$e^{-\frac{\beta}{2m} \vec{E}_1 \vec{P}_1} = e^{-\frac{\beta}{2m} P_{x_1}}, \quad e^{-\frac{\beta}{2m} \vec{E}_2 \vec{P}_2} = e^{-\frac{\beta}{2m} P_{x_2}}$$

$$Z_P = \left(\sqrt{\frac{\pi}{(\beta/m)}} \right)^{3N}$$

$$= (2\pi m k_B T)^{3N/2}$$

$$\left[I = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\pi/\alpha} \right] \xrightarrow{\text{Feynman trick}}$$

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

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

$$\Rightarrow \langle P \rangle_V = N k_B T$$

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

$$\text{internal energy } \langle E \rangle = - \frac{\partial \ln Z}{\partial \beta}$$

heat capacity (at constant vol.)

$$C_V = \frac{\partial \langle E \rangle}{\partial T} \propto \langle E^2 \rangle - \langle E \rangle^2 \propto \frac{\partial^2 \ln Z}{\partial \beta^2}$$

Helmholtz free energy $F = -k_B T \ln Z$

$$\text{entropy } S = -k_B \sum_j P_j \ln P_j$$

Ideal gas:

$$Z = \frac{1}{h^{3N}} \int \int \int e^{-\beta H(C_i, \vec{P})} d\{x\} d\vec{P}$$

$$H(\{\vec{p}\}, \vec{P}) = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{P}_i \rightarrow \text{sum of } 3N \text{ terms}$$

simple case

$$N=1$$

2 dimensional (P_x, P_y)

$$x P_x = h$$

$$y P_y = h_y$$

$$Z_2 = \frac{1}{h^2} \left[\int_{x=0}^L \int_{y=0}^L dx dy \right] \left(\int_{P_x=-\infty}^{\infty} \int_{P_y=-\infty}^{\infty} e^{-\frac{\beta}{2m} (\vec{P}_x + \vec{P}_y)^2} dP_x dP_y \right) = \frac{1}{h^2} L^2 \int_{P_x=-\infty}^{\infty} e^{-\frac{\beta P_x^2}{2m}} dP_x \int_{P_y=-\infty}^{\infty} e^{-\frac{\beta P_y^2}{2m}} dP_y$$

$$Z_2 = \frac{L^2}{h^2} \int_{x=-\infty}^{\infty} \left(e^{-\frac{\beta x^2}{2m}} dx \right)^2 = \frac{L^2}{h^2} \left(\sqrt{\frac{\pi m}{\beta}} \right)^2 \text{ for 2 dimensions}$$

$$Z_n = \frac{(L^3)^n}{h^{3n}} \left(\sqrt{\frac{\pi m}{\beta}} \right)^{3n} \cancel{\text{for}}$$

$$= \frac{V^n}{h^{3n}} \left(\sqrt{\frac{\pi m}{\beta}} \right)^{3n}$$

$$= \frac{V^n}{h^{3n}} (2\pi m k_B T)^{3n/2}$$

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

$$= V^N \sigma$$

Pressure $\langle P \rangle = n k_B T \frac{\partial \ln Z}{\partial V}$

$$\ln Z_n = \ln V^N + \ln \sigma$$

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

(ideal gas equation)

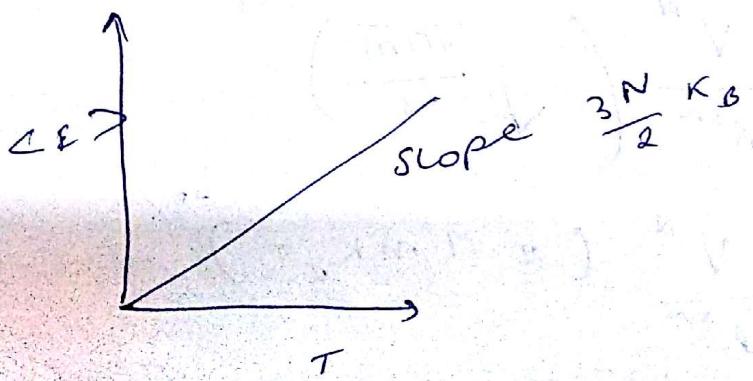
$$\langle P \rangle V_n = k_B T N$$

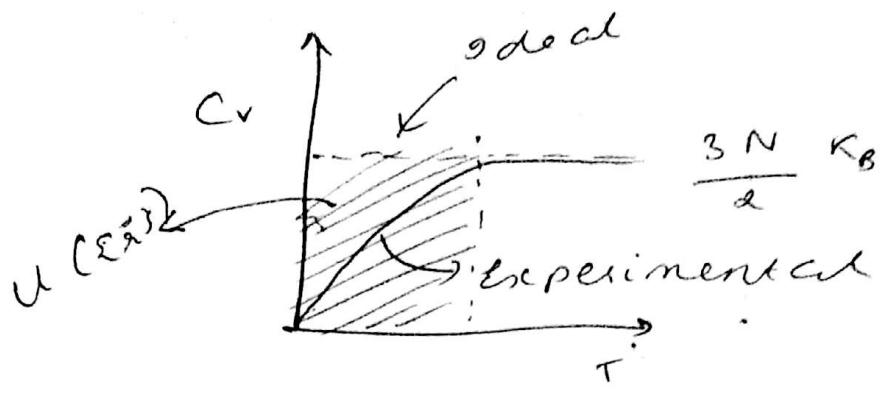
(equation of state of ideal gas)

internal energy $\langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} = - \partial \left[\frac{1}{h^{3N}} \frac{V^N (2\pi m)^{3N/2}}{\beta} \right] / \partial \beta$

$$\langle E \rangle = \frac{3}{2} \frac{N}{\beta} K_B T$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{3}{2} N K_B \quad (C_V \text{ is independent of temp.})$$





heat capacity is independent of temperature. (Dulong Petit law).

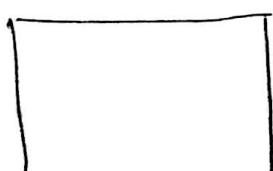
\therefore at high T , C_V is not relevant (gas is not ~~a non-ideal gas~~)

Entropy is an extensive property (when system size changes, certain parameters change)

intrinsic properties

e.g. Temperature (T independent of system size)

To show that entropy is extensive,

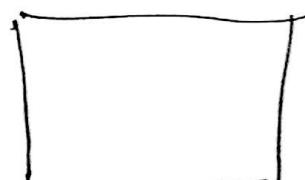


System 1

$$\frac{N}{V}$$

S_1 (entropy)

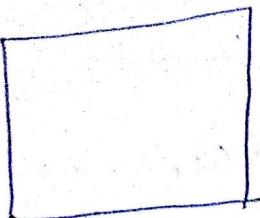
$$T$$



System 2

$$\frac{N}{V} \frac{S_2}{T}$$

After combining both systems,



2N

2V

S

T

we need to check if $S = S_1 + S_2$

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

$$= k_B [\ln 2 + \beta \langle E \rangle]$$

$$S_1 = S_2$$

$$S_1 = N k_B [\ln V + \frac{3}{2} \ln T + \lambda]$$

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

$S_2 = S_1$ (since volume and temp. are same)

$$S = 0 \quad N \rightarrow 2N \\ V \rightarrow 2V$$

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

acc. to thermodynamics

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

But,

$S = CS_1 +$
Capita
This
Zeros

$S = k_B$

use all
in N

from

$S = C$

when

$\frac{N}{V}$

For

$N \rightarrow$

$V \rightarrow$

$T \rightarrow$

ode

Rea

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

(paradox)

This is Gibbs paradox.

$$S_{\text{correct}} = \frac{2}{N!} \rightarrow \text{Gibbs correction}$$

$$S = k_B [\ln S_{\text{correct}} + P \langle E \rangle]$$

use Stirling's approx.,

$$\ln N! \approx N \ln N - N \text{ for large } N$$

from this,

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

when $\begin{cases} N \rightarrow \infty \\ V \rightarrow \infty \end{cases} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{thermodynamic limit.}$
 η_V is finite

for real gases, $U(\vec{r}_i) \neq 0$

$N \rightarrow$ No. of particles

$V \rightarrow$ volume

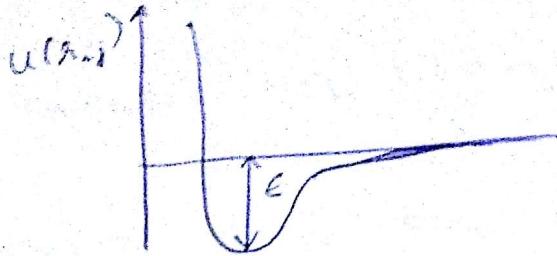
$T \rightarrow$ temp.

ideal gas \rightarrow a point is an atom
real gas has a size. let
 σ be diameter

 σ is diameter

let there be two atoms i and j and distance between them be R_{ij} . when far away,
 $U(r_{ij}) = 0$.

To calculate
 $U(r^2)$



$$U(r_{ij}) = +\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

[For uncharged]

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

ϵ is min. potential energy.

Gradient zero at minimum

$$\frac{dU(r_{ij})}{dr_{ij}} = -\frac{16\epsilon}{2} = 0$$

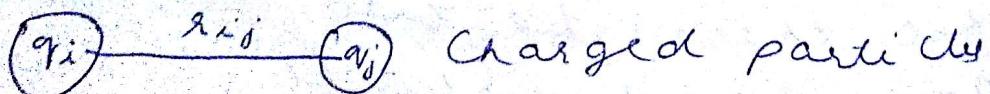
$$\Rightarrow r_{ij} = 2^{1/6} \sigma$$

$U(r_{ij}) = 0$ in two cases:

(i) $r_{ij} = \infty$

(ii) $r_{ij} = \sigma_{ij}$ i.e., when the particles touch each other.

This was for uncharged particles / inert gases / van der waal's interactions



For charged,

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

To calculate partition function

$$u(\{\vec{r}\}, \{\vec{p}\}) = k(\{\vec{p}\}) + u(\{\vec{r}\})$$

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

Total potential energy can be written as sum of pairwise atom interaction.

$$u(\{\vec{r}\}) = u_{1,2} + u_{1,3} + \dots + u_{n-1,n}$$
$$= \frac{1}{2} \sum_{j=1}^N \sum_{\substack{k=1 \\ j \neq k}}^N u_{jk}$$

$$Z = \frac{1}{h^{3N} N!} \int_{\{\vec{r}\}} \int_{\{\vec{p}\}} e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})} \cdot d\{\vec{r}\} \cdot d\{\vec{p}\}$$

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

$$\left(\int_{\{\vec{r}\}} e^{-\beta u(\{\vec{r}\})} \cdot d\{\vec{r}\} \right)$$

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

$$Z_u = \int_{\{\vec{r}\}} e^{-\beta u(\{\vec{r}\})} \cdot d\{\vec{r}\}$$

For an ideal gas, $u(\{\vec{r}\}) = 0$

$$\Rightarrow Z_u = V^N$$

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

$$= -\frac{\partial \ln Z_u}{\partial \beta}$$

$$\frac{\partial \ln Z_u(\beta)}{\partial \beta} = -\langle u \rangle \rightarrow \textcircled{2}$$

We know that when $\beta \rightarrow 0$

$$Z_u(\beta \rightarrow 0) = V^n \quad (\text{since } \beta = 1/k_b T)$$

and T increases when $\beta \rightarrow 0$
and it behaves like an ideal
gas)

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

(Integrating \textcircled{2})

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

$$\ln Z_u(\beta) = n \ln V - \int_0^{\beta} \langle u \rangle \cdot d\beta' \rightarrow \textcircled{A}$$

There are $\frac{n(n-1)}{2}$ atom pairs

in a system of n particles

$$\Rightarrow \langle u \rangle = \frac{1}{2} \cdot n(n-1) \overbrace{\langle u \rangle}^{\substack{\text{small} \\ u}} \rightarrow$$

average energy
per pair

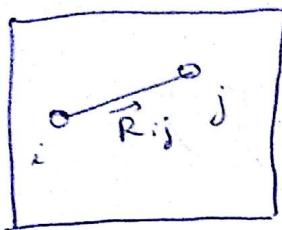
$$N \rightarrow \infty$$

$$V \rightarrow \infty$$

$$\langle u \rangle \approx \frac{1}{2} N^2 \langle u \rangle$$

calculate $\langle u \rangle$?

$$\langle u \rangle = \frac{\int_{\vec{R}} e^{-\beta u(\vec{R}')} \cdot u(\vec{R}') \cdot d\vec{R}'}{\int_{\vec{R}} e^{-\beta u(\vec{R}')} \cdot d\vec{R}'}$$



\vec{R}_{ij} is
displace-
ment
vector

distance
between
2 particles

$$\langle u \rangle = -\frac{\partial}{\partial \beta} \ln \left[\int_{\vec{R}} e^{-\beta u(\vec{R}')} \cdot d(\vec{R}') \right] \rightarrow ③$$

Consider

$$\begin{aligned} & \int_{\vec{R}} e^{-\beta u(\vec{R}')} \cdot d\vec{R}' \\ &= \int_{\vec{R}} [1 + (e^{-\beta u(\vec{R}')} - 1)] \cdot d\vec{R}' \\ &= \int_{\vec{R}} d\vec{R}' + \int_{\vec{R}} (e^{-\beta u(\vec{R}')} - 1) \cdot d\vec{R}' \quad \text{3 Dimensional} \\ &= V + I(\beta) \end{aligned}$$

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

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

from 3D to
spherical polar

$$\therefore \langle u \rangle = -\frac{\partial}{\partial \beta} \ln \left[V \left(1 + \frac{I(\beta)}{V} \right) \right] \quad (\text{from } ③)$$

$V \rightarrow \infty$, $T \ll V$
(dilute gas)

$$\langle u^2 \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \ln \left(1 + \frac{I}{V} \right)$$

$$= 0 - \frac{\partial}{\partial \beta} \ln \left(1 + \frac{I}{V} \right)$$

$$= -\frac{\partial}{\partial \beta} \left(\frac{I}{V} + \dots \right)$$

negligible
further terms

$$= -\frac{1}{V} \frac{\partial I}{\partial \beta}$$

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

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

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

$$= \frac{K_B T}{V} \frac{\partial}{\partial V} \ln Z_u(\beta)$$

$Z = \frac{1}{N!} \left(\frac{2 \pi m K_B T}{n^2} \right)^{3N/2}$ Z_u does
not depend on volume]

$$\underbrace{\langle P \rangle}_{K_B T} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I$$

Ideal gas
part

Interaction

$$\frac{\langle P \rangle}{K_B T} = \rho - \frac{1}{2} \rho^2 I$$

where ρ is density , $\rho = \frac{N}{V}$

In general,

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



Initial equation

- ~1890 - electron discovery (J.J. Thompson)
 ~1911 - nucleus discovery (Rutherford)
 ~1913 - Bohr's atom model

THERMODYNAMICS

- 1) Zeroeth law of thermodynamics
 → defines temperature
 → thermal eqbm. \Rightarrow equality of temp.
 → thermometer
- 2) First law of thermodynamics (energy)

$$dU = dQ + dW \quad (\text{conservation of energy})$$

(heat supplied to system) \downarrow
 Change in internal energy \uparrow
 work done on system

$$dQ = Q_{\text{final}} - Q_{\text{initial}} \quad (\text{is} + \text{ee})$$

heat supplied to system

$$dW \quad (\text{is} - \text{ee})$$

work done by system

- 3) Second law of thermodynamics
- = spontaneous process (Processes that do not require external work)
 - (i) $(\Delta S)_{\text{total}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}}$
 ≥ 0

Total entropy increases in spontaneous process

(ii) system specific definition of second law

$$(ds)_{\text{system}} \geq \frac{dQ}{T} \xrightarrow{\substack{\text{heat} \\ \text{supplied to} \\ \text{system}}} \xrightarrow{\text{temperature}} \text{ Clausius' inequality}$$

4) third law of thermodynamics

it talks about absolute value of entropy (in comparison to second which deals with change)

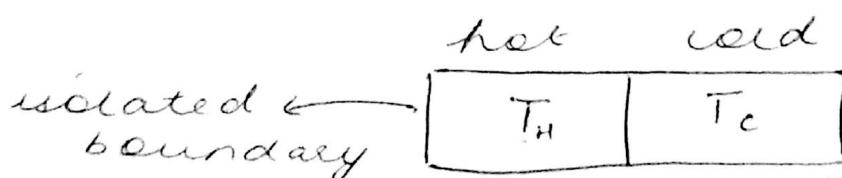
$$\text{when } T \rightarrow 0, S_{\text{system}} \rightarrow 0$$

$$(ds)_{\text{system}} \geq \frac{dQ}{dT}$$

$$\text{when } dQ = 0 \Rightarrow (ds)_{\text{system}} > 0$$

The inequality is valid only for reversible (quasistatic) process.

case ① : spontaneous cooling



keep a hot object next to a cold object.

$dq_H \rightarrow$ heat change in hot
 $dq_C \rightarrow$ " cold

$|dq_H| = |dq_C|$ { since isolated}
this is done reversibly

$$dS_H = \frac{dq_H}{T_H}$$

$$dS_C = \frac{dq_C}{T_C}$$

- (a) heat flow from cold \rightarrow hot
(b) " hot \rightarrow cold

$$(a) dS_{\text{tot}} = -\frac{|dq_C|}{T_C} + \frac{|dq_H|}{T_H}$$

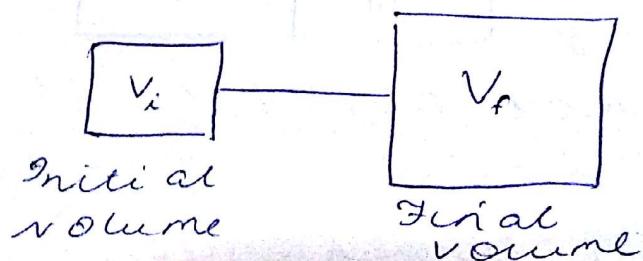
$$\Rightarrow dS = dq_C \left(\frac{1}{T_H} - \frac{1}{T_C} \right)$$

$$\Rightarrow dS < 0 \quad (\text{non spontaneous})$$

$$(b) dS = -\frac{|dq_H|}{T_H} + \frac{|dq_C|}{T_C}$$

$$\Rightarrow dS > 0 \quad (\text{spontaneous})$$

case ② : Expansion of an ideal gas (reversible, isothermal)



$$V_f > V_i$$

$$PV = nRT \quad (\text{equation of state})$$

$dU = 0$ ($T = \text{constant}$)
internal energy is constant

$dQ_{\text{rev}} = -W_{\text{rev}}$ \rightarrow reversible
work done by
the system

$$\Delta S = \frac{1}{T} \int_i^f dQ_{\text{rev}} = \frac{Q_{\text{rev}}}{T}$$

$$W_{\text{rev}} = -PdV$$
$$= -nRT \frac{dV}{V}$$

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$W = -nRT \ln \frac{V_f}{V_i}$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Cases

(a) if $V_f < V_i$ (compression)

(b) $V_f > V_i$ (expansion)

$\Rightarrow \Delta S > 0$
(spontaneous)

$\Rightarrow \Delta S < 0$
(non spontaneous)

Thermodynamic Potentials

From the second law of thermodynamics

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

(a) heat transfer at constant volume (work done = 0)

$$dV = 0$$

$$\Rightarrow dS \geq \frac{dU}{\cancel{\partial F}} \quad [\text{since } dU = dQ + dW]$$

$$TdS - dU \geq 0$$

constant entropy $\Rightarrow dS = 0$

$(dU)_{S,V} \leq 0$ (internal energy will be minimized)

For constant volume, constant entropy process

$$U(S, V)$$

(b) Define a new function
Enthalpy $\leftarrow H = U + PV$

$$dH = dU + PdV + VdP$$

$$dH = dq - PdV + PdV + VdP$$

$$dH = dq + VdP$$

if P is constant

$$dH = dQ$$

heat supplied to a system
at constant:

- (i) pressure is called enthalpy
- (ii) volume is internal energy

$$TdS \geq dH$$

if ~~enthalpy~~^{entropy} is constant

$$dS = 0$$

$$\Rightarrow (dH)_{P,S} \leq 0$$

→ H will be minimized
at constant P and S

(c) at constant V and T,

$$A = U - TS$$

→ helmholtz
free energy

$$dA = -PdV - SdT$$

at constant T and V,

$$(dA)_{V,T} \leq 0$$

→ helmholtz free energy will
be minimized at constant
T and V.

(d) constant P and T

(most processes follow this)

gibbs
free energy $G = U + PV - TS$

$$\xleftarrow{\text{minimized}} (dG)_{T,P} \leq 0$$

minimized at constant T, P

Maurice's relations

$$U = U(S, V) \rightarrow \textcircled{1} \quad \begin{array}{l} \text{internal energy} \\ \text{Enthalpy} \end{array}$$

$$H = H(P, S)$$

$$A = A(T, V) \quad \begin{array}{l} \text{Helmholtz} \\ \text{free energy} \end{array}$$

$$G = G(T, P) \quad \begin{array}{l} \text{Gibbs free} \\ \text{energy} \end{array}$$

$$dU = T dS - P dV \quad (\text{First law})$$

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

(from \textcircled{1})

$$\left[\left(\frac{\partial U}{\partial S}\right)_V = T ; \left(\frac{\partial U}{\partial V}\right)_S = P \right]$$

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

[state function - second derivative's order is the same]

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

Maurice's relation

$$\text{From } H = H(P, S)$$

$$\Rightarrow \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 U}{\partial S \partial P}$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

from $A = A(T, V)$

$$\Rightarrow \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial^2 A}{\partial V \partial T}$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

from $G = G(P, T)$

$$\Rightarrow \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$$

$$(a) \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \Leftrightarrow S \geq 0$$

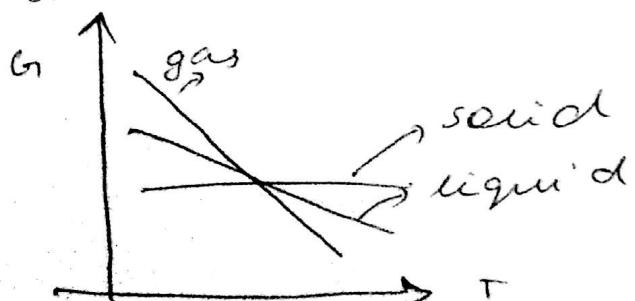
[entropy can't be negative so G decreases with temperature]

$$(b) \left(\frac{\partial G}{\partial P}\right)_T = V$$

[since $S = k_B \ln(\Omega)$ and a gas can have more microstates]

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}} \quad [\text{from (a)}]$$

[since $S = k_B \ln(\Omega)$ and a gas can have more microstates]



$$\left(\frac{\partial G}{\partial T}\right)_P < \left(\frac{\partial G}{\partial T}\right)_L < \left(\frac{\partial G}{\partial T}\right)_S$$

solid liquid gas
Response
greater

$$\left(\frac{\partial G}{\partial P}\right)_T > 0, \quad V \geq 0 \quad [\text{From (b)}]$$

α must increase with increasing P .

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

Response of α to P is highest for gas.

Measuring S experimentally is not that easy.

Gibbs-Helmholtz equation:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad [G = H - TS]$$

$$\text{we know } S = \frac{H - G}{T}$$

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

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

Multiply by T on both sides

$$\frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G_1}{T^2} = -\frac{\mu}{T^2} \quad [\text{Product rule of } \frac{\partial}{\partial T} \text{ and } \frac{1}{T}]$$

$$\boxed{\left(\frac{\partial G}{\partial T} \right)_P = -\frac{\mu}{T^2}} \quad \text{Gibbs Helmholtz equation}$$

using calorimetric experiment
 μ can be measured.

using G_f , determine stability
 For fixed no. of moles,

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

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

A phase with the least G_f
 at a given T or P would
 be the most stable phase.

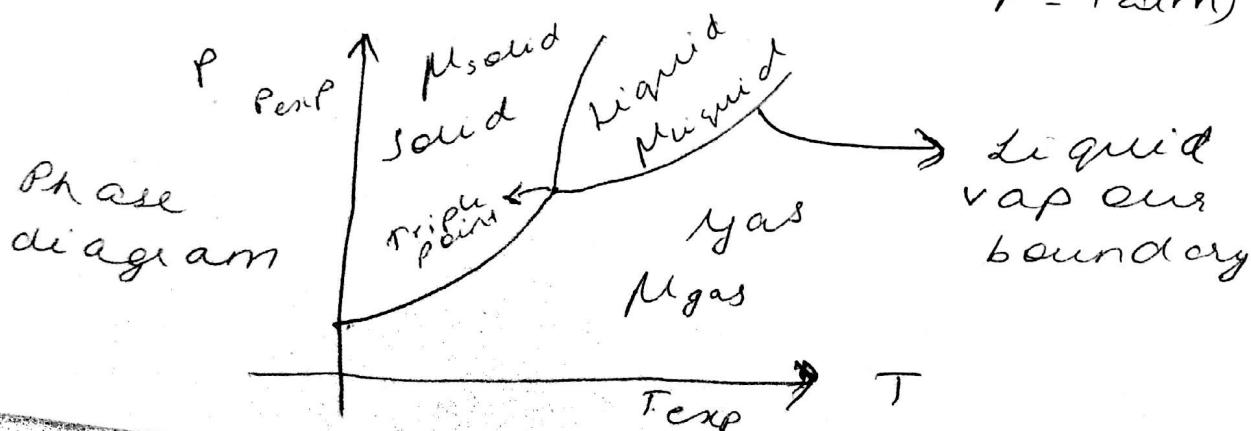
chemical Potential (μ)

Gibbs free energy per mole

$$\mu(T, P) = \frac{G(T, P)}{n} \rightarrow \text{no. of moles}$$

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

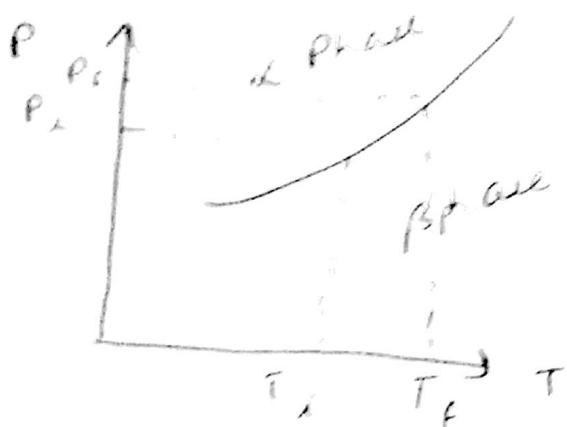
$< \mu_{\text{ice}} (T=300K, P=1 \text{ atm})$



point μ_{gas} at which vapor boundary (and similar boundaries) meet (undisturbed)

Triple point belongs to all three phase point $= \mu_{solid} = \mu_{gas}$

$$P = f(T)$$



$$\mu_d(T_{ideal}, P_{ideal}) - \mu_d(T_{real}, P_{real})$$

$$\mu_d(T_i, P_i) = \mu_d(T_e, P_e) \rightarrow ①$$

$$\mu_d(T_f, P_f) = \mu_d(T_e, P_e) \rightarrow ②$$

$$② - ①$$

$$\mu_d(T_e, P_e) - \mu_d(T_i, P_i)$$

$$= \mu_d(T_e, P_f) - \mu_d(T_i, P_e)$$

If difference is small

$$d\mu_d(T, P) = d\mu_d(T, P) \rightarrow ③$$

we know that

$$dG = -SdT + VdP$$

by no. of moles on both side

$$d\mu = -S_m dT + V_m dP$$

↓ ↓
Entropy per mole molar volume

From ③,

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

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

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

$$\frac{dP}{dT} = \frac{S_{m,\beta} - S_{m,\alpha}}{V_{m,\beta} - V_{m,\alpha}} = \frac{\Delta_{\text{trans}} S}{\Delta_{\text{trans}} V}$$

Clay-Peyron equation gives
slope of boundary at a
given T and P)

For a solid liquid boundary:
melting

at constant pressure,

$$\Delta_{\text{trans}} S = \frac{\Delta_{\text{fusion}} H}{T} \quad [\text{second law of thermodynamics}]$$

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad [\text{from Clay-Peyron}]$$

ΔH is +ve because liquid entropy is higher than solid. ΔV is +ve ($V_{\text{liquid}} > V_{\text{solid}}$)

$\therefore \frac{\Delta H}{\Delta V}$ is +ve.

$$\int_{P^*}^P dP \approx \frac{\Delta H}{\Delta V} \int_{T^*}^T \frac{dT}{T}$$

(Assumption ΔH & ΔV does not change much with T & P)

P^*, T^* \rightarrow transition pressure, temp.

$$P \approx P^* + \frac{\Delta H}{\Delta V} \ln \frac{T}{T^*}$$

when $T \approx T^*$

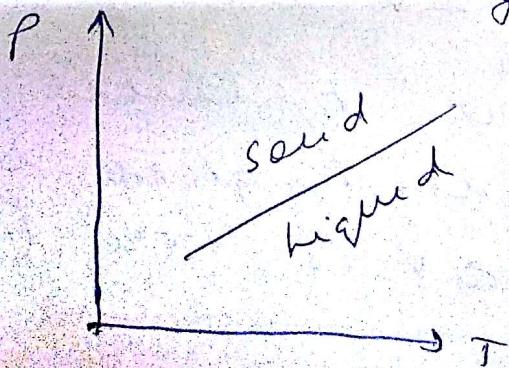
$$\ln \frac{T}{T^*} = \ln \left(1 + \frac{T - T^*}{T^*} \right) \\ \approx \frac{T - T^*}{T^*}$$

[Expanding $\ln(1+x)$]

$$\Rightarrow P^* \approx$$

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

(Equation of straight line)



Phase
a given
phase
eg year
temp.
to do
(T)
Mgraph
Diamo
graph
Types

- 1) Fir
- 2) sec
- heat

- 1) Fir

$$\frac{\partial \mu}{\partial P}$$

P^* ,
Gm

- 2) sec

$$\frac{\partial P}{\partial \mu}$$

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

e.g. graphite is more stable at room temp. and pressure compared to diamond.

$$\mu_{\text{graphite}}(T, P) < \mu_{\text{diamond}}(T, P)$$

Diamond is slowly converting to graphite

Types of phase transition

- 1) First order phase transition
- 2) second ..

Created by Paul Ehrenfest

- 1) First order phase transition

$$\frac{\partial \mu(T, P)}{\partial P_*}; \frac{\partial \mu(T, P)}{\partial T_*} \Rightarrow \text{discontinuous}$$

P_* , T_* are transition pressure, temp.

- 2) second order phase transition

$$\frac{\partial \mu(T, P)}{\partial P_*}; \frac{\partial \mu(T, P)}{\partial T_*} \rightarrow \text{continuous}$$

$$\frac{\partial^2 \mu(T, P)}{\partial P_*^2}; \frac{\partial^2 \mu(T, P)}{\partial T_*^2} \rightarrow \text{Discontinuous}$$

chemical equilibrium

constant $\mu(T, P)$

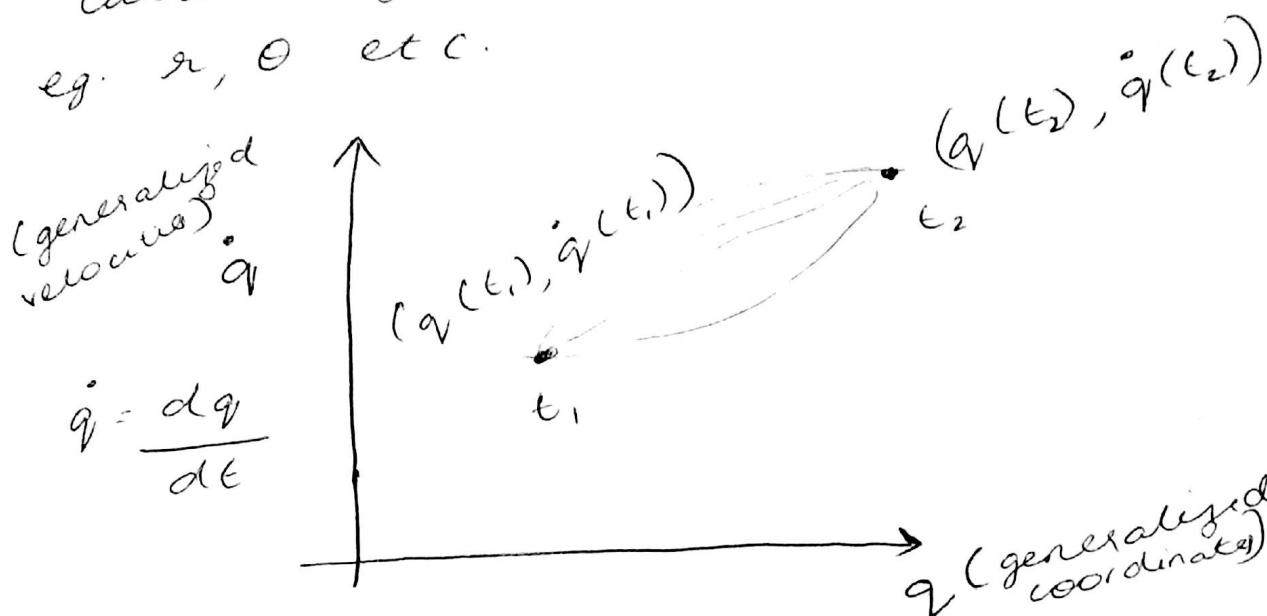
thermal equilibrium

constant T

CLASSICAL MECHANICS

The principle of least action
or Hamilton's principle

q is position parameter
called generalized coordinate
e.g. r, θ etc.



Find the optimum path that
the system takes (least
action principle)

$L(q, \dot{q}; t)$ implicit time
dependency
{
Z Lagrangian (q and \dot{q} may
depend on time)}

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

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

The path with the least action
is the most probable path
that the system would take.

$$S = \int_{t_1}^{t_2} K(\dot{q}) \cdot dt - \int_{t_1}^{t_2} U(q) \cdot dt$$

↓
related to
mean kinetic
energy

Let $q(t), \dot{q}(t)$ ($\forall t, t_1 \leq t \leq t_2$)

→ define the least action path

Create a neighbouring path :

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

We know that $\delta q(t_1) = \delta q(t_2) = 0$

(Because all paths converge at
the end points)

Change in action :

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

↓
action for
neighbouring
path

↓
action for
least action
path

$$= \delta \int_{t_1}^{t_2} L(q, \dot{q}) \cdot dt$$

$$= \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \delta \dot{q} \right) \cdot dt$$

$$\text{Note: } \delta \dot{q} = \frac{d(\delta q)}{dt}$$

$$S_S = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \frac{d(\delta q)}{dt} \right) dt$$

consider the second term

$$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \frac{d(\delta q)}{dt} dt$$

Integration by parts

$$\left[\frac{\partial L}{\partial \dot{q}} \delta q \right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \delta q dt$$

$$= 0 - \int_{t_1}^{t_2} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \delta q dt$$

$$(\because \delta q(t_1) = \delta q(t_2) = 0)$$

$$S_S = \int_{t_1}^{t_2} \frac{\partial L}{\partial q} \delta q dt - \int_{t_1}^{t_2} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \delta q dt$$

$$= \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \right] \delta q dt$$

[Bringing neighbouring path
to least action path]

$$\Rightarrow S_S = 0$$

This is true for any arbitrary

to get action path

$$\boxed{\frac{\partial L}{\partial q_i} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) = 0}$$

→ Lagrange's equation

$$L = K(\dot{q}) - U(q)$$

$$\frac{\partial L}{\partial \dot{q}} = \frac{\partial K(\dot{q})}{\partial \dot{q}}$$

$$K = \frac{1}{2} m \dot{q}^2$$

$$\Rightarrow \left. \begin{array}{l} \frac{\partial K}{\partial \dot{q}} = m \dot{q} \\ \frac{\partial L}{\partial \dot{q}} = m \ddot{q} \end{array} \right\} \rightarrow \textcircled{1}$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = m \ddot{q}$$

acceleration ($\ddot{q} = \frac{d\dot{q}}{dt}$)

$$\Rightarrow \frac{d}{dt} \dot{q} = \frac{1}{m} \left(\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \right)$$

$$\frac{\partial L}{\partial q} = - \frac{\partial U(q)}{\partial q}$$

From Lagrange's equation,

$$m \dot{q} = - \frac{\partial U}{\partial q} \rightarrow \text{force on this degree of freedom}$$

Equation of motion

This tells how \dot{q} evolves with time

$$\frac{d\dot{q}}{dt} = -\frac{1}{m} \frac{\partial U}{\partial q} = \frac{1}{m} \frac{\partial L}{\partial q}$$

$$\frac{dq}{dt} = \frac{1}{m} \frac{\partial L}{\partial \dot{q}} \quad (\text{From (1)})$$

By solving the equation, we can study the evolution of the system in phase space.

$$L(q_i, \dot{q}_i; t) \quad i = 1, 2, 3, \dots \quad n \text{ is } \# \text{ of degrees of freedom}$$

$$\frac{dL}{dt} = \sum_{i=1}^n \frac{\partial L}{\partial q} \ddot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i$$

From Lagrange's equation,

$$\left(\frac{d\dot{q}_i}{dt} \right) = \sum_{i=1}^n \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \frac{d\dot{q}_i}{dt}$$

$$\frac{dL}{dt} = \sum_{i=1}^n \frac{d}{dt} \left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right) \quad [\text{product rule}]$$

$$\Rightarrow \frac{d}{dt} \left[\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \right] = 0$$

$$\Rightarrow \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = \text{constant}$$

What is $\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$?

$$L = K - U$$

$$\frac{\partial L}{\partial \dot{q}_i} = m \ddot{q}_i$$

$$\Rightarrow \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = \sum_i m \dot{q}_i^2 - L$$

$$= \frac{1}{2} K - K + U$$

$$= K + U$$

= hamiltonian

Therefore, total energy is constant.

Total energy is conserved.

$$H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$$



Hamiltonian is the ~~Lagrangian~~
~~Legendre~~ transform of
Lagrangian

Legendre transform

Let some $f = f(x, y)$

and change $x \rightarrow x + dx$

$$y \rightarrow y + dy$$

$$f \rightarrow f + df$$

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

$$df = u dx + v dy \rightarrow ①$$

$$\left[u = \frac{\partial f}{\partial x}; v = \frac{\partial f}{\partial y} \right]$$

consider $d(vy) = y dv + v dy \rightarrow ②$

$$\Rightarrow d(vy - f) = -u dx + y dv \rightarrow ③$$

consider another function
 $g(x, v)$

$$dg = \frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial v} dv \rightarrow ④$$

compare ③ and ④

$$\boxed{g(x, v) = vy - f(x, y)} \quad [\text{from LHS}]$$

Legendre transform

therefore since $H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L(q, \dot{q})$

$$\Rightarrow H(p, q)$$

$H(p, q, t) \rightarrow$ consider only one degree of freedom
 $n = 1 \rightarrow$

$$dH = \frac{\partial H}{\partial p} dp + \frac{\partial H}{\partial q} dq + \frac{\partial H}{\partial t} dt$$

(6)

since $H = p\dot{q} - L$ (for one degree of freedom, no summation)

$$\Rightarrow dH = p d\dot{q} + \dot{q} dp - \frac{\partial L}{\partial q} dq$$

$$dH = p d\dot{q} + \dot{q} dp - \frac{\partial L}{\partial q} dq$$

(6) \rightarrow

$$- \frac{\partial L}{\partial \dot{q}} d\dot{q} - \frac{\partial L}{\partial t} dt$$

use Lagrange's equation

$$\cancel{dH = p d\dot{q} + \dot{q} dp - \dot{p} dq - pd\dot{q}} - \frac{\partial L}{\partial t} dt$$

$$dH = p d\dot{q} + \dot{q} dp - \dot{p} dq - pd\dot{q} - \frac{\partial L}{\partial t} dt$$

$$dH = \dot{q} dp - \dot{p} dq - \frac{\partial L}{\partial t} dt$$

(7)

compare (6), (7)

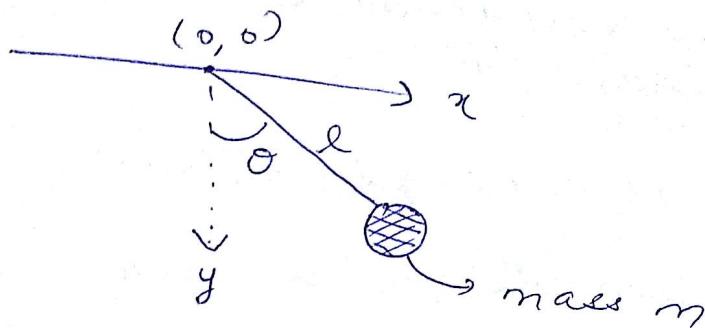
$\ddot{q} = \frac{\partial H}{\partial p}$	$\dot{p} = -\frac{\partial H}{\partial q}$
--	--

Hamilton
equations
of motion

$$\text{and } \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$$

If H is constant
 $\Rightarrow L$ should also be conserved
simple case studies

Simple pendulum:



$$q = \theta$$

$\theta, \dot{\theta} \rightarrow$ measure with time

calculate Lagrangian / Hamiltonian

$$x = l \sin \theta$$

$$y = l \cos \theta$$

$$\dot{x} = \frac{dx}{dt} = l \cos \theta \dot{\theta}$$

$$\dot{y} = \frac{dy}{dt} = -l \sin \theta \dot{\theta}$$

$$K = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2) = \frac{1}{2} m l^2 \dot{\theta}^2$$

$$U = -m g l \cos \theta$$

$$L(\theta, \dot{\theta}) = K - U$$

$$= \frac{1}{2} m l^2 \dot{\theta}^2 + m g l \cos \theta$$

million
allow
ratio

Lagrange's equation?

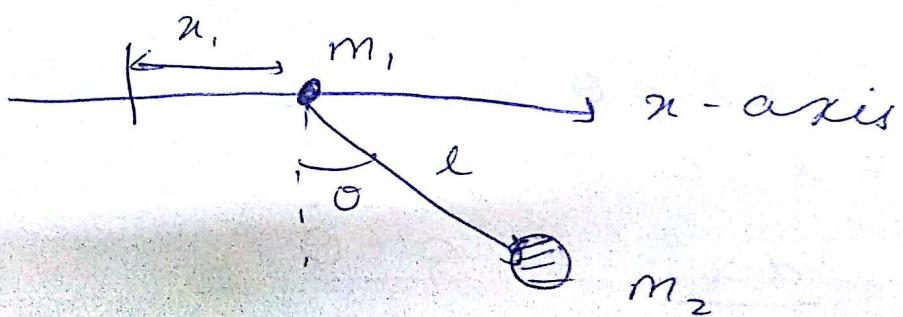
$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = \frac{\partial L}{\partial \theta}$$

$$\Rightarrow m l^2 \ddot{\theta} + mgl \sin \theta = 0$$

The equation of motion of the pendulum.

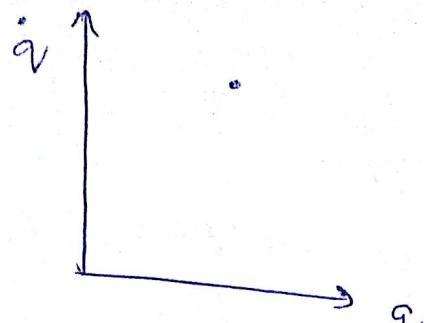
② Sliding pendulum

A simple pendulum of mass m_2 with a mass m_1 at the point of support which can move on a horizontal line lying in the plane in which m_2 moves



conservation laws

homogeneity of time : L need not depend on time explicitly



\Rightarrow law of conservation of energy

homogeneity of space ; L does not change by translation of the whole system.

\Rightarrow conservation of linear momentum

isotropy of space ; L does not change by rotation of whole system

\Rightarrow conservation of angular momentum

conservation of momentum

\rightarrow homogeneity of space

\rightarrow mechanical properties of a closed system are unchanged by any parallel displacement of the entire system in space

Displace every degree of freedom by ϵ

$$q_i \rightarrow q_i + \epsilon \quad (\forall i)$$

$(q_i \rightarrow \text{unchanged})$

change in L

$$\delta L = \sum_i \frac{\partial L}{\partial q_i} \delta q_i$$

$$= \epsilon \sum_i \frac{\partial L}{\partial q_i}$$

homogeneity in space $\Rightarrow \delta L = 0$

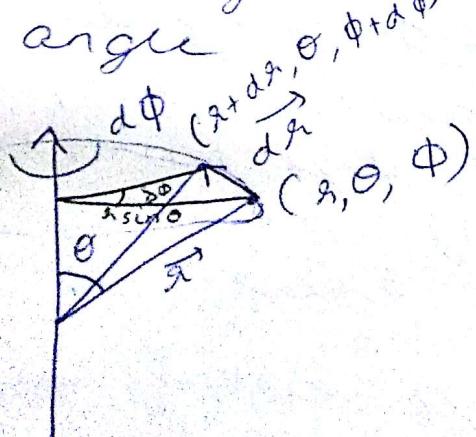
$$\Rightarrow \frac{d}{dt} \sum_i \frac{\partial L}{\partial \dot{q}_i} = 0 \quad [\text{Lagrange's equation}]$$

$$\Rightarrow \frac{d}{dt} \sum_i m_i \dot{q}_i = 0$$

$\underbrace{\quad}_{\text{Total}}$
momentum is
constant

conservation of angular momentum

rotopy of space - Lagrangian is invariant under the rotation of the whole system by an arbitrary angle



$$|\vec{d\alpha}| = r \sin \theta d\phi$$

$$\vec{\delta \alpha} = \vec{\delta \phi} \times \vec{\alpha}$$

$$L = L(\vec{\alpha}_i, \vec{v}_i)$$

$$\delta L = \sum_i \frac{\partial L}{\partial \vec{\alpha}_i} \cdot \vec{\delta \alpha}_i + \frac{\partial L}{\partial \vec{v}_i} \cdot \vec{\delta v}$$

$$\vec{\delta v} = \vec{\delta \phi} \times \vec{v}$$

$$\left[\frac{\partial L}{\partial \vec{\alpha}_i} = i \frac{\partial L}{\partial x_i} + j \frac{\partial L}{\partial y_i} + k \frac{\partial L}{\partial z_i} \right]$$

$$\delta L = \sum_i \vec{p}_i \cdot (\vec{\delta \phi} \times \vec{\alpha}_i) + \vec{p}_i \cdot (\vec{\delta \phi} \times \vec{v})$$

scalar triple product is invariant under a circular shift of its three operands

$$\vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$$

$$\Rightarrow \delta L = \sum_i \vec{\delta \phi} \cdot (\vec{\alpha}_i \times \vec{p}_i) + \vec{\delta \phi} \cdot (\vec{v}_i \times \vec{p}_i)$$

$$= \vec{\delta \phi} \cdot \sum_i (\vec{\alpha}_i \times \vec{p}_i) + (\vec{v}_i \times \vec{p}_i)$$

we know that

$$\frac{d}{dt} (\vec{A} \times \vec{B}) = \vec{A} \times \dot{\vec{B}} + \vec{A} \times \vec{B}$$

$$\delta L = \vec{\delta \phi} \cdot \frac{d}{dt} \sum_i \vec{\alpha}_i \times \vec{p}_i$$

Now we know that $\delta L = 0$
(isotropy of space)

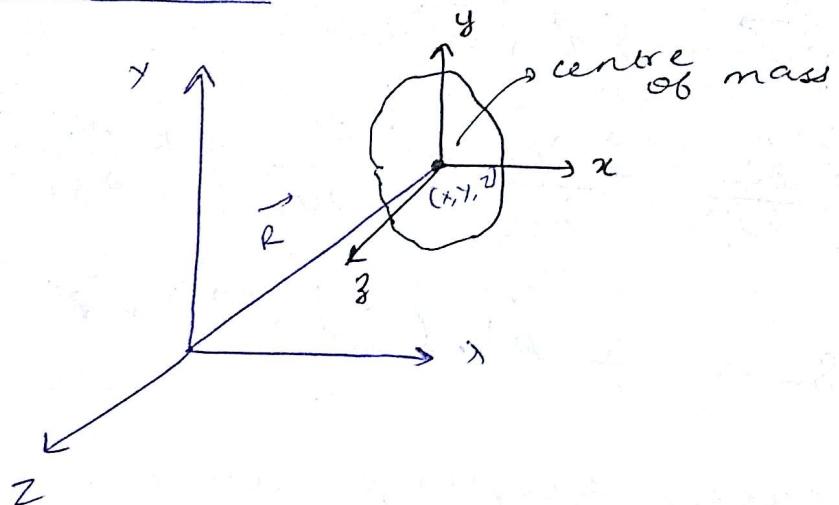
$$\therefore \text{LHS} = 0$$

But $\vec{\omega} \neq 0$

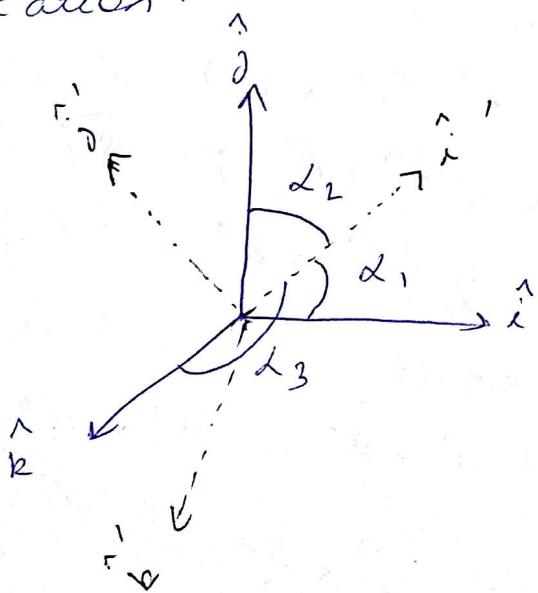
$$\Rightarrow \frac{d}{dt} (\vec{\epsilon} \cdot \vec{r}_i \times \vec{p}_i) = 0$$

\Rightarrow total angular momentum is conserved.

Rotation Matrix



Rotation:



Express \hat{i}' in terms of $\hat{i}, \hat{j}, \hat{k}$

$$\hat{i}' = (\hat{i} \cdot \hat{i}) \hat{i} + (\hat{i} \cdot \hat{j}) \hat{j} + (\hat{i} \cdot \hat{k}) \hat{k}$$

$\hat{i}' = \hat{i}$
 $\hat{j}' = \hat{j}$
 $\hat{k}' = \hat{k}$

Now
free
(in
air)

$\hat{i} \cdot \hat{j}$
 $\hat{i} \cdot \hat{i}$

sin
 \Rightarrow co
= 0

$$\begin{aligned} \hat{i}' &= (\hat{j} \cdot \hat{i}) \hat{i} + (\hat{j} \cdot \hat{j}) \hat{j} + (\hat{j} \cdot \hat{k}) \hat{k} \\ \hat{j}' &= (\hat{k} \cdot \hat{i}) \hat{i} + (\hat{k} \cdot \hat{j}) \hat{j} + (\hat{k} \cdot \hat{k}) \hat{k} \\ \hat{k}' &= \end{aligned}$$

$$\begin{pmatrix} \hat{i}' \\ \hat{j}' \\ \hat{k}' \end{pmatrix} = \begin{pmatrix} (\hat{i} \cdot \hat{i}) & (\hat{i} \cdot \hat{j}) & (\hat{i} \cdot \hat{k}) \\ (\hat{j} \cdot \hat{i}) & (\hat{j} \cdot \hat{j}) & (\hat{j} \cdot \hat{k}) \\ (\hat{k} \cdot \hat{i}) & (\hat{k} \cdot \hat{j}) & (\hat{k} \cdot \hat{k}) \end{pmatrix} \begin{pmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{pmatrix}$$

rotation matrix
(will consist of
cosine of angles
between unit vectors)

$$\begin{pmatrix} \hat{i}' \\ \hat{j}' \\ \hat{k}' \end{pmatrix} = \begin{pmatrix} \cos \alpha_1 & \cos \alpha_2 & \cos \alpha_3 \\ \cos \beta_1 & \cos \beta_2 & \cos \beta_3 \\ \cos \gamma_1 & \cos \gamma_2 & \cos \gamma_3 \end{pmatrix} \begin{pmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{pmatrix}$$

however only 3 degrees of freedom are required
(instead of 9) since constraints exist:

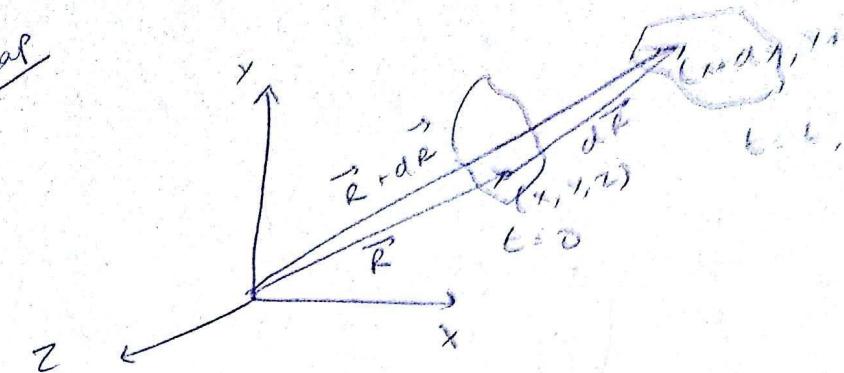
$$\hat{i} \cdot \hat{j} = \hat{j} \cdot \hat{k} = \hat{k} \cdot \hat{i} = 0$$

$$\hat{i} \cdot \hat{i} = \hat{j} \cdot \hat{j} = \hat{k} \cdot \hat{k} = 1$$

$$\text{Similarly } \hat{i}' \cdot \hat{j}' = 0$$

$$\Rightarrow \cos \alpha_1 \cos \beta_1 + \cos \alpha_2 \cos \beta_2 + \cos \alpha_3 \cos \beta_3 = 0$$

Recall



Rotable
w.r.t.
1. angle
2) $\alpha = 0$
3) $\beta = 90^\circ$
 $\gamma = 90^\circ$

Three degrees of freedom required in the case of translation.

For rotation, another three degrees of freedom are required.

Hence, for motion of rigid body, 6 degrees of freedom required.

$$\vec{i}' \cdot \vec{j}' = 0$$

$$\Rightarrow \cos \alpha, \cos \beta, + \cos \delta, \cos \beta_2 + \cos \delta_3 \text{ resp.} = 0$$

$$\vec{r} = x \vec{i} + y \vec{j} + z \vec{k}$$

Express \vec{r} with relation to $\vec{i}', \vec{j}', \vec{k}'$

$$x' = \vec{r} \cdot \vec{i}'$$

$$x' = x (\vec{i}' \cdot \vec{i}) + (\vec{i}' \cdot \vec{j}) y + (\vec{i}' \cdot \vec{k}) z$$

thus for y' & z'

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \alpha, & \cos \delta, \cos \delta_3 \\ \cos \beta, & \cos \beta_2, \cos \beta_3 \\ \cos \gamma, & \cos \gamma_2, \cos \gamma_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Proper
success

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

rotate a point (x, y, z) about z axis by θ
 \Rightarrow angle between i and i' is zero
 $\Rightarrow \alpha_1 = 0$
 $\Rightarrow \alpha_2 = 90^\circ, \alpha_3 = 90^\circ, \beta_1 = 90^\circ, \beta_2 = \theta,$
 $\Rightarrow \beta_3 = 90 - \theta$ (or $90 + \theta$ depending on clockwise or anticlockwise rotation)

$$\therefore \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix}$$

Inverse of this matrix is the transpose of this matrix

Let $A =$ rotation matrix $\begin{pmatrix} \cos \alpha_1 & \cos \alpha_2 & \cos \alpha_3 \\ \cos \beta_1 & \cos \beta_2 & \cos \beta_3 \\ \cos \gamma_1 & \cos \gamma_2 & \cos \gamma_3 \end{pmatrix}$

Properties Of A:

successive rotations \Rightarrow Product of corresponding rotation matrices

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow[A_1]{\alpha_1} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \xrightarrow[A_2]{\alpha_2} \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix}$$

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = A_2 A_1 \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Inverse rotation $\Rightarrow A^{-1}$

Transpose of $A \Rightarrow \tilde{A}$

$$\tilde{A} = A^{-1}$$

$$(AB)C = A(BC)$$

Euler angles (θ, ϕ, ψ)

Any rotation can be described by three successive rotations about linearly independent axes.

→ start from xyz frame of reference

→ rotate by ϕ counterclockwise about ~~Z~~ axis.

$$A_1 = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

→ $x'y'z'$ (here $z' = z$)

→ rotate by θ counterclockwise about x' axis

$$A_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix}$$

→ $x''y''z''$ (here $x'' = x'$)

→ see all 4 counterclockwise
about z'' axis

$$A_3 = \begin{pmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

→ $x'y'z'$ (here $z' = z$)

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = A_3 A_2 A_1 \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

bed
nions
t