

Science - 1.

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Quiz 1 : 15 %

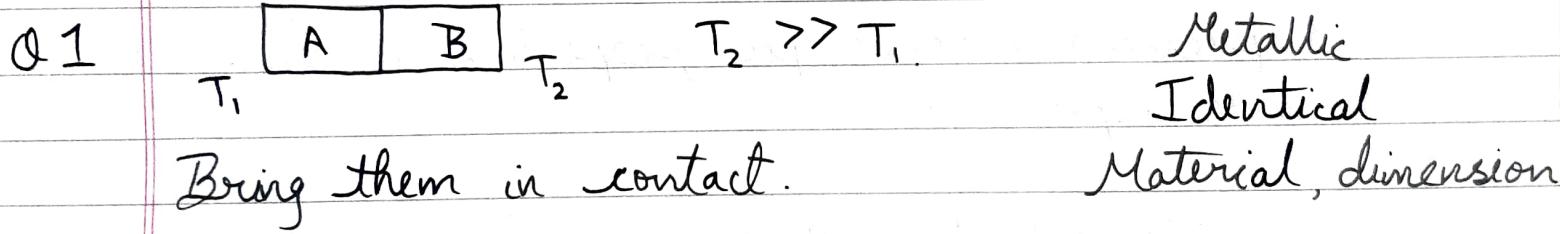
Quiz 2 : 15 %

Mid : 20 %

Final : 35 %

Asn : 15 %

Syllabus : On Moodle



Heat flows from B to A.

Why is $A \rightarrow B$ heat flow prohibited? Proof.

- + Molecules in B oscillate more vigorously than those in A.
 - + heat
- + Law of Entropy
 - + system + states
 - entropy of system increases - initial state to final state through intermediate states
 - Interested : how the system evolves.
 - the process (fast, slow)
 - paths

• Entropy : Measure of Randomness.

→ Macroscopic / Microscopic

Parameters, Variables to define macroscopic properties : (P, T, V)



Thermodynamics

Microscopic : Define $\{\vec{r}\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

- coordinates of molecules 1 to N.

$\{\vec{p}\} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$: Momentum, Velocity.

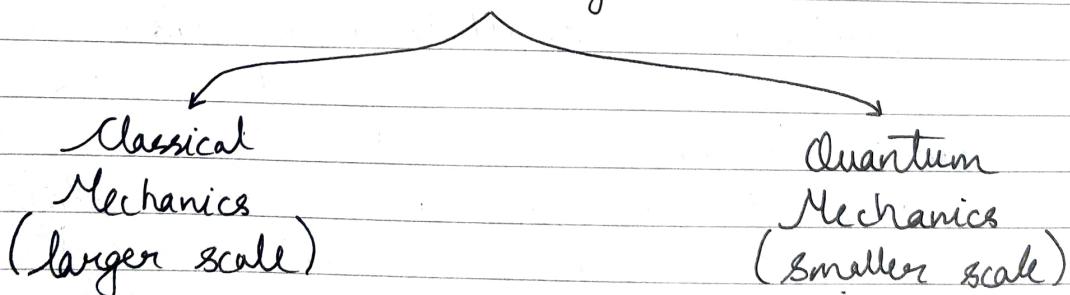
Any Property $\leftarrow A(\{\vec{r}\}, \{\vec{p}\})$

Expressing Macroscopic properties in terms of microscopic ones.

→ Classical to Quantum
(larger) (femto, fast)

length scale : 10^{-18} to 10^{18} m

time scale : 10^{-15} s to years



* Laptop : Not Dissipate heat

Theoretically Yes : 2nd law of Thermo

Lec 2

1) Science is based on measurements & observations.

Length	$6 \times 10^6 \text{ m}$
Scale	$9 \times 10^3 \text{ m}$
	1.7 m
	10^{-8} m
	$5 \times 10^{-11} \text{ m}$
	10^{-15} m

Radius of earth

Mt. Everest

Human

Length of typical virus

Radius of H-atom

Radius of proton

Time	$5 \times 10^{17} \text{ s}$
Scale	$8 \times 10^{-1} \text{ s}$

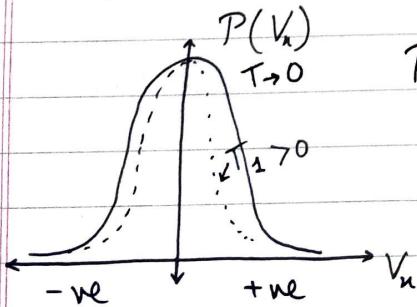
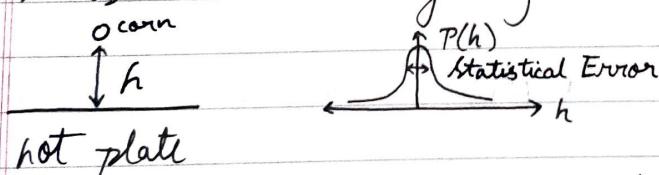
Age of universe

Heart rate

$$10^{-23} \text{ s}$$

Life of most unstable particle

2) Measurements do not give you unique values.



$$P(V_n) \propto e^{-\frac{1}{2k_B T} m V_n^2}$$

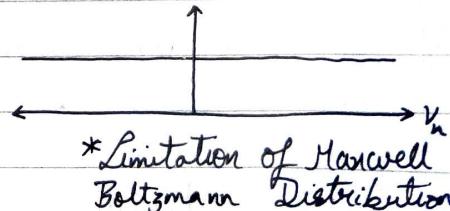
given this

how to calculate:

$$\langle V_n^2 \rangle \rightarrow \text{average } V_n^2$$

$$\langle V_n^2 \rangle = \int_{-\infty}^{\infty} V_n^2 P(V_n) dV_n$$

As $T \rightarrow \infty$



*Limitation of Maxwell Boltzmann Distribution

$$\int_c^{\infty} P(V_n) dV_n \neq 0 \text{ at high temperature}$$

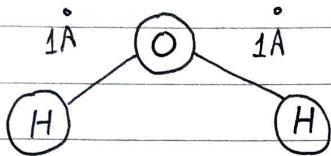
$$\langle (V_x - \langle V_x \rangle)^2 \rangle : s.d$$

Function symmetric about y-axis. $\Rightarrow \langle V_x \rangle = 0$

$$\therefore \frac{m}{2} \langle V_x^2 \rangle = \frac{m}{2} \int_{-\infty}^{\infty} V_x^2 P(V_x) dV_x = \frac{1}{2} K_B T$$

\rightarrow Most probable speed of Nitrogen Molecule at room temperature : 1600 km/h

$H_2O :$



Intergalactic event : bond length changes by $\sim 1 \text{ \AA}$
 \rightarrow everyone dies.

- \rightarrow What about molecular vibration? Shape change.
- \rightarrow Prove molecules moving around - Add a drop of ink - diffuses
- Measure energy of water molecules - Add energy - Pump - Spectroscopy
- Missile timing example : 5-8 mins. Islamabad to Delhi

Time taken t $- t\tau \sim k$ (constant) • Run from A to B experiment • Ice cube Volume Time to Melt	Relaxation time τ
--	------------------------

- Stability : Graphite more stable than diamond. Diamond wants to go back to graphite state.

Stability determined by thermodynamic laws.

$$G(T, P) = 0 \text{ stability}$$

- Gibbs free energy

→ Cool water very fast : Water Gas.
Kinetics Dominates.

- 4 ways of understanding system using science

1) Energy : heat, work, free energy, enthalpy, entropy
(Thermodynamic Approach)

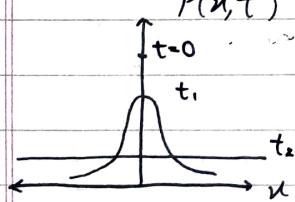
2) Matter : System made up of particles (Atoms / molecules) → define microstate of the system
↳ Statistical Mechanics ↳ Solid State Physics

3) Waves : EM waves, Quantum Mechanics

4) Mathematical : Diffusion equation, Random Walk Problem
Modelling
↳ Drop ink at origin
↳ Assume 1 D

↳ Diffusion both sides

Diffusion



Molecule : A random walker.
Left or Right with prob. $\frac{1}{2}$.

Lec 3

Energy : Thermodynamics \Rightarrow Work \Rightarrow Heat
 \Rightarrow Thermodynamic potentials (internal energy, Gibbs free energy, enthalpy, Helmholtz free energy)

P, V, T, \dots $P = f(V, T)$: Arbitrary Function
 : equation of state of system.

$$V = g(P, T)$$

$\frac{dV}{dP} \Big|_T$ \rightarrow compressibility representation

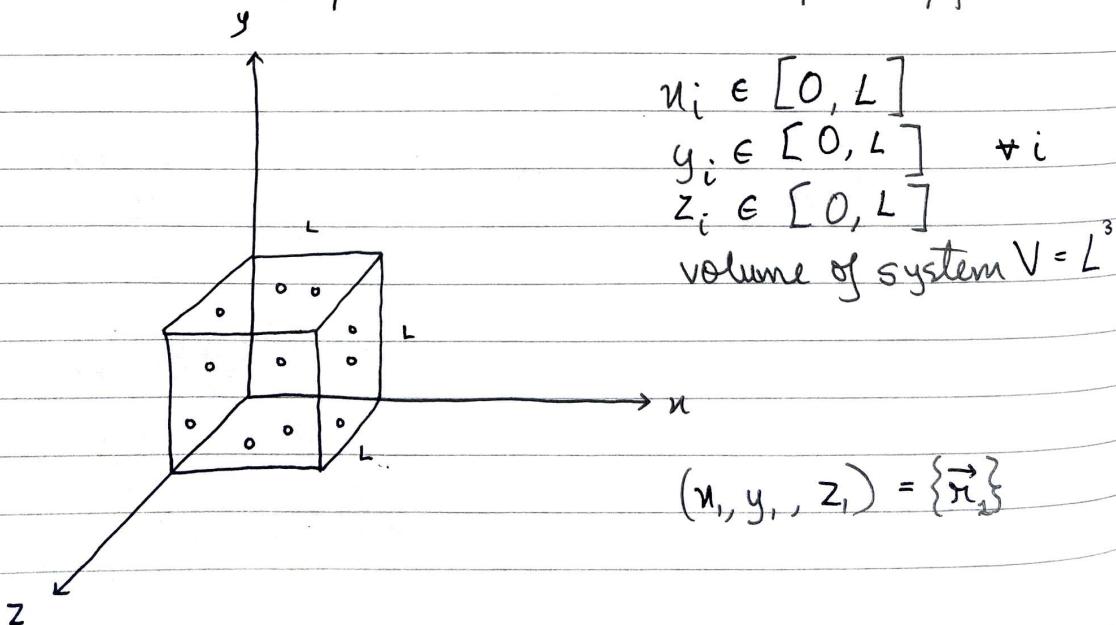
Normalize w.r.t volume : $\frac{1}{V} \frac{dV}{dP} \Big|_T$

$$P \rightarrow P + dP : V \rightarrow V + dV$$

↳ Everything can be explained in terms of these 4 variables — Macroscopic variables : have rules & laws.

Matter :

- System consists of N particles
- position & momenta of the particles are known
 - ↳ Microscopic variables - microscopic approach



$$\{\vec{r}\} \text{ set} = (u_1, y_1, z_1, u_2, y_2, z_2, \dots, u_N, y_N, z_N)$$

$$\vec{r}_i = (u_i, y_i, z_i)$$

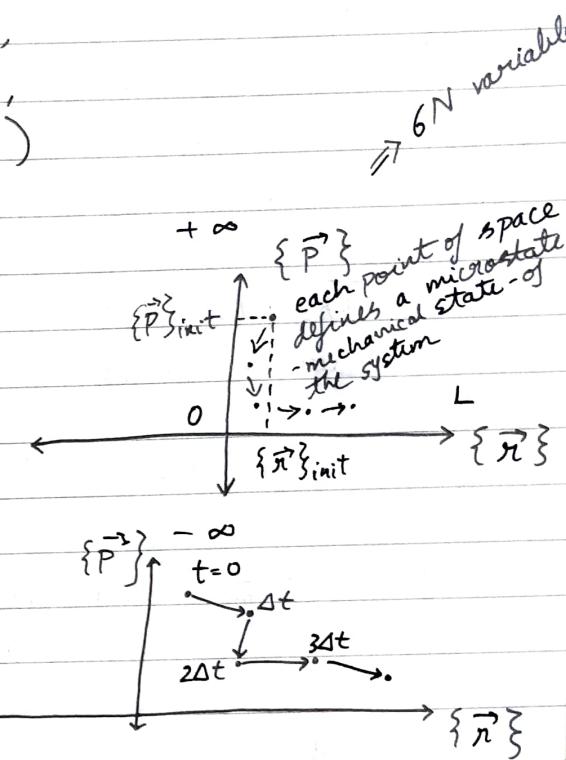
$$\{\vec{p}\} = (P_{x1}, P_{x2}, P_{x3}, \dots, P_{xn},$$

$$\begin{cases} P_{y1}, P_{yz}, \dots, P_{yn}, \\ P_{z1}, \dots, P_{zn} \end{cases}$$

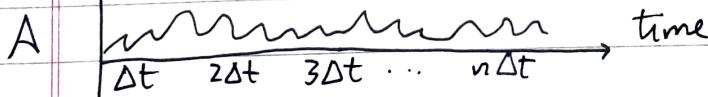
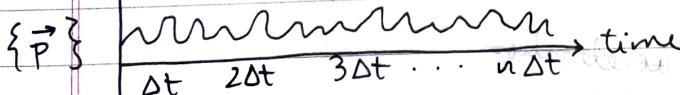
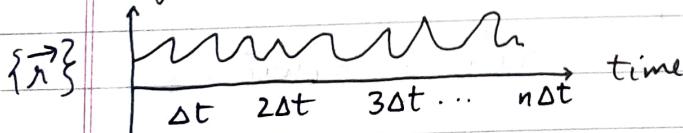
set of momenta

$$|\{\vec{r}\}| = |\{\vec{p}\}| = 3n$$

- unstable: visits different states
- trajectory



• Any arbitrary property of interest can be expressed as a function of $\{\vec{r}\}$ & $\{\vec{p}\}$: $A = A(\{\vec{r}\}, \{\vec{p}\})$



$\langle A \rangle_{\text{time}}$
average A over time

case 1

$N \rightarrow \text{small}$

$V \rightarrow \text{small}$

case 2

$V \rightarrow \infty$

$N \rightarrow \infty$

→ Will Results differ?

$\frac{N}{V}$: finite OR $N \rightarrow \infty$ } thermodynamic unit
 $V \rightarrow \infty$

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

↓

Potential energy function

Scalar function

Hamiltonian function

(Total energy of the system)

Isolated System ~ Doesn't exchange energy with the surroundings.

$$\frac{dH(\{\vec{r}\}, \{\vec{p}\})}{dt} = 0$$

$$\rightarrow \sum_{i=1}^N \left\{ \frac{\partial H}{\partial \vec{r}_i} \cdot \frac{d\vec{r}_i}{dt} + \frac{\partial H}{\partial \vec{p}_i} \cdot \frac{d\vec{p}_i}{dt} \right\} = 0$$

$$\frac{d\vec{r}_i}{dt} = \left(\frac{dx_i}{dt}, \frac{dy_i}{dt}, \frac{dz_i}{dt} \right)$$

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

force

Hamilton's equations

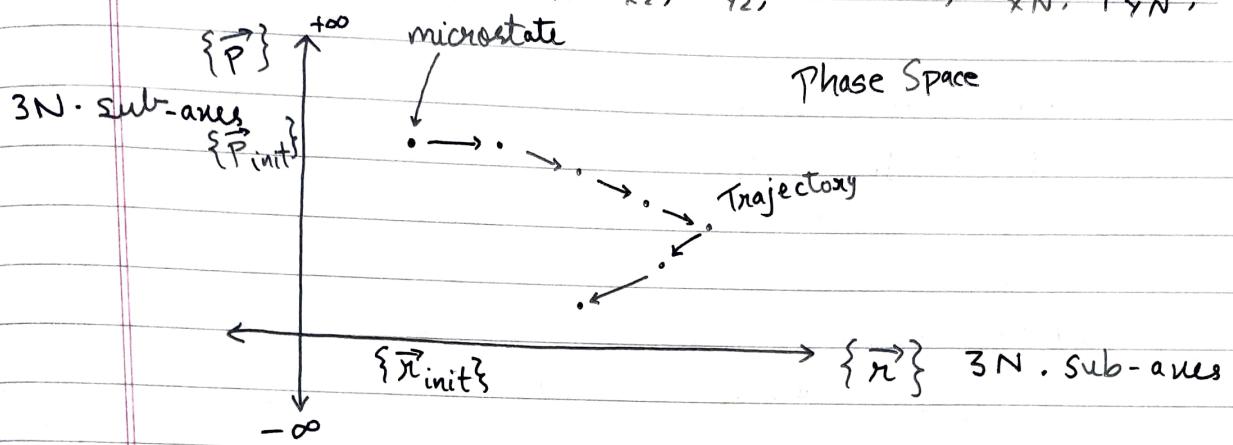
$$\frac{\partial H}{\partial \vec{p}_i} = \frac{d\vec{r}_i}{dt}$$

velocity

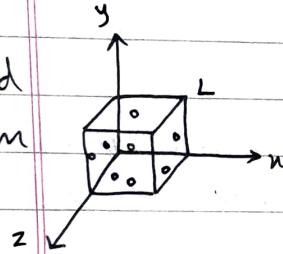
Lec 4 → Microstate of a system consisting of N particles
 $(\{\vec{r}\}, \{\vec{p}\})$

$$\{\vec{r}\} = (x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N)$$

$$\{\vec{p}\} = (p_{x_1}, p_{y_1}, p_{z_1}, p_{x_2}, p_{y_2}, \dots, p_{x_N}, p_{y_N}, p_{z_N})$$



Isolated System



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

[Scalar hamiltonian function - Total energy]

U : potential energy (interaction of particles)

K : kinetic energy (thermal)

$$\frac{dH}{dt} = 0, \text{ isolated, constant total energy.}$$

→ Hamilton's equations of motion:

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

$$\text{Now, } \vec{F}_i = \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{r}_i} = -\frac{\partial U}{\partial \vec{r}_i} (\{\vec{r}\})$$

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

$$F_{n,i} = -\frac{\partial U}{\partial n_i}$$

$$F_{z,i} = -\frac{\partial U}{\partial z_i}$$

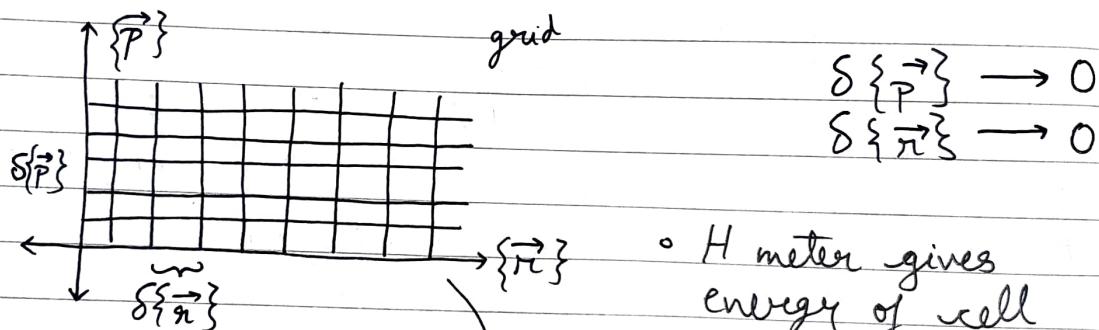
$$F_{y,i} = -\frac{\partial U}{\partial y_i}$$

$$\therefore n_i \rightarrow n_i + \delta n_i$$

$$y_i \rightarrow y_i + \delta y_i$$

$$z_i \rightarrow z_i + \delta z_i$$

$$U(n_i + \delta n_i, y_i + \delta y_i, z_i + \delta z_i) - U(n_i, y_i, z_i)$$



- Create energy ladder

◦ H meter gives energy of cell
◦ place cells on this ladder acc. to their energy values

E_{max}



$E_i \rightarrow S(E_i)$: #cells with energy E_i

$\Delta E \{$

(lowest possible energy for the system)

$E_{min} + 2 \Delta E$

$E_{min} + \Delta E$

E_{min}

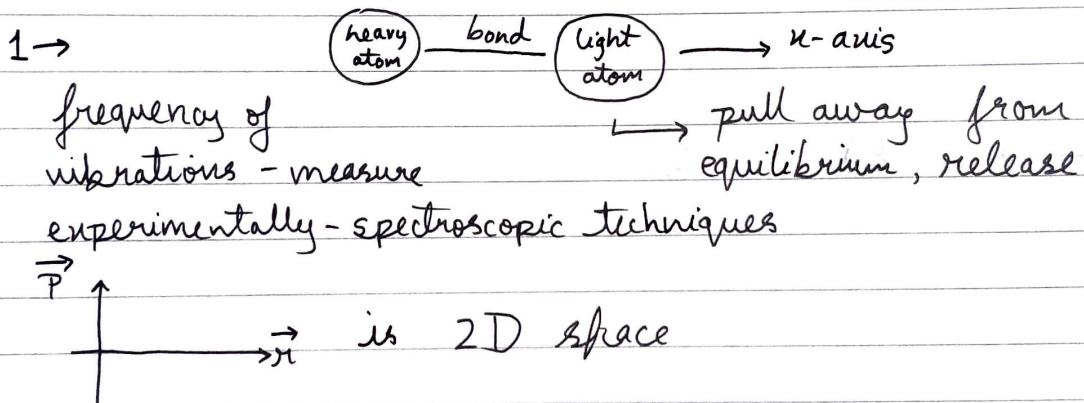
System can travel b/w various cells with the same energy — changes mechanical state

Boltzmann: entropy $S \propto \ln(-\Omega(E_i))$] statistical
 thermodynamic [$S = k_B \ln\{-\Omega(E_i)\}$] quantity
 quantity Boltzmann's constant
 : Microscopic definition of entropy

$$-\Omega(E_i) \rightarrow 1 \text{ for ice.}$$

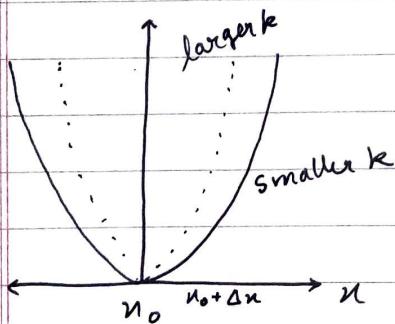
1) Model: 1D harmonic oscillator

2) Model: Ideal Gas. $U(\{\vec{r}\}) = 0$ - Simple.



m : Mass of light atom

$$H(n, p) = \frac{p^2}{2m} + \frac{1}{2} k(n - n_0)^2 = E \quad \begin{matrix} \nearrow \text{initial energy} \\ \end{matrix}$$



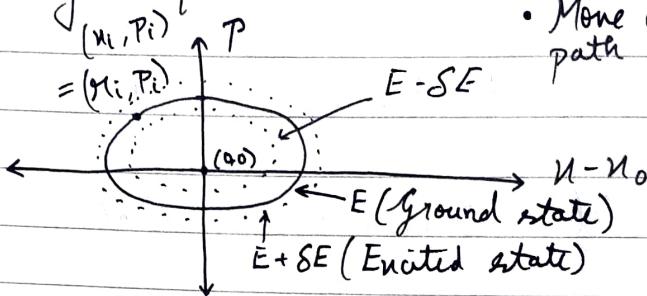
$$U(n) = \frac{1}{2} k(n - n_0)^2$$

$$\frac{\partial^2 U}{\partial n^2} = k \rightarrow \begin{matrix} \text{how} \\ \text{easy to} \\ \text{compress} \end{matrix}$$

• Spring connecting train coaches - high k

$$\therefore \frac{(n - n_0)^2}{\left(\sqrt{\frac{2E}{K}}\right)^2} + \frac{P^2}{\left(\sqrt{2mE}\right)^2} = 1$$

↳ equation of ellipse



- Move on the elliptical path

$$\begin{aligned}\Omega(E) &= \text{circumference of ellipse} / \delta E \\ &= \pi \left(\sqrt{\frac{2E}{K}} + \sqrt{2mE} \right) / \delta E\end{aligned}$$

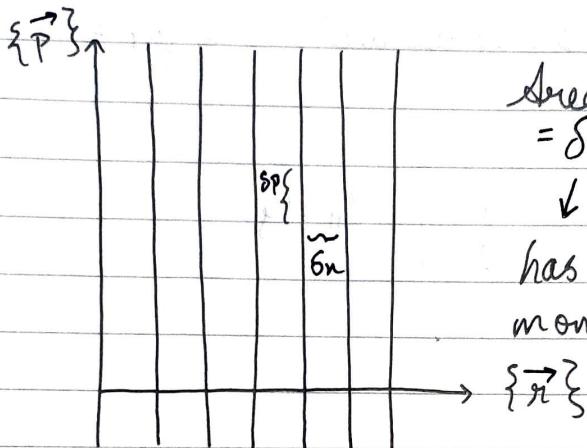
$$\propto \pi \left(\sqrt{\frac{2E}{K}} + \sqrt{2mE} \right)$$

$$\longrightarrow \Omega(E_i) \propto \sqrt{E_i}$$

Lec 5 $S = K_B \ln (\Omega(E))$

for crystals at low temperatures, $\Omega(E) \rightarrow 1$
 $\Rightarrow S \rightarrow 0$.

Model 1 : 1D Harmonic Oscillator



$$\text{Area of cell } n \\ = \delta n \cdot \delta P = h$$

↓

has dimensions of angular momentum

$$\{n\}$$

Model 2 : Ideal Gas

$$H(\{n\}, \{\vec{P}\}) = U(\{n\}) + K(\{\vec{P}\})$$

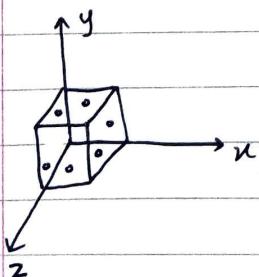
↑
as ideal gas

if $U(\{n\}) = 0$, atoms do not interact with each other \rightarrow ideal gas

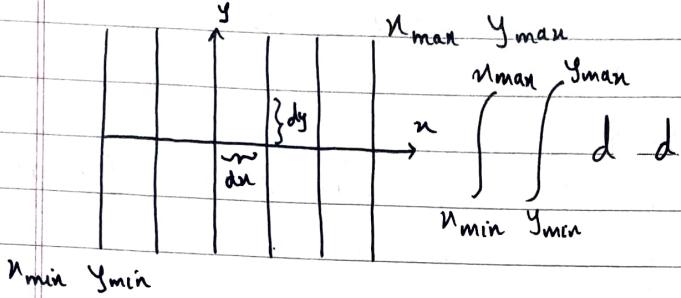
$N \rightarrow$ # ideal gas atoms

$V \rightarrow$ volume = L^3

$E \rightarrow$ initial energy of the system
isolated system



$$\begin{aligned} & \text{Volume of } 6N \text{ dimensional cell} \\ &= \delta \{n\} \cdot \delta \{\vec{P}\} \\ &= \frac{\delta n_1 \delta P_{x1}}{\delta n_N \delta P_{xN}} \frac{\delta y_1 \delta P_{y1}}{\delta y_N \delta P_{yN}} \frac{\delta z_1 \delta P_{z1}}{\delta z_N \delta P_{zN}} \dots \\ &= h^{3N} \end{aligned}$$

$h \rightarrow 0$ h is arbitrary in classical mechanics h : Planck's constant in quantum mechanicsWant: Calculate $\Omega(E)$ - dependency on N . $\Omega(N, V, E) \rightarrow$ number of accessible microstates→ find all cells in space with energy E .→ Visit all cells in $6N$ dimensional phase space:

$$\int \int \delta\{\vec{r}\} \delta\{\vec{p}\}$$

$$\{\vec{r}\} \{\vec{p}\}$$

$$\int \int \delta(H - E) \delta\{\vec{r}\} \delta\{\vec{p}\}$$

$$\{\vec{r}\} \{\vec{p}\}$$

$\xleftarrow[3N]{}$
integrals
each

$$\rightarrow \delta(H - E) = \begin{cases} 1 & \text{when } H = E \\ 0 & \text{otherwise} \end{cases} \quad \left. \begin{array}{l} \text{Dirac delta} \\ \text{function} \end{array} \right.$$

· like carrying a Hamiltonian meter around

$$\Omega(N, V, E) = \frac{1}{h^{3N}} \int \int \delta(H - E) \delta\{\vec{r}\} \delta\{\vec{p}\}$$

The Hamiltonian function:

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

↓
mass of atom

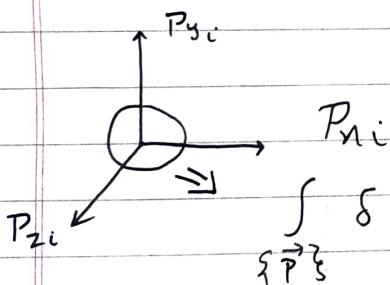
$$\begin{aligned} \Omega(N, V, E) &= \frac{1}{h^{3N}} \int d\{\vec{r}\} \int \delta(H-E) \delta\{\vec{p}\} \\ &\quad \{\vec{r}\} = 0 \quad \{\vec{p}\} \\ &= \frac{1}{h^{3N}} \cdot V^N \int \delta(H-E) \delta\{\vec{p}\} \end{aligned}$$

looking for p 's s.t.:

$$\frac{P_{x_1}^2}{2m} + \frac{P_{y_1}^2}{2m} + \frac{P_{z_1}^2}{2m} + \dots + \frac{P_{x_N}^2}{2m} + \frac{P_{y_N}^2}{2m} + \frac{P_{z_N}^2}{2m} = E$$

$$\Rightarrow P_{x_1}^2 + P_{y_1}^2 + P_{z_1}^2 + \dots + P_{x_N}^2 + P_{y_N}^2 + P_{z_N}^2 = (\sqrt{2mE})^2$$

($3N$ -dimensional sphere) (radius : $\sqrt{2mE}$)



$$\int \delta(H-E) \delta\{\vec{p}\} \propto \text{surface area of } 3N \text{ dimensional sphere of radius } \sqrt{2mE}$$

$$\propto (\sqrt{2mE})^{3N-1}$$

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

$S = k_B \ln(\Omega(N, V, E))$: valid for isolated system

Lec 6

Recap:

- isolated system

- ideal gas

- $\Omega(N, V, E) \propto \frac{1}{h^{3N}} V^N (E)^{\frac{3N-1}{2}} \equiv 6N$ phase space

1D Harmonic Oscillator $\Omega(E) \propto E^{1/2}$

Energy

Isolated

 E_{initial}

time

 $P(E)$ E_{initial}

Energy

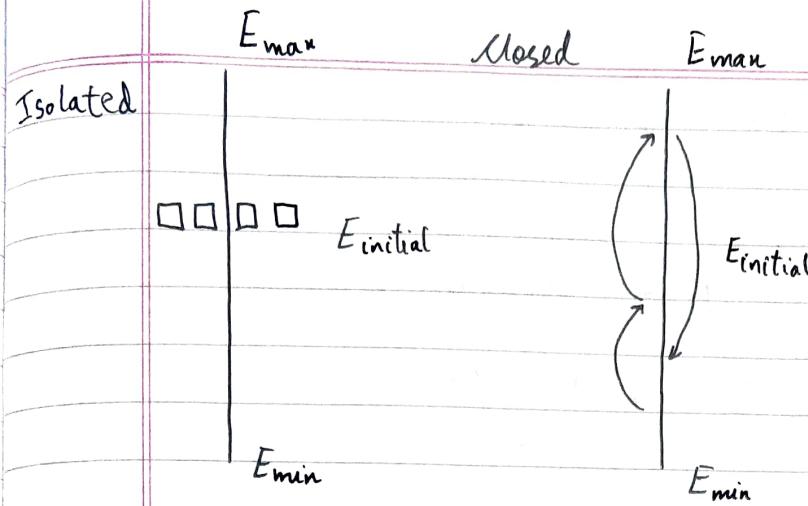
Closed

 $P(E)$ $\langle E \rangle$

time

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3N}{2} k_B T \rightarrow \text{temperature}$$

to keep T constant, keep avg. kinetic energy of the system constant.



$P(E_i) = P[\text{finding the system in a given energy level with energy } E_i]$

$$P(E_i) \propto e^{-\beta E_i}, \text{ where } \beta = 1/k_B T$$

$$P(\{\vec{r}\}, \{\vec{p}\}) \propto e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}$$

$$P(\{\vec{r}\}, \{\vec{p}\}) = A e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}$$

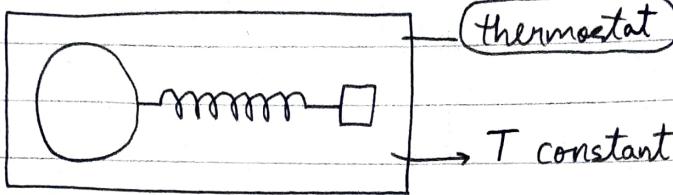
$$\int_{\{\vec{r}\}} \int_{\{\vec{p}\}} P(\{\vec{r}\}, \{\vec{p}\}) d\{\vec{r}\} d\{\vec{p}\} = 1$$

$$\Rightarrow P(\{\vec{r}\}, \{\vec{p}\}) = \frac{e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}}{Z}$$

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

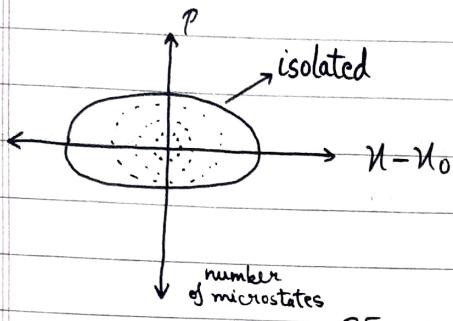
- Z is called the partition function of the system
- Given Z , we can calculate all thermodynamic properties of the system.

Model - 1 [Closed] 1D harmonic oscillator



$$H(x, p) = \frac{1}{2} k(x - x_0)^2 + p^2/2m$$

$$P(n, p) \propto e^{-\beta/2 k(x - x_0)^2} \cdot e^{-\beta p^2/2m}$$



$Z = \sum_{i=1} e^{-\beta E_i}$, from Z we calculate thermodynamic properties of the system.

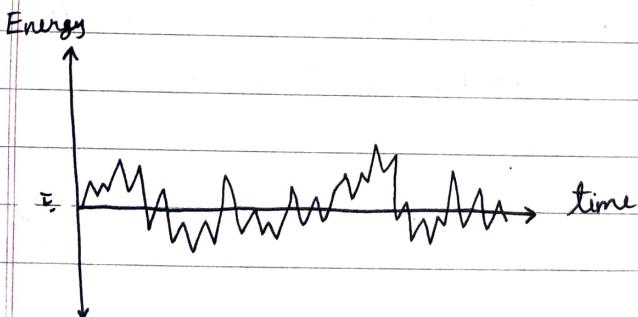
$$\ln Z = \ln \left(\sum_i e^{-\beta E_i} \right)$$

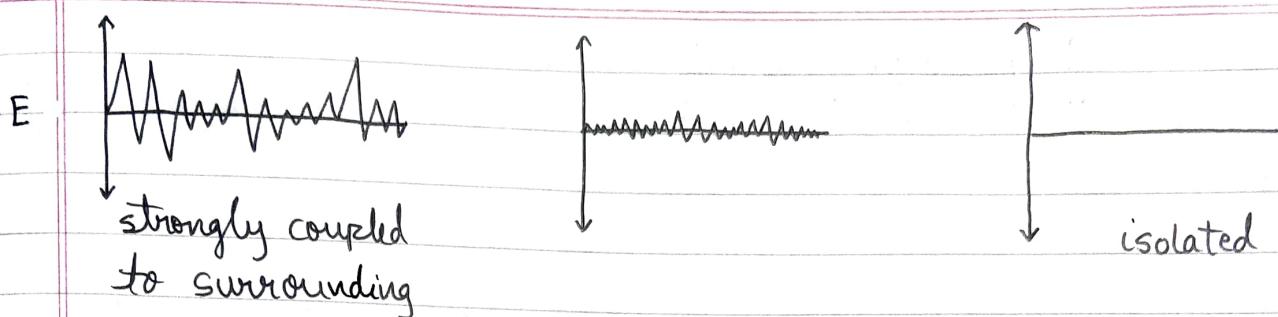
$$\left\{ -\frac{\partial (\ln Z)}{\partial \beta} = \frac{1}{\sum_i e^{-\beta E_i}} \sum_i E_i e^{-\beta E_i} \right\} \quad (i)$$

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

$$= \sum_i E_i \cdot P[E_i] = \langle E \rangle^* \text{ Internal Energy of the system}$$

— Average total energy of system





: s.d. gives useful information. - fluctuation of energy

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

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

$$\hookrightarrow \frac{\partial}{\partial \beta} \left[\sum E_i e^{-\beta E_i} \right] = \frac{\partial}{\partial \beta} \left(-Z \frac{\partial \ln Z}{\partial \beta} \right)$$

$$\Rightarrow - \sum_i E_i^2 e^{-\beta E_i} = - \frac{\partial Z}{\partial \beta} \cdot \frac{\partial \ln Z}{\partial \beta} - Z \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\Rightarrow \sum_i E_i^2 \left(\frac{e^{-\beta E_i}}{Z} \right) = \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \cdot \frac{\partial \ln Z}{\partial \beta} + \frac{\partial^2 \ln Z}{\partial \beta^2}$$

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

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

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

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

$$\beta = 1/k_B T$$

$$\langle E^2 \rangle - \langle E \rangle^2 = \left(\frac{-\frac{\partial}{\partial T} \langle E \rangle}{\frac{\partial \beta}{\partial T}} \right) = \frac{-C_V}{(\frac{\partial \beta}{\partial T})} \quad \langle E \rangle \uparrow T$$

$$C_V = +\frac{\partial}{\partial T} \langle E \rangle$$

— energy fluctuations is related to the heat capacity C_V of the system

$$\frac{\partial \beta}{\partial T} = \frac{1}{\partial T} \left[\frac{1}{k_B T} \right]$$

$$= \frac{1}{k_B} \cdot -\frac{1}{T^2}$$

$$\therefore \frac{-\frac{\partial}{\partial T} \langle E \rangle}{\frac{\partial \beta}{\partial T}}$$

$$\frac{\partial \beta}{\partial T}$$

$$= \frac{-C_V}{\frac{-1}{k_B T^2}} = C_V k_B T^2$$

Lec 7

Recap:

Isolated System : $\Omega(N, V, E)$ Closed System : Partition Function $Z = \sum_i e^{-\beta E_i}$

$$\text{where } \beta = 1/k_B T$$

$$P(E_i) = e^{-\beta E_i} / Z$$

$$P(\{\vec{r}\}, \{\vec{p}\}) = e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}$$

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

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Z \rightarrow \text{Internal Energy}$$

$$-\text{Fluctuation of energy} \quad \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{\partial^2 \ln Z}{\partial \beta^2} = C_V k_B T^2$$

$$\left[C_V = \frac{\partial \langle E \rangle}{\partial T} \right]$$

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

$\rightarrow C_V$ Always (+)ve

Experimental :

Find C_V : slope

- Recall for any isolated system - entropy $S = k_B \ln \Omega$

$$S = -k_B \sum_i P_i \ln P_i = -k_B \langle \ln P \rangle$$

Probability of finding the system in the i th microstate

If the system was isolated : $P_i = \frac{1}{\Omega}$

[The principle of equal a priori probabilities]

For closed systems : $P_i = \frac{e^{-\beta E_i}}{Z}$

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

$$= \beta K_B \sum_i E_i P_i + K_B \ln Z \sum_i P_i$$

$$\Rightarrow S = \frac{\langle E \rangle}{T} + K_B \ln Z$$

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

Helmholtz Free Energy $A = U - TS$
 $A = -K_B T \ln Z$

$$\hookrightarrow S = -K_B \sum_i P_i \ln P_i$$

□ Microscopic Definition of Pressure

$$\text{pressure of system in microstate } i \quad P_i \equiv -\frac{\partial E_i}{\partial V} = -\left[\frac{E_i(v+\Delta v) - E_i(v)}{\Delta v} \right] \quad \text{where } \lim \Delta v \rightarrow 0$$

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

$$\frac{\partial P}{\partial V} = \frac{\partial}{\partial V} \left(\frac{1}{\beta} \frac{\partial (\ln Z)}{\partial V} \right)$$

Ideal Gas (closed)

$N \rightarrow$ number of ideal gas atoms

$V \rightarrow$ volume

$T \rightarrow$ temperature

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

Goal → calculate Z

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

$$= \frac{1}{h^{3N}} \int_{\{\vec{r}\}} d\{\vec{r}\} \int_{\{\vec{p}\}} e^{-\beta \left[\frac{1}{2m} \sum_j \vec{p}_j \cdot \vec{p}_j \right]} d\{\vec{p}\}$$

$$\rightarrow Z = \frac{1}{h^{3N}} V^N \left(\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} x^2} dx \right)^{3N} e^{-\beta/2m [P_{x1}^2 + P_{y1}^2 + P_{z1}^2 + \dots + P_{xN}^2 + P_{yN}^2 + P_{zN}^2]} *$$

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

$$\langle p \rangle^{\text{pressure}} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{1}{\beta} \frac{N}{V}$$

$$\Rightarrow \boxed{\langle p \rangle V = N k_B T} \quad \text{ideal gas equation of state}$$

- Feynmann's Trick

$$I = \int_{-\infty}^{\infty} e^{-\alpha n^2} dn, \quad I = \int_{-\infty}^{\infty} e^{-\alpha y^2} dy$$

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

$$x^2 + y^2 = r^2, \quad dx dy = r dr d\theta$$

$$\begin{aligned} I^2 &= \int_0^{\infty} \int_0^{2\pi} e^{-\alpha r^2} r dr d\theta \\ \Rightarrow I^2 &= 2\pi \int_0^{\infty} e^{-\alpha r^2} d\left(\frac{r^2}{2}\right) \end{aligned}$$

$$\begin{aligned} &= \pi \int_0^{\infty} e^{-\alpha u} du \\ \Rightarrow I &= \sqrt{\frac{\pi}{\alpha}} \end{aligned}$$

$$x = r \cos \theta$$

$$dx = r \cdot -\sin \theta d\theta$$

$$y = r \sin \theta$$

$$dy = r \cos \theta d\theta$$

$$dx dy = r^2 \cdot -\sin \theta \cos \theta (d\theta)^2$$

$$= r (-\sin \theta \cos \theta r d\theta) d\theta$$

$$dx = dr \cos \theta$$

$$dy = dr \sin \theta$$

lec 8

Recap:

ideal gas (closed)

partition function Z pressure from Z

ideal gas eqn. of state was derived

 Z was related to all thermodynamic functions

- 1 → Calculate the entropy of an ideal gas [fixed N, V, T]

$$2 \rightarrow \begin{array}{c|c} S \\ N, V, T & N, V, T \end{array} \xrightarrow{\downarrow} S$$

Combined $2N, 2V, T$ is $S_{\text{com}} = S + S$
entropy

 S_{com}

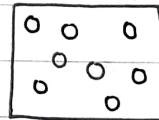
$$\text{if: } S(2N, 2V, T) = 2S(N, V, T)$$

Thermodynamics : = } Gibbs Paradox
from Z : ≠ }

$$S(2N, 2V, T) - 2S(N, V, T) = 2N K_B \ln 2$$

Gibbs Corrections:

$$Z_{\text{cor}} = \frac{Z}{N!}$$



Use Z_{cor} to calculate S . S would become an extreme quantity.

[Sterling's Approximation: $\ln N! \approx N \ln N - N$ for large N]

- Entropy - Extensive Property
- Temperature - Not extensive

Interacting Systems : Molecular Interactions

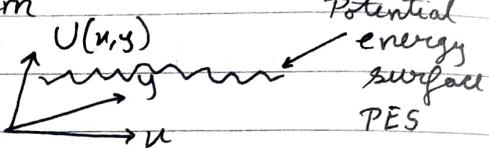
$$U(\{r\}) = 0 \quad [\text{Ideal gas}]$$

what if $U(\{r\}) \neq 0$. \rightarrow Real Gases / Interacting systems

$$\{r\} = (n_1, y_1, z_1, \dots, n_N, y_N, z_N)$$

$U(\{r\}) \Rightarrow 3N$ degrees of freedom determine the potential energy of the system

Simple : 2D system : $U(n, y)$



$$F_n = -\frac{\partial}{\partial n} U(n, y), \quad F_y = -\frac{\partial}{\partial y} U(n, y)$$

gives depth/
shallowness of
the energy
well

$3N \times 3N$

$$\begin{bmatrix} \frac{\partial^2 U(n,y)}{\partial n^2} & \frac{\partial^2 U(n,y)}{\partial n \partial y} \\ \frac{\partial^2 U(n,y)}{\partial y \partial n} & \frac{\partial^2 U(n,y)}{\partial y^2} \end{bmatrix}$$

→ related to vibrational frequencies of the system
 $(3N+1)D$ PES
for N -particle system

1D
Case:
Harmonic
Oscillator

$$U(n) = \frac{1}{2} k (n - n_0)^2 = \frac{1}{2} k [n^2 + n_0^2 - 2n n_0]$$

$$\rightarrow \frac{\partial U}{\partial n} = \frac{1}{2} k [2n - 2n_0] = kn - kn_0$$

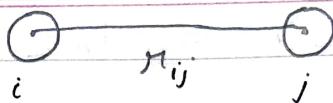
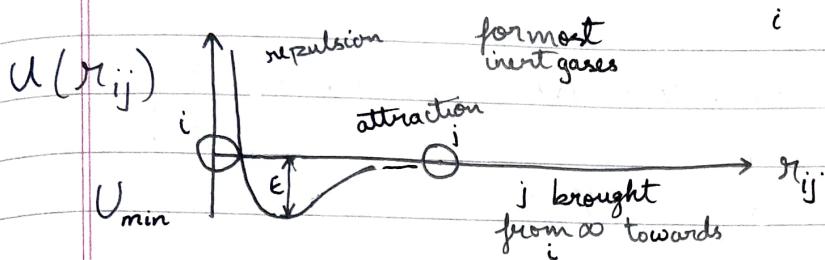
$$\rightarrow \frac{\partial^2 U}{\partial n^2} = k \quad \therefore \omega = \sqrt{\frac{k}{m}}$$

→ Force \vec{F} points towards nearest minima. At minima, $F=0$, hence the system stays put.

→ \exists a $(3N+1)D$ PES — Oscillation about minima — conversion of PE into KE & vice versa.

→ Frequency of oscillation calculated by 2nd degree derivative of P.E.

• Interatomic Potentials



σ is the diameter of the atom. $\epsilon \rightarrow$ strength of attraction

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

Find values of r_{ij} at which :

$$\rightarrow U(r_{ij}) \text{ is minimum} \rightarrow r_{ij} = 2^{1/6} \sigma$$

$$\rightarrow \text{Find the values of } r_{ij} \text{ where } U(r_{ij}) = 0$$

$$Z = \frac{1}{h^{3N}} \underbrace{\int e^{-\beta U(\{\vec{r}\})} d\{\vec{r}\}}_{\substack{\text{Potential Energy Factor} \\ \{\vec{r}\}}} \underbrace{\int e^{-\frac{\beta}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i} \prod_{i=1}^N p_i d\{\vec{p}\}}_{\{\vec{p}\}}$$

$$1) \text{ Entropy of an ideal gas: } \frac{\langle E \rangle}{T} + k_B \ln Z$$

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

$$\therefore S = \frac{\langle E \rangle}{T} - k_B N \ln h + k_B N \ln V + \frac{3Nk_B}{2} \ln (2\pi m K_B T)$$

$$2) S = \frac{\langle E \rangle}{T} - k_B N \ln h + k_B N \ln V + \frac{3N}{2} k_B \ln (2\pi m K_B T)$$

$$\begin{aligned} S_{\text{com}} &= \frac{\langle E_2 \rangle}{T} - k_B 3(2N) \ln h + k_B (2N) \ln(2V) + k_B 3 \frac{2N}{2} \ln \overline{(2\pi m K_B T)} \\ &= \frac{\langle E_2 \rangle}{T} - k_B 6N \ln h + k_B 2N \ln(2V) + k_B 3N \ln \overline{(2\pi m K_B T)}^2 \end{aligned}$$

$$S_{\text{com}} - 2S = \frac{\langle E_2 \rangle - 2\langle E_1 \rangle}{2} + 2N \left(\ln^2 \frac{x}{y} \right) K_B$$

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

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

$$= \frac{3N}{2} \cdot \frac{1}{\frac{2\pi m}{K_B T}} \cdot \frac{2\pi m}{K_B T} \cdot -\frac{\partial}{\partial \beta} (K_B T)$$

$$= \frac{-3N}{2} \cdot \frac{1}{K_B T} \cdot \frac{\partial}{\partial \beta} \left(\frac{1}{\beta} \right) = -\frac{3N}{2} \cdot \frac{1}{K_B T} \cdot -\frac{1}{\beta^2} = \frac{3N}{2} \cdot \frac{1}{K_B T} \cdot \frac{1}{\beta^2}$$

$$= \frac{3N}{2} K_B T$$

$$\therefore \frac{\langle E_2 \rangle - 2\langle E_1 \rangle}{2} = \left(\frac{3(2N)}{2} K_B T - 2 \cdot \frac{3N}{2} K_B T \right)/2 = 0$$

$$\therefore S_{\text{com}} - 2S = K_B 2N \ln 2.$$

$$3) U(r_{ij}) = 4\epsilon \left[\frac{\sigma^{12}}{r_{ij}^{12}} - \frac{\sigma^6}{r_{ij}^6} \right]$$

$$\frac{dU}{dr_{ij}} = 4\epsilon \left[\frac{\sigma^{12} \cdot -12}{r_{ij}^{13}} - \frac{\sigma^6 \cdot -6}{r_{ij}^7} \right]$$

$$\frac{d^2 U}{dr_{ij}^2} = 4\epsilon \left[\frac{\sigma^{12} \cdot 12 \cdot 13}{r_{ij}^{14}} - \frac{\sigma^6 \cdot 6 \cdot 7}{r_{ij}^8} \right]$$

$$\frac{dU}{dr_{ij}} = 0 \Rightarrow \frac{\sigma^{12} \cdot 12}{r_{ij}^{13}} = \frac{\sigma^6 \cdot 6}{r_{ij}^7}$$

$$\text{Now: } \sigma, r_{ij} \neq 0$$

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

[r_{ij} is real & +ve]

$\therefore r_{ij} = 2^{1/6} \sigma$ is a critical point for U .

$$\left[\frac{\partial^2 U}{\partial r_{ij}^2} \right]_{r_{ij} = 2^\frac{1}{6}\sigma} = 4\epsilon \left[\frac{12 \cdot 13 \sigma^{12}}{2^{14/6} \sigma^{14}} - \frac{6 \cdot 7 \sigma^6}{2^{8/6} \sigma^8} \right]$$

$$= \frac{4\epsilon}{\sigma^2} \left[\frac{12 \cdot 13}{2^{14/6}} - \frac{6 \cdot 7}{2^{8/6}} \right] \approx \frac{4\epsilon}{\sigma^2} \times 14 \cdot 29 > 0.$$

Clearly, $r_{ij} = 2^\frac{1}{6}\sigma$ is a minima for U .

$$U_{\min} = U(2^\frac{1}{6}\sigma) = 4\epsilon \left[\frac{\sigma^{12}}{2^2 \sigma^{12}} - \frac{\sigma^6}{2 \cdot \sigma^6} \right]$$

$$= 4\epsilon \left[\frac{1}{4} - \frac{1}{2} \right] = -\epsilon.$$

4) $U(r_{ij}) = 0 \Rightarrow \frac{\sigma^{12}}{r_{ij}^{12}} = \frac{\sigma^6}{r_{ij}^6}$

$$\Rightarrow \sigma^{12} r_{ij}^6 - \sigma^6 r_{ij}^{12} = 0$$

$$\Rightarrow \sigma^6 r_{ij}^6 (\sigma^6 - r_{ij}^6) = 0$$

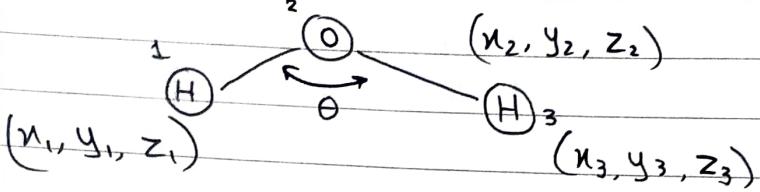
$$\Rightarrow r_{ij}^6 = \sigma^6 \quad \text{As } \sigma \neq 0 \text{ & } r_{ij} \neq 0$$

$$\therefore r_{ij} = \sigma. \text{ i.e } U(\sigma) = 0.$$

Lecture 9

1) There is a system of N independent particles. Each can have only one of two energies: $-\epsilon_0, \epsilon_0$. Calculate thermodynamic properties of system. $\langle E \rangle, S, C_V$.

2) Consider a water molecule:



$$\text{Potential Energy} = \frac{1}{2} k (r_{12} - l)^2 + \frac{1}{2} k (r_{23} - l)^2 + \frac{1}{2} T (\Theta_{123} - \Theta_0)^2$$

l : equilibrium bond length

Θ_0 : equilibrium bond angle

K, T : spring constants

Calculate the force on atoms.

3) N monomeric units are arranged along a straight line to form a chain molecule. Each monomer unit is capable of being in either α or β state (assume)

Lec 10 Non Interacting Systems

→ Ideal Gas

$$\rightarrow Z \propto \int d\{\vec{r}\} \int e^{-\frac{\beta}{2m} \sum_{i=1}^N \vec{P}_i \cdot \vec{P}_i} d\{\vec{p}\}$$

$$\frac{\langle P \rangle}{K_B T} = \frac{N}{V} = e \{ \text{Number Density} \}$$

- Ideal Gas equation of state

For interacting Systems

$$Z \propto \int_{\{\vec{r}\}} e^{-\beta U(\{\vec{r}\})} d\{\vec{r}\} \int_{\{\vec{p}\}} e^{-\frac{\beta}{2m} \sum_{i=1}^N \vec{P}_i \cdot \vec{P}_i}$$

$$\begin{aligned} \frac{\langle P \rangle}{K_B T} &= e + B_2(T) e^2 + B_3(T) e^3 + \dots \\ &= \sum_{i=1}^{\infty} B_i(T) e^i \end{aligned}$$

$$\frac{\langle P \rangle}{K_B T} = \sum_{i=1}^{\infty} B_i(T) e^i$$

virial equation of state

$B_i(T) \rightarrow$ virial coefficient : depend on temperature

$$U(\{\vec{r}\}) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N u_{ij}(r_{ij})$$

□ Thermodynamics

→ In thermodynamics world, atoms & molecules do not exist.

◦ Laws of thermodynamics

1st: The internal energy of the system can be changed by 2 ways: supply/absorb heat to the system
work on/by the system.

$$dU = dW + dQ$$

↓

Change in
internal energy
of the system

- Conservation
of energy

Correction:

Work done by the system: $-dW$

Work done on the system: dW

Heat supplied to the system: dQ

Heat extracted from the system: $-dQ$

2nd: Spontaneous Processes - Change in entropy of a spontaneous process.

Statement: $(\Delta S)_{\text{total}} \geq 0$

$$(\Delta S)_{\text{total}} \equiv (\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}}$$

The total entropy of any spontaneous process must increase.

→ For reversible/quasi-static (done very slowly)
spontaneous process -

$$(\Delta S)_{\text{total}} = 0$$

Statement: Clausius Inequality: (System specific)
 change in $(dS)_{\text{system}} \geq \frac{dQ}{T}$ → heat supplied
 entropy of at temperature
 the system — equality is valid
 for reversible processes

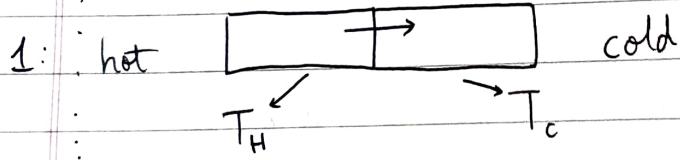
3rd: The second law didn't mention about the absolute value of entropy but it did quantify the change in entropy.

$((\Delta S)_{\text{total}} \text{ or } (dS)_{\text{system}})$

when $T \rightarrow 0, S \rightarrow 0$

Consider the following 2 spontaneous processes:

- 1) Heat flow
- 2) Gas expansion



Insulated: System doesn't interact with surroundings.

$$T_H \gg T_C$$

case 1: heat flowing from colder object to hotter object.

change in entropy of the colder object: $-\frac{dQ}{T_C}$

change in entropy of the hotter object = $\frac{dQ}{T_H}$

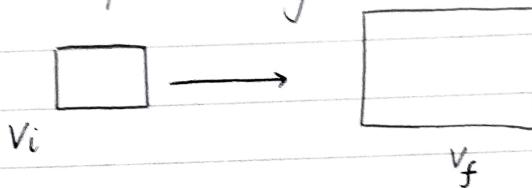
$$\text{Total change in entropy} : \Delta S = dQ \left[\frac{1}{T_H} - \frac{1}{T_C} \right]$$

$$\text{Since } T_H \gg T_C \Rightarrow \underline{\Delta S < 0}$$

- Not a spontaneous process.

case 2: heat flowing from hotter object to colder object.
 $\Delta S > 0$.

Process 2: Free expansion of an ideal gas.



let molecules expand.

: whether it expands or tries to compress itself.

case 1: $V_f < V_i$: compression } Isothermal.

case 2: $V_f > V_i$: expansion

$$S_{\text{ideal gas}} = \frac{\langle E \rangle}{T} - K_B 3N \ln h + K_B N \ln V + \frac{3N}{2} K_B \ln (2m \pi k_B T)$$

$\langle E \rangle$: function of temperature \rightarrow change in internal energy is 0. $\rightarrow dQ = -dW$.

$$S_f = c_1 \ln V_f + c_2$$

$$S_i = c_1 \ln V_i + c_2$$

(Max sign convention)

$$\therefore S_f - S_i = c_1 [\ln V_f - \ln V_i]$$

$$P = \frac{nRT}{V}$$

\ln : increasing function

\therefore for $\Delta S > 0$, $V_f > V_i$

for the process to be spontaneous, $V_f > V_i$

→ An ideal gas can expand spontaneously while compression of an ideal gas is not a spontaneous process.

Lec 11

Thermodynamics

Recap: P, V, T, n : number of moles (not $\{\vec{r}\}, \{\vec{p}\}$)

$$1st\ law: dU = dq + dW$$

$$2nd\ law: (\Delta S)_{total} = (\Delta S)_{system} + (\Delta S)_{surroundings} \geq 0$$

$$\Rightarrow (\Delta S)_{system} \geq dq/T$$

$$3rd\ law: T \rightarrow 0; S \rightarrow 0.$$

→ Spontaneous Process

↳ heat flow from hotter to colder object

↳ expansion of a gas.

1) Freezing of water : liquid water \rightarrow solid ice
 $(S_{liquid}) > (S_{ice})$

Violate 2nd law? NO - surroundings.

- Thermodynamic Potentials :

→ internal energy U

→ enthalpy H

→ Helmholtz free energy A

→ Gibbs free energy G .

- Rewrite 2nd law in terms of thermodynamic potentials :

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

(i) Constant Volume $\rightarrow dq = dU$
 $dW = 0$ as constant volume.

$$dS \geq \frac{dU}{T} \Rightarrow T.dS - dU \geq 0$$

ii) Constant entropy: $(dU)_{s,v} \leq 0$

Processes carried out at constant volume & constant entropy would minimize the internal energy of the system.

$$[dU = dq + dW]$$

→ Define enthalpy: $H = U + P.V$

$$dH = dU + PdV + Vdp = dq - PdV + PdV + Vdp$$

$$dW = -P.dV \quad [\text{System only does expansion work, in mechanical equilibrium with surroundings}]$$

i) Constant Pressure

ii) Constant Entropy

$$dH = dq + Vdp$$

$$(dH)_{P,S} = dq \quad ds \quad V.dp = 0$$

$$T.ds - dH \geq 0 \Rightarrow (dH)_{P,S} \leq 0$$

- H will be minimized at constant S & P .
- Process carried out at constant pressure & constant entropy would minimize the enthalpy of the system.

→ Helmholtz Free Energy

$$A = U - TS$$

i) Constant Volume

ii) Constant Temperature

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

Processes carried out at constant volume & temperature minimizes Helmholtz Free Energy.

→ Gibbs free energy.

$$G = U + P.V - TS$$

i) Constant Temperature

ii) Constant Pressure

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

Gibbs free energy will be minimized at constant Pressure & Temperature.

$$U = U(S, V)$$

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

$$A = A(T, V)$$

$$G = G(T, P)$$

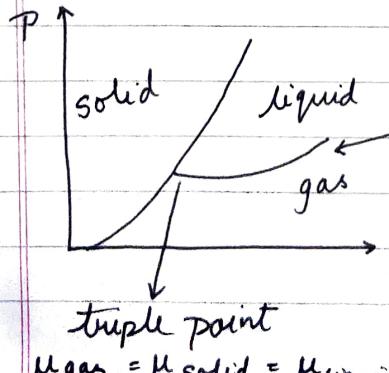
$$G(T, P) \quad > \quad G(T, P)$$

Phase 1 Phase 2

→ Phase with the least G at a given T & P is the most stable phase. (For same #molecules)

- G would vary with the number of moles of the substance.
- Chemical Potential $\mu(T, P) = \frac{G(T, P)}{n}$
 - Gibbs free energy per-mole of a substance.
- The phase with the least μ at a given T & P would be its stable phase.

→ Phase Diagram :



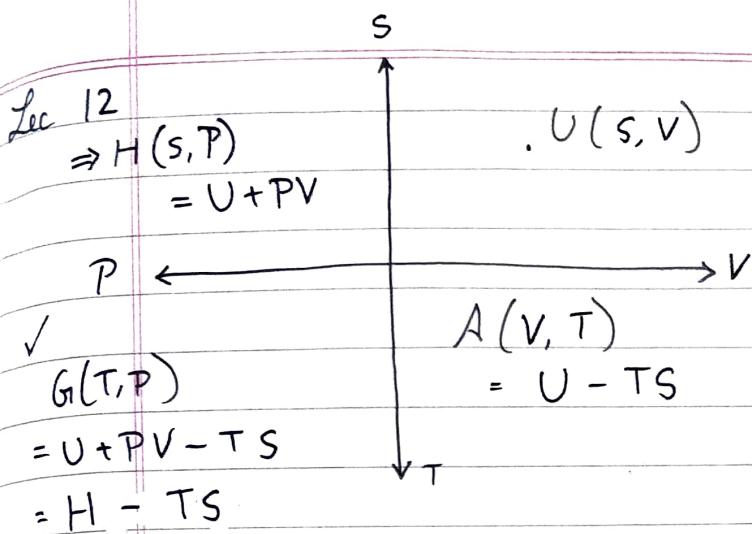
$$\mu_{\text{gas}}(T, P) = \mu_{\text{liquid}}(T, P)$$

- both phases are stable on the boundary.

- phase boundary - two phases are equally stable

$$\mu_{\text{gas}} = \mu_{\text{solid}} = \mu_{\text{liquid}}$$

- crossing the phase boundary leads to phase transition.



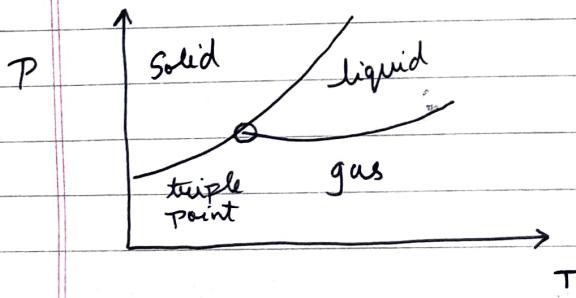
- $G(T, P) \rightarrow$ Determines stability for phases.

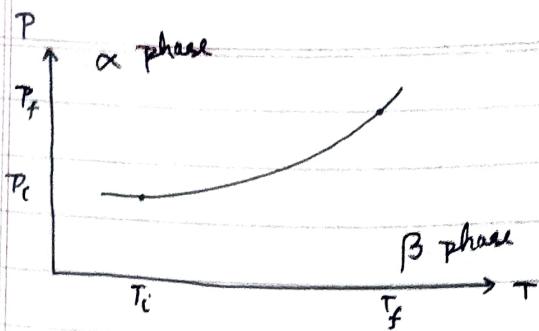
\rightarrow Chemical Potential $\rightarrow \mu(T, P) = \frac{G(T, P)}{n}$

n : #moles

\rightarrow the phase with the least μ at a given T, P would be the most stable phase at that specific $T \& P$.

- Recap: Phase Boundary & Phase Diagram





initial : $\mu_\alpha(T_i, P_i) = \mu_\beta(T_i, P_i) \quad \text{--- 1}$

final : $\mu_\alpha(T_f, P_f) = \mu_\beta(T_f, P_f) \quad \text{--- 2}$

$$\begin{aligned} (2) - (1) : & \mu_\alpha(T_f, P_f) - \mu_\alpha(T_i, P_i) \\ &= \mu_\alpha(T_f, P_f) - \mu_\beta(T_i, P_i) \\ \hookrightarrow d\mu_\alpha &= d\mu_\beta \quad \text{--- 3} \end{aligned}$$

From definition of Gibbs free energy:

$$dG = -SdT + VdP$$

- dividing both sides with n : # moles

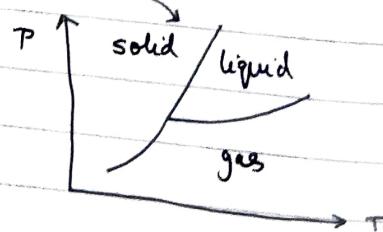
$$\hookrightarrow d\mu = \underset{\substack{\uparrow \text{molar entropy}}}{-S_m dT} + \underset{\substack{\uparrow \text{molar volume}}}{V_m dP}$$

$$3 \rightarrow -S_{\alpha,m}dT + V_{\alpha,m}dP$$

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

$$\frac{dP}{dT} = \frac{S_{\beta,m} - S_{\alpha,m}}{V_{\beta,m} - V_{\alpha,m}} \quad \left. \right\} \text{Clapeyron Equation.}$$

For solid-liquid boundary: P vs T curve is a straight line.



→ Maxwell's Relations.

internal energy : $U(S, V)$ - State function

- change Δ is independent of path b/w initial & final states

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

$$\text{First Law : } dU = T dS - P dV$$

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

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

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Maxwell's Relation}$$

→ Using $H(S, P)$

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

using
exactness
condition

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

with A & T :

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

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

Lec 13 Lagrangian Mechanics / Dynamics

- Newtonian
- Lagrangian
- Hamiltonian

↓ Chronological Order

- Define a new function - called Lagrangian.

Scalar:

$$L(q, \dot{q}; t) \rightarrow \dot{q} = \frac{dq}{dt}$$

↓
generalized velocity ↓ implicit dependence on time

depends on t
implicitly & not explicitly
; implicit time depend

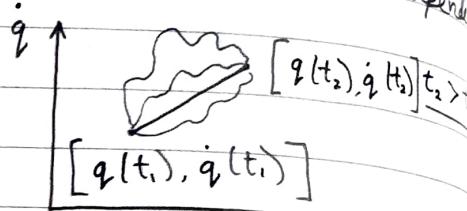
: describe degrees of freedom of the system : 3D: x, y, z

$$= K(\dot{q})$$

Kinetic energy function

$$- U(q)$$

Potential energy function



$$\dot{\theta} = \frac{\partial \theta}{\partial t}$$

(u, y, z)

(+) for Hamiltonian

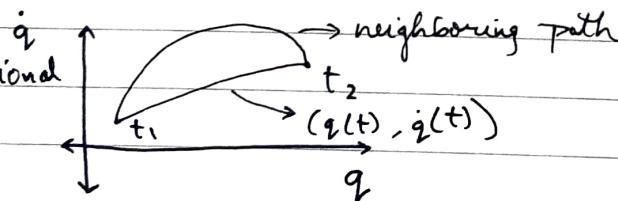
- Principle of least action

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

Consider 2 paths:

$$(q(t), \dot{q}(t)) \rightarrow \text{least action path}$$

$$(q(t) + \delta q(t), \dot{q}(t) + \delta \dot{q}(t)) \rightarrow \text{neighbouring path}$$



$$\begin{aligned} \text{Paths meet at } t_1, t_2 \\ \delta q(t_1) \\ = \delta q(t_2) = 0 \end{aligned}$$

$$\text{Change in } S : \int_{t_1}^{t_2} L(q + \delta q, \dot{q} + \delta \dot{q}; t) dt$$

$$- \int_{t_1}^{t_2} L(q, \dot{q}; t) dt = SS$$

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

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

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

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

Consider the 2nd term: $\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \frac{d}{dt} (\dot{q}) dt$

Integrating by parts:

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

As \dot{q} is
0 at t_1 & t_2 ,
 \dot{q} is
continuous

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

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

$$\rightarrow \text{Since least action} \quad \delta S = 0.$$

$$\delta S = 0 \nabla \dot{q}$$

$$\Rightarrow \boxed{\frac{\partial L}{\partial \dot{q}} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = 0} \quad \text{Lagrange's Equation of Motion.}$$

$$\text{Now, } \frac{\partial L}{\partial \dot{q}} = - \frac{\partial U}{\partial q} \quad \text{As } L = K(\dot{q}) - U(q)$$

KE
independent
of
coordinates.

\downarrow
force

$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \equiv$ rate of change
of generalized
momentum

- How do we get Hamiltonian from the lagrangian?

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

$\curvearrowleft N$ generalized coordinates

→ from Lagrange's Equation:

$$\begin{aligned} \frac{dL}{dt} &= \sum_i \dot{q}_i \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) + \sum_i \frac{\partial L}{\partial \dot{q}_i} \frac{d}{dt} (\dot{q}_i) \\ &= \sum_i \frac{d}{dt} \left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right) \end{aligned}$$

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

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

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

External forces on system: $\frac{dL}{dt} \neq 0$.

Isolated System
 $\frac{dL}{dt} = 0$.

Hamiltonian

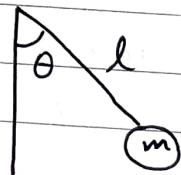
$$\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial K}{\partial \dot{q}_i} = m\dot{q}_i \rightarrow \sum_i \dot{q}_i (m\dot{q}_i) - L = \text{constant}$$

$$\equiv 2K - K + U \rightarrow \boxed{K+U} = \text{constant}$$

Hamiltonian: $H \equiv K + U$

- Simple Pendulum:

Step 1: Construct L
 $K(\dot{\theta})$, $U(\theta)$



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

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

$$\frac{\partial L}{\partial \theta} = -mgl \sin\theta, \quad \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = ml^2 \ddot{\theta}$$

$$\rightarrow ml^2 \ddot{\theta} + mg l \sin \theta = 0$$

Reference : Mechanics by Landau.

Lec 14

If L was time explicit

$$\frac{dL}{dt} = \sum_i \left[\frac{\partial L}{\partial q_i} \cdot \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \cdot \ddot{q}_i \right] + \cancel{\frac{\partial L}{\partial t}}$$

(L is not an explicit function of time, so $\frac{\partial L}{\partial t} = 0$)
 $L \rightarrow$ homogeneity in time
 [for isolated system]

- Homogeneity of time
 - ' of an isolated system does not depend on time explicitly \rightarrow energy will be conserved.
- Homogeneity in time leads to energy conservation
- Conservation of momentum
 - \rightarrow Homogeneity of Space - the mechanical properties (i.e L) would not change by any parallel displacement of the entire system.
- Displace energy particles by ϵ , velocities remaining fixed.

$$: q_i \rightarrow q_i + \epsilon, \quad SL = \sum_i \frac{\partial L}{\partial q_i} \delta q_i$$

$$\therefore \delta q_i = \epsilon$$

Homogeneity of space $\Rightarrow SL = 0$ [Lagrangian does not change on translation]

$$\Rightarrow \epsilon \cdot \sum_i \frac{\partial L}{\partial q_i} = 0 \quad (\because \text{every } \delta q_i = \epsilon)$$

• Using Lagrange's equation:

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

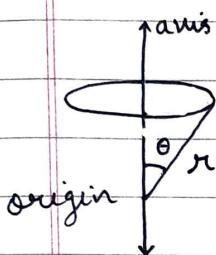
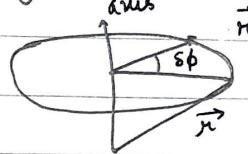
$$\Rightarrow \frac{d}{dt} \left[\sum_i m \dot{q}_i \right] = 0 \Rightarrow \sum_i m \dot{q}_i = \text{constant}$$

i.e total linear momentum should be conserved.

- Conservation of Angular Momentum

→ isotropy of space

→ L is invariant under the rotation of the whole system by an arbitrary angle.



change in \vec{r} due to rotation by $\delta\phi$ angle.
 $\delta\vec{r} = \delta\phi \times \vec{r}$

- $\delta\vec{\phi}$ has magnitude of $\delta\phi$ & direction along axis of rotation.

Similarly, for change in velocity:

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

$$\delta L = \sum_i \left(\frac{\partial L}{\partial \vec{r}_i} \cdot \delta\vec{r}_i + \frac{\partial L}{\partial \vec{v}_i} \cdot \delta\vec{v}_i \right)$$

Isotropy of Space : $\delta L = 0$

Use Lagrange's eqn: $\sum_i \{ \vec{p}_i \cdot (\delta\vec{\phi} \times \vec{r}_i) + \vec{p}_i \cdot (\delta\vec{\phi} \times \vec{v}_i) \}$

$$= 0$$

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

$$\delta\vec{\phi} \cdot \sum_i (\vec{r}_i \times \dot{\vec{p}}_i + \vec{v}_i \times \vec{p}_i) = 0$$

$$\delta\vec{\phi} \cdot \frac{d}{dt} \left(\sum_i \vec{r}_i \times \vec{p}_i \right) = 0$$

Since $\delta\vec{\phi}$ is arbitrary $\rightarrow \frac{d}{dt} \left(\sum_i \vec{r}_i \times \vec{p}_i \right) = 0$

$$\Rightarrow \sum_i \{ \vec{r}_i \times \vec{p}_i \} = \text{constant}$$

[Conservation of Angular Momentum]
- Position & Momentum are coupled.

Lec 15 Mathematical Modelling

- Diffusion (Process)
- Random Walk (Model)

• 1D Random Walk

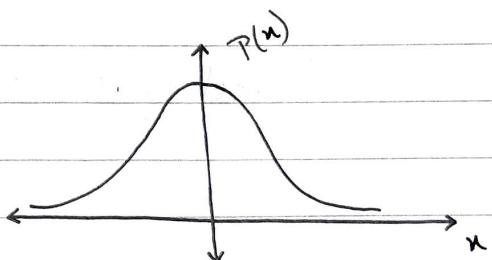


- A drunk starts at $n=0$
 - Each step of equal length l
 - Direction of each step (l or $-l$) is random
 - At each point in time, Probability to go right P , left is q .
- P [Finding him at a certain point from origin after N steps]

- How related is this to diffusion ?
 - Drop of ink added to water. Consider 1D.
 - P [finding ink molecules at a certain distance after some time t] → $P(t)$
- each ink molecule is a drunk molecule. Assumption -random walk. We have no such ink molecules

Gaussian → as $t \uparrow$

$$\text{at } t=0, P[n=0] = 1.$$



N : total # steps

n_1 : # steps to the right

n_2 : # steps to the left

$$N = n_1 + n_2$$

Displacement m : $(n_1 - n_2) l$
 l being the length of each step.
 $-Nl \leq m \leq Nl$

$P[n_1 \text{ out of } N \text{ steps taken to the right}]$

$$= \frac{N!}{n_1! n_2!} \cdot P^{n_1} q^{n_2} = W_N(n_1)$$

Simple Case : $N=3, n_1=2, n_2=1$

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

with $l=1$.

Mean # steps to the right

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

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

$$\text{Now, } n_1 P^{n_1} = P \frac{\partial}{\partial P} P^{n_1}$$

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

- Interchange the order of summation & differentiation

$$P \frac{\partial}{\partial P} \left[\sum_{n_1=0}^N \frac{N!}{n_1! (N-n_1)!} P^{n_1} q^{N-n_1} \right]$$

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

$$\langle n_1 \rangle = Np \quad \left\{ \begin{array}{l} \text{if } P+q=1 \text{ i.e } P[\text{Not Moving}] = 0. \\ \langle n_2 \rangle = Nq \end{array} \right.$$

Similarly

- Mean Displacement

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

if $p = q = 1/2$, on average: $p = q$.

electrons in a metal were w/o bias - drunk person
- same random walk model.

- Mean Squared Displacement: $\langle m^2 \rangle \neq 0$.

$$\langle m^2 \rangle \neq 0$$

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

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

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

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

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

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

$$= p \frac{\partial}{\partial p} \left(p \frac{\partial}{\partial p} \{ p+q \}^N \right)$$

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

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

$$= p (p+q)^{N-2} \left[Np + Nq + p N^2 - p N \right]$$

$$= (pN)^2 + Npq \quad [\text{if } p+q = 1]$$

$$= \langle n_1 \rangle^2 + Npq$$

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

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

$$p = q = 1/2$$

$$\begin{aligned} \cdot \langle m^2 \rangle &= 4 \langle (\Delta n_1)^2 \rangle = 4 Npq \\ &= 4 \cdot 1/2 \cdot 1/2 \cdot N \\ &= N \end{aligned}$$

$$\langle m^2 \rangle = N$$

$$\text{Now, } m = n_1 - n_2 \\ = 2n_1 - N$$

$$\Delta m = 2 \Delta n_1$$

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

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

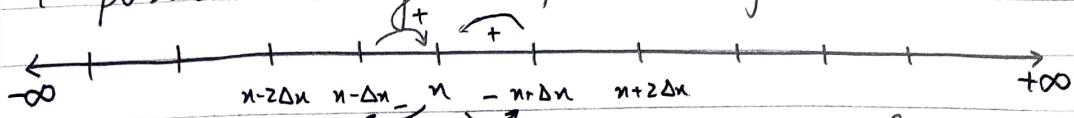
As $\langle m \rangle = 0$.

$$\therefore \langle (\Delta m)^2 \rangle = \langle m^2 \rangle = 4 \langle (\Delta n_1)^2 \rangle = N.$$

i.e Mean Squared Displacement varies linearly with time OR # steps taken.

Lec 16 Derive Diffusion equation from Random Walk Model

4 possible changes in probability.



Δn : step length. if $\Delta n \rightarrow 0$, space becomes continuous \rightarrow diffusion.

$\Delta t \rightarrow$ time step. Random walker
Random walker \rightarrow count velocity

$P(n, t) = P[\text{finding random walker at } n \text{ at time } t]$

Change in probability at n

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

$$P(n, t + \Delta t) - P(n, t) = \underbrace{\frac{1}{2} [P(n + \Delta n, t) - 2P(n, t) + P(n - \Delta n, t)]}_{\text{time variation}} \\ \underbrace{\qquad\qquad\qquad}_{\text{spatial variation}}$$

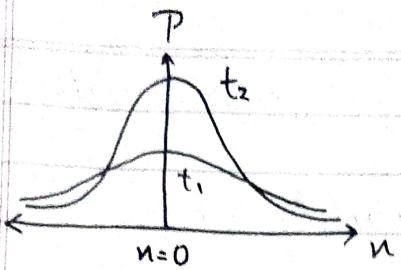
— Dividing by $(\Delta t)(\Delta n)^2$ on both sides,

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

Set : $\Delta t \rightarrow 0, \Delta n \rightarrow 0$

$$\left\{ \frac{\partial P(n, t)}{\partial t} = D \frac{\partial^2 P(n, t)}{\partial n^2} \right\}$$

} $D \rightarrow$ Diffusion count
depends on medium
- for environmental effects



$t_2 > t_1$, P increases as a function of t .

- Prove by computation:

after $t > 0$:

- $\langle n \rangle = 0$

- $\langle n^2 \rangle \propto t$

Lec 17 Recap:

- diffusion

- random walk: mean displacement $\langle m \rangle = 0$

mean squared displacement $\langle m^2 \rangle \propto N$
at

- diffusion equation: $\frac{\partial P(n, t)}{\partial t} = D \frac{\partial^2 P(n, t)}{\partial n^2}$

$$\frac{\partial C(n, t)}{\partial t} = D \frac{\partial^2 C(n, t)}{\partial n^2}$$

C: concentration

- One Dimensional $P(n, t) \propto e^{-\frac{n^2}{4Dt}}$

$$(x^2 + y^2 + z^2)/(4Dt)$$

- Three Dimensional $P(\vec{r}, t) \propto e^{-\frac{r^2}{4Dt}}$

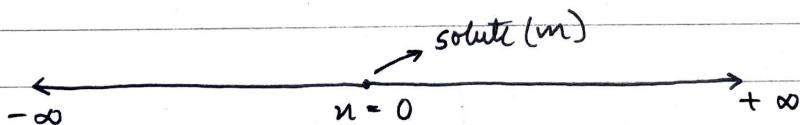
: 3D diffusion equations: $\frac{\partial}{\partial t} P(\vec{r}, t)$

$$= D \left[\frac{\partial^2}{\partial x^2} P(\vec{r}, t) + \frac{\partial^2}{\partial y^2} P(\vec{r}, t) + \frac{\partial^2}{\partial z^2} P(\vec{r}, t) \right]$$

↳ isotropic diffusion.

↪ 1D: $\langle u \rangle = 0$, $\langle u^2 \rangle \propto t$

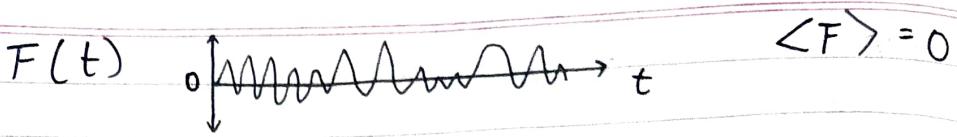
[Draw parallel with Random walk experiment]



$$\dot{n} = \frac{dn}{dt}, m \frac{d\dot{n}}{dt} = \text{damping force.} + \text{random force}$$

$$= -\alpha \dot{n} + F(t) \quad \text{--- (i)}$$

Positive Constant
(Friction Constant)

(i) $\times n \rightarrow$

$$m n \frac{d\dot{n}}{dt} = -\alpha n \dot{n} + n F$$

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

- Average on both sides.

$$\begin{aligned} &\Rightarrow m \left[\left\langle \frac{d}{dt} (n\dot{n}) \right\rangle - \left\langle \dot{n}^2 \right\rangle \right] \\ &= -\alpha \left\langle n \dot{n} \right\rangle + \left\langle n F \right\rangle \end{aligned}$$

$\stackrel{\text{!!}}{=}$

• Uncorrelated Noise $\langle n F \rangle = \langle n \rangle \langle F \rangle = 0$.- From equipartition theorem: $\frac{1}{2} m \langle \dot{n}^2 \rangle = \frac{1}{2} k_B T$

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

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

$$\rightarrow \text{Solution: } \langle n \dot{n} \rangle = C e^{-\Gamma t} + k_B T / \alpha$$

$$\Gamma = \alpha/m$$

$$\text{Initial condition: At } t=0, n=0, C = -\frac{k_B T}{\alpha}$$

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

$$\left\{ \begin{array}{l} \langle n \dot{n} \rangle = C e^{-\Gamma t} + k_B T / \alpha \\ \Rightarrow \frac{1}{2} \frac{d}{dt} \langle n^2 \rangle = C e^{-\Gamma t} + \frac{k_B T}{\alpha} \end{array} \right.] \text{ Integrate wrt } t$$

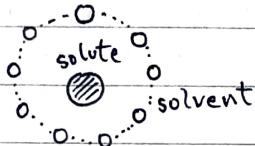
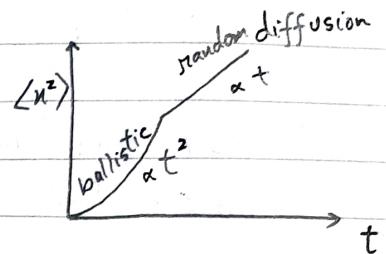
Limit 1: $t \gg 1/\tau \rightarrow e^{-\tau t} \rightarrow 0$

$$\langle n^2 \rangle \approx \frac{2 k_B T}{\alpha} t$$

Limit 2: $t \ll 1/\tau$ (Smaller Time Scale)

$$e^{-\tau t} \approx 1 - \tau t + 1/2 \tau^2 t^2$$

$$\langle n^2 \rangle \approx (k_B T/m) t^2$$



- when inside: ballistic
- once outside: random

Heat Equation.

$T(n, t)$: temperature at n at time t .

$$\frac{\partial T}{\partial t}(n, t) = D_T \frac{\partial^2 T}{\partial n^2}(n, t)$$

Thermal Diffusivity

$$D_T = \frac{\sigma_T}{\rho c}, \quad \sigma_T = \text{thermal conductivity}$$

$\rho = \text{density}$

Class Assignment: $\Pi(n, t) \propto e^{-\frac{n^2}{4 D_T t}}$

Calculate $\langle n \rangle, \langle n^2 \rangle$

Lec 18

Quantum Mechanics.

- End of 19th century

1895: Discovery of X-rays

1896: Discovery of Radioactivity

1897: Discovery of electron

1) Black Body Radiation ↗

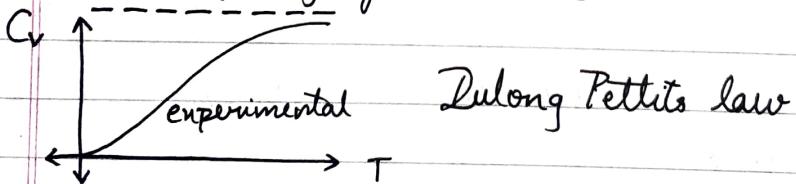
2) Photoclectric effect ↗

3) Hydrogen Spectrum:

Hamiltonian gives continuous range of energies. But, when Hydrogen atoms are excited, they emit light of specific frequencies.

↳ Something classical physics cannot explain.

4) Heat capacity of solids (at low temperatures)



- Einstein used quantum principles to propose valid changes/reasoning.

5) Diffraction of electrons by crystals.

- Was believed that the electron is a particle
- electron diffraction indicates wave nature

6) Spin/Angular Momentum could not be explained.

Framework of Quantum Mechanics.

In order to understand any quantum system, compute

$\psi(n, t)$ → time \equiv Wave function for 1D
analogous ↓
to 2 spatial degree of freedom system

- Properties of ψ

- finite - single valued - continuous

- unique values for n [cannot map to 2 different probabilities].

→ Also, $\psi^*(n, t) \cdot \psi(n, t)$ \equiv probability density, complex conjugate of $\psi(n, t)$, P [finding the particle in dn] $= \psi^*(n, t) \psi(n, t) dn$
- concept by Max Born

- Multiplying $\psi^*(n, t) \cdot \psi(n, t)$ by a small length dx (for 1D) or small volume dv (for 3D)

In QM, all physical properties are expressed as mathematical operators

- momentum $\hat{P} = -i \hbar \frac{\partial}{\partial n}$

$$\hbar = \frac{h}{2\pi} \rightarrow \text{planck's constant}$$

- kinetic energy $\hat{k} = \frac{\hat{P} \cdot \hat{P}}{2m} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial n^2}$

- On using this operator on the wave function, we'll get the k.E of the particle at that state which can be compared with experimental results

- Defining the Hamiltonian:

$$\hat{H} = \hat{K} + \hat{U} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} + U(n)$$

- this is also an operator.

• for an ideal gas, $U(n) = 0$.

→ Schrödinger's Equation

Eigenvalue problem

$$\hat{H}(\psi(n, t)) = E \cdot \psi(n, t)$$

↳ scalar total energy of
the system

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} \psi(n, t) + U(n) \psi(n, t)$$

$$= E \psi(n, t)$$

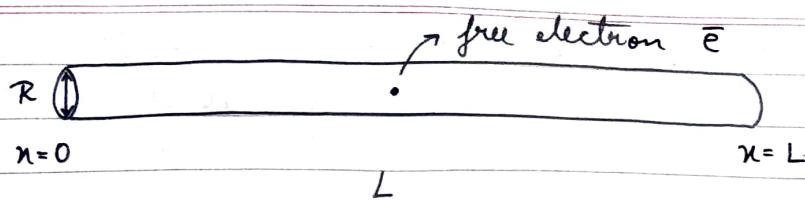
- for a fixed instant of time, tells us how ψ is distributed over n .
- we can solve the above differential equations to find $\psi(n, t)$ & E .
- in general, for any operator:
 $\hat{O} \psi(n, t) = O \psi(n, t)$
 ↓ scalar: measure of property of interest.

- Model 1:

Quantum particle in a 1D box. Consider a metallic wire of length L & diameter R s.t $L \gg R$.

- we therefore treat like a 1D object.

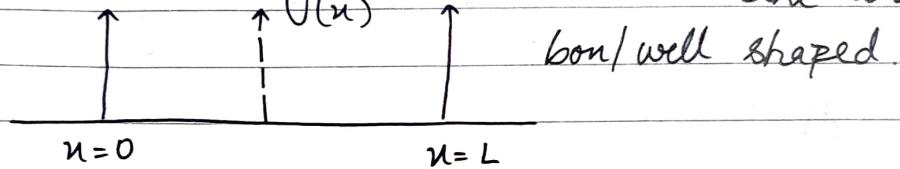
hypothetical { Place a single electron in the wire.
 Assume free electron
 s.t potential inside the wire is 0



if \bar{e} executes random motion, then $\langle n \rangle = 0$
- this is a classical result.

$$U(n) = 0 \text{ for } 0 < n < L$$

$U(n) = \infty$ if $n=0$ or $n=L$ - \bar{e} cannot leave the wire.



- Solving the Schrodinger equation:

- Inside the bon :-

$$U(n) = 0$$

$$\therefore -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} \psi(n, t) = E \psi(n, t)$$

- free particle, dynamics controlled by kinetic energy.

- rewriting this as :

[dropping t , consider a particular time instant, hence t is fixed]

$$\frac{d^2}{dn^2} \psi(n, t) + k^2 \psi(n, t) = 0 \dots \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

we get a simple harmonic oscillation equation
guessed solution : $\psi(n) = A \cos kn + B \sin kn$.

$$\text{At } n=0, \psi(n=0) = 0 \Rightarrow A=0$$

$$\text{at } n=L, \psi(n=L) = 0 \Rightarrow B \sin kL = 0 \\ \text{but } B \neq 0.$$

$$\Rightarrow \sin kL = 0 \Rightarrow kL = n\pi$$

$$\Rightarrow k = n \frac{\pi}{L}, \quad n \in \mathbb{I}$$

- n : Quantum Number.

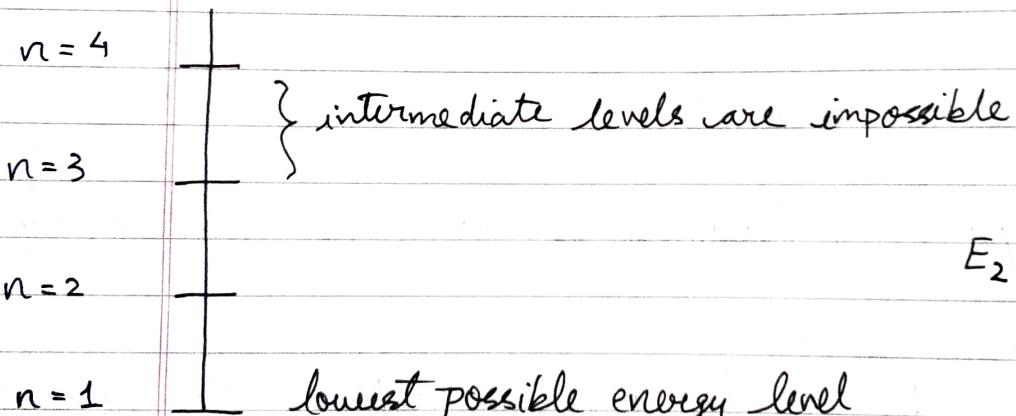
1D: a single quantum number; increase # dimensions
increase in # quantum numbers

$$k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow E = \frac{k^2 \hbar^2}{2m} = \left(\frac{n\pi}{L}\right)^2 \left(\frac{\hbar}{2\pi}\right)^2 \frac{1}{2m}$$

$$= \frac{n^2 \pi^2}{L^2} \cdot \frac{\hbar^2}{4\pi^2} \cdot \frac{1}{2m} = \frac{n^2 \hbar^2}{8mL^2}$$

→ energy is quantised

- Energy level diagram for the above.



$$E_2 = 4 \frac{\hbar^2}{8mL^2}$$

$$E_1 = \frac{\hbar^2}{8mL^2}$$

→ explain why H-atoms on returning to the ground state, emits radiations of only certain frequencies

$$\therefore \psi(n) = B \sin\left\{\frac{n\pi}{L}x\right\}$$

- Using a normalization condition -

$$P[\text{finding the electron within the wire}] = 1$$

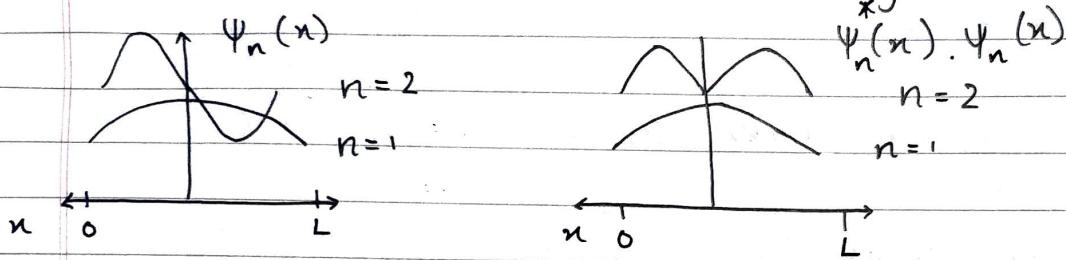
$$n=0 \quad n=L$$

$$\int_{n=0}^{n=L} \psi^*(n) \psi(n) dx = 1$$

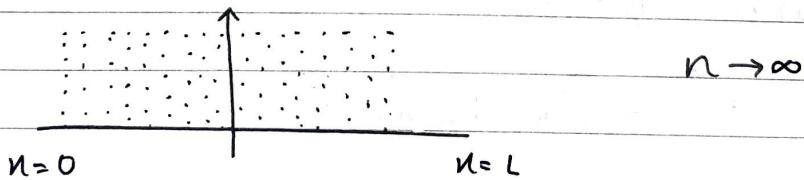
solving $\Rightarrow B = \sqrt{2/L}$

$$\therefore E = \frac{n^2 h^2}{8m L^2} \quad \psi_n(n) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi}{L} n\right)$$

- the system can exist in various states
- $\therefore \psi(n)$ depends on n , the state of the particle.



- probability of finding a particle varies depending on the state
- with increase in n , the probability becomes more & more delocalized.
- $n \rightarrow \infty$: all points are equally likely — transcend to classical concepts



Lec 19

Wave Function $\psi(n, t) \Rightarrow 1D; \text{ single particle}$
 $\psi(n_1, y_1, z_1, n_2, y_2, z_2, \dots, n_N, y_N, z_N, t)$
 $\hookrightarrow N \text{ particle system}$

\rightarrow All physical observables can be expressed as operators.
En: linear momentum } $\hat{P}_n \equiv -i\hbar \frac{\partial}{\partial n}$

$$i = \sqrt{-1}$$

$$\hbar = \frac{h}{2\pi} \rightarrow \text{Planck's Constant} \quad 6.62 \times 10^{-34} \text{ Js}$$

$$\text{Kinetic Energy } \hat{K} = \frac{\hat{P} \cdot \hat{P}}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2}$$

$$\hat{P}_n \psi(n, t) = -i\hbar \frac{\partial}{\partial n} \psi(n, t)$$

$$= \propto \psi(n, t)$$

\hookrightarrow scalar measure of linear momentum

- Schrodinger equation:

$$\hat{H} = \hat{K} + \hat{U} - \text{Hamiltonian}$$

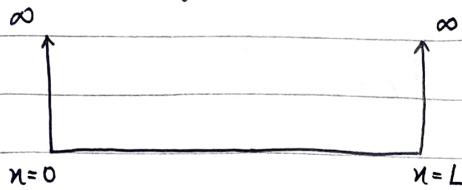
$$\hat{H} \psi(n, t) = E \psi(n, t) \rightarrow \text{scalar (total energy)}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} \psi(n, t) + \hat{U}(n) \psi(n, t) = E \psi(n, t)$$

• time independent schrodinger
 \downarrow

At a given t , how ψ varies with n .

- Particle confined in a one-dimensional box.



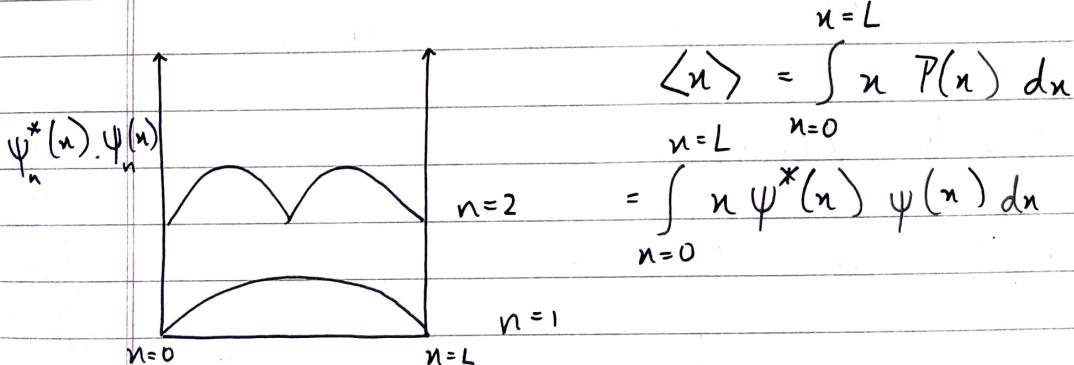
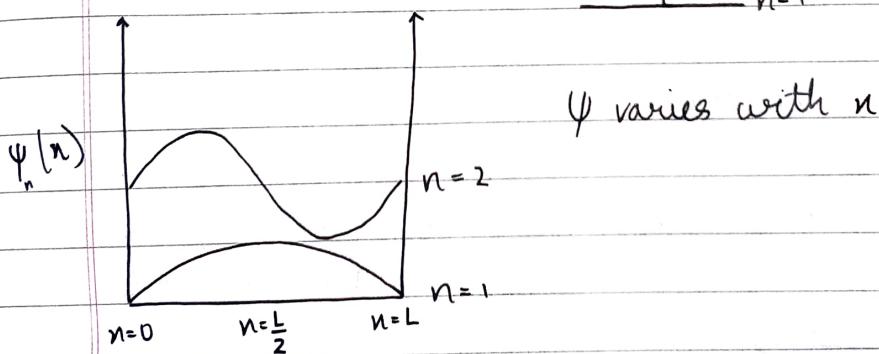
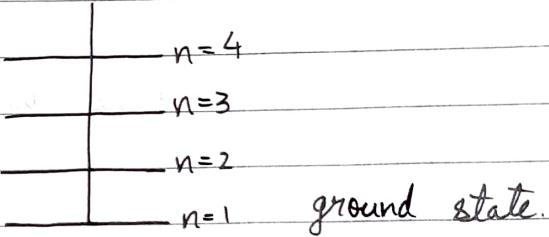
$$V(x) = 0, \quad 0 < x < L$$

$$V(x) = \infty \quad \text{if} \quad x = 0 \quad \text{or} \quad x = L$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$\psi_n^*(x) \psi_n(x) \Rightarrow$ Probability Density.

$$E_n = n^2 \frac{h^2}{8mL^2}$$

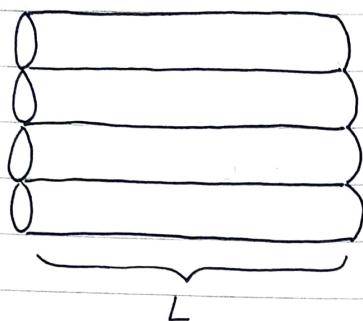
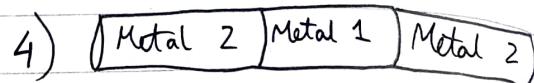


$$\langle x \rangle = \int_{n=0}^{n=L} x P(n) dx$$

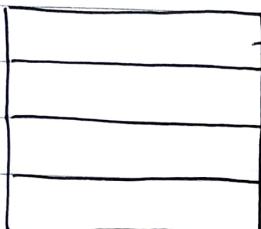
$$= \int_{n=0}^{n=L} n \psi_n^*(x) \psi_n(x) dx$$

Extension of 1D Model

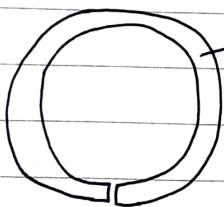
1)

 \Rightarrow Metallic Sheet / film

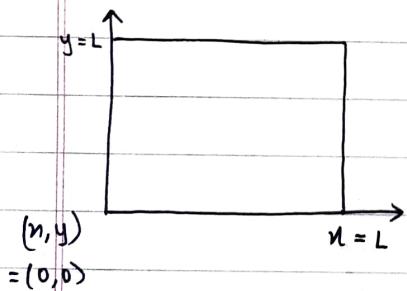
2)

 \Rightarrow film sheet

3)

 \Rightarrow single wire (circular loop)

- Particle in a 2D box.



$$V(n, y) = \infty ; n \leq 0 \quad | \quad y \leq 0 \\ n \geq L \quad | \quad y \geq L$$

$$V(n, y) = 0 ; \text{ inside sheet}$$

Wave Function $\psi(n, y)$

- Inside the sheet : $V(n, y) = 0$

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial n^2} + \frac{\partial^2}{\partial y^2} \right] \psi(n, y) = E \psi(n, y)$$

$$\psi(n, y) = X(n) Y(y)$$

$$\rightarrow Y(y) \cdot \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} X(n) \right) + X(n) \cdot \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} Y(y) \right) = E \cdot X(n) \cdot Y(y)$$

$\hookrightarrow E_1 + E_2$

divide by $X(n) Y(y)$ on both sides.

$$\frac{1}{X(n)} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} X(n) \right) = E_1$$

$$\frac{1}{Y(y)} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} Y(y) \right) = E_2$$

$$E_1 = \frac{n_1^2 h^2}{8mL^2} ; E_2 = \frac{n_2^2 h^2}{8mL^2}$$

$$E = E_1 + E_2 = (n_1^2 + n_2^2) \frac{h^2}{8mL^2}$$

$$\Psi_{n_1, n_2}(n, y) = \frac{2}{L} \sin\left(\frac{n_1 \pi n}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right)$$

$$\text{Ground State} : n_1 = n_2 = 1 : E_{1,1} = \frac{2 h^2}{8mL^2}$$

$$\text{1st excited State} : n_1 = 1, n_2 = 2 ; E_{1,2} = E_{2,1} = \frac{5h^2}{8mL^2}$$

Lec 20

Particle in a 1D box

→ ground state ($n=1$)

$$\text{wave function } \psi_1(n) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n}{L}\right)$$

Calculate $\langle n \rangle$, $\langle n^2 \rangle$, $\langle P \rangle$, $\langle P^2 \rangle$

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

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

$$\text{Note: } \langle A \rangle = \overline{\int_n \psi^*(n) \hat{A} \psi(n) dn}$$

$$\langle n \rangle = \overline{\int_0^L \frac{2}{L} \sin^2\left(\frac{\pi n}{L}\right) n dn}$$

I₁

$$= \overline{\int_0^L \frac{2}{L} \sin^2\left(\frac{\pi n}{L}\right) dn} = I_2$$

$$I_2 = \frac{2}{L} \cdot \frac{1}{2} \int_0^L \left[1 - \cos \frac{2\pi n}{L} \right] dn$$

$$= \frac{1}{L} \int_0^L \left(1 - \cos \frac{2\pi n}{L} \right) dn$$

$$= \frac{1}{L} \left\{ \left[n \right]_0^L - \left[\frac{\sin \frac{2\pi n}{L}}{\frac{2\pi}{L}} \right]_0^L \right\}$$

$$= \frac{1}{L} \left\{ L - \frac{L}{2\pi} \sin 2\pi \right\} = 1$$

$$\begin{aligned}
 I_1 &= \int_0^L \frac{2}{L} \sin^2\left(\frac{\pi n}{L}\right) n \, dx \\
 &= \frac{2}{L} \left[\left[n \int \sin^2\left(\frac{\pi n}{L}\right) dx \right]_0^L - \int_0^L \int \sin^2\left(\frac{\pi n}{L}\right) dx \cdot du \right] \\
 &= \frac{2}{L} \left[\left[\frac{n}{2} \left(u - \frac{\sin \frac{2\pi n}{L}}{\frac{2\pi}{L}} \right) \right]_0^L - \int_0^L \left(\frac{n}{2} - \frac{1}{2} \frac{\sin \frac{2\pi n}{L}}{\frac{2\pi}{L}} \right) du \right] \\
 &= \frac{2}{L} \left[\frac{L}{2} (L - 0) - \left[\frac{n^2}{4} + \frac{1}{2} \frac{\cos \frac{2\pi n}{L}}{\left(\frac{2\pi}{L}\right)^2} \right]_0^L \right] \\
 &= \frac{2}{L} \left[\frac{L^2}{2} - \frac{L^2}{4} - \frac{1}{2} \cdot \frac{L^2}{4\pi^2} + \frac{1}{2} \cdot \frac{L^2}{4\pi^2} \right] \\
 &= \frac{2}{L} \times \frac{L^2}{4} = \frac{L}{2}
 \end{aligned}$$

$$\langle n^2 \rangle = \int_0^L n^2 \sin^2\left(\frac{\pi n}{L}\right) dx = \frac{L^2}{6} \left(2 - \frac{3}{\pi^2} \right)$$

$$\langle P \rangle = \int_0^L \psi^*(x) \left(-i \hbar \frac{\partial}{\partial x} \psi(x) \right)$$

$$-i\hbar \sqrt{\frac{2}{L}} \int_0^L \left(\frac{\pi n}{L} \right) \sqrt{\frac{2}{L}} \cos\left(\frac{\pi n}{L}\right) \cdot \frac{\pi}{L} dx$$

$$= -i\hbar \frac{2}{L} \cdot \frac{\pi}{L} \int_0^L \cos\left(\frac{\pi n}{L}\right) \sin\left(\frac{\pi n}{L}\right) dx$$

$$= -i\hbar \frac{\pi}{L^2} \int_0^L \sin\left(\frac{2\pi n}{L}\right) dx = -\frac{i\pi\hbar}{L^2} \left[\frac{\cos \frac{2\pi n}{L}}{\frac{2\pi}{L}} \right]_0^L$$

$$= -\frac{i\pi\hbar}{L^2} \left[\frac{1}{\frac{2\pi}{L}} - \frac{1}{\frac{2\pi}{L}} \right] = 0.$$

$$\langle P^2 \rangle = \frac{\hbar^2}{4L^2}$$

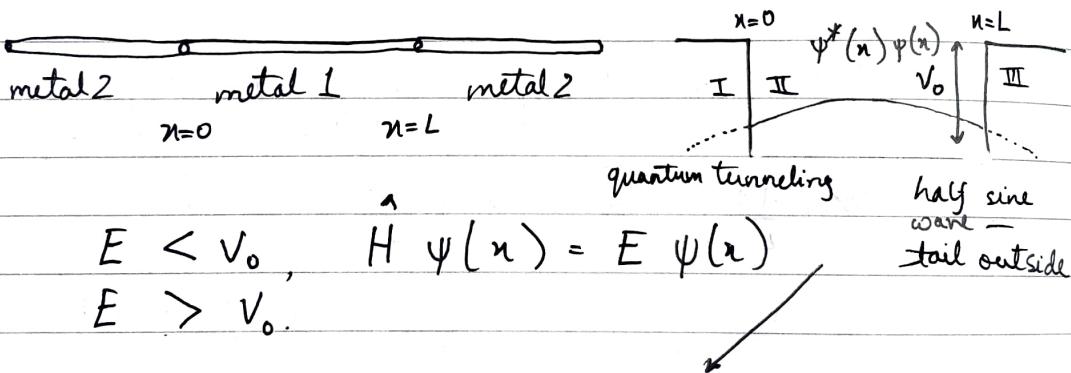
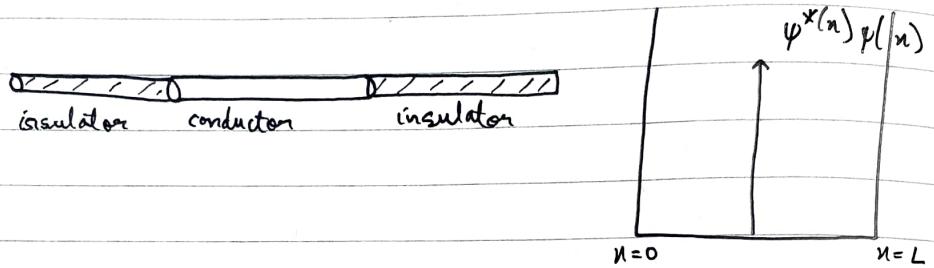
$\Delta n \equiv$ Uncertainty in n

$$= \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$$

$\Delta p \equiv$ Uncertainty in p

$$= \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

$\Delta n \cdot \Delta p \geq \frac{\hbar}{2} -$ Uncertainty Principle.



Scanning Tunneling Microscopy (STM)
 $10^{-6} \text{ m} \rightsquigarrow 10^{-9} \text{ m}$

Region I : $U(n) = 0$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial n^2} \psi_I(n) = E \psi(n)$$

$$\Rightarrow \psi_I(n) = C_1 e^{k_1 n} \quad k_1 = \sqrt{\frac{2m|E|}{\hbar^2}}$$

$$\psi_{III}(n) = C_3 e^{-k_1 n}$$

Boundary Conditions

$$\psi_I(n = -a) = \psi_2(n = -a)$$

[ψ should be single valued]

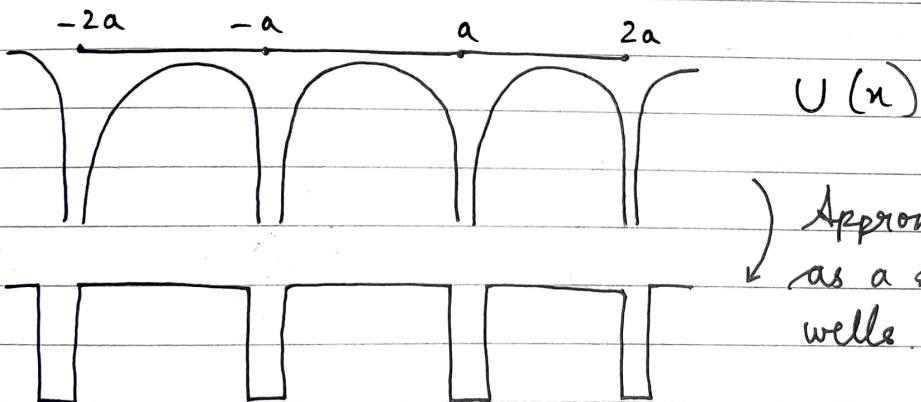
$$\frac{d}{dn} \psi_I(n = -a) = \frac{d}{dn} \psi_{II}(n = -a)$$

[ψ should be continuously differentiable]

Similarly :

$$\psi_{II}(n = a) = \psi_{III}(n = a)$$

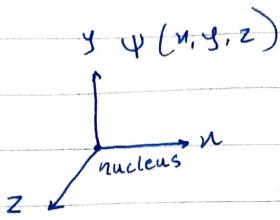
$$\frac{d}{dn} \psi_{II}(n = a) = \frac{d}{dn} \psi_{III}(n = a)$$



) Approximation
as a series of
wells.

Dec 21

Atoms



$\psi^*(n, y, z) \psi(n, y, z)$: Probability density of finding electron at (n, y, z) .

Potential energy $V(n, y, z) \neq 0$.

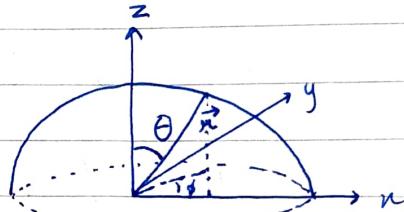
- electron-nucleus interaction is not zero.

$$\psi(n, y, z) \sim \psi(r, \theta, \phi)$$

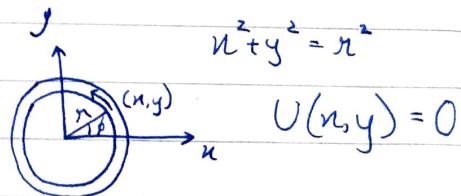
$$r \rightarrow 0 \text{ to } \infty$$

$$\theta \rightarrow 0 \text{ to } \pi$$

$$\phi \rightarrow 0 \text{ to } 2\pi$$



- One-Dimensional atom



$$\text{Schrodinger Equation} : -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] \psi(x, y) = E \psi(x, y)$$

Cartesian to Polar : $x = r \cos \phi$, $y = r \sin \phi$
 r is a constant

$$\phi \in [0, 2\pi)$$

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] = \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right]$$

To Derive :

$$\frac{\partial f(r,y)}{\partial r} = \frac{\partial f}{\partial r} \cdot \frac{\partial r}{\partial r} + \frac{\partial f}{\partial y} \cdot \frac{\partial y}{\partial r}$$

- for this problem : r is fixed.

$$\frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \phi^2}$$

Schrodinger equation in polar coordinates :

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \psi(r, \phi) = E \psi(r, \phi)$$

|||

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \phi(\phi) = E \phi(\phi)$$

$$\psi(r, \phi) = R(r) \phi(\phi)$$

Given : $I = m r^2 \Rightarrow \text{Moment of Inertia}$

$$-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \phi(\phi) = E \phi(\phi)$$

$$\frac{\partial^2}{\partial \phi^2} \phi(\phi) = -\frac{2IE}{\hbar^2} \phi(\phi)$$

→ general solution $\Phi(\phi) = A e^{im_e \phi}$

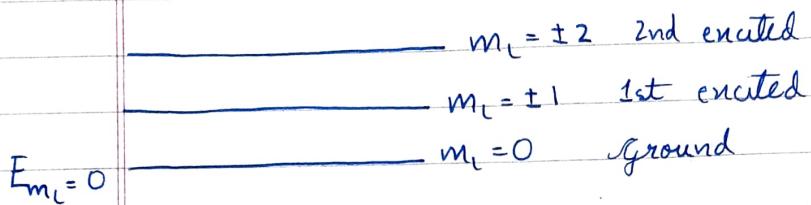
$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

$$A e^{im_e(\phi + 2\pi)} = A e^{im_e \phi}$$

$$e^{im_e 2\pi} = 1 ; m_e = 0, \pm 1, \pm 2, \pm 3, \dots$$

Substitute : $\Psi(\phi) = Ae^{im_e \phi}$ in the Schrodinger equation & determine E .

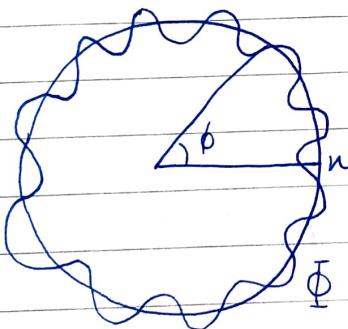
$$\Rightarrow E_{m_e} = \frac{m_e \hbar^2}{2I} \quad m_e = 0, \pm 1, \pm 2, \dots$$



Find A : normalize : $\Psi(\phi) = A e^{im_e \phi}$

$$\int_0^{2\pi} \Psi^*(\phi) \Psi(\phi) d\phi = 1 \longrightarrow A = \frac{1}{\sqrt{2\pi}}$$

$$\therefore \Psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_e \phi}; m_e = 0, \pm 1, \pm 2, \dots$$



Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p}$$

$$\hat{i} L_x + \hat{j} L_y + \hat{k} L_z = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ n_x & n_y & n_z \\ p_x & p_y & p_z \end{vmatrix}$$

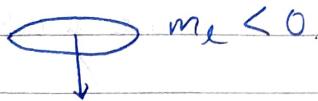
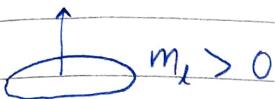
$$L_z = x P_y - y P_x, \quad \hat{L}_z = \hat{x} \left(-i \hbar \frac{\partial}{\partial y} \right) - \hat{y} \left(-i \hbar \frac{\partial}{\partial x} \right)$$

$$\text{Polar: } \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

$$\hat{L}_z \dot{\phi}(\phi) = m_e \hbar \dot{\phi}(\phi)$$

Angular Momentum = $m_e \hbar$
 ↳ quantised

$$m_e = 0, \pm 1, \pm 2, \dots$$



- Particle on a sphere



Angular Momentum quantum number
 $l = 0, 1, 2, \dots$

$$\begin{aligned} m_e &= 0, \pm 1, \dots, \pm l, \dots \\ &= E \psi(n, y, z) \end{aligned}$$

$r \rightarrow \text{fixed}$

$\theta \rightarrow 0 \text{ to } \pi$

$\phi \rightarrow 0 \text{ to } 2\pi$

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(n, y, z)$$

Lec 22 Atomic Structure / Spectra.

Recap:



1) Polar : $(x, y) \rightarrow (r, \phi)$

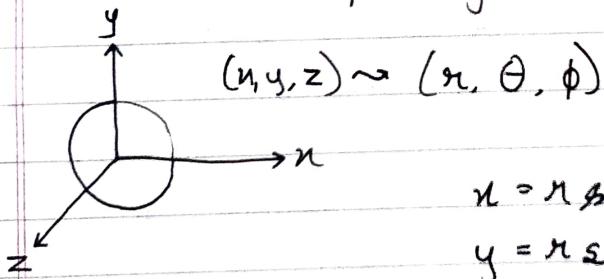
2) $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \rightarrow \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$

3) \rightarrow Schrodinger equation in polar coordinates :

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) \Phi(\phi) = E \Phi(\phi)$$

4) Apply the boundary condition : $\Phi(\phi + 2\pi) = \Phi(\phi)$
 $\Rightarrow \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$, m being the magnetic quantum number.

- Particle on a sphere of radius r.



$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

Step 1: express : $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

in terms of r, θ, ϕ .

Step 2 : rewrite the Schrodinger equation in terms of r, θ, ϕ .

$$\nabla^2 = \cancel{\frac{\partial^2}{\partial r^2}} + \frac{2}{r} \cancel{\frac{\partial}{\partial r}} + \frac{1}{r^2} \Lambda^2$$

$$\Lambda^2 \equiv \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)$$

Schrödinger equation

$$\nabla^2 \psi(r, \theta, \phi) = -\left(\frac{2IE}{\hbar^2}\right) \psi(r, \theta, \phi)$$

$$I = m r^2$$

Solution : Spherical harmonics $Y_{lm}(\theta, \phi)$
 ↳ 2 quantum numbers : l, m

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{lm}(\cos \theta) e^{im\phi}$$

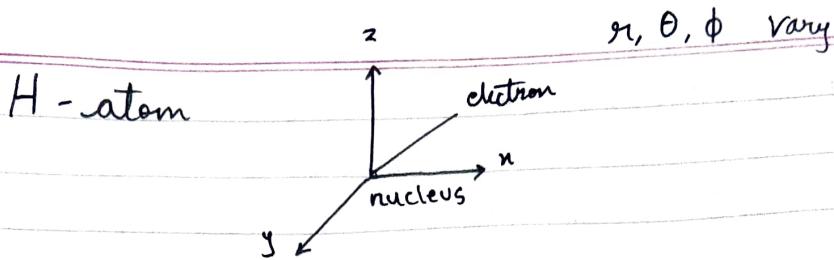
$$\psi(r, \theta, \phi) = Y_{lm}(\theta, \phi)$$

- here $P_{lm}(\cos \theta)$ is called the associated Legendre Polynomial
- $m \rightarrow$ magnetic quantum number $[0, \pm 1, \pm 2, \dots]$
- $l \rightarrow$ angular momentum quantum number $[0, 1, 2, \dots]$

Spherical Harmonics

l	m	$Y_{lm}(\theta, \phi)$
0	0	$\frac{1}{2} \sqrt{\pi}$
1	0	$\frac{1}{2} \sqrt{3\pi} \cos \theta$
1	± 1	$\mp \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$

$l=0 \rightarrow$ s orbitals [spherical]



$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad [\text{Derive}]$$

$$\rightarrow -\frac{\hbar^2}{2m} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right) \psi(r, \theta, \phi)$$

$$\begin{aligned} & * -\frac{\hbar^2}{2m} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \\ & - \frac{e^2}{4\pi\epsilon_0 r} \end{aligned} \quad \left. \begin{array}{l} \text{Kinetic energy} \\ \text{Potential energy} \end{array} \right\}$$

- Method of separation of variables:

$$\psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$$

radial angular

$$\Rightarrow -\frac{\hbar^2}{2m} Y(\theta, \phi) \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} R(r) \right) \right)$$

$$\text{radial} + \text{angular} = 0.$$

↪ using the particle on a sphere model

$Y_{lm}(\theta, \phi)$: solution to angular part

$R_{nl}(r)$:

3 quantum numbers : $n = 1, 2, 3, \dots$

$$l = 0, 1, 2, \dots, n-1$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

$$\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi)$$

- Principal Quantum Number

$1s$	n	l	m	Ψ
	1	0	0	$\Psi_{100} = \sqrt{\pi} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$

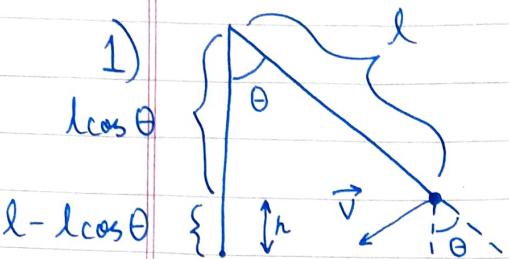
orbital

$$r = \frac{a_0}{a_0}, a_0 = \text{Bohr Radius.}$$



Assignment 2

Simple Pendulum



l : length of pendulum string

$$\text{Lagrangian } L = K - U$$

Kinetic energy Potential energy

For isolated system, Lagrange's equations of motion gives:

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

$$K = \frac{1}{2} m (\vec{v} \cdot \vec{v}) = \frac{1}{2} m \|\vec{v}\|^2$$

& $v = l \dot{\theta} = l \frac{d\theta}{dt}$ is the linear velocity.

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

$$U = mgh = mg(l - l \cos \theta) = mgl(1 - \cos \theta)$$

$$\therefore L = \frac{1}{2} m l^2 \dot{\theta}^2 - mgl + mgl \cos \theta$$

$$\frac{\partial L}{\partial \theta} = -mgl \sin \theta, \quad \frac{\partial L}{\partial \dot{\theta}} = ml^2 \dot{\theta}$$

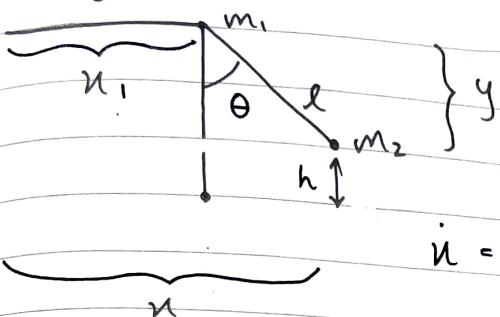
$$\& \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = ml^2 \ddot{\theta}$$

$$\begin{aligned} \text{from (I): } & -mgl \sin \theta = ml^2 \ddot{\theta} \\ & \Rightarrow \ddot{\theta} = -\frac{g \sin \theta}{l} \end{aligned}$$

$$\begin{aligned} \text{In this case, the hamiltonian } H &= -L + \dot{\theta} L' \dot{\theta} \\ &= mgl(1 - \cos \theta) - \frac{ml^2 \dot{\theta}^2}{2} + \dot{\theta} ml^2 \dot{\theta} \end{aligned}$$

$$\begin{aligned} &= mgl(1 - \cos \theta) + \frac{ml^2 \dot{\theta}^2}{2} \\ &= U + K \end{aligned}$$

2) Sliding Pendulum



$$x = n_1 + l \sin \theta$$

$$y = +l \cos \theta$$

$$\dot{x} = \dot{n}_1$$

$$L = K - U$$

$K =$ Kinetic energy of m_1 + Kinetic energy of m_2

$$= \frac{1}{2} m_1 \dot{n}_1^2 + \frac{1}{2} m_2 \vec{v} \cdot \vec{v}$$

$$\begin{aligned} \text{Velocity of } m_2 &= \vec{v} = \frac{d}{dt} [(n_1 + l \sin \theta) \hat{i} + (l \cos \theta) \hat{j}] \\ &= (\dot{n}_1 + l \cos \theta \cdot \dot{\theta}) \hat{i} - (l \sin \theta \cdot \dot{\theta}) \hat{j} \end{aligned}$$

$$\begin{aligned} \text{K.E. of } m_2 &= \frac{1}{2} m_2 \vec{v} \cdot \vec{v} = \frac{1}{2} m_2 (\dot{n}_1^2 + l^2 \dot{\theta}^2 \cos^2 \theta \\ &\quad + 2 \dot{\theta} \dot{n}_1 l \cos \theta + l^2 \dot{\theta}^2 \sin^2 \theta) \\ &= \frac{1}{2} m_2 (\dot{n}_1^2 + 2 \dot{\theta} \dot{n}_1 l \cos \theta + l^2 \dot{\theta}^2) \end{aligned}$$

$$\therefore K = \frac{1}{2} m_1 \dot{n}_1^2 + \frac{1}{2} m_2 \dot{n}_1^2 + m_2 \dot{\theta} \dot{n}_1 l \cos \theta + \frac{1}{2} m_2 l^2 \dot{\theta}^2$$

$$U = m_2 g h = m_2 g (l - l \cos \theta)$$

$$L = K - U$$

$$= \frac{1}{2} (m_1 + m_2) \dot{n}_1^2 + \frac{1}{2} m_2 l^2 \dot{\theta}^2 + m_2 \dot{\theta} \dot{n}_1 l \cos \theta - m_2 g l + m_2 g l \cos \theta$$

Let's calculate :

$$\frac{\partial L}{\partial \dot{n}_1} = (m_1 + m_2) \dot{n}_1 + m_2 \dot{\theta} l \cos \theta$$

$$\frac{\partial L}{\partial n_1} = 0$$

$$\text{iii) } \frac{\partial L}{\partial \theta} = -m_2 \dot{\theta} \dot{r}_1 l \sin \theta - m_2 g l \sin \theta$$

$$\text{iv) } \frac{\partial L}{\partial \dot{\theta}} = m_2 l^2 \ddot{\theta} + m_2 \ddot{r}_1 l \cos \theta$$

Using Lagrange's Equations of Motion:

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

$$\therefore -m_2 \dot{\theta} \dot{r}_1 l \sin \theta - m_2 g l \sin \theta = \\ m_2 l^2 \ddot{\theta} + m_2 \ddot{r}_1 l \cos \theta - m_2 \dot{r}_1 \sin \theta \dot{\theta}$$

$$\Rightarrow -m_2 g l \sin \theta = m_2 l^2 \ddot{\theta} + m_2 \ddot{r}_1 l \cos \theta$$

$$\Rightarrow (l \ddot{\theta} + \ddot{r}_1 \cos \theta + g \sin \theta) = 0 \quad \text{As } ml > 0$$

$$\text{II) } \frac{\partial L}{\partial r_1} = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_1} \right)$$

$$\Rightarrow 0 = (m_1 + m_2) \ddot{r}_1 + m_2 l (\dot{\theta} \cos \theta + \theta \cdot -\sin \theta \cdot \dot{\theta}) \\ = (m_1 + m_2) \ddot{r}_1 + m_2 l (\ddot{\theta} \cos \theta - \dot{\theta} \dot{\theta} \sin \theta) \\ = (m_1 + m_2) \ddot{r}_1 + m_2 l \ddot{\theta} \cos \theta - (\dot{\theta})^2 \sin \theta \cdot m_2 l$$

$$\Rightarrow m_2 l \sin \theta \dot{\theta}^2 = m_2 l \ddot{\theta} \cos \theta + (m_1 + m_2) \ddot{r}_1$$

$$\text{Now, } H = K + U$$

$$= \frac{1}{2} \dot{r}_1^2 (m_1 + m_2) + \frac{1}{2} m_2 l^2 \dot{\theta}^2 + m_2 \dot{r}_1 l \dot{\theta} \cos \theta \\ - m_2 g l \cos \theta + m_2 g l$$

Using Hamilton's Equations of Motion:

$$\text{III) } \frac{\partial H}{\partial \theta} = -\frac{dP_\theta}{dt} \text{ yields (I)}$$

$$\text{IV) } \frac{\partial H}{\partial n_1} = -\frac{dP_{n_1}}{dt} \text{ yields (II)}$$

where $\dot{P}_\theta = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right)$ & $\dot{P}_{n_1} = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{n}_1} \right)$

$$\dot{P}_\theta = m_2 l^2 \ddot{\theta} + m_2 \dot{n}_1 l \cos \theta - m_2 l \dot{n}_1 \dot{\theta} \sin \theta$$

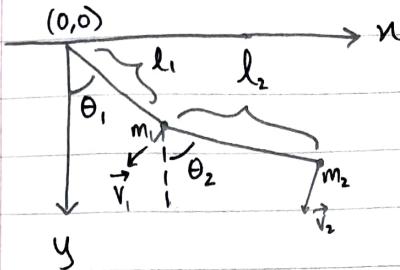
$$\dot{P}_{n_1} = (m_1 + m_2) \ddot{n}_1 + m_2 l \ddot{\theta} \cos \theta - \dot{\theta}^2 \sin \theta m_2 l$$

$$\frac{\partial H}{\partial n_1} = 0, \quad \frac{\partial H}{\partial \theta} = -m_2 \dot{n}_1 l \dot{\theta} \sin \theta + m_2 g l \dot{\theta} \sin \theta$$

$$\text{III) } -m_2 \dot{n}_1 l \dot{\theta} \sin \theta + m_2 g l \dot{\theta} \sin \theta = -m_2 l^2 \ddot{\theta} + m_2 \dot{n}_1 l \cos \theta$$

$$\text{IV) } \frac{\partial H}{\partial n_1} = 0 = -\dot{P}_{n_1}$$

3) Double Pendulum

Positions: $m_1 : (x_1, y_1), m_2 : (x_2, y_2)$

$x_1 = l_1 \sin \theta_1, x_2 = l_1 \sin \theta_1 + l_2 \sin \theta_2$

$y_1 = l_1 \cos \theta_1, y_2 = l_1 \cos \theta_1 + l_2 \cos \theta_2$

$\dot{x}_1 = l_1 \dot{\theta}_1 \cos \theta_1, \dot{x}_2 = l_1 \dot{\theta}_1 \cos \theta_1 + l_2 \dot{\theta}_2 \cos \theta_2$

$\dot{y}_1 = -l_1 \dot{\theta}_1 \sin \theta_1, \dot{y}_2 = -l_1 \dot{\theta}_1 \sin \theta_1 - l_2 \dot{\theta}_2 \sin \theta_2, \dot{y}_1 = -l_1 \dot{\theta}_1 \sin \theta_1$

Lagrange's equation for a simple pendulum
yields: $l \ddot{\theta} = -g \sin \theta$ [see 1]

$$\begin{aligned} K &= \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \\ &= \frac{1}{2} m_1 l_1^2 \dot{\theta}_1^2 + \frac{1}{2} m_2 (l_1^2 \dot{\theta}_1^2 + l_2^2 \dot{\theta}_2^2 + 2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \cos(\theta_2 - \theta_1)) \\ &= \frac{1}{2} (m_1 + m_2) l_1^2 \dot{\theta}_1^2 + \frac{1}{2} m_2 l_2^2 \dot{\theta}_2^2 + m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \cos(\theta_2 - \theta_1) \end{aligned}$$

Using $v_1^2 = \dot{x}_1^2 + \dot{y}_1^2$,
 $v_2^2 = \dot{x}_2^2 + \dot{y}_2^2$

$$\begin{aligned} U &= -m_1 g h_1 - m_2 g h_2 \quad [\text{Since } y\text{-axis} \\ &\text{for us is directed below}] \\ &= -m_1 g l_1 \cos \theta_1 - m_2 g (l_1 \cos \theta_1 + l_2 \cos \theta_2) \\ &= -(m_1 + m_2) g l_1 \cos \theta_1 - m_2 g l_2 \cos \theta_2 \end{aligned}$$

$$\begin{aligned} L &= K - U = \frac{1}{2} (m_1 + m_2) l_1^2 \dot{\theta}_1^2 + \frac{1}{2} m_2 l_2^2 \dot{\theta}_2^2 \\ &+ m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \cos(\theta_2 - \theta_1) + (m_1 + m_2) g l_1 \cos \theta_1 \\ &+ m_2 g l_2 \cos \theta_2 \end{aligned}$$

Now:

$$i) \frac{\partial L}{\partial \dot{\theta}_1} = (m_1 + m_2) l_1^2 \dot{\theta}_1 + m_2 l_1 l_2 \dot{\theta}_2 \cos(\theta_2 - \theta_1)$$

$$ii) \frac{\partial L}{\partial \theta_1} = m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \sin(\theta_2 - \theta_1) - (m_1 + m_2) g l_1 \sin \theta_1$$

By Lagrange's Equations of Motion:

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

$$\Rightarrow m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \sin(\theta_2 - \theta_1) - (m_1 + m_2) g l_1 \sin \theta_1 \\ = (m_1 + m_2) l_1^2 \ddot{\theta}_1 + m_2 l_1 l_2 \dot{\theta}_2 \cos(\theta_2 - \theta_1) \quad \text{--- (I)}$$

Similarly, for $\dot{\theta}_2$:

$$\text{iii) } \frac{\partial L}{\partial \dot{\theta}_2} = m_2 l_2^2 \ddot{\theta}_2 + m_2 l_1 l_2 \dot{\theta}_1 \cos(\theta_2 - \theta_1)$$

$$\text{iv) } \frac{\partial L}{\partial \theta_2} = -m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \sin(\theta_2 - \theta_1) - m_2 g l_2 \sin \theta_2$$

Using Lagrange's Equations of Motion:

$$\frac{\partial L}{\partial \theta_2} = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}_2} \right)$$

$$\Rightarrow -m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \sin(\theta_2 - \theta_1) - m_2 g l_2 \sin \theta_2 \\ = m_2 l_2^2 \ddot{\theta}_2 + m_2 l_1 l_2 \dot{\theta}_1 \cos(\theta_2 - \theta_1) \quad \text{--- (II)}$$

Now, $H = K + U$

$$= \frac{1}{2} (m_1 + m_2) l_1^2 \dot{\theta}_1^2 + \frac{1}{2} m_2 l_2^2 \dot{\theta}_2^2 + m_2 l_1 l_2 \dot{\theta}_1 \dot{\theta}_2 \cos(\theta_1 - \theta_2) \\ - (m_1 + m_2) g l_1 \cos \theta_1 - m_2 g l_2 \cos \theta_2$$