

Contents

1) Applications of Quantum Mechanics

- Particle in a box & tunnel effect - T. M. F.
- Harmonic Oscillator
- Finite potential well & tunnel effect
- Magnetic moment & spin - T. M. F.

2) Laws of Thermodynamics & Thermodynamic Potential

3) Statistical Mechanics

- Bridging the micro and macro
- Statistical basis of thermodynamics
- Statistical distributions
- Maxwell-Boltzmann distributions
- Distribution of molecular speeds
- Specific heat of Solids.

4) Periodic Potentials, Solid State, Metallic bonding, Semiconductors.

5) Quantum statistics

6) Nuclear physics

7) Electromagnetism

Ref. Books

- 1) Concepts of Modern Physics - Arthur Beiser
- 2) Feynman lectures - Vol 3 - R. Feynman
- 3) Physical Chemistry - P.W. Atkins
- 4) Fundamentals of statistical & thermal physics - F. Reif.
- 5) Quantum chemistry by E.N. Levine

Thermodynamics:

- $P, V, T \Rightarrow$ Pressure, Volume & Temperature.

- $P = f(V, T)$ } Equation of state

$$P = \frac{nRT}{V} \text{ for an ideal gas}$$

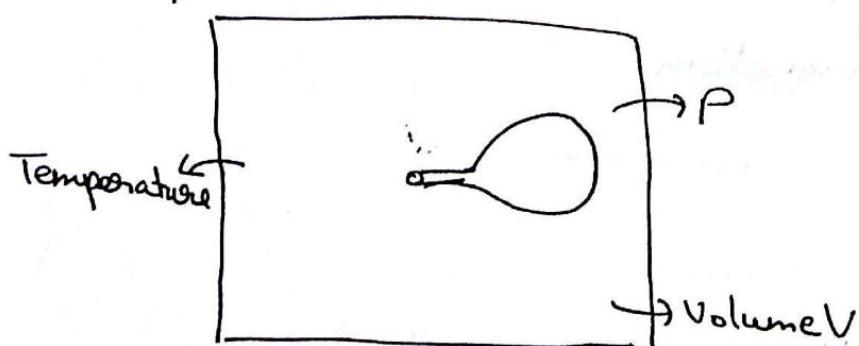
- i) \Rightarrow Coefficient of thermal expansion of the system, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$
- * ii) Isothermal compressibility, $\chi = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$
- iii) Coefficient of tension, $\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$

- Spontaneous process \rightarrow When no external force (Have specific direction) (Natural) is applied.

e.g.: Gas expansion is spontaneous, gas compression is not.

* Dispersal of Energy (By molecules)

- Experiment:



- Gas molecules want to expand & explore so balloon deflates

- In different conditions, different kinds of energies are minimized.

- $A = A(T, V)$ or $U = U(S, V)$ } Different kinds of energies
- $\Delta S \propto \ln(V_f/V_i)$

1) Internal Energy:

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

- Internal energy is ~~minimized~~ minimized under constant entropy & constant volume.

2) Helmholtz free energy:

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

- 'A' will be minimized under constant T & V.

3) Gibbs free energy: (Most experiments)

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

- G will be minimized under constant P & T.

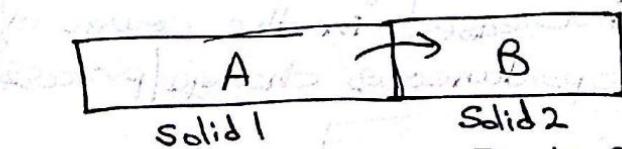
4) Enthalpy:

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

- H will be minimized under constant P & S.

⇒ We need different forms of energy measures because of the various parameters we perform the experiment under.

• Experiment 2:



initial: T_A temp, T_B temp ($T_A \gg T_B$)

- Something flows from A → B (Spontaneous)

$$\bullet \Delta S \propto \left[\frac{1}{T_B} - \frac{1}{T_A} \right]$$

System:

- a) Exchange energy and matter with the surrounding
(Open System)
- b) Exchange only energy with the surrounding
(Closed system)
- c) Do not exchange energy & matter
(Isolated system)

* Boundary:

- a) Adiabatic boundary (do not allow heat flow)
- b) Diabatic boundary (allow heat flow)

* Laws of Thermodynamics:

- First Law: Every thermodynamic system possesses a characteristic property called energy. The energy of system is increased by a quantity of heat (dQ) added to it and is increased by external work (dW) performed on it.

$$\Rightarrow dU = dQ + dW$$

- Second Law: The entropy of an isolated system increases in the course of a spontaneous change/process

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

$$(\Delta S)_{\text{total}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$$

• Clausius inequality:

$$(DS)_{\text{system}} \geq \frac{dQ}{T}$$

- dQ is the heat supplied to the system at a given temperature T .

\Rightarrow For an isolated system $(DS)_{\text{system}} \geq 0$

• Third Law: Defines the absolute value of entropy of the system.

• When $T \rightarrow 0, S \rightarrow 0$

$$\frac{dS = 0}{dU = 0} \quad \xrightarrow{\text{From first law}}$$

① Heat transfer at constant volume & S:

- No work done by the system ($\therefore dV = 0$)

* $\Rightarrow dU = dQ + dW = dQ$ (From first law) $\therefore dW = 0$

$$dS \geq \frac{dQ}{T} \Rightarrow dS \geq \frac{dU}{T} \quad \text{if } dV = 0$$

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

- If S is constant, $dS = 0$

$$\Rightarrow (dU)_{S,V} \leq 0 \Rightarrow U_{\text{fin}} \leq U_{\text{init}}$$

(At constant ~~temp~~ & entropy, dU is -ve, so U is minimized (Internal energy = minimized))

• This inequality is valid for quick processes, spontaneous

(($(dU)_{S,V} = 0$ for quasi-static processes)

② Enthalpy at constant pressure & S:

* \Rightarrow Define $H = U + PV$

$$dH = dU + PdV + VdP$$

$$dH = dQ + VdP \quad (dW = -PdV)$$

$$\Rightarrow dH = dQ + VdP$$

From Clausius inequality, $TdS \geq dQ$

$$TdS \geq dH - VdP$$

\Rightarrow If P, S are constant,

$$(dH)_{P,S} \leq 0 \Rightarrow dH_{fin} < dH_{init}$$

(Minimization of enthalpy at constant pressure & entropy).

③ Isothermal expansion, change in entropy:

* $dS = \frac{dQ}{T}$ (For a reversible process)

$$\Rightarrow T = \text{constant}, dT = 0, V_i \rightarrow V_f \\ V_f > V_i$$

$$dS = \int \frac{dQ}{dT} = \frac{1}{T} \int dQ = \frac{Q}{T}$$

From the first law, $dU = Q + W$

$$Q = Q + W, dU = 0 \quad (\text{For an isolated system})$$
$$\Rightarrow Q = -W$$

But, $W = - \int_{V_i}^{V_f} P dV$

$$\Rightarrow PV = nRT, P = \frac{nRT}{V}$$

$$W = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

$$W = -nRT \ln(V_f/V_i)$$

$$\Rightarrow dS = \frac{nR \ln(V_f/V_i)}{T}$$

$$dS = nR \ln(V_f/V_i)$$

$\therefore V_f > V_i, \Delta S > 0$ (Entropy increases on isothermal expansion of ideal gas)

④ Helmholtz free energy & constant T, V:

Helmholtz free energy (A)

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

Const T,

$$dA = dU - TdS \quad , \text{ we know } dU - TdS \leq 0$$

$$\therefore (dA)_{T,V} \leq 0 \quad \therefore dW = 0$$

\therefore (Helmholtz free energy is minimized at const temperature & volume)

⑤ Gibbs free energy & const P, T:

$$G = H - TS$$

$$dG = \underbrace{dH - TdS - SdT}_{\leq 0} \quad (\because dH = dQ + VdP = dQ \text{ & from clausius})$$

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

(Gibbs free energy is minimized at const pressure & temperature).

Note: $dU = TdS - PdV$ } $U(S, V)$

~~* * *~~ $dH = TdS + VdP$ } $H(S, P)$

$dA = -PdV - SdT$ } $A(V, T)$

$dG = VdP - SdT$ } $G(P, T)$

Maxwell's Equations:

$$1) \Rightarrow U = U(S, V)$$

$$dU = \frac{\partial U}{\partial S} \Big|_V dS + \frac{\partial U}{\partial V} \Big|_S dV$$

$$\text{From, } dU = TdS - PdV,$$

$$\text{Comparing, } \frac{\partial U}{\partial S} \Big|_V = T, \quad \frac{\partial U}{\partial V} \Big|_S = -P$$

$$\Rightarrow \frac{\partial}{\partial V} \left[\frac{\partial U}{\partial S} \Big|_V \right]_S = \frac{\partial}{\partial S} \left[\frac{\partial U}{\partial V} \Big|_S \right]_V$$

$$\Rightarrow \boxed{\frac{\partial T}{\partial V} \Big|_S = -\frac{\partial P}{\partial S} \Big|_V} \rightarrow \text{1st Maxwell equation}$$

$$2) H = H(S, P)$$

$$dH = \frac{\partial H}{\partial S} \Big|_P dS + \frac{\partial H}{\partial P} \Big|_S dP$$

$$\text{From, } dH = TdS + VdP,$$

$$\Rightarrow \frac{\partial H}{\partial S} \Big|_P = T, \quad \frac{\partial H}{\partial P} \Big|_S = V$$

$$\frac{\partial}{\partial P} \left[\frac{\partial H}{\partial S} \Big|_P \right]_S = \frac{\partial}{\partial S} \left[\frac{\partial H}{\partial P} \Big|_S \right]_P$$

$$\therefore \boxed{\frac{\partial T}{\partial P} \Big|_S = \frac{\partial V}{\partial S} \Big|_P}$$

$$3) A = A(V, T)$$

$$dA = \frac{\partial A}{\partial V} \Big|_T dV + \frac{\partial A}{\partial T} \Big|_V dT$$

From, $dA = -PV - SdT$

$$\frac{\partial A}{\partial V} \Big|_T = -P, \quad \frac{\partial A}{\partial T} \Big|_V = -S$$

$$\frac{\partial}{\partial T} \left[\frac{\partial A}{\partial V} \Big|_T \right]_V = \frac{\partial}{\partial V} \left[\frac{\partial A}{\partial T} \Big|_V \right]_T$$

$$\Rightarrow \boxed{+\frac{\partial P}{\partial T} \Big|_V = +\frac{\partial S}{\partial V} \Big|_T}$$

$$4) G_r = G_r(P, T)$$

$$dG_r = \frac{\partial G_r}{\partial P} \Big|_T dP + \frac{\partial G_r}{\partial T} \Big|_P dT$$

From, $dG_r = VdP - SdT$

$$\frac{\partial G_r}{\partial P} \Big|_T = V, \quad \frac{\partial G_r}{\partial T} \Big|_P = -S$$

$$\frac{\partial}{\partial T} \left[\frac{\partial G_r}{\partial P} \Big|_T \right]_P = \frac{\partial}{\partial P} \left[\frac{\partial G_r}{\partial T} \Big|_P \right]_T$$

$$\Rightarrow \boxed{\frac{\partial V}{\partial T} \Big|_P = -\frac{\partial S}{\partial P} \Big|_T}$$

Note: Kinetics deals with time & variations in the system's states.

kinetic energy terms \times

if \dot{x} is a velocity, \dot{x}^2 is a kinetic energy term

$$\text{kinetic energy} = \frac{1}{2} m \dot{x}^2$$

* Melting of Ice:

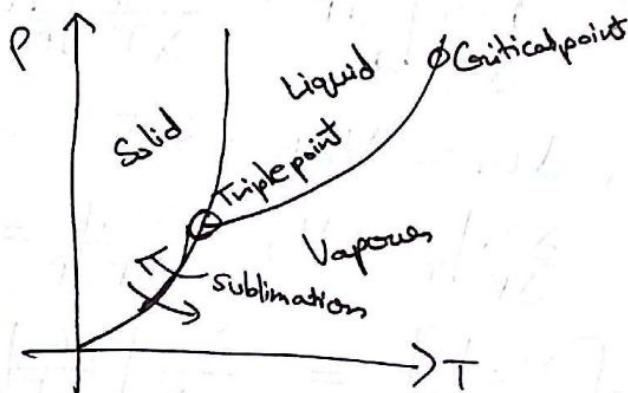
- $G_{\text{ice}}(T_{\text{room}}, P_{\text{atm}}) > G_{\text{water}}(T_{\text{room}}, P_{\text{atm}})$

→ Gibbs free energy is a measure of stability of materials/phases.

Note: $G_{\text{diamond}}(T_{\text{room}}, P_{\text{atm}}) > G_{\text{graphite}}(T_{\text{room}}, P_{\text{atm}})$

∴ Over a long time, diamond gets converted to graphite.

- Using Gibbs free energy measurements, we can come up with a phase diagram.



⇒ On the phase boundaries, element exists at both adjacent states.

- * At triple point, all three phases can coexist.

* ⇒ Critical point = Highest T after which distinguishing liquid & gas is not possible (super critical region)

- * Chemical potential = Gibbs free energy per mole (μ)

$$\mu_{\text{ice}}(T, P) = G_{\text{ice}}(T, P) / N_{\text{mole}} \rightarrow \text{Num of moles}$$

- Note: Temp gradient: Flow of ~~mass~~ energy (heat)
 Pressure gradient: Flow of work
 Chem. potential gradient: Flow of particles

Measuring Gibbs free energy:

$$G(T, P) \equiv H(S, P) - T \cdot S$$

$$dG = dH - TdS - SdT$$

We know, $H = U + PV$,
 $\therefore dH = TdS - PdV + \cancel{dU} + VdP$

$$\Rightarrow dH = TdS + VdP$$

$$\therefore dG = TdS + VdP - TdS - SdT$$

$$\therefore \boxed{dG = VdP - SdT} \rightarrow ①$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \rightarrow ②$$

From ①, ②,

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

(Similar to Maxwell's equations)

*). If $S = +ve$, $\left(\frac{\partial G}{\partial T}\right)_P = -ve$. So increasing T at const P , G_f would decrease.

\Rightarrow If S is large, the slope increases, so G_f decreases more w.r.t T at a given P .

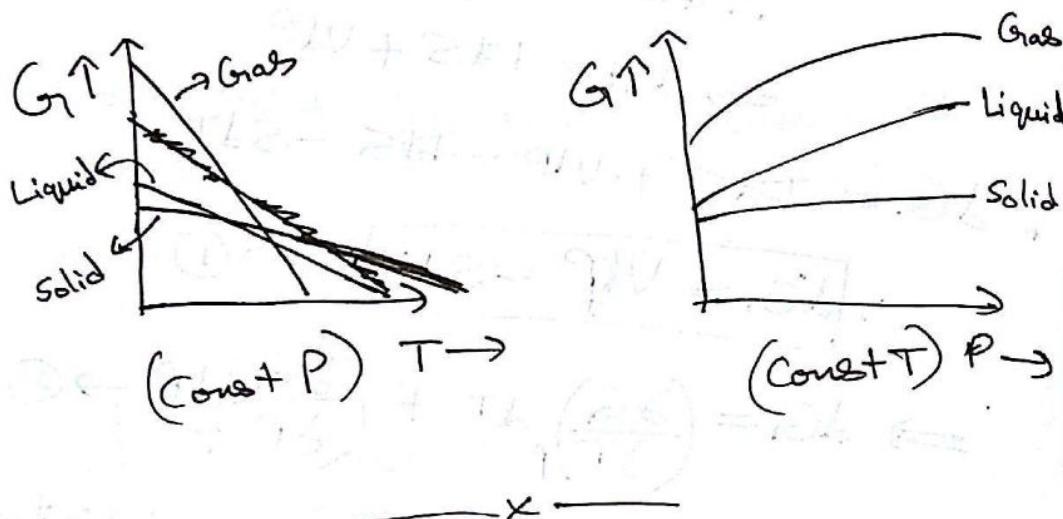
\Rightarrow We know $S_{gas} \gg S_{liq}$ (In general)

• Gases are more sensitive to temp changes compared to liquids.

* ii) $\because V = \text{true}$,

$$\left(\frac{\partial G}{\partial P}\right)_T \Rightarrow \text{Always true.}$$

- G_r would increase as P increases at const temperature.
- Systems with larger volume are more sensitive to pressure. So G_r of gases are more sensitive to pressure than the solid & liquid phases.



* Gibbs Helmholtz equation:

- You can determine G_r from the enthalpy of the system.

$$\Rightarrow \left(\frac{\partial G_r}{\partial T}\right)_P = -S, S = \frac{H - G_r}{T}$$

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

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

$$\Rightarrow \frac{1}{T} \left(\frac{\partial G_f}{\partial T} \right)_P - \frac{G_f}{T^2} = -H/T^2$$

$$\Rightarrow \boxed{\left(\frac{\partial \left(\frac{G_f}{T} \right)}{\partial T} \right)_P = -H/T^2} \xrightarrow{\text{Gibbs Helmholz equation}}$$

- H can be measured from calorimetry experiments & from that on integration we can estimate G_f .

Note: Quiz on Monday (23/1/17)

gibbs free energy (standard) = $\Delta_f G^\circ$

(calorimetry) = $\Delta_f H^\circ$

(enthalpy of combustion) = $\Delta_f U^\circ$

To prove which method is more accurate, we will compare both values against Hess's law.

• Derivation of standard $\Delta_f G^\circ$

standard free energy (standard) = $(\Delta_f G^\circ)^\circ$

(GDT, DFT) = enthalpy (standard) = $\Delta_f H^\circ$

(calorimetry) = $(\Delta_f U^\circ)^\circ$

(enthalpy of combustion) = $\Delta_f U^\circ$

(enthalpy of combustion) = $\Delta_f U^\circ$

• Relationship between $\Delta_f G^\circ$ and $\Delta_f H^\circ$

• Relationship between $\Delta_f G^\circ$ and $\Delta_f U^\circ$

Statistical Mechanics

- Macroscopic variables $P, V, T \rightarrow$ Thermodynamics.
- Microscopic view: System of interest consists of many atoms.
 - Positions & velocities of the atoms are known. $\vec{r}_i = (x_i, y_i, z_i)$ } Position
 $\{\vec{r}_i\}$ = Set of positions of all atoms.
 $\{\vec{r}_i\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$
= $(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_n, y_n, z_n)$
 - $\vec{v}_i = (v_{xi}, v_{yi}, v_{zi})$ } Velocity
 $\{\vec{v}_i\} = (\vec{v}_1, \vec{v}_2, \dots, \vec{v}_n)$
= $(v_{x1}, v_{y1}, v_{z1}, \dots, v_{xn}, v_{yn}, v_{zn})$
- Assume system is isolated, total energy of system should not change with time \rightarrow it's a constant

* Hamiltonian function (H):

- $H(\{\vec{r}_i\}, \{\vec{v}_i\})$ = Total energy of the system.
 - \vec{v}_i & \vec{r}_i vary with time $\Rightarrow \vec{r}_i(t), \vec{v}_i(t)$
- $\Rightarrow \frac{dH(\{\vec{r}_i\}, \{\vec{v}_i\})}{dt} = 0$ $(\because$ It's an isolated system)

- Let $\vec{p}_i = m \cdot \vec{v}_i$ (m = Mass of a particle)
Linear momentum \hookrightarrow Consider $H(\{\vec{r}_i\}, \{\vec{p}_i\})$
from now on.

$$\begin{aligned}\bullet \frac{dH}{dt} = \frac{\partial H}{\partial x_1} \cdot \frac{dx_1}{dt} + \frac{\partial H}{\partial y_1} \cdot \frac{dy_1}{dt} + \frac{\partial H}{\partial z_1} \cdot \frac{dz_1}{dt} \\ + \dots + \frac{\partial H}{\partial x_i} \cdot \frac{dx_i}{dt} + \frac{\partial H}{\partial y_i} \cdot \frac{dy_i}{dt} + \frac{\partial H}{\partial z_i} \cdot \frac{dz_i}{dt} \\ \uparrow \text{For all particles}\end{aligned}$$

$$\Rightarrow \frac{dH}{dt}(\{\bar{q}_i\}, \{\bar{p}_i\}) = \sum_{i=1}^N \frac{\partial H}{\partial \dot{q}_i} \cdot \frac{d\bar{q}_i}{dt} + \sum_{i=1}^N \frac{\partial H}{\partial \dot{p}_i} \cdot \frac{d\bar{p}_i}{dt} = 0$$

- $\frac{d\bar{p}_i}{dt} = \bar{F}_i = \text{Force on atom } i$
- $\frac{d\bar{q}_i}{dt} = \bar{v}_i = \text{Velocity of atom } i$

$$\Rightarrow \because \frac{dH}{dt} = 0, \quad \boxed{\begin{aligned} \frac{\partial H}{\partial \dot{q}_i} &= -\frac{d\bar{p}_i}{dt} \\ \frac{\partial H}{\partial \dot{p}_i} &= \frac{d\bar{q}_i}{dt} \end{aligned}} \quad \left. \begin{array}{l} \text{Choosing these satisfies} \\ \frac{dH}{dt} = 0. \\ (\text{So it is a possible solution}) \end{array} \right\}$$

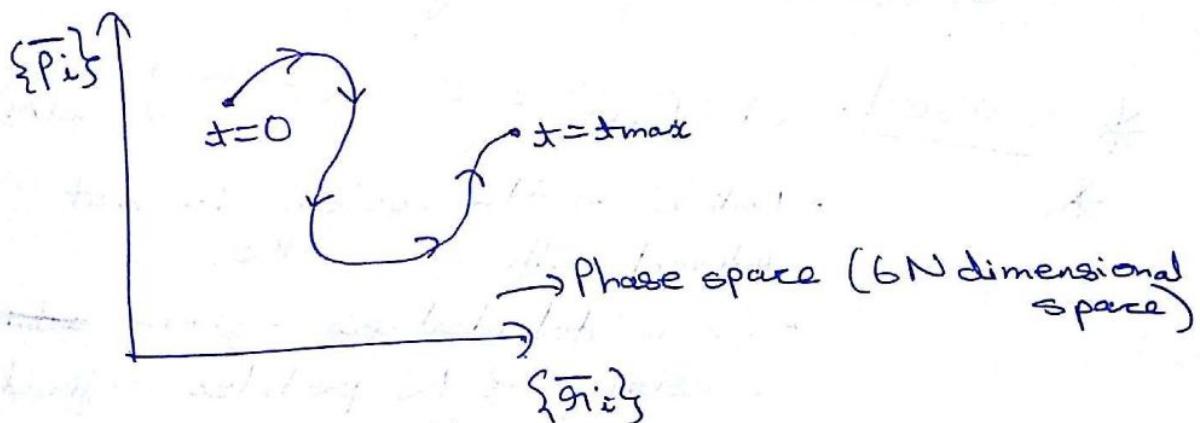
Hamilton's approach (equations of motion)

- All the properties of the system of interest can be expressed as a function of $\{\bar{q}_i\}$ and $\{\bar{p}_i\}$

$$A = A(\{\bar{q}_i\}, \{\bar{p}_i\}; t)$$

↳ The parameters of function vary with t , A does not explicitly depend on t .

- $\langle A(t) \rangle = \text{Time average of } A(t)$



- Limitations of Hamiltonian equations:

- 1) Only applicable to isolated systems.
- 2) Fails for quantum systems.

* What is $H(\{\bar{r}_i\}, \{\bar{p}_i\})$?

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

Potential energy Kinetic energy

$$\Rightarrow \frac{d\bar{p}_i}{dt} = -\frac{\partial H}{\partial \bar{r}_i} = -\frac{\partial U(\bar{r}_i)}{\partial \bar{r}_i}$$

↑
 Force on each particle
 is due to $U(\bar{r}_i)$

- For all atomic systems

$$K(\{\bar{p}_i\}) = \sum_{i=1}^N \frac{\bar{p}_i \cdot \bar{p}_i}{2m_i}$$

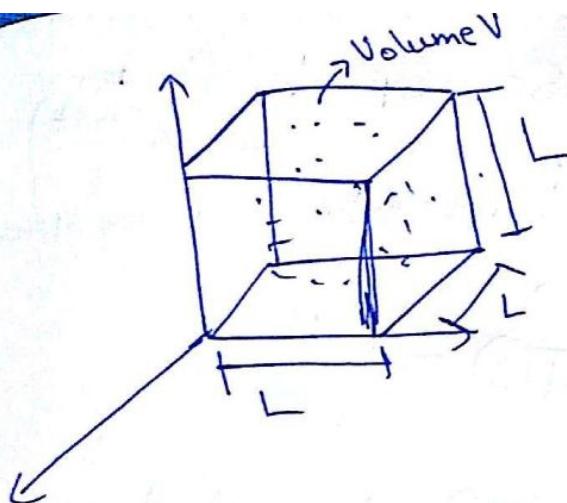
where m_i is
 the mass
 of the i^{th}
 particle.

- $U(\{\bar{r}_i\})$ is different for different systems.
- The nature of $U(\{\bar{r}_i\})$ for a given system is not known precisely.

* Case 1: $U(\{\bar{r}_i\}) = 0$ (Isolated ideal gas system)

*

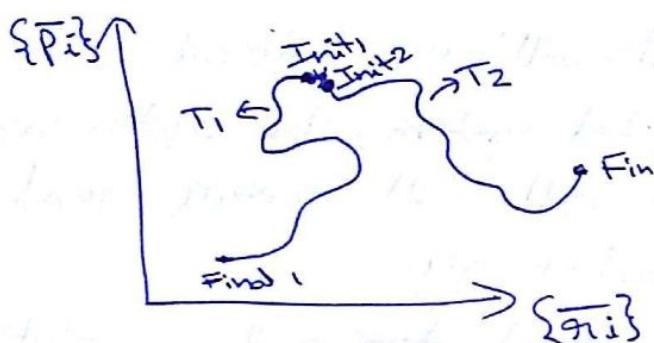
- Particles in the system do not interact with each other.
- An isolated ideal gas system consisting of N particles confined in a volume V .



$$0 \leq x_i \leq L \\ 0 \leq y_i \leq L \\ 0 \leq z_i \leq L$$

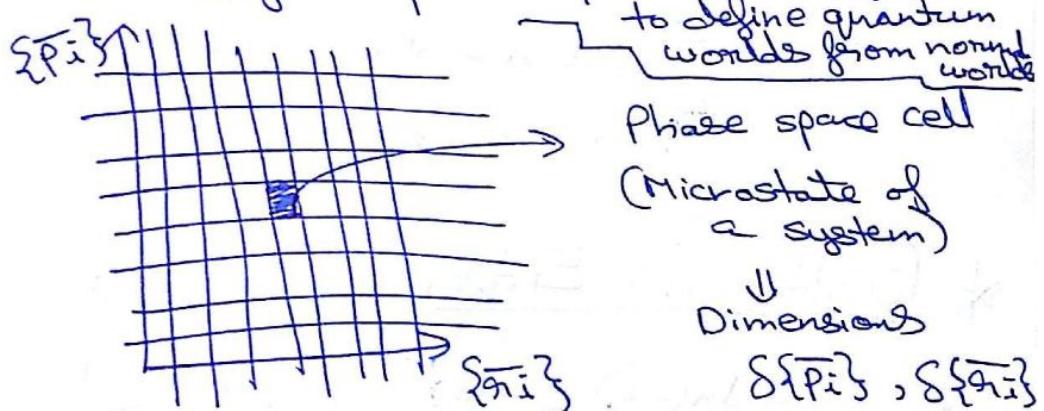
$$\bullet \frac{dH}{dt} = \frac{dK}{dt} = 0 \quad (\text{Isolated system})$$

$$\bullet U(\{\bar{q}_i\}) = 0 \quad (\text{Ideal gas})$$



- The phase space points on the trajectory are special compared to the remaining phase space points.
- Same system studied at two different kinetic energies trace out two different trajectories.

\Rightarrow Dividing the phase space into a grid,



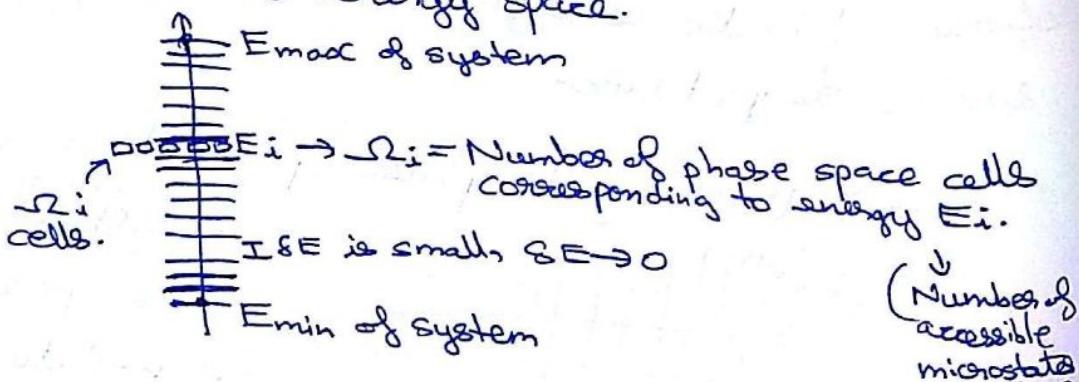
$$\delta(\{\bar{q}_i\}) = \delta x_1 \delta y_1 \delta z_1 \dots \delta x_N \delta y_N \delta z_N$$

$$\delta(\{\bar{p}_i\}) = \delta p_{x_1} \delta p_{y_1} \delta p_{z_1} \dots \delta p_{x_N} \delta p_{y_N} \delta p_{z_N}$$

\Rightarrow For one dimension, $\delta x \cdot \delta p \sim h$ (Planck's
 $h = 10^{-34}$ const)

\Rightarrow Volume of a given hypercube in phase space
 (phase space cell) is,

$$\delta(\{\bar{q}_i\}) \cdot \delta(\{\bar{p}_i\}) = h^{3N}$$

- Measure $H(\{\bar{q}_i\}, \{\bar{p}_i\})$ at each phase space cell.
- Different cells will have different energies.
- For an isolated system, the system visits only those cells with energy equal to the set initial energy.
- * • Any cell visited during the evolution of the system is called a microstate of the system.
- * • Observing & Analyzing $6N$ dimensional phase space is hard, so we also use a 1D energy space.


$\Omega_i \rightarrow \Omega_i =$ Number of phase space cells corresponding to energy E_i .
 R_i cells.
 $E \in E$ is small, $S \rightarrow 0$

* Boltzmann's Entropy Formula:

$$\bullet S \propto \ln(\Omega_i) \quad \Rightarrow S = k_B \ln \Omega_i$$

\downarrow
 Entropy Boltzmann constant

Note: At low temperatures, S is large, at very low temperatures $S \approx 0$, $S = 0$ (for crystals).
 Only 1 microstate is visited. (3rd law of thermodynamics)

$\langle \bar{r}_i \rangle \Rightarrow$ average position of the i^{th} atom
 $\langle \bar{r}_i \rangle = \text{constant}$ (for crystals)
 $\langle \bar{r}_i \rangle \Rightarrow$ Varies with time (for liquids and gases)

* Entropy is the measure of delocalization of probability of an atom's position.

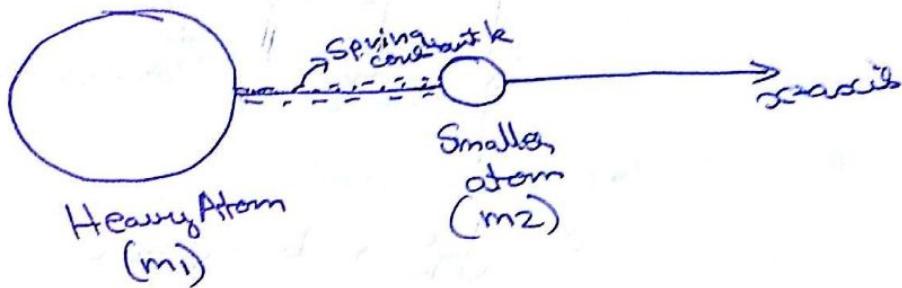
→ Determine $\omega(E)$ for two model systems,

* Case 1: One-dimensional harmonic oscillator

Case 2: A system of N ideal gas atoms

confined in a volume V .

1) \Rightarrow Case 1:



• $m_1 \gg m_2$

• Strength of bond → represented with spring constant k . ($k = \text{Strength of spring}$)

• Smaller atom vibrates along x-axis.

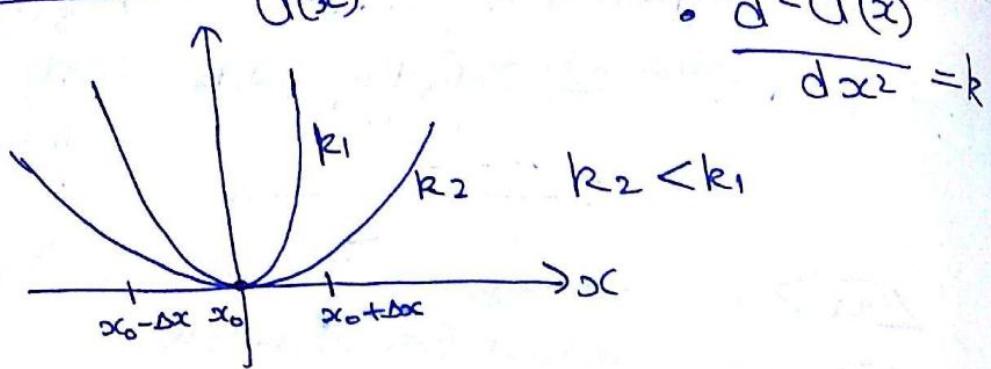
• $x_0 = \text{Equilibrium bond length}$.

• time evolution = $x(t)$

• Potential energy of system $\Rightarrow U(x)$

$$U(x) = \frac{1}{2}k(x - x_0)^2$$

- Potential functions:

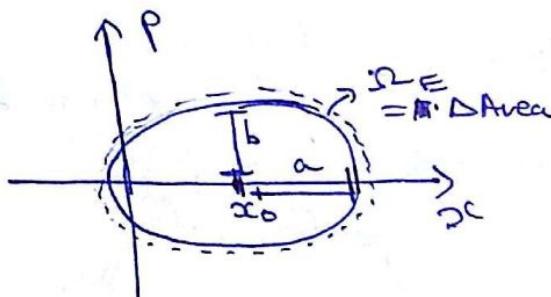


- $H(x, p) = \frac{1}{2m_2} p^2 + \frac{1}{2} k(x - x_0)^2$

* • Isolated system, initial energy of the system = E.

$$\Rightarrow E = \frac{p^2}{2m_2} + \frac{1}{2} k(x - x_0)^2$$

$$\Rightarrow \frac{(x - x_0)^2}{(\sqrt{\frac{2E}{k}})^2} + \frac{p^2}{(2m_2 E)^2} = 1 \quad \left. \right\} \text{Equation of ellipse}$$



• The ellipse represents the trajectory we take in phase space.

$$a = \sqrt{\frac{2E}{k}}, \quad b = \sqrt{2m_2 E}$$

- Now since $a, b \propto \sqrt{E}$, as $E \uparrow$, $a, b \uparrow$
so a larger ellipse is accessible.
- Area of ellipse \Rightarrow ~~small region~~ is the number of accessible states Ω_E
- Given the semi major and semi minor lengths of the elliptical orbit of the system calculate Ω_E .

$$\Rightarrow \text{Area} = \pi ab$$

$$\text{Circumference} = \pi(a+b) \rightarrow \text{The number of states} \approx$$

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

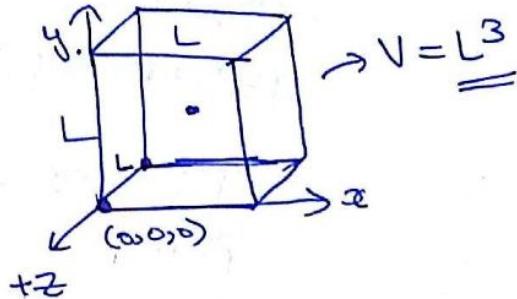
(Since we take a very small region boundary around the ellipse)

2) Case 2:

- Ideal gas with N atoms of volume V .

$$\text{Simplify: } N=1$$

($E = \text{Initial energy}$)



$$U(x, y, z) = 0$$

$$K = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

- Isolated system: Constant energy $E = K$

$$\Omega_E = \frac{1}{h^3} \int_{x=0}^{x=L} \int_{y=0}^{y=L} \int_{z=0}^{z=L} \delta(p_x = 0, p_y = 0, p_z = 0) \delta(H(x, y, z; p_x, p_y, p_z) - E) \cdot dx dy dz dp_x dp_y dp_z$$

*

- Define $\delta(x - x_0) = 1$ when $x = x_0$, 0 otherwise

\Rightarrow We know ~~H~~ H can be split into potential and kinetic components, therefore

$$\Omega(E) = \frac{1}{h^3} \iiint_{x,y,z} dx dy dz \iint_{p_x, p_y, p_z} \delta(H - E) dp_x dp_y dp_z$$

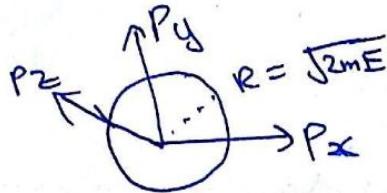
($\because H$ only depends on p_x, p_y, p_z here)

$$\Rightarrow \Omega(E) = \frac{1}{h^3} \cdot V \cdot ?$$

We calculate this next.

$$\Rightarrow \frac{p_x^2 + p_y^2 + p_z^2}{2m} = E$$

$$\Rightarrow p_x^2 + p_y^2 + p_z^2 = (\sqrt{2mE})^2 = R^2 \text{ (Sphere)}$$



- All points on the surface of sphere satisfy $p_x^2 + p_y^2 + p_z^2 = R^2$.

$$\Rightarrow \iiint_{p_x p_y p_z} \delta(H - E) dp_x dp_y dp_z \propto \text{Surface area of sphere.}$$

$$\therefore \Omega(E) \propto V \cdot R^2$$

$$\Rightarrow \Omega(E) \propto V \cdot (\sqrt{2mE})^2$$

$$\Rightarrow \Omega(E) \propto V \cdot E$$

- This can be extended to N particles where $U(\dots) = 0$ since they are ideal gas atoms.

$$\therefore \text{We will get } \Omega(E) \propto V^N \cdot E$$

(Sphere in $3N$ dimensions for momentum where again surface area $\propto R^{3N-1}$)

$$(\text{Here also } R \propto \sqrt{E})$$

$$\therefore \propto R^{3N-1} \Rightarrow \propto E^{\frac{3N-1}{2}}$$

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

\rightarrow For N particles

\xrightarrow{x}

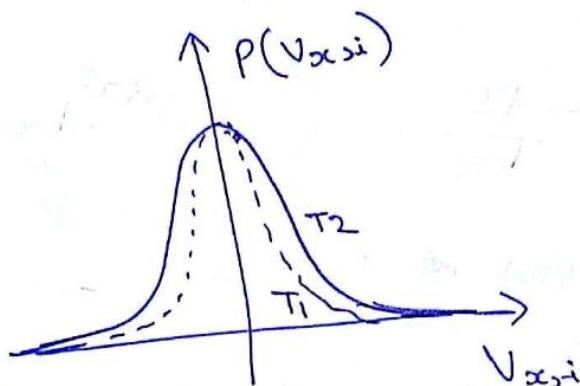
- For practical purposes, we want the temperature to be constant, so we allow for energy exchange.

$\Rightarrow \frac{dH}{dt} = 0 \Rightarrow$ Does not mean the temperature is constant.

* Maxwell Boltzmann Velocity Distribution:

$$P(V_{xi}) \propto e^{-\frac{1}{2K_B T} \cdot m V_{xi}^2}$$

Prob of x^{th} component of velocity of i^{th} atom.



Width increases as $T \uparrow$
 \Rightarrow Width \propto Temp

(Proofs for
these in assignment
photos)

$$\textcircled{1} \quad I = \int_{-\infty}^{\infty} P(V_{xi,i}) \cdot dV_{xi,i} \Rightarrow \text{determine proportionality constant } A$$

$$P(V_{xi,i}) = A \cdot e^{-\frac{1}{2K_B T} \cdot m V_{xi,i}^2}$$

$$I = \int_{-\infty}^{\infty} A e^{-\frac{1}{2K_B T} \cdot m V_{xi,i}^2} \cdot dV_{xi,i}$$

$$\bullet A = \sqrt{\frac{m}{K_B \cdot T \cdot \pi \cdot 2}}$$

(Bell curve
integral
known;
convert
to require
form)

$$\textcircled{2} \quad \langle V_{xi,i} \rangle = \int_{-\infty}^{\infty} A e^{-\frac{m V_{xi,i}^2}{2K_B T}} \cdot V_{xi,i} \cdot dV_{xi,i} \quad (\text{Odd function}) = 0$$

$$\textcircled{3} \quad \langle (V_{xi,i} - \langle V_{xi,i} \rangle)^2 \rangle = \int_{-\infty}^{\infty} (V_{xi,i} - \langle V_{xi,i} \rangle)^2 \cdot A \cdot e^{-\frac{m V_{xi,i}^2}{2K_B T}} \cdot dV_{xi,i}$$

$$= \frac{K_B \cdot T}{m}$$

$$\textcircled{4} \quad \frac{1}{2} m \langle (v_{x,i} - \langle v_{x,i} \rangle)^2 \rangle \Rightarrow \begin{array}{l} \text{Average kinetic} \\ \text{energy per} \\ \text{velocity} \\ \text{component} \end{array}$$

$$= \frac{N}{2} \cdot k_B \cdot T$$

$$\textcircled{5} \quad \frac{m}{2} \sum_{i=1}^N \left[\langle (v_{x,i} - \langle v_{x,i} \rangle)^2 \rangle + \langle (v_{y,i} - \langle v_{y,i} \rangle)^2 \rangle + \langle (v_{z,i} - \langle v_{z,i} \rangle)^2 \rangle \right]$$

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

Note: If $I = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$

$$\Rightarrow -\frac{dI}{dx} = \int_{-\infty}^{\infty} x^2 \cdot e^{-\alpha x^2} dx$$

$$\text{But } I = \sqrt{\frac{\pi}{\alpha}}$$

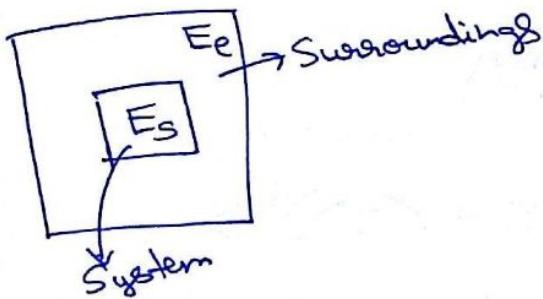
$$\Rightarrow -\frac{dI}{dx} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}} \quad \rightarrow \text{Use this to prove (3)}$$

- The average kinetic energy of the system is related to the temperature,

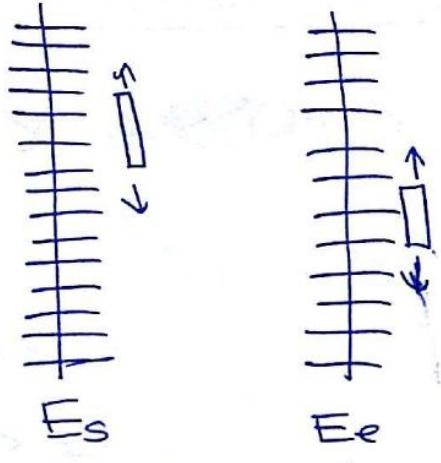
*
$$T = \frac{2 \langle K \rangle}{3 \cdot N \cdot k_B} \quad \begin{array}{l} \text{Average} \\ \text{kinetic} \\ \text{energy.} \end{array}$$

\Rightarrow To keep the system at a constant temperature T , $\langle K \rangle$ should be constant.

* Closed System:



$$E_s + E_e = \text{constant}$$



- The system's energy can vary since it's no longer isolated.

⇒ How does it vary? Given,

Microstate probability $P(E_i) \propto e^{-\frac{E_i}{k_B T}}$, $\beta = \frac{1}{k_B T}$

$$\Rightarrow P(E_i) = A e^{-\beta E_i}$$

- $\sum_{\text{all energy levels}} P(E_i) = 1 \Rightarrow A = \frac{1}{\sum_{\text{all energy levels}} e^{-\beta E_i}}$

$$\Rightarrow P(E_i) = \frac{e^{-\beta E_i}}{\sum_{\text{all energy levels}} e^{-\beta E_j}} \{ Z \}$$

* $Z \equiv \sum_{\text{all energy levels}} e^{-\beta E_j}$ = Partition function of system.

- Given Z , we can calculate all thermodynamic properties.

* Internal Energy $\Rightarrow -\frac{\partial \ln Z}{\partial \beta} = \sum_{\text{all energy levels}} E_i e^{-\beta E_i}$

$$\frac{\sum_{\text{all energy levels}} E_i e^{-\beta E_i}}{\sum_{\text{all energy levels}} e^{-\beta E_i}} = \sum_{\text{all energy levels}} E_i P(E_i)$$

$$1) \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \text{Internal Energy of the System}$$

* 2) Fluctuation in energy

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle \\ &= \langle E^2 + \langle E \rangle^2 - 2 E \langle E \rangle \rangle \\ &= \langle E^2 \rangle + \langle E \rangle^2 - 2 \langle E \rangle \langle E \rangle \\ &= \underbrace{\langle E^2 \rangle}_{\substack{\text{what} \\ \text{is this?}}} - \underbrace{\langle E \rangle^2}_{\substack{\text{we know this}}} \end{aligned}$$

From (1), $-\frac{\partial \ln Z}{\partial \beta} \cdot Z = \sum E_i e^{-\beta E_i}$

$$\Rightarrow -\frac{\partial}{\partial \beta} \left(\sum E_i e^{-\beta E_i} \right) = + \left[Z \frac{\partial^2 \ln Z}{\partial \beta^2} + \frac{\partial \ln Z}{\partial \beta} \frac{\partial Z}{\partial \beta} \right]$$

$$\Rightarrow \sum E_i^2 e^{-\beta E_i} = \left[Z \frac{\partial^2 \ln Z}{\partial \beta^2} + \frac{\partial \ln Z}{\partial \beta} \frac{\partial Z}{\partial \beta} \right]$$

Divide by Z on both sides,

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

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

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

3) Heat capacity (at const volume (C_V))

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

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

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

Here, $\frac{\partial \langle E \rangle}{\partial T} = C_V \rightarrow$ Heat capacity of the system at constant volume.

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

$$\left(\beta = \frac{1}{K_B T} \right)$$

$$\therefore \frac{\partial T}{\partial \beta} = -\frac{1}{K_B \beta^2}$$

$$\therefore \langle E^2 \rangle - \langle E \rangle^2 = C_V \cdot K_B \cdot T^2$$

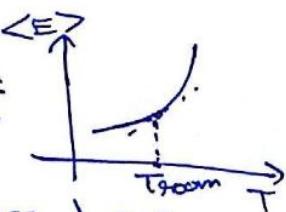
$$\langle \Delta E \rangle^2 = \langle (E - \langle E \rangle)^2 \rangle$$

LHS is always positive (can be zero)

$\Rightarrow C_V$ should be positive for all systems

_____ x _____

* Experimental determination of C_V :



• $\langle E \rangle$ is measured at different temperatures.

\Rightarrow Calculate slope of $\langle E \rangle$ vs T at a given temperature. $(C_V = \frac{\partial \langle E \rangle}{\partial T})$

- Theoretically C_V can be calculated by measuring/monitoring the time evolution E_i at a given temperature.

4) Entropy:

* $S = k_B \ln \Omega \quad \{ \text{Boltzmann's formula}$

- Shannon's entropy

$$S = -k_B \sum p_i \ln(p_i)$$

where p_i = Probability of finding the system at a given microstate.

\Rightarrow For an isolated system,

$$p_i = \frac{1}{\Omega}$$

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

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

$$\Rightarrow S = k_B \cdot \ln(\Omega) //$$

\Rightarrow For closed systems,

$$p_i = \frac{e^{-\beta E_i}}{Z}$$

$$S \Rightarrow -k_B \cdot \sum_i e^{-\beta E_i} \ln \left(\frac{e^{-\beta E_i}}{Z} \right)$$

$$S = k_B \left[\beta \sum_i E_i p_i + \ln Z \right] //$$

$$\Rightarrow S = K_B \left[\beta \langle E \rangle + \ln Z \right]$$

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

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

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

$$= K_B \cdot \sum_i \frac{e^{-\beta E_i}}{Z} (\beta E_i + \ln Z)$$

$$= K_B \cdot \left[\sum_i p_i \cdot \beta \cdot E_i + \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z \right]$$

$$= K_B \left[\beta \sum_j E_j p_j + \frac{\ln Z}{Z} \right]$$

$$\therefore \boxed{S = K_B [\beta \langle E \rangle + \ln Z]}$$

- Now, consider

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

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

~~# 5).~~ Helmholtz free energy:

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

$$\boxed{F = -K_B \cdot T \cdot \ln Z}$$

? hour

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

Average pressure \downarrow Volume of the system

* System with continuous energy spectrum:

- N atoms

- Potential energy, $U = (\bar{q}_1, \bar{q}_2, \dots, \bar{q}_N)$

- Kinetic energy, $K = (\bar{p}_1, \bar{p}_2, \dots, \bar{p}_N)$

$$\Rightarrow \text{Partition function}, Z = \prod_{i=1}^N \int_{\{\bar{q}_i\}} \int_{\{\bar{p}_i\}} e^{-\beta H(\bar{q}_i, \bar{p}_i)} \cdot d(\bar{q}_i) \cdot d(\bar{p}_i)$$

$H = \text{Hamiltonian.}$

$$\Rightarrow Z = \frac{1}{h^{3N}} \prod_{i=1}^N \int_{\{\bar{q}_i\}} \int_{\{\bar{p}_i\}} e^{-\beta U(\bar{q}_i, \dots, \bar{q}_N)} \cdot e^{-\frac{\beta}{2m} \sum_{i=1}^N \bar{p}_i \cdot \bar{p}_i} \cdot d(\bar{q}_i) \cdot d(\bar{p}_i)$$

$$\Rightarrow Z = \frac{1}{h^{3N}} \prod_{i=1}^N \int_{\{\bar{q}_i\}} \int_{\{\bar{p}_i\}} e^{-\frac{\beta}{2m} \sum_{i=1}^N \bar{p}_i \cdot \bar{p}_i} \times e^{-\beta U(\bar{q}_1, \dots, \bar{q}_N)} \cdot d(\bar{q}_i) \cdot d(\bar{p}_i)$$

↓ —————— κ ——————

* * Ideal gas of N atoms in a volume V:

$$U(\bar{q}_1, \bar{q}_2, \dots, \bar{q}_N) = 0$$

$$\Rightarrow Z = \frac{1}{h^{3N}} \prod_{i=1}^N \int_{\{\bar{q}_i\}} d(\bar{q}_i) \int_{\{\bar{p}_i\}} e^{-\frac{\beta}{2m} \sum_{i=1}^N \bar{p}_i \cdot \bar{p}_i} \cdot d(\bar{p}_i)$$

$$\therefore Z = \frac{V^N}{h^{3N}} \left(\int_{p=-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} \cdot dp \right)^{3N}$$

$$\Rightarrow \text{We know, } \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\Rightarrow Z = \frac{V^N}{h^{3N}} \cdot \left(\frac{2\pi m}{B} \right)^{\frac{3N}{2}}$$

Now consider, $\langle P \rangle = \frac{1}{B} \frac{\partial (\ln Z)}{\partial V}$

$$\begin{aligned}\Rightarrow \langle P \rangle &= \frac{1}{B} \cdot \frac{1}{Z} \frac{\partial Z}{\partial V} \\ &= \frac{1}{B} \cdot \frac{1}{\cancel{const} \cdot V^N} \cdot N \cdot V^{N-1} \\ &= \frac{1}{B} \cdot \frac{N}{V} = k_B \cdot T \cdot \frac{N}{V}\end{aligned}$$

$$\Rightarrow \langle P \rangle V = k_B \cdot T \cdot N$$

$$\Rightarrow \boxed{\langle P \rangle V = N \cdot k_B \cdot T} \rightarrow \text{Equation of state for an ideal gas.}$$

* Now $C_V = \frac{\partial (\langle E \rangle)}{\partial T}$

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

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

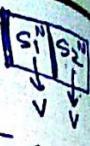
$$\text{Now } C_V = \frac{\partial (\langle E \rangle)}{\partial T} = \frac{\partial \left(\frac{3N}{2} k_B \cdot T \right)}{\partial T}$$

$$\Rightarrow C_V = \frac{3N}{2} k_B \quad \left(C_V = \frac{3R}{2} \right)$$

\uparrow
Independent of T for ideal gases.

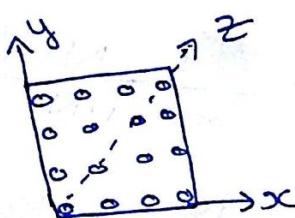
Note: Gibbs Paradox $\rightarrow S \neq S_1 + S_2$

* (Exam) solved by considering $Z_{\text{new}} = \frac{Z}{N!}$
(Split closed system into 2 parts)



(Stirlings approx: $\log N! = N \log N - N$)

* Heat Capacity of Solids:



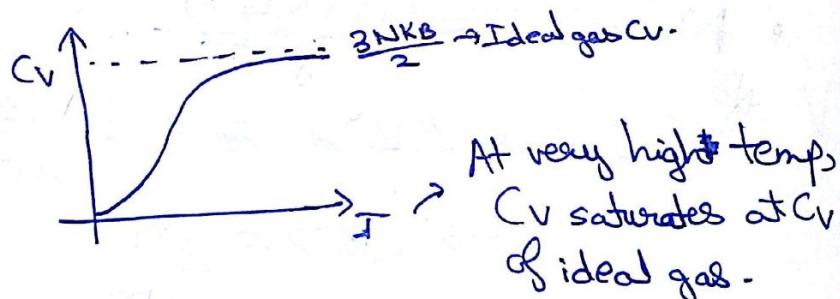
- N atoms in solid
- Vibrations of atoms can be considered as $3N$ different harmonic oscillators.

$$\Rightarrow E_n = (n + \frac{1}{2})\hbar\omega \quad \text{where } \hbar = \frac{h}{2\pi}$$

$C_V = 3 \times N \times C_{V,1}$ Each harmonic oscillator
 $n=0, 1, 2, \dots$

- We then calculate Z and C_V .

\Rightarrow Unlike C_V of ideal gases which is constant here C_V varies based on temperature.



* 1-D Harmonic Oscillator: (Closed System) (Classical)

$$\bullet U(x) = \frac{1}{2} k(x - x_0)^2$$

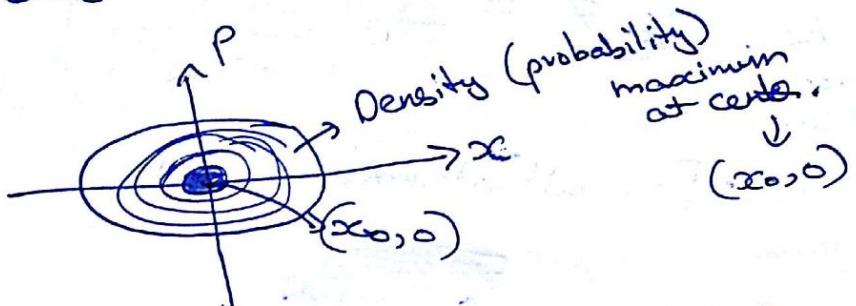
$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} k(x - x_0)^2$$

For closed system!

$$\Rightarrow P(x, p) \propto e^{-\beta E} \rightarrow \text{Probability in phase space}$$

$$\Rightarrow P(x, p) \propto e^{-\beta \left[\frac{p^2}{2m} + \frac{1}{2} k(x-x_0)^2 \right]} \times e^{-\frac{\beta p^2}{2m}} \cdot e^{-\frac{\beta k}{2}(x-x_0)^2}$$

- This probability is maximum when $p=0$, $x = x_0$



(Note: For isolated system $P(x, p) = \frac{1}{n(E)}$)

* Heat capacity of Harmonic Oscillators: (Normal)
(Classical)

* $3N$ classical oscillators, with spring constants
(Independent oscillators)

k .

$$\Rightarrow Z = \sum_{\text{all energies}} e^{-\beta E_j}$$

$$\bullet U(x_0, y_0, z_0) = \frac{1}{2} k (x - x_0)^2 + \frac{1}{2} k (y - y_0)^2 + \frac{1}{2} k (z - z_0)^2$$

$$\Rightarrow H = U + K = \left(\frac{1}{2} k x^2 + \frac{1}{2} k y^2 + \frac{1}{2} k z^2 + \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right) N$$

For all atoms

$$\Rightarrow \text{Partition function } Z = \frac{1}{h^{3N}} \left\{ \int_{\{x\}} e^{-\beta H(\{x, p\})} \cdot d(\{x\}) \cdot d(\{p\}) \right\}$$

$$\Rightarrow Z = \frac{1}{h^{3N}} \left(\int e^{-\frac{\beta k x^2}{2}} dx \cdot \int e^{-\frac{\beta k y^2}{2}} dy \cdot \int e^{-\frac{\beta k z^2}{2}} dz \cdot N \cdot \int e^{-\frac{\beta p_x^2}{2m}} dp_x \cdot \int \dots \right)$$

~~We know~~ We know $I = \int e^{-\frac{E}{kT}} dE = \frac{1}{\sqrt{\pi}}$

$$\therefore Z = \frac{1}{h^{3N}} \cdot \left(\frac{2\pi}{Bk} \cdot \frac{2\pi}{Bk} \cdot \frac{2\pi}{Bk} \cdot \left(\frac{\sqrt{2\pi m}}{B} \right)^3 \right)^N$$
$$Z = \frac{1}{h^{3N}} \left(\frac{(2\pi)^3 \cdot m^{3/2}}{B^3 k^{3/2}} \right)^N$$

- For all atoms, we get

~~for~~

$$Z = \left(\frac{2\pi}{Bh} \right)^{3N} \cdot \left(\frac{m}{k} \right)^{3N/2}$$

$$\Rightarrow \langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} = - \frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta}$$

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

$$\bullet C_V = \frac{\partial \langle E \rangle}{\partial T}, \quad \beta = \frac{1}{k_B T}$$

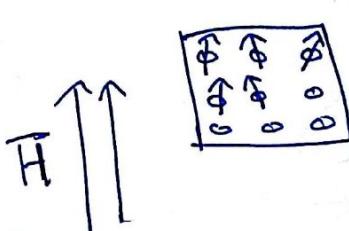
$$\therefore C_V = \frac{\partial}{\partial T} (3Nk_B T) = 3Nk_B$$

~~for~~ ~~for~~

* Paramagnetic Materials:

* H = external magnetic field

* μ = magnetic moment of an atom



$$\cdot \mu = g \cdot \mu_0 \cdot \bar{J}$$

($g = g$ factor of an atom)

($\mu_0 = \text{Bohr magneton}$)

($\bar{J} = \text{Angular momentum of an atom}$)

$$\Rightarrow \mu_0 = \frac{e\hbar}{2me \cdot c} \quad (\text{me = electron mass, } c = \text{speed of light})$$

• Magnetic interaction energy of an atom, $E = -\mu \cdot H$

(Atoms do not interact with each other)

• If magnetic field is only along z -axis,

$$E = -g \mu_0 J_z \cdot H$$

$\Rightarrow J_z$ can only take discrete values

(Q-Mech
science 1)
Notes

$$J_z = \underbrace{-J, -J+1, \dots, J-1, J}_{2J+1 \text{ values}}$$

(Only those J 's allowed whose components along z (J_z) are one of above).

• Partition function of an atom $Z_\alpha = \sum_{J_z=-J}^J e^{+\beta g \mu_0 J_z H}$

$$\Rightarrow \eta = \beta g \mu_0 H \quad \} \text{ Consider}$$

$$* \therefore Z_\alpha = \sum_{J_z=-J}^J e^{n J_z} \quad \} \text{ For } \alpha^{\text{th}} \text{ atom.}$$

$$Z_\alpha = \frac{e^{-nJ} - e^{n(J+1)}}{1 - e^n} \quad (\text{G.P series sum})$$

$$\bullet Z_\alpha = \frac{e^{-n(J+1/2)} - e^{n(J+1/2)}}{e^{-n/2} - e^{n/2}}$$

$$Z_\alpha = \frac{\sinh((J+1/2)n)}{\sinh(n/2)}$$

$$\Rightarrow \ln Z_\alpha = \ln \sinh((J+1/2)n) - \ln \sinh(n)$$

$\bullet M_i$ = Magnetic moment of i^{th} atom

$$M = \sum_{i=1}^N M_i \quad \{ \text{Magnetization}$$

$M = 0$ in paramagnetic substances
(Since magnetic moments are randomly aligned)

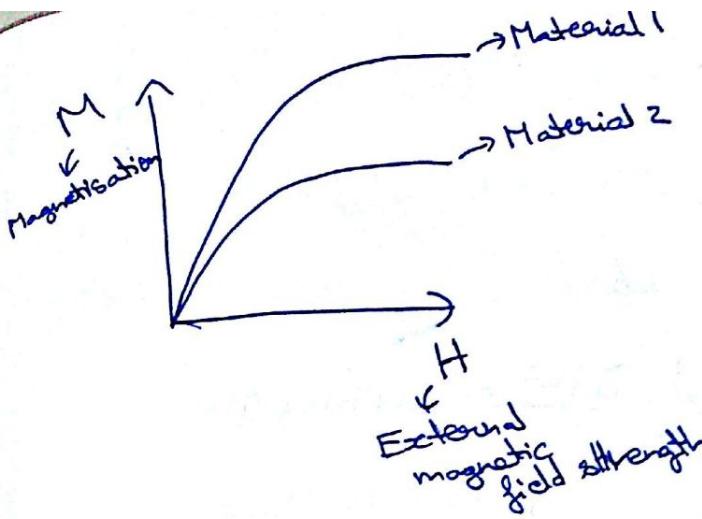
1) \Rightarrow Ferromagnetic substances,

$|M| \neq 0$, the magnetic moments are aligned in a certain manner.

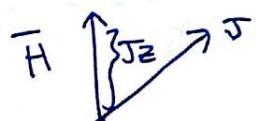
* 2) Paramagnetic substances,

$|M| = 0$ in the absence of external magnetic field

$|M| \neq 0$ in the presence of a magnetic field.



$$\Rightarrow \langle \mu \rangle = \frac{1}{N} \sum_{i=1}^N \mu_i$$



$\epsilon = -\mu \cdot H$ if H is along z -axis.
 $\epsilon \propto J_z H$

$$\Rightarrow J_z = -J, -J+1, \dots, J \quad (2J+1 \text{ values})$$

$$\Rightarrow Z_\alpha = \sum_{J_z=-J}^J e^{\beta g H_0 J_z H} = \frac{\sinh((J+1/2)n)}{\sinh(n/2)}$$

For α^{th} atom
 $\ln Z_\alpha = n \ln \sinh((J+1/2)n) - n \ln \sinh(n/2)$

$$\Rightarrow M_z = g H_0 J_z \quad \text{From earlier}$$

$$\langle M_z \rangle = g H_0 \langle J_z \rangle$$

$$\boxed{\langle M_z \rangle = \frac{1}{\beta} \cdot \frac{\partial \ln Z_\alpha}{\partial H}} \rightarrow \text{Prove this} \rightarrow ①$$

$$\Rightarrow \frac{\partial \ln Z_\alpha}{\partial H} = \frac{1}{Z_\alpha} \cdot \frac{\partial Z_\alpha}{\partial H} = \frac{1}{Z_\alpha} \cdot$$

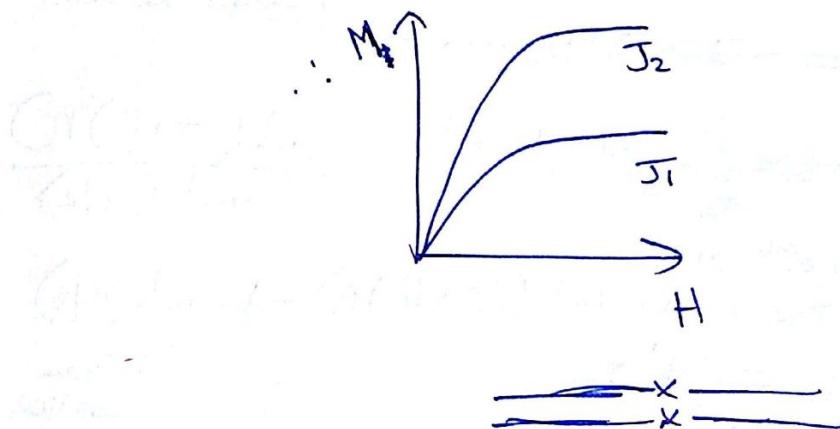
$$\Rightarrow \langle M_z \rangle = \frac{1}{\beta} \frac{\partial \ln z_\alpha}{\partial H} \rightarrow \text{Using } ①,$$

↓

Mean
magnetization
of the α th atom

$$\langle M_z \rangle = g \mu_0 \left[\frac{(J + \frac{1}{2}) \cosh((J + \frac{1}{2})n)}{\sinh(J + \frac{1}{2})n} - \frac{1}{2} \frac{\cosh n}{\sinh \frac{n}{2}} \right]$$

$$\Rightarrow M = N \langle M_z \rangle \quad (\text{Assume they are non-interacting atoms})$$



- For different substances, J 's differ and therefore M, H even vary.

Note: $\langle A(\{\bar{r}_{ij}\}, \{\bar{p}_{ij}\}) \rangle_{\text{time}}$ } Time average of the function



$$\langle A \rangle_{\text{ensemble}} = \iint_{\{\bar{r}_{ij}\} \{\bar{p}_{ij}\}} A(\{\bar{r}_{ij}\}, \{\bar{p}_{ij}\}) \cdot P(\{\bar{r}_{ij}\}, \{\bar{p}_{ij}\}) \cdot d\{\bar{r}_{ij}\} \cdot d\{\bar{p}_{ij}\}$$

ex: $\langle x \rangle_{\text{time}} = \frac{1}{N} \sum_{i=1}^N x_i$ } Roll a die

↑ N experiments with single die

$$\langle x \rangle_{\text{ensemble}} = \frac{1}{Ns} \cdot \sum_{i=1}^{Ns} x_s = \sum_{i=1}^{Ns} p_i \cdot x_i //$$

• Statistical mechanics says,

* $\langle x \rangle_{\text{time}} = \langle x \rangle_{\text{ensemble}}$

(This is ergodicity | ergodic theory)

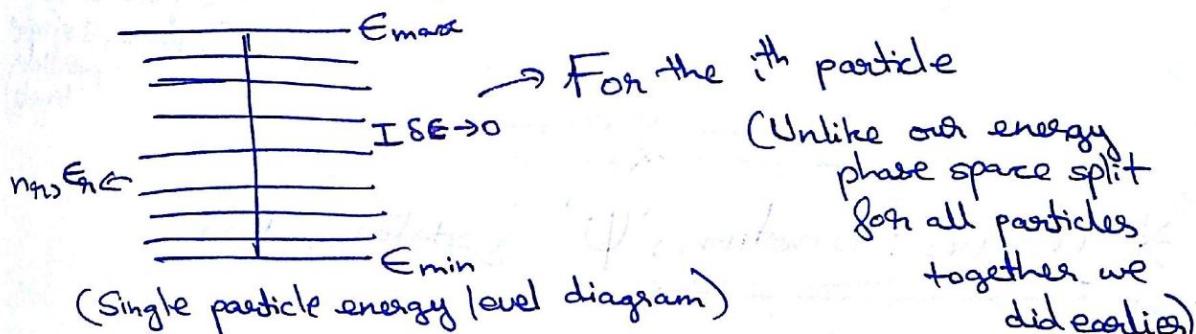
===== X =====

Quantum Statistics:

- Maxwell - Boltzmann statistics [Classical gases]
- Fermi - Dirac statistics [Fermions]
- Bose - Einstein statistics [Bosons]

Single Particle energy states / levels

- Potential energy of i^{th} atom = U_i
- Kinetic energy of i^{th} atom = K_i
- Hamiltonian for i^{th} atom $E_i = U_i + K_i$



- n_g = No. of atoms with energy E_g

$\Rightarrow \langle n_g \rangle =$ mean number of atoms to be found
in a state with energy E_g .

Changes with time, different for fermions/bosons ~~& classical~~ particles

$N=2$ • Consider 3 single particle levels
 (Consider 2 particles) (E_1, E_2, E_3)

- Particles are distinguishable (O ⊗)

(How many ways can we distribute these particles in the energy levels?)
 $\hookrightarrow 3 \times 3 = 9$ states possible

* Maxwell-Boltzmann Statistics (MB Statistics)

- Particles are distinguishable (9 possibilities $N=2, 3$ single particle levels)
- $n_g = 0, 1, 2, \dots, N$

* Bose-Einstein Statistics (BE Statistics)

- Particles are indistinguishable (6 possibilities $N=2, 3$ single particle levels)
- $n_g = 0, 1, 2, \dots, N$

* Fermi-Dirac Statistics (FD Statistics)

- Particles are indistinguishable
- Particles will satisfy the Pauli's exclusion principle
 $(n_g = 0 \text{ or } 1)$

(3 possibilities
 $N=2, 3$ single particle levels)



* Wave Function: ' Ψ ' { State function

- $\Psi(\vec{r}, t) \rightarrow$ Position space
- $\Psi(\vec{p}, t) \rightarrow$ Momentum space

→ Eigen value equation,

$$\hat{A} \Psi \xrightarrow{\substack{\text{Eigen function} \\ \downarrow \text{Operator}}} a \Psi$$

→ Eigen value { Operator's result

- i) position operator $\hat{x} \rightarrow x$ (self operator)
- ii) momentum $\hat{p} \rightarrow i\hbar \frac{\partial}{\partial x}$ Gradient in multiple dimensions.
- iii) Kinetic energy $\hat{K} \rightarrow \frac{\hbar^2}{2m} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2$

$$\hat{K} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Laplacian in multiple dimensions

* Schrodinger Wave function:

$$\hat{H}\psi = E\psi$$

- $\hat{H} = \hat{K} + \hat{V}$ } Kinetic + Potential

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

* $\Rightarrow \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi = E\psi$ } Time independent

- In 3D,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] \psi = E\psi$$

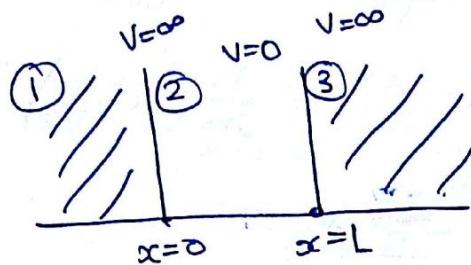
ψ = Solution of this S.W equation.

\Rightarrow Considering time dependence,

$$\hat{H}\psi = E\psi = i\hbar \frac{\partial}{\partial t} \psi$$

* $\Rightarrow \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t) = i\hbar \frac{\partial}{\partial t} \psi(x,t)$

* Particle in a 1-D Box:



- Regions ① & ③ are prohibited.
- In Region ②, $V=0$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + 0 = E\psi \rightarrow ①$$

$$\bullet \frac{d\psi^2}{dx^2} = -k^2\psi(x) \rightarrow ②$$

From ①, ②, $k^2 = \frac{2mE}{\hbar^2}$

$$\psi(x) = A\sin(kx) + B\cos(kx) \quad \left. \begin{array}{l} \\ \text{Consider this} \end{array} \right\}$$

Boundary conditions:

$$\bullet \text{At } x=0, \psi(x)=0$$

$$0 = A\sin(0) + B\cos(0) = B \quad \therefore B=0$$

$$\psi(x) = A\sin(kx)$$

$$\bullet \text{At } x=L, 0 = A\sin(kL)$$

$$kL = n\pi \quad \text{where } n=0, 1, 2, \dots$$

$$\therefore k = \frac{n\pi}{L}, \quad k \neq 0 \text{ since } \psi = 0 \text{ if } k=0$$

$$\therefore n=1, 2, \dots$$

~~Zero Point Energy~~ ~~If $n=0$, $E \neq 0$~~

$$k^2 = \frac{2mE}{\hbar^2}, \quad k = \frac{n\pi}{L}, \quad n=1, 2, \dots$$

$$E = \frac{\hbar^2 \cdot n^2 \pi^2}{L^2 \cdot 2m} \doteq \frac{\hbar^2 \cdot n^2 \cdot \pi^2}{4\pi^2 \cdot L^2 \cdot 2m}$$

$$\Rightarrow E = \frac{\hbar^2 n^2}{8mL^2}, \quad n=1, 2, \dots$$

- In classical mechanics $n=0$ is allowed and if $n=0, E=0$.
- Here $E \neq 0$ so n starts from 1.

? ~~Zero Point Energy~~

⇒ Quantization of energy:

* \rightarrow As $n \uparrow$, energy gap \uparrow
 \rightarrow Energy only occurs in these quantized states.

$$\bullet \psi(x) = A \sin(kx)$$

$$\int_0^L \psi^2 dx = 1 \Rightarrow \int_0^L A^2 \sin^2 kx dx = 1$$

Wave function must satisfy the

$$\Rightarrow \cos 2kx = 1 - 2 \sin^2 kx$$
$$\sin^2 kx = \frac{1 - \cos 2kx}{2}$$

$$\therefore \int_0^L \psi^2 dx = \int_0^L \frac{A^2(1 - \cos 2kx)}{2} dx = \frac{A^2}{2} \left[x - \frac{A^2 \sin 2kx}{2 \cdot 2k} \right]_0^L$$

$$\Rightarrow 1 = \frac{A^2}{2} \left[L - \frac{\sin 2kL}{2k} - 0 + 0 \right]$$

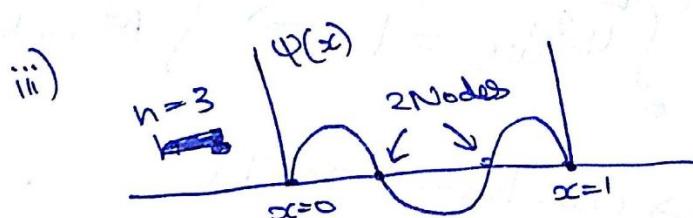
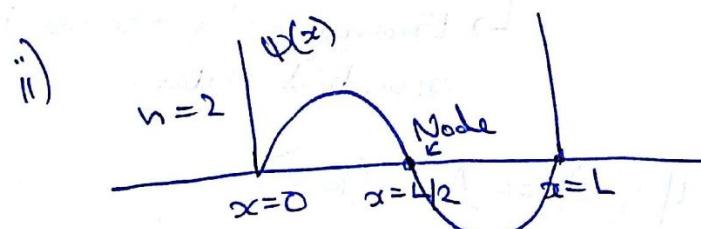
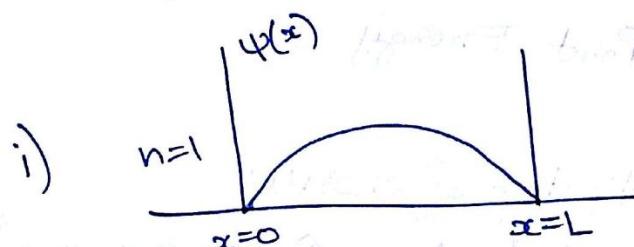
$$\Rightarrow \frac{A^2}{2} \left[L - \frac{1}{2k} \sin(2n\pi) \right] = 1 \quad (k = n\pi)$$

$$\Rightarrow \frac{A^2 L}{2} = 1$$

$$\therefore A = \sqrt{\frac{2}{L}}$$

We have derived our wave functions,

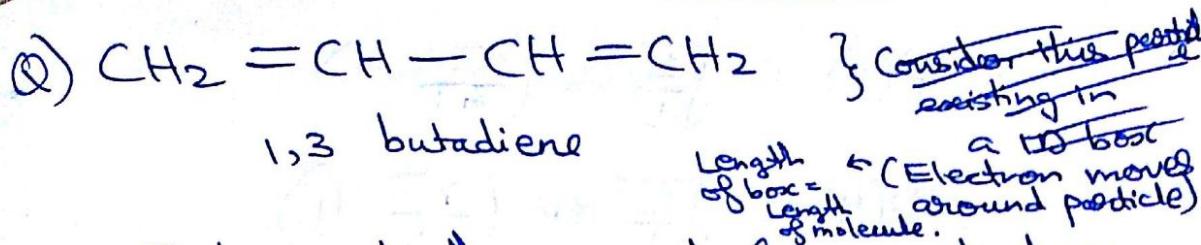
$$\Psi(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi}{L}x\right)$$



\Rightarrow At some n , we have $n-1$ nodes

- As n increases, nodes increase

- * \hookrightarrow This is continuum for very high value of n .



- Find wavelength required for an electron to move from $n=2$ to $n=3$
 (Box length = Molecule length)

$$\bullet E = \frac{n^2 h^2}{8mL^2} \rightarrow E_3 - E_2 = h\nu = \frac{hc}{\lambda}$$

$$\Rightarrow \frac{9h^2}{8mL^2} - \frac{4h^2}{8mL^2} = \frac{hc}{\lambda} = \frac{5h^2}{8mL^2}$$

$$\Rightarrow \lambda = \frac{8mcL^2}{5h}$$

* • C-C, C=C average bond length is 1.4 \AA

$$\Rightarrow m = 9.1 \times 10^{-31} \text{ kg} \} \text{ mass of electron}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

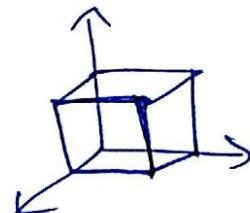
$$h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kg/s}, \lambda =$$

$$\Rightarrow L = 4 \times 1.4 \text{ \AA}$$

————— X —————

* Particle in 3D Box:

$$\rightarrow H\Psi = E\Psi$$



$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) = E\Psi$$

$$\Rightarrow \Psi(x, y, z) = X(x) \cdot Y(y) \cdot Z(z) \} \text{ They can be considered independently.}$$

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

$$\Psi(y) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} \cdot y\right)$$

$$\Psi(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} \cdot z\right)$$

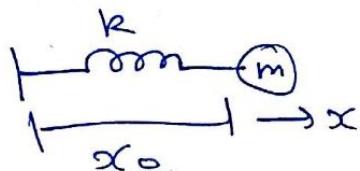
$$\therefore \Psi(x, y, z) = \frac{2\sqrt{2}}{\sqrt{L^3}} \cdot \sin\left(\frac{n\pi x}{L}\right) \cdot \sin\left(\frac{n\pi y}{L}\right) \cdot \sin\left(\frac{n\pi z}{L}\right)$$

— x —

* Harmonic Oscillator:

- $F = -kx$

$$F = -\frac{dV}{dx}$$



$$\Rightarrow V = - \int F dx \quad \{ \text{Potential}$$

$$V = \int kx dx = \frac{1}{2} kx^2 = \frac{1}{2} m\omega^2 x^2$$

$(\omega = \sqrt{\frac{k}{m}})$

$$\Rightarrow \hat{H} = \hat{K} + \hat{V}$$

$$\hat{K} = \frac{\hat{p}^2}{2m}$$

$$\Rightarrow (\hat{K} + \hat{V})\Psi = E\Psi$$

$$\hat{p} = -i\hbar \frac{d}{dx}$$

$$\therefore \frac{-\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \Psi = E\Psi$$

$$\Rightarrow \frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} m\omega^2 x^2 \right) \Psi = 0$$

(Differential equation)

①

$$\text{Let } y = \left(\frac{m\omega}{\hbar}\right)^{1/2} x, \quad \lambda = \frac{2E}{\hbar\omega}$$

$$\Rightarrow \frac{d^2\psi}{dy^2} + (\lambda - y^2)\psi = 0 \quad \begin{matrix} \text{(After substituting)} \\ \text{in (1)} \end{matrix} \quad \rightarrow (2)$$

(As a simplified case)

$$\text{If } y \rightarrow \infty \rightarrow \frac{d^2\psi}{dy^2} - y^2\psi = 0 \rightarrow (3)$$

$\psi = e^{\pm y^2/2}$ is a solution to (3)

- If $\psi = e^{y^2/2}$ then $y \rightarrow \infty \Rightarrow \psi \rightarrow \infty$,
but ψ should have valid values
(should not diverge)
- ∴ $\psi = e^{-y^2/2}$ } This is an approx
solution to (3)

⇒ We now assume that the actual
solution is,

$$\psi = e^{-y^2/2} \cdot H(y) \rightarrow (4)$$

- Substituting (4) in (2),

$$\frac{d\psi}{dy} = e^{-y^2/2} \cdot \frac{d(H)}{dy} + e^{-y^2/2} \cdot -\frac{2y}{2} \cdot H$$

$$\Rightarrow \frac{d^2\psi}{dy^2} = e^{-y^2/2} \frac{d^2H}{dy^2} + \frac{dH}{dy} \cdot e^{-y^2/2} \cdot -y \cdot \frac{dH}{dy}$$

$$+ e^{-y^2/2} \cdot -y \cdot \frac{dH}{dy} + H \cdot \left(e^{-y^2/2} \cdot -1 \right)$$

$$\Rightarrow \frac{d^2H}{dy^2} - 2y \frac{dH}{dy} + (\lambda - 1)H = 0 \rightarrow (5)$$

(Hermite Differential Eqn)

Series solution $\Rightarrow H_n(y) = \sum_{n=0}^{\infty} a_n y^n$
 (Often used to solve differential equations)

• Substituting equation ⑤ in ⑤ \rightarrow ⑥

$$\Rightarrow \frac{dH}{dy} = \sum_{n=0}^{\infty} n a_n y^{n-1}$$

$$\frac{d^2H}{dy^2} = \sum_{n=0}^{\infty} n(n-1) a_n y^{n-2}$$

$$\Rightarrow \sum_{n=0}^{\infty} n a_n (n-1) y^{n-2} - 2y \sum_{n=0}^{\infty} n a_n y^{n-1} + \sum_{n=0}^{\infty} (\lambda-1) \cdot a_n \cdot y^n = 0$$

$$\Rightarrow \sum_{n=0}^{\infty} a_n \left[(n)(n-1) y^{n-2} - 2ny^{n-1} + (\lambda-1)y^n \right] = 0$$

• Coeff of $y^k = 0$,

$$\Rightarrow a_{k+2} \cdot (k+2)(k+1) + (-2k + \lambda - 1)a_k = 0$$

$$\Rightarrow a_{k+2} = \frac{(2k+1-\lambda)a_k}{(k+2) \cdot (k+1)}$$

• The series terminates when coeff becomes zero.

$$\Rightarrow n \rightarrow \text{Finite num of terms } \} \text{ After this it terminates}$$

$$2n+1-\lambda = 0 \Rightarrow \lambda = 2n+1$$

$$\Rightarrow \lambda = \frac{2E}{\hbar\omega} \Rightarrow 2n+1 = \frac{2E}{\hbar\omega}$$

$$\Rightarrow E = \left(n + \frac{1}{2}\right)\hbar\omega, E_{n+1} - E_n = \hbar\omega$$

∴ For the simple harmonic oscillator, we have shown that the energy is quantized and separation b/w energy levels is always $\hbar\omega$.

$$\Rightarrow \Psi_n = e^{-y^2/2} \cdot H_n(y) \cdot N_n, \int \Psi^* \Psi = 1$$

↑
Normalizing constant

• Hermite Polynomials,

$$H_0(y) = 1$$

$$H_1(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

$$H_3(y) = 8y^3 - 12y$$

$$H_n(y) = (-1)^n \exp(y^2) \frac{d^n \exp(-y^2)}{dx^n}$$

• Normalisation constant,

$$N_n = \left[\left(\frac{m\omega}{\hbar\pi} \right)^{1/2} \cdot \frac{1}{2^n \cdot n!} \right]^{1/2}$$

$$\boxed{\Psi_n(y) = \left[\left(\frac{m\omega}{\hbar\pi} \right)^{1/2} \cdot \frac{1}{2^n \cdot n!} \right]^{1/2} \cdot e^{-y^2/2} \cdot H_n(y)}$$

(Substitute back ω into the expression)

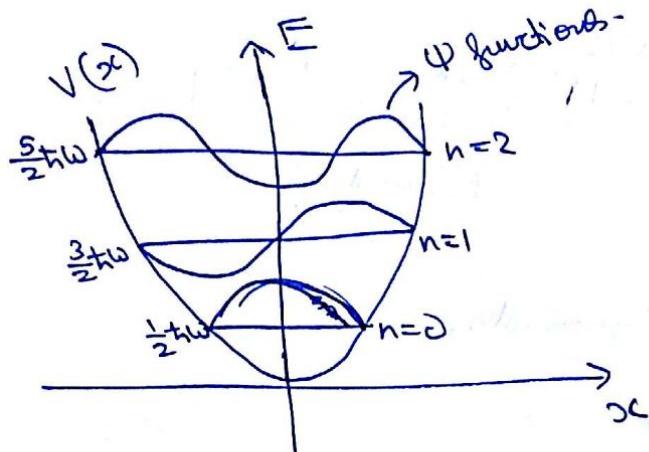
⇒ Ground state wave function, $n=0$

$$\Psi_0(x) = \left(\frac{m\omega}{\hbar\pi} \right)^{1/4} \cdot \exp \left(-\frac{m\omega x^2}{2\hbar} \right)$$

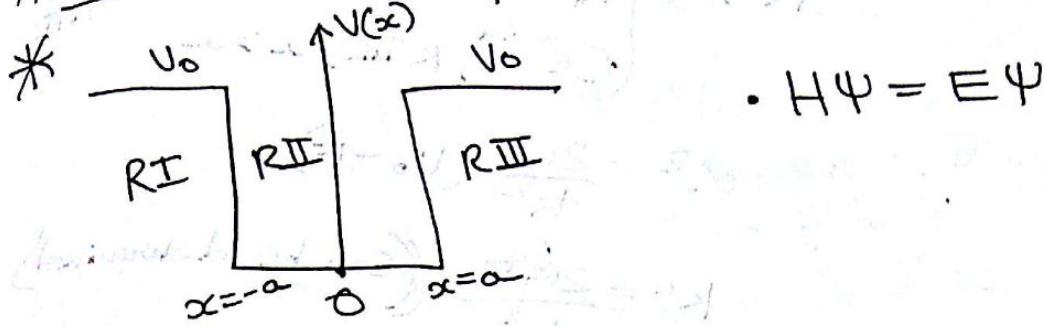


$$V = \frac{1}{2} m \omega^2 x^2, E = (n + \frac{1}{2}) \hbar \omega$$

$$\psi = N_n \cdot e^{-\frac{x^2}{2}} \cdot H_n(y)$$



* Square well potential with finite walls:



$$\cdot H\psi = E\psi$$

R_{II}:

$$\Rightarrow -\frac{\hbar^2}{2m} \cdot \frac{d^2\psi}{dx^2} + 0 = E\psi \quad \left. \begin{array}{l} \text{Use to} \\ \text{determine} \\ k. \end{array} \right\}$$

$$\psi(x) = A\sin kx + B\cos kx$$

(n=1, 3, ...) \Rightarrow Symmetric wave functions
 (n=2, 4, ...) \Rightarrow Anti symmetric wave functions

R_I, III

$$\Rightarrow H\psi = E\psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} (V_0 - E)\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = \alpha^2\psi, \quad \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$E > V_0, \quad E < V_0$$

* Case 1: $E < V_0$

$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x}, \quad \psi(x) \rightarrow \infty \text{ if } D \neq 0$$

$$\underset{R_{III}}{x \rightarrow \infty} \quad \therefore \psi(x) = Ce^{-\alpha x}$$

$$\underset{R_I}{x \rightarrow -\infty}, \quad \psi(x) \rightarrow \infty \text{ if } C \neq 0$$

$$\therefore \psi(x) = De^{\alpha x}$$

$$\therefore \Psi(x) = \begin{cases} De^{\alpha x}, R\text{I}, x < -a \\ A\sin kx + B\cos kx, -a < x < a \\ Ce^{-\alpha x}, R\text{III}, x > a, \end{cases}$$

$$\alpha^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$k^2 = \frac{2mE}{\hbar^2} \quad (\text{Can be determined})$$

Boundary conditions,

i) Consider, Symmetric wave fn: $A=0$

in RI

$$\Psi(x) = B\cos kx$$

Intersection:

$$\cdot \left. \Psi(x) \right|_{RI, x=-a} = \left. \Psi(x) \right|_{R\text{II}, x=-a}$$

$$\cdot \left. \frac{d\Psi}{dx} \right|_{RI, x=-a} = \left. \frac{d\Psi}{dx} \right|_{R\text{II}, x=-a}$$

$$\Rightarrow De^{\alpha x} \Big|_{x=-a} = B\cos kx \Big|_{x=-a}$$

$$\Rightarrow De^{-\alpha a} = B\cos ka$$

$$\Rightarrow \alpha De^{\alpha x} \Big|_{x=-a} = Bk\sin kx \Big|_{x=-a}$$

$$\Rightarrow \alpha De^{-\alpha a} = Bk\sin ka$$

→ ①

ii) Consider, Anti-symmetric wave fn:

Intersection 2

in R III

$$\cdot \left. \Psi(x) \right|_{R\text{III}, x=a} = \left. \Psi(x) \right|_{R\text{II}, x=a}$$

$$\cdot \left. \frac{d\Psi}{dx} \right|_{R\text{III}, x=a} = \left. \frac{d\Psi}{dx} \right|_{R\text{II}, x=a}$$

$$\Rightarrow C e^{-\alpha a} = B \cos k a$$

$$\Rightarrow \alpha C e^{-\alpha a} = \beta B \sin k a \rightarrow ②$$

From ①, ②,

$$C=0 \text{ & } \alpha k \tan k a = \alpha a$$

$$\beta \tan \beta = \gamma$$

ii) Consider, Anti-symmetric wave fn: $B=0$

$$\Psi(x) = A \sin k x$$

Apply same boundary conditions,

$$\Psi(x)|_{R^I, x=-a} = \Psi(x)|_{R^III, x=-a}$$

At $x=-a$,

$$De^{\alpha a} = A \sin k a$$

$$\alpha De^{\alpha a} = Ak \cos k a$$

$$\rightarrow De^{\alpha a} = A \sin k a$$

$$\alpha De^{-\alpha a} = Ak \cos k a$$

$$\Psi(x)|_{R^III, x=a} = \Psi(x)|_{R^II, x=a}$$

replaced \rightarrow exterior $\Psi(x)$

At $x=a$,

$$Ce^{-\alpha a} = A \sin k a$$

$$-\alpha Ce^{-\alpha a} = Ak \cos k a$$

$$\rightarrow Ce^{-\alpha a} = A \sin k a$$

$$-\alpha Ce^{-\alpha a} = Ak \cos k a$$

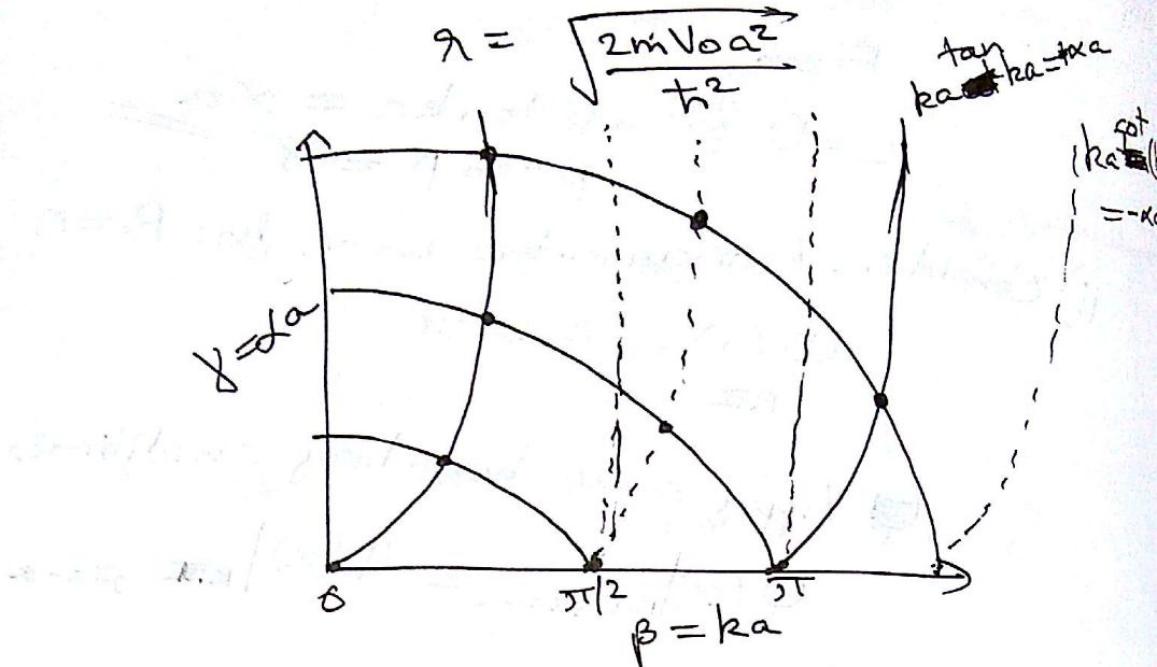
$$C=-0; k a \cot(k a) = -\alpha a$$

$$\beta \cot \beta = -\gamma$$

• Define, $\beta = ka, \gamma = \alpha a$.

$$\Rightarrow \beta^2 + \gamma^2 = k^2 a^2 + \alpha^2 a^2 = (k^2 + \alpha^2) a^2$$

$$\Rightarrow \beta^2 + \gamma^2 = \frac{2mV_0\alpha^2}{t^2} \quad \left. \right\} \text{Equation of circle}$$



For any γ : $0 < \gamma < \pi/2 \rightarrow$ ① intersections symm-1
anti-0
~~in orange~~ $\pi/2 < \gamma < \pi \rightarrow$ ② ~~symm-1~~ anti-1
 $\pi < \gamma < 3\pi/2 \rightarrow$ ③ symm-2, anti-1

* Case 2: $E > V_0$ (see assignment)

$$\psi(x) = A \sin kx + B \cos kx$$

Probability distribution

• Consider a particle moving in a rectangular box of length a and width b .
 • The particle has to start from one corner and end at another corner.
 • The probability of finding the particle at a point x is given by $P(x)$.

Qualitative concepts are also discussed. It is said that if the particle moves randomly, it will eventually cover the entire area of the box.

Qualitatively, the probability distribution is shown as follows:

The shaded region is labeled "most probable".

Postscript: ~~Assignment~~ Standardized with $\frac{1}{\pi}$

Plot $P(a+\Delta x) \text{ vs } V_0$

Note: Assignment: Square well potential with finite walls

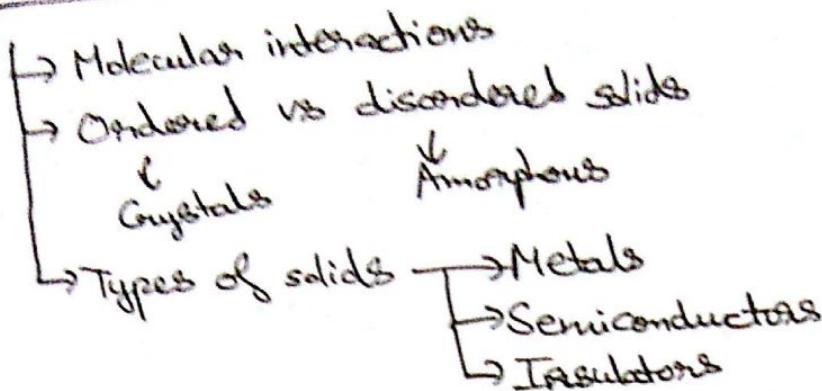
Case 1 $\rightarrow V_0 \rightarrow \infty$

Case 2 $\rightarrow V_0 \rightarrow 0$

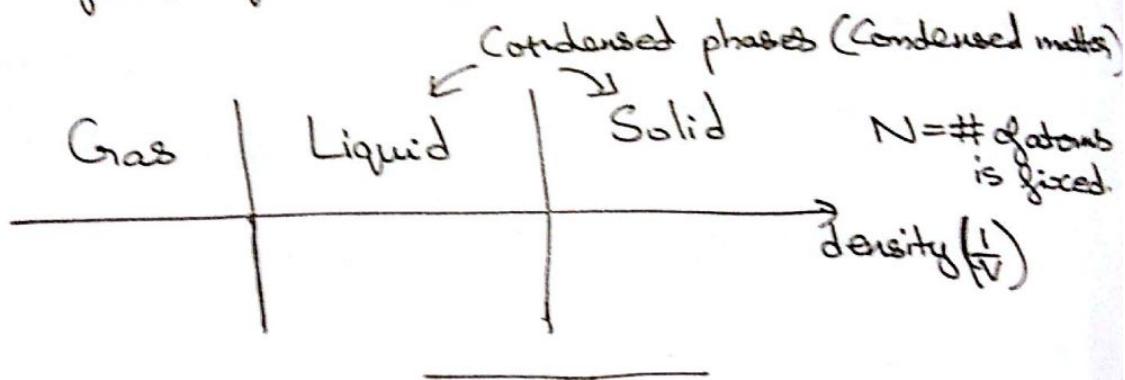
Case 3 $\rightarrow V_0 = 0 \pm \Delta V_0$, $V_0 = \frac{\infty}{\Delta V_0}$ in steps of ΔV_0

• Probability of finding the particle at $x = a + \Delta x$.

Solid State Physics



- In Statistical mech, we ignored interactions between the molecules. Upon cooling an ideal gas, liquids & solids would not form.



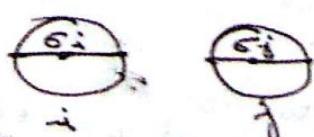
Classical ← Interaction Energy → Quantum

• $U(R_1, R_2, \dots, R_N)$
 R_i = position of i^{th} atom

• $U(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N, \vec{q}_1, \vec{q}_2, \dots, \vec{q}_n)$
 $N = \# \text{ of nuclei}$
 $n = \# \text{ of electrons}$

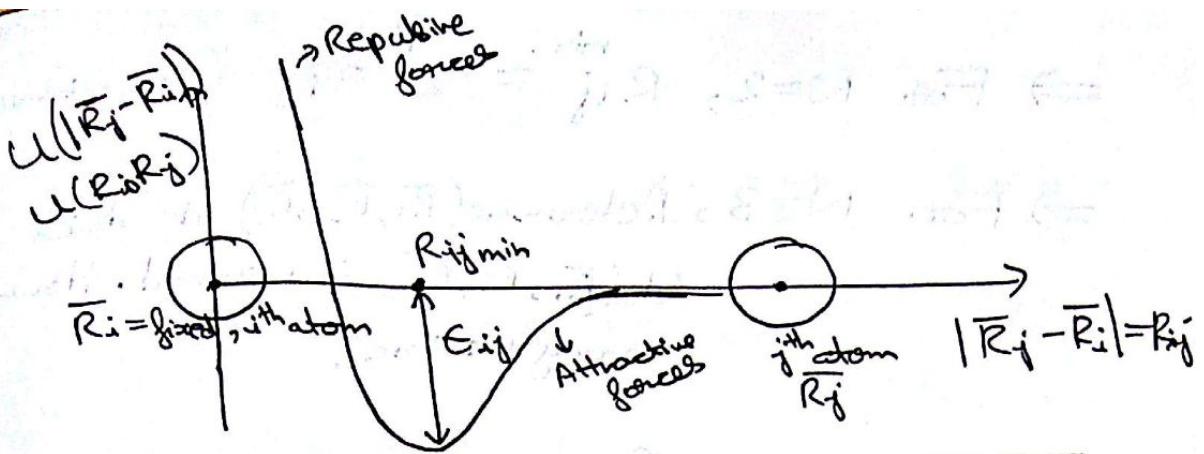
* Van der Waals Solids: (Argon, Krypton)

* • $U(R_i, R_j) = ?$



} Identical atoms

$\sigma_i = \sigma_j \Rightarrow$ Diameter of



$$U(R_{ij}) = 4\pi \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right]$$

$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$ $\rightarrow \epsilon_{ij}$ = Disassociation energy of strength of attraction.

\Rightarrow Find $R_{ij\min}$

$$\frac{dU}{dR_{ij}} = 0$$

$$\frac{dU}{dR_{ij}} = 4\pi \epsilon_{ij} \left[-12 \frac{\sigma_{ij}^{12}}{R_{ij}^3} - 6 \frac{\sigma_{ij}^6}{R_{ij}^7} \right] = 0$$

$$\frac{12 \sigma_{ij}^{12}}{R_{ij}^3} - \frac{6 \sigma_{ij}^6 R_{ij}^6}{R_{ij}^7} = 0$$

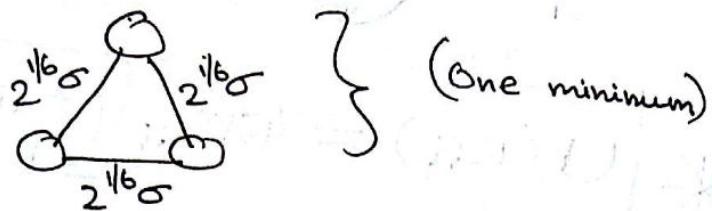
$$\Rightarrow R_{ij} = \infty \text{ or } R_{ij} = 2^{1/6} \sigma_{ij}$$

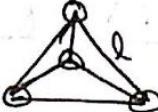
$$R_{ij\min} = 2^{1/6} \sigma_{ij}$$

$\bullet R_{ij\min} > \sigma_{ij}$ } At least energy, the atoms don't touch each other but have a small gap between them.

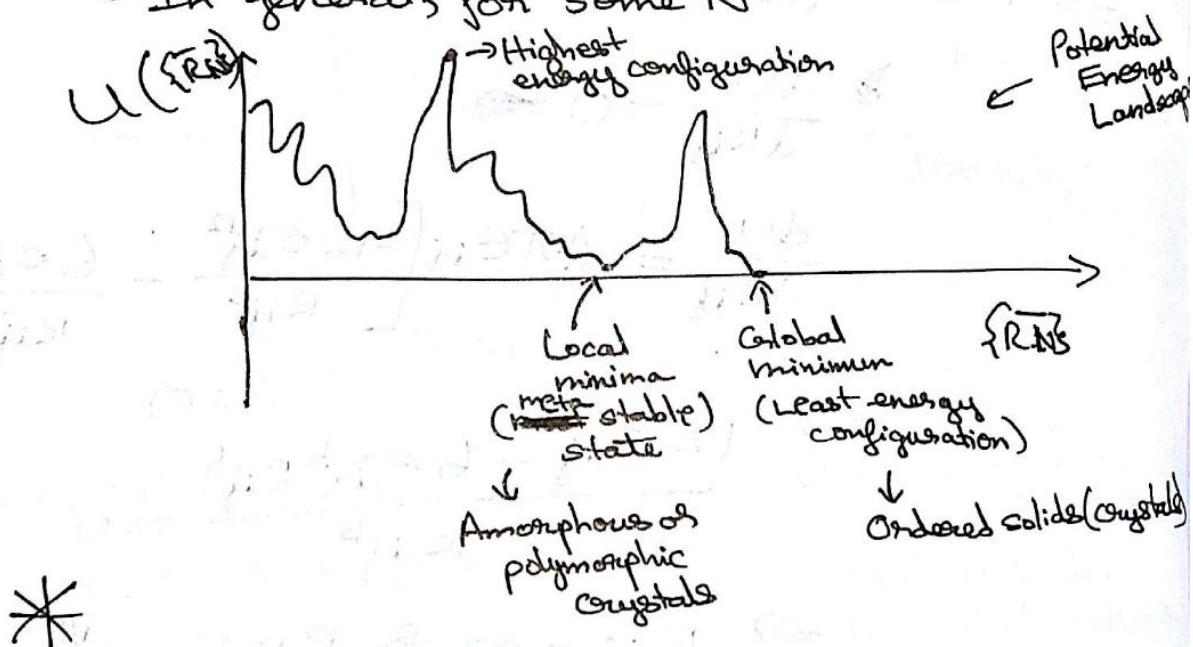
\Rightarrow For $N=2$, $R_{ij}^{\min} = 2^{1/6}\sigma_{ij}$ (One minimum)

\Rightarrow For $N=3$, Determine $(\bar{R}_1, \bar{R}_2, \bar{R}_3)$ at which $U(\bar{R}_1, \bar{R}_2, \bar{R}_3)$ is minimal. How many minima?



\Rightarrow For $N=4$,  } Tetrahedron $l = 2^{1/6}\sigma$

- In general, for some N



i) Upon cooling, liquids can form crystals (slow cooling) or amorphous (fast cooling) solids.

ii) Amorphous solids would correspond to metastable states of the potential energy landscape.

iii) Crystals correspond to the global minimum.

⇒ For a crystal,

$$U(\{\bar{R}^{\min}\}) = U(\bar{R}_1^{\min}, \bar{R}_2^{\min}, \dots, \bar{R}_N^{\min})$$

$$\cdot U(\{\bar{R}^{\min} + \delta \bar{R}\}) = U(\bar{R}_1^{\min} + \delta \bar{R}_1, \bar{R}_2^{\min} + \delta \bar{R}_2, \dots, \bar{R}_N^{\min} + \delta \bar{R}_N)$$

(Displaced ~~slightly~~ slightly from the minimum)

Using Taylor expansion,

$$f(x + \delta x) = f(x) + \frac{\partial f}{\partial x} \Big|_x \cdot \delta x + \frac{1}{2!} \frac{\partial^2 f}{\partial x^2} \Big|_x \delta x^2 + \dots$$

$$\Rightarrow U(\{\bar{R}^{\min} + \delta \bar{R}\}) = U(\{\bar{R}^{\min}\})$$

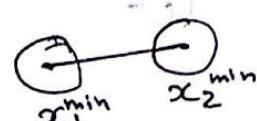
$$\text{Let } \delta R = \sum \frac{\partial U}{\partial R} \Big|_{\bar{R}^{\min}} \cdot \frac{\delta \bar{R}_i}{R_i^{\min}} + \underbrace{\frac{\partial U}{\partial \delta R} \Big|_{\delta \bar{R}}} \cdot \{\delta \bar{R}\} + \dots$$

zero at min

$$\therefore U(\{\bar{R}^{\min} + \delta \bar{R}\}) = U(\{\bar{R}^{\min}\}) + \frac{1}{2!} (\delta \bar{R}_1, \delta \bar{R}_2, \dots, \delta \bar{R}_N)^T \begin{pmatrix} \frac{\partial^2 U}{\partial R^2} & \frac{\partial^2 U}{\partial R_1 \partial R_2} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \delta \bar{R}_1 \\ \delta \bar{R}_2 \\ \vdots \\ \delta \bar{R}_N \end{pmatrix}$$

(Only) $\frac{\partial^2 U}{\partial R^2}$ will be non-zero since $\frac{\partial U}{\partial R} = 0$

⇒ Consider solid with 2 atoms, (1 dimensional solid)



$$U(x_1^{\min}, x_2^{\min}) \rightarrow U(x_1^{\min} + \delta x_1, x_2^{\min} + \delta x_2)$$

⇒ ~~solid~~ (Note: Displacement from minima, it will start to oscillate)

$$\Rightarrow U(x_1^{\min}, x_2^{\min}) + \frac{1}{2!} (\delta_{x_1} \delta_{x_2}) \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} \\ \frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} \end{pmatrix}$$

$\blacksquare U(x) = \frac{1}{2} k x^2$, comparing with 1D form we can see that the Hessian is the Spring constant matrix

$$\omega = \sqrt{\frac{k}{m}}$$

- Diagonalize the Hessian matrix

\Rightarrow Eigen vectors (Direction of vibration)

\Rightarrow Eigen values (Related to vibrational frequencies)

Types of Solids

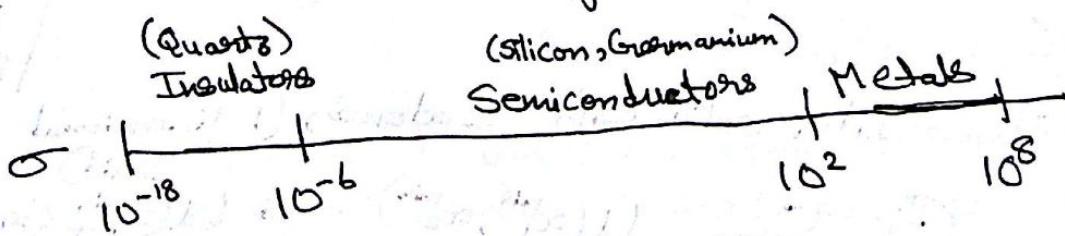
\rightarrow Crystalline solids } Based on potential
 \rightarrow Amorphous solids } energy landscape

- Another kind of classification is

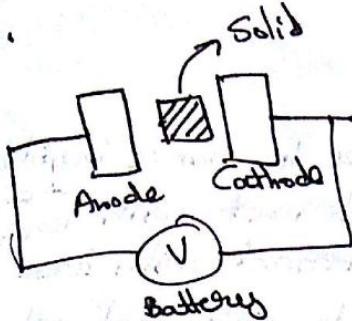
\rightarrow Metals
 \rightarrow Semiconductors
 \rightarrow Insulators

(Based on conductivity $\sigma (\Omega m)^{-1}$)

σ varies from 10^{-18} to 10^8



- Metals
 - Debye's model.
 - Free electron gas model.



\vec{E} = Electric field

I = Current flowing through the material

R = Resistance of the material.

- $V = IR$ } Ohm's Law

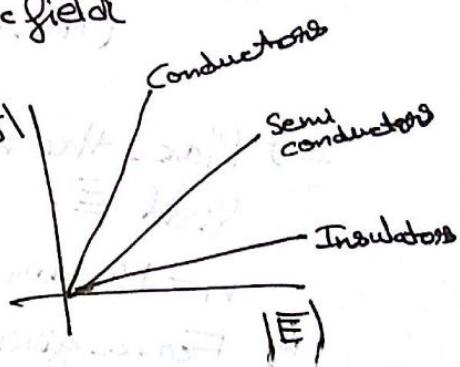
can also be expressed as

$$\vec{J} = \sigma \cdot \vec{E}$$

(conductivity σ)

Electric field

Current density
(Charge through material per unit area)



ex: Copper (29 electrons)

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

28 core electrons

1 valence electron

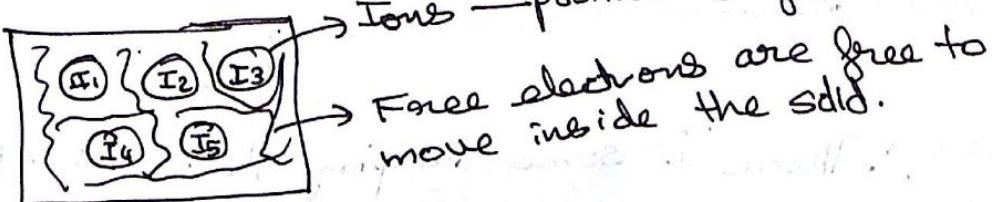
\bullet Ion = Nucleus + Core electrons

\bullet Conduction electrons = valence electrons

$\Rightarrow z$ = Number of valence electrons,
here $z = 1$ for Copper.

* Draude's Model:

* Ions — position is fixed



Free electrons are free to move inside the solid.

• Assumptions

- Ions are fixed
- Free electrons are free to move inside the solid
- Electrons do not interact with each other
- Electrons do not interact with ions.
- Ions do not interact with each other
- Electrons follow Newton's laws of motion
- Kinetic theory of gases can be applied to an ideal gas of free electrons.
(Maxwell's probability distribution)

⇒ Place the metal in an external electric field \bar{E} .

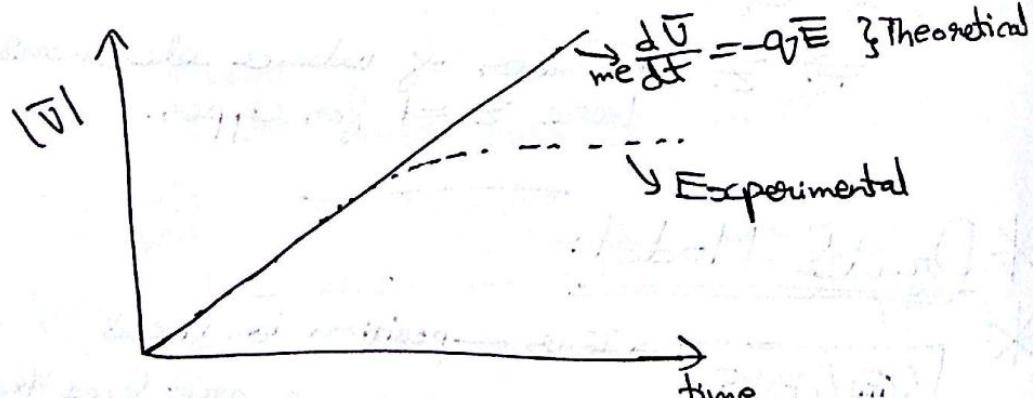
n = Number of free electrons per unit volume.
For a given electron,

$$m_e \cdot \frac{d\bar{V}}{dt} = F$$

$$\Rightarrow m_e \cdot \frac{d\bar{V}}{dt} = -q\bar{E} \quad \left. \begin{array}{l} q = \text{charge} \\ \text{of electron.} \end{array} \right.$$

if \bar{E} is constant,

$\frac{d\bar{V}}{dt} = \text{constant} \Rightarrow \bar{V} \text{ increases linearly with time.}$



∴ There is some damping that takes place,

Damping

$$m_e \cdot \frac{d\bar{V}}{dt} = -q\bar{E} - \gamma \bar{V}, \gamma = \text{Damping coefficient}$$

↓
Damping term

Equation of motion
describing the transport
of free electrons in metals.

Long-time limit: ($t \rightarrow \infty$)
From experimental observation

$$\frac{d\bar{V}}{dt} = 0, \bar{V}_{\text{saturation}} \Rightarrow \text{Saturation velocity}$$

$$\boxed{\bar{V}_{\text{saturation}} = -\frac{q\bar{E}}{\gamma}}$$

(n = Total number of free electrons per unit volume)

$$\therefore \bar{J} = -nq\bar{V}_{\text{saturation}}$$

$$\bar{J} = \frac{nq^2 \bar{E}}{\gamma}$$

$$\text{Since } \bar{J} = \sigma \bar{E},$$

$$\boxed{\sigma = \frac{nq^2}{\gamma}}$$

→ Microscopic definition of σ given by Drude model.

- From Kinetic theory of gases,
 \Rightarrow In the absence of the external electric field, the mean velocity of a free electron is zero.

$$\Rightarrow \langle \bar{V}_0 \rangle = 0$$

- \Rightarrow For an electron with an arbitrary velocity \bar{V}_0 (at time $t=0$)

- Now, in the presence of an external electric field $\bar{V} = \bar{V}_0 - \frac{q\bar{E}}{m_e} t$

- The mean velocity is now,

$$\langle \nabla \rangle = \langle v_0 \rangle - \frac{qE}{me} \cdot T$$

where T = Mean collision time.

(Mean time between two successive collisions)

$$\Rightarrow \langle \nabla \rangle = - \frac{qE}{me} \cdot T$$

$$\cdot \bar{J} = -nq \left(-\frac{qE}{me} \cdot T \right)$$

$$\bar{J} = \frac{nq^2 T}{me} \cdot E$$

$$\sigma = \frac{nq^2 T}{me}$$

$$\text{Comparing with } \sigma = \frac{hq^2}{\gamma} \quad , \quad \boxed{\gamma = \frac{me}{T}}$$

\downarrow
Microscopic relations
(blur damping coefficient
by mean collision time)

ex: Copper (Cu)

Molecular weight $M = 63.5 \times 10^{-3} \text{ kg}$

Density $\rho = 8.96 \times 10^3 \text{ kg/m}^3$

Conductivity $\sigma = 5.8 \times 10^7 (\Omega \text{ m})^{-1}$

No. of free electrons, $z = 1$
per atom

• Estimate T (Mean collision time)

Mean free path $l = \langle v \rangle \cdot T$

$$n = \frac{z \cdot e \cdot N_A}{M} \quad \leftarrow$$

$$\Rightarrow n = 1 \times \frac{8.96 \times 10^3}{63.5 \times 10^{-3}} \times 6.023 \times 10^{23} = 8.49 \times 10^{28}$$

Free electrons per $\text{m}^3 \text{ of Cu}$

$$\frac{1}{2}me\langle v^2 \rangle = \frac{3}{2}k_B T, \sqrt{\langle v^2 \rangle} \approx 10^7 \text{ cm/s}$$

$$l = \sqrt{\langle v^2 \rangle} \cdot r \approx 1-10 \text{ Å}$$

Note: Failures of Drude's model (Reading Assignment)

(Exam)

* Drawbacks of the Drude's model:

→ Electrons do not follow the Newton's Law of motion.

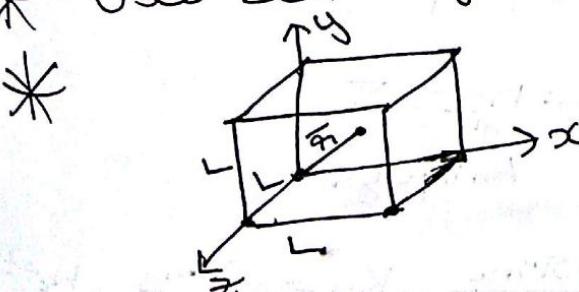
↳ Improvement: Apply quantum mechanics

→ Kinetic theory of gases is not applicable (Electrons are fermions)

↳ Improvement: Use Fermi-Dirac statistics instead of Boltzmann statistics

* Free Electron Model:

* • Uses Schrödinger's equation



• Cubic model

• Potential energy of a free electron is zero inside the box.

• Electrons are free to move inside the box but cannot move out of the box.

? • An electron in a metal
particle confined in a 3D box.

$$\bullet H\psi = E\psi$$

$$+ \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2}$$

$$= -\frac{2mE}{\hbar^2} \psi(x, y, z)$$

We get,

$$\Rightarrow \psi(x, y, z) = \frac{1}{V} \cdot e^{i\vec{k} \cdot \vec{r}}$$

Volume $V = L^3$

$$\text{where } \vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k}$$

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

Apply boundary conditions,

$$\psi(x+L, y, z) = \psi(x, y, z)$$

$$\psi(x, y+L, z) = \psi(x, y, z)$$

$$\psi(x, y, z+L) = \psi(x, y, z)$$

$$\bullet \text{Considering } \psi(x+L, y, z) = \psi(x, y, z)$$

$$\frac{1}{V} \cdot e^{i[k_x \cdot (x+L) + k_y y + k_z z]}$$

$$= \frac{1}{V} \cdot e^{i[k_x x + k_y y + k_z z]}$$

$$\Rightarrow e^{i k_x \cdot L} = 1$$

$\therefore k_x \cdot L = n_x \cdot 2\pi$
An integer

Using all
the boundary
conditions. $\left\{ \begin{array}{l} k_x = \frac{2\pi \cdot n_x}{L}, k_y = \frac{2\pi \cdot n_y}{L}, k_z = \frac{2\pi \cdot n_z}{L} \end{array} \right.$

Calculate the total energy of a particle,

$$E = \frac{\hbar^2}{2m} \vec{k} \cdot \vec{k} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

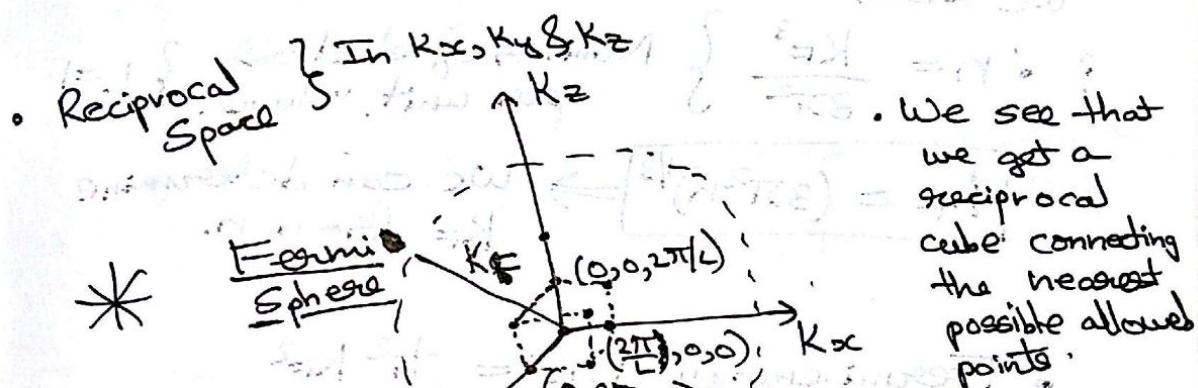
From operator

$$= \frac{\hbar^2}{2m} \left[\left(\frac{2\pi n_x}{L} \right)^2 + \left(\frac{2\pi n_y}{L} \right)^2 + \left(\frac{2\pi n_z}{L} \right)^2 \right]$$

State 1: $n_x = n_y = n_z = 0$, $E = 0$

State 2: $n_x = 1$, $n_y = 0, n_z = 0$

$$E = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2$$



(Each \vec{k} -point is an energy state)

$$\Rightarrow \text{Volume of cube} = \left(\frac{2\pi}{L} \right)^3$$

$$\Rightarrow \text{Density} = \frac{1}{8} \times 8 = 1 \text{ effective point per } 8 \text{ neighbours cell.}$$

$$\Rightarrow k_x^2 + k_y^2 + k_z^2 = \left(\frac{2\pi E}{\hbar^2} \right)^2$$

$$\Rightarrow \text{Volume of Fermi sphere} = \frac{4}{3} \pi k_F^3$$

$$\# \text{ of } \vec{k}-\text{points inside the Fermi sphere} = \frac{4}{3} \pi k_F^3 \times \frac{L^3}{(2\pi)^3} \times 1$$

- At max, two electrons can occupy one \vec{k} -point (spin up & spin down).

- Electrons are filled in based on the energy values of each k-point. (Lowest energies filled first)

⇒ Fermi surface: Surface that divides filled states of electrons from unfilled states.

(The outermost layer with filled electrons) → Higher energy

$$\bullet E_F = \frac{\hbar^2 K_F^2}{2m} \quad \left\{ \begin{array}{l} \text{Fermi Energy} \\ \downarrow \end{array} \right.$$

We know,

$$\bullet n = \frac{K_F^3}{3\pi^2} \quad \left\{ \begin{array}{l} \text{Number of electrons} \\ \text{per unit volume.} \end{array} \right. \quad \left\{ L=1 \right.$$

$$\boxed{K_F = (3\pi^2 n)^{1/3}} \Rightarrow \text{We can determine } K_F \text{ from } n.$$

$$\bullet \text{Fermi energy } E_F = \frac{\hbar^2 K_F^2}{2m}$$

$$\bullet \text{Highest energy possible for a given free electron} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad \rightarrow \text{Number of electrons per unit volume.}$$

$$\bullet \text{Highest momentum } p_F = \hbar K_F \quad \left\{ \begin{array}{l} \text{From } E_F \\ \text{and } p_F^2 = 2m E_F \end{array} \right.$$

$$\text{Maximum velocity } v_F = \frac{p_F}{m}$$

$$v_F = \frac{\hbar}{m} (3\pi^2 n)^{1/3}$$

For Copper, n is known

$$v_F \approx 10^8 \text{ cm/s} \quad (\text{Quantum mechanics})$$

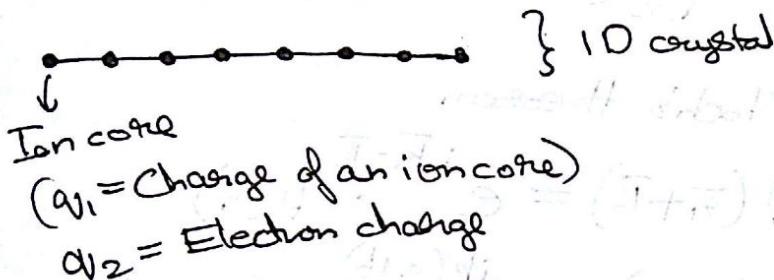
(Drude's model $v_F \approx 10^7 \text{ cm/s}$)

* Origin of band gap in solids: (Final exam) Question

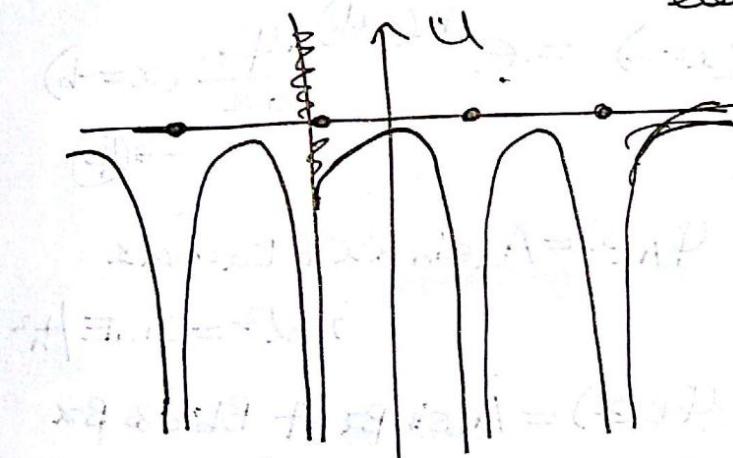
- Electron in a periodic lattice

- Kronig Penny model.

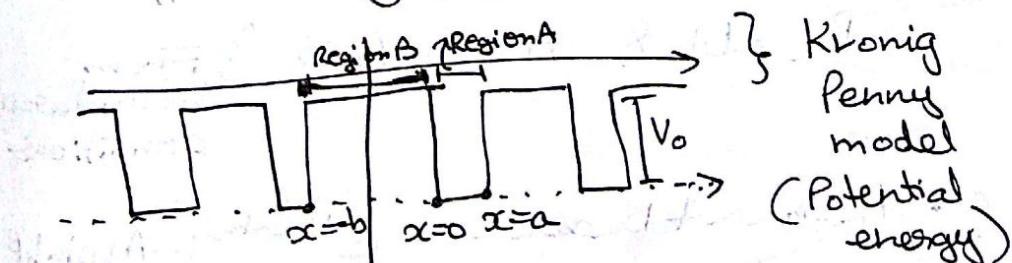
⇒ Electron-Ion interaction potential:



$$\Rightarrow U \propto \frac{q_1 q_2}{r}, r = \text{distance between the ion core and the electron.}$$



(i) Exact (ii) Approximation



V_0 = Barrier height

$$L = a + b$$

- Region A : $0 < x < a$ ($V = 0$)
- Region B : $-b < x \leq 0$ ($V = V_0$)

- Step 1: Write Schrödinger equation for regions A and region B.

$$\bullet \Psi_A(x) \& \Psi_B(x)$$

- Step 2: Apply boundary conditions,

$$\Psi_A(x=0) = \Psi_B(x=0) \rightarrow ①$$

$$\frac{d\Psi_A}{dx}(x=0) = \frac{d\Psi_B}{dx}(x=0) \rightarrow ②$$

- * • Use Bloch's theorem

$$\Psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \cdot \Psi(\vec{r})$$

for 1D, $\Psi_A(x=a) = e^{ik(a+b)} \Psi_B(x=-b)$

$$\frac{d\Psi_A}{dx}(x=a) = e^{ik(a+b)} \frac{d\Psi_B}{dx}(x=-b) \rightarrow ④$$

- We get $\Psi_A(x) = A_a \sin \alpha x + B_a \cos \alpha x$
 $\alpha^2 = 2mE/\hbar^2$

$$\Psi_B(x) = A_b \sin \beta x + B_b \cos \beta x$$

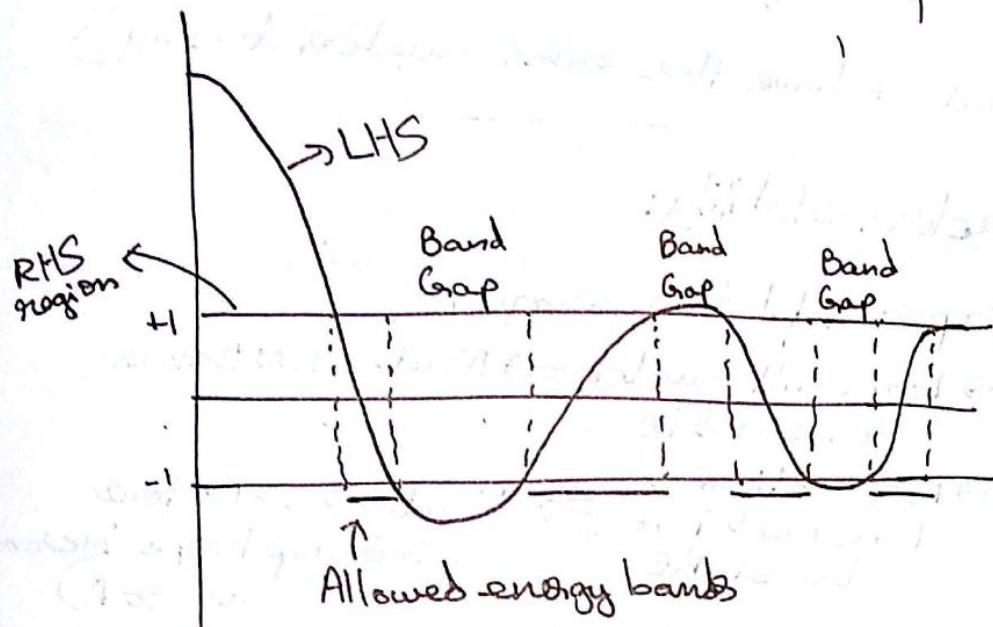
$$\beta^2 = \frac{2m}{\hbar^2} (E - V_0)$$

- $B_a = B_b \& A_a \alpha = A_b \beta \quad \left. \right\} \text{From boundary conditions}$

From Bloch's conditions

- $A_a \sin \alpha x + B_a \cos \alpha x = e^{ik(a+b)} (-A_b \sin \beta b + B_b \cos \beta b)$
- $A_a \cos \alpha x - B_a \sin \alpha x = e^{ik(a+b)} (A_b \beta \cos \beta b + B_b \beta \sin \beta b)$

Plotting these, we get



∴ Not all energies are allowed and there are only certain bands of allowed energy.

- * • Last band with electrons = Valence band
- Next band after valence is the conduction band.
→ Free electron model can be applied for this case.
- ⇒ Metals: Bands overlap (Valence & conduction)
- ⇒ Semiconductors: Have a small band gap (Valence & conduction)
- ⇒ Insulators: Huge band gap (Valence & conduction)

Nuclear Physics

- $e = -1.6 \times 10^{-19}$
 - electron mass = $9.1 \times 10^{-31} \text{ kg}$
 - proton & neutron masses = $1.67 \times 10^{-27} \text{ kg}$
- $$\Rightarrow r_0 = r_0 A^{1/3} \quad \left\{ \begin{array}{l} \text{Radius} \\ \text{of nucleus} \end{array} \right.$$
- $A = \text{Mass Number}$
- $$A \times \left\{ \begin{array}{l} \text{nucleons (Mass} \\ \text{number)} \end{array} \right.$$
- \downarrow
- $$Z \quad \left\{ \begin{array}{l} \text{Rutherford} \\ \text{Scattering} \\ \text{experiments} \end{array} \right.$$
- \downarrow
- $$Z \quad \left\{ \begin{array}{l} \text{Protons} \end{array} \right.$$
- $$r_0 = 1.2 \times 10^{-15} \text{ m}$$

* (All atoms have the same nuclear density)

Nuclear Stability:

- Experimental data suggests,
 - For small nuclei \Rightarrow Neutrons \approx Protons to be stable
 - For medium & large nuclei to be stable \Rightarrow Neutrons $>$ Protons (This gap keeps increasing as $Z \uparrow$)
- Unstable nuclei emit radioactive rays and decay into stable nuclei.

* Binding Energy (Mass Defect)

- If we bring all protons & neutrons together there is a mass deficit.
- \Rightarrow Binding energy = $Dm \cdot c^2$
- (Nucleus + Binding energy \rightarrow Separated nucleons)
(Fusion reactions release energy)

- Plotting binding energy per nucleon as we increase nucleon number A , initially it increases and then slowly starts dropping.

↳ To understand this, we use the liquid drop model.

Liquid Drop Model: (To investigate binding energy)

K. A nucleus behaves like a liquid drop.

- Heat of vaporization is the amount of energy required to convert molecules from liquid to gaseous phase. (Can be considered an analogy to binding energy)

$$\Rightarrow E_B = \underbrace{avA}_{\text{Volume term}} - \underbrace{asA^{2/3}}_{\text{Surface term}} - \underbrace{ac \frac{z(z-1)}{A^{1/3}}}_{\text{Coulomb term}}$$

(Proportional to number of nucleons since av can be thought of as the average interaction energy per nucleon)

- Surface nucleons don't have all neighbours so our overall energy just considering the volume term is an overapproximation.
→ Number of nucleons on surface $\propto r^2$

$$\Rightarrow A \propto \text{volume of nucleons} \propto r^3$$

$$\therefore r^2 \Rightarrow A^{2/3}$$

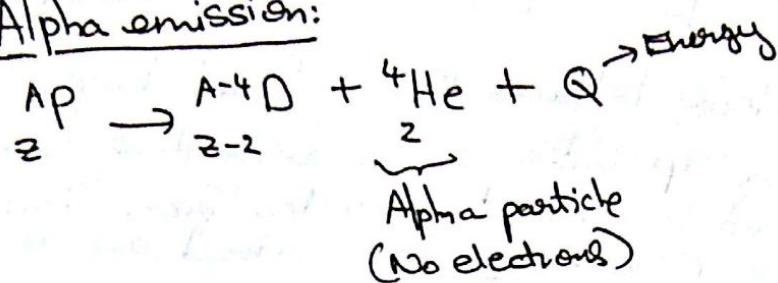
∴ $as \cdot A^{2/3}$ is our surface term.

- The coulomb term takes care of the interactions between protons.
→ Proton-proton pairs = $\frac{z(z-1)}{2}$
 $r \propto A^{1/3}$, so the average distance $\propto A^{1/3}$
So the denominator has it. ($\frac{q_1 q_2}{r} = \frac{F_n}{E_{\text{Energy}}}$)

* Radioactivity:

- Radioactive material emits particles. On applying a magnetic field we can split charged & uncharged particles | gamma rays photons etc.

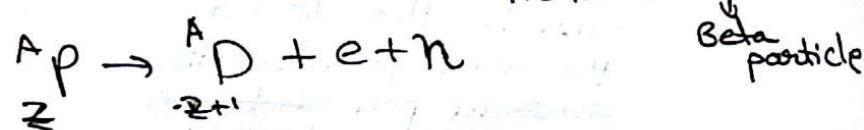
i) Alpha emission:



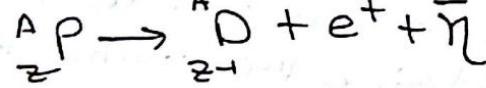
$$Q = [m(P) - m(D) - m(He)]c^2$$

ii) Beta emission:

- a) Excess of neutrons \rightarrow Neutron switches into Proton + Electron Neutrino



- b) Excess of protons \rightarrow Proton switches into Neutron + Positron + Anti Neutrino



iii) Gamma emission:

