

For any gas,

$$\frac{\langle \bar{P} \rangle}{k_B T} = B_1(T) p + B_2(T) p^2 + B_3(T) p^3 + \dots$$

$$\frac{\langle \bar{P} \rangle}{k_B T} = \sum_{i=1}^{\infty} B_i(T) p^i \rightarrow \text{virial expansion of gas}$$

$B_1(T), B_2(T), \dots \rightarrow$ virial coefficients
(can be determined from experiments)

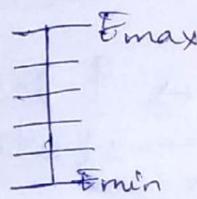
For ideal gas, $B_1 = 1, B_2 = B_3 = B_4 = \dots = 0$

Quantum Statistics

- Bosons (follows Bose-Einstein statistics)
- Fermions (Fermi-Dirac statistics)
- Classical particles (Maxwell-Boltzmann statistics)

New approach: single particle energy levels

System (N, V, T)



single particle

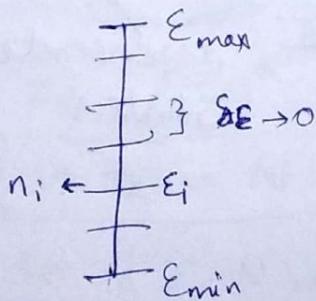
$$H_i(\vec{r}_i, \vec{p}_i) = U_i(\vec{r}_i) + K_i(\vec{p}_i)$$

↓ ↓ ↓
Total energy PE of KE of
of i^{th} atom atom i atom i



→ PE of i is calculated
wrt ~~the~~ other particles

Single particle energy level diagram



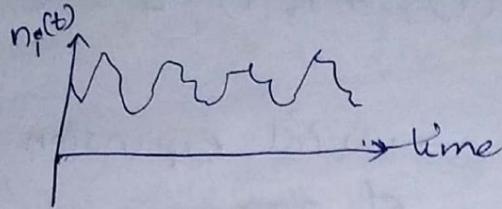
$E \rightarrow$ energy of system
 $\epsilon \rightarrow$ " single part"

For each particle, find ϵ and place on the ladder.

The distribution on the ladder changes with time.

~~n_i~~ → No. of particles present in
energy level ϵ_i

Since the PEs and KEs of individual atoms change with time, n_i also changes with time.



Average of n_i ,
 $\langle n_i \rangle = ?$

It is different for different types of particles

Total energy of the system,

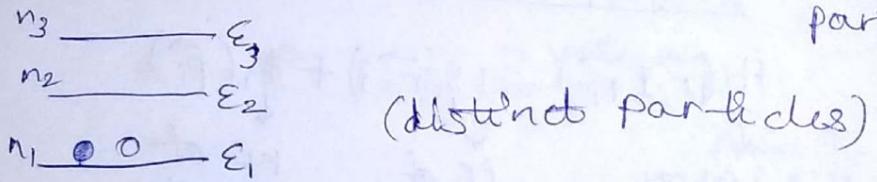
$$E = n_1 \epsilon_1 + n_2 \epsilon_2 + \dots$$

Total no. of particles in the system,

$$N = n_1 + n_2 + \dots \quad 0 \leq n_i \leq N$$

Can the partition function (Z) be expressed in terms of z for a single atom?

Model system $N=2$, with 3 possible single particle levels



→ 9 possible states

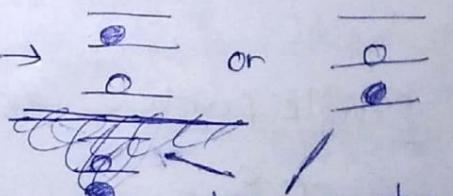
$$\hookrightarrow n_1 = 2, n_2 = 0, n_3 = 0 \Rightarrow E = 2 \epsilon_1$$

$$n_1 = 0, n_2 = 2, n_3 = 0 \Rightarrow E = 2 \epsilon_2$$

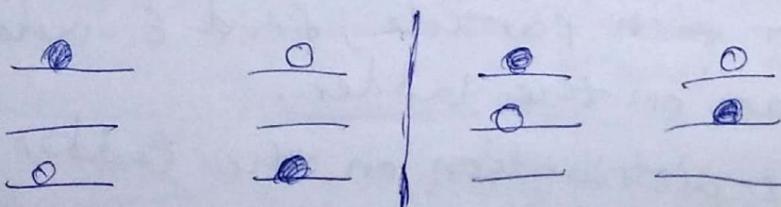
$$n_1 = 0, n_2 = 0, n_3 = 2 \Rightarrow E = 2 \epsilon_3$$

$$n_1 = 1, n_2 = 1, n_3 = 0 \Rightarrow E = \epsilon_1 + \epsilon_2 \rightarrow \begin{array}{c} \bullet \\ \text{---} \\ \bullet \end{array} \text{ or } \begin{array}{c} \text{---} \\ \bullet \\ \bullet \end{array}$$

DEGENERACY



degenerate states



$$n_1 = 1, n_2 = 0, n_3 = 1 \quad n_1 = 0, n_2 = 1, n_3 = 1$$

$$E = \epsilon_1 + \epsilon_3 \\ (\text{degenerate})$$

$$E = \epsilon_2 + \epsilon_3 \\ (\text{degenerate})$$

* $\frac{N!}{n_1! n_2!} \rightarrow$ multiplicity / degeneracy factor
 \rightarrow no. of possible states for a given n_1, n_2
 (degenerate states)

Eg: $n_1=1, n_2=1 \quad \frac{N!}{n_1! n_2!} = \frac{2!}{1! 1!} = 2$

$n_1=2, n_2=0 \quad \frac{N!}{n_1! n_2!} = 1$

$$Z_R = \sum_{i=1}^q e^{-\beta E_i}$$

↓
partition function of the system

$$Z_r = \sum_{\text{all single particle levels}} e^{-\beta E_i} = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}$$

↓
partition function for a particle

$$Z_R = \sum_{n_1, n_2} \left(\frac{N!}{n_1! n_2!} \right) e^{-\beta(n_1 E_1 + n_2 E_2)}$$

$0 \leq n_i \leq N$

↓
Sum is done with a constraint $\sum_i n_i = N$

$$Z_R = \sum \frac{N!}{n_1! n_2!} (e^{-\beta E_1})^{n_1} (e^{-\beta E_2})^{n_2}$$

(Binomial expansion)

$$Z_R = (e^{-\beta E_1} + e^{-\beta E_2})^N$$

For multiple particles,

$$Z_R = (e^{-\beta E_1} + e^{-\beta E_2} + \dots)^N$$

$$Z_R = (Z_r)^N$$

$$\boxed{\ln Z_R = N \ln Z_r}$$

$$\ln Z_R = N \ln (\sum_i e^{-\beta E_i}) \rightarrow ①$$

$$\langle n_s \rangle = ?$$

$$\text{Ansatz} \quad \langle n_s \rangle = \frac{\sum_{\text{possible states}} n_s e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}{\sum_{\text{possible states}} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}$$

$$(\because z_R = \sum e^{-\beta(n_i \epsilon_i + \dots)})$$

$$\cancel{\frac{\partial \ln z_R}{\partial \epsilon_s} = \frac{\partial}{\partial \epsilon_s}}$$

$$\Rightarrow \langle n_s \rangle = -\frac{1}{\beta} \frac{\partial \ln z_R}{\partial \epsilon_s} \quad (\text{from ①})$$

$$\langle n_s \rangle = \frac{1}{\beta} \frac{N(-\beta e^{-\beta \epsilon_s})}{\sum e^{-\beta \epsilon_s}}$$

$$\boxed{\langle n_s \rangle = N \frac{e^{-\beta \epsilon_s}}{\sum e^{-\beta \epsilon_s}}} \rightarrow \text{Maxwell Boltzmann statistics}$$

Maxwell Boltzmann $\rightarrow 0 \leq n_i \leq N, n_i = 0, 1, 2, \dots, N$
 (9 states) $\xrightarrow{\text{for model system}}$ particles are distinct

Bose Einstein $\rightarrow n_i = 0, 1, 2, \dots, N$
 (6 states) \rightarrow particles are indistinguishable

Fermi-Dirac $\rightarrow n_i = 0, 1$ (\because no two particles can have same state)
 (3 states) \rightarrow particles are indistinguishable

$$\boxed{\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}} \rightarrow \text{Bose Einstein}$$

$$\boxed{\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}} \rightarrow \text{Fermi Dirac}$$

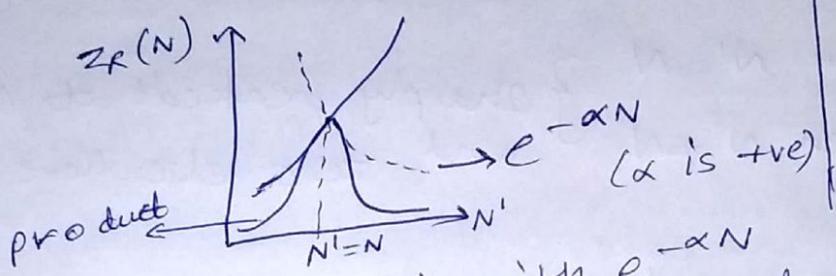
$\mu \rightarrow$ chemical potential of system
 $(\mu = \frac{\partial F}{\partial N})$

Bose Einstein

$N \rightarrow \text{no. of particles}$

$$Z_R(N) = \sum_{\substack{R \\ \text{all states}}} e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}$$

$Z_R(N)$ varies rapidly with N .



Multiply $Z_R(N)$ with $e^{-\alpha N}$ to get a gaussian distribution.

$$Z = \sum_{N'} Z_R(N') e^{-\alpha N'}$$

\Rightarrow no. of atoms in the system

α is chosen such that $Z_R(N') e^{-\alpha N'}$ is max. at $N' = N$ \rightarrow approximated as S function (sharp)

n_s varies with time.

$$\langle n_s \rangle = N \left(\frac{e^{-\beta E_s}}{\sum e^{-\beta E_s}} \right)$$

Fermions $\rightarrow n_s = 0, 1$
 \downarrow
 particles are indistinguishable
 difficult to condense

$\langle n_s \rangle$ for bosons?

$$Z(N) = \sum_{\substack{R \\ \text{over all states}}} e^{-\beta E_R}$$

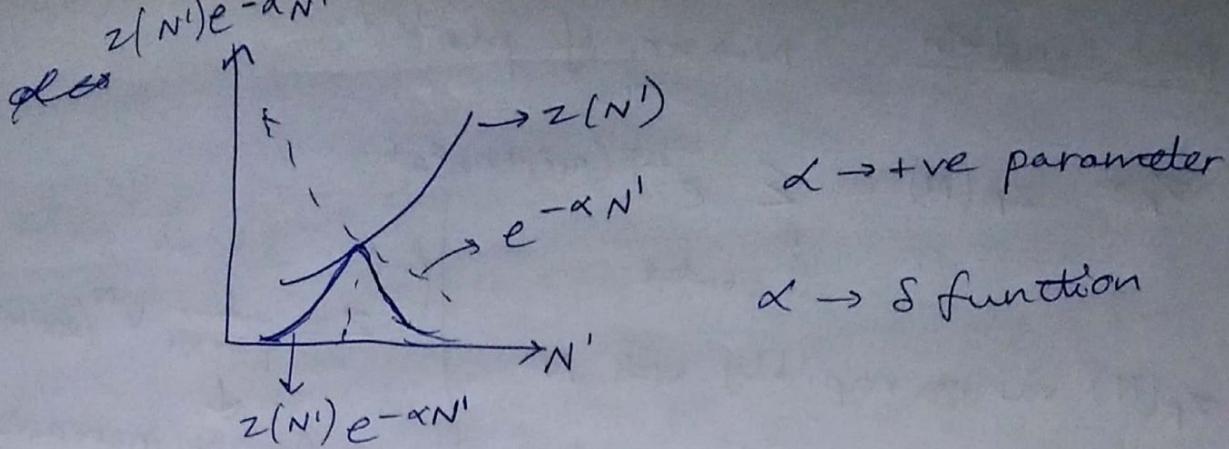
$$\sum_R = \sum_{i=1}^q = \sum_{n_1, n_2} \frac{N!}{n_1! n_2!} e^{-\beta(n_1 E_1 + n_2 E_2)}$$

$N=2 \Rightarrow 3$ states

$\overline{0}$	$\overline{1}$
\bullet	\circ

$n_1=1, n_2=1, n_3=0$

multiplicity/degeneracy = 2



$$S(N' - N) = 1, \text{ when } N' = N \\ = 0, \text{ when } N' \neq N \quad \left. \begin{array}{l} \text{sharply peaked at } N \\ \text{and zero elsewhere} \end{array} \right\}$$

$$Z = \sum_{N'} z(N') e^{-\alpha N'} S(N' - N) \quad (\text{only 1 term contributes})$$

$$Z = z(N) e^{-\alpha N}$$

$$\ln Z = \ln z(N) - \alpha N \rightarrow ①$$

$$z = \sum_{n_1, n_2} e^{-(\alpha + \beta \epsilon_1)n_1 - (\alpha + \beta \epsilon_2)n_2} \dots$$

$$Z = \left[\sum_{n_1=0}^{\infty} e^{-(\alpha + \beta \epsilon_1)n_1} \right] \left[\sum_{n_2=0}^{\infty} e^{-(\alpha + \beta \epsilon_2)n_2} \right] \dots$$

Thermodynamic limit: $N \rightarrow \infty$ $(\because 1 + x + x^2 + \dots = \frac{1}{1-x})$

$$Z = \left(1 - \frac{1}{e^{-(\alpha + \beta \epsilon_1)}} \right) \left(1 - \frac{1}{e^{-(\alpha + \beta \epsilon_2)}} \right) \dots$$

$$\ln Z = - \sum_s \ln \left(1 - e^{-(\alpha + \beta \epsilon_s)} \right)$$

$$\text{from ①, } \ln Z(N) = \alpha N + \ln Z$$

$$\ln Z(N) = \alpha N - \sum_s \ln \left(1 - e^{-\alpha - \beta \epsilon_s} \right)$$

Since $Z(N)e^{-\alpha N}$ is max. at $N' = N$,

$$\frac{\partial}{\partial N'} \left[\ln Z(N') - \alpha N' \right]_{N'=N} = 0$$

$$\frac{\partial}{\partial N} \ln Z(N) - \alpha = 0 \rightarrow \textcircled{2}$$

From ①,

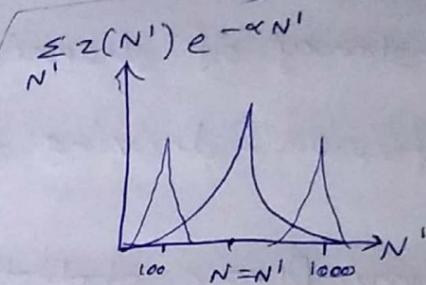
$$\ln \mathbb{E}Z(N) = \alpha N + \ln Z_1$$

$$\frac{\partial}{\partial N} \ln \mathbb{E}Z(N) = \alpha + N \frac{\partial \alpha}{\partial N} + \frac{\partial \ln Z_1}{\partial \alpha} \frac{\partial \alpha}{\partial N}$$

$$\Rightarrow \left(N + \frac{\partial \ln Z_1}{\partial \alpha} \right) \frac{\partial \alpha}{\partial N} = 0$$

$$N + \frac{\partial \ln Z_1}{\partial \alpha} = 0$$

(from ②)



$$\Rightarrow N - \sum S \frac{e^{-\alpha - \beta \epsilon_s}}{1 - e^{-\alpha - \beta \epsilon_s}} = 0$$

$\alpha \rightarrow$ function of N

$$\frac{\partial \alpha}{\partial N} \neq 0$$

(\because for different N , α would be different)

~~$\alpha \propto \frac{1}{N}$~~

$$\Rightarrow \sum S \frac{1}{e^{\alpha + \beta \epsilon_s} - 1} = N$$

$$\langle n_s \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s}$$

$$\langle n_s \rangle = -\frac{1}{\beta} \left[\frac{-\beta e^{-\alpha - \beta \epsilon_s}}{1 - e^{-\alpha - \beta \epsilon_s}} + \frac{\partial \ln Z}{\partial \alpha} \frac{\partial \alpha}{\partial \epsilon_s} \right]$$

$$\langle n_s \rangle = \frac{e^{-\alpha - \beta \epsilon_s}}{1 - e^{-\alpha - \beta \epsilon_s}} = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1}$$

$$\text{Bose Einstein} \rightarrow \langle n_s \rangle = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1}$$

Chemical Potential

$$\mu = \frac{\partial F}{\partial N}$$

$F \rightarrow$ Helmholtz free energy

$$F = -k_B T \ln Z, \quad F(N) = -k_B T \ln Z(N)$$

$$\mu = \frac{F(N+\Delta N) - F(N)}{\Delta N}$$

From ②, $\frac{\partial \ln Z}{\partial N} = \alpha$

$$\mu = \frac{\partial F}{\partial N} = -k_B T + \frac{\partial \ln Z}{\partial N}$$

$$\Rightarrow \mu = -k_B T \alpha \Rightarrow \alpha = -\beta \mu = \frac{-\mu}{k_B T}$$

$$\langle n_s \rangle = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1}$$

Constancy of chemical potential - chemical eq

Diffusion - driving force - variation in conc.

Fermi Dirac statistics

$$n_s = 0 \text{ or } 1$$

$$\langle n_s \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_s} \quad * \sum_{n_i=0}^1$$

$$Z = \sum_{n_1, n_2} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots)} - \alpha(n_1 + n_2 + \dots)$$

$$Z = (1 + e^{-\alpha - \beta \varepsilon_1}) (1 + e^{-\alpha - \beta \varepsilon_2})$$

$$\ln Z = \sum_s \ln (1 + e^{-\alpha - \beta \varepsilon_s})$$

$$\begin{cases} \ln Z = \ln Z(N) - \alpha N \\ \frac{\partial \ln Z}{\partial \alpha} = N + \frac{\partial}{\partial \alpha} \ln Z \end{cases}$$

Resatz

$$\frac{\partial \ln Z}{\partial \alpha} = N - \frac{\sum_s e^{-\alpha - \beta \varepsilon_s}}{1 + e^{-\alpha - \beta \varepsilon_s}}$$

$$\langle n_s \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{1}{1 + e^{-\alpha - \beta \varepsilon_s}}$$

$$\langle n_s \rangle = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}$$

Thermodynamics

The laws of thermodynamics:

① There are two ways of changing the internal energy of a thermodynamic system

- supply / extract heat (dq)

- work on/by the system (dW)

\Rightarrow Internal energy, $dU = dq + dW \xrightarrow{\text{Change in}} \text{Conservation of energy}$

② - Spontaneous processes
- ^{*defines} change in entropy

First version: $(\Delta S)_{\text{total}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$
of the universe as a whole

For any spontaneous process,

$(\Delta S)_{\text{total}} \geq 0 \rightarrow$ Equality holds when the process is quasi-static / reversible

$$(\Delta S)_{\text{total}} = (\Delta S)_{\text{final}} - (\Delta S)_{\text{initial}}$$

Second version:

- system specific (doesn't include surroundings)

- Clausius inequality

Change in entropy, $(\Delta S)_{\text{system}} \geq \frac{dq}{T} \rightarrow$ heat supplied to the system at temp. T

of system

The equality holds when for quasi-static or reversible processes.

③ Second law doesn't talk about the absolute value of entropy. It defines only $(\Delta S)_{\text{total}}$ or $(\Delta S)_{\text{system}}$

Third law - when $T \rightarrow 0$, $(S)_{\text{system}} \rightarrow 0$

0th law: If A, B are in thermal eq; B, C are also in thermal eq, then A, C are in thermal eq.

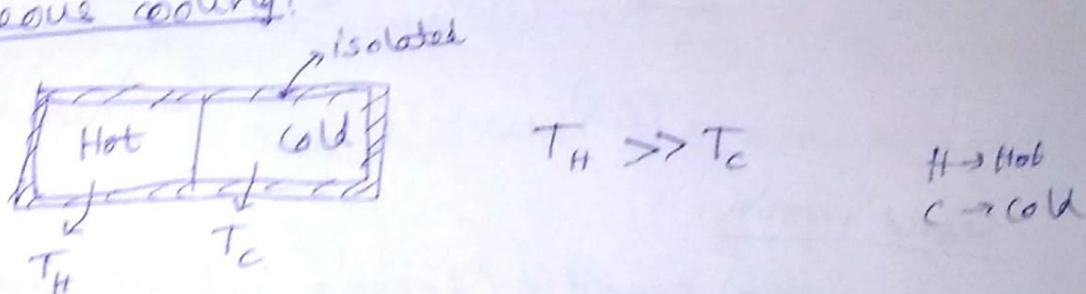
Ex: Thermometer

Even if dU is constant, dS can change.
(2nd & 3rd laws)

Consider two spontaneous processes

1. flow of heat from a hotter obj' to a colder obj'
→ spontaneous ~~expans~~ cooling
2. Spontaneous expansion of an ideal gas

Spontaneous cooling:



$$|dq_H| = |dq_C| \quad (\text{assume reversibility})$$

charge

Case 1: Heat goes from C to H → not spontaneous

$$(dS)_C = -\frac{dq_C}{T_C}, \quad (dS)_H = \frac{dq_H}{T_H}$$

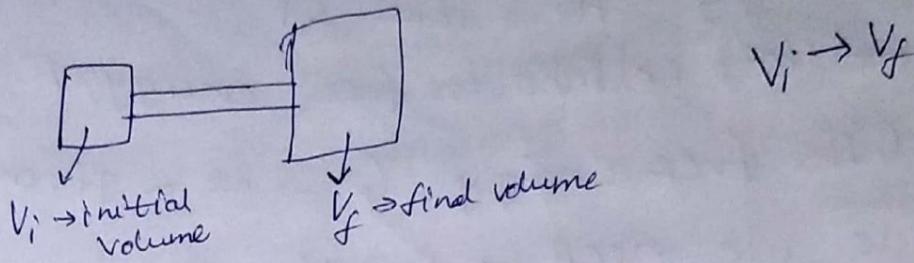
$$dS = -\frac{dq_C}{T_C} + \frac{dq_H}{T_H} \quad (\because |dq_H| = |dq_C| \& T_H > T_C)$$

$\Rightarrow dS < 0 \rightarrow$ violates the 2nd law

→ not spontaneous process (prohibited)

Case 2: Heat goes from H to C
 $dS > 0 \rightarrow$ permitted by the 2nd law
 \rightarrow spontaneous process

Spontaneous expansion of an ideal gas: (isothermal expansion)



Since it is isothermal process,

$$\Delta U = 0 \quad (\text{ideal gas})$$

From the 1st law, $q_{\text{rev}} = -w_{\text{rev}}$

$$dS = \frac{1}{T} \int_{\text{initial}}^{\text{final}} dq = \frac{q_{\text{rev}}}{T}$$

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad \left(\because PV = nRT \right) \quad P = \frac{nRT}{V}$$

$$\Rightarrow dS = nR \ln \frac{V_f}{V_i}$$

$dq > 0 \rightarrow$ heat supplied to the system

$dq < 0 \rightarrow$ heat extracted from the system

$dw > 0 \rightarrow$ work done by the system

$dw < 0 \rightarrow$ work done on the system

Case 1: $V_f < V_i \rightarrow$ not spontaneous since $dS < 0$
 (compression)

Case 2: $V_f > V_i \Rightarrow dS > 0 \rightarrow$ spontaneous

* For any ^{spontaneous} process, a direction is defined. That direction holds all the above properties.

* Is freezing a spontaneous process? If so, does it violate the 2nd law.

Thermodynamic potential functions:

- Internal energy, $U \rightarrow \text{const. } S, V$
- Enthalpy, $H \rightarrow \text{const. } S, P$
- Helmholtz free energy, $F \rightarrow \text{const. } T, V$
- Gibbs free energy, $G \rightarrow \text{at a given } T \& P$

Why do we need 4 functions?

A. Each function gives the direction of the spontaneous process under various conditions at ~~at~~ ^{which} the experiments are performed.

Eg: G is used at const. T, P
($\because G$ is minimized at const T, P)

From the 2nd law,

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

① At const. V , no work is done ($\therefore w = -P\Delta V \stackrel{V \neq 0}{=} 0$)
 \Rightarrow From 1st law, $dU = dq$

$$\Rightarrow dS - \frac{dq}{T} \geq 0$$

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

At const. S , ($ds=0$)

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

criterion for a spontaneous process
at const. S and V

② Define a new function, $H = U + PV$

$$\Rightarrow dH = dq + V dP$$

At const V , $dH = dq + V dP$

At const P , $\boxed{dH = dq}$

Heat supplied to the system at constant P is called enthalpy.

At const P , $T dS \geq dH$

At const S , $\boxed{(dH)_{S,P} \leq 0}$

* Experimentally S can't be controlled. So, we introduce F and G where T can be controlled.

③ At const T and V ,

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

④ At const T and P ,

$\boxed{(dG)_{T,P} \leq 0}$ → Generally this is used

$H(S,P)$; $F(T,V)$; $G(P,T)$

Stability of phases

$G(P,T)$ determines the stability of a phase at given T and P .

* The state with lowest G is stable at given T, P .

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

Room temp.

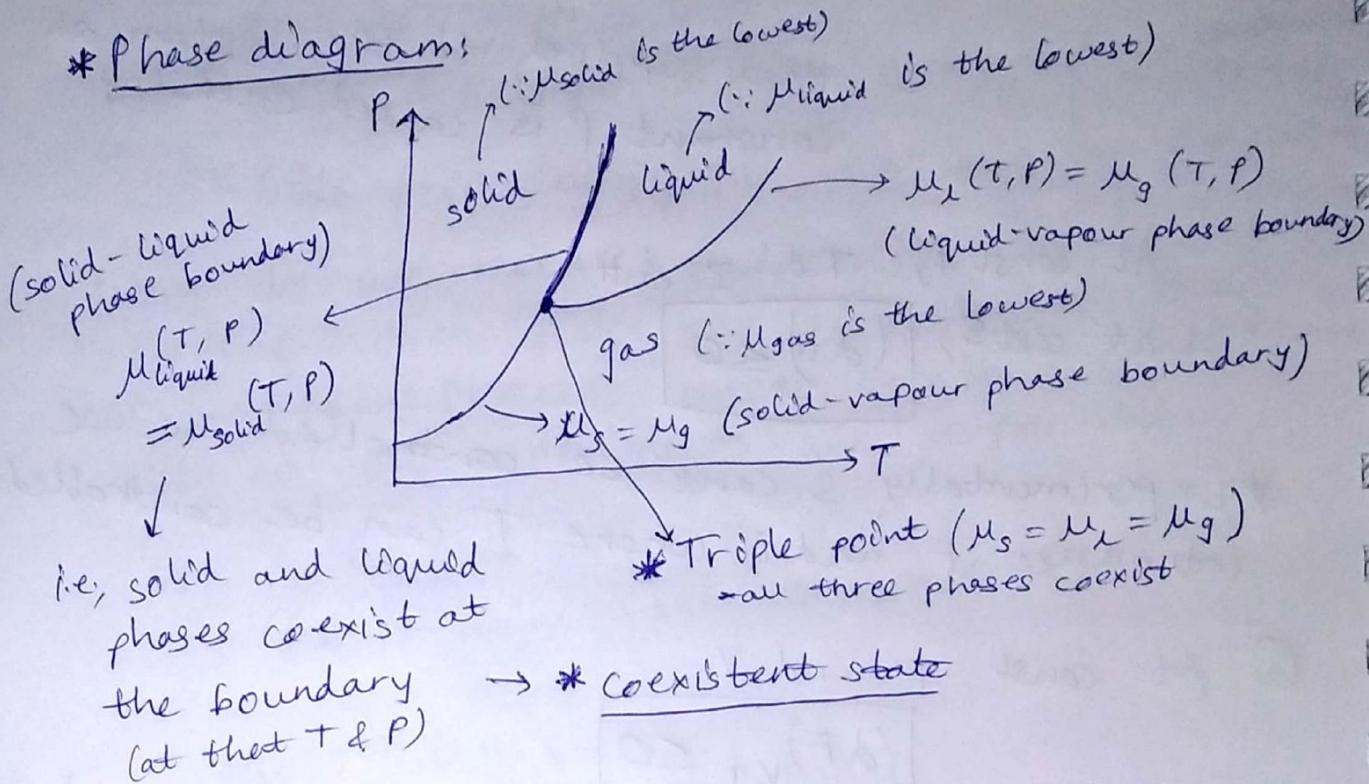
⇒ Ice is less stable.

Chemical potential (μ) = Gibbs free energy per mole

$$\mu(T, P) = \frac{G(T, P)}{n} \rightarrow \text{Normalise form of } G$$

For stability, we use μ instead of G .

* Phase diagrams:



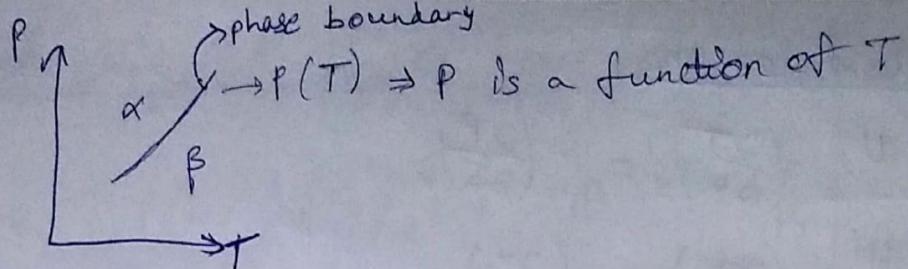
• At const P , as T increases, we cross the solid-liquid boundary → Melting transition (gas \rightarrow l)

- $S \rightarrow g \Rightarrow$ Sublimation
- $l \rightarrow g \Rightarrow$ Evaporation

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

$\mu_x(T, P) = \mu_\beta(T, P) \Rightarrow$ Phases α, β coexist at that T and P .

⇒ Both α, β are stable



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

$$F(T, V) = U(S, V) - TS$$

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

} Maxwell's relations

$U, H, F, G \rightarrow$ don't depend on the path we take
 \rightarrow they are called perfect differentials

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

\rightarrow They are ~~called~~ state functions

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

From the first law,

$$dU = TdS - PdV \rightarrow ①$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \rightarrow ②$$

const. S

From ① and ②,

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

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

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

(\because they are state functions,

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

Maxwell's relations

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

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

- From F, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

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

$\frac{\partial S}{\partial V}, \frac{\partial S}{\partial P}$ can't be measured experimentally, but they can be calculated using $\frac{\partial P}{\partial T}, \frac{\partial V}{\partial T}$ experimentally

$$G(T, P) = H(S, P) - TS$$

$$dG = dH - TdS - SdT \quad (\because H = U + PV)$$

$$dG = Tds + Vdp - Tds - SdT \quad \Rightarrow dH = dU + PdV + VdP$$

$$dG = Vdp - SdT \rightarrow \textcircled{3}$$

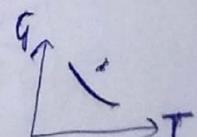
$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \rightarrow \textcircled{4}$$

From \textcircled{3} and \textcircled{4},

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

\downarrow
S is +ve $\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P$ is -ve

$$\left(\frac{\partial G}{\partial T}\right)_P \leq 0 \Rightarrow \text{As } T \uparrow, G \downarrow$$



As $S_{solid} < S_{liquid} \ll S_{gas}$

\Rightarrow change of G wrt T is highest for ~~the~~ gas

~~Solid - liquid~~ phase boundary

$$\mu_\alpha(T_i, P_i) = \mu_\beta(T_i, P_i) \rightarrow ①$$

$$\mu_\alpha(T_f, P_f) = \mu_\beta(T_f, P_f) \rightarrow ②$$

② - ①

$$\mu_\alpha(T_f, P_f) - \mu_\alpha(T_i, P_i) = \mu_\beta(T_f, P_f) - \mu_\beta(T_i, P_i)$$

$$d\mu_\alpha = d\mu_\beta \rightarrow ③$$

We know that

$$dG = -SdT + VdP$$

Dividing by n,

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

From ③,

$S_m \rightarrow$ molar entropy

$V_m \rightarrow$ molar volume

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

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{S_{\beta,m} - S_{\alpha,m}}{V_{\beta,m} - V_{\alpha,m}}} \rightarrow \text{Clapeyron equation}$$

→ gives slope of the boundary

Integrating $\frac{dP}{dT} \rightarrow$ gives $P(T) \rightarrow$ how P varies with T along the boundary

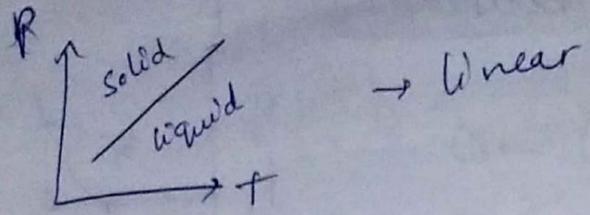
For solid - liquid boundary,

$$P \approx P^* + \frac{\Delta H_{\text{fusion}}}{T^* \Delta V_{\text{fusion}}} (T - T^*) \Rightarrow P \text{ is a linear function of } T$$

To find P use $\int_{P^*}^P dP$

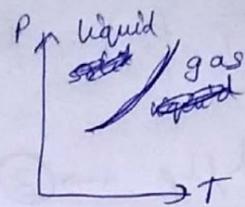
$$\Delta V = V_{\beta,m} - V_{\alpha,m}$$

$$\frac{\Delta H}{T} = \Delta S = S_{\beta,m} - S_{\alpha,m}$$



For liquid - vapour boundary

$$P = P^* e^{-\frac{\Delta \text{Evaporation}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)}$$



Quantum Mechanics

$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \rightarrow \text{Wave function}$

$$\hat{H}\psi = E\psi \rightarrow \text{Schrodinger equation}$$

↓
 Hamiltonian operator
 Energy

$$\hat{H} = \hat{K} + \hat{U}$$

↓
 KE op
 PE op

All the physical properties can be expressed as operators

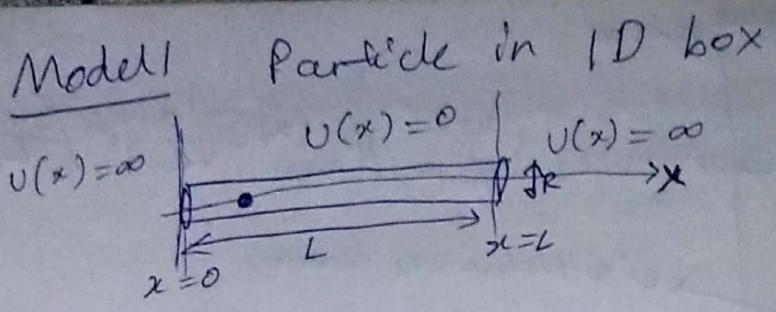
$$\hat{A}\psi = a\psi$$

↓
 Eigen value of operator \hat{A}

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} \quad i = \sqrt{-1}$$

$$\text{1D case: } \frac{\hat{P}_x \cdot \hat{P}_x}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

$$\begin{aligned} \text{3D case: } \hat{K} &= \frac{\hat{P} \cdot \hat{P}}{2m} = \frac{1}{2m} [\hat{P}_x \cdot \hat{P}_x + \hat{P}_y \cdot \hat{P}_y + \hat{P}_z \cdot \hat{P}_z] \\ &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \end{aligned}$$



Inside box

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

$$\frac{d^2 \psi(x)}{dx^2} + k^2 \psi(x) = 0$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

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

A, B are arbitrary const.

Boundary conditions

① At $x=0$, $\psi(x=0) = 0$
 $\Rightarrow A = 0$

$$\hat{A} \cdot \psi_n(x) = A_n \psi_n(x)$$

② At $x=L$, $\psi(x=L) = 0$
 $\Rightarrow B \sin kL = 0$

$$\Rightarrow kL = n\pi \quad \hbar = \frac{\hbar}{2\pi}$$

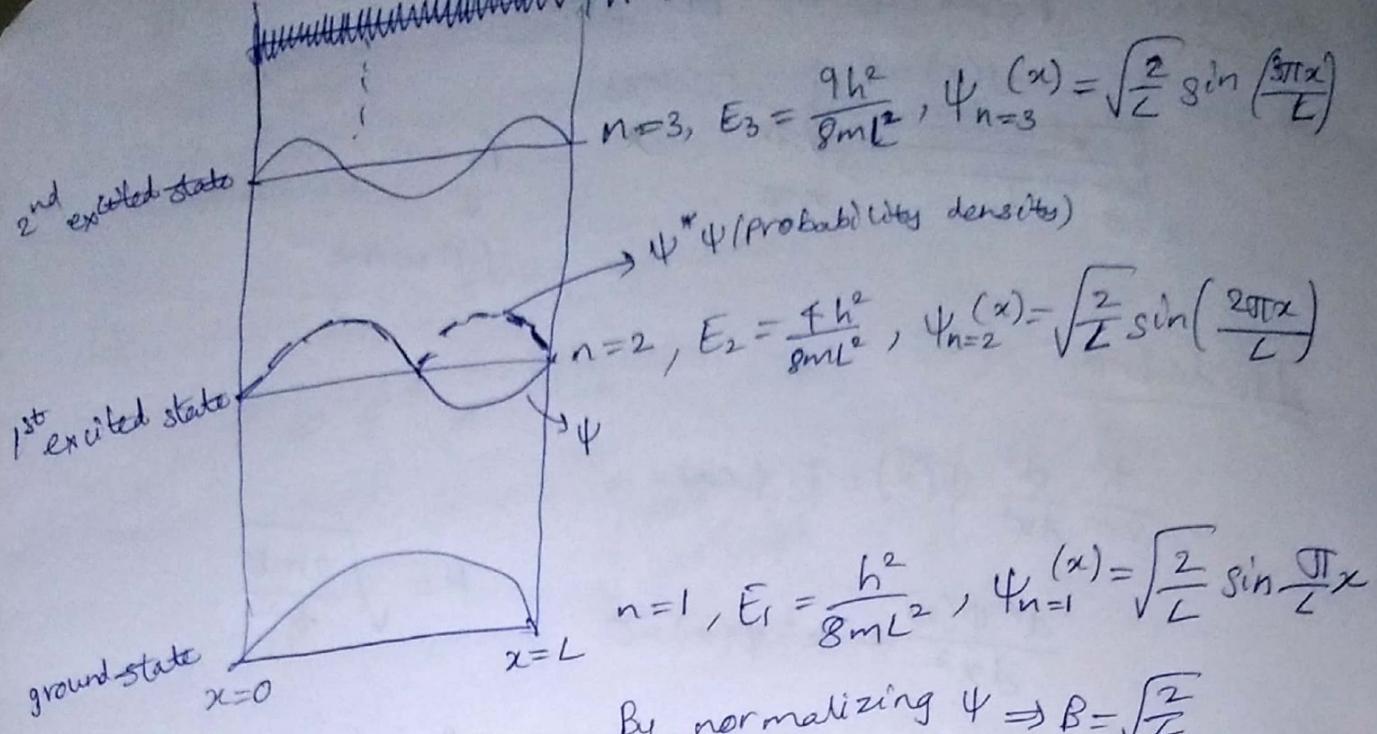
$$n = 1, 2, 3, \dots$$

$$\Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow E = \frac{n^2 \hbar^2}{(8mL^2)}$$

Energy of the free
e⁻ in a wire bound
by ∞ potentials is

* quantized

~~It's~~ $\frac{\hbar^2}{8mL^2}$ is a fundamental
unit of energy.



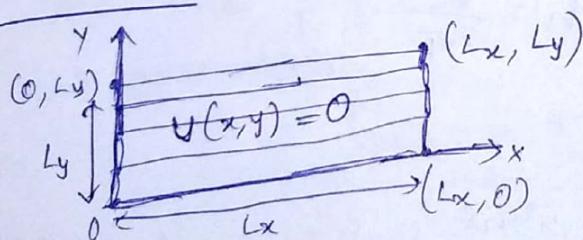
$n \rightarrow$ principal quantum no.

As $n \rightarrow \infty$,
the probability is uniform in the box.

AS $n \uparrow$, KET $\left(\because \hat{p}_x = -i\hbar \frac{\partial \Psi}{\partial x} \right)$
 $n \uparrow \Rightarrow \hat{p}_x \cdot \hat{p}_x \uparrow$

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

Model 2 particle in 2D box



$$V(x,y) = 0, 0 < x < L_x \text{ &} 0 < y < L_y$$

$V(x,y) = \infty$ at the boundary
and beyond

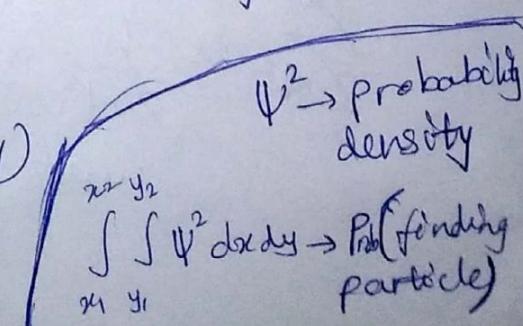
$$V(x,y) = \infty, x \leq 0$$

$$x \geq L_x$$

$$y \leq 0$$

$$y \geq L_y$$

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



On solving,

$$\Psi_{n_1, n_2}(x, y) = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right)$$

$$n_1 = 1, 2, 3, \dots$$

$$n_2 = 1, 2, 3, \dots$$

$$E_{n_1, n_2} = \frac{(n_1^2 + n_2^2) h^2}{8m L^2} \quad (L_x = L_y = L)$$

Ground state $n_1 = 1, n_2 = 1$

$$\Psi_{1,1}(x, y) = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sin\left(\frac{\pi x}{L_x}\right) \sin\left(\frac{\pi y}{L_y}\right)$$

$$E_{1,1} = \frac{2 h^2}{8m L^2}$$

1st excited state $n_1 = 1, n_2 = 2$

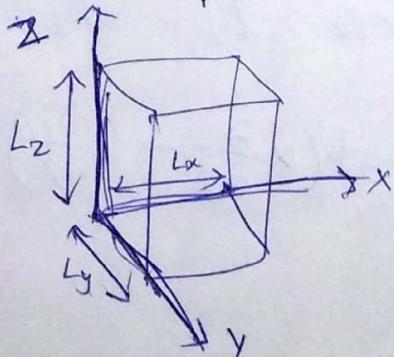
$$E_{1,2} = \frac{5 h^2}{8m L^2}, \quad \Psi_{1,2}(x, y) = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sin\left(\frac{\pi x}{L_x}\right) \sin\left(\frac{2\pi y}{L_y}\right)$$

$$n_1 = 2, n_2 = 1$$

$$E_{2,1} = \frac{5 h^2}{8m L^2}, \quad \Psi_{2,1}(x, y) = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sin\left(\frac{2\pi x}{L_x}\right) \sin\left(\frac{\pi y}{L_y}\right)$$

$n_1 = 1, n_2 = 2$ and $n_1 = 2, n_2 = 1$ are degenerate states.

Model 3 particle in 3D box



Assume $L_x = L_y = L_z = L$

$V(x, y) = \infty$, outside the box

$V(x, y) = 0$, inside the box

Wood doesn't shine.

Metals shine due to transport of e^- . ~~Because~~
(optical & electrical properties of metal)

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

obtained using separation of variables \rightarrow

$$\Psi(x, y, z) = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right) \sin\left(\frac{n_3 \pi z}{L_z}\right)$$

$$E_{n_1, n_2, n_3} = (n_1^2 + n_2^2 + n_3^2) \frac{\hbar^2}{8m L^2} \quad (L_x = L_y = L_z = L)$$

Periodic boundary conditions \rightarrow for solids that extend infinitely

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

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

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

Angular momentum

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

$$= \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= \hat{x}(y p_z - z p_y) - \hat{y}(x p_z - z p_x) + \hat{z}(x p_y - y p_x)$$

$$= \hat{x} L_x + \hat{y} L_y + \hat{z} L_z$$

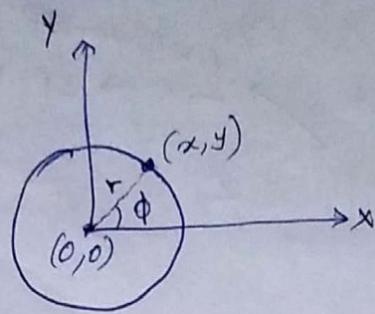
$$L_x = y p_z - z p_y, \quad L_y = z p_x - x p_z, \quad L_z = x p_y - y p_x$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} + y \frac{\partial}{\partial z} \right) = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

Particle in a circular ring



$$x = r \cos \phi, y = r \sin \phi$$

$$r = \sqrt{x^2 + y^2}$$

r is a constant.

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

$$(x, y) \rightarrow (\phi, r) \quad 0 \leq \phi \leq 2\pi$$

ϕ is the only degree of freedom.

$$\hat{H} \text{ in polar coordinates, } \boxed{\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)}$$

$$\text{If } r \text{ is constant, } \hat{H} = -\frac{\hbar^2}{2mr^2} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

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

$$-\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2} \psi = E\psi$$

$$I = mr^2$$

↓ moment of Inertia

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

The general solution is

$$\psi = A e^{im_\phi \phi}$$

Apply periodic boundary condition

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

$$\Rightarrow Ae^{im_x\phi} = Ae^{im_x(\phi+2\pi)}$$

$$\Rightarrow e^{im_x 2\pi} = 1 \quad \begin{array}{l} \text{f ve} \rightarrow \text{spin up} \\ \text{-ve} \rightarrow \text{spin down} \end{array}$$

$$\Rightarrow m_x = 0, \pm 1, \pm 2, \dots, \pm \infty$$

$$E_{m_x} = \frac{m_x^2 \hbar^2}{2I} \rightarrow \text{energy is quantized}$$

Angular momentum,
 $(L_x = 0, L_y = 0)$ as the
 particle is moving circularly
 in xy plane)

$$\hat{L}_z \psi = \frac{\hbar}{i} \frac{\partial}{\partial \phi} (Ae^{im_x \phi})$$

$$\hat{L}_z \psi = \underbrace{m_x \hbar}_{\downarrow} \psi$$

angular momentum
 is quantized

* Express \hat{L}_z in polar coordinates.

Spin \equiv Angular momentum

$m_x > 0 \rightarrow$ spin up

$m_x < 0 \rightarrow$ spin down

3D case (r, θ, ϕ) on sphere

$$E_l = l(l+1) \frac{\hbar^2}{2I}$$

Laplacian,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- Express ∇^2 in spherical polar coordinates (SPC)
 - Solve the Schrodinger equation in SPC

$$m_x = -l, -l+1, \dots, 0, 1, \dots, l-1, l$$

$\Rightarrow 2l+1$ possible values

$r \rightarrow$ constant

$\theta, \phi \rightarrow$ degrees of freedom

$l \rightarrow$ orbital quantum no.

$m_l \rightarrow$ magnetic quantum no.

$\text{H}\vec{w}$

$$\cdot \vec{\nabla} = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$$

$$\cdot \nabla^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

' $\hat{L}_x, \hat{L}_y, \hat{L}_z$

Express all the above in spherical polar coordinates

Hint:

$$\text{If } \vec{s} = x\hat{i} + y\hat{j} + z\hat{k}, \quad \hat{i} = \frac{\partial \vec{s}}{\partial x}, \quad \hat{j} = \frac{\partial \vec{s}}{\partial y}, \quad \hat{k} = \frac{\partial \vec{s}}{\partial z}$$

$$\text{Similarly, use } \hat{r} = \frac{\partial \vec{s}}{\partial r}, \quad \hat{\theta} = \frac{\partial \vec{s}}{\partial \theta}, \quad \hat{\phi} = \frac{\partial \vec{s}}{\partial \phi}$$

$$x^2 + y^2 + z^2 = r^2, \quad x = r \sin\theta \cos\phi, \quad y = r \sin\theta \sin\phi, \\ z = r \cos\theta$$

Free e⁻ in a periodic solid

Similar to *particle in 3D box, but periodic boundary condition should be applied

Schrodinger equation $\hat{H} \Psi(x, y, z) = E \Psi(x, y, z)$

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

Periodic boundary conditions,

$$\textcircled{1} \quad \psi(x+L, y, z) = \psi(x, y, z)$$

$$\textcircled{2} \quad \psi(x, y+L, z) = \psi(x, y, z)$$

$$\textcircled{3} \quad \psi(x, y, z+L) = \psi(x, y, z)$$

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

$$\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

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

$$V^3 = V \rightarrow \text{volume of box}$$

Applying $\textcircled{1}$, $i(k_x L + k_y y + k_z z)$

$$\frac{1}{\sqrt{V}} e^{i(k_x L + k_y y + k_z z)} = \frac{1}{\sqrt{V}} e^{i(k_x L + k_y y + k_z z)}$$

$$e^{i k_x L} = 1$$

$$\Rightarrow k_x L = n_x 2\pi, \quad n_x = 0, \pm 1, \pm 2, \dots$$

From $\textcircled{2}$ and $\textcircled{3}$,

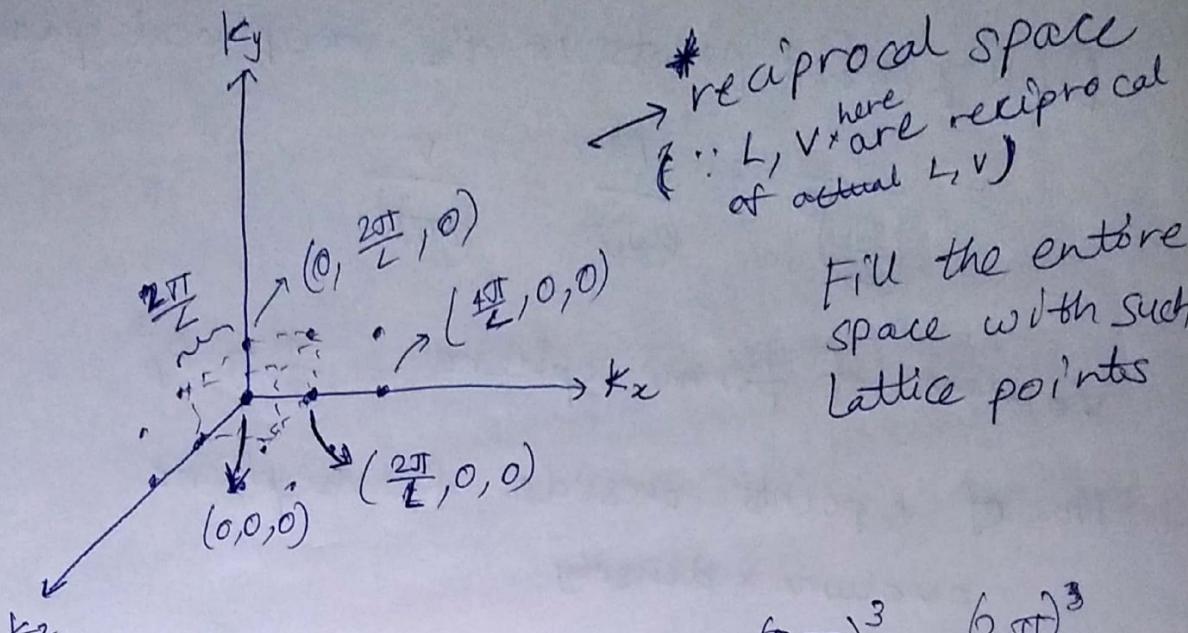
$$k_y L = n_y 2\pi, \quad n_y = 0, \pm 1, \pm 2, \dots$$

$$k_z L = n_z 2\pi, \quad n_z = 0, \pm 1, \pm 2, \dots$$

Energy of the free electron

$$\begin{aligned} E &= \frac{\hbar^2}{2m} \vec{k} \cdot \vec{k} \\ &= \frac{\hbar^2}{2m} \left[\left(\frac{2\pi n_x}{L} \right)^2 + \left(\frac{2\pi n_y}{L} \right)^2 + \left(\frac{2\pi n_z}{L} \right)^2 \right] \\ E_{n_x, n_y, n_z} &= (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2}{2m L^2} \end{aligned}$$

Various states are defined by n_x, n_y, n_z



Fill the entire space with such lattice points

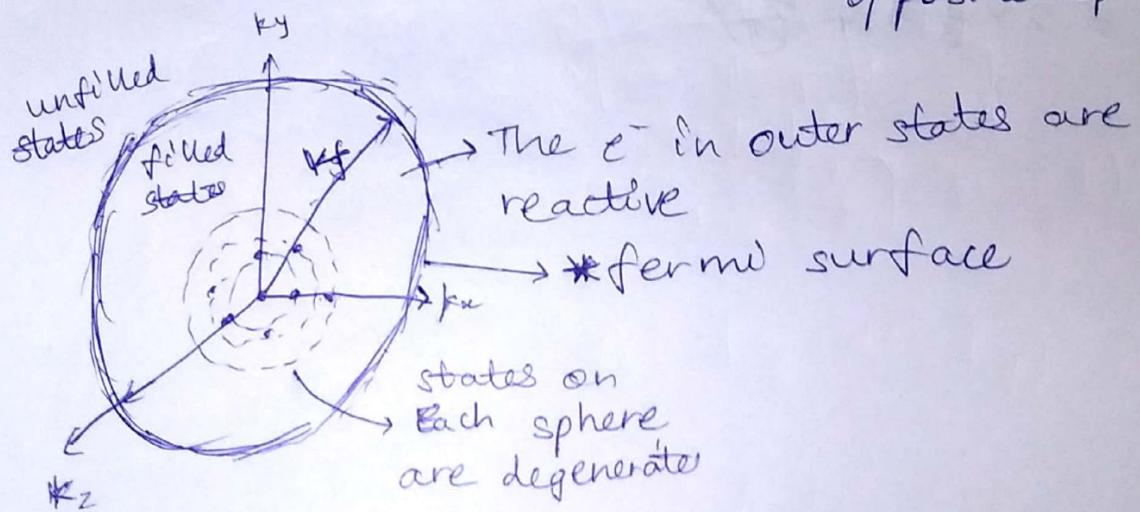
$$\text{Volume of a unit cell} = \left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$$

reciprocal

Consider each point to be a state.

Each state can occupy $2 e^-$.

Pauli's exclusion principle \rightarrow the $2 e^-$ are of opposite spin



Fermi surface \rightarrow separates filled and unfilled states

Fermi radius \rightarrow radius of fermi surface (k_f)

The free e^- on or near the fermi surface can be excited by external perturbations.

\downarrow this leads to the optical properties of metals (metals shine)

Density of k points in the reciprocal space

$$= \frac{1}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{(2\pi)^3} = \frac{V}{(2\pi)^3}$$

Volume of fermi sphere = $\frac{4}{3}\pi k_f^3$

No. of k points inside fermisphere

$$= \text{volume} \times \text{density}$$

$$= \frac{4}{3}\pi k_f^3 \times \frac{V}{(2\pi)^3}$$

Each k-point would have 2 e⁻.

⇒ Total no. of free e⁻ in a metal

$$= 2 \times \frac{4}{3}\pi k_f^3 \frac{V}{(2\pi)^3}$$