

Kinetic theory  $\rightarrow$  Laws of classical mechanics to individual atoms

Thermodynamics  $\rightarrow$  phenomenological relations between macroscopic observables.

(Microfactors combine + appropriate sum)  $\Rightarrow$  macropredictions

↓

statistical mechanics - / stat thermodynamics

↙

will not talk about behaviours of individual particles etc... but will give probable behaviour

{ Classical stat mech  $\rightarrow$  Maxwell Boltzmann  
Quantum  $\rightarrow$  Fermi Dirac, BE

Statistical mechanics

↙

→ mechanics of classical or quantum system

It makes statistical

predictions - inexact or

average!

deviation from exact behaviour

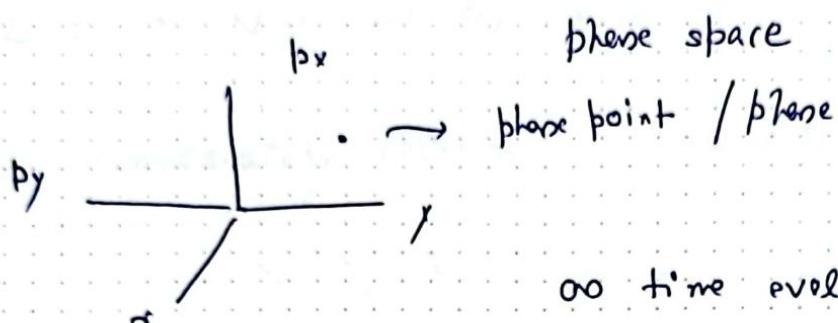
decreases as # of particles

increases!

Phase space: Consider noninteracting monoatomic gas particles -

for each particle  $x, y, z, p_x, p_y, p_z$   
(dynamical specification)

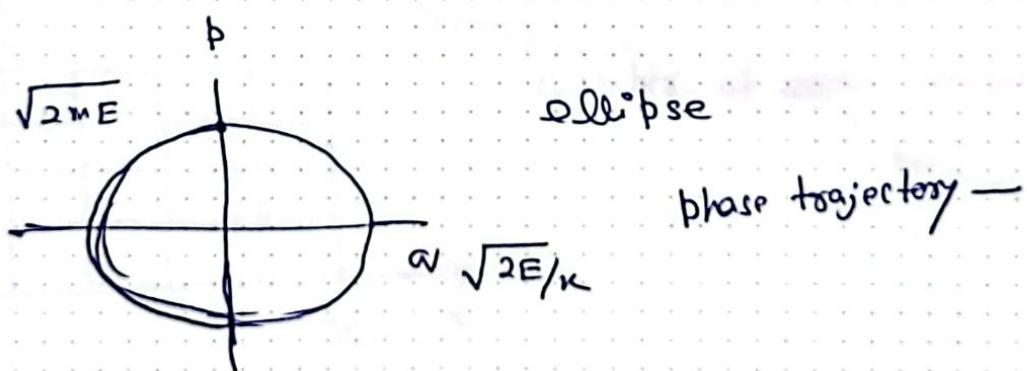
Geometrise it six dimensional space -



as time evolves the point moves  $\rightarrow$  phase path / trajectory.

One-D S.H.O :

$$H = \frac{p^2}{2m} + \frac{1}{2} kx^2$$



If  $E_1 < E_2$  then trajectory will lie between a cell.

Can phase trajectory cross itself?

→ trajectory of a dynamical system, if crosses, violates  
if you know  $(p, q)|_{t=0} \rightarrow$  it uniquely predicts

Is it always going to be closed?  $\rightarrow$  stone at rest falls freely  
 ↴  
 parabola.

For  $N$ -particles  $\in N$  dimensional  $\rightarrow$  r-space!

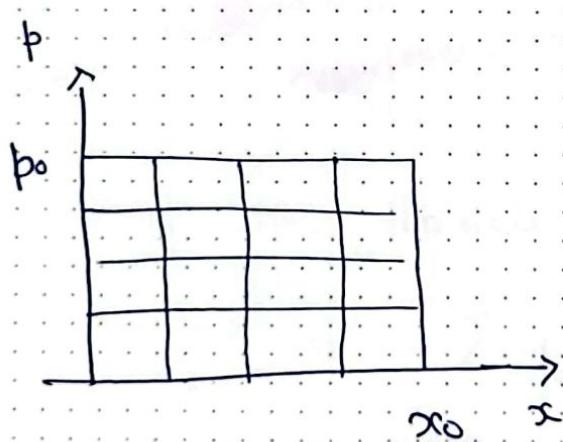
point in phase space?

$$\Omega = \# V = \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$$

uncertainty relation  $\Delta x \Delta p_x \gg \hbar$

$$V \gg \hbar^3$$

A point in phase space  $\rightarrow$  six dimensional phase cell (momentum compartments)



$$\text{Volume} \sim \hbar^3$$

Number of states available

$$n = \frac{\omega_0 p_0}{\Delta x \Delta p_x}$$

$$= \frac{x_0 p_0}{\hbar}$$

- Calculate # of quantum state of ~~p~~  $p^+$  inside a nucleus.

## specification of a state :

$$E = \frac{n^L \pi^L + L}{2m L^2} \quad \text{one-D box}$$

$$E = \frac{\pi^L + 2}{2m} \left( \frac{n_x^L}{L_{x^L}} + \frac{n_y^L}{L_{y^L}} + \frac{n_z^L}{L_{z^L}} \right) \quad E = (n_1, n_2, n_3)$$

N-particles in 3-D box :

Ignore interactions.  $E = E_1 + E_2 + \dots + E_N$

For each particle state defined by  $n_{ix}, n_{iy}, n_{iz}$

~~Take all possible states~~

just do 1D case  
 multiple parti.  
 All possible state will be defined by  $\vec{p}$   
 Corresponding energy  $E$

Say  $N_j$  particle in  $j^{th}$  energy state

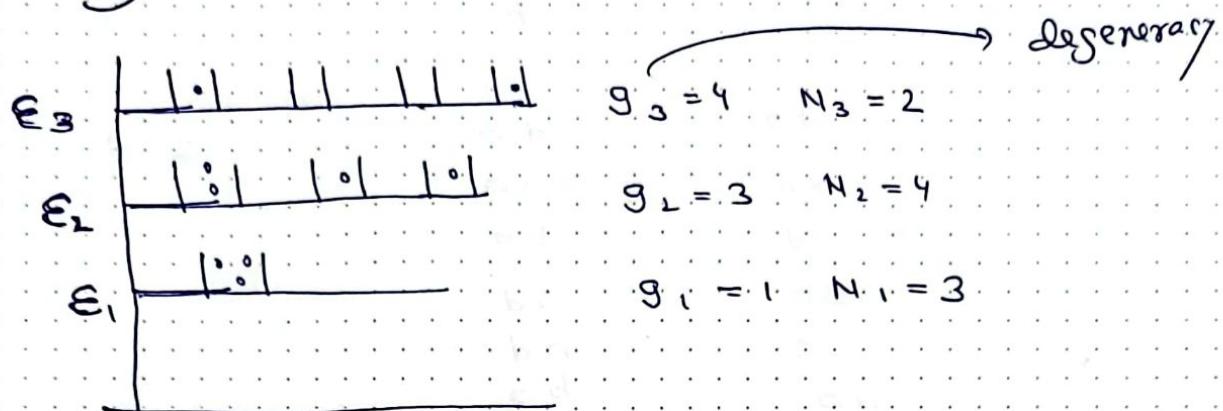
$$N = \sum N_j$$

Occupation number

$$E = \sum_j \varepsilon_j N_j$$

## Macrostate & Microstate

Macrostate of a system is that state which can be described by specifying only those quantities which can be determined by macroscopic measurement without any ref to microscopic details.



Assume indistinguishable —

$$\checkmark N = N_1 + N_2 + N_3 = 2+4+3$$

$$\begin{aligned}\checkmark E &= E_3 N_3 + E_2 N_2 + E_1 N_1 \\ &= 2E_3 + 4E_2 + 3E_1\end{aligned}$$

Many microstates correspond to the same macrostate!

excl In level 3 put the particles in state 2  
or 3

Diff microstate

o  
o  
o

For distinguishable particles — which particle where will matter. / # of microstates for distinguishable particle

E.3 Four distinguishable particles - o, b, c, d

<u>Macrostate</u>	<u>Comp 1</u>	<u>Comp 2</u>	<u># of microstates</u>
0, 4	o	abcd	1
1, 3	a b c d	bcd acd abd abc	4
2, 2	ab ac ad bc bd cd	cd bd bc ad ac ab	6
3, 1	bcd cad deb abc	i i !	4
4, 0	abcd	o	1

Total # of macrostate  $(n+1)$

$${}^n C_x \quad n=4, \quad x = 4, 3, 2, 1$$

Total microstate when four distinguishable particles are to be distributed in two identical compartments

$$2^4 = 16$$

Consider ideal gas in a box  $V$

$$\int \frac{d^3 p d^3 x}{h^3} = \frac{4\pi V}{h^3} \int p^2 dp$$

particles have access of whole volume  $V$

as interactions

non relativistic  $\epsilon = \frac{p^2}{2m}$  negligible!

$$p^2 dp = \sqrt{2m\epsilon} m dE$$

$$= \sqrt{2} m^{3/2} \sqrt{\epsilon} dE$$

$$\sum_{\text{state}} = \frac{2\pi V}{h^3} (2m)^{3/2} \int \sqrt{\epsilon} dE$$

$$= \int D(\epsilon) d\epsilon \quad \xrightarrow{\text{density of states!}}$$

# of states available states per unit energy.

$$D(\epsilon) d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon} d\epsilon$$

(1)

A particle in a 3D box:

$$E = \frac{\pi^2 \hbar^2}{2m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right]$$

$n_x, n_y, n_z$  taken 1, 2, 3

$$L^3 = V \Rightarrow L^2 = V^{2/3}$$

$$E_j = \frac{\pi^2 \hbar^2}{2m V^{2/3}} (n_x^2 + n_y^2 + n_z^2) = C n_j^2$$

$$\frac{\hbar^2}{8m V^{2/3}} = C \equiv \frac{\pi^2 \hbar^2}{2m V^{2/3}} ; \quad n_j^2 = n_x^2 + n_y^2 + n_z^2$$

Lowest energy levels  $n_x = n_y = n_z = 1$

$$j = 1 \quad n_1^2 = 3 \quad E_1 = \frac{3 \hbar^2}{8m V^{2/3}}$$

Only ONE state corresponds to this energy!  
(non-degenerate)

↗  $j = 2 \Rightarrow (n_x, n_y, n_z)$

$$(2, 1, 1), (1, 2, 1), (1, 1, 2)$$

$$n_2^2 = 6 \quad E_2 = \frac{6 \hbar^2}{8m V^2}$$

These states same energy.  $\rightarrow$  3-fold degeneracy

(3)

Total number of particles in an energy state corresponding to a particular level is occupation number  $N_j$ :

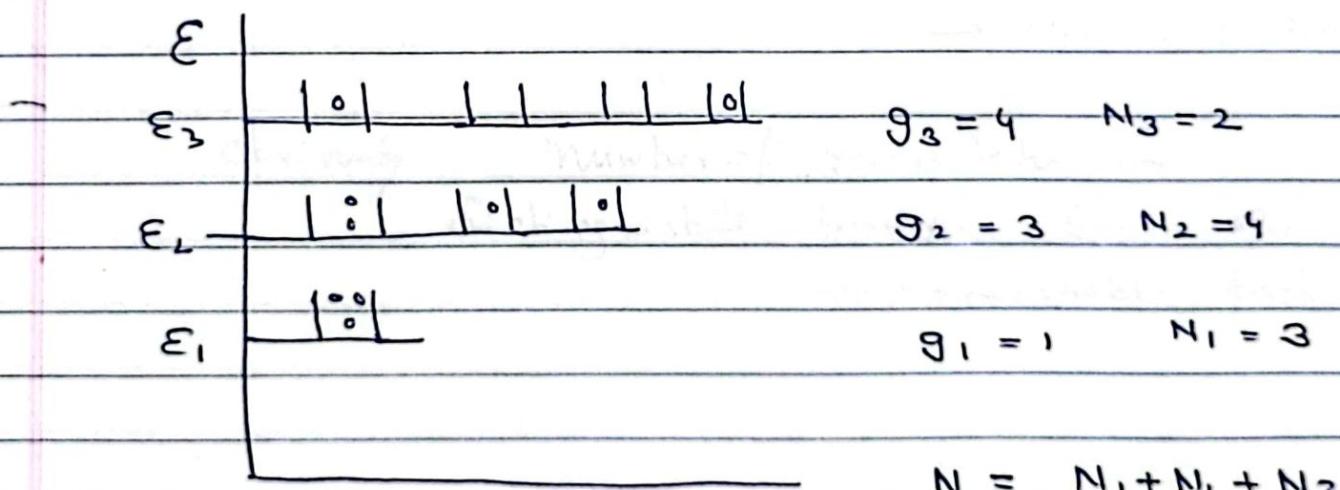
$$N = \sum_j N_j \quad \checkmark$$

All particles:

$$E = \sum_j E_j N_j \quad \checkmark$$

### Macrostate & Microstate

Macrostate of a system described by variables which can be determined by macroscopic measurements.



$$E = N_1 \times E_1 + N_2 \times E_2 + N_3 \times E_3$$

(4)

✓ Assume indistinguishable particles -

Look at  $E_3$  state.

Change of move particle from (1) state to  
 (2) state  $\rightarrow$  diff microstate, but  
 some macrostate  $N_g = 2$

Many microstate  $\Rightarrow$  single macrostate!

Possible ways these particles can be

✓ Distinguishable particles. ✓

specify which particles are in

Each distribution.

Exchange particles between (1) & (4)

$\rightarrow$  New microstate!

Obviously number of microstates for

distinguishable particles larger than  
 indistinguishable particles.

(5)

Consider FOUR distinguishable particles,  
a, b, c, d

Distribute these in two identical compartments  
in an open box

Compartments are alike, so each particle  
has probability of  $\frac{1}{2}$

Possible ways these particles can be  
distributed  $(0, 4), (1, 3), (2, 2),$   
 $(3, 1), (4, 0)$

Each distribution a macrostate!

Macrostate	Compt 1	Compt 2	No of micro	
0, 4	a	b c d	1	total $(4+1)$ macrostate
1, 3	a b c d	b c d c d a d a b a b c	4	general: $(n+1)$ "
2, 2	a b a c a d b c b d c d	c d. b d. b c. a d. a c. a b.	6	→ No of microstate $n_c = 4$ $n = 4$
3, 1	b c d c d a d a b a b c	a b c d	4	Total # of micro state $2^4 = 16$
4, 0	a b c d	0	1	

(6)

System tends to equilibrate - @ equilibrium  
macroscopic variables do not change! -



- { An isolated system is in equilibrium when probabilities of it being in the various accessible states do not vary with time.
- { e.g. open a perfume bottle at the corner of a room. → At large time perfume molecules will fill up whole room such that molecules are equally likely to ~~be found~~ be found anywhere in the room.

How do we calculate probability?

Fundamental Postulate: An isolated system in equilibrium is equally likely to be in any of its accessible states.

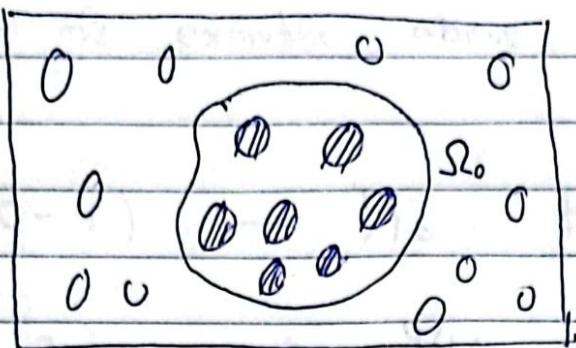


Over a long period of time one microstate would occur as often as another ]

postulate of equal a priori probability

- Macrostates are NOT equally probable as different macrostates correspond to diff number of microstates

(7)



Among all possible microstate  $\Omega_0$  is consistent with constraints

e.g. No compartment should be empty.

$(0, 4) \& (4, 0)$  excluded

and associated microstates

No of accessible microstate  $\Omega_0$

The probability of finding in eq state  $\frac{1}{\Omega_0}$

Probability of finding the system in a certain set of accessible states is

$$P_i = \left( \frac{\Omega_i}{\Omega_0} \right)$$

*The probability of certain macrostate occurring is proportional to total number of states in the set.*

$$\sum_{i=1}^m P_i = 1$$

$\bar{Y}$  is called In stat mech. mean value of a physical quantity about which

the several values  $\bar{Y} = \sum_{i=1}^n P_i Y_i = \frac{1}{\Omega_0} \sum_{i=1}^n \Omega_i Y_i$

⑧

For the example above total # of microstates

16

$E_1$  } <sup>Say, these are macro variables</sup>  $(0-4) \rightarrow 1/16$  probability

$E_L$  }  $(1, 3) \rightarrow 4/16$

$E_3$  }  $(2, 2) \rightarrow 6/16$

$E_L$  }  $(3, 1) \rightarrow 4/16$

$E_{\bullet 1}$  }  $(4, 0) \rightarrow 1/16$

Mental constraint

$$\langle E \rangle = E_1 \times \frac{1}{16} + E_1 \times \frac{1}{16}$$

$$+ E_L \cdot \frac{4}{16} + E_L \times \frac{6}{16}$$

$$+ E_3 \times \frac{6}{16}$$

$$= \frac{E_1}{8} + \frac{E_L}{2} + E_L \cdot \frac{3}{8}$$

(9)

Ensemble : (mental "photocopies")

We want average behaviour (statistical / probabilistic)

make measurements again & again as we cannot control microstates ✓

Gibbs

Macroscopically alike but microscopically distinct

Mental construct

1. Microcanonical ensemble : fixed  $E, V, N$   
(isolated system)

2. Canonical ensemble : fixed  $T, V, N$   
can exchange energy  $E$

*Closed  
isothermal* ↴ in touch with heat reservoir

3. Grand Canonical ensemble : can exchange both  $E \& particles$ .

$\mu, V, T$  fixed

If energy fluctuations fixed (to a narrow range)  
Canonical  $\rightarrow$  micro ;

(10) e

Example :Consider  $N$  particles. (Isolated system)

- spinless, identifiable, distinguishable (classical)
- no worry about uncertainty relation or exclusion principle.

$$\delta N = \sum \delta n_i = 0$$

$n_i$  = number  
of particles in  
ith energy state

Conservation of

non interacting

number of particles

$$\psi = \sum n_i \epsilon_i$$

$$\delta \psi = \sum \epsilon_i \delta n_i = 0$$

constraint conditions!

 $n_1 \dots n_n$  in energy states  $\epsilon_1 \dots \epsilon_n$  $g_1 \dots g_n$  degeneracyTotal number of ways  $N$  particles can be distributed.

$$W_1 = \frac{N!}{n_1! n_2! \dots n_n!} = \frac{N!}{\prod_{i=1}^n n_i!}$$

number of ways  
 $n_1 \dots n_n$  could be  
chosen for  $N$   
particles.

(11)

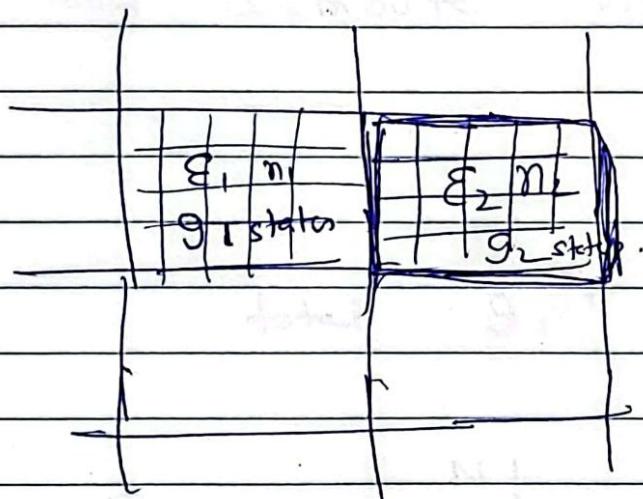
## Calculation of $S_{MB}$

$N$  - distinguishable particles in  $V$  &  
each particle can have only energy

to mathematically simplify  $\epsilon_1, \epsilon_2, \dots, \epsilon_g$  states <sup>energy</sup>

Occupation number  $\rightarrow n_1, n_2, \dots, n_g$

each state with degeneracy  $g_1, g_2, \dots, g_g$ .



phase space!

small boxes cubes

big box room!

- $n_1$  particles out of  $N$  particles

$$N_{C_{n_1}}$$

You are left with  $(N - n_1)$

You choose  $n_2$

$$N - n_1 \quad C_{n_2} \quad \text{so on}$$

(12)

Total number of ways  $n_1$ , occupies first  
 $n_2$ , , and etc.

$$N = N C_{n_1} \times (N - n_1) C_{n_2} \dots \dots$$

$$= \frac{N!}{\prod_i n_i!} = \frac{N!}{n_1! n_2! \dots n_i! \dots}$$

Now distribute  $n_i$  particles in  $g_i$  states

$$\text{total } g_1^{n_1} g_2^{n_2} \dots = \prod_i g_i^{n_i}$$

$$\Omega_{MB} = \frac{N!}{\prod_i n_i!} \left( \prod_i g_i^{n_i} \right)$$

Thermodynamic probabilities of  $N$  distinguishable particles when there is no limit on the number of particles occupies a cell!

(13)

$$N = 3$$

$$\epsilon_1, \epsilon_2, \epsilon_3$$

$$g_1 = 1 \quad g_2 = 2 \quad g_3 = 1$$

$$\Omega_{MB} = \frac{3!}{1! \times 2!} \cdot \begin{pmatrix} 1 & 0 & 2 \\ 1 & 2 & 1 \end{pmatrix}$$

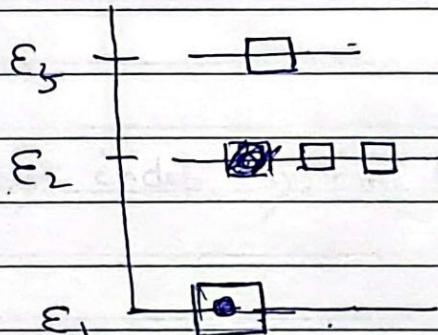
$\epsilon_1 \quad n_1 = 1$   
 $\epsilon_2 \quad n_2 = 0$   
 $\epsilon_3 \quad n_3 = 2$

a      b c  
 b      a c  
 c      a b

$$n_1 = 1 \quad n_2 = 2, \quad n_3 = 0$$

$$\Omega_{MB} = \frac{3!}{1! 2!} \cdot 1^1 \cdot 2^2 \cdot 1^0$$

$$= 12$$



$$\epsilon_1 \rightarrow a$$

$$\epsilon_2$$

b c.

c b..

bc o.

o bc

exchange a by b c  $\rightarrow 4 \times 3 = 12$

o If you put constraint e.g. total energy then states are restricted!

(14)

A system attains maximum entropy

state of equilibrium

spontaneously move to less probable state to more probable state:

Suggests  $\rightarrow$  thermodynamic quantity S related to

probability, statistical

Boltzmann

$$S = f(\Omega)$$

Consider two completely indep system having entropies  $S_1$  &  $S_2$

Entropy extensive quantity

Entropy of the combined system  $S_1 + S_2 = S_0$

Now if  $\Omega_1$  &  $\Omega_2$  are probabilities of the system

probability of the combined system

$$\Omega_0 = \Omega_1 \Omega_2$$

for every microstate of one system, the other system may be in any of the possible states.

such that

Expect  $f$ ,  $s$  increase with  $\Omega$  is to consider.

$\Downarrow$

product into "sum -

$$s_1 + s_2 = f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \Omega_2)$$

take  $\frac{\partial}{\partial \Omega_1}$  for fixed  $\Omega_2$

$$\left. \frac{\partial f(\Omega_1)}{\partial \Omega_1} \right|_{\Omega_2} = \frac{df(\Omega_1)}{d\Omega_1} \quad \begin{matrix} f(\Omega_1) \\ \text{as } f \text{ is fun of} \\ \Omega_1 \text{ only.} \end{matrix}$$

$$\text{on } \left. \frac{\partial f(\Omega_2)}{\partial \Omega_1} \right|_{\Omega_1} = 0$$

$$\begin{aligned} \left. \frac{\partial}{\partial \Omega_1} f(\Omega_1 \Omega_2) \right|_{\Omega_2} &= \frac{df(\Omega_1 \Omega_2)}{d(\Omega_1 \Omega_2)} \frac{\partial}{\partial \Omega_1} (\Omega_1 \Omega_2) \\ &= \Omega_2 \frac{df(\Omega_1 \Omega_2)}{d(\Omega_1 \Omega_2)} \end{aligned}$$

$$\text{Then } \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_1 \Omega_2)}{d(\Omega_1 \Omega_2)}$$

$$\text{Similarly } \frac{df(\Omega_2)}{d\Omega_2} = \Omega_1 \frac{df(\Omega_1 \Omega_2)}{d(\Omega_1 \Omega_2)}$$

$$\therefore \Omega_1 \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_2)}{d\Omega_2}$$

(16)

1st term only  $f(\Omega_1)^2$  of  $\Omega_1$  & 2nd term only  $f(\Omega_2)^2$  of  $\Omega_2$

$$\text{Then } \Omega_1 \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_2)}{d\Omega_2} = \text{Constant}$$

$$\text{Then } f(\Omega_1) = K \ln \Omega_1 + C_1$$

$$f(\Omega_2) = K \ln \Omega_2 + C_2$$

$$\text{or } f(\Omega) = S = K \ln \Omega + C$$

$f(\Omega)^2$  logarithmic & constant  $K$  is same for all system!

Derived by Boltzmann, but did not determine  $K \& C$

Planck at  $T = 0$ ,  $S = 0$  &  $\Omega = 1$

Third law of Thermodynamics

Apply for a perfect crystal

i.e.  $C = 0$

Also identified

$\Omega \propto$

Thermodynamic probability

## Lagrange Multiplier:

Find local max/min of a fun<sup>n</sup> subject to equality constraint

find max/min of  $f(x)$  subject to  $g(x) = 0$

construct  $\mathcal{L}(x, \lambda) = f(x) + \lambda g(x)$

find stationary point of  $\mathcal{L}$ , i.e. considering  $\mathcal{L} \approx f^n$  of  $x \& \lambda$

$$\frac{\partial \mathcal{L}}{\partial x} = 0, \quad \frac{\partial \mathcal{L}}{\partial \lambda} = 0$$

i.e.  $\frac{\partial f}{\partial x} + \lambda \frac{\partial g}{\partial x} = 0$  &  $g(x) = 0$

Ex.  $f(x, y) = x + y$  subject to  $x^L + y^L = 1$

~~$\mathcal{L} = x + y + \lambda (x^L + y^L - 1)$~~

$$\frac{\partial \mathcal{L}}{\partial x} = 0 \Rightarrow 1 + 2\lambda x = 0$$

$$\frac{\partial \mathcal{L}}{\partial y} = 0 \Rightarrow 1 + 2\lambda y = 0$$

$$\frac{\partial \mathcal{L}}{\partial \lambda} = 0 \Rightarrow x^L + y^L - 1 = 0$$

$$\lambda = y = -\frac{1}{2x} \quad (x \neq 0)$$

plug back to last eqn  $\frac{1}{4x^2} + \frac{1}{4y^2} - 1 = 0$ .

$$\Rightarrow \lambda = \pm \frac{1}{\sqrt{2}}$$

(19)

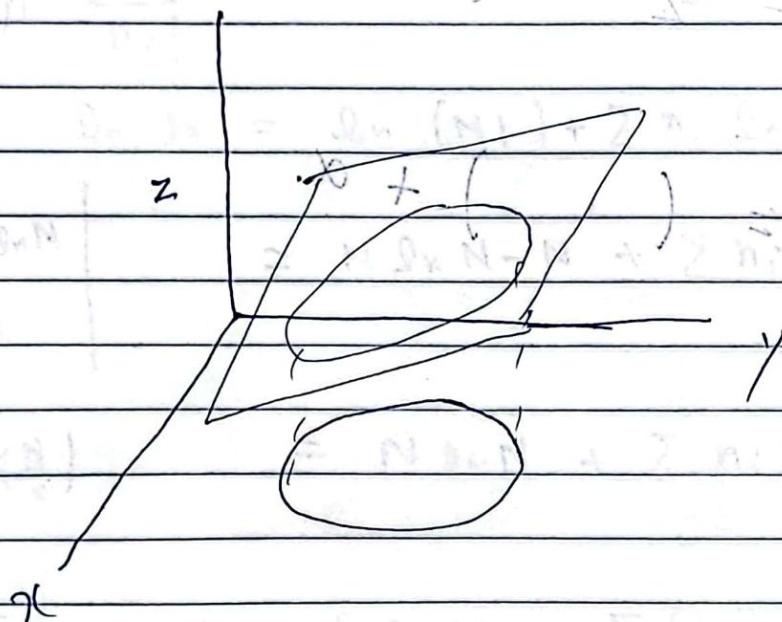
stationary points of  $\mathcal{L}_W$

$$(x, y, z) = \left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right), \left( -\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)$$

$$f\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right) = \sqrt{2}, \quad f\left(-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right) = -\sqrt{2}$$

Constrained max value is  $\sqrt{2}$

$$\min " " = -\sqrt{2}$$



$$\text{Time } T = \sum_{i=1}^n (t_i - t_{i-1})$$

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## MB Distribution or (Most probable distribution)

→ for most probable distribution  $S_{\text{ext}}$  is to be extremised

$$\delta S = 0 \Rightarrow \delta(\ln W) = 0$$

subject to  $\delta N = \sum \delta n_i = 0$

$$W = N! \prod \frac{(g_i)^{n_i}}{n_i!} \quad \delta U = \sum \varepsilon_i \delta n_i = 0$$

$$\ln W = \ln(N!) + \sum n_i \ln g_i - \sum \ln(n_i!)$$

Stirling approx

$$\ln N! \approx N \ln N - N$$

$$\approx N \ln N - N + \sum n_i \ln g_i - \sum n_i \ln n_i$$

-N

(large N)

$$= N \ln \left( \frac{N}{e} \right)$$

$$+ \sum n_i$$

$$= N \ln N + \sum n_i \ln g_i - \sum n_i \ln n_i$$

$$N! \approx \frac{N^N}{e^N}$$

$$\text{Then } \delta \ln W = \sum (\ln g_i - \ln n_i - 1) \delta n_i$$

subject to  $\sum \delta n_i = 0$

Now  $N = 2^{m_e} = 18 \times 2 \quad \& \sum \varepsilon_i \delta n_i = 0$

Then  $\sum (\ln g_i - \ln n_i - \alpha - \beta \varepsilon_i) \delta n_i = 0$

absorb  $\pm \ln \alpha$

(21)

~~Now  $n_i$ 's are indep~~ Now  $n_i$ 's are indep the bracket term mu vanishes for all  $i$ 's

$$\ln g_i - \alpha n_i - \alpha - \beta \varepsilon_i = 0$$

$$\Rightarrow \ln n_i = \ln g_i + \ln(e^{-\alpha - \beta \varepsilon_i})$$

$$\Rightarrow n_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

$$\left(\frac{n_i}{g_i}\right) = f(\varepsilon_i) = e^{-\alpha - \beta \varepsilon_i}$$

Ratio of number of particles  $n_i$  to the

number of states  $g_i \rightarrow$  distribution fun.

Average number of particles per momentum state

Distribution for spinless distinguishable particles!

$$\text{Now. } N = \sum n_i = \sum g_i e^{-\alpha - \beta \varepsilon_i}$$

$$= e^{-\alpha} \sum g_i e^{-\beta \varepsilon_i}$$

$$Z = \sum_i g_i e^{-\beta \varepsilon_i}$$

Partition fun

num of states.

$$e^{-\alpha} = \frac{N}{Z}$$

$$\text{Th} \quad f(\varepsilon_i) = \left( \frac{n_i}{g_i} \right) = \frac{N}{Z} e^{-\beta \varepsilon_i}$$

$$\text{Now } d_n W = N \ln N - \sum n_i \ln n_i + \sum n_i \ln g_i$$

$$= N \ln N - \sum n_i (\ln N - \ln Z - \beta \varepsilon_i + \ln g_i) + \sum n_i \ln g_i$$

$$= N \ln' N - \sum n_i \ln' N + (\ln Z) \otimes N + \beta \sum \varepsilon_i n_i - \sum n_i \ln' g_i + \sum n_i \ln g_i$$

$$= N \ln Z + \beta U \quad U = \sum n_i \varepsilon_i$$

$\uparrow$  total energy

$$S = K \ln W = N K \ln Z + K \beta U$$

For a system of non-interacting particles  $U =$   
 $\checkmark$  internal energy

Introduce  $T$  by thermodynamics |  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V$

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$$\left(\frac{\partial S}{\partial V}\right)_V = \frac{Nk}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial V}\right)_V + k\beta.$$

$$\frac{n_i}{g_i} = \frac{N}{Z} e^{-\beta \varepsilon_i}$$

$Z \equiv \sum g_i e^{-\beta \varepsilon_i}$

$$+ k \cdot \nu \cdot \left(\frac{\partial \beta}{\partial V}\right)_V$$

Now  $\left(\frac{\partial Z}{\partial \beta}\right)_V = - \sum g_i \varepsilon_i e^{-\beta \varepsilon_i}$

$\sum g_i \varepsilon_i n_i e^{-\beta \varepsilon_i}$

$= - \frac{\nu Z}{N}$

$$= \sum n_i \varepsilon_i \frac{Z}{N} e^{\frac{\beta \varepsilon_i}{\nu}} \left(\frac{\partial S}{\partial V}\right)_V = \frac{Nk}{Z} \left(-\frac{\nu Z}{N}\right) \left(\frac{\partial \beta}{\partial V}\right)_V + k\beta$$

$$+ k \nu \left(\frac{\partial \beta}{\partial V}\right)_V$$

$$= \frac{Z}{N} \nu$$

$$= k\beta$$

$$\Rightarrow \beta = \frac{1}{k} \left(\frac{\partial S}{\partial V}\right)_V = \frac{1}{kT}$$

Then  $f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{N}{Z} e^{-\frac{\varepsilon_i}{kT}}$

Maxwell Boltzmann distribution!

## Partition function & Thermodynamic Properties.

Ideal monoatomic gas system of  $n$  identical distinguishable particles in  $V$  & total internal energy  $U$ .

$$U = \sum \varepsilon_i n_i = \frac{N}{Z} \sum g_i e^{-\frac{\varepsilon_i}{kT}}$$

$$Z = \sum g_i e^{-\frac{1}{kT} \varepsilon_i}$$

$$\frac{\partial Z}{\partial T} = \frac{1}{kT^2} \sum g_i \varepsilon_i e^{-\frac{\varepsilon_i}{kT}}$$

$$\checkmark \text{ so } U = N k T \ln \left( \frac{\partial}{\partial T} (\ln Z) \right)$$

Now  $S = k \ln W = N k \ln Z + N U \frac{1}{kT}$

$$= N k \ln Z + U/T.$$

Helmholtz free energy  $F = U - TS$

$$= -N k T \ln Z$$

Also  $S = N \ln Z + N k T \left( \frac{\partial \ln Z}{\partial T} \right)_V$

Now  $P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{N k T}{Z} \left( \frac{\partial Z}{\partial V} \right) \checkmark$

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$$H = U + PV = NkT \left[ T \left( \frac{\partial \ln z}{\partial T} \right)_V + V \left( \frac{\partial \ln z}{\partial V} \right)_T \right]$$

$$G = F + PV = NkT \left[ -\ln z + V \left( \frac{\partial \ln z}{\partial V} \right)_T \right]$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = Nk \left[ 2T \frac{\partial}{\partial T} (\ln z) + T^2 \frac{\partial}{\partial T} (\ln z) \right]_V$$

Ideal Gas: Dilute gas

$$\sum \epsilon_i = \sum k \cdot E$$

$$\int \frac{\partial^3 p \partial^3 \epsilon}{h^3} = \frac{4\pi V}{h^3} \int p^2 dp$$

$$\# \text{ of states} = \frac{2\pi V}{h^3} (2m)^{3/2} \int \sqrt{\epsilon} F dE$$

$$Z = \sum g_i e^{-\epsilon_i/kT}$$

$$N_{\text{gas}} = \int_0^\infty g(\epsilon) e^{-\epsilon/kT} d\epsilon \quad \begin{matrix} \text{energy level} \\ \text{closely packed} \end{matrix}$$

$$= \int_0^\infty \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon$$

$$= \frac{2\pi V}{h^3} (2m)^{3/2} (kT)^{3/2} \int_0^\alpha x^{1/2} e^{-x} dx \quad x = \frac{\epsilon}{kT}$$

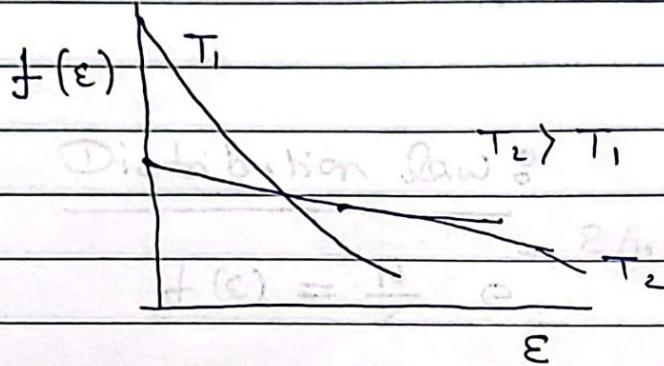
$$= \frac{2\pi V}{h^3} (2m kT)^{3/2} \Gamma\left(\frac{3}{2}\right) = \frac{V}{h^3} (2\pi m kT)^{3/2}$$

$$e^{-\alpha} = \frac{N}{Z} = \frac{N}{V} \left( \frac{h^2}{2\pi m k T} \right)^{3/2}$$

Then MB distribution fun

$$f(\varepsilon) = e^{-\alpha} e^{-\varepsilon/kT}$$

$$= e^{-\varepsilon/kT} \frac{N}{V} \left( \frac{h^2}{2\pi m k T} \right)^{3/2}$$



- For electrons gas obeying MB, Z must be multiplied by 2 for two spin orientations

$$\underline{\text{Now}} \quad F = -NkT \ln Z$$

$$= -NkT \left[ \ln V - \ln h^3 + \frac{3}{2} \ln (2\pi m k T) \right]$$

$$\left( \frac{\partial F}{\partial V} \right)_T = -\frac{NkT}{V}$$

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

$$\Rightarrow P V = n R T$$

$$U = N k T^L \frac{\partial}{\partial T} \ln Z$$

$$= N k T^L \frac{3}{2} \frac{1}{T} = \frac{3}{2} N k T$$

$$N(\epsilon) d\epsilon = \frac{2\pi m}{(2\pi mkT)^{3/2}} e^{-\epsilon/kT} = \frac{3}{2} n R T$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} R$$

Distribution law :-

$$f(\epsilon) = \frac{N}{Z} e^{-\epsilon/kT}$$

$$\underline{N(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon}$$

$$= \frac{N}{Z} e^{-\epsilon/kT} \frac{2\pi m (2m)^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

$$= \frac{N h^3}{V} (2\pi m kT)^{-3/2} e^{-\epsilon/kT}$$

$$= \frac{2\pi m (2m)^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

$$N(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon$$

Maxwell's energy distribution

→ Number of molecules having energy between  $\epsilon$  and  $\epsilon + d\epsilon$

$$\text{Now } \mathcal{E} = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

$$d\mathcal{E} = m v d\mathbf{v}$$

$$N(v) dv = \frac{2\pi N}{(\pi kT)^{3/2}} \left( \frac{1}{2} m v^2 \right)^{1/2} e^{-\frac{1}{2} \frac{mv^2}{kT}} dv$$

$$dN_v = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

Velocity distribution law  $\rightarrow$

number of molecules  $N(v)$  with speed (velocity) between  $v$  &  $v+dv$ .

$$\checkmark N(p) dp = \frac{\sqrt{2\pi N}}{(\pi m kT)^{3/2}} p^2 e^{-\frac{p^2}{2mkT}} dp$$

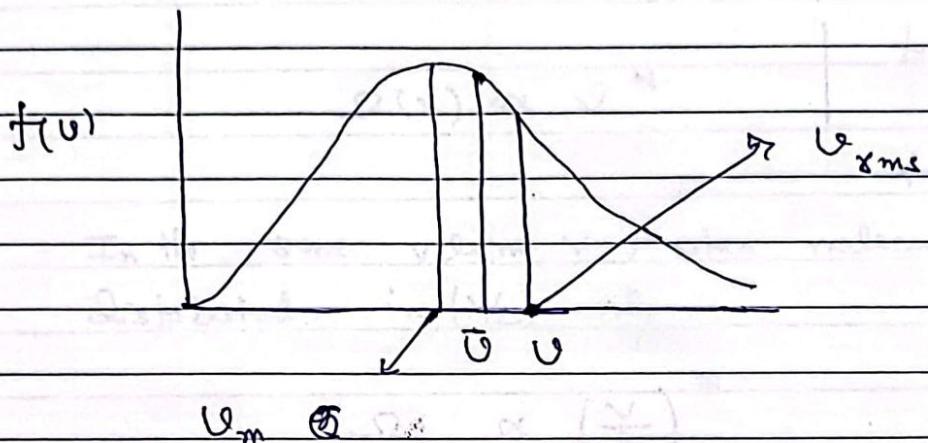
$$\bar{v} = \frac{1}{N} \int_0^\infty v dN_v$$

$$\bar{v} = \sqrt{\frac{8kT}{m\pi}}$$

$$\bar{v^2} = \frac{1}{N} \int_0^\infty v^2 dN_v = \frac{3kT}{m}$$

$$f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

~~for~~  $\frac{df}{dv} = 0 \Rightarrow v_{\text{most prob}} = \sqrt{\frac{2kT}{m}}$



(20)

Consider a box of volume  $V$  with  $N$  molecules!

→ we see "always" that molecules are homogeneously distributed!

→ For homogeneous distribution of  $N$  molecules in volume  $V$  can be realised by MANY microstates!

when molecules are distributed over  $V$

$$\Omega(v) \propto v^N.$$

for single molecule  
 $\Omega \propto v$

$$\text{for } N, \Omega \propto v^N$$

In the same volume  $V$ , when molecules are distributed in  $(V/2)$  only

$$\Omega \propto \left(\frac{v}{2}\right)^N$$

This is less probable by  $\left(\frac{1}{2}\right)^N$  factor

$$\sim \left(\frac{1}{2}\right)^{10^{23}}$$

$$\frac{1}{2^N} \rightarrow 0 \text{ for } N \rightarrow \infty$$

Gathering in  $(V/2)$  is possible but highly unlikely.

Will hold for any small volume  $\omega$

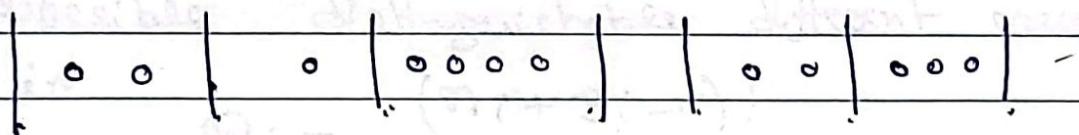
$$\omega^N \rightarrow 0 \text{ for } \omega < 1, N \rightarrow \infty$$

## Bose Einstein Statistics:

- Identical particles  $\rightarrow$  indistinguishable.
- Do not obey Pauli's exclusion principle.  
Any number of bosons may occupy any momentum level.
- $\delta N = \sum \delta n_i = 0$  (isolated)
- non interacting particle  $\delta u = \sum \epsilon_i \delta n_i = 0$

$g_i \rightarrow$  # eigenstate having  $E_i$  energy.

each eigenstate can have arbitrary num of particles.



Each line a state & no dots fall below the line  $\Rightarrow$  no. of particles in that state

$$g_i = 7, n_i = 12$$

First state 2 particles

Four .. 0 particle.

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There are  $(g_i + n_i)$  quantum states + particles.

$\propto (S_i + n_i)$  objects. ✓

Q Keep the first line fixed, and we have

$(S_i + n_i - 1)$  objects  $\rightarrow$  all permutations  
possible

$$(S_i + n_i - 1)!$$

Among them  $n!$  permutations of  $n_i$  particles.

among them  $(S_i - 1)$  lines among themselves do not affect the distribution.

Possible distinguishable different arrangement  
of  $n_i$  particles in  $S_i$  states.

$$\Omega_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$:= n_i! (g_i - 1)!$$

Total number of ways of distribution of  
N particles in n energy levels

$$\Omega = \prod_i^n \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$:= n_i! (g_i - 1)!$$

3(B)

Most probable distribution -

$$\delta S = 0 \text{ subject to } \delta N = 0$$



$$\delta V = 0$$

$$f(\varepsilon_i) = \left( \frac{n_i}{g_i} \right) = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} + \alpha + \beta \varepsilon_i}$$

$$\alpha = \frac{N}{Z}$$

$$\beta = \frac{1}{kT}$$

- For photons number of particles are not conserved

Number of photons i.e.  $\alpha = 0$

$$f(\varepsilon_i) = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}$$

Now  $S = k \ln \Omega$

stably

$$\sum [(n_i + s_i) \ln (n_i + s_i)]$$

$$- n_i \ln n_i - s_i \ln s_i$$

Put  $n_i$  formula

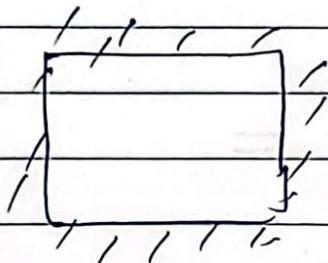
3(4)

Some steps ...

$$S_{\max} = \frac{4}{3} A \nu T^3.$$

$$\text{with } A = \frac{8\pi^5 k^4}{15 c^3 h^3}$$

BE start to Planck's law -



Black body chamber of vol V  
at T.

Ses of photons

$$n_i = \frac{g_i}{e^{\alpha + \epsilon/kT} - 1}$$

Number of photons with energ  $\epsilon \rightarrow \epsilon + d\epsilon$

$$dN = N(\epsilon) d\epsilon = \frac{g(\epsilon)}{e^{\epsilon/kT} - 1} d\epsilon$$

$g(\epsilon) d\epsilon \rightarrow$  # quantum states of photons ✓

Number of quantum states with  $p \rightarrow p + dp$ .

~~$$g(p) dp = \frac{V}{h^3} 4\pi p^2 dp$$~~

$$dN = \left( \frac{d^3 \times d^3 p}{h^3} \right) \cdot \frac{1}{e^{\beta E} - 1}$$

3(5)

*polarization*

$$= 2 \sqrt{\left( \frac{4\pi p^2 dp}{h^3} \right)} \frac{1}{e^{\beta E} - 1}$$

$$\epsilon = p^c$$

$$\text{ie } p^c \frac{dp}{\epsilon^2 d\epsilon} = \frac{8\pi V}{h^3 c^3} \frac{\epsilon^c d\epsilon}{e^{\beta \epsilon} - 1}$$

$$p = \frac{h v}{c}$$

$$= \frac{8\pi V}{h^2 c^2} \frac{h^2 v^2}{c} \frac{dv}{e^{\beta h v} - 1}$$

$$= \frac{8\pi V}{c^3} \frac{1}{e^{\beta h v} - 1} v^2 dv$$

Total number of particles !

Total number of particles

$$\int dN = \int \frac{8\pi V}{h^3 c^3} \frac{\epsilon^c d\epsilon}{e^{\beta \epsilon} - 1}$$

$$N = 2 \times 10^7 V T^{-3}$$

3(6)

number density of photons  $\propto T^3$

at 273 K,  $1 \text{ m}^3 \rightarrow 10^{14}$  photons!

Ideal gas  $10^{25}$  molecules!

Distribution of photon energy

$$dE = \epsilon dN$$

$$= \epsilon \cdot \frac{8\pi v}{h^2 c^3} \frac{e^{-\beta \epsilon}}{e^{\beta \epsilon} - 1} d\epsilon$$

1. energy density  $u = \frac{8\pi}{c} \left( \frac{E}{v} \right)$

$$u(T, \epsilon) d\epsilon \quad \boxed{d\epsilon = \frac{8\pi \epsilon^2}{h^3 c^3} \frac{d\epsilon}{e^{\beta \epsilon} - 1}}$$

$$= \frac{8\pi h}{c^3} \frac{v^3}{e^{\beta hv} - 1} dv = u(v, T) \frac{dv}{dv}$$

$$= \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{\beta hc/\lambda} - 1} = u(\lambda, T) d\lambda$$

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$$U(T) = \int_0^\infty \frac{8\pi n c}{\lambda^5} \frac{d\lambda}{e^{\beta hc/\lambda} - 1}$$

$$= \frac{8\pi^5 k_B^4}{15 h^3 c^3} T^4 = a T^4$$

3 (6)

## FD statistics:

$$\Omega = \frac{n}{T} = \frac{g_i!}{n_i! (g_i - n_i)!}$$

$$f(\varepsilon_i) = \left( \frac{n_i}{g_i} \right) = \frac{1}{e^{\alpha + \beta \varepsilon_i} + 1}$$

$$N(\varepsilon) d\varepsilon = \frac{g(\varepsilon)}{\alpha + \beta \varepsilon_i/kT + 1}$$

$$\varepsilon = -\frac{\varepsilon_F}{kT} \quad \varepsilon_F = \text{Fermi energy}$$

highest occupied state

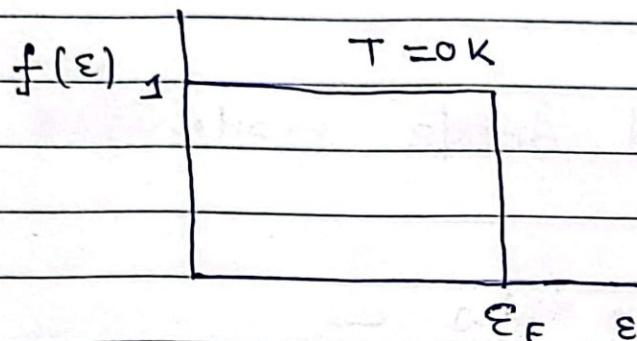
$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} + 1}$$

3(9)

$$\text{at } T = 0 \text{ K}$$

$$f(\varepsilon) = \begin{cases} 1 & \varepsilon_i < \varepsilon_F \\ 0 & \varepsilon_i > \varepsilon_F \end{cases}$$



ie at  $T = 0$ , for all states  $\varepsilon < \varepsilon_F$   
occupation probability = 1

$$\varepsilon > \varepsilon_F \rightarrow \text{occupation}$$

$$prob = 0$$

ie at  $T = 0$   $\varepsilon = \varepsilon_F$  def<sup>n</sup>s highest  
occupied energy level

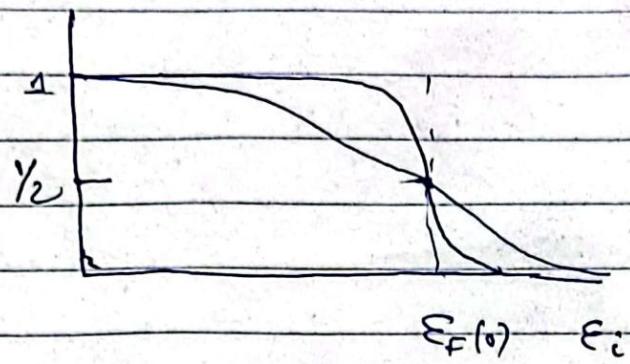
$$\leftarrow T_F = \varepsilon_F / k$$

from temp ✓

$$\text{at } T \neq 0 \text{ when } \varepsilon_i = \varepsilon_F \rightarrow f = \frac{1}{e^{\frac{\varepsilon_i - \varepsilon_F}{kT}} + 1}$$

$$= \frac{1}{2}$$

40 (20)



Application → specific heat of free electron  
in metal,

→ white dwarf etc.