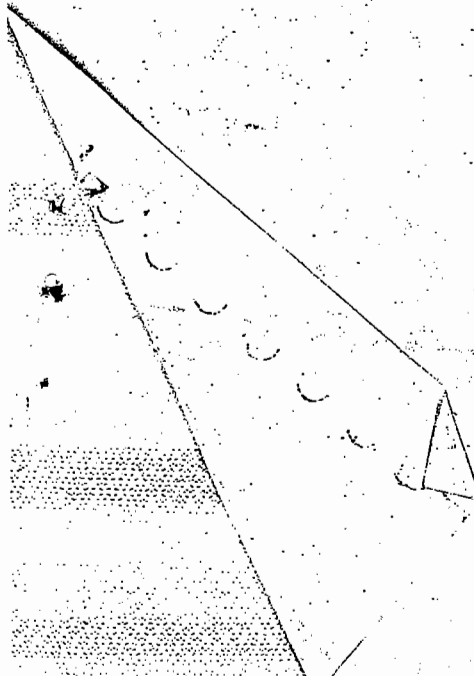
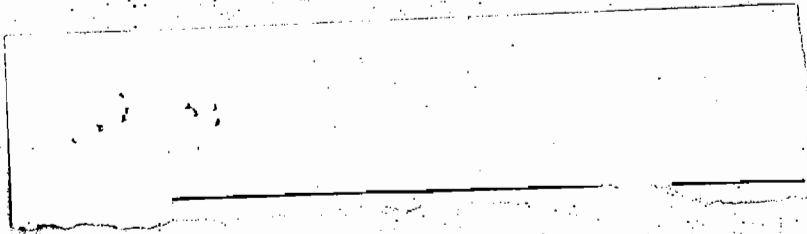
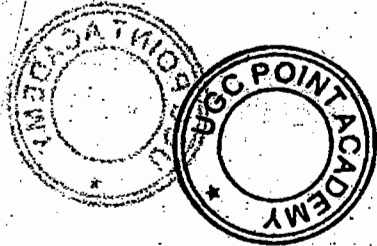


Jai Maa Saraswati

UGC POINT ACADEMY

Statistical Mechanics




$$(a+b)^2 \xrightarrow{\substack{\downarrow \\ \text{macro}}} a^2 + 2ab + b^2 \xrightarrow{\substack{\downarrow \\ \text{micro}}}$$

→ One coin : Two macrostate, Two microstate

→ 3 coin : 4-macrostate & 8-micro.

Toss of n-coins;

$$(a+b)^n \rightarrow (n+1) \rightarrow \text{macrostate}$$



$$2^n \rightarrow \text{microstate.}$$

Pro. of equally LPE is  $\rightarrow \frac{1}{2^n}$

→ If degeneracy of state are exist then No. of ways of distn

$$\Omega = \frac{1}{\prod_i n_i!} \prod_i g_i^{n_i}$$

Q. 10 similar coins are tossed together. what is the prob. of getting 4 heads.

$${}^{10}C_4 \left(\frac{1}{2}\right)^4 \left(\frac{1}{2}\right)^6$$

$$\rightarrow \frac{{}^{10}C_4}{2^{10}}$$

Q. A random walker may take a step towards right or left at random, what is the prob. that the walker comes to its initial pos. after taking 6 steps  $\rightarrow {}^6C_3 \left(\frac{1}{2}\right)^6$

# Statistical Mechanics:

(Based on distribution of particle)

Branch of mechanics which deals with the <sup>prob. of</sup> system involving large no. of molecule/particles.

How?

→ S.M. solve the prob. of <sup>macroscopic</sup> system by microscopic pt. of view.

→ In thermodynamics we solve the prob. of a macroscopic system by macroscopic pt. of view.

→ By S.M. we can calculate the average properties of Bulk material. As the no. of molecules involve in the calculation increases the result of calculations becomes more perfect.

→ This mechanics is based on distribution of particle. By knowing the distribution of particles in system we calculate the physical properties of the system.

→ Initially, this mechanics was developed by Maxwell, Boltzmann, Gibbs etc.

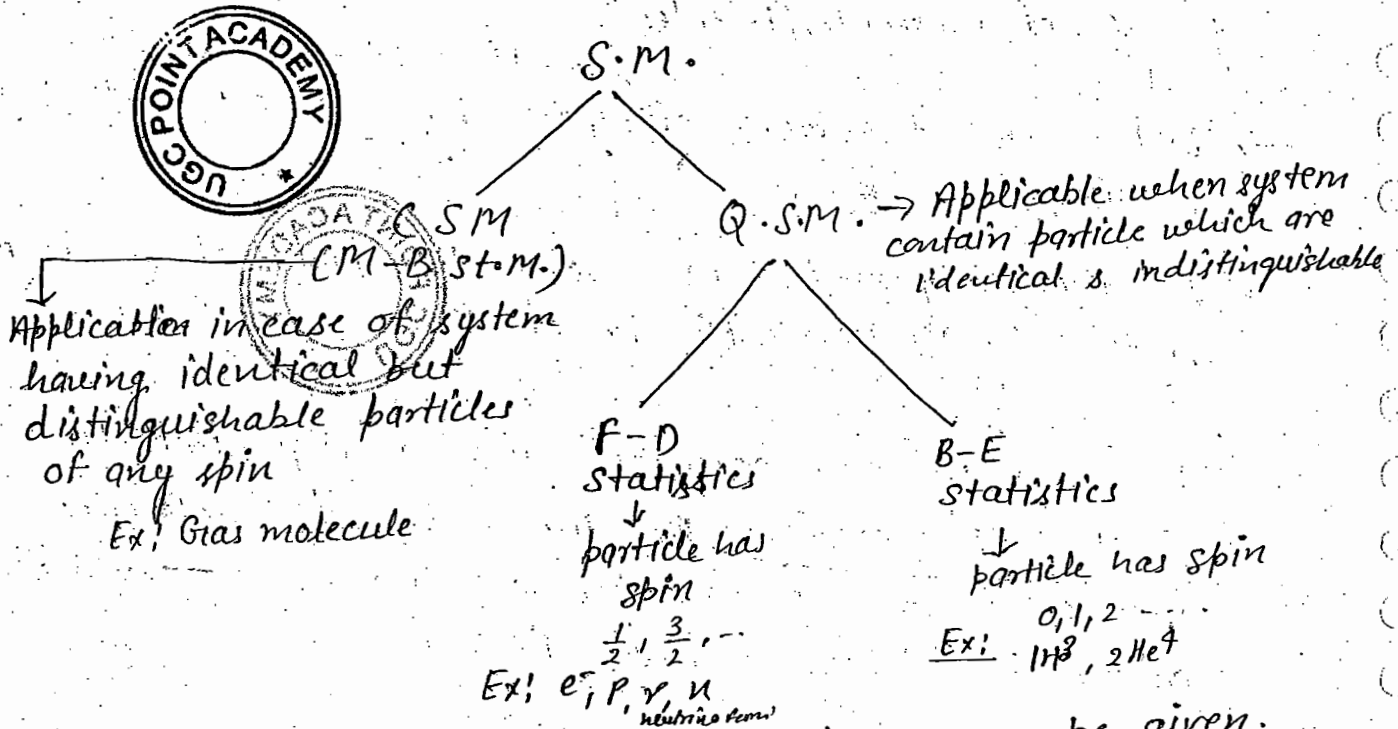
→ This branch of S.M. is known as M-B statistical mechanics or classical statistical mechanics.

By it we can calculate the average energy ( $\bar{E}$ ), Ave. ( $\bar{P}$ ), Ave. temp ( $\bar{T}$ ), Av. value of chemical potential ( $\bar{\mu}$ ) etc.

→ But later it fails to explain BBR, specific heat of solids at low temp., BEC (Bose-Einstein condensation)

Then another branch of S.M. is developed by terms Dirac, Bose, Einstein etc. which is based on Planck's quantum idea (discrete exchange of energy b/w radiation & matter).

→ This new branch is Kias Q.S.M.



→ Classical particle (A, B, C, etc) Name can be given.

→ Quantum particles (.....) represented by dots of same size or same letter.

→ Total No. of particles ( $e^-, p, n$ )

$$= Z + A \quad (\text{atom})$$

A

(nucleus)

Even → Bosons

Odd → fermions

${}_{3}Li^7$  is atom  
Then Boson

if  ${}_{3}Li^7$  is nucleus  
Then it's fermions.

$N \rightarrow$  fermions

→ A photon is boson, An  $e^-$  is fermion.

## C.S.M. :

### Distribution :

Prob: find the no. of ways of distribution, when 3 distinguishable particles are to be distributed in a box such that

a) A box, contain 1 particle only  $r=1$

Ans: 3

$\boxed{A}$  or  $\boxed{B}$  or  $\boxed{C}$

b.) Box contains two particles.

Ans: 3

$\boxed{AB}$  ,  $\boxed{BC}$  ,  $\boxed{CA}$

c.) Box contains 3 particles.

Ans: 1

$\boxed{ABC}$

→ Thus the no. of ways of distribution of  $N$  particles such that box contain  $r$  out of  $N$  distinguishable particles =  $N C_r = \Omega$

### Macrostate or Macroscopic state :

The state which represents the observable property of the system, is called macrostate.

#### Observable properties :

$N$  (No. of particles), Volume ( $V$ )  
Energy ( $E$ ), momentum ( $P$ ) etc.

→ A macrostate has large no. of microstates.  
(Accessible under given restriction)

Microstate: The states which represents the unobservable property of the system.



→ No. of  $\Omega$ -state in a macrostate is called Thermodynamical probability ( $\Omega$ ).  $> 1$ . explain or represent No. or ways of distribution.

$$S = k_B \ln \Omega \rightarrow \text{As we increase no. of particles, more no. of microstate, so the system moves toward most prob. state}$$

Prob:

$N$  particles are to be distributed into two boxes such that box 1 contain  $n_1$  particles and 2 box contain  $n_2$  particles &  $N = n_1 + n_2$ . find the no. of ways of distribution? or thermodynamical probability/no. of  $\Omega$ -state

$$\Omega = {}^N C_{n_1} \text{ or } {}^N C_{n_2}$$



$$\text{or } \frac{N!}{n_1! n_2!}$$

$N$  particles are to be distributed in large No. of boxes having  $n_1, n_2, n_3, \dots$  particles

$$N = n_1 + n_2 + \dots$$

No. of ways of distribution:

$$= {}^N C_{n_1} \times {}^N C_{n_2} \times \dots \times {}^N C_{n_3} \times \dots$$

$$\Omega = \frac{N!}{n_1! n_2! n_3! \dots} = \frac{N!}{\prod n_i!}$$

Prob: 1000 particles are to distributed in 3 boxes having (500, 400 & 100) particles. find the entropy of the system.

$$\ln N = N \ln N - N \quad \text{Stirling's formula}$$

(provided  $N$  large)



$$\ln N = \ln(1, 2, 3, \dots, N)$$

$$= \sum_{x_i=1}^N \ln x_i$$

$$= \int_{x=1}^N \ln x dx$$

$$= x \ln x - x \Big|_1^N$$

$$= N \ln N - N + 1$$

Prob: Two spin  $\frac{1}{2}$  particles <sup>of mag. moment  $(\mu_B)$</sup>  are placed in a mag. field in z-dir. find the total no. of ways of distributions.

U U  
U D  
D U  
D D

$$\Omega = (2s+1)^N$$

		En. of particle		En. of system
U	U	$-4B$	$-4B$	$-24B$
U	D	$-4B$	$4B$	0
D	U	$4B$	$-4B$	0
D	D	$4B$	$4B$	$24B$

→ Total No. of  $\mu$ -state = 4

→ The No. of  $\mu$ -state corresponding to  $E=0$   
= 2

→ In all  $\mu$ -state are equally probable find the probability of finding the system in most probable macrostate.

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

Prob: Consider a system of 3 spin  $1/2$  particles. The z-component of spin of system is given by

$$S_z = S_z(1) + S_z(2) + S_z(3)$$

each of  $S_z(1)$ ,  $S_z(2)$ ,  $S_z(3)$  can take value  $\pm 1/2$

find

- (i) Total no. of  $M$ -state of the system  $\rightarrow 8$
- (ii) No. of  $M$ -states in macrostate  $S_z = 1/2 \rightarrow 3$
- (iii) If all  $M$ -states are equally probable of finding the system in  $S_z = -1/2 \rightarrow 3/8$

Prob: Consider the case of 10 unbiased coins, tossed simultaneously.

find the no. of ways of distribution

- i) 3 H uppermost (3H, 7T)

$${}^{10}C_3$$

Probability  $\rightarrow$



The quantitative value of qualitative statements.

Spin  $1/2$  particles

Coins related prob.

dice related "

Random walker

Particle distr. in two boxes

baby births

particle in given volume  $u$  of a box of vol.  $v$ .

$\rightarrow$  Prob. of equally likely probable even  $= \frac{1}{2^n}$



Distribution of probability:

Binomial distribution: Is discrete distribution and applicable when  $p$  &  $q (=1-p)$  are not too low. The prob.  $p$  of one trial is known.

$(p+q)^N = 1 = \sum_{r=0}^N {}^N C_r p^r q^{N-r}$   
 Total Prob. in  $n$ -trial. w/for event

$P(r, N-r) = {}^N C_r p^r q^{N-r}$



Prob: An unbiased coin is tossed 10 times. find the prob. of getting

- (i) 1 H uppermost  $r=1$   $\frac{{}^N C_r p^r q^{N-r}}{p^N q^0}$
- (ii) 9 T uppermost
- (iii) At least 9 H uppermost  ${}^N C_r - 1, r=1$   ${}^{10} C_1$
- (iv) 5 T uppermost  $(\frac{1}{2})^{10}$  max. prob.
- (v) (5T, 5H) distribution prob.
- (vi) Prob. of least probable distribution  $\frac{{}^{10} C_5 (\frac{1}{2})^5 (\frac{1}{2})^5}{10}$
- (vii) Probability of most probable distri
- (viii) Prob. At least 1 T uppermost  $= \sum_{r=1}^N {}^N C_r (\frac{1}{2})^N$

$q = 1-p$

$p = \frac{1}{2}, q = \frac{1}{2}, N = 10$   
 (ix) At most 1 H uppermost  $P(0) + P(1)$

$\Rightarrow {}^{10} C_1 (\frac{1}{2})^1 (\frac{1}{2})^9$



${}^{10} C_0 (\frac{1}{2})^0 (\frac{1}{2})^{10} + {}^{10} C_{10} (\frac{1}{2})^{10} (\frac{1}{2})^0$

least  $\Rightarrow {}^{10} C_0 (\frac{1}{2})^{10} (\frac{1}{2})^0$

Q. 10 unbiased coin is tossed 1 time.

coin - baby  
tail  $\rightarrow$  girl  
H  $\rightarrow$  girl  
Tail  $\rightarrow$  Boy

coin  $\rightarrow$  Dice

toss  $\rightarrow$  Throw

$p$  (prob. of coming a no. uppermost 1, 3, 4, 5, 6)

$$= \frac{1}{6}$$

$$q = 1 - p = \frac{5}{6}$$



Q. A dice is thrown 10 times find probability that

(i) no. 1 comes uppermost all times  ${}^{10}C_{10} \left(\frac{1}{6}\right)^{10} \left(\frac{5}{6}\right)^0$

(ii) least probable case

(iii) No. 4 comes uppermost atleast 8 times.

$$P(8) + P(9) + P(10) = {}^{10}C_8 \left(\frac{1}{6}\right)^8 \left(\frac{5}{6}\right)^2 + {}^{10}C_9 \left(\frac{1}{6}\right)^9 \left(\frac{5}{6}\right)^1 + {}^{10}C_{10} \left(\frac{1}{6}\right)^{10} \left(\frac{5}{6}\right)^0$$

(iv) No. 6 doesn't appear uppermost

$${}^{10}C_0 \left(\frac{1}{6}\right)^0 \left(\frac{5}{6}\right)^{10}$$

Q. 10 dice are thrown simultaneously.

Q. 10 balls are distributed into 2 boxes with equal prob.  
find prob. of

(a.) all balls occupy 1st box  $(10, 0) = {}^{10}C_{10} \left(\frac{1}{2}\right)^{10}$

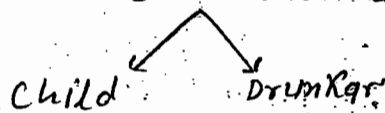
(b.) Prob. of distribution  $(8, 2) = P(r, n-r) = {}^{10}C_8 \left(\frac{1}{2}\right)^{10}$

(c.) Most probable distri.





Random Walker problem: One who don't care of taking steps



Prob: A one dim. random walker takes 10 steps in left right with equal prob.

4 step - 4C2

find prob. of

(i) Starting from origin, it will be at origin after all steps.

$${}^{10}C_5 \left(\frac{1}{2}\right)^{10}$$



(ii) Starting from 0, He will be one step away from 0, after all steps. Prob  $\begin{cases} n_1 + n_2 = 10 \\ n_1 - n_2 = 1 \end{cases} \Rightarrow n_1 = 5.5$   
 Not happening 0

(iii) Most probable distribution  ${}^{10}C_5 \left(\frac{1}{2}\right)^5 \left(\frac{1}{2}\right)^5$

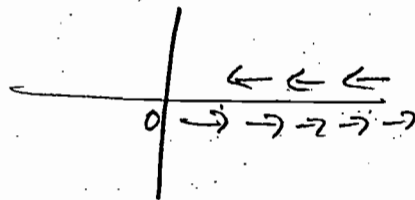
(iv) Least prob. distribution.  ${}^{10}C_{10} \left(\frac{1}{2}\right)^{10}$

(v) Start from 0 will be 2 steps from 0 after all steps.

$$\begin{cases} n_1 + n_2 = 10 \\ n_1 - n_2 = 2 \end{cases} \Rightarrow \begin{matrix} (6, 4) \text{ or } (4, 6) \\ {}^{10}C_6 + {}^{10}C_4 \end{matrix}$$

$${}^{10}C_4 \frac{1}{2^{10}}$$

$$\text{Ans: } 2 \times {}^{10}C_6 \left(\frac{1}{2}\right)^{10}$$



Prob: If 1-D random walker takes steps to right or left with equal prob. find the prob. that the random walker starting from the origin is back to origin after taking  $N$  even no. of steps.

$$N C_{N/2} \left(\frac{1}{2}\right)^N = \frac{N!}{\left(\frac{N}{2}!\right)^2} \left(\frac{1}{2}\right)^N$$

Sol<sup>n</sup>:

$$N C_{N/2} \left(\frac{1}{2}\right)^N$$

$$= \frac{N!}{\left(\frac{N}{2}!\right)^2} \left(\frac{1}{2}\right)^N$$



Prob: A drunkard starts from a certain lamp-post on the street and he is trying to get his destination at a distance  $x$ . Some of steps he take in forward dir<sup>n</sup> with prob. ( $p$ ) & some steps in backward dir<sup>n</sup> with prob. ( $q = 1 - p$ ), and each step is of equal length. What is the prob. that the drunkard will reach its destination after  $N$ -steps.

Sol<sup>n</sup>:

$$n_f + n_b = N$$

$$n_f L - n_b L = x$$

$$\text{Prob. } P(n_f) = N C_{n_f} p^{n_f} q^{N-n_f}$$

$$= N C_{n_f} p^{n_f} (1-p)^{n_b}$$



$$N = 10$$

$$L = 1m$$

$$x = 2m$$

$$p = \frac{2}{3}$$

$$q = \frac{1}{3}$$

$$n_f + n_b = 10$$

$$n_f - n_b = 2$$

$$n_f = 6$$

$$n_b = 4$$

$$= {}^{10}C_6 \left(\frac{2}{3}\right)^6 \left(\frac{1}{3}\right)^4$$

$$n_f + n_b = 10$$

$$n_f L - n_b L = x$$

→  $N = 10$  (when step is uncorrelated)

$$l_f = 2m, \quad l_b = 1m$$

$$x = 2m$$

$$p = \frac{2}{3}, \quad q = \frac{1}{3}$$

$$n_f + n_b = 10$$

$$2n_f - n_b = 2$$

$$n_f = 4$$

$$n_b = 6$$



$$= 10 C_4 \left(\frac{2}{3}\right)^4 \left(\frac{1}{3}\right)^6$$

Q. A random walker takes a step of unit length in +ve dir<sup>n</sup> with prob.  $\frac{2}{3}$  & a step of unit length in the -ve dir<sup>n</sup> with prob.  $\frac{1}{3}$ . The mean displacement of walker after  $n$  steps is

$$n/3, \quad n/8, \quad 2n/3, \quad 0$$

Sol<sup>n</sup>:

Mean displacement

$$\langle x \rangle = \frac{P_0 x_0 + P_1 x_1 + P_2 x_2 + \dots + P_n x_n}{P_0 + P_1 + P_2 + \dots + P_n}$$

$$= 0 + n C_1 \left(\frac{2}{3}\right)^1 \left(\frac{1}{3}\right)^{n-1} \cdot 1 + n C_2 \left(\frac{2}{3}\right)^2 \left(\frac{1}{3}\right)^{n-2} \cdot 2 + \dots + n C_n \left(\frac{2}{3}\right)^n \left(\frac{1}{3}\right)^0 \cdot n$$

OR

$$\langle x \rangle = \frac{P_f x_f - P_b x_b}{P_f + P_b}$$

$$= \frac{\frac{2}{3}(n \times 1) - \frac{1}{3}(n \times 1)}{\frac{2}{3} + \frac{1}{3}}$$

$$\langle x \rangle = \frac{n}{3}$$

Ave. distance travelled by the walker in forward dir<sup>n</sup> in  $n$  steps with prob.  $\frac{2}{3}$  of each step of length unit

$$= \frac{2n}{3}$$

In Backward: mean  $\frac{n}{3}$

$$\langle x \rangle = P x = \sum P_i x_i$$

Steps	Prob.	More ← Most Prob
left	1/8	
Right	7/8	

Q. A coin is tossed

Event	Prob.
0H	—
1H	
2H	
⋮	
⋮	
10H	



$$\text{Ave Head} = 0H \times P_0 + 1 \times P_1 + \dots$$

→ Statistical Error  $\propto \frac{1}{\sqrt{N}}$   
 or deviation  
 or uncertainty  $\propto \frac{1}{\sqrt{N}}$

→ Unbiased → Biased coin

$$NCr p^r q^{N-r}$$

$$P_H = \frac{1}{3}$$

$$Q_H = \frac{2}{3}$$

$P_T$

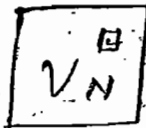
$$N = 10$$

$$P(4H) = {}^{10}C_4 \left(\frac{1}{3}\right)^4 \left(\frac{2}{3}\right)^6$$

Q. Consider a box of volume  $V$  containing  $N$  identical but distinguishable particles find

a.) The prob. that a given particle is in given volume  $v$  of the box.

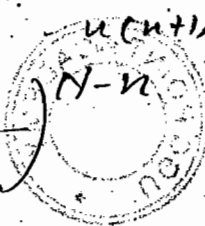
$$\frac{v}{V}$$



b.) The prob. that a given set of  $n$  particles are in a given volume  $v$  & all other particles are in the remaining volume.



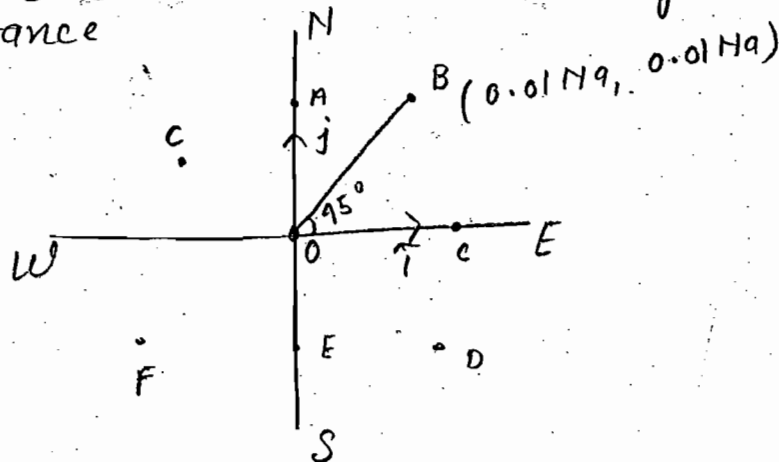
$$\left(\frac{v}{V}\right)^n \left(\frac{V-v}{V}\right)^{N-n}$$



c.) Prob. of finding any  $n$  particles in volume  $v$  & rest  $(N-n)$  in remaining volume

$$= N C_n \left(\frac{v}{V}\right)^n \left(1 - \frac{v}{V}\right)^{N-n}$$

Q. A child make a random walk on a square lattice of lattice const.  $a$  taking step in north, east, south & west dir<sup>n</sup> with prob.  $0.255, 0.255, 0.245, 0.245$  respectively. After a large No. of steps,  $N$ , the expected position of the child w.r. to the starting pt  $O$  is at a distance



$$\sqrt{2} \times 10^{-2} Na \text{ in N-E dir}^n$$

$$\sqrt{2} N \times 10^{-2} a \text{ in N-E dir}^n$$



$$\langle \vec{r} \rangle = \frac{P_1 \vec{r}_1 + P_2 \vec{r}_2 + P_3 \vec{r}_3 + P_4 \vec{r}_4}{P_1 + P_2 + \dots}$$

$$= 0.255 \text{ Na} \uparrow + 0.255 \text{ Na} \downarrow - 0.245 \text{ Na} \uparrow - 0.24$$

$$= 0.01 \text{ Na} \uparrow + (0.015) \text{ Na}$$

Prob:

Spin  $\frac{1}{2}$  particles are kept in a m.f. find prob.

(i) Most probable distri  
 $N C_{N/2} \left(\frac{1}{2}\right)^N$

(ii)  $\left(\frac{2N}{3}, \frac{N}{3}\right)$  most prob.  $N C_{2N/3} \left(\frac{1}{2}\right)^N$

(iii)  $(0, N)$  least prob.

$$\rightarrow N C_0 \left(\frac{1}{2}\right)^N$$



Prob:

Three fair dice are thrown simultaneously  
 find the probability of getting

a.) Sum 18 uppermost

$$(6, 6, 6) \quad \frac{1}{216}$$

b.) Sum of 12 uppermost

$$(6, 6) \quad \frac{1}{36}$$

c.) Most probable sum

$$(6, 1), (1, 6)$$

$$(3, 4), (4, 3)$$

$$(2, 5), (5, 2)$$

$$\rightarrow \frac{1}{6}$$

m.p.  
 $\frac{7+0+12}{6}$

as 8

$$6 \ 2$$

$$2 \ 6$$

$$5 \ 3$$

$$3 \ 5$$

$$4 \ 4$$

8 fm  
 13 6.9

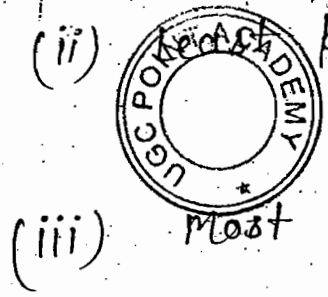
Prob: An unfair dice has prob. to appear 1, 2, 3, ..., 6 respectively as  $\frac{1}{21}, \frac{2}{21}, \frac{3}{21}, \dots, \frac{6}{21}$ . In throwing such a dice 4 times find prob.

(i) No. 1 appear in uppermost 2 times  

$${}^4C_2 \left(\frac{1}{21}\right)^2 \left(\frac{20}{21}\right)^2 \quad NCr P^N q^{N-r}$$

(ii) probable case  

$${}^4C_4 \left(\frac{1}{21}\right)^4 \left(\frac{20}{21}\right)^0 \quad NCr P^N q^0$$



(iii) Most probable case  

$${}^4C_0 \left(\frac{6}{21}\right)^0 \left(\frac{15}{21}\right)^4$$



(iv) If this dice is thrown 2 time. find the prob. of getting sum even uppermost

- $(1,1)$   $(1,3)$   $(1,5)$   $(2,2)$   $(2,4)$   $(2,6)$   
 $(3,3)$   $(4,4)$   $(4,6)$   $(5,3)$   $(5,5)$   $(6,6)$

(v) In throwing such a dice 3 times find prob. of getting sum  $\neq$  uppermost  $\rightarrow$  [1-odd sum]

(iv) 
$$\frac{1}{441} [1+6+10+4+16+48+9+46+30+25+36]$$
  

$$= \frac{225}{441}$$

(v) 
$$1 - [(1,2) (1,4) (1,6) (3,2) (3,4) (3,6) (5,2) (5,4) (5,6)]$$
  

$$1 - \frac{2}{441} [2+4+6+6+12+18+10+20+30]$$

Q. A system has 3 particles having energy

$$E = -\epsilon_0 [J_1 J_2 + J_2 J_3 + J_3 J_1]$$

each of  $J_1, J_2, J_3$  has values  $\pm 1$ . Find

- 1.) min<sup>m</sup> energy of the system  $\rightarrow -3\epsilon_0$   
*all -ve*
- 2.) max. en. of the system  $\rightarrow \epsilon_0$  (Any 2 +ve or -ve)
- 3.) No. of  $\mu$ -state in microstate  $E = \epsilon_0 = 6$   
 $3C_2$   
 $3+3=6$

$E = -3\epsilon_0$  (macrostate)  
having 24 state

Total no. of  $\mu$ -state  
 $= 8$



Sol<sup>n</sup>:

Q. Consider a system having 3 parameter  $J_A, J_B$  &  $J_C$  each of  $J_A, J_B, J_C$  can take value  $\pm 1$ . The prob. of changing the value of these parameter is  $2/3$  & not changing is  $1/3$ . Let  $J_A = 1, J_B = 1, J_C = -1$  at a given instant. In the next instant the prob. that  $J_A + J_B + J_C$  remain unchanged is  $\frac{2}{3}, \frac{1}{3}, \frac{2}{9}, \frac{4}{9}$  sum at <sup>given</sup> instant.

given instant:  $J_A + J_B + J_C = +1$   
 $\begin{matrix} 1 & 1 & -1 \end{matrix}$

On next, either

$$\frac{1}{27} + \frac{1}{9} \times \frac{2}{3} + \frac{1}{9} \times \frac{2}{3}$$

$$= \frac{12}{27}$$

or

$$\begin{matrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{matrix}$$

when it change

$$\rightarrow \frac{1}{27} + \frac{4}{27} + \frac{4}{27} = \frac{9}{27}$$

## Fundamental postulates of Statistical Mechanics:

→ Any gas under consideration may be considered to be composed of large no. of molecules which are constantly in motion. And behave like very small elastic spheres.

→ The configuration of the particle is completely described by six co-ordinates  $(x, y, z, p_x, p_y, p_z)$ . This six dim space is called phase-space. This phase is divided into large no. of elementary cells called phase cells, each having equal size  $h^3$ .

→ The most fundamental postulate of S.M. is "principle of equal a priori prob." i.e. all accessible macrostate are equally probable.

→ The equilibrium state of gas corresponds to the macrostate of max prob.

→ The total no. of molecules  $N = \sum_i n_i = \text{const}$  (conservation of mass)

→ Total energy of the system remains const.  
 $E = n_1 \epsilon_1 + n_2 \epsilon_2 + \dots = \sum_i n_i \epsilon_i = \text{const}$  (energy conservation)

← constraints on system:

Prob: 10 particles are distributed in 3 given cells, with energy per particle  $0, \epsilon, 3\epsilon$  such that

$$n_1 = 3, \quad n_2 = 5, \quad n_3 = 5$$

If total En of the system remains same. Then find  $\delta n_1$  &  $\delta n_2$  when  $\delta n_3 = -1$ . Also find the thermodynamical prob. for odd's new distribution.

Sol<sup>n</sup>:

$$n_1 + n_2 + n_3 = 13 = \text{constt}$$

$$\delta n_1 + \delta n_2 + \delta n_3 = 0$$

$$\delta n_1 + \delta n_2 = 1$$

$$E = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 = \text{constt}$$

$$\Rightarrow E = n_2 \epsilon + 3n_2 \epsilon$$

$$0 = \epsilon \delta n_2 + 3\epsilon \delta n_3$$

$$\delta n_2 = 3$$

new distribution (1, 8, 4)

No. of accessible  $\mu$ -state / thermodynamic prob.

$$\Omega = \frac{\Omega_1 \Omega_2 \Omega_3}{\Omega_1 \Omega_2 \Omega_3} = \frac{13}{11 \cdot 8 \cdot 4}$$



$$\Omega_{\text{old}} = \frac{13}{3 \cdot 5 \cdot 5} \quad \text{most prob. distri.} \\ \text{(equilibrium state)} \\ \text{maxim entropy state}$$

Phase-space: To describe the configuration of a particle completely, six co-ordinate ( $x, y, z, p_x, p_y, p_z$ ) required.

Six dim. space is called phase space.

Volume element in phase space

$$d\tau = dx dy dz dp_x dp_y dp_z$$

$$= (dx dp_x) (dy dp_y) (dz dp_z)$$

$$dx dp_x \sim h$$

$$d\tau \sim h^3$$

$$(d\tau)_{\text{min}} = h^3$$

Thus elementary cell in phase space or phase cell has volume  $h^3$ .

In cartesian co-ordinate

$(dT)_{\min} = 0 \rightarrow$  point element can never be possible in phase space.

$\rightarrow$  Volume of phase space :

$$= \iiint dx dy dz dp_x dp_y dp_z$$



$$-\infty < x, y, z < +\infty$$

$$-\infty < p_x, p_y, p_z < +\infty$$

macro-state

$$\begin{cases} p_x \rightarrow p_x + dp_x \\ p_y \rightarrow p_y + dp_y \\ p_z \rightarrow p_z + dp_z \end{cases}$$

$$p \rightarrow p + dp$$

or

$$E = E + dE$$

macrostate

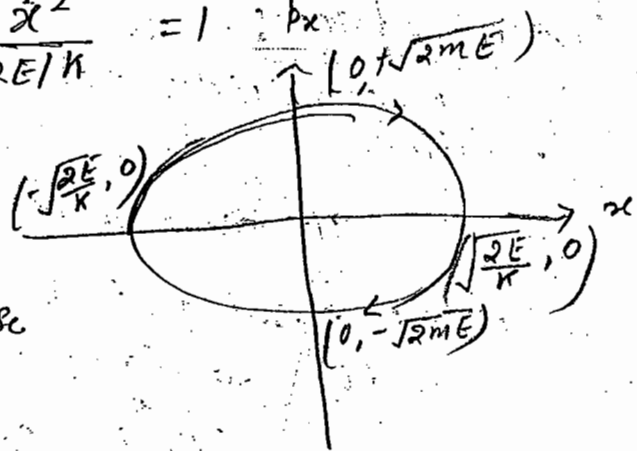


Application of phase space :

Ex: 1-D H.O.

$$E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2$$

$$\Rightarrow \frac{p_x^2}{2mE} + \frac{x^2}{2E/k} = 1$$



Accessible area to the O.s.c

$$= \pi ab$$

$$= \pi \sqrt{2mE} \sqrt{\frac{2E}{k}}$$

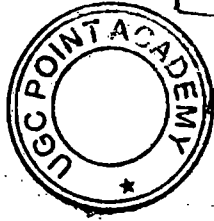
$$= E \cdot 2\pi \sqrt{\frac{m}{k}} = \frac{E}{\nu}$$

No. of possible H-state :

$$= \frac{\text{Accessible area to the Osc}}{\text{Area of 1 phase cell}}$$

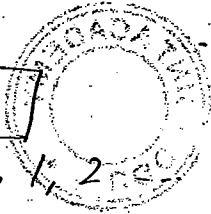
$$n = \frac{E/\nu}{dx dy dz dp_x} = \frac{E}{h\nu}$$

$$n = \frac{E}{h\nu}$$



$$E = nh\nu$$

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



\* free particle:

$$P.E. = 0$$

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

No. of  $n$ -state in momentum range  $p \rightarrow p+dp$   
or

In energy range  $E \rightarrow E+\delta E$

$$\Omega(p) dp = \frac{\text{Volume of phase space in mom. range } p \rightarrow p+\delta p}{\text{Volume of phase cell}}$$

$$\Omega(p) dp = \frac{\iiint dx dy dz dp_x dp_y dp_z}{h^3}$$

$$= \frac{\iiint dx dy dz \iiint dp_x dp_y dp_z}{h^3}$$

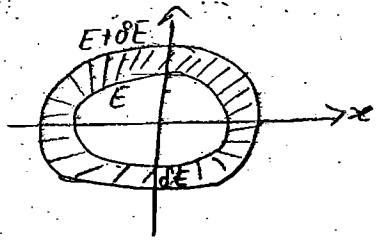
$$\Omega(p) dp = \frac{V}{h^3} \int_p^{p+dp} d^3p$$

$$\int_0^\infty \int_0^\infty \int_0^\infty p^2 \sin\theta d\theta d\phi dp$$

$$0 < r < \infty$$

$$0 < p < \infty$$

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



$$\delta n = \frac{\delta E}{h\nu}$$

$$\frac{\delta n}{\delta E} = \frac{1}{h\nu}$$

$$D(E) = \frac{1}{h\nu}$$

OR

$$D(E) \delta E = \frac{\delta E}{h\nu} = \delta n$$

↓  
Density of state i.e. no. of states per unit energy range.

$$E \rightarrow E + \delta E$$

no. of states in  $E$ -range  $\delta E = \frac{\delta E}{h\nu}$

$$\Omega(E) \delta E = \frac{\delta E}{h\nu}$$

$$0 \rightarrow E$$

$$\int_0^E \Omega(E) \delta E = \Omega = \text{Total no. of } n\text{-states in range } E$$

$$\Omega(p) dp = \frac{V}{h^3} \left[ \frac{4}{3} \pi (p+dp)^3 - \frac{4}{3} \pi p^3 \right]$$

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

$$p = \sqrt{2mE}$$

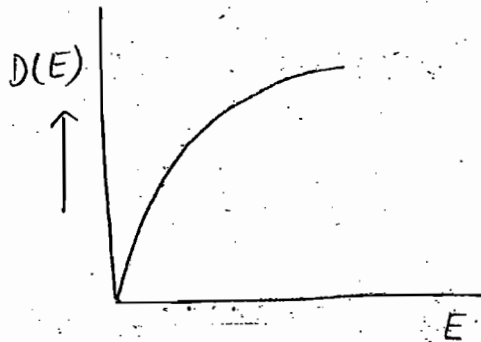
$$dp = \sqrt{2m} \frac{1}{2} E^{-1/2} dE$$

$$dn = \Omega(E) dE = \frac{4\sqrt{2} V \pi m^{3/2} E^{1/2} dE}{h^3}$$

$$\Omega(E) = \frac{dn}{dE} = D(E) = \frac{4\sqrt{2} V \pi m^{3/2} E^{1/2}}{h^3}$$

Density of state

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



\* Non-interacting photon gas:  
 No. of states available for photon is  
 mom. range  $p \rightarrow p+dp$   
 or  $E \rightarrow E+dE$

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

In terms of energy  $p = E/c$   
 $dp = dE/c$



$$\rho(E) dE = \frac{V 4\pi E^2 dE}{c^3 h^3}$$

$$\rho(E) = \frac{V 4\pi E^2}{c^3 h^3}$$

$$\parallel$$

$$D(E)$$

$$\parallel$$

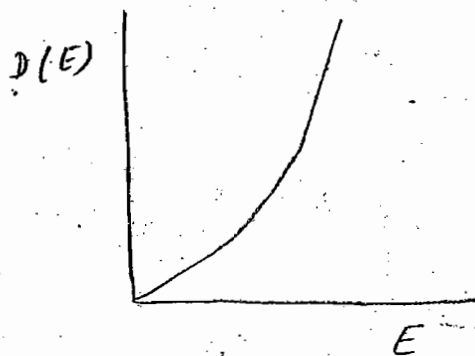
$$\frac{dN}{dE}$$

In terms of frequency

$$E = h\nu$$

$$dE = h d\nu$$

$$D(\nu) = \frac{V 4\pi \nu^2 d\nu}{c^3}$$



Phonon gas:

Expression are same as photon gas.

\* Density of states:

1-D: Consider a linear crystal of length  $L$

The periodic boundary cond<sup>n</sup>

$$\psi_k(x) = \psi_k(x+L)$$

$$\begin{array}{c} \text{-----} \\ x=0 \qquad \qquad \qquad x=L \end{array}$$

$$A e^{ikx} = A e^{ik(x+L)}$$

$$e^{ikL} = 1 = e^{\pm i2n\pi}$$

$$k = \pm \frac{2n\pi}{L} = \dots -\frac{4\pi}{L}, -\frac{2\pi}{L}, 0, +\frac{2\pi}{L}, +\frac{4\pi}{L}$$

No. of  $n$ -state in range  $k \rightarrow k + dk$

$$dn = \frac{\text{range of } k}{\text{length require for 1 state}}$$



$$= \frac{dk}{\left(\frac{2\pi}{L}\right)}$$

$$dn = \frac{L dk}{2\pi}$$

$$\frac{dn}{dk} = \frac{L}{2\pi}$$

OR

$$\boxed{D(k) = \frac{L}{2\pi}}$$

DOS



$$D(p) = \frac{L}{2\pi \hbar}$$

from

$$D(k) dk = \frac{L}{2\pi} dk$$

$$D(p) dp = \frac{L}{2\pi} \frac{dp}{\hbar}$$

$$\boxed{D(p) = \frac{L}{2\pi \hbar}}$$

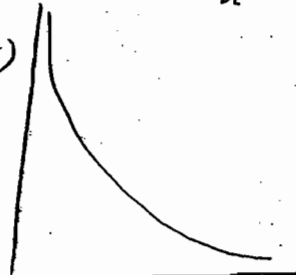
In terms of  $E$

$$p = \sqrt{2mE} \Rightarrow dp = \sqrt{\frac{m}{2}} E^{-1/2} dE$$

$$D(E) dE = \sqrt{2m} \frac{1}{2} E^{-1/2} dE = \sqrt{\frac{m}{2}} E^{-1/2} dE \frac{L}{\hbar}$$

$$\boxed{D(E) dE = \frac{L}{\hbar} \sqrt{\frac{m}{2}} E^{-1/2} dE}$$

$D(E)$



## DOS in 2-D :

No. of  $\mu$ -state in range  $k \rightarrow k+dk$

$$dn = \frac{\text{Area available in phase space}}{\text{Area required for 1 state}}$$



$$\frac{2\pi k dk}{\left(\frac{2\pi}{L}\right)^2}$$

$$dn = \frac{Ak dk}{2\pi}$$

$$L^2 = A$$

$$D(k) dk = \frac{Ak dk}{2\pi}$$

$$k = \frac{p}{\hbar}$$

$$dk = \frac{dp}{\hbar}$$

$$D(p) dp = \frac{Ap dp}{2\pi \hbar^2}$$

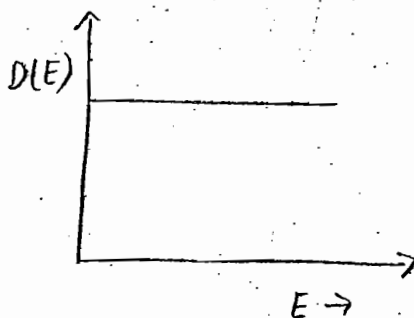
$$p^2 = 2mE$$

$$2p dp = 2m dE$$

$$p dp = m dE$$

$$D(E) dE = \frac{2\pi A m dE}{L^2}$$

$$D(E) \propto E^0$$



DOS in 3-D:

No. of 4-state in range

$$k \rightarrow k + dk$$

or

$$k_x \rightarrow k_x + dk_x, \quad k_y \rightarrow k_y + dk_y$$

$$k_z \rightarrow k_z + dk_z$$

$$dn = \frac{\text{Volume available in phase space}}{\text{Volume required for 1 state}}$$

$$dn = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = \frac{V k^2 dk}{2\pi^2}$$



$$L^3 = V$$

$$D(k) dk = \frac{V k^2 dk}{2\pi^2}$$

$$k = \frac{p}{\hbar}$$

$$dk = \frac{dp}{\hbar}$$

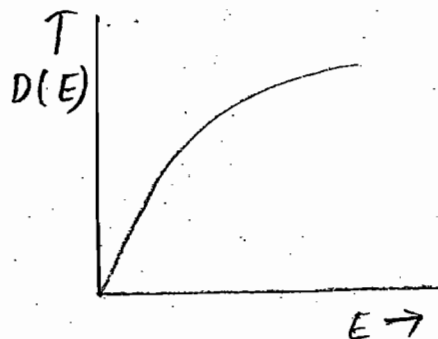
$$D(p) dp = \frac{V 4\pi p^2 dp}{\hbar^3} \rightarrow G.E.$$

$$p = \sqrt{2mE}$$

$$dp = \sqrt{\frac{m}{2}} E^{-1/2} dE$$

$$D(E) dE = \frac{4\sqrt{2}\pi m^{3/2} E^{1/2} dE}{\hbar^3}$$

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



$$\rightarrow \omega = v_0 k$$
$$\frac{\hbar\omega}{v_0} = p = \frac{E}{v_0}$$

ask  $\rightarrow E \propto p^2$  (given)

$s=1$  irrepy...  
 $s=1$  for photon or phonon

$D(E) \propto E^{d/s-1}$  in  $d$ -dim.

$\rightarrow E \propto p^2$  3-dim  
 $D(E) \propto E^{1/2}$

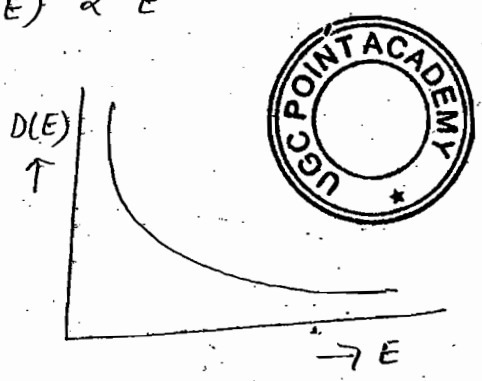
$\rightarrow E \propto \sqrt{p}$  3-D  
 $D(E) \propto E^{3 \times 2 - 1} \propto E^5$

Particle in 1-D rigid box  $\rightarrow$

$V(x) = 0$   $0 < x < L$   
 $= \infty$  elsewhere

$D(E) \propto E^{-1/2}$

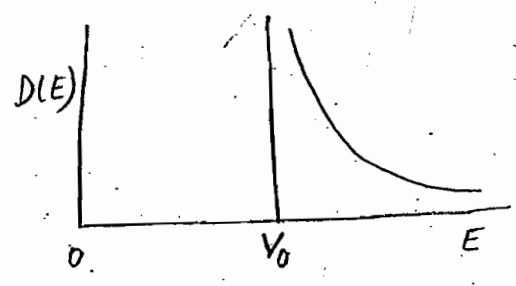
$E = \frac{p^2}{2m} + 0$   
 $D(E) \propto E^{\frac{1}{2}-1}$



$\rightarrow V(x) = V_0$   $0 < x < L$   
 $= \infty$  elsewhere

$D(E) \propto (E - V_0)^{-1/2}$

$E = \frac{p^2}{2m} + V_0$



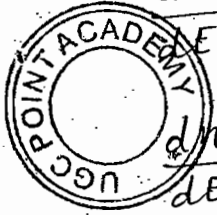
$E \propto p^s$   
 $E \propto k^s$   
 $\omega \propto k^s$   
 all are same things.

$$\rightarrow D(E) = \frac{dn}{dE}$$

$$E = \frac{n^2 h^2}{8mL^2} + V_0$$

$$dE = \frac{n h^2 dn}{4mL^2}$$

$$\frac{dn}{dE} = \frac{4mL^2}{h^2} \cdot \frac{1}{n}$$

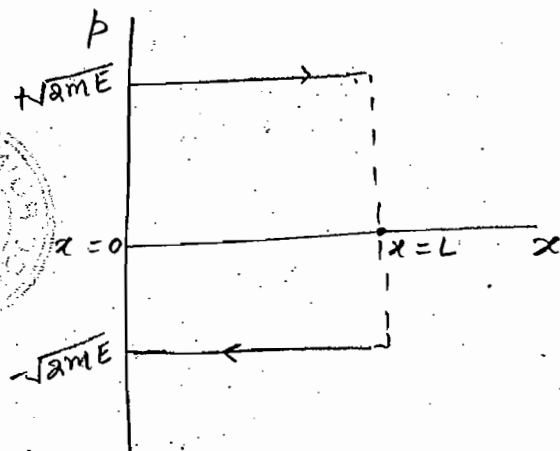


$$\frac{dn}{dE} \propto \frac{1}{n} \propto \frac{1}{(E-V_0)^{1/2}}$$

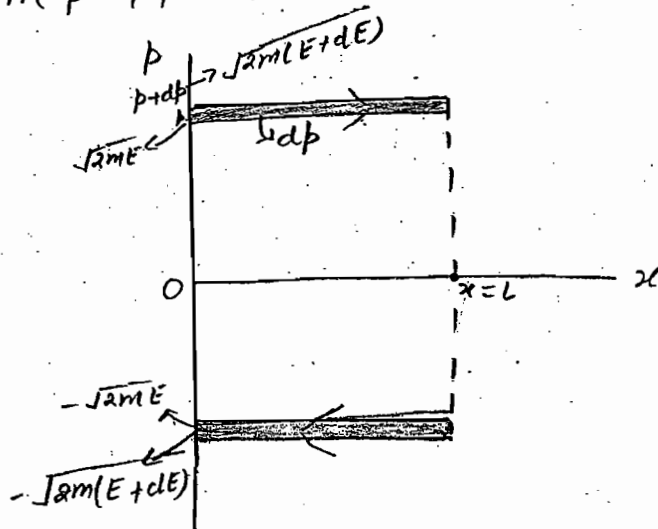
Phase-space diagram:

$$E = \frac{p^2}{2m}, \quad 0 < x < L$$

$$p = \pm \sqrt{2mE}$$



$\rightarrow$  If  $p$  varies from  $p \rightarrow p+dp$



Prob: The Hamiltonian of a particle is given by

$$H = \frac{p^2}{2m} - \frac{\alpha z^2}{2}$$

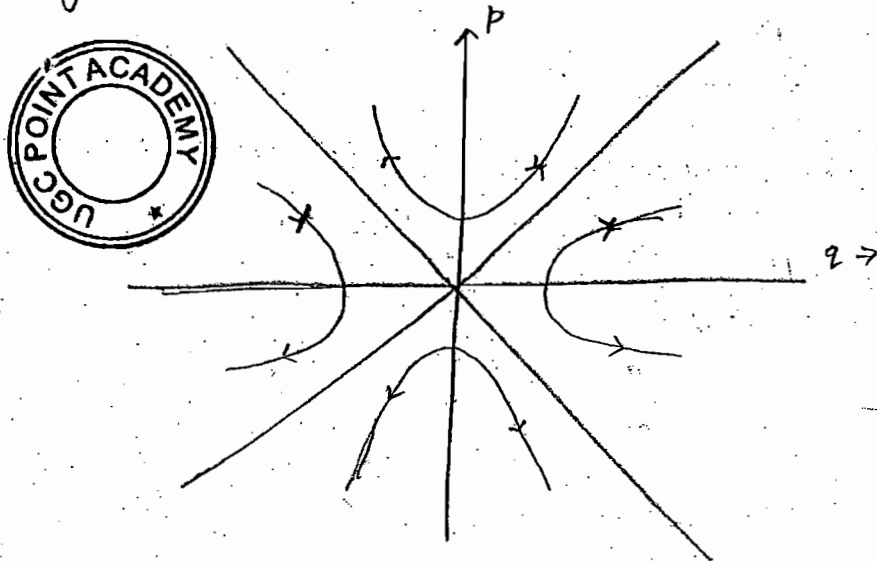
which of the following fig represents the motion of the particle in phase space.

$$H = \frac{p^2}{2m} - \frac{\alpha z^2}{2}$$

$E \rightarrow \text{constt.}$

P-S-diagram: Parabola

$V(x) = -\frac{\alpha z^2}{2}$  i.e. eq<sup>n</sup> of para



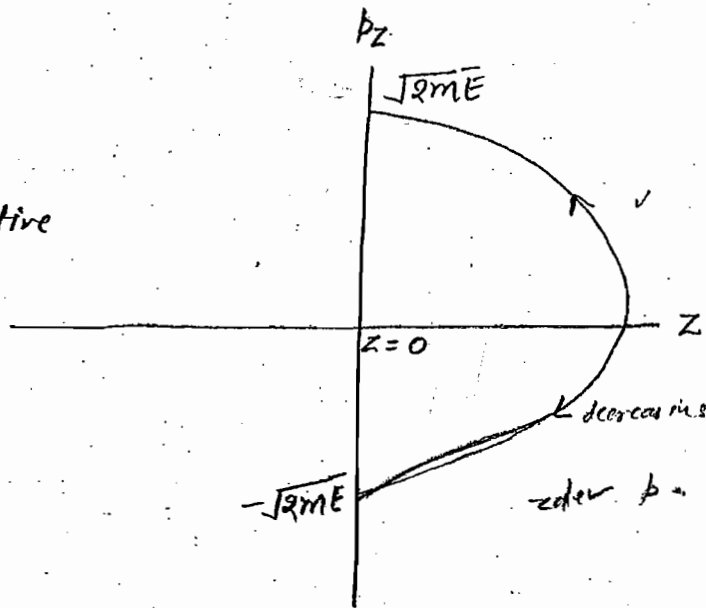
$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m}$$

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

\* The trajectory (Phase space diagram) on  $z$ - $p_z$  plan of ball bouncing from a perfect elastic hard sphere.

$$H = \frac{p_z^2}{2m} + mgz$$

$E = \text{constt}$   
system is conservative



→ It the particle is bouncing from inelastic sphere:

Elastic

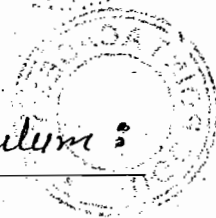
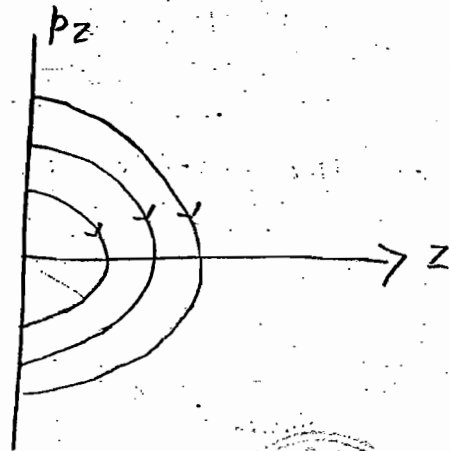
$$P = P', \quad T = T'$$

$$\vec{P} \neq \vec{P}'$$

$P \neq P'$  Inelastic

$$\vec{P} \neq \vec{P}'$$

$$T = T'$$



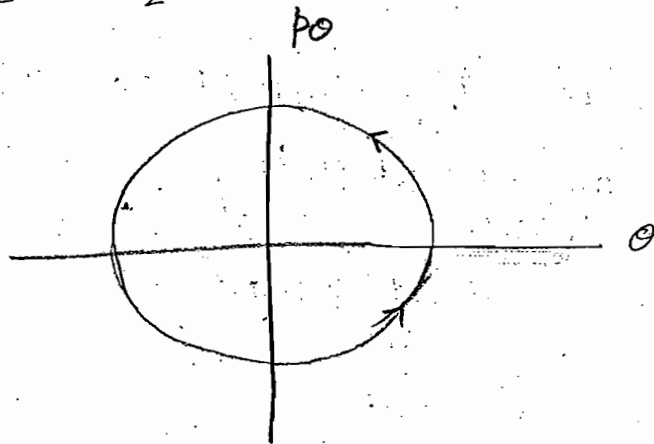
→ Phase space diagram of simple pendulum:

$$H = \frac{p_\theta^2}{2ml^2} + mgl(1 - \cos\theta)$$

$\theta$  is small

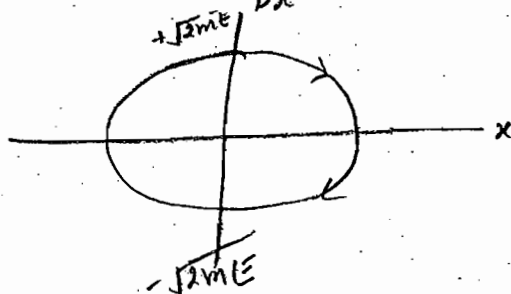
$$\cos\theta = 1 - \frac{\theta^2}{2}$$

$$H = \frac{p_\theta^2}{2ml^2} + \frac{mgl}{2} \theta^2$$



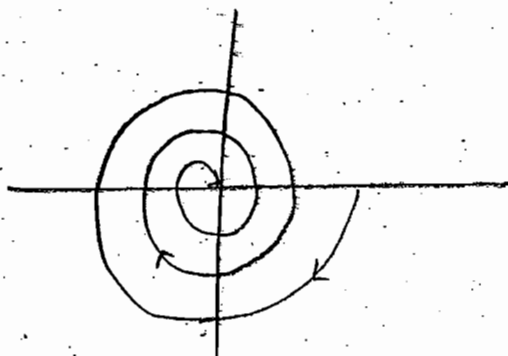
$$E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2$$

$$p_x = -\frac{Kx}{Dx} \Rightarrow \frac{dp_x}{dt} = -Kx$$





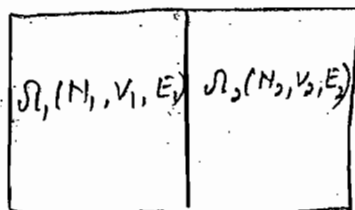
→ If bob is immersed in water then phase space diagram



\* Boltzmann's Definition of Entropy →

$$S = k_B \ln \Omega$$

Consider two independent system having macrostates are described by  $(N_1, V_1, E_1)$  &  $(N_2, V_2, E_2)$  with thermodynamical probabilities  $\Omega_1(N_1, V_1, E_1)$  &  $\Omega_2(N_2, V_2, E_2)$  respectively.



Thermodynamical probability of composition

$$\Omega = \Omega_1 \times \Omega_2 \quad \text{--- (1), En. of composition } E = E_1 + E_2 \quad \text{--- (2)}$$

If energy is allowed to exchange

$$\Omega = \Omega_1(E_1) \times \Omega_2(E_2)$$

Let equilibrium energy is  $\bar{E}$

$$\Omega = \max$$

$$\left. \frac{\partial \Omega}{\partial E_1} \right|_{E=\bar{E}} = 0$$

$$0 = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} \frac{\partial E_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \frac{\partial E_2}{\partial E_1}$$

$$\frac{1}{\Omega_1} \frac{\partial \Omega}{\partial E_1} = - \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2}$$

$$\frac{1}{\Omega} \frac{\partial \Omega}{\partial E} = \text{const} \quad \text{--- (3)}$$

$$\frac{\partial (\ln \Omega)}{\partial E} = \text{const} \quad \text{--- (4)}$$

$\beta = \frac{1}{k_B T}$       $S = \text{entropy} = \frac{1}{T}$

By thermodynamic

$$\left. \frac{\partial S}{\partial E} \right|_{N, V} = \frac{1}{T} \quad \text{--- (4)}$$

from  $TdS = dE + PdV - \mu dN$

Dividing (5) by (4)

$$\frac{\partial S}{\partial (\ln \Omega)} = \frac{1}{\beta T} = k_B$$

$$S = k_B \ln \Omega + C$$

$$C = 0 \quad \text{at } T \rightarrow 0K$$

$S \rightarrow 0$

$$S = k_B \ln \Omega$$



$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

→ If we allow volume to exchange

$$\frac{\partial (\ln \Omega)}{\partial V} = \eta = \frac{P}{k_B T} = \frac{P}{T}$$

If allow  $N$  to exchange

$$\frac{\partial (\ln \Omega)}{\partial N} = \gamma = -\frac{\mu}{k_B T}$$

$$\left. \frac{\partial S}{\partial E} \right|_{N, V} = \frac{1}{T}$$

$$\left. \frac{\partial S}{\partial V} \right|_{N, E} = \frac{P}{T}$$

$\sigma \rightarrow$  statistical entropy

$T \rightarrow$  statistical temp.

$\beta =$  inverse temp.

$$\text{Ph. E. } \boxed{S = k_B \sigma \rightarrow S.E.}$$

$$\left. \frac{\partial \sigma}{\partial E} \right|_{N, V} = \frac{1}{T}$$

$$\left. \frac{\partial \sigma}{\partial V} \right|_{E, N} = \frac{P}{T}$$

$$\left. \frac{\partial \sigma}{\partial N} \right|_{E, V} = -\frac{\mu}{T}$$

Prob: Consider a system of  $N$  magnetic ions with spins  $1/2$ . At low temp. the system is ferromagnetic while at high temp.  $T$  it is paramagnetic. Neglecting all DOF except spins, find entropy of the system at

(i)  $T \rightarrow 0$       b.)  $T \rightarrow \infty$

(i)  $T \rightarrow 0K$

Distribution of spins

→ Almost all spins are aligned in same dir<sup>n</sup>.

No. of ways of distribution

$$\Omega \rightarrow 1$$

$$S = k_B \ln \Omega$$

$$S \rightarrow 0$$



grp  
(ii)

$T \rightarrow \infty$

System attain equilibrium.

$$\Omega = \text{max.}$$

No. of distr.  
Max. No. of  
microstate

$$= (2S+1)^N = \left(2 \times \frac{1}{2} + 1\right)^N = 2^N$$

$$\begin{aligned} \text{Entropy } S &= k_B \ln(2^N) \\ &= (\ln 2^N) k_B \end{aligned}$$

Q. Consider a system of  $N$  paramagnetic atoms each have mag. moment  $M$ , are placed in mag. field  $B$ .  $n$  atoms are allined  $\parallel^e$  to  $B$  &  $(N-n)$  allined antill<sup>e</sup> to  $B$ . find

(i) Internal En. of the system

(ii) Entropy of the system

(iii) The thermodynamic temp. of the system.

(i)  $E = nE_{\parallel} + (N-n)E_{\text{antill}}$

$$= n(-MB) + (N-n)MB$$

$$E = (N-2n)MB$$

$$(ii) \quad \Omega = \Omega^n = \frac{N!}{n! (N-n)!}$$

$$S = k_B \ln \Omega \\ = k_B \ln \left( \frac{N!}{n! (N-n)!} \right)$$



$$= N k_B \ln N - N k_B - N k_B \ln n + n k_B \\ - (N-n) k_B \ln (N-n) + (N-n) k_B$$

$$S = k_B \left[ N \ln \left( \frac{N}{N-n} \right) - n \ln \left( \frac{n}{N-n} \right) \right]$$

$$(iii) \quad \frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n} \cdot \frac{\partial n}{\partial E}$$

$$= \frac{\partial S}{\partial n} \left( \frac{-1}{2\mu B} \right)$$

$$= \frac{k_B}{2\mu B} \ln \left( \frac{n}{N-n} \right)$$

$$T = \frac{2\mu B}{k_B \ln \left( \frac{n}{N-n} \right)}$$

$$\tau = \frac{2\mu B}{\ln \left( \frac{n}{N-n} \right)}$$

## Distribution Laws :-

### Boltzmann's distribution law:

→ Applicable to classical particles (identical, distinguishable of any spin.)

Consider a system of  $N$  particles system has different energy states having energies  $E_1, E_2, \dots$ . The no. of ways of distributions of particles such that:

$E_1$  energy state has  $n_1$  particles.  
 $E_2$  energy state has  $n_2$  particles.

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

$$= \frac{N!}{n_1! n_2! n_3! \dots}$$

$$= \frac{N!}{\prod_i n_i!}$$



when state are non-degenerate

If energy state are degenerate  
 i.e.  $E_1$  energy state has degeneracy  $g_1$   
 $E_2$  " " " " "  $g_2$

No. of ways of distribution

$$\Omega = \frac{N!}{\prod_i n_i!} \underbrace{g_1^{n_1} \times g_2^{n_2} \times \dots}_{\prod_i g_i^{n_i}} \quad \text{--- (1)}$$

$E_1, E_n$  states has two particles A, B  
 If deg. of this state is 3.



of degenerate  $g \rightarrow$  No. of particle  $\rightarrow$

Q.  $N=3$   
 No. of state  $\epsilon_1, \epsilon_2$   
 $g_1=3 \quad g_2=1$   
 $n_1=2 \quad n_2=1$

find No. of ways of distribution

→ At equilibrium

$$\Omega = \max. = \ln \Omega$$

with constraints



$$N - \sum_i n_i = 0$$

$$E - \sum_i n_i \epsilon_i = 0$$

$$\frac{\partial f}{\partial x_i} + \sum_k \lambda_k \frac{\partial \phi_k}{\partial x_i} = 0$$

$$\frac{\partial \ln \Omega}{\partial n_i} + \alpha \frac{\partial \phi_1}{\partial n_i} + \beta \frac{\partial \phi_2}{\partial n_i} = 0$$

$$\ln \frac{g_i}{n_i} - \alpha - \beta \epsilon_i = 0$$

OR

$$\frac{\partial (\ln \Omega)}{\partial n_i} + \alpha \frac{\partial \phi_1}{\partial n_i} + \beta \frac{\partial \phi_2}{\partial n_i} = 0$$

from eq<sup>n</sup> ①

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

$$\frac{\partial (\ln \Omega)}{\partial n_i} = - \ln n_i - \frac{n_i}{n_i} + 1 + \ln g_i$$

$$\ln \frac{g_i}{n_i} = \alpha + \beta \epsilon_i$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i}$$

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}$$

$$f(x, y, z) = \max$$

$$\phi_1(x, y, z) = 0$$

$$\phi_2(x, y, z) = 0$$

$$\frac{\partial f}{\partial x} + \sum_k \lambda_k \frac{\partial \phi_k}{\partial x} = 0$$

$\lambda_k \rightarrow$  undetermined multiplier

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz = 0$$

$$d\phi_1 = \frac{\partial \phi_1}{\partial x} dx + \frac{\partial \phi_1}{\partial y} dy + \dots$$

$$d\phi_2 = \frac{\partial \phi_2}{\partial x} dx + \dots$$

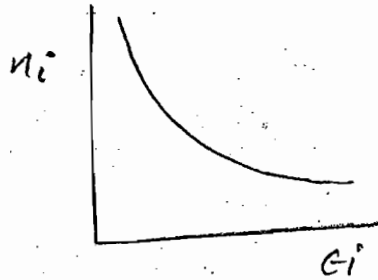
$$df + \lambda_1 d\phi_1 + \lambda_2 d\phi_2 = 0$$

$\alpha, \beta$  are undetermined multipliers.

$$n_i \propto g_i$$

$g_i$  = priori probability  
or  
degeneracy of the  $E_i$  energy state

$$\begin{aligned} \rightarrow n_i &= g_i e^{-\alpha} e^{-\beta E_i} \\ &= A g_i e^{-\beta E_i} \\ A &= e^{-\alpha} = \text{const} \end{aligned}$$



$$\sum n_i = N = \sum_i A g_i e^{-\beta E_i}$$

$$A = \frac{N}{\sum_i g_i e^{-\beta E_i}}$$



$$n_i = \frac{N g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

Probability:

$$P(E_i) = \frac{n_i}{N} = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

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

↓  
Partition fun<sup>n</sup>

→ when states are non-degenerate i.e.  $g_i = 1$

$$Z = \sum_i e^{-\beta E_i} = \text{Sum of all Boltzmann's factor}$$

Prob: calculate the partition fun<sup>n</sup> in case of 1D H.O.

$$E_n = (n + \frac{1}{2}) \hbar \omega \quad \text{Q. osc}$$

$$E = \frac{p^2}{2m} + \frac{1}{2} kx^2 \quad \text{cl. osc}$$

$$Z = \sum_n g_n e^{-\beta E_n}$$



$$Z = \sum_n e^{-\beta E_n}$$

$$= \sum_{n=0}^{\infty} e^{-\beta(n + \frac{1}{2}) \hbar \omega}$$



$$Z = e^{-\beta \hbar \omega / 2} + e^{-3\beta \hbar \omega / 2} + \dots$$

$$= \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

Partition fun<sup>n</sup> for 1D cl. osc:

$$E = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$Z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dx dp}{h} e^{-\beta E}$$



rigid rot:

$$E_J = (J^2 + J) \frac{\hbar^2}{2I}$$



$$= \int_0^{\infty} (2J+1) e^{-\beta E_J} dJ$$

Q. If two ideal dice are rolled once, what is the probability of getting at least one 6.

$$\frac{11}{36}, \frac{1}{36}, \frac{10}{36}, \frac{5}{36}$$

Partition function:

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

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

$$= \frac{1}{h} \int e^{-\beta E_j} dx dp_x$$

$$= \frac{1}{h^3} \iiint e^{-\beta E} dq_1 dq_2 dq_3 dp_1 dp_2 dp_3$$

$$= \text{tr}(e^{-\beta \hat{H}})$$

1-D Q.H.O:

$$E_n = (n + \frac{1}{2}) \hbar \omega$$

non-degenerate case =  $g_n = 1$

$$Z = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

1-D Classical oscillator:

$$Z = \frac{1}{\beta \hbar \omega} = \frac{k_B T}{\hbar \omega}$$

Partition fun<sup>n</sup> of rigid rotator:

$$Z = \frac{2 I k_B T}{\hbar^2}$$

Partition fun<sup>n</sup> for a molecule of classical ideal gas -

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

$$Z = \frac{1}{h^3}$$

$$Z = \int g(p) dp e^{-\beta E}$$

No. of microstate or No. of non-degenerate state

$$Z = \iiint \frac{dx dy dz dp_x dp_y dp_z}{h^3} e^{-\beta \left( \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right)}$$



$$= \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-\beta p_x^2 / 2m} dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2 / 2m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2 / 2m} dp_z$$

$$Z = \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-\beta p_x^2 / 2m} dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2 / 2m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2 / 2m} dp_z$$

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

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

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

$$Z = \frac{V}{\lambda^3}$$

where  $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

↓  
De-Broglie wavelength.

Q. Write the partition function for a particle of mass  $m$  whose pot. energy is given

$$V(x, y, z) = ax^2 + b(y^2 + z^2)^{1/2}$$

Sol<sup>n</sup>:

$$E = \frac{p^2}{2m} + V$$

$$= \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + ax^2 + b(y^2 + z^2)^{1/2}$$

$$Z = \frac{1}{h^3} \iiint e^{-\beta \left[ \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + ax^2 + b(y^2 + z^2)^{1/2} \right]} dx dy dz dp_x dp_y dp_z$$

$$= \frac{1}{h^3} \int_{-\infty}^{\infty} e^{-\beta ax^2} dx \int_{-\infty}^{\infty} e^{-\beta p_x^2 / 2m} dp_x$$

$$= \frac{1}{h^3} \sqrt{\frac{\pi}{\beta a}} \left( \frac{2m\pi}{\beta} \right)^{3/2} 2\pi \left( \frac{1}{\beta b} \right)^2$$



Q. In a system of particle fixed in space, each particle has total q. no.  $J$ , the mag. q. no.  $m_j$ , which has  $(2J+1)$  values  $-J, (-J+1), \dots, +J$ .

In presence of mag. field  $B$ , the energy of a level is given by:

$$E = -m_j \mu_B B g$$

$g \rightarrow$  Lande  $g$ -factor

find partition fun<sup>n</sup> for such an atom in mag. field

Sol<sup>n</sup>:

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

$$= \sum_{m_j = -J}^{+J} 1 \cdot e^{+\beta m_j \mu_B B g}$$

$$= e^{-\beta J \mu_B B g} + e^{\beta(-J+1) \mu_B B g} + \dots + e^{\beta J \mu_B B g}$$

G.P.  
 $\frac{a(1-r^n)}{1-r}$

$$= \frac{\sinh(\beta \mu_B B g (J+1))}{\sinh\left(\frac{\beta \mu_B B g}{2}\right)}$$

$$Z = e^{-\beta J M_B B \eta} [1 + e^{\beta J M_B B \eta} + e^{-\beta J M_B B \eta} + \dots + e^{2\beta J M_B B \eta}]$$

$$= \frac{e^{-\beta J M_B B \eta} [e^{\beta J M_B B \eta (2J+1)} - 1]}{e^{\beta J M_B B \eta} - 1}$$

$$= \frac{e^{\beta J M_B B \eta (J+1)} - e^{-\beta J M_B B \eta}}{e^{\frac{\beta J M_B B \eta}{2}} [e^{\frac{\beta J M_B B \eta}{2}} - e^{-\frac{\beta J M_B B \eta}{2}}]} = \frac{\sinh(\beta J M_B B \eta (J+1))}{\sinh(\frac{\beta J M_B B \eta}{2})}$$



\* for a system of  $N$  distinguishable particles the partition fun<sup>n</sup>.

$$Z_{\text{system}} = (Z_i)^N$$

Prob: Consider a 1-D Ising model of  $N$  spins at very low temp. where all spins are aligned  $\parallel$  to each other. There will be few spins flip at temp.  $T$ . With each spin flip  $2J$  energy is added.

In a configuration of  $N$  spins,  $r$  spins are flip, the energy of the system is

$$E = -NJ + 2rJ \quad \begin{matrix} \text{all spin are } \parallel \\ \text{flip spin energy} \end{matrix}$$

No. of configuration is  $N C_r$ ,  $r$  varies from 0 to  $N$ . The partition fun<sup>n</sup> of the system is.

Sol<sup>n</sup>:

$$Z = \sum_r g_r e^{-\beta E_r}$$

$$= \sum_{r=0}^N N C_r e^{-\beta(-NJ + 2rJ)}$$

$$= (2 \cosh \beta J)^N$$

Boltzmann's definition of probability:

$$P(\epsilon_i) = \frac{N_i}{N} = \frac{g_i e^{-\beta \epsilon_i}}{\sum_i g_i e^{-\beta \epsilon_i}}$$

$$N_1 = \frac{N_0 e^{-1}}{2}$$

$$N_1 = \frac{N_0}{2}$$

Prob: In a system, there are three energy states, having energies,  $0, K_B T$  &  $2K_B T$ . The total energy of the system is  $1000 K_B T$ . find the no. of particles in different states & average en. of each particle.

Soln:  $N_2$  —————  $2K_B T$

$N_1$  —————  $K_B T$

$N_0$  —————  $0$



find  $N_0, N_1, N_2$

$$N = ?$$

$$\bar{E} = ?$$

decay formula

$$N = N_0 + N_1 + N_2$$

$$N = N_0 + \frac{N_0}{e} + \frac{N_0}{e^2}$$

$$\frac{N_1 (E = K_B T)}{N_0} = \frac{N e^{-\beta K_B T} / z}{N e^{-0} / z}$$

$$N_0 = \frac{N}{1}$$

$$N_1 = \frac{N e^{-1}}{2}$$

$$\frac{N_1}{N_2} = \frac{g_1 e^{-(E_1 - E_2)\beta}}{g_2}$$

$$E = 1000 K_B T = N_0 \epsilon_0 + N_1 \epsilon_1 + N_2 \epsilon_2$$

$$= N_0 \times 0 + N_1 K_B T + N_2 2K_B T$$

$$1000 = N_1 + 2N_2$$

$$= \frac{N_0}{e} + \frac{2N_0}{e^2} \Rightarrow N_0 = \frac{1000 e^2}{(e^2 + 2)}$$

$$\bar{E} = \frac{E}{N} = \frac{K_B T (2 + e)}{(1 + e + e^2)}$$

Prob: A system of 5 identical but distinguishable particles having energy  $3\epsilon$ . The single particle state are available at energies,  $0, \epsilon, 2\epsilon, 3\epsilon$ .

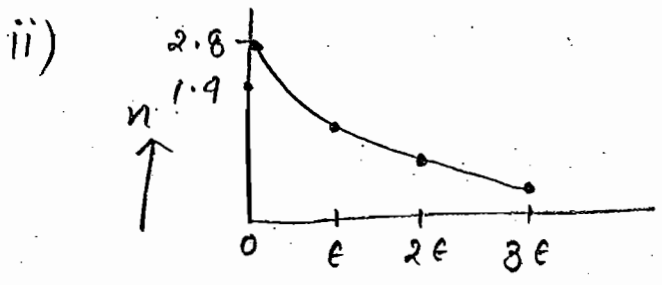
- i) find the ave no. of particles in each energy state  
 ii) sketch  $n(\epsilon)$  with energy.

Sol <sup>n</sup>	En. of the system	Energy of the state			No. of ways of distribution.	
		0	$\epsilon$	$2\epsilon$		$3\epsilon$
	$3\epsilon$	4	0	0	1	$\frac{15}{4!0!0!1!} = 5$
		3	1	1	0	20
		2	3	0	0	10
					Probabilities	
(1) $n(\epsilon) = n_1 p_1 + n_2 p_2 + \dots$ $= 4 \times \frac{5}{35} + 3 \times \frac{20}{35} + 2 \times \frac{10}{35}$ $= 2.8$					$\frac{5}{35}$ $\frac{20}{35}$ $\frac{10}{35}$	

$20 + 10 + 5 = 35$



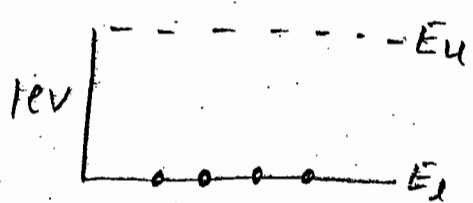
$n(\epsilon) = 1.4$   
 $n(2\epsilon) = 0.571$   
 $n(3\epsilon) = 0.14$





Prob: The energy required to create a lattice vacancy in a crystal is 1eV. find out the ratio of vacancies at temp 1200K & 300K. a)  $e^{-30}$  b)  $e^{30}$  ✓ c)  $e^{-10}$  d)  $e^{10}$

Sol<sup>n</sup>:



$$n(T) \propto e^{-\Delta E / k_B T}$$

$$n(1200) \propto e^{-1\text{eV} / k_B \times 1200}$$

$$n(300) \propto e^{-1\text{eV} / k_B \times 300}$$

$$\frac{n(1200)}{n(300)} = \frac{e^{-1\text{eV} / k_B \times 1200}}{e^{-1\text{eV} / k_B \times 300}} = \frac{e^{-1200}}{e^{-300}}$$



Q. The states with energy diff<sup>n</sup>  $4.83 \times 10^{-21}$  J occurs w<sup>th</sup> relative probability  $e^2$ . find temp. (Ans 175K)

ask Q. in A system can take only 3 different energy states in terms of energy  $E_1 = 0$ ,  $E_2 = 1.38 \times 10^{-21}$  J,  $E_3 = 2.76 \times 10^{-21}$  J

These 3 states occur in 2, 5, 4 different ways respectively find the probability that at 100K, the system may be

1.) In one of 4-state of energy  $E_3$   $P(E_3) = ? \frac{4e^{-\beta E_3}}{Z}$

2.) In the cr.s.  $P(E_1) = \frac{2e^{-\beta 0}}{Z}$

①  $\frac{P(E_1)}{P(E_2)} = e^2 = e^{\Delta E / k_B T}$



Q. A system has two normal modes of vibrations with frequencies of vibrations with  $\omega_1$  &  $\omega_2 (=2\omega_1)$ . Let is the pot. en. of the system. Also find the probability that at temp.  $T$ , the system has energy less than  $4\hbar\omega_1$ .

Sol<sup>n</sup>:

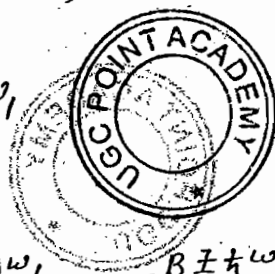
$$V = ax^2 + 4ay^2$$

OR

$$V = \frac{1}{2} m \omega_1^2 (x^2 + 4y^2)$$

$$E_{n_x, n_y} = (n_x + \frac{1}{2}) \hbar \omega_1 + (n_y + \frac{1}{2}) \hbar \omega_2 \rightarrow 2\omega_1$$

$$= (n_x + 2n_y + \frac{3}{2}) \hbar \omega_1$$



$$P(< 4\hbar\omega_1) = \frac{1 \cdot e^{-\beta \frac{3}{2} \hbar \omega_1} + 1 \cdot e^{-\beta \frac{5}{2} \hbar \omega_1} + 2 e^{-\beta \frac{7}{2} \hbar \omega_1}}{Z}$$

$$n_x \quad n_y = \frac{e^{-\frac{3}{2} \beta \hbar \omega_1}}{Z} (1 + e^{-\beta \hbar \omega_1} + 2e^{-2\beta \hbar \omega_1})$$

$$\frac{3}{2} \hbar \omega_1$$

$$0$$

$$0$$

$$\frac{5}{2} \hbar \omega_1$$

$$1$$

$$0$$

$$\frac{7}{2} \hbar \omega_1$$

$$0$$

$$1$$

$$2$$

$$0$$

} degeneracy

$$x = e^{-\beta \hbar \omega_1}$$

Ensembles: Gibbs

- A collection of large no. of macroscopically identical but essentially independent system, is called Ensemble
- OR
- A system is defined as "coll. of large no. of particles"

Macroscopic identical ÷ System having the same macroscopic quantities like,  $T, V, N, E, \mu, P$  etc.

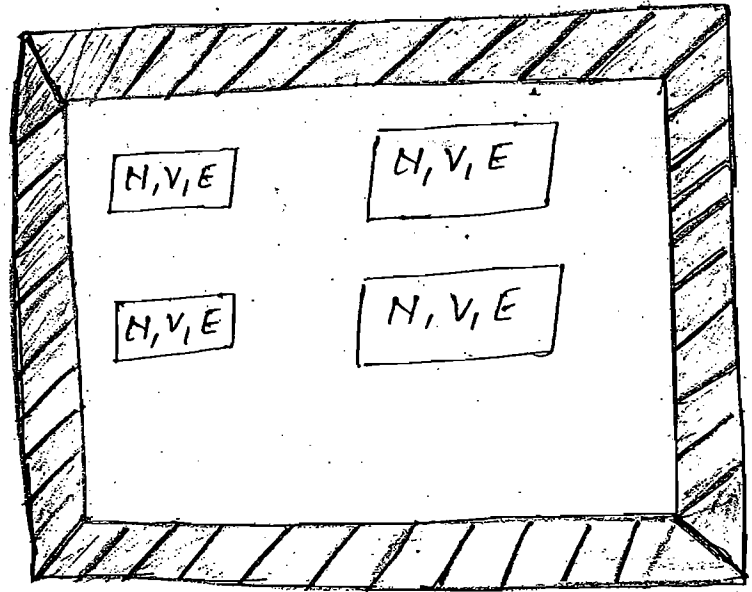
- If we have a coll. of large no. of independent system having macroscopic properties



- 1.)  $N, V, E$  more restriction → microcanonical ensemble
- 2.)  $T, V, \mu$  less restriction → canonical ensemble
- 3.)  $T, V, \mu$  same → Grand canonical ensemble No restriction.

System → Involving in time → We take the time averaged quantity.

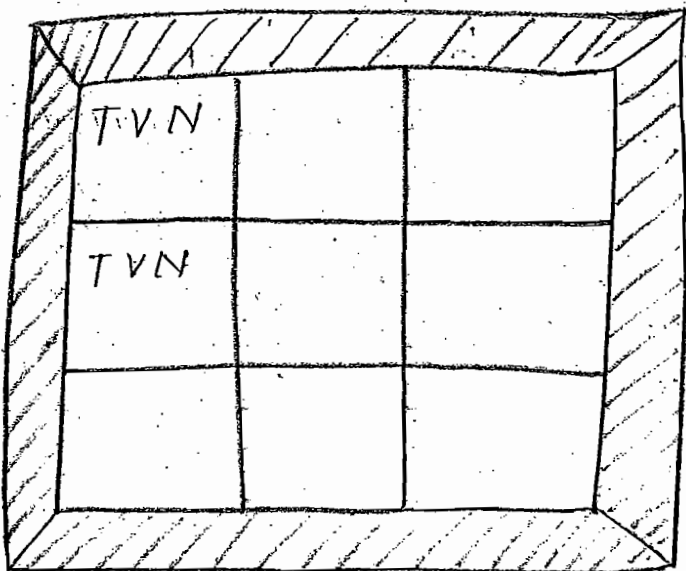
$\langle \text{Time ave behaviour} \rangle = \langle \text{ensemble averaged behaviour} \rangle$



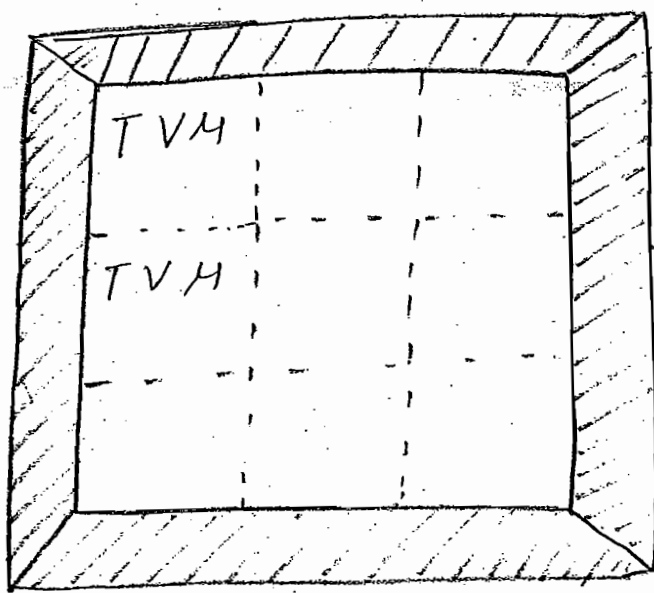
MCE

\* Ensemble average of any property would be very close to time average value of that property over a single system.

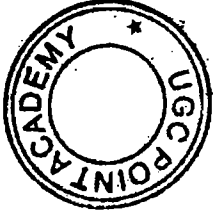
Properties	MCE
Contact with the environment	No contact ie isolated. ie, No exchange of Energy & matter (particle). ie, walls should be rigid, impenetrable & not conducting $(V=0) \quad dN=0$



Canonical Ensembles



G. C. E.

Properties	M.C.E.	C.E.	G.C.E.
Contact with the environment 	No contact ie isolated.	System in thermal contact with heat reservoir. Walls should be conducting rigid & impenetrable	System can exchange both energy & matter.
Fluctuations	None	fluctuation in energy only	fluctuation in energy & no. of particle both.
Density function $P(E)$	$P(E) = \frac{N}{V} = \text{const}$	$P(E) = Ae^{-E/k_B T}$	$P(E) = e^{-(\Omega + N_H - E)/k_B T}$
Partition function (Z)	$Z = \Delta T$	$Z = \int e^{-\beta E} d\Gamma$	$Z = \sum_n e^{4n/T} \cdot Z_n$
What is the use of Ensembles	→ Internal energy of an ideal monoatomic gas $\rightarrow \frac{3}{2} NKT$		

## Average properties of different quantities →

$$\bar{E}, \bar{E}^2, \bar{P}, \bar{M}, \Delta E \text{ etc}$$

$$\begin{aligned} \rightarrow \bar{X} &= \frac{n_1 x_1 + n_2 x_2 + \dots}{n_1 + n_2 + \dots} \\ &= \frac{n_1}{N} x_1 + \frac{n_2}{N} x_2 + \dots \\ &= p_1 x_1 + p_2 x_2 + \dots \end{aligned}$$

$$\bar{X} = \sum_i p_i x_i$$

$$\begin{aligned} \rightarrow \bar{E} &= \sum_i p_i \epsilon_i \\ &= \sum_i \frac{e^{-\beta \epsilon_i}}{Z} \epsilon_i \\ &= \frac{\sum_i e^{-\beta \epsilon_i} \epsilon_i}{\sum_i e^{-\beta \epsilon_i}} \end{aligned}$$

$$\boxed{\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}}$$

OR

$$\bar{E} = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

where  $\beta = \frac{1}{k_B T}$

$$\begin{aligned} \rightarrow \bar{E}^2 &= \sum_i p_i \epsilon_i^2 \\ &= \frac{\sum_i e^{-\beta \epsilon_i} \epsilon_i^2}{\sum_i e^{-\beta \epsilon_i}} \end{aligned}$$

$$\boxed{\bar{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}$$



$$\begin{aligned} \rightarrow (\overline{\Delta E})^2 &= (\overline{E^2}) - (\overline{E})^2 \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \end{aligned}$$

$$\boxed{(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z}$$

OR

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

$$= -\frac{\partial}{\partial \beta} (\overline{E})$$

$$= K_B T^2 \frac{\partial \overline{E}}{\partial T}$$

$$= K_B T^2 \left( \frac{3}{2} N K_B \right)$$



for ideal gas

$$(\Delta E)^2 = K_B T^2 C_V$$

$$\boxed{\Delta E = K_B T \sqrt{\frac{3N}{2}}}$$

$$\frac{\overline{\Delta E}}{\overline{E}} = \frac{K_B T \left( \frac{3}{2} N \right)^{1/2}}{\frac{3}{2} N K_B T}$$

$$\frac{\overline{\Delta E}}{\overline{E}} = \left( \frac{3}{2} N \right)^{-1/2} = \left( \frac{2}{3N} \right)^{1/2}$$



Relative fluctuation in energy

$$\frac{\Delta E}{E} < N^{-1/2} \text{ or } \frac{1}{\sqrt{N}}$$

$10^{22}$  atoms

$$< 10^{-11}$$

$\rightarrow 0$ , In ideal gas, fluctuations in en. is approx to zero.

Average Pressure:

$$\bar{p} = \sum_i p_i \cdot P_i$$

$p \rightarrow$  Probability

$P_i \rightarrow$  Pressure

$$\bar{p} = \sum_i \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \left( -\frac{\partial E_i}{\partial V} \right)_N \quad \text{--- (1)}$$

We know

$$T ds = dE + p dv - \mu dN$$

At equilibrium

$$T ds \rightarrow 0$$

OR Entropy fixed state

$$p = \left( -\frac{\partial E}{\partial V} \right)_N$$

from eq<sup>n</sup> (1)

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \Big|_{T, N} \quad \text{pascal}$$

OR

$$= \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial V} \Big|_{T, N}$$

$$\bar{p} = \frac{N}{\beta V} = \frac{N k_B T}{V}$$

$$\bar{p} = \frac{2}{3} \frac{E}{V}$$



Average chemical potential  $\rightarrow$

$$\begin{aligned}\bar{M} &= \sum_i P_i M_i \\ &= \frac{\sum_i e^{-\beta E_i} \left( \frac{\partial E_i}{\partial N} \right)_V}{Z}\end{aligned}$$

$$\boxed{\bar{M} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial N} \Big|_{V, T}}$$

Helmholtz free energy (F) and Entropy in terms of Z  $\rightarrow$

$$F = U - TS$$

$$dF = dU - Tds - SdT$$

we KIT:  $Tds = dU + PdV$

Then

$$dF = -PdV - SdT$$

$$\rightarrow \text{If } dV = 0$$

$$dT = 0$$

$$dF = 0$$

when  $F \rightarrow$  min<sup>m</sup> energy, then system is in equil<sup>m</sup>



$$d[\ln Z(T, V, N)] = \frac{\partial \ln Z}{\partial \beta} \Big|_{V, N} d\beta + \frac{\partial \ln Z}{\partial V} \Big|_{T, N} dV + \frac{\partial \ln Z}{\partial N} \Big|_{T, V} dN$$

$$d[\ln Z(T, V, N)] = -E d\beta + \beta P dV - \beta \mu dN \quad \text{--- (1)}$$

$$d(\beta E) = \beta dE + E d\beta \quad \text{--- (2)}$$

Add (1) + (2)

$$\begin{aligned}
 d[\ln Z + \beta \bar{E}] &= \beta [dE + PdV - \mu dN] \\
 &= \beta T ds \\
 &= \frac{1}{k_B} ds
 \end{aligned}$$

$$ds = d[k_B \ln Z + k_B \beta \bar{E}]$$

$$S = k_B \ln Z + \frac{E}{T}$$

$$F = E - TS = -k_B T \ln Z$$



$$\rightarrow F = E - TS$$

$$\begin{aligned}
 dF &= dE - T ds - S dT \\
 &= dE - (dE + PdV - \mu dN) - S dT
 \end{aligned}$$

$$dF = -PdV + \mu dN - S dT$$

From this rel<sup>n</sup>, we can find that

$$P = -\left. \frac{\partial F}{\partial V} \right|_{N, T}$$

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{V, T}$$

Entropy  $S = -\left. \frac{\partial F}{\partial T} \right|_{N, V}$

$$\rightarrow E = F + TS$$

$$E = F - T \left. \frac{\partial F}{\partial T} \right|_{N, V}$$

Helmholtz free energy.



Prob

1-DCH.O.

$$E = \frac{p^2}{2m} + \frac{1}{2} Kx^2$$

The partition fun<sup>n</sup>  $Z = \frac{K_B T}{h\omega}$

find ave thermal En.

Sol<sup>n</sup>:

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



$$= -\frac{\partial}{\partial \beta} \ln \left( \frac{1}{\beta h\omega} \right)$$

$$= -\beta h\omega \times \frac{1}{h\omega} \times -\frac{1}{\beta^2}$$

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

$$= K_B T$$

$$\langle E \rangle = \frac{1}{2} K_B T + \frac{1}{2} K_B T$$

Q. The hamiltonian of a particle of classical ideal gas is  $H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$

What is the ave. energy of the molecule.

Ans  $\frac{3}{2} K_B T$

Sol<sup>n</sup>: Use KIT

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

Q. A system can have three energy levels  $E = 0, \pm \epsilon$ . level  $E = 0$  is doubly degenerate while other are non-degenerate. Find the ave. energy of the system.

Soln:

$$\begin{aligned} \text{Partition fun}^n Z &= 2e^{-0} + e^{-\beta\epsilon} + e^{\beta\epsilon} \\ &= 2 + e^{\beta\epsilon} + e^{-\beta\epsilon} \\ &= (e^{\beta\epsilon/2} + e^{-\beta\epsilon/2})^2 \\ &= (2\cosh\beta\epsilon/2)^2 \end{aligned}$$

$$\bar{E} = \frac{-2 \ln Z}{\beta}$$

$$= \frac{-2}{\beta} \ln (2\cosh\beta\epsilon/2)^2$$

$$= \frac{-2}{2} \frac{1}{\cosh\frac{\beta\epsilon}{2}} \cdot \sinh\beta\epsilon/2 \cdot \beta\epsilon/2$$

$$= -\tanh\frac{\beta\epsilon}{2} \cdot \epsilon$$

$$\bar{E} = -\epsilon \tanh\beta\epsilon/2 \quad \text{Ans}$$

Q. Av. thermal En. 1-D q. Osc.

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$\bar{E} = \frac{-2 \ln Z}{\beta}$$

$$= \frac{\frac{1}{2} \hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$\bar{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$\begin{aligned} * P &= E/c, E = \hbar\omega \\ \omega &= 2\pi\nu = \frac{2\pi c}{\lambda} = kc \end{aligned}$$

$$\omega = \frac{E}{\hbar}, k = p/\hbar$$

$$\frac{\frac{1}{2} \hbar \cdot 2\pi\nu}{e^{\frac{\beta \hbar}{2\pi} \cdot \nu} - 1}$$



Q.  $N$  gas of molecules enclosed in a volume  $V$  at temp.  $T$ .  
The logarithm of partition fun<sup>n</sup> is given by

$$\ln Z = N \ln [(V - bN)(k_B T)^{3/2}]$$

find (i) Av. Internal En.  $\frac{3}{2} N k_B T$

(ii) Eq<sup>n</sup> of state of the gas.

Sol<sup>n</sup>: (ii)  $p = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \Big|_{N, T}$

$$p = \frac{N k_B T}{V - bN}$$

$$p(V - bN) = N k_B T \quad (\text{semi-vander-wall eq<sup>n</sup>})$$

(i)  $\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$

$$= -\frac{\partial}{\partial \beta} [N \ln (V - bN)(k_B T)^{3/2}]$$



Q. The partition fun<sup>n</sup> for a system of  $N$  particles is  

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

find

- (i)  $\langle E \rangle = \frac{3}{2} N k_B T$   
 (ii) Eq<sup>n</sup> of state  $PV = N k_B T$

Q. A gas of  $N$  non-interacting particles is in thermal equilibrium at temp.  $T$ . Each particle can be any of the possible non-degenerate states of energy  $0, 2\epsilon$  &  $4\epsilon$ . The average energy per particle of the gas, when  $\beta\epsilon$  is  $2\epsilon, 3\epsilon, 2\epsilon/3, \epsilon$ .

Q. The partition fun<sup>n</sup> of 1-D H.O. is

$$Z = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \quad \langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

find the average no. of oscillations or quanta.

Q.2 
$$Z = 1 + e^{-2\beta\epsilon} + e^{-4\beta\epsilon}$$

$$\langle E \rangle = \frac{-\partial \ln Z}{\partial \beta} = \frac{0 + 2\epsilon e^{-2\beta\epsilon} + 4\epsilon e^{-4\beta\epsilon}}{1 + e^{-2\beta\epsilon} + e^{-4\beta\epsilon}}$$

$\beta\epsilon \ll 1$

$$\frac{6\epsilon}{3} = 2\epsilon$$

Ave En. of System.

(3) Ave. Osc  $\langle n \rangle = \sum_{n=0}^{\infty} \frac{n e^{-\beta E_n}}{Z} \quad E_n = (n + \frac{1}{2}) \hbar \omega$   
 $n = 0, 1, 2, \dots$

$$= \frac{0 e^{-\beta \hbar \omega / 2} + 1 \cdot e^{-\frac{3}{2} \beta \hbar \omega} + 2 e^{-\frac{5}{2} \beta \hbar \omega} + \dots}{Z}$$

$$\langle n \rangle = \frac{e^{-\frac{3}{2} \beta \hbar \omega} (1 + 2e^{-\beta \hbar \omega} + 3e^{-2\beta \hbar \omega} + \dots)}{Z}$$



$$1 + 2x + 3x^2 + \dots = (1-x)^{-2}$$

$$1 + x + x^2 + \dots = (1-x)^{-1}$$

$$\langle n \rangle = \frac{e^{-\frac{3}{2}\hbar\omega}}{z} \frac{1}{(1 - e^{-\beta\hbar\omega})^2}$$

$$= \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Ave. No. of photon or phonons or quanta.

→ Oscillator emits & absorbed energy in the form of quanta.

$$\begin{array}{l} 2 \text{ ————— } \frac{5}{2} \hbar\omega \\ 1 \text{ ————— } \frac{3}{2} \hbar\omega \\ n=0 \text{ ————— } \frac{1}{2} \hbar\omega \end{array}$$

$$E_n = (n + \frac{1}{2}) \hbar\omega$$

$$E_n = n h\nu$$

$$E_n = 0, h\nu, 2h\nu, \dots$$

$$\begin{array}{l} \text{Av. No. of qu.} \\ = 0, 1, 2, 3 \end{array}$$



Total No. of Oscillator :

$$\begin{array}{l}
 2 \text{ --- } N_2 \text{ --- } \vdots \\
 1 \text{ --- } N_1 \text{ --- } \frac{3}{2} \hbar \omega \\
 n=0 \text{ --- } N_0 \text{ --- } \frac{1}{2} \hbar \omega
 \end{array}$$

$$\begin{aligned}
 N &= N_0 + N_1 + N_2 + \dots \\
 &= N_0 + N_0 e^{-\hbar \omega \beta} + N_0 e^{-2\hbar \omega \beta} + \dots
 \end{aligned}$$

$$N = \frac{N_0}{1 - e^{-\beta \hbar \omega}}$$

Total No. of Osc.

$$E = N_0 E_0 + N_1 E_1 + \dots$$

$$= N_0 \left( \frac{1}{2} \hbar \omega \right) + N_0 e^{-\beta \hbar \omega} \left( \frac{3}{2} \hbar \omega \right) + \dots$$

$$= \frac{1}{2} N_0 \hbar \omega \left[ 1 + 3e^{-\beta \hbar \omega} + 5e^{-2\beta \hbar \omega} + \dots \right]$$

$$= \frac{1}{2} \frac{N_0 \hbar \omega}{(1 - e^{-\beta \hbar \omega})^2}$$

wrong



$$Av. E_n = \frac{N \hbar \omega}{e^{\beta \hbar \omega} - 1} = N \langle E \rangle =$$

→

If G is given

$$G = N k_B T (1 - \ln Z)$$

$$G = E + PV - TS$$

Q. 
$$Z = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

Calculate Av. no. of oscillators.

Sol<sup>n</sup>:

Av. En. of osc =  $\frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$

Av. no of osc =  $\frac{1}{e^{\hbar \beta \omega} - 1}$



Q. for a non-relativistic fermi gas

$$E \propto \frac{N^{5/3}}{V^{2/3}}$$

The pressure of gas is.

$\frac{1}{3} \frac{E}{V}, \frac{2}{3} \frac{E}{V}, \frac{5}{2} \frac{E}{V}$

Sol<sup>n</sup>:

$$\bar{p} = \left( - \frac{\partial E}{\partial V} \right)_N$$

$$\bar{p} = \frac{2}{3} \frac{E}{V}$$

Q. for a certain system the energy of each state is given by

$$E_s = f_s(T) - N k_B T \ln \left( \frac{V}{V_0} \right)$$

$V_0 = \text{const}$

(i) Write the partition fun<sup>n</sup> of the system.

(ii) Ave Pressure of the system

(iii)

$$Z = \sum_s e^{-\beta E_s} \rightarrow \text{value}$$

$$\bar{p} = \frac{N k_B T}{V}, \quad \bar{p} = - \frac{1}{\beta} \frac{\partial}{\partial N} \ln Z \Big|_{T, V}$$

Sol<sup>n</sup>!

$$Z = \sum_s e^{-\beta E_s} = \left(\frac{V}{V_0}\right)^{1/2} \sum_s e^{-\beta E_s(T)}$$
$$= \sum_s e^{-}$$

$$A = -\frac{1}{\beta} \frac{\partial}{\partial N} \left[ N \ln\left(\frac{V}{V_0}\right) \right]$$

$$= -\frac{1}{\beta} \ln\left(\frac{V}{V_0}\right)$$

$$= -k_B T \ln\left(\frac{V}{V_0}\right)$$

$$\bar{p} = \frac{N k_B T}{V}$$



Q. for a certain system

$$Z(T, V, N) = \left(\frac{\beta}{\beta_0}\right)^{\frac{3N}{2}} \left(\frac{V}{V_0}\right)^N$$

find  $\bar{E}$ ,  $F$ ,  $\bar{p}$ ,  $\bar{A}$ ,  $\xi$ , eq<sup>n</sup> of state, &  $\Delta E / \bar{E}$

Sol<sup>n</sup>!



CHAD

Q. The partition function for a certain system is given as

$$Z = \left(\frac{\beta}{\beta_0}\right)^{-N} e^{-N\left(\frac{V}{V_0}\right) - 10}, \quad \beta_0, V_0 \text{ are const}$$

find  $\bar{E}$ ,  $F$ ,  $\bar{P}$ ,  $\bar{M}$ ,  $S$ , eq<sup>n</sup> of states.  $\Delta E/\bar{E}$



Average thermal energy of 1-D classical gas →

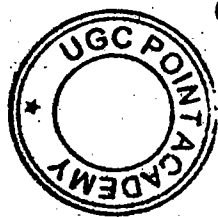
Some important formula:

$$\begin{aligned} H &= E + PV \\ &= Nk_B T^2 \left[ \frac{\partial}{\partial T} (\ln Z) \right]_V + Nk_B T \end{aligned}$$

$$\begin{aligned} G &= H - TS \\ &= Nk_B T^2 \left[ \frac{\partial}{\partial T} (\ln Z) \right]_V + Nk_B T - Nk_B \ln Z - E \end{aligned}$$

$$G = k_B T (1 - \ln Z)$$

Specific heat



$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V$$

$$= -T \left( \frac{\partial^2 f}{\partial T^2} \right)_V$$

Isothermal compressibility

$$\kappa_T = \frac{1}{B} = -V \left( \frac{\partial P}{\partial V} \right)_T$$

$$= V \left[ \frac{\partial^2 f}{\partial V^2} \right]_T$$

$$= \left[ V \frac{\partial^2}{\partial V^2} (-Nk_B T \ln Z) \right]_T$$

Q. The partition function for an interacting gas (real) is assumed to

$$Z = \left( \frac{V - Nb}{N} \right)^N \left( \frac{mK_B T}{2\pi h^2} \right)^{3N/2} e^{-N^2 a^2 / V K_B T}$$

$a, b$  are constt

Show that the pressure of the gas

$$P = \frac{NK_B T}{(V - Nb)} - \frac{N^2 a^2}{V^2} \Rightarrow \left( P + \frac{N^2 a^2}{V^2} \right) (V - Nb) = NK_B T$$

Sol<sup>n</sup>:



Q. A system containing  $N$  non-interacting identical particles of spin  $1/2$  & mag. moment  $\mu$ , each kept in const. external m.f.  $H$  is normal equilibrium at temp.  $T$ . The magnetisation of the system is  $N\mu \coth\left(\frac{\mu H}{k_B T}\right)$ ,  $N\mu \tanh\left(\frac{\mu H}{k_B T}\right)$

Sol<sup>n</sup>:

$$M = \left. \frac{-\partial F}{\partial H} \right|_{T, V, N}$$

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

$$= -Nk_B T \ln \left[ 2 \cosh\left(\frac{\mu H}{k_B T}\right) \right]$$

$$M = N\mu \tanh\left(\frac{\mu H}{k_B T}\right)$$

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

$$= e^{-\beta(\mu H)} + e^{\beta \mu H}$$

$$Z = 2 \cosh \beta \mu H$$

Q. An ensemble of  $N$ , three level system with energies  $-\epsilon_0, 0, +\epsilon_0$  in thermal equilibrium at temp.  $T$ . If  $\beta \epsilon_0 = 2$ . What is the prob. of finding the system in the level  $\epsilon = 0$  Probability  $P = \frac{g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}}$

$$\frac{\cosh 2}{2}, (\cosh 2)^{-1}, (2 \cosh 2)^{-1}, (1 + 2 \cosh 2)^{-1}$$

Q.  $E = \frac{bS^3}{VN}$ ,  $T = ?$   $\frac{bS^2}{VN}$ ,  $\frac{3bS^2}{VN}$  etc

Sol<sup>n</sup>:

$$Z = \sum_i e^{-\beta E_i} = 1 + e^{-\beta \epsilon_0} + e^{\beta \epsilon_0}$$

$$P = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} \Rightarrow \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{1 + e^{-2} + e^2}$$

$$= \frac{1}{1 + \left(\frac{e^{-2} + e^2}{2}\right)^{1/2}}$$

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

$$= (1 + 2 \cosh 2)^{-1}$$



~~Imp~~  $T = \left. \frac{\partial E}{\partial S} \right|_{V, N}$

~~$d\bar{E} = Tds$~~

✓  $Tds = dE + PdV - \mu dN$

✓  $dF = -SdT - PdV + \mu dN$



Average thermal energy of 1-D classical osc →

1-D cl. H.O.

$$E = \frac{p_x^2}{2m} + \frac{1}{2} k x^2$$

$$\langle E \rangle = \frac{1}{2m} \langle p_x^2 \rangle + \frac{1}{2} k \langle x^2 \rangle$$

$$= \frac{1}{2m} m k_B T + \frac{1}{2} k_B T$$

$$= \frac{1}{2} k_B T + \frac{1}{2} k_B T$$



$$\langle E \rangle = k_B T$$

→ Average thermal energy corresponding to each quadratic term of momentum & position is  $\frac{1}{2} k_B T$ . (Equipartition theorem)

$$\langle E \rangle = \frac{\int H(q, p) e^{-\beta H(q, p)} dq dp}{\int e^{-\beta H(q, p)} dq dp}$$

If

$$\bar{x} = \sum x_i p_i$$

$$= \frac{\sum x e^{-\beta H(q, p)}}{\sum e^{-\beta H(q, p)}}$$

$$\langle E \rangle = \frac{\iint \left( \frac{p_x^2}{2m} + \frac{1}{2} k x^2 \right) e^{-\beta \left( \frac{p_x^2}{2m} + \frac{1}{2} k x^2 \right)} dx dp_x}{\iint e^{-\beta \left( \frac{p_x^2}{2m} + \frac{1}{2} k x^2 \right)} dx dp_x}$$

unit

$dq dp \rightarrow \text{Joule} \cdot \text{sec}$

Average thermal energy of 3-D cl. osc.  $\rightarrow$

$$\langle E \rangle = 3k_B T$$

Q. A system has  $N$  particles having p.e.  $ax^2 + by^2$ . The Av. thermal en. of the system is

$$= 2Nk_B T$$

$$H = \frac{1}{2m} (p_x^2 + p_y^2) + ax^2 + by^2$$

$$\langle E \rangle = 2k_B T$$

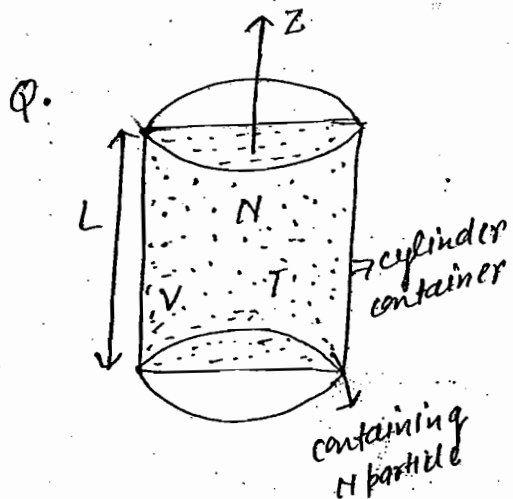


\* Non-interacting cl. ideal gas having  $N$  particles, Av. thermal en.

$$\langle E \rangle = \frac{3}{2} Nk_B T$$

Q. A system of  $N$  cl. non-interacting particles each of mass  $m$  at temp.  $T$  and is confined by the external pot.  $V = \frac{1}{2} Ar^2$ , where  $A = \text{const.}$  in 3-D find the Av. Int. En. of the system.

$$\frac{3}{2} Nk_B T, \frac{5}{2} Nk_B T, 3 Nk_B T, \frac{1}{2} Nk_B T$$



$$L \ll R$$

$$mgL \gg k_B T$$

$\langle E \rangle$  of the system

$$\frac{3}{2} Nk_B T, \frac{5}{2} Nk_B T$$

Soln: Hamiltonian of the particle

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + mgz$$

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

$$\langle E \rangle = \frac{\iiint H e^{-\beta H} dx dy dz dp_x dp_y dp_z}{\iiint e^{-\beta H} dx dy dz dp_x dp_y dp_z}$$



Q. A particle contained in a region  $x \geq 0$  by a pot. which linearly increases with  $x$  as  $V(x) = 4_0 x$ ,  $4_0$  const. Find mean position of the particle at temp.  $T$

$$\frac{k_B T}{4_0}, \frac{k_B T}{2H_0} \text{ etc}$$

$$\int_0^{\infty} t^4 e^{-at} dt = \frac{4!}{a^{n+1}}$$

Sol<sup>n</sup>:

$$\langle x \rangle = \frac{\iint x e^{-\beta H(q,p)} dq dp}{\iint e^{-\beta H(q,p)} dq dp}$$

$$= \frac{\int_0^{\infty} x e^{-\beta 4_0 x} dx}{\int_0^{\infty} e^{-\beta 4_0 x} dx}$$



## Thermal Expansion of Solids:

Av. value of thermal expansion

$$\langle x \rangle = \frac{\iint x e^{-\beta H} dx dp_x}{\iint e^{-\beta H} dx dp_x}$$

Cl. H.O. treatment

$$H = \frac{p_x^2}{2m} + ax^2 \quad \text{H.O.}$$

Parabolic pot.



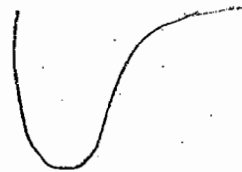
$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-\beta ax^2} dx}{\int_{-\infty}^{\infty} e^{-\beta ax^2} dx} = 0$$



Cl. An H.O. treatment:

$$V(x) = ax^2 - bx^3 - cx^4$$

Anharmonic terms  
b, c are smaller than a



$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-\beta(ax^2 - bx^3 - cx^4)} dx}{\int_{-\infty}^{\infty} e^{-\beta(ax^2 - bx^3 - cx^4)} dx}$$

(1 + b x^3 + c x^4)

$$\langle x \rangle = \frac{3b}{4a^2} (k_B T)$$

Coeff. of thermal expansion:

Linear<sup>OR</sup> expansion coeff.

$$\alpha = \frac{d\langle x \rangle}{dT} = \frac{3}{4a^2} b k_B = \text{const}$$

but expansion

$$\alpha \rightarrow 0 \quad \text{at } T \rightarrow 0$$

Quantum anharmonic osc. treatment:

$$\langle x \rangle = \frac{3}{4a^2} b \langle E \rangle$$

$$\langle x \rangle = \frac{3}{4a^2} b \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right)$$

$$\alpha = \frac{d\langle x \rangle}{dT}$$

$$= \frac{3}{4a^2} b \left[ \frac{(\hbar \omega)^2}{k_B T^2} \frac{e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2} \right]$$

$$\text{AT } T \rightarrow 0$$

$$\alpha \rightarrow 0$$

Q. Consider a system of two Ising spins  $s_1$  &  $s_2$  taking values  $\pm 1$  with internal energy  $E = -J s_1 s_2$ . It is in thermal equilibrium at temp.  $T$ . The ave. en. varies as  $C/k_B T$  for large  $T$ .

Then  $C$  varies as  $-J^2, J^2, -J, +J$

Soln:

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

$$Z = \sum g e^{-\beta E} = 2e^{-\beta J} + 2e^{\beta J}$$

$E = +J$	$s_1$	$s_2$
	+1	-1
	-1	+1
$-J$	+1	+1



$$\langle E \rangle = \frac{-[-2J e^{-\beta J} + 2J e^{\beta J}]}{2e^{-\beta J} + 2e^{\beta J}}$$

$\tanh x \rightarrow x$   
 $x \rightarrow 0$   
 $x \rightarrow 0$   
 $\cos \rightarrow 1$   
 $\sin \rightarrow x$

$$= \frac{J [e^{-J/k_B T} + e^{J/k_B T}]}{e^{-J/k_B T} + e^{J/k_B T}}$$

$$\langle E \rangle = \frac{J \left[ 1 - \frac{J}{k_B T} - 1 - \frac{J}{k_B T} \right]}{2}$$



$$\langle E \rangle = -\frac{J^2}{k_B T}$$

Q. The partition fun<sup>n</sup> of a system is  $Z = e^{\alpha T^3 V}$ , find  $\mu, \bar{P}, S, U$   
 $\alpha$  is constt.  $\bar{M} = 0$

$$\bar{P} = \alpha k_B T^4, \quad S = 4\alpha k_B T^3 V, \quad U = 3\alpha k_B T^4 V$$

Q. The free en. of a gas having  $N$  particle, volume  $V$  & temp.  $T$  is given as

$$F = -N k_B T \ln \left[ \frac{q_0 V (k_B T)^{5/2}}{N} \right]$$

$$\ln Z = \ln \left[ \frac{q_0 V}{N \beta^{5/2}} \right]$$

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

find internal energy of the gas.  $= \frac{5}{2} \frac{N}{\beta}$

Q. The entropy  $S = N k_B \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N k_B$  in MCE

obtain (i) I.E.  $\rightarrow \frac{3}{2} N k_B T$

Sacur-Tetrode eq<sup>n</sup>

- (ii)  $C_V$
- (iii)  $P \Rightarrow \frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{N, T}$
- (iv)  $\sigma = \frac{S}{k_B}$   
 ↓  
 Statistical Error



for system of  $N$ -particle  $\Gamma = -Nk_B \ln(Z)$

$$\ln Z = \ln z_1^N \\ = N \ln \left[ \frac{90 \text{ V}}{N \beta^{5/2}} \right]$$

Q. The helmholtz energy  $F$  in case of canonical ensemble is given as

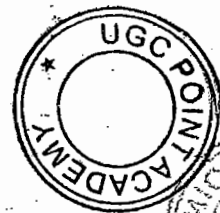
$$F = -Nk_B T \ln \left( \frac{eV}{N \beta^{5/2}} \right)$$

$$\lambda = \frac{h}{\sqrt{2\pi m T}}, \quad \tau = k_B T$$

find  $\sigma$  &  $U$  (I.E.)

$$\sigma = - \frac{\partial F}{\partial T} = N \ln \left( \frac{eV}{N \beta^{5/2}} \right)$$

$$U = -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right)_{V, N} = \frac{3}{2} N T$$



The entropy of mixing of two ideal gases -

(Gibbs paradox)

for a molecule of ideal gas

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

$$z_1 = \frac{V}{\lambda^3} = V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

for  $N$  molecules

$$Z_{\text{system}} = (z_1)^N$$



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

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

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

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

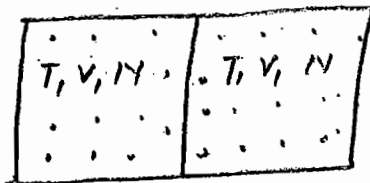
$$\bar{p} = \frac{2}{3} \frac{\bar{E}}{V} = \frac{N k_B T}{V}$$

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

$$S = k_B \ln V^N + \frac{3}{2} N k_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \frac{3}{2} N k_B$$

→

Now we consider the mixing of two ideal gas



ideal gas molecule is non-interacting so entropy remain same after & before.

Before mixing the entropy of the system

$$S = S_1 + S_2 = 2S_1$$

$$S = 2Nk_B \ln V + 3Nk_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + 3Nk_B$$

After mixing the entropy of the system

$$N \rightarrow 2N, \quad V \rightarrow 2V, \quad T \rightarrow T$$

$$S' = 2Nk_B \ln 2V + 3Nk_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + 3Nk_B$$

Change in entropy

$$\Delta S = S' - S$$

$$\Delta S = 2Nk_B \ln 2$$

→ Mixing of two same ideal gases is reversible process  
 $\Rightarrow \Delta S = 0$

Two results are contradictory  
particle is distinguishable.

This contrary result is called Gibbs paradox.

\* How to treat the problem arise in the result  
→ modifying the partition function

$$Z = \frac{(Z_1)^N}{N!} \quad (\text{particle is indistinguishable})$$

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

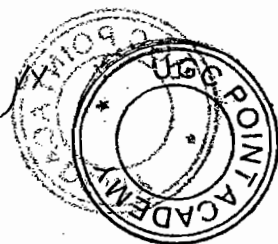
Entropy before mixing

$$S = 2Nk_B \ln V - 2k_B \ln N! + 3Nk_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + 3Nk_B$$

||  
2S<sub>1</sub>

After mixing

$$S' = S$$



$$S^I = Nk_B \ln V - k_B \ln LN + \frac{3}{2} Nk_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \frac{3Nk_B}{2}$$

$$V \rightarrow 2V, N \rightarrow 2N, T \rightarrow T$$

$$S^I = 2Nk_B \ln 2V - k_B \ln 2N + 3Nk_B \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \frac{3Nk_B}{2}$$

$$\Delta S = S^I - S$$



$$= 2Nk_B \ln 2V - 2Nk_B \ln V - k_B \ln 2N + 2k_B \ln LN$$

$$= 2Nk_B \ln 2 - [2Nk_B \ln 2N - 2Nk_B] + 2Nk_B \ln N - 2Nk_B$$

$$\Delta S = 0$$

→ Thus the Gibbs paradox is removed by taking into account the indistinguishable of particles. The modifying & correct expression of  $Z(N, V, T)$  ideal gas

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

$$E = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} Nk_B T$$

$$P = \frac{2}{3} \left( \frac{E}{V} \right)$$

$$S = Nk_B \ln \left[ \left( \frac{V}{N} \right) \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5}{2} Nk_B$$

Which is called Sackur-Tetrode eq<sup>n</sup>.

Maxwell's DISTRIBUTION LAW OF MOLECULAR SPEEDS (C) →

Used Boltzmann's distribution law.

$dN(c)dc \Rightarrow$  No. of molecules in a range

	$dc$
$c$	$c+dc$
	$dN(c)dc$
$p$	$p+dp$
$E$	$E+dE$
$K$	$K+dK$

If gas contain  $N$  molecules  $\rightarrow$  momentum

$$\frac{dN}{N} = dP = \frac{g(p) dp e^{-\beta E}}{Z}$$

$\downarrow$  Probab.       $\downarrow$  No. of microstate or degeneracy



$$= A g(p) dp e^{-\beta E}$$

$$= A \frac{V 4\pi p^2 dp e^{-\beta E}}{h^3}$$

$$dP = \frac{AV p^2 e^{-\beta(p^2/2m)}}{2\pi^2 h^3} dp$$

$$\int dP = \frac{AV}{2\pi^2 h^3} \int_0^{\infty} e^{-\beta(p^2/2m)} p^2 dp$$

$$1 = \frac{AV}{2\pi^2 h^3} \sqrt{\frac{2\pi}{(\beta/4m)^3}}$$

$$A = \frac{(2\pi)^{3/2} h^3}{V} \left(\frac{\beta}{4m}\right)^{3/2}$$

$$dP = \frac{4}{\sqrt{\pi}} \left( \frac{2}{2m k_B T} \right)^{3/2} p^2 e^{-p^2/2m} dp$$

$$p = me$$

$$dP = \frac{dN}{N} = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mc^2/2k_B T} c^2 dc$$

$$dN = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mc^2/2k_B T} c^2 dc$$

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

Average speed: ( $\bar{c}$ )



$$\bar{c} = \frac{\int c dP}{\int dP}$$

$$\int dP = 1$$

$$\bar{c} = \int c dP$$

$$= \int_0^{\infty} c \frac{dN}{N} = \frac{\int c dN}{\int dN}$$

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}}$$

Average speed

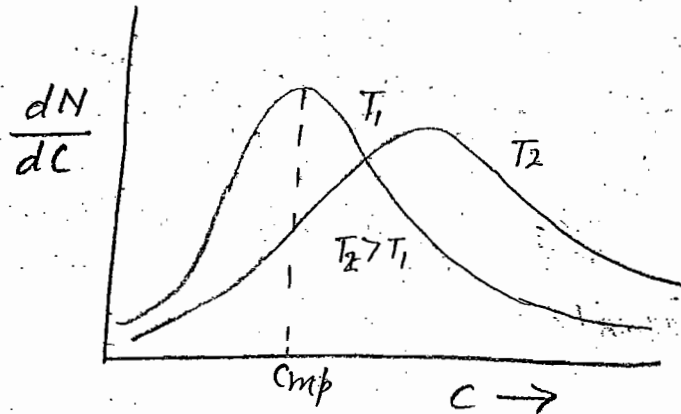
$$\overline{c^2} = \frac{\int c^2 dN}{\int dN}$$

$$= \frac{3k_B T}{m}$$

$$\left( \overline{c^2} \right)^{1/2} = \sqrt{\frac{3k_B T}{m}} = c_{\text{rms}} \text{ (root mean square)}$$

$$c_{\text{rms}} > \overline{c} > c_{\text{mp}} \text{ (most probable)}$$

$\sqrt{3} \quad ; \quad \sqrt{\frac{8}{\pi}} \quad ; \quad \sqrt{2}$



$$A_1 = A_2 \text{ (area)}$$

$$\int \frac{dN}{dc} dc = N$$

Breaththxhrg!



Most probable speed ( $c_{\text{mp}}$ ):

followed by max. no. of molecules

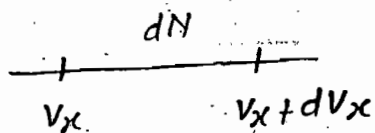
at  $c = c_{\text{mp}}$

$$\frac{d}{dc} \left( \frac{dN}{dc} \right) = 0$$

$$\rightarrow \frac{dN}{dc} = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} c^2 e^{-mc^2/2k_B T}$$


peak depend upon temp.

# Maxwell's distribution law of velocity distribution →

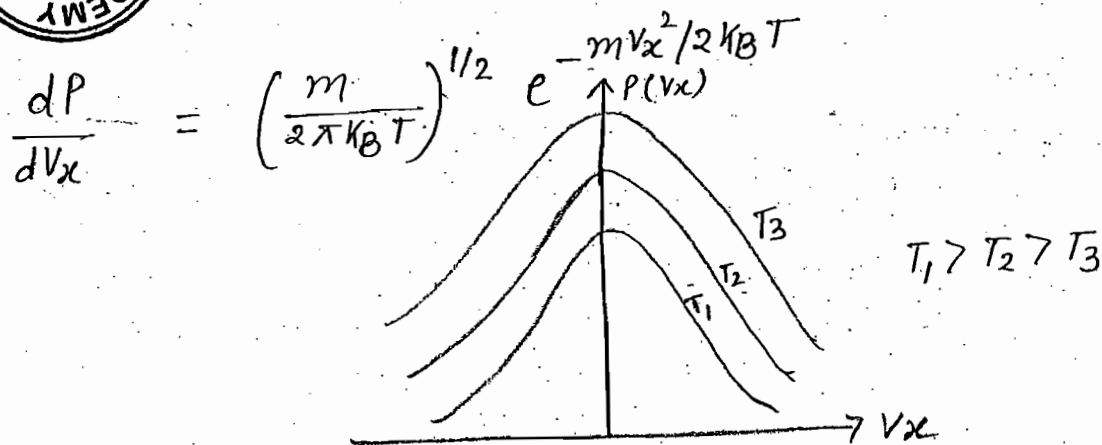


$$dP = \frac{dN(v_x)}{N} = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv_x^2/2k_B T} dv_x$$

$$dP(v) = \frac{dN(v)}{N} = \frac{dN(v_x) dN(v_y) dN(v_z)}{N}$$



$$= \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} \underbrace{dv_x dv_y dv_z}_{dv}$$



i)  $\frac{dP(v_x)}{dv_x} = \text{max. at } v_x = 0$

ii) Probability distribution curve is symmetric  
 $P(-v_x) = P(v_x)$

Most Probable velocity

$$\Rightarrow \frac{d}{dv_x} \left( \frac{dP}{dv_x} \right) = 0 \text{ wrong}$$

$$\text{OR } \frac{d}{dv_x} [P(v_x)] = 0 \text{ right}$$



Max. value of

$$\times \frac{dP(v_x)}{dv_x} \Big|_{\max} = \frac{dP(v_x)}{dv_x} \Big|_{v_x=0} = \left( \frac{m}{2\pi k_B T} \right)^{1/2}$$

or

$$P(v_x) \Big|_{\max} = P(v_x) \Big|_{v_x=0} = \left( \frac{m}{2\pi k_B T} \right)^{1/2}$$

iv) Average velocity:

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x P(v_x) dv_x$$

$$= 0$$

v)  $\langle v_x^2 \rangle$

$$= \int_{-\infty}^{\infty} v_x^2 P(v_x) dv_x$$

$$= \frac{k_B T}{m}$$

vi)

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$= \frac{k_B T}{m} + \frac{k_B T}{m} + \frac{k_B T}{m}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

vii) Velocity at which  $P(v_x)$  falls 1/e time of max. value =

$$v_x = \sqrt{\frac{2k_B T}{m}}$$



$$\text{viii)} \quad \overline{v_x v_y} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x v_y P(v_x v_y) dv_x dv_y$$

$$= 0$$

$$\text{ix)} \quad \overline{v_x^2 v_y v_z} = 0$$

$$\text{x)} \quad \overline{(\alpha + \beta v_x)^2} = \alpha^2 + \beta^2 \frac{k_B T}{m}$$

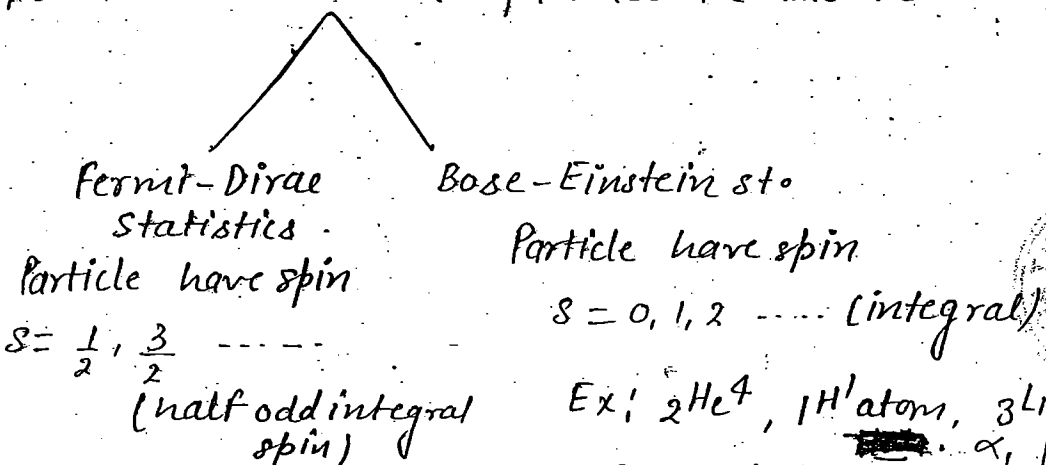


$$\text{xi)} \quad \overline{(\alpha v_x - \beta v_y)^2} = (\alpha^2 + \beta^2) \frac{k_B T}{m}$$

$$\text{xii)} \quad \overline{(\alpha v_x + \beta v_y - v_z)^2} = (\alpha^2 + \beta^2 + 1) \frac{k_B T}{m}$$

# Quantum Statistical Mechanics :

→ Applicable when the particles are identical & indistinguishable



**Fermi-Dirac Statistics**  
 Particle have spin  
 $s = \frac{1}{2}, \frac{3}{2}$  -----  
 (half odd integral spin)

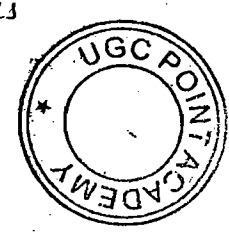
**Bose-Einstein st.**  
 Particle have spin  
 $s = 0, 1, 2$  ----- (integral)



Ex:  $e^-, p, n$  etc.  $\pi^-,$  Hole  
 These particles are klas fermions.

Ex:  ${}^4\text{He}, {}^1\text{H}^+, {}^3\text{Li}^+$  etc  
~~...~~  $\alpha,$  positron!  
 These particles are klas  ${}^1\text{H}^+$   
**Bosons**

→ fermions follow the Pauli exclusion principle.  
 → Condensation property not exist.



→ Bose-Eins condensation is possible.  
 → They donot follow P. Ex.,  
 → No. of distribution is greater than fermions.  
 → In case of Boson  
 ${}^{11}\text{Na}^{23}$

In case of atom  $= n + p + e$   
 $= A - Z + Z + Z$   
 $= A + Z \rightarrow \text{even} \rightarrow \text{Boson}$

Nucleus  
 $A - Z + Z = A \rightarrow \text{even}$

Ex:  ${}^{11}\text{Na}^{23}$  Bosons,  ${}^{11}\text{Na}^{24}$  fermions

→

a                  b  
 \                  /  
   q. states

MB.  
 $\psi_{ab}(1, 2) = \phi_a(1) \phi_b(2)$

$$\psi_{ab}^F(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]$$

F-D st<sup>n</sup> wave fun<sup>n</sup> is antisymmetric.

$$\psi_{ab}^F(1, 2) = 0, \text{ when } a \equiv b$$



$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_a(2) \\ \phi_b(1) & \phi_b(2) \end{vmatrix}$$

Slater Determinant.

for Bosons:

$$\psi_{ab}^B(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]$$

→ wave fun<sup>n</sup> is symmetric.

$$a \equiv b$$

$$\psi_{ab}^B(1, 2) = \sqrt{2} \phi_a(1)\phi_a(2)$$

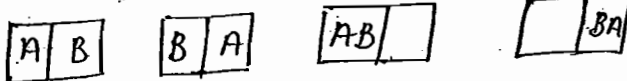
a ≡ b

Distribution of two particles in two degenerate cells →



Case-1) M-B/classical:

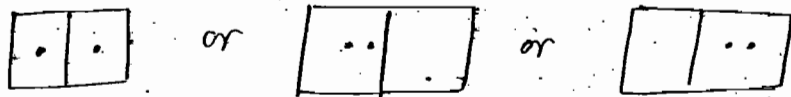
$$\Omega = g_i^{n_i}$$



2.) Bosons :

No. of ways  
of distribution

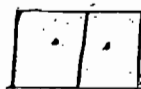
$$\Omega = \frac{n_i + g_i - 1}{g_i} C_{n_i}$$



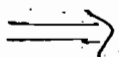
$$\Omega_{B-E} = \frac{2+2-1}{2} C_2 = 3 C_2 = 3$$



3.) Fermions :



$$\Omega_{F-D} = g_i C_{n_i}$$



No. of ways of distribution of  $N$  particles in different cells  $1, 2, \dots, i, \dots$  having degeneracies  $g_1, g_2, \dots$  etc.

(i) when particles are classical :

$$\Omega_{M-B} = \prod_i \frac{N!}{n_i!} (g_i)^{n_i}$$



2.) Bosons :

$$\Omega_B = \prod_i \frac{n_i + g_i - 1}{g_i} C_{n_i}$$

3.) Fermions :

$$\Omega_{F-D} = \prod_i (g_i C_{n_i})$$

Imp → ratio of probabilities of finding the two particles in some state to that probability of finding particles in different states.

$$\gamma_{MB} : \gamma_{BE} : \gamma_{FD} = 1 : 2 : 0$$

Q. Partition fun<sup>n</sup> for a system of two particles each of which can occupy any one of energy level 0 or  $\epsilon$ .

Sol<sup>n</sup>:

(i) If particles are classical:

Distrib.	Energy	Energy
AB	0	0
AB	$\epsilon$	$\epsilon$
A B	$\epsilon$	$\epsilon$
B A	$\epsilon$	$\epsilon$



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

$$= g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2} + g_3 e^{-\beta \epsilon_3}$$

$$= 1 \cdot e^{-0} + 2 e^{-\beta \epsilon} + e^{-2\beta \epsilon}$$

$$Z = (1 + e^{-\beta \epsilon})^2$$

(ii) Fermions:

Distrib.	Energy	Energy
•	0	$\epsilon$
•	$\epsilon$	$\epsilon$

$$Z = e^{-\beta \epsilon}$$

iii) Bosons:



$$Z = e^{-\beta\epsilon} + e^{-0} + e^{-2\beta\epsilon}$$

$$Z = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$$



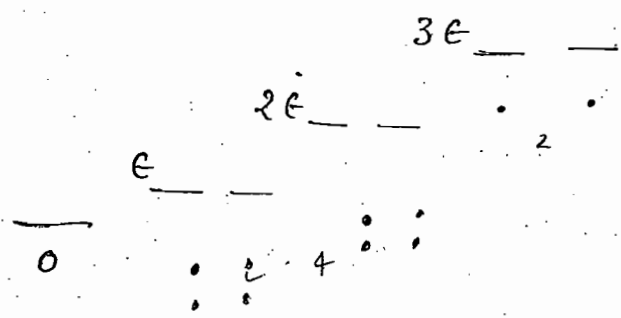
Q. Two particles are to be distributed in different cells having energies 0, ε, 2ε ---

The gr state is non-degenerate, while the excited states are doubly degenerate.

Find the ways of distribution such that the En of the system is 3ε if particles are:

Sol<sup>n</sup>:

(i) Fermions:



ways of distribution = 6

$${}^4C_2 = \frac{4!}{2!2!} = \frac{4 \times 3 \times 2}{2 \times 2} = 6$$

ii) Bosons ;  
ask

No. of ways = 6

$$n_i + g_i - 1 \text{ C } n_i$$

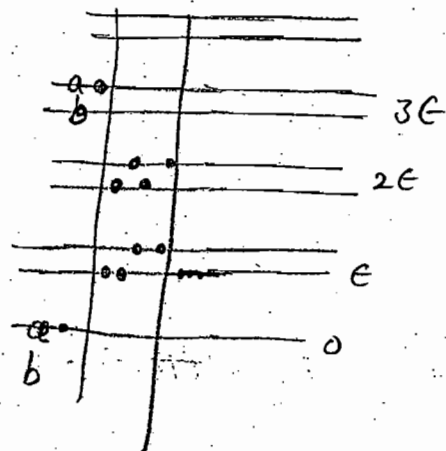
$$\frac{5 \text{ C } 2}{2! 3!} = \frac{5 \times 4 \times 3 \times 2}{2 \times 3 \times 2 \times 3} = 10$$

iii) classical :

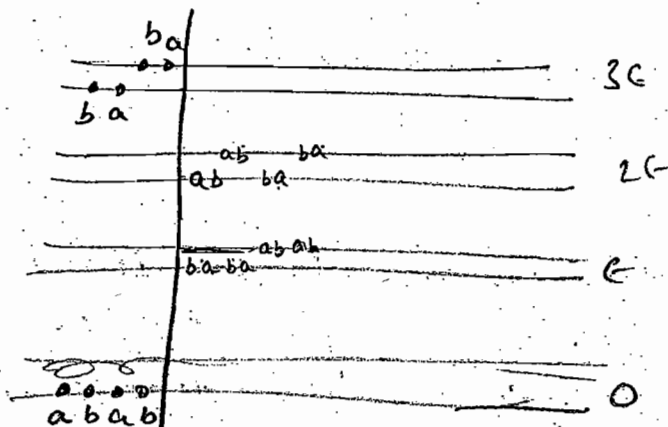
No. of ways = 12

$$3^2 = 9$$

$$g_i \cdot n_i$$



a b



$$8 + 4 = 12$$





## Fermi-Dirac statistics:

Distribution fun<sup>n</sup> for fermions  $f(\epsilon) \rightarrow$

We KIT, for M-B st.

$$f(\epsilon_i) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i}} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T}}$$

In F-D st.

$$\Omega_{F-D} = g_i c_{n_i}$$

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

At equil<sup>m</sup>

$$d(\log \Omega_{F-D}) = 0$$

$$N - \sum_i n_i = 0$$

$$E - \sum_i n_i \epsilon_i = 0$$

} constraints eq<sup>n</sup>s

$$f(\epsilon_i) = \frac{n_i}{g_i} = \langle n_i \rangle$$

$$= \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

2nd method:

Partition fun<sup>n</sup>

$$Z = \sum_i e^{-\beta(\epsilon_i - \mu)}$$



$$Z = \sum_{n_1, n_2, \dots} e^{-\beta(\mu_1 n_1 + \mu_2 n_2 + \dots) - \beta(\epsilon_1 n_1 + \epsilon_2 n_2 + \dots)}$$

or

$$Z = \sum_{n_1=0}^{\infty} e^{-n_1 \beta(\epsilon_1 - \mu)} \sum_{n_2=0}^{\infty} e^{-n_2 \beta(\epsilon_2 - \mu)}$$



or

$$Z = (1 + e^{-\beta(\epsilon_1 - \mu)}) \times (1 + e^{-\beta(\epsilon_2 - \mu)})$$

$$Z = \prod_i (1 + e^{-\beta(\epsilon_i - \mu)})$$

$$\log_e Z = \sum_i \log (1 + e^{-\beta(\epsilon_i - \mu)})$$

$$\sum_i \langle n_i \rangle = N = + \frac{1}{\beta} \frac{\partial}{\partial \mu} (\log_e Z) = \frac{1}{\beta} \sum_i \frac{\beta e^{-\beta(\epsilon_i - \mu)}}{(1 + e^{-\beta(\epsilon_i - \mu)})}$$

$$Tds = dE + PdV - \mu dN + Nd\mu$$

$$N = - \frac{\partial E}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}$$

$$\mu = - \frac{1}{\beta} \frac{\partial}{\partial N} \ln Z |_{T, V}$$

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

Ave. no. of  $\geq$  Occupation no.  
particle in  $i$ th  
cells

Occupation probability:

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$

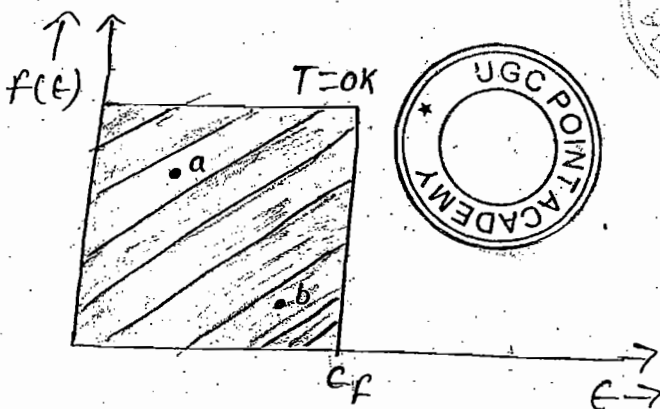
$$f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_f)/k_B T} + 1}$$

$$\beta = \frac{1}{k_B T} \quad \mu \sim \epsilon_f$$

at  $T = 0K$

$$f(\epsilon) = 1 \quad \epsilon < \epsilon_f$$

$$= 0 \quad \epsilon > \epsilon_f$$



Expression for

$\epsilon_f(T=0K)$  for fermions or fermi gas at  $0K \rightarrow$

No. of states in  $\epsilon$ -range

$$\epsilon \rightarrow \epsilon + d\epsilon$$

$$p \rightarrow p + dp$$

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

$$g(\epsilon) d\epsilon = \frac{V 4\sqrt{2} \pi m^{3/2} \epsilon^{1/2} d\epsilon}{h^3}$$

No. of  $e^-$  (fermions)

$$dn(\epsilon) = \underbrace{g(\epsilon) d\epsilon}_{\substack{\downarrow \\ \text{No. of filled} \\ \text{states}}} \times \underbrace{f(\epsilon)}_{\substack{\rightarrow 1 \\ \text{at } 0^{\circ}K}} \times g_s \rightarrow (2s+1) \frac{\text{fermions}}{\text{state}}$$

No. of filled states

Total no. of fermions

$$N = \int dN(\epsilon) = \int dn(\epsilon)$$

$$= (2s+1)V \frac{4\sqrt{2} \pi m^{3/2}}{h^3} \int_0^{E_f(0)} f(\epsilon) \epsilon^{1/2} d\epsilon$$

↓  
1 If  $T=0K$



$$N = \frac{(2s+1) 4\sqrt{2} \pi m^{3/2} E_f^{3/2}}{h^3 \cdot 3/2}$$

$$E_f(0) = \frac{h^2}{2m} \left[ \frac{3N}{4\pi V g_s} \right]^{2/3}$$

$$E_f(0) \propto \left( \frac{N}{V} \right)^{2/3}$$

$$E_f(0) \propto n^{2/3}$$

$n \rightarrow$  fermion density

Average energy of fermion in fermi-Dirac stats  $\rightarrow$

$$\bar{\epsilon} = \frac{\int_0^{E_f(0)} \epsilon dn}{\int_0^{E_f(0)} dn}$$

$$= \frac{\int_0^{E_f(0)} \epsilon \epsilon^{1/2} dn}{\int_0^{E_f(0)} \epsilon^{1/2} dn}$$

$$\bar{\epsilon} = \frac{3}{5} E_f(0)$$

Ave. En. of gas:

$$\bar{E}_{\text{gas}} = N \bar{E} = \frac{3}{5} N E_f(0)$$

At 0K →

$$E_f(0) = \frac{p_f^2}{2m} = \frac{\hbar^2 k_f^2}{2m}$$

$k_f \rightarrow$  fermi wave vect

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

$$k_f \propto n^{1/3}$$

$$p_f \propto n^{1/3}$$

$$v_f \propto n^{1/3}$$

(velocity)

$$t_f \propto n^{-1/3}$$

$$T_f \propto n^{2/3}$$

fermi temp  $\rightarrow$  Energy

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

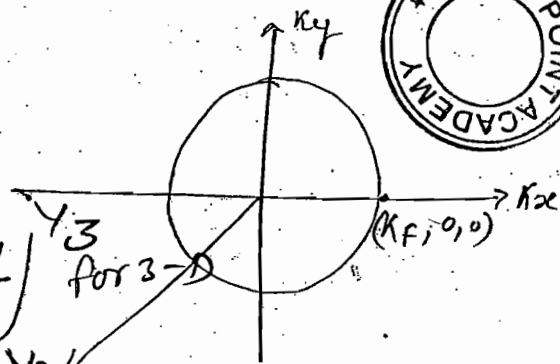
for 3-D

$$k_f = \left( \frac{2\pi N}{A} \right)^{1/2}$$

$k_z \rightarrow$  2D fermi surface at 0K  $\rightarrow$  spherical

$$k_f = \left( \frac{N\pi}{2a} \right)$$

$\rightarrow$  1-D



Pressure of the gas:

$$= \frac{1}{3} g_s \left( \frac{\bar{E}_{\text{gas}}}{v} \right)$$

$$= \frac{1}{3} (2s+1) \frac{\frac{3}{5} N E_f(0)}{V}$$

$$= \frac{1}{5} (2s+1) \left( \frac{N}{V} \right) E_f(0) \quad \text{--- (1)}$$

$$PV = \frac{1}{3} g_s \bar{E}$$

$$PV = \frac{2}{3} \bar{E}$$

$$\bar{E} = a \left( \frac{N}{V} \right)^{5/3} \cdot \frac{1}{V^{2/3}} = a \frac{N^{5/3}}{V^{2/3}}$$

$$P = - \left. \frac{\partial E}{\partial V} \right|_N = \frac{2}{3} a (N)^{5/3} V^{-5/3}$$

$$PV = \frac{2}{3} \bar{E} = \frac{1}{3} \rho \bar{E}$$



from ①

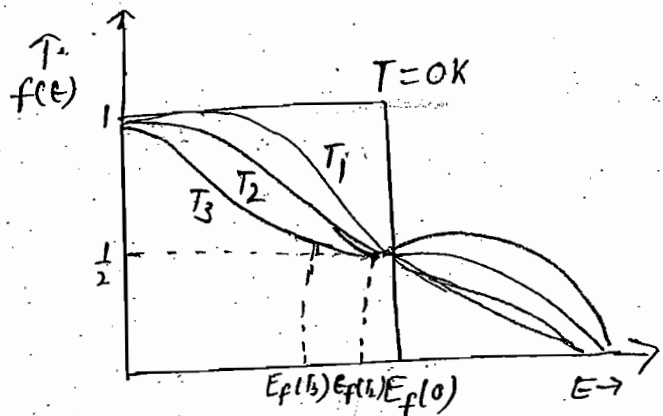
$$P = \frac{1}{3} \left( \frac{N}{V} \right)^{5/3} \left( \frac{6\pi^2}{2s+1} \right)^{2/3} \frac{\hbar^2}{m}$$

$$P \propto N^{5/3}$$

At 0K

$$P_{MB} = 0$$

$$P_{FD} > P_{MB}$$



$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

$$T \neq 0K$$

$$E = E_F$$

$$f(E) = \frac{1}{2}$$

$$E_F(T) = E_F(0) \left[ 1 - \frac{5\pi^2}{12} \left( \frac{k_B T}{E_F(0)} \right)^2 \right]$$

→ Pressure increases when avg  $E$  is less.

Q. Show that at  $T=0K$  in  $e^-$  gas, where  $e \ll E_F(0)$

$$\frac{N(E_F - e \rightarrow E_F)}{N_{total}} = \frac{3}{2} \frac{e}{E_F}$$

Sol<sup>n</sup>:

$$\frac{\int_{E_F - e}^{E_F} dn}{\int_0^{E_F} dn} = \frac{\int_{E_F - e}^{E_F} E^{1/2} dE}{\int_0^{E_F} E^{1/2} dE}$$

$$= \left[ 1 - \left( \frac{E_F - e}{E_F} \right)^{3/2} \right]$$

$$= \left[ 1 - \left( 1 - \frac{e}{E_F} \right)^{3/2} \right]$$

$$= \frac{3}{2} \frac{e}{E_F}$$



Q. for a 2-D  $e^-$  gas no. of  $e^-$  per unit area is given by

$$n = \frac{4\pi m k_B T}{h^2} \log(e^{E_F/k_B T} + 1)$$

Sol<sup>n</sup>:

$$\frac{N}{A} = n = \frac{4\pi m k_B T}{h^2} \log(e^{E_F/k_B T} + 1)$$

$$\frac{dN}{A} = dn = g_s \times g(k) dk \times f$$

$$= 2 \times \frac{k}{2\pi} dk \times \frac{1}{e^{(E - E_F)/k_B T} + 1}$$

$$= \frac{2m}{2\pi h^2} \int_0^\infty \frac{1}{e^{(E - E_F)/k_B T} + 1} dE$$

Q. Show that the de Broglie wavelength of  $e^-$  at Fermi surface at 0K is

$$2 \left( \frac{\pi}{3n} \right)^{1/2}$$

Hint:  $\lambda_{dB} = \frac{h}{p_f} = \frac{h}{\sqrt{2mE_f}}$



Q. Show that the partition fun<sup>n</sup> of a relativistic gas of  $N$  monoatomic molecule having the energy momentum relation  $E = pc$  is

$$\frac{1}{N} \left[ \frac{8\pi V}{h^3} \left( \frac{k_B T}{c} \right)^3 \right]^N$$

$$\rightarrow g(p) dp = g(E) dE$$

Also find  $\langle E \rangle$ ,  $\langle p \rangle$

Sol<sup>n</sup>:

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

$$= \int g(E) dE e^{-\beta E}$$

$$= \int g(p) dp e^{-\beta pc}$$

$$= \int_0^\infty \frac{4\pi p^2 dp V}{h^3} e^{-\beta pc}$$

$$= \frac{8\pi V}{h^3} \left( \frac{k_B T}{c} \right)^3$$



$$Z_{\text{gas}} = \frac{1}{N!} (z_1)^N$$

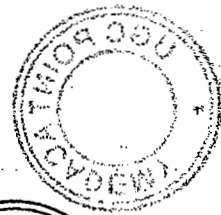
$$= \frac{1}{N!} \left[ \frac{8\pi V}{h^3} \left( \frac{k_B T}{c} \right)^3 \right]^N$$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln z \Big|_{V, N}$$

=

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial}{\partial V} \ln z \Big|_{T, N}$$

$$\langle P \rangle = \frac{1}{\beta} \frac{\langle E \rangle}{V}$$



→ If case is non-relativistic then  $E = p^2/2m$  treated this prob

Q. Show that the partition fun<sup>n</sup> of a non-relativistic gas of  $N$  monoatomic molecules having the eu. mono rel<sup>n</sup>

$$E = p^2/2m$$

$$\langle P \rangle = \frac{2}{3} \frac{\langle E \rangle}{V}$$

$$z_1 = \sum g_i e^{-\beta E_i}$$

$$z_1 = \frac{V}{\lambda^3}$$

Q. Calculate the Fermi energy & average energy of  $e^-$  in eV for sodium assuming it has one free  $e^-$  per atom.

Given  $\rho = 0.977 \text{ gm/cm}^3$   $A = 23$

Soln:

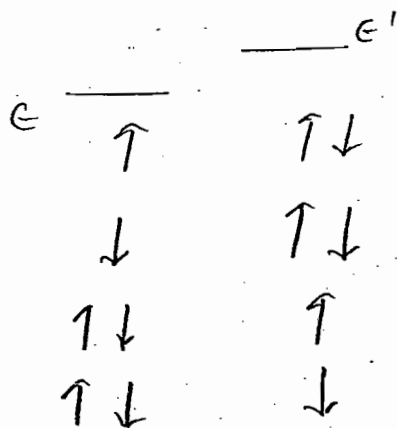
$$E_f = \frac{h^2}{2m} \left( \frac{3N}{8\pi v} \right)^{2/3}$$

$\frac{3}{5} E_0$

$$\rho = \frac{M}{V} = \frac{N \cdot m}{V}$$



Q. 3 spin  $1/2$  fermions are distributed in 2 non-degenerate cells  
no. of ways of distribution



4 ways

4 spin  $1/2$

1-way

5 spin  $1/2$

→ 0-way

## Bose-Einstein statistics:

Distribution fun<sup>n</sup>:

$$Z = \sum_i e^{-\beta(\epsilon_i - \mu)}$$

$$= \sum_{n_1, n_2} e^{-\beta[(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots) - \mu(n_1 + n_2 + \dots)]}$$

$$= \sum_{n_1=0}^{\infty} e^{-\beta n_1 (\epsilon_1 - \mu)} \times \sum_{n_2} e^{-\beta n_2 (\epsilon_2 - \mu)}$$

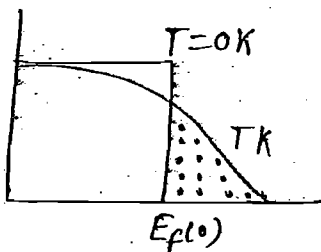
$$\sum x^n = \frac{1}{1-x}$$

$$Z = \frac{1}{1 - e^{-\beta(\epsilon_1 - \mu)}} \times \frac{1}{1 - e^{-\beta(\epsilon_2 - \mu)}} \times \dots$$

$$Z = \prod_i \frac{1}{[1 - e^{-\beta(\epsilon_i - \mu)}]}$$



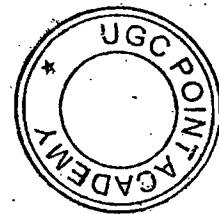
## Electronic specific heat ( $c_e$ )



No. of excited e<sup>s</sup> in range  $d\epsilon$

$$N_{\text{excited}} = \frac{8\sqrt{2} V \pi m^{3/2}}{h^3} d\epsilon e^{-\frac{\epsilon - \mu}{k_B T}}$$

$$N_{\text{excited}} = \frac{3}{2} \frac{N k_B T}{E_f(0)}$$



Excitation energy

$$E = N_{\text{exc}} \times k_B T$$

$$= \frac{3}{2} \frac{N k_B^2 T^2}{E_f(0)} = k_B T^2$$

$$c_e = \frac{dE}{dT} = \frac{3 N k_B^2 T}{k_B T^2}$$

$$c_e = 3 N k_B \left( \frac{T}{T_F} \right)$$

$$c_e \propto T$$

$$c_e = AT$$

# Bose-Einstein distribution

1st page



$$Z = \prod_i \frac{1}{[1 - e^{-\beta(\epsilon_i - \mu)}]}$$

$$\ln Z = - \sum_i \ln [1 - e^{-\beta(\epsilon_i - \mu)}]$$

$$\sum \langle n_i \rangle = N = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} \Big|_{T, V}$$

$$\sum_i \langle n_i \rangle = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

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

Occupation no. for Bosons:

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

$$f_{BE} = \langle n \rangle = \frac{1}{e^{\beta\epsilon} \cdot e^{-\beta\mu} - 1}$$

$$e^{-\beta\mu} \gg 1$$

$$f_{BE} = f_{MB}$$

Q. st change into cl. st

Classical ideal gas:

$$\mu = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial N} \Big|_{T, V}$$

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

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

$$\mu = -\frac{1}{\beta} \left[ \ln \left\{ \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right]$$

for validity of csm

$$e^{-\beta \mu} \gg 1$$

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

$$\Rightarrow \frac{1}{n \lambda^3} \gg 1$$

$$\boxed{n \lambda^3 \ll 1}$$

validity cond<sup>n</sup> for csm.

when T high

$$n = \frac{N}{V} = \text{low}$$

particle behave like cl. gas

when T is low

$$n = \frac{N}{V} = \text{High}, n \lambda^3 \gg 1$$

particle behave like quantum gas particle.

Ideal Bose gas →  
(Photon gas)

for photons

$$Z_{ph} = \prod_i \frac{1}{[1 - e^{-\beta(\epsilon_i - \mu)}]}$$

with  $\mu = 0$ , (min en. of a particle or photon  
 $E = mc^2 = 0$ )

$$Z_{\text{photon}} = \prod_i \frac{1}{(1 - e^{-\beta \epsilon_i})}$$



$$\ln Z = \sum_i \ln \frac{1}{(1 - e^{-\beta \epsilon_i})}$$

$$\ln Z |_{\text{photon gas}} = 2 \times \int g(p) dp \ln Z |_{\text{photon}}$$



$$= 2 \times \int g(\omega) d\omega \ln \left( \frac{1}{1 - e^{-\beta \hbar \omega}} \right)$$

we freq find 2 mods.

Transverse mode

for photon

$\omega \rightsquigarrow Z$  dir'n

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

$$E = \hbar \omega$$

$$g(\omega) d\omega = \frac{V \times 4\pi \hbar^3 \omega^2 d\omega}{h^3 c^3}$$

$$\ln Z |_{\text{ph. gas}} = - \int_0^{\infty} \frac{\omega^2 V}{\pi^2 c^3} \ln(1 - e^{-\beta \hbar \omega}) d\omega$$

$$\ln Z |_{\text{ph. gas}} = \frac{V \pi^2}{45 c^3 (\beta \hbar)^3}$$

$$F = -k_B T \ln Z = -k_B T \frac{V \pi^2}{45 c^3 (\beta \hbar)^3}$$

Avg. En. of photon gas:

$$\langle E \rangle = \frac{-\partial \ln Z}{\partial \beta} \Big|_{N, V}$$

$$= \frac{3V \pi^2}{45 c^3 \hbar^3} \left( \frac{1}{\beta^4} \right)$$

$$\langle E \rangle \propto T^4$$

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \Big|_{T, N}$$

$$= \frac{\pi^2}{45 c^3 h^3 \beta^4}$$

$$\boxed{\langle P \rangle \propto T^4}$$

$$\rightarrow \frac{\langle P \rangle}{\langle E \rangle} = \frac{1}{3V}$$

$$\frac{\Delta \cdot R}{PV} = \frac{S}{3} \langle E \rangle$$

$$\langle P \rangle = \frac{2}{3} \frac{\langle E \rangle}{V}$$

$$\Rightarrow \langle P \rangle = \frac{1}{3} \frac{\langle E \rangle}{V} \rightarrow \text{Relativistic case}$$

$$\boxed{\langle P \rangle = \frac{\langle U \rangle}{3}}$$

$\langle U \rangle \rightarrow$  En. density

specific heat at constt volume

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

$$= \frac{32 \pi^5 V k_B^4 T^3}{15 (hc)^3}$$

$$\boxed{C_V \propto T^3}$$

\*

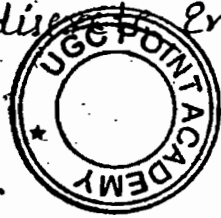
$$\text{Entropy } S = \frac{-\partial F}{\partial T} \Big|_{N, V}$$

$$= \frac{32 \pi^5 k_B^4 V T^3}{45 (hc)^3}$$

$$\boxed{S \propto T^3}$$

Planck's radiation formula of BBR  $\rightarrow$

B.B. has atomic oscillators  
and radiation has discrete  $E_n$  packets  
(photons)



Energy of osc.

$$E_n = nh\nu$$

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

Total no. of osc.

$$N = N_0 + N_1 + N_2 + \dots = \frac{N_0}{1 - e^{-h\nu/k_B T}}$$

Total  $E_n$  of osc.

$$E = E_0 N_0 + E_1 N_1 + \dots = \frac{N_0 h\nu e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})^2}$$

Avg.  $E_n$  of an osc.

$$= \frac{E}{N}$$

$$= \frac{h\nu}{e^{h\nu/k_B T} - 1} = \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

No. of oscillators in freq. range  $\nu \rightarrow \nu + d\nu$

$$= 2 \times \frac{4\pi p^2 dp \nu}{h^3}$$

Energy density of black body having freq.  $\nu \rightarrow \nu + d\nu$

$$u_\nu d\nu = \frac{\text{no. of osc. in range } \nu \rightarrow \nu + d\nu \times \bar{E}_{\text{osc}}}{\text{volume}}$$

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} d\nu$$

Planck's radiation formula



$$p = E/c = h\nu/c$$

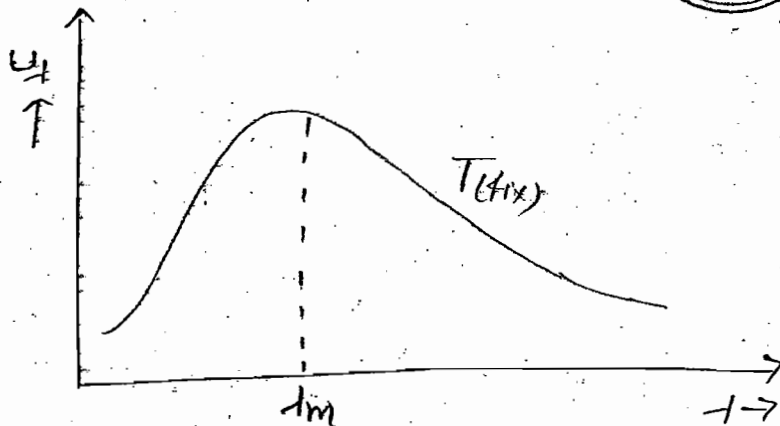
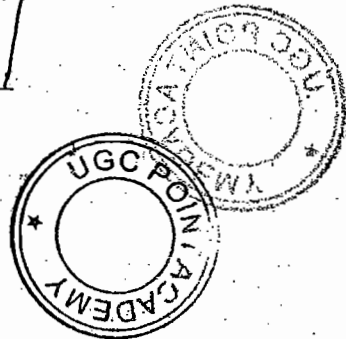
In terms of wavelength

$$\nu = c/\lambda$$

$$d\nu = -\frac{c}{\lambda^2} d\lambda$$

$$U_\lambda d\lambda = \frac{8\pi^5 k_B^4 T^4}{15} \frac{1}{e^{hc/\lambda k_B T} - 1} d\lambda$$

$$U_\lambda = \frac{8\pi^5 k_B^4 T^4}{15} \frac{1}{e^{hc/\lambda k_B T} - 1}$$



→ BB spectra is continuous. (ie. it absorb completely, completely emits)

(i) In low wavelength limit

$$\frac{hc}{\lambda k_B T} \gg 1$$

$$U_\lambda d\lambda = \frac{8\pi^5 k_B^4 T^4}{15} \times \left[ e^{-hc/\lambda k_B T} \right]$$

$$U_\lambda d\lambda = \frac{8\pi^5 k_B^4 T^4}{15} e^{-hc/\lambda k_B T} d\lambda$$

This is Wein's Law.

(ii) long wavelength limit

$$\frac{hc}{\lambda k_B T} \ll 1 \Rightarrow e^{hc/\lambda k_B T} = 1 + \frac{hc}{\lambda k_B T}$$

$$u_{\lambda} d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$$

Rayleigh's - Jean's law.



(iii)  $u_{\lambda}$  max. at  $\lambda = \lambda_m$

$$\Rightarrow \frac{du_{\lambda}}{d\lambda} = 0$$

$$\Rightarrow \frac{3(e^{hc/\lambda_m k_B T} - 1)}{e^{hc/\lambda_m k_B T}} = \frac{hc}{\lambda_m k_B T}$$

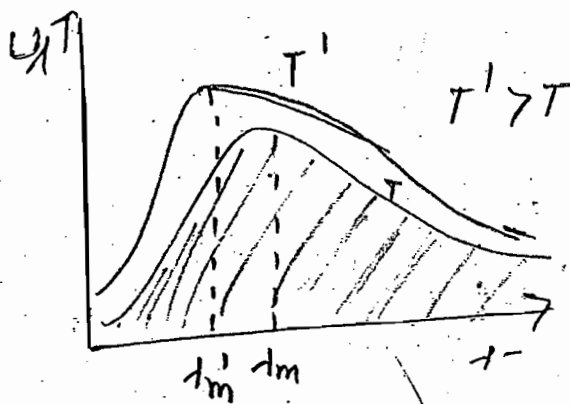
$$\Rightarrow 3 = \frac{hc}{\lambda_m k_B T}$$

$$\Rightarrow \lambda_m \cdot T = \frac{hc}{3k_B} = \text{const.}$$

$$\lambda_m \cdot T = \frac{hc}{2.965 k_B} = b$$

Wien's displacement law

$$\lambda_m T' = \lambda_m T$$



(iv) Area enclosed by the curve

$$\propto T^4$$

(Stefan's Law)

$$\text{Area} = \int_0^{\infty} U_f dt$$

$$= \int_0^{\infty} \frac{8\pi hc}{15} \frac{1}{e^{hc/\lambda kT} - 1} d\lambda$$

$$\frac{hc}{\lambda kT} = x$$

$$= \propto T^4 \int_0^{\infty} x^3 \frac{dx}{e^x - 1}$$



Stefan's Law:

$$E = \sigma A e (T^4 - T_0^4) t$$

$e = 1$  for B.B.

$$\sigma = 5.67 \times 10^{-8} \text{ watt/m}^2$$

$$\sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2}$$

Q.  $T_0 = 27^\circ\text{C}$ ,  $T_A^{\text{sup}} = 373^\circ\text{C}$ ,  $T_B^{\text{sup}} = 573^\circ\text{C}$ , Body A & B are spherical of radius  $\frac{r_A}{r_B} = \frac{1}{2}$ . find

$$\frac{\text{Rate of cooling of body A}}{\text{Rate of cooling of body B}} = \frac{1}{4} \left( \frac{T_A^4 - T_0^4}{T_B^4 - T_0^4} \right)$$

⇒

Rate of cooling  $\propto (T - T_0)$

if  $(T - T_0)$  is small

This is Newton's Law of cooling.



Adiabatic expansion of black body →

$$dQ = dU + PdV$$

In adiabatic  $\leftarrow 0 = dU + PdV$

$$= d(UV) + PdV$$

$$= u dv + v du + PdV$$

$$= v dv + v du + \frac{2}{3} v du$$

$$\Rightarrow 0 = \frac{4v}{3} dv + v du$$

$$= \frac{4}{3} \frac{dv}{v} + \frac{du}{u}$$

$$\boxed{u v^{4/3} = \text{const}}$$

$$u \propto T^4$$

$$\boxed{T^4 v^{4/3} = \text{const}}$$

$$\Rightarrow p^{1/4} v^{1/3} = \text{const}$$

$$\boxed{p v^{4/3} = \text{const}}$$

$$\boxed{T v^{1/3} = \text{const}}$$

or  $\boxed{V T^3 = \text{const}}$

$$\boxed{T v^{\gamma-1} = \text{const}}$$

$$\gamma = \frac{C_p}{C_v} = \frac{4}{3} \rightarrow \text{Triatomic gas}$$

If adiabatically in case of BB.

$$T \rightarrow 2T$$

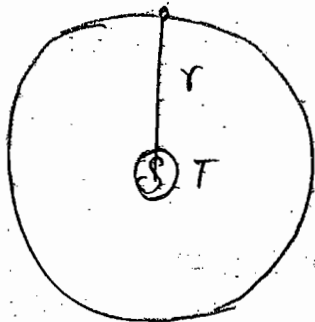
$$V \rightarrow \frac{V}{8}$$

### Measurement of Sun's temp $\rightarrow$

By pyrometer

Total radiation pyrometer  
(Based on Stefan's law)

optical pyrometer  
(Based on Wien's displacement)



En. radiated by the sun/sec

$$= \sigma \cdot 4\pi R_s^2 T_s^4$$

$$= S \times 4\pi r^2$$

↓  
En. falling/Area sec on earth's surface. (solar const)

(Poynting vector) unit  $\text{w/m}^2$

$$S = 2 \text{ cal/min-cm}^2$$

BOSE-EINSTEIN CONDENSATION:  
 particle-den Cr. S.  $\rightarrow$  sharp increase  $\rightarrow$  condensation.

Occupation No.

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

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

for gr. state  $\epsilon = 0$

$$\langle n \rangle = \frac{1}{e^{-\beta\mu} - 1}$$

for Bosons  $\mu$  must be -ve.  
 as  $\langle n \rangle$  can never be -ve.

$$\Rightarrow \langle n \rangle = \frac{1}{e^{|\beta\mu|} - 1}$$

$T \rightarrow$  Increases

$|\mu| \rightarrow$  Increases

$T \rightarrow$  Decreases

$|\mu| \rightarrow$  decreases.

As no. of particle is conserved.  
 The temp. at which  $|\mu| \rightarrow 0$ , when  $T$  is very low

is called  $T \rightarrow T_B$  (Bose temp. or condensation temp.)

No. of Bosons in the Bose gas

$$N = \int g(p) dp \times \frac{f(\epsilon)}{\beta \epsilon}$$

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

$$N = \frac{V}{2\pi^2 h^3} \int_0^{\infty} \frac{p dp}{e^{\beta(p^2/2m - \mu)} - 1}$$

$$\text{at } T = T_B, \mu = 0$$

$$N = \frac{V}{2\pi^2 h^3} \int_0^{\infty} \frac{p^2 dp}{(e^{p^2/2mk_B T} - 1)}$$

$$\text{let } y^2 = \frac{p^2}{2mk_B T}$$

$$2y dy = \frac{2p dp}{2mk_B T}$$

$$dp = \sqrt{2mk_B T} dy$$

$$N = \frac{V(2mk_B T)^{3/2}}{2\pi^2 h^3} \int_0^{\infty} \frac{y^2 dy}{e^{y^2} - 1}$$

$$N = \frac{V(2mk_B T)^{3/2}}{2\pi^2 h^3} \left( \frac{2.612 \sqrt{\pi}}{4} \right)$$

$$T_B = \left[ \frac{N}{2.612 V} \right]^{2/3} \frac{2\pi h^2}{m k}$$

$$T_B \propto \left( \frac{N}{V} \right)^{2/3}$$

$$T_B \propto n^{2/3}$$

$$T_B \propto \frac{1}{m}$$

→ what happens when T decreases beyond  $T_B$   
 ( $T < T_B$ )

There is a problem:

Problem is that zero weightage is given to the gr. st.  $\epsilon=0$  as  $g(\epsilon) \propto \epsilon^{1/2}$

If  $\epsilon=0$ ,  $g(\epsilon=0)=0$



But  $\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$

if  $\epsilon=0$  &  $\mu=0$

$\langle n \rangle = \infty$

This problem can be solved by isolating the state & let gr. st. has  $N_0$  particles.

Then

$$N = N_0 + \frac{V}{2\pi^2 h^3} \int_0^\infty \frac{p^2 dp}{(e^{\beta^2/2m k_B T} - 1)} \rightarrow \frac{V (2m k_B T)^{3/2} (0.6125)^{3/2}}{2\pi^2 h^3 (T_B)^{3/2}}$$

$$N = N_0 + N \left( \frac{T}{T_B} \right)^{2/3}$$



$$N_0 = N \left[ 1 - \left( \frac{T}{T_B} \right)^{2/3} \right]$$

$T < T_B$

$T \rightarrow 0$

$N_0 \rightarrow N$  (ie, all particles goes over to the gr. state) (population increases in gr. st.)

Energy of Bosonic system below  $T_B \rightarrow$

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

$T < T_B$

$E_{in}(E)$  of Bosonic system below  $T_B$

$$E = \int g(\epsilon) d\epsilon \times f(\epsilon) \times \epsilon$$

$$= \frac{V}{2\pi^2 h^3} \int \frac{p^2}{2m} \frac{p^2 dp}{e^{\beta(p^2/2m)} - 1}$$



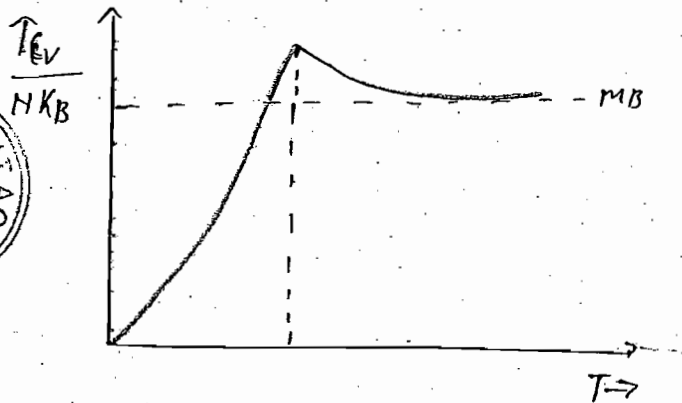
$$= \frac{V}{4\pi^{4/3} m} (2m k_B T)^{5/2} \int_0^{\infty} \frac{y^4}{e^{y^2} - 1} dy$$

$$E = \frac{V}{4\pi^{4/3} m} (2m k_B T)^{5/2} \frac{3}{8} \times 1.391 \sqrt{\pi}$$

$$E = 0.77 \frac{N k_B T^{5/2}}{T_B^{3/2}}$$

$$C_V = \frac{dE}{dT}$$

$$C_V \propto T^{3/2}$$



Q. Determine the Bose temp. of Bosons each of mass of  $6.65 \times 10^{-27} \text{ kg}$  and spin 0, their concentration being  $10^{26}/\text{m}^3$ . Then also determine the fraction  $N_0/N$  of the Bosons in gr. st. at a temp.  $0.2 T_B$

$$T_B = 1.32 \text{ K}, \quad \frac{N_0}{N} = 0.91$$

Q. The excitation of 3-D solid are bosonic in nature with their freq.  $\omega$  & wave vector  $k$ , which are related as  $\omega \propto k^2$ . In large wavelength limit the chemical pot. is zero the behaviour of sp. heat depends on  $T$  as

$$T, T^3, T^{3/2}, T^{5/2}$$

Ans:  $E = \int \epsilon(\epsilon) d\epsilon f(\epsilon)$

$$= \int e^{-\frac{4\pi^2 p^2}{h^2}} \frac{1}{e^{\beta E} - 1}$$

$$\propto \int e^{-E} e^{1/2} \frac{1}{e^{\beta E} - 1}$$



$$\int_0^{\infty} \frac{e^{-3/2}}{e^{\beta E} - 1} dE$$

$$\propto T^{5/2} \int_0^{\infty} \frac{x^{3/2} dx}{e^x - 1}$$

$\propto T^{3/2}$

→ Condensation of photons does not possible.

$$\langle n \rangle = \frac{1}{e^{\beta E} - 1}$$

No. is not conserved in case of photon.

$E \propto p^2$   
 $S=1$  condensation not possible.

Q. condensation is possible for

$$0 < S < 1$$

$$0 < S < 2$$

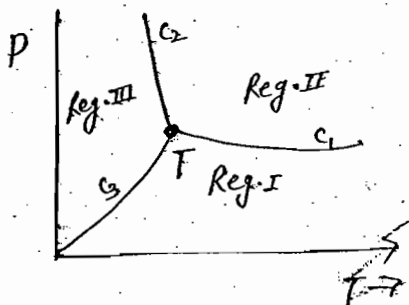
$$S < 2$$

$$0 < S < 3$$



Phase transition :

Ex: Water - vapour



T → Triple pt

Point where all the three phase, solid, liquid & gas coe. in equilibrium with each other.

In case of water the co-ordinate of triple pt  
 (0.075°C, 760mm)

Reg. I

Gas

Curve 1

Curve of vaporisation

Reg. II

liquid

Curve 2

Curve of fusion

Reg. III

solid

Curve 3

Curve of sublimation.

Critical point:

The pt. at which liquid vapour equilibrium lying ends.  
Above critical point, there is no further phase transition.

Prob: The vapour pressure  $P$  (in mm of Hg) of a solid at temp.  $T$  is expressed by  $\ln P = 23 - \frac{3863}{T}$  & that of liquid phase by  $\ln P = 19 - \frac{3063}{T}$



Q. At transition pt. which is correct  $\xrightarrow{P}$   
one-state to other  $\xrightarrow{T}$

$$G_1 = 0$$

$$dG_1 = \text{const}$$

$$dG_1 = 0$$

None

free En  $G_1$  i.e.  $G_1(T, P)$  is continuous at T.P.

$$dG_1 = 0$$

$$* G_1 = H - TS = U + PV - TS$$

$$dG_1 = \underline{dU + PdV + VdP} - TdS - SdT$$

$$dG_1 = VdP - SdT$$

or

$$dG_1 = VdP - SdT - MdH$$

# Types of transitions



I<sup>st</sup> order

1<sup>st</sup> derivative of  $G$  is discontinuous

Ex:  $V$ ,  $S$ ,  $M$ , Density  
 ↓ ↓ ↓  
 volume Entropy magnetization

II<sup>nd</sup> order

2<sup>nd</sup> order derivative is discontinuous & 1<sup>st</sup> order derivative is continuous

$C$ ,  $\chi_m$ , compressibility  
 $K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)$

## Ising model :-

A model used to explain ferromagnetism easily.



$$E = -J \sum_{i,j} S_i S_j - MH \sum_i S_i$$

↓ pole moment of atom  
 ↓ mag. field

Interaction En. with nearest neighbouring atom  $S_i, S_j$  can take value  $\pm 1$  only.

$J \rightarrow$  exchange En.

If  $H = 0$

$$E = -J \sum_{i,j} S_i S_j$$



let there are 2 atom

$$E = -J \sum S_1 S_2 = -J \sum_{S_1} S_1 \sum_{S_2} S_2$$

$$E = e^{\beta J \sum_{S_1, S_2 = \pm 1} S_1 S_2} \quad \text{or} \quad \sum_{S_1} \sum_{S_2} e^{\beta J S_1 S_2}$$

$$E = e^{\beta J \sum_{S_1} S_1 (+1)} + e^{\beta J \sum_{S_1} S_1 (-1)} = \sum_{S_1} e^{\beta J S_1 (+1)} + \sum_{S_1} e^{\beta J S_1 (-1)}$$

$$\boxed{Z_2 = 2^2 (\cosh \beta J)}$$

If there are 3 atom

$$Z_3 = 2^3 (\cosh \beta J)^2$$

In case of  $N$ -particle

$$Z_n = 2^N (\cosh \beta J)^{N-1}$$

$$F = -k_B T \ln Z_N$$

If  $H \neq 0$

$$Z_N = 2^N (\cosh \beta J)^{N-1} (2 \cosh \beta H)^N$$

126



Handwritten notes and markings on the right margin, including a vertical line of small circles and some illegible text.