Statistical Mechanics

Classical Stat. Mech.
(deals with classical particle)
Ex- gas molecules
Maxwell-Boltzmann's Stat.

Quantum Stat. Mech.
(deals with quantum particles)
Ex.

- Particles with half integral spin
  (Ex- e^-, p', He^3 atom, μ meson)
  Fermi-Dirac Statistics
- Particles with integral spin
  (Ex- photon, phonon, He^4, π-meson)
  → Bose-Einstein Statistics

Basic concept of Energy Levels, Energy States or Quantum state and Degeneracy :

a) for a bond e^-.

$$E_n = -\frac{me^4z^2}{8\epsilon_0^2 n^2 h^2} = -\frac{13.6\, z^2}{n^2}\, eV$$

Quantum States (n, l, m_l, m_s)

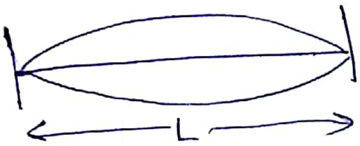
Energy Level	n	l	m_l	m_s	Energy States
2 $E_n = \frac{-13.6 z^2}{4} eV$	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	$(2,0,0,+\frac{1}{2})$; $(2,0,0,-\frac{1}{2})$
		1	$+1$	$+\frac{1}{2}, -\frac{1}{2}$	$(2,1,1,+\frac{1}{2})$; $(2,1,1,-\frac{1}{2})$
			0	$+\frac{1}{2}, -\frac{1}{2}$	$(2,1,0,+\frac{1}{2})$, $(2,1,0,-\frac{1}{2})$
			-1	$+\frac{1}{2}, -\frac{1}{2}$	$(2,1,-1,+\frac{1}{2})$, $(2,1,-1,-\frac{1}{2})$

Many and different energy state may correspond to a particular energy level, the no. of energy states corresponding to a particular energy level is known as degeneracy no. (g_i).

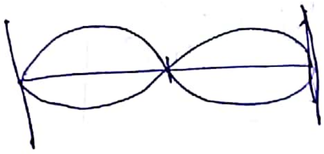
for $g_j = 1 \Rightarrow$ the energy level is called non-degenerate energy level.

for $g_j > 1 \rightarrow$ degenerate energy level.

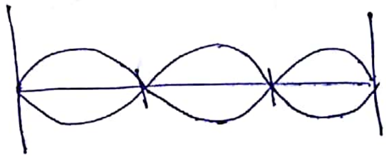
b) for a free particle



$\xrightarrow{n=1} \lambda/2 = L \Rightarrow \lambda_1 = 2L$



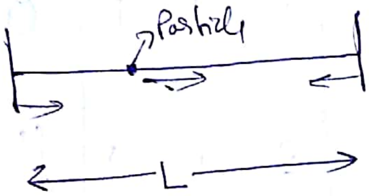
$\lambda = L \Rightarrow \lambda_2 = \frac{1}{2} \times 2L$



$\lambda_3 = \frac{1}{3} \times 2L$

and so on - -

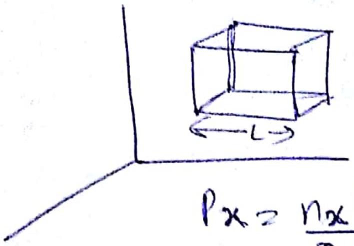
so, $\boxed{\lambda_j = \frac{1}{n_j} \times 2L}$



$p = \frac{h}{\lambda}$ → from de Broglie's hypothesis

$$P_j = \frac{h}{\lambda_j}$$

$$\boxed{P_j = \frac{n_j \times h}{2L}}, \quad n_j = 1, 2, \ldots$$



Considering the particle to be in a cubicle box

$$P_x = \frac{n_x h}{2L}$$

$$P_y = \frac{n_y h}{2L} \quad , \quad P_z = \frac{n_z \times h}{2L}$$

$$\underset{(\text{resultant})}{P^2} = P_x^2 + P_y^2 + P_z^2$$

$$\boxed{E_{(n_x, n_y, n_z)} = \frac{P^2}{2m} = \left(n_x^2 + n_y^2 + n_z^2\right) \frac{h^2}{8mL^2}}$$

has 4 quantum states

n_x, n_y, n_z & spin quantum no. (m_s)

$$E_{(1,1,1)} = \frac{3h^2}{8mL^2}$$

Energy Level	Energy Value	n_x	n_y	n_z	Energy states / Quantum States
1) Ground state or lowest energy	$\frac{3h^2}{8mL^2}$	1	1	1	(1, 1, 1)
2) 1st excited	$\frac{6h^2}{8mL^2}$	2	1	1	(2, 1, 1)
		1	2	1	(1, 2, 1)
		1	1	2	(1, 1, 2)
3) 2nd	$\frac{9h^2}{8mL^2}$	2	2	1	(2, 2, 1)
		2	1	2	(2, 1, 2)
		1	2	2	(1, 2, 2)
3rd	$\frac{11h^2}{8mL^2}$	3	1	1	(3, 1, 1)
		1	3	1	(1, 3, 1)
		1	1	3	(1, 1, 3)
4th	$\frac{12h^2}{8mL^2}$	2	2	2	(2, 2, 2)

$$\underset{\text{(resultant)}}{P^2} = P_x^2 + P_y^2 + P_z^2$$

$$\boxed{E_{(n_x, n_y, n_z)} = \frac{P^2}{2m} = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mL^2}}$$

→ has 4 quantum states
n_x, n_y, n_z & spin quantum no. (m_s)

$$E_{(1,1,1)} = \frac{3h^2}{8mL^2}$$

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		1	1	2	(1,1,2)
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		2	1	2	(2,1,2)
		1	2	2	(1,2,2)
3rd	$\frac{11h^2}{8mL^2}$	3	1	1	(3,1,1)
		1	3	1	(1,3,1)
		1	1	3	(1,1,3)
4th	$\frac{12h^2}{8mL^2}$	(2,	2,	2)	(2, 2, 2)

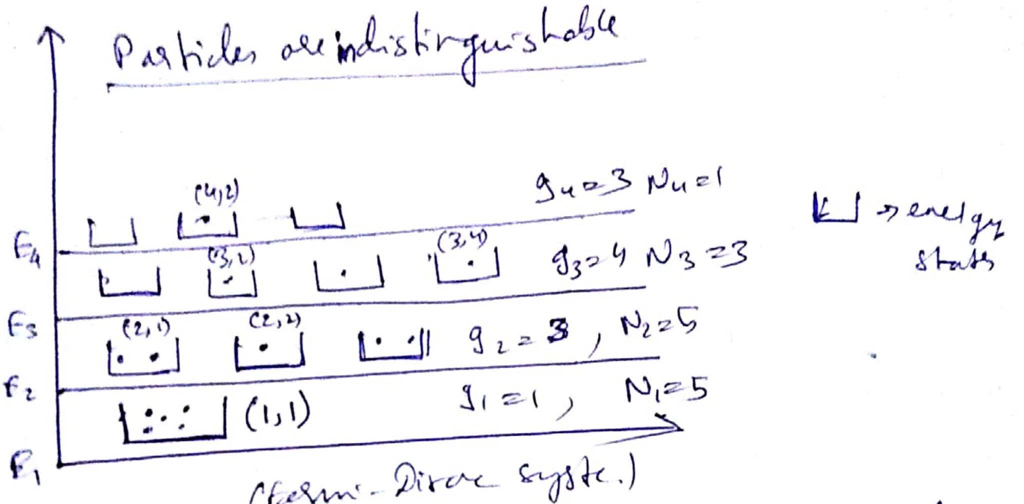
Degeneracy

$g_1 = 1$ → Non-degenerate level

$g_2 = 3$ → Degenerate level

$g_3 = 3$ → Degenerate level

Schematic Representation of Energy Level, Energy States & degeneracy



- Occupation No. (N_i) No. of particles in a particular energy level of the system.

- Total no. of particles of the system,

$$N = N_1 + N_2 + N_3 + \cdots + N_i$$

for closed system $N = \sum N_i$ = constant

- Each particle energy in ith energy level has the energy E_i irrespective of the energy states it occupies at that level.

- The total energy of the system —

$$U = N_1 E_1 + N_2 E_2 + \cdots + N_i E_i$$

for an isolated system.

$$U = \sum N_i E_i = \text{constant}$$

$U = \int$

• <u>Macrostates</u> – A specification of the set of occupation no. i.e. the no. of particles in each <u>energy level</u> of the system is defined as the macrostate of the system.

$$M(N_1, N_2, N_3 \ldots N_i)$$

In this case ← $M(5,5,3,1)$

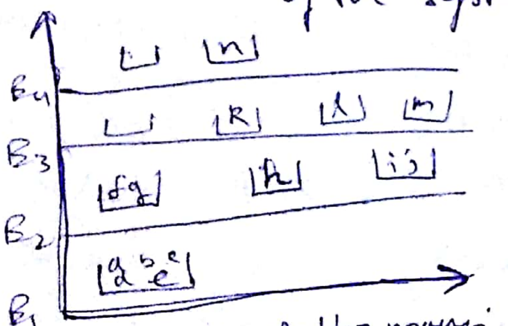
• <u>Microstate</u> – i) If the particles are indistinguishable (W) a specification of the set of no. of particles in each <u>energy states</u> of the system is defined as the microstate of the syste.

← <u>Microstats</u>

(1,1) Energy states contains 5 particle
(2,1) " " 2 "
(2,2) " " 1 "
⋮
(4,2) " " 1 "

} 1 Microstate

ii) If the particles are distinguishable, a specification of the quantum state of each particle of the system is defined microstate of the system.



(Maxwell – Boltzmann system)

(1,1) Energy states contain a,b,c,d,e
(2,1) " " " f h
(2,2) " " " g
⋮
(4,2) " " " n

Each particle can only be in one quantum state at a time. The system taken as a whole can only be 1 microstate at a time

Changing the quantum state of any one particle of the system will change the microstate of the system as a whole.

There are actually a large no. of ways in which this transfer can be made without changing the macrostate of the system.

The no. of microstate (W) to a particular macrostate (M) is known as Thermodynamic Probability of the given macrostate

Macrostate $M(N_1, N_2, N_3, \ldots N_i)$

$\downarrow$

Microstates $\rightarrow W = ??$

$N = \Sigma N_i \rightarrow$ closed

$U = \Sigma E_i N_i \rightarrow$ Isolated.

$E_1 = 1\,eV$
$E_2 = 2\,eV$
$E_3 = 3\,eV$
$E_4 = 4\,eV$

Ex: $\left.\begin{matrix} N = 14 \\ U = 28\,eV \end{matrix}\right\} M_1(5,5,3,1) \rightarrow W_1 = ??$

Constant values of total energy U (with $U = \Sigma E_i N_i$) and total no. of particles N (with $N = \Sigma N_i$) are possible even if the occupation no. of the energy levels are varied. But, every time we change this no. we get a new macrostate.

// Corresponding to each of this macrostate (M_k) there are a large no. of microstate (W_k).

The total no. of microstate of the system is known as the Thermodynamic Probability of the given ~~macro~~ System.

$$\boxed{\Omega = W_1 + W_2 + \cdots + W_K}$$

$$= \Sigma W_K$$

($W_1 \rightarrow$ is Thermodynamic probability of given macrostate M_1)

and so on

The fundamental postulate of statistical mechanics states that in an isolated and closed system all the possible microstates (Ω) are equally probable.

- The probability of a given microstate:

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

- The probability of a given macrostate:

$$P_{M_K} = \frac{W_K}{\Omega}$$

- Most probable State - is simply the macrostate which has the maximum no. of microstate.

Scanned by CamScanner

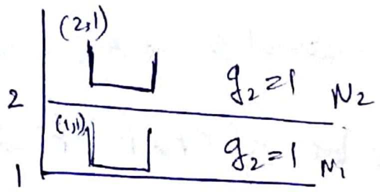
Q1) 4 particles are distributed over 2 non-degenerate energy level. Find the macrostate & microstate of the system if the particles

i) Distinguishable

ii) Indistinguishable.

Distinguish

N=4 → a, b, c, d



Macrostate	Microstate
$M_1=(4,0)$	$W_1=1$
$M_2=(3,1)$	$W_2=4$
$\boxed{M_3=(2,2)}$ → Most probable state	$W_3=6$
$M_4=(1,3)$	$W_4=4$
$M_5=(0,4)$	$W_5=1$

W_1:

(1,1)	(2,1)
ab,cd	

W_2 = 4:

bcd	a
acd	b
abd	c
abc	d

W_3 = 6:

cd	ab
bd	ac
bc	ad
a,d	bc
a,c	bd
ab	cd

$M=5$

$W=16$

Indistinguishable

Macrostate	Microstate
$M_1=(4,0)$	$W_1=1$
$M_2=$	$W_2=1$
M_3	$W_3=1$
M_4	$W_4=1$
M_5	$W_5=1$

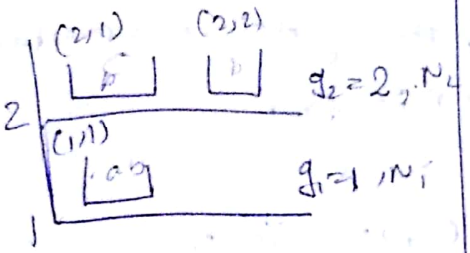
$^4C_2=\frac{4\times 3}{2}$ same

$M=5$

5

Q2) 2 particles are distributed in 2 energy levels, with $g = 1, 2$ respectively. Find the macro & microstate.

Distinguishable	Indistinguishable



macrostate

$M_1 (2, 0)$ — $W_1 = 1$

$M_2 (1, 1)$ — $W_2 = 4$

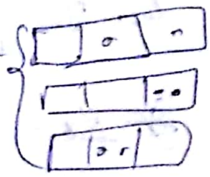
$M_3 (0, 2)$ — $W_3 = 4$

$\overline{\quad 9 \quad}$

M_1 — $W_1 = 1$

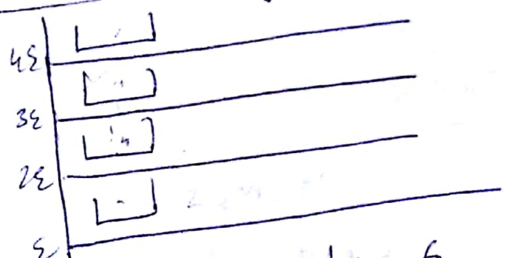
M_2 — $W_2 = 2$

M_3 — $W_3 = 3$



Q3) 3 particles each of which can be in any one of the $\varepsilon, 2\varepsilon, 3\varepsilon, 4\varepsilon$ energy states, have the total energy of the system $= 6\varepsilon$, Find all possible distribution of all the particles of the system. If the particles are

Distinguishable	Indistinguishable



$M_1 (1, 1, 1, 0) \rightarrow W_1 = 6$

$M_2 (2, 0, 0, 1) \rightarrow W_2 = 3$

$M_3 (0, 3, 0, 0) \rightarrow W_3 = 1$

$\boxed{10}$

$W_1 = 1$

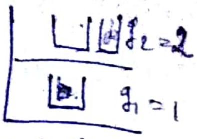
$W_2 = 1$

$W_3 = 1$

$\boxed{3}$

Maxwell-Boltzmann Statistics (MBS)

distinguish particle



$M(1,1) \Rightarrow W = 4$

$N = 2$

Basic of postulate of M.B.

1. The particles are considered to be identical and distinguishable

2. The total no. of particles of the system is constant

$$N = N_1 + N_2 + \cdots + N_i = \text{const.}$$

$$\boxed{N = \Sigma N_i = \text{const.}}$$

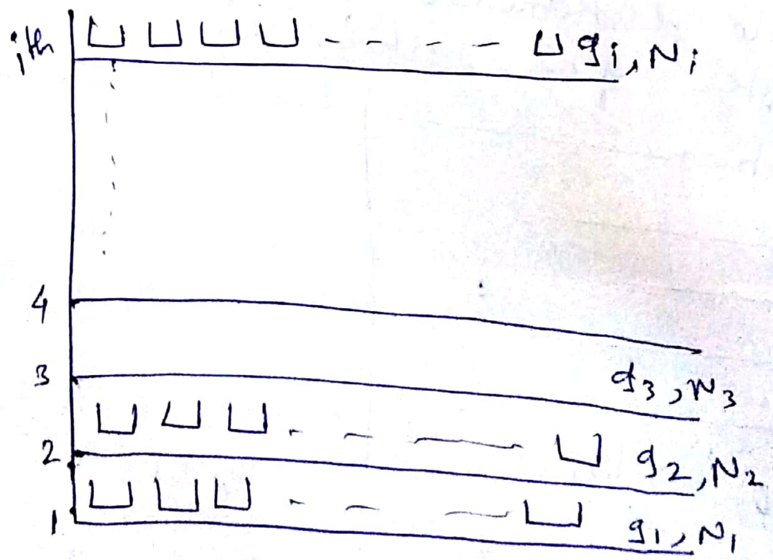
3. $U = E_1 N_1 + E_2 N_2 + \cdots + E_i N_i = \text{const.}$

$$\boxed{U = \Sigma E_i N_i = \text{const}}$$

4. The particles do not obey Pauli's Exclusion principle.

Ex – Gas molecules

Now we will calculate the no. of possible microstate (i.e. Thermodynamic Probability) corresponding to a macrostate $M(N_1, N_2, N_3 \cdots N_i)$ for a system of particles (Gas molecules) obeying Maxwell-Boltzmann statistics.



1. The no. of ways to collect N_1 particles from N particles in 1st Energy Level $= {}^{N}C_{N_1}$ ways

Similarly, N_2 particles from $(N-N_1)$ - - in 2nd Energy Level

$${}^{N-N_1}C_{N_2}$$

and so on - - -

Total no. of ways to collect $N_1, N_2, \ldots N_i$ particles in 1st, 2nd, . . . ith Energy Level resp.

$${}^{N}C_{N_1} \times {}^{N-N_1}C_{N_2} \times \cdots \times$$

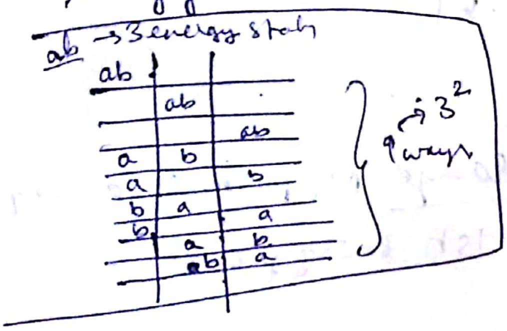
$$= \frac{N!}{N_1!\,\cancel{(N-N_1)!}} \times \frac{\cancel{(N-N_1)!}}{N_2!\,(N-N_1-N_2)!} \times \cdots$$

$$= \frac{N!}{N_1!\,N_2!\,\cdots N_i!}$$

2. The no. of ways to arrange N_1 particles among g_1 energy state in 1st Energy Level

$$\downarrow$$

$$g_1^{N_1}$$



Similarly -

N_2 particles among g_2 energy state in 2nd Energy Level

$= g_2^{N_2}$ ways.

and so on - -

The effective no. of ways to distribute n particles under the macrostate $M(N_1, N_2, \ldots N_i)$ obeying MB statistics.

$$W = \underbrace{\frac{N!}{N_1!\,N_2!\cdots N_i!}}_{\text{collect}} \times \underbrace{g_1^{N_1} \times g_2^{N_2} \times \cdots \times g_i^{N_i}}_{\text{arrange}}$$

$$\boxed{W_{MB} = N!\,\prod_i \frac{g_i^{N_i}}{N_i!}}$$

Quantum Statistics :-

Fermi - Dirac Statistics (FDS)

1. The particles are considered to be identical and indistinguishable.

2. $N = \sum N_i = \text{const.}$

3. $U = \sum E_i N_i = \text{const.}$

4. The particles have half integral spin

5. The particles have asymmetric wave function.

6. Particles obey Pauli's Exclusion Principle

Ex- e^-, p, n, He^3 atom, μ-meson etc. (Fermions)

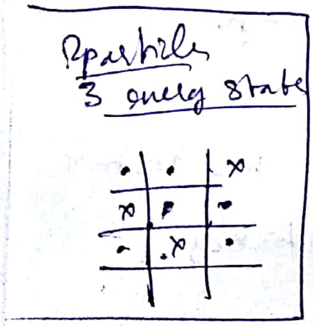
Calculation -

1. Total no. of ways to collect $N_1, N_2, \ldots N_i$ particles in 1st, 2nd ... ith energy level.

$= 1 \times 1 \times 1 \cdot - - - \cdot \times 1$

$= 1$ ways.

2. The no. of ways to arrange N_1 particles amongst g_i energy states in 1st energy level:



$$= \frac{g_1 \times (g_1-1) \times (g_1-2) \times \cdots \times (g_1 - N_1 + 1)}{N_1!}$$

[$\because$ Particles are indistinguishable]

$$= \frac{g_1 \times (g_1-1) \times (g_1-2) \times \cdots \times (g_1-N_1+1) \times (g_1-N_1) \times (g_1-N_1-1) \times 3 \times 2 \times 1}{N_1! \times (g_1-N_1)(g_1-N_1-1) \times \cdots \times 3 \times 2 \times 1}$$

$$= \frac{g_1!}{N_1!(g_1-N_1)!} = {}^{g_1}C_{N_1}$$

$$W = \underbrace{1 \times 1 \times \dots \times 1}_{\text{collect}} \times \underbrace{{}^{g_1}C_{N_1} \times {}^{g_2}C_{N_2} \times \dots \times {}^{g_i}C_{N_i}}_{\text{arrange}}$$

$$\boxed{W_{FD} = \prod_i {}^{g_i}C_{N_i}}$$

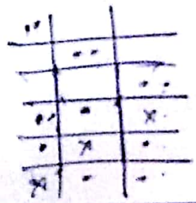
Bose – Einstein's Statistics

1. The particles are considered identical & indisting.
2. $N = \sum N_i = \text{const.}$
3. $U = \sum E_i N_i = \text{const}$
4. The particles have integral spin.
5. Symmetric wave function
6. Particles do not obey Pauli's Excl. Principle

Ex – photon, phonon, He^4 atom, π-meson

Calculate

2 particle
3 energy state



6 ways

1. Total ways to collect = 1 way
2. 1 2 3 4 ... g_1

fix

Consider Energy state & particle to be distinguishable

the total no. of object $= g_1 + N_1$ (considering distinguishable)

Remaining object $= (g_1 + N_1 - 1)$

Permutation

$(g_1 + N_1 - 1)!$

No. of ways to fix $= g_1$

So, total permutations $= \dfrac{(g_1) \cdot (g_1 + N_1 - 1)!}{g_1!\, N_1!}$

Here both are indistinguishable

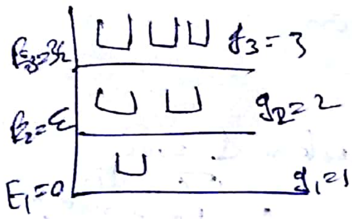
$$= \frac{(g_1 + N_1 - 1)!}{N_1!\,(g_1 - 1)!}$$

$$= \boxed{{}^{g_1 + N_1 - 1}C_{N_1}} \text{ ways}$$

$$W_{BE} = \underbrace{1 \times 1 \times 1 \times \dots 1}_{\text{collect}} \times {}^{g_1+N_1-1}C_{N_1} \times \cdots \times {}^{g_i+N_i-1}C_{N_i}$$

$$\boxed{W_{BE} = \pi_i \; {}^{g_i+N_i-1}C_{N_i}}$$

Ex 1. 4 particles are distributed in 3 energy levels with energies $0, \varepsilon, 3\varepsilon$ so that the total energy is 4ε. Energy levels are degenerate with degeneracy 1, 2, 3 resp.
Find all possible distribution of all the particles if the particles obey –



1) MB
2) F-D
3) BE statistics.

Ans

M-B

$$W_{MB} = N! \, \pi_i \frac{g_i^{N_i}}{N_i!}$$

Macrostates   Microstates

$M_1 = (0,4,0) \rightarrow W_1 = 4! \times \dfrac{1^0 \times 2^4 \times 3^0}{0!\, 4!\, 0!} = 16$

$M_2\ (2,1,1) \rightarrow W_2 = 4! \times \dfrac{1^2 \times 2^1 \times 3^1}{2! \times 1! \times 1!} = 72$ 24 ?

$W = 88$

F-D

No macrostate possible.

B-E

$M_1 (0,4,0) \longrightarrow W_1 = {}^{1+0-1}C_0 \times {}^{2+4-1}C_4 \times {}^{3+0-1}C_0$

$= 5$

$M_2 (2,1,1) \longrightarrow W_2 = {}^{1+2-1}C_2 \times {}^{2+1-1}C_1 \times {}^{3+1-1}C_1$

$= 1 \times 2 \times 3 = 6$

$W = 11$

– Distribution law –

- $\sum N_i = \text{const}$ ①
- $\sum E_i N_i = \text{const}$ ②

Bose-Einstein

$$W = \pi_i \, {}^{g_i+N_i-1}C_{N_i} = \pi_i \frac{(g_i+N_i-1)!}{N_i!\,(g_i-1)!}$$

$$\Rightarrow \ln W = \sum_i \left[\ln(\underbrace{g_i+N_i}_{\text{very large}} - \underbrace{1}_{\text{neglect}})! - \ln(N_i!) - \ln(g_i-1)! \right]$$

$\Rightarrow$ [Applying sterling approx
$\ln x! = x\ln x - x$, x is very large]

$$\ln W = \sum_i \Big[(g_i+N_i)\ln(g_i+N_i) - (g_i+N_i) - N_i \ln N_i + N_i - (g_i-1)\ln(g_i-1) + (g_i-1) \Big]$$

$$\Rightarrow d[\ln W] = \sum dN_i \ln(g_i+N_i) + \cancel{dN_i} - \cancel{dN_i} - dN_i \ln N_i - \cancel{dN_i} + \cancel{dN_i}$$

$$\Rightarrow d[\ln W] = \sum \ln\left(\frac{g_i+N_i}{N_i}\right) dN_i$$

For most prob. state W is max.
$\ln W$ is also max.