

Macroscopic System :

The specification of no. of phase points [ie, system or molecule] in each cell of Phase Space.

→ A system containing a small no. of particles whose motion can be described individually by dynamic particle is called as macroscopic system.

→ Example : System of the bodies which may collide System containing a ball and The Earth.

Microscopic System :

In order to define the microstate of the ensemble we must specify the individual position of phase points for each system or molecule of the ensemble.

→ A system containing a large no. of particles whose motion cannot be described individually by dynamic particle is called as microscopic system

Degrees of Freedom :

→ It is used to describe the position and configuration of the system.

→ A system comprising one molecule has F degrees of freedom.

→ If there are N molecules in the system it has NF degrees of freedom.

→ Rigid body has 6 degrees of freedom.
(3 translatory + 3 rotational) motion

Phase Space :

→ A combination of position space and momentum space is known as phase space.

→ There are 6 dimensions

[3 position + 3 momentum Co-ordinates]

→ A small element in phase space is denoted by $d\tau$.

$$d\tau = (dx \, dy \, dz) (dp_x \, dp_y \, dp_z)$$

→ According to Heisenberg Uncertainty Principle,

$$dx \cdot dp_x \approx \hbar$$

$$dy \cdot dp_y \approx \hbar$$

$$dz \cdot dp_z \approx \hbar$$

$$\text{So, } d\tau = \hbar^3$$

→ Unit of phase space = $[J \cdot \text{Sec}]^3$ (or) $[Nms]^3$

→ Dimension of phase space,

$$= \text{Length} \times \text{momentum}$$

$$= m \times \text{kg m/s}$$

$$= \text{kg m}^2/\text{s}$$

→ 6 dimensional phase-space is called μ space (or) Γ space representation.

→ No. of phase points per unit volume is called the phase density

→ An element of volume in phase space is called a cell.

→ F degrees of freedom per molecule,

- Position Space - F dimensional

- Momentum Space - F dimensional

- μ Space - $2F$ dimensional (one Particle)

- Γ space - $2FN$ dimensional (N Particle)

Macrostates and Microstates :

- Let us consider an ensemble consisting of a large No. of independent system (or) a gas consisting of a large no. of molecules in the phase space. Each system (or) molecule may be represented by point known as phase point in the phase space.
- Let the phase space be divided into cells numbered $1, 2, 3, \dots$
- A phase point for any system (or) molecule may be supposed to lie inside one of these cells.
- In order to define the microstate of the ensemble we must specify the individual position of phase point for each system (or) molecule of the ensemble.

→ A macrostate of the ensemble may be defined by the specification of the number of phase point in each cell of phase space.

→ Such as n_1 phase points are in cell 1 and n_2 phase points are in cell 2, n_3 phase points are in cell 3 and so on.

→ The no. of microstates corresponding to a given macrostate is called thermodynamic probability of that macrostate.

→ Thus the probability that the ensemble will possess energy E is proportional to $W(E)$

$$P(E) = C W(E)$$

where, C - constant of proportionality

$W(E)$ - Thermodynamic probability

Four distinguishable coins are tossed for a large no. of times. Write down different microstate which may be observed and macrostate into which they would fall.

Solution:

Let us denote the coins by a, b, c, d. If they are tossed for a large no. of times, we shall have the micro & macro states as shown in table.

Macrostate	Possible Arrangement		No. of microstate
	Compartment 1	Compartment 2	
0, 4	0	abcd	1
1, 3	a b c d	bcd acd abd abc	4
2, 2	ab bc cd da ac bd	cd da ab cb db ac	6
3, 1	abc bcd dab acd	d a c b	4
4, 0	abcd	0	1

⑤

No. of microstate = 16

No. of macrostate = 5

⑩

→ Total no. of microstates for n particles is $n+1$

→ A given macrostate may consist of
4 distinguishable particles.

$$= n+1$$

$$= 4+1 = 5$$

But total particles is 4.

→ In general for a system of n particles,
the total no. of microstates are 2^n .

$$n = 4$$

$$2^n = 2^4 = 16 \text{ microstates}$$

→ The no. of microstates corresponding to any
given macrostate is called its thermodynamic
probability and it is represented by W (or) Ω

→ The probability (or) occurrence of a macrostate
is defined as,

$$P_{\text{macro}} = \frac{\text{No. of microstate in the macrostate}}{\text{Total no. of microstate of system.}}$$

$$P_{\text{macro}} = \frac{W}{2^n}$$

→ The probability of a microstate is,

$$P_{\text{micro}} = \frac{1}{2^n}$$

$$P_{\text{macro}} \propto W$$

→ Probability of macrostate \propto Thermodynamic Probability

→ There may be many different microstates may correspond to the same macrostates.

Stirling's Formula:

→ For a large value of n , the calculation of $n!$ becomes very troublesome. Stirling's formula gives a suitable analytic approximation of $\log n!$. For large value of n ,

$$n! = n(n-1)(n-2)\dots 4 \times 3 \times 2 \times 1$$

$$\rightarrow \log n! = n \log n - n$$

$$\log N! = N \log N - N$$

$$\log n_i! = n_i \log n_i - n_i$$

Stirling's

Formula

Most Probable Distribution :

→ "The most probable state of a system is that macrostate which has maximum probability of occurrence."

→ "Equilibrium state of a system is state of maximum probability"

[Most Probable State \Rightarrow Equilibrium State of the System]

→ The most probable distribution is a no. of particles in each cell is proportional to the size of the cell.

$$g_z = \frac{n_z}{n}$$

where, g_z - Probability of any one particle in cell

n_z - No. of particle in cell z

n - Total no. of particle.