STATISTICAL PHYSICS

(Part-1)

B.Sc. III (paper-1)

<u>Unit-II</u>

Dr. A.K. DWIVEDI

DEPARTMENT OF PHYSICS
HARISH CHANDRA P. G. COLLEGE VARANASI

STATISTICAL PHYSICS

THE STATICAL BASIC OF THERMODYNAMICS

Introduction

The primary goal of statistical thermodynamics (also known as equilibrium statistical mechanics) is to derive the classical thermodynamics of materials in terms of the properties of their constituent particles and the interactions between them. In other words, statistical thermodynamics provides a connection between the macroscopic properties of materials in thermodynamic equilibrium, and the microscopic behaviors and motions occurring inside the material.

Whereas statistical mechanics proper involves dynamics, here the attention is focused on statistical equilibrium (steady state). Statistical equilibrium does not mean that the particles have stopped moving (mechanical equilibrium), rather, only that the ensemble is not evolving.

Fundamental postulate

A sufficient (but not necessary) condition for statistical equilibrium with an isolated system is that the probability distribution is a function only of conserved properties (total energy, total particle numbers, etc.).There are many different equilibrium ensembles that can be considered, and only some of them correspond to thermodynamics.[1] Additional postulates are necessary to motivate why the ensemble for a given system should have one form or another.

A common approach found in many textbooks is to take the equal a priori probability postulate. This postulate states that

> For an isolated system with an exactly known energy and exactly known composition, the system can be found with equal probability in any microstate consistent with that knowledge.

The equal a priori probability postulate therefore provides a motivation for the microcanonical ensemble described below. There are various arguments in favour of the equal a priori probability postulate:

- **Ergodic hypothesis**:

  An Ergodic system is one that evolves over time to explore "all accessible" states: all those with the same energy and composition. In an ergodic system, the microcanonical ensemble is the only possible equilibrium ensemble with fixed energy. This approach has limited applicability, since most systems are not ergodic.

- **Principle of indifference:**

  In the absence of any further information, we can only assign equal probabilities to each compatible situation.

- **Maximum information entropy**:

  A more elaborate version of the principle of indifference states that the correct ensemble is the ensemble that is compatible with the known information and that has the largest Gibbs entropy (information entropy).

STATIC AND DYNAMICS SYSTEM

Static System

A system is said to be static if the constituent particles of the system remain at rest in a particular microstate.

Example: A system of tossed coin is an example of static system. After every toss, the coins remain permanently latched in the last state.

Dynamic System

A system is said to be dynamics if the constituent particles of the system can move so that the system goes from one microstate to another.

Example: Any gas is an example of dynamics system. Thus, molecules of gas are always is constant, random motion, continuously colliding with one another, following Brownian motion. During this, they change their position, momentum and energy continuously.

CONSTRAINT, ACCESSIBLE AND INACCESSIBLE STATES

Constraint

A set of conditions or restrictions that must be obeyed by a system are known as constraints.

Let us take an example of the distribution of 3 particles in two compartments, the system must obey the constraint that total no. of particles in two compartments must be 3.

In general, if there are N particles to be distributed in two compartments and there are n_1 particles in compartment no. 1 and n_2 particles in compartment no. 2, then we must have

$$n_1 + n_2 = N$$

This relation is known as equation of constraint on the system.

Accessible States

The macrostates which are allowed under a constraint are called Accessible states.

For ex- in distributing 3 particle in 2 compartment under the constraint that no compartment will remain empty, the only accessible macrostates are (2, 1) and

(1, 2).

Inaccessible States

The macrostates which are not allowed under a constraint are called inanccessible states.

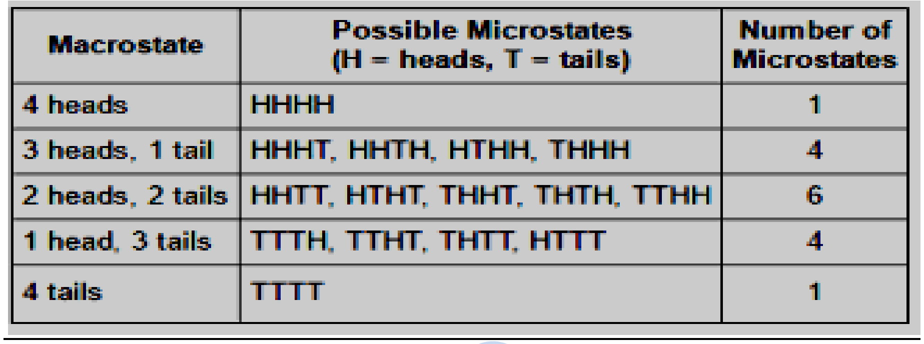
For ex- in distributing 3 particle in 2 compartment under the constraint that no compartment will remain empty, the only macrostates are (3, 0) and (0, 3) are inaccessible macrostates.

MACROSTATE AND MICROSTATE

In statistical mechanics, a microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuations. In contrast, the macrostate of a system refers to its macroscopic properties, such as its temperature, pressure, volume and density. Treatments on statistical mechanics define a macrostate as follows: a particular set of values of energy, the number of particles, and the volume of an isolated thermodynamic system is said to specify a particular macrostate of it. In this description, microstates appear as different possible ways the system can achieve a particular macrostate.

A macrostate is characterized by a probability distribution of possible states across a certain statistical ensemble of all microstates. This distribution describes the probability of finding the system in a certain microstate. In the thermodynamic limit, the microstates visited by a macroscopic system during its fluctuations all have the same macroscopic properties.

Example…



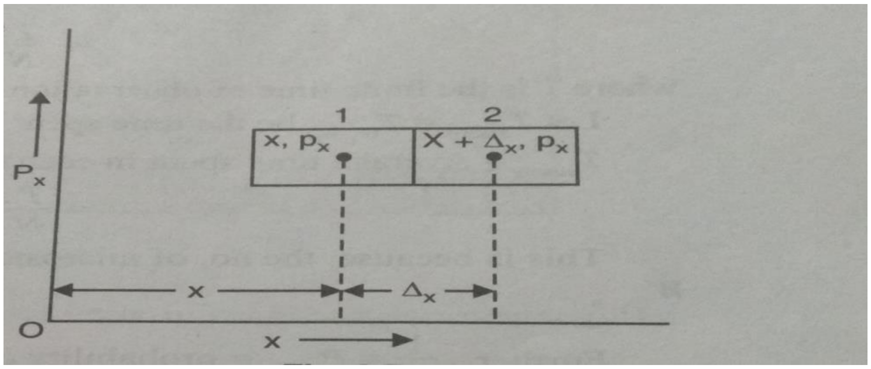
Macrostate	Possible Microstates (H = heads, T = tails)	Number of Microstates
4 heads	HHHH	1
3 heads, 1 tail	HHHT, HHTH, HTHH, THHH	4
2 heads, 2 tails	HHTT, HTHT, THHT, THTH, TTHH	6
1 head, 3 tails	TTTH, TTHT, THTT, HTTT	4
4 tails	TTTT	1

Lift Time Of A Microstate and Macrostate:

Lift Time of a Microstate

The life time of a microstate is the average time taken by a particle of a system to move from one phase compartment to an adjascent phase compartment.

Let us consider a particle in a phase plane (x, p_x), moving from compartment 1 to compartment 2, with change in position coordinate from (x, p_x) to (x+ Δx, p_x) in time T_{micro}, keeping its momentum p_x constant in below fig. If m is the mass of the particle, then its velocity



$$V_x = \Delta x / T_{micro}$$

$$= p_x / m$$

$$T_{micro} = \Delta x / V_x \qquad \ldots (1)$$

This T_{micro} is called the life time of the microstate. According to the law of equipartition of energy, the average K.E of a gas molecule at temperature T Kelvin by

$$\frac{1}{2} \text{ m } v_x = \frac{1}{2} \text{ Kt}$$

$$v_x = \sqrt{kT/m}$$

Substituting in eq. (1), we get

$$\mathbf{T_{micro} = \Delta x / \sqrt{kT/m}}$$

Lift Time of a Macrostate

In above fig. the no. of particles in each compartment, we will need some finite time. This finite time would be of the order of one millionth (10^{-6}) of a second, even if we use a superfast camera. This finite time T would be very large of the order of 10^{-7} as compared to the life time of microstate, as calculated below

$$\mathbf{T/\,T_{micro}=10^{-6}/10^{-13}=10^{7}}$$

The average time spend in each microstate

$$\mathbf{T_{micro}= T/\ \text{total no. of microstates (N)}}$$

$$=T/N \qquad \ldots(1)$$

Where, T is the finite time of observation.

Let $T_{macro} = T(n_1,n_2)$ be the time spent in the microstate(n_1,n_2) then,

T_{macro}=Average time spent in each microstate* No. of microstates in a given macrostate

$$=\frac{T}{N}*\mathbf{W\ (n_1,\ n_2)} \qquad \ldots..\ (2)$$

This is Because, the no. of microstates in a given macrostate in a given thermodynamic probability $W_{(n1,\ n2)}$

Further,

$$1/N = P_{micro} = \text{probability of microstate.}$$

$$T_{macro} = T.P_{micro} * W\ (n_1,\ n_2) \qquad \ldots.\ (3)$$

$$T_{macro} / T = P_{micro} * W(n_1, n_2) \quad \text{..... (4)}$$

$$\boldsymbol{\frac{Tmacro}{T} \propto W(n_1, n_2)} \quad \textbf{.... (5)}$$

Thus, the fraction of the time spent by a system in a macrostate is proportional to the thermodynamic probability (W) of the state.

Reference books:

Statistical mechanics by **Satya Prakash**.

Relativity and statistical physics by **J.C. Agarwa**l.

Heat thermodynamics and statistical by **Dr. N. Subramaniam Brijlal**.