* What is Statistical Mechanics

Some important ideas which are fundamental in our understanding of St. Mechanics, These are –

① System → particles ~~an~~ or collection of particles with basels.

② Process → Procedure to change the undergoing from one system to another System.

③ Microstate → defined as a state of the system where all the parameters of the ~~contict~~ constituents (particles) are specified.

The ~~a~~ many microstates exist for each state of the system specified in ~~micro~~ macroscopic variables (E, V, N - - -) and there are many parameters for each state, We have two perspectives to approch in looking at a microstate –

ⓐ Classical Mechanics

The position (x, y, z) and momentum (P_x, P_y, P_z) ~~20~~ well given 6N degrees of freedom and this is put in a phase space representation.

ⓑ Quantum Mechanics :– The energy levels and the state of particles in terms of quantum numbers are used to specify the parameters of a microstate.

(4) Macrostate :- defined as a state of the system where the distribution of particles over the energy levels is specified having distinct microstates.

In macrostate macroscopic variable we need only 3 specific variables (P.V.T) or (P,V,N) or (E,V,N) are in equilibrium.

In st. mechanics, the equilibrium tends towards a macrostate which is the stable. The stability of the macrostate depends on the perspective of microstate.

* "St. Mechanics as its name implies is not concerned with the actual motions or interactions of the individual particles but explores the most probable behaviour of assembly of particles"

Need: If we attempt to determine the actual behaviour of a gas consisting of, say 10^{23} molecules whose position and velocities are known at any initial time, we have to solve 10^{23} equations of motion.

Moreover it is not possible to have a complete knowledge regarding the positions & velocities of all the molecules. It enables to predict the average properties of the system without a detailed knowledge about the initial condition of its component. For exmple, radioactive decay is a good example of the statistical nature of the phenomenon. In radioactive decay one cannot say which atom of the radioactive material will decay first and when. Applying this principle of St. mechanics, it can be said that a certain average number of atoms will decay at any instant of time.

The study of St. Mechanics can be classified mainly two categories —

① Classical St. Mech.
→ Maxwell-Boltzmann statistics

② Quantum St Mech —
Fermi-Dirac St. → (half spin)
Bose Einstein St. Mech (0 zero and integral spin)

Some Basic definition

① **Phase Space :-**

In classical mechanics → for position - have degree (3)

⇒ Momentum Coordinates (P_x, P_y & P_z)

⇒ The position of a single particle can be specified in terms of Cartesian Co-ordinate x, y, z, and their corresponding momentum components P_x, P_y, P_z, we imagine a six dimensional space in which the six coordinates x, y, z and P_x, P_y & P_z mutual perpendicular to each other.

Thus the combination of position and momentum space known as phase space. A point in the space phase space represents the position and momentum of the particle at some particular instant. The meaning of a point in phase space can be understood with the help of uncertainty principle.

The phase space is divided into six dimensional cells whose sides $dx, dy, dz, dP_x, dP_y, dP_z$. Further we approach close to the limit of a point in phase space by reducing the size of a cell. The volume of each cell given by

$$d\tau = dx\, dy\, dz\, dP_x\, dP_y\, dP_z$$

But a/c to uncertainty principle

$dx\,dp_x \geq h, \quad dy\,dp_y \geq h, \quad dz\,p_z \geq h.$

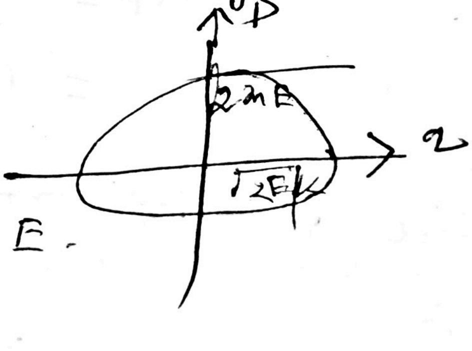
$\therefore d\tau \geq h^3$.

A point in the phase-space is actually considered to be a cell whose minimum volume is of the order h^3 being a complex system. Since an assembly of N-systems can be described in terms of 6N co-ordinates i.e. 3N position co-ordinates and 3N momentum co-ordinates. i.e 6N dimensional space known as phase space or Γ space. The set of numbers $(q_1, q_2 \ldots q_f; p_1, p_2 \ldots p_f)$ is regarded as a point in phase space of 2f - dimensions.

"Thus the dimensional state of a system may be specified by locating a point in a 2n dimensional (in general); the co-ordinates of the point being the values of the n for coordinates & n for momentum which is specify. The space is referred to as phase and the point is called a "PHASE POINT"

For 3 dimensional harmonic oscillator of mass m and spring constant K, The energy is given by

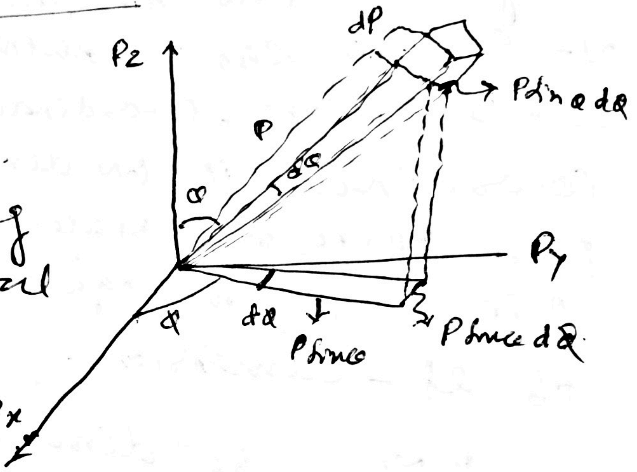
$$E = \frac{p^2}{2m} + \frac{1}{2}kq^2$$



$\frac{p^2}{2m} \to$ K.E & $\frac{1}{2}kq^2 \to$ Pot. E.

where $q \to$ position & P – momentum
For a constant energy E, equation describes an ellipse in space i.e in the qP plane with Semi major axis $\sqrt{\frac{2E}{K}}$ and minor axis.
$\sqrt{2mE}$.

② Volume in Phase Space P_o



Let the volume of the momentum space lying between the values of total momentum P and P+dP ranges to θ to θ+dθ and ϕ to ϕ + dϕ i.e shown in the figure
The element is considered in polar coordinates P, θ & dθ, (like polar coordinates r, θ & ϕ)

The volume of the element is given by

$$d\tau_p = dP \, P d\theta \, d\phi \, P \sin\theta$$

$$= P^2 dP \sin\theta \, d\theta \, d\phi$$

...ire volume element in between P and P+dP

$$\Delta \tau_p = p^2 dp \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$= 4\pi p^2 dp$$

This volume is the same as the volume of a spherical shell of thickness dp lying between p & $p+dp$.

Now $\Delta\tau$ be the product of $\Delta\tau_p$ a of momentum space and the volume V of ordinary space.

i.e. $\Delta\tau = \Delta\tau_p \int_V dx\,dy\,dz$

$$= 4\pi p^2 dp \, V \quad \text{—— (1)}$$

Again we know that

$$\epsilon_p = \frac{p^2}{2m}$$

$$\therefore p^2 = 2m\epsilon_p \quad \& \quad dp = \left(\frac{m}{2\epsilon_p}\right)^{1/2} d\epsilon_p$$

$$\therefore \text{Hence } \Delta\tau = d\tau = 4\pi (2m\epsilon_p) \left(\frac{m}{2\epsilon_p}\right)^{1/2} d\epsilon_p \, V$$

$$\therefore \boxed{d\tau = 2\pi (2m)^{3/2} \epsilon_p^{1/2} d\epsilon_p \, V} \quad \text{—— (2)}$$

This equations (1) & (2) widely used to solve st. mechanical problem.

ENSEMBLES :– The collection single particle shall ~~refere~~ refer to a ~~single~~ system and to the collection of particles as a ~~whole~~ whole as an assemble. The collection of a large no. of assembles is known as an "ENSEMBLE".

The volume, energy, total no. of particles etc are known as ELEMENT. If elements ~~differ~~ differ in their states i.e they should differ in co-ordinates and velocity ad ~~hence~~ hence momentum too.

∴ Thus an ensemble is defined as a collection of a very large no. of assembles which are essentially independent of one another but which have been made macroscopically as identical as possible. By using macroscopically identity ~~we~~ mean that each assemble is charaterised by the same values of sets of macroscopic parameters which uniquely determine the equilibrium state of the assembly.

In an ensemble, the system play the same role as the non interacting molecules do in a gas. The macroscopic identity of the systems constituting an assemble can be achieved by choosing the same values of some set of macroscopic parameters. These parameters uniquely determine the equilibrium state of the system. There are three type of ~~ensemblee~~ ensembles —

(a) Micro canonical Ensemble.
(b) Canonical Ensemble.
(c) Grand canonical Ensemble.

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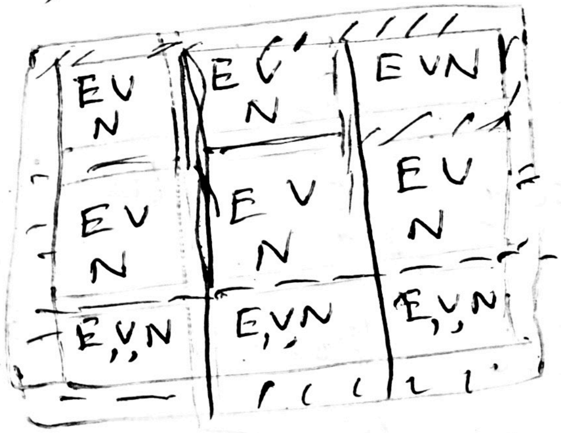
(1) **Micro canonical Ensemble** :- The micro canonical ensemble is a collection of essentially independent assemblies having the same energy (E), volume (V) and number of particles (N) of ~~systems~~ identical systems. The individual assemblies are seperated by rigid rigid ~~[illegible]~~ impermeable and well insulated walls so that the values of E, V & N are not affected other system. ~~This~~ This means that macroscopic en

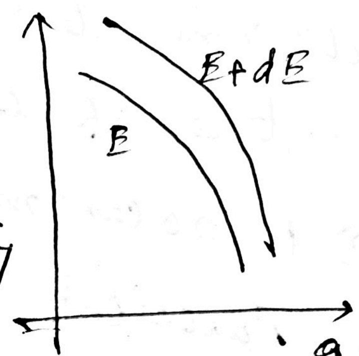


microcanonical ensemble is constant. i.e

H (Total energy) = E remains constant,

$E(q_1 \ldots q_f, p_1 \ldots p_f) =$ constant.

The locus of all the phase points having equal energies in phase space is called an energy surface or <u>ergodic surface</u>.



Let we considering ensemble can be obtained by taking the density as equal to zero for all values of the energy except in a selected narrow range E and E + dE. Using the terminology of Gibbs, such an ensemble specified by

$$\rho = \text{constant} \left(\text{Energy flow, range } E \text{ to } E+dE \right)$$

$$\rho = 0$$

may be called a microcanonical ensemble.

We should observe the following properties –

(1) As ρ is a function of energy, this ensemble is in st. equilibrium.

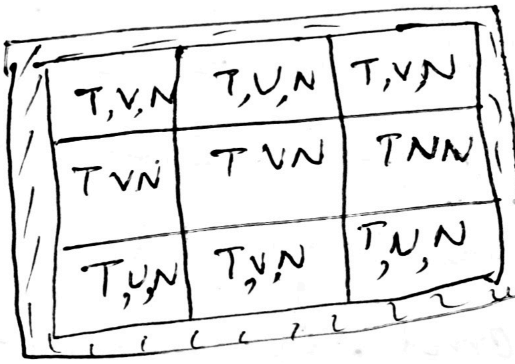
(ii) The average properties of ~~energy~~, predicted by such ensemble will not vary in time being of equilibrium.

(iii) As ρ is constant within the energy shell, the distribution of phase points is uniform (by Liouville's theorem)

---x---x---

(2) Canonical Ensemble :-

This type of ensemble is the collection of essentially independent assemblies having the same temp T, volume V and number of particles N

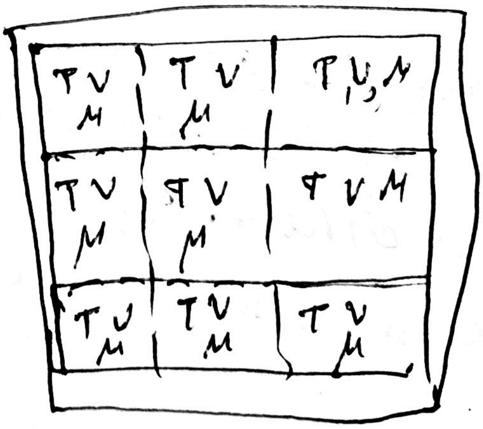


are constant. In canonical ensemble all the assemblies should be acting here have the same temp that could simply bring reservoir at temp T as we could simply bring all of the ~~ass~~ assemblies in thermal contact with each other. Thus in for canonical ensemble, system can exchange energy but not particles.

(3) Grand Canonical Ensemble :-

The micro canonical ensemble is a collection of independent assemblies having the same energy (E), volume (V) and number N of system and the canonical ensemble is a collection of independent assemblies having the same

- The ensemble in which exchange of energy as well as of particles take place with the heat reservoir is known as grand canonical ensemble. In grand canonical is the essentially independent assemblies having the same temperature (T) volume V and a chemical potential μ. that occupying a seperate volume V but can exchange energy and molecules with each other.



The individual assemblies systems are seperated by rigid, permeable diathermic walls.

The grand canonical ensemble will thus correspond to the situation when we know both the average energy and the average number of particles in assembly, but are otherwise completely ignorant about the state of the system.

Lect - III

Uses of the Ensemble :-

These Three ensemble basically usefull for two main reason -

① They are approximately to the types of thermodynamic measurements most frequently made in practices.

② In large assemblies, it is useful to find that the values of thermodynamic equations are not very sensitive to the method of measurement.

For example, in the measurement of specific heat of a liquid is ~~isolated at constant temp~~ of known mass at below the boiling point.