M.SC. PHYSICS – I YEAR

DKP11 : CLASSICAL AND STATISTICAL MECHANICS

SYLLABUS

Unit 1: Lagrangian and Hamiltonian formulations

Hamilton's principle - Derivation of Lagrange's equations from Hamilton's principle - Principle of Least Action and its applications, Canonical Transformation : The Hamiltonian Formalism, Canonical formalism, Hamiltonian equations of motion, Cyclic coordinates, Rauthian procedure and equations, Derivation of Generating functions, examples, properties, Derivation of Hamiltonian equations from variational principle.

Unit 2: Poisson bracket and theory of small oscillations

Poisson bracket, Special cases of Poisson bracket , Poisson theorem, Poisson bracket and canonical transformation, Jacobi identity and its derivation, Lagrange bracket and its properties, the relationship between Poisson and Lagrange brackets and its derivation, the angular momenta and Poisson bracket, Liouville's theorem and its applications; Theory of small oscillations:

Formulation of the problem, Eigenvalue equation and the principle axis transformation, frequencies of free vibration and normal coordinates, free vibrations of a linear triatomic molecule

Unit 3: Two - body central force problem and H - J theory

Two body central force problem: Reduction to the equivalent one body problem, the equation of motion and first integrals, classification of orbits, the virial theorem, the differential equation for the orbit, integral power law in time in the Kelper's problem ,scattering in central force field;

H-J Theory: H-J equation and their solutions, use of H-J method for the solution of harmonic oscillator problem, Hamilton's principle function, Hamilton's characteristic function and their properties, Action angle variable for completely separable systems, the Kelper's problem in action angle variables

Unit 4: Classical Statistical Mechanics

Foundation of Statistical Mechanics: The macroscopic and microscopic states, postulate of equal a priori probability, Contact between statistics and thermodynamics; Ensemble theory: Concept of ensemble, phase space, Density function, Ensemble average, Liouville's theorem, Stationary ensemble; The microcanonical ensemble, Application to the classical ideal gas; The canonical and grand canonical ensembles, Canonical and grand canonical partition functions, Calculation of statistical quantities; Thermodynamics of a system of non-interacting classical harmonic oscillators using canonical ensemble, and of classical ideal gas using grand canonical ensemble, Energy and density fluctuations; Entropy of mixing and the Gibb's paradox, Sackur-Tetrode equation .

Unit 5: Quantum Statistical Mechanics

Quantum-mechanical ensemble theory: Density matrix, Equation of motion for density matrix, Quantum- mechanical ensemble average; Statistics of indistinguishable particles, Two types of quantum statistics- Fermi-Dirac and Bose-Einstein statistics, Fermi-Dirac and Bose-Einstein distribution functions using microcanonical and grand canonical ensembles (ideal gas only), Statistics of occupation numbers; Ideal Bose gas: Internal energy, Equation state, Bose-Einstein Condensation and its critical conditions; Bose-Einstein condensation in ultra-cold atomic gases: its detection and thermodynamic properties: Ideal Fermi gas: Internal energy, Equation of state, Completely degenerate Fermi gas.

Books for Study and Reference

1.Classical Mechanics (3rd ed.,2002) by H. Goldstein, C.Poole and J. Safko, Pearson Edition
2. Classical Mechanics - J. C. Upadhyaya- Second Edition-2005-Himalaya Publishing House
3.Classical Mechanics - G. Aruldhas-2008-PHI Learning Pvt.Ltd.
4.Classical Mechanics-A Text Book-Suresh Chandra-Narosa Publications
5.Statistical Mechanics by R. K. Pathira (2nd edition)
6.Statistical Mechanics by R.K. Pathira and P.D. Beale (3rd edition)
7.Statistical Mechanics by K.Huang
8.Statistical Mechanics by L.D.Landau and I.M.Lifshitz

UNIT 1: LAGRANGIAN AND HAMILTONIAN FORMULATIONS

Hamilton's principle - Derivation of Lagrange's equations from Hamilton's principle - Principle of Least Action and its applications, Canonical Transformation : The Hamiltonian Formalism, Canonical formalism, Hamiltonian equations of motion, Cyclic coordinates, Rauthian procedure and equations, Derivation of Generating functions, examples, properties, Derivation of Hamiltonian equations from variational principle.

LAGRANGIAN AND HAMILTONIAN FORMULATIONS

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1.1 HAMILTON'S PRINCIPLE:

The motion of the system from time t_1 to time t_2 is such that the line integral

$$I = \int_{t_1}^{t_2} L\,dt$$

Where L = T – V, is an extremum for the path of motion

(or) $$\delta I = \delta \int_{t_1}^{t_2} L\,dt = 0$$

δ is the variation symbol.

Deduction of Lagrange's equations:

Consider a conservative system of particles. The integral can be written as

$$\int_{t_1}^{t_2} \left[T\left(q_j, \dot{q}_j\right) - V\left(q_j\right)\right] dt.$$

According to Hamilton's variational principle, we have

$$\delta \int_{t_1}^{t_2} \left[T\left(q_{j,} \dot{q}_j\right) - V\left(q_j\right)\right] dt = 0$$

$$\int_{t_1}^{t_2} \sum_j \left[\left(\frac{\partial T}{\partial q_j}\delta q_j + \frac{\partial T}{\partial \dot{q}_j}\delta \dot{q}_j\right) - \frac{\partial V}{\partial q_j}\delta q_j\right] dt = 0$$

$$\int_{t_1}^{t_2} \sum_j \left(\frac{\partial T}{\partial q_j} - \frac{\partial V}{\partial q_j}\right)\delta q_j \; dt + \int_{t_1}^{t_2} \sum_j \frac{\partial T}{\partial \dot{q}_j}\delta \dot{q}_j \; dt = 0$$

$$\int_{t_1}^{t_2}\sum_j\left(\frac{\partial T}{\partial q_j}-\frac{\partial V}{\partial q_j}\right)\delta q_j\ dt+\int_{t_1}^{t_2}\sum\frac{\partial T}{\partial \dot{q}_j}\ \frac{d}{dt}\left(\delta q_j\right)dt=0$$

Integrating by parts the second term, we get

$$\int_{t_1}^{t_2}\sum_j\left(\frac{\partial T}{\partial q_j}-\frac{\partial V}{\partial q_j}\right)\delta q_j\ dt+\sum_j\frac{\partial T}{\partial \dot{q}_j}\delta q_j\Big|_{t_1}^{t_2}-\int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right)\delta q_j\,dt=0$$

There is no coordinate variation at end points and hence

$$\delta q_j\Big|_{t_1}^{t_2}=0\,.$$

Now equation reduces to

$$\int_{t_1}^{t_2}\sum_j\left(\frac{\partial T}{\partial q_j}-\frac{\partial V}{\partial q_j}\right)\delta q_j dt-\int_{t_1}^{t_2}\sum_j\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right)\delta q_j dt=0$$

$$\int_{t_1}^{t_2}\sum\left[\frac{\partial T}{\partial q_j}-\frac{\partial V}{\partial q_j}-\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right)\right]\delta q_j dt=0$$

each δq_j are independent of each other, the coefficient of every δq_j should be equated to zero. And we get

$$\left[\frac{\partial T}{\partial q_j}-\frac{\partial V}{\partial q_j}-\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right)\right]=0$$

$$\left[\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right)-\frac{\partial}{\partial q_j}(T-V)\right]=0$$

V is not a function of $\dot{q}_j$ and therefore

$$\frac{d}{dt}\left[\frac{\partial (T-V)}{\partial \dot{q}_j}\right]-\frac{\partial}{\partial q_j}(T-V)=0$$

T – V = L = Lagrangian for a conservation system

L = Scalar function of $q_j, \dot{q}_j\ and\ t$

$$\left[\frac{\mathrm{d}}{\mathrm{dt}}\left(\frac{\partial \mathrm{L}}{\partial \dot{\mathrm{q}}_{\mathrm{j}}}\right)-\frac{\partial \mathrm{L}}{\partial \mathrm{q}_{\mathrm{j}}}\right]=0 \qquad \text{J = 1, 2,......n.}$$

This set of equations is called Lagrange’s equations of motion and each is a second order differential equation in terms of the time as independent variable.

1.2 DERIVATION OF LAGRANGE’S EQUATIONS FROM HAMILTON’S PRINCIPLE:

The Lagrangian L is a function of generalized co-ordinates q_j ′s and generalized velocities $\dot{q}_j$ ′s and time t.

That is $L = L[q_j(t), \dot{q}_j(t), t]$

According to Hamilton's variational principle, motion of a conservative system from finite time t_1 to time t_2 is such that the line integral

$$I = \int_{t_1}^{t_2} L[q_j(t), \dot{q}_j(t), t] dt$$

is zero. That is $$\delta I = \delta \int_{t_1}^{t_2} L[q_j(t), \dot{q}_j(t), t] dt = 0$$

If the Lagrangian does not depend on time t explicitly, then the variation δL can be written as

$$\delta L = \sum_{j=1}^{n} \frac{\partial L}{\partial q_j} \delta q_j + \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j$$

Integrating both sides from $t = t_1$ to $t = t_2$

$$\int_{t_1}^{t_2} \delta L dt = \int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial q_j} \delta q_j \; dt + \int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j \, dt = 0$$

But from Hamilton's principle

$$\int_{t_1}^{t_2} \delta L dt = 0$$

Therefore $$\int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial q_j} \delta q_j \; dt + \int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j \, dt = 0$$

$$\delta \dot{q}_j = \frac{d}{dt}(\delta q_j)$$

Integrating by parts the second term, we get

$$\int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j \, dt = \sum_j \left[\frac{\partial L}{\partial q_j} \delta q_j \right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \sum_j \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) \delta q_j \, dt$$

There is no coordinate variation at end points and hence

$$\sum_j \left[\frac{\partial L}{\partial q_j} \delta q_j \right]_{t_1}^{t_2} = 0.$$

Now equation reduces to

$$\int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial q_j} \delta q_j \; dt - \int_{t_1}^{t_2} \sum_j \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) \delta q_j \, dt = 0$$

(or)

$$\int_{t_1}^{t_2} \sum_j \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) \delta q_j \, dt - \int_{t_1}^{t_2} \sum_j \frac{\partial L}{\partial q_j} \delta q_j \; dt = 0$$

$$\int_{t_1}^{t_2}\sum_j\left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}\right]\delta q_j\,dt=0$$

For holonomic system the generalized co-ordinates δq_j are independent of each other. Therefore the coefficients of each δq_j must vanish. And we get

$$\left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}\right]=0 \qquad J = 1, 2, \ldots\ldots n.$$

This set of equations is called Lagrange’s equations of motion and each is a second order differential equation in terms of the time as independent variable.

1.3 PRINCIPLE OF LEAST ACTION:

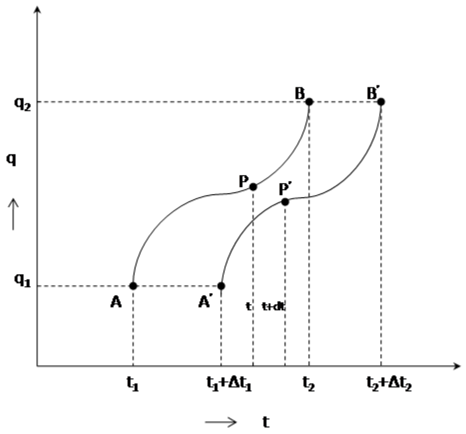
The time integral of twice the K.E is called the action. The principle of least action states that

$$\Delta\int_{t_1}^{t_2} 2T\,dt=0$$

But in systems for which H remains constant

$$2T=\sum_j p_j\dot{q}_j$$

$$\therefore \Delta\int_{t_1}^{t_2}\sum_j p_j\dot{q}_j\,dt=0$$



Δ represents variation of the path which allows time as well the position coordinates to vary.

In Δ variation

1. time as well as the position coordinates are allowed to vary.
2. time t varies even at the end points.
3. the position coordinates are held fixed at the end points. ie $\Delta q_j = 0$

Let APB be the actual path and AP′B be the varied path. The end points A and B after time Δt take the positions A′ and B′ such that A and B are fixed while time is not fixed.

A point P on the actual path gives P′ on the varied path.

$$q_j \rightarrow q_j' = q_j + \Delta q_j$$

If α is the variational parameter, then in δ process t is independent of α. But in Δ process t is a function of α even at the end points. ie t = t (α).

q_j depends on t and α

$$\Delta q_j = \frac{dq_j}{d\alpha}d\alpha$$

$$= \left[\frac{\partial q_j}{\partial \alpha} + \frac{\partial q_j}{\partial t}\frac{\partial t}{\partial \alpha}\right] d\alpha$$

$$= \frac{\partial q_j}{\partial \alpha} d\alpha + \dot{q}_j \frac{\partial t}{\partial \alpha} d\alpha$$

$$= \delta q_j + \dot{q}_j\, \Delta t$$

Since $\delta q_j = \frac{\partial q_j}{\partial \alpha} d\alpha$ *and* $\dot{q}_j \frac{\partial t}{\partial \alpha} d\alpha = \dot{q}_j\, \Delta t$

Any function $f = f(q_j, \dot{q}_j, t)$

$$\Delta f = \sum_j \left[\frac{\partial f}{\partial q_j}\Delta q_j + \frac{\partial f}{\partial \dot{q}_j}\Delta \dot{q}_j + \frac{\partial f}{\partial t}\Delta t\right]$$

$$= \sum_j \frac{\partial f}{\partial q_j}\left(\delta q_j + \dot{q}_j\, \Delta t\right) + \sum \frac{\partial f}{\partial \dot{q}_j}\left(\delta \dot{q}_j + \ddot{q}_j\, \Delta t\right) + \frac{\partial f}{\partial t}\Delta t$$

$$= \delta f + \frac{\partial f}{\partial t}\Delta t$$

$$\Delta = \delta + \Delta t \frac{\partial}{\partial t} \qquad \text{....(1)}$$

Here Δ operation and time differentiation cannot be interchanged.

Proof:

$$A = \int_{t_1}^{t_2} \sum_j p_j \dot{q}_j\, dt$$

$$= \int_{t_1}^{t_2} (L + H)\, dt$$

$$= \int_{t_1}^{t_2} L\, dt + H(t_2 - t_1) \quad \text{[since H is conserved]} \qquad \text{....(2)}$$

$$\Delta A = \Delta \int_{t_1}^{t_2} L\, dt + H\, \Delta (t_2 - t_1)$$

$$= \Delta \int_{t_1}^{t_2} L\, dt + H\, \Delta t \Big|_{t_1}^{t_2} \qquad \text{....(3)}$$

To Solve $\Delta \int_{t_1}^{t_2} L\, dt$:

Let $\int_{t_1}^{t_2} L\, dt = I$ so that $\dot{I} = L$

Now $\Delta I = \delta I + \dot{I}\,\Delta t$

ie $$\Delta\int_{t_1}^{t_2} L\ dt = \delta\int_{t_1}^{t_2} L\,dt + L\,\Delta t\,\Big|_{t_1}^{t_2} \qquad .....(4)$$

Substituting equation (4) in equation (3) we get

$$\Delta A = \delta\int_{t_1}^{t_2} L\ dt + L\,\Delta t\,\Big|_{t_1}^{t_2} + H\,\Delta t\,\Big|_{t_1}^{t_2} \qquad ....(5)$$

$\delta\int_{t_1}^{t_2} L\,dt$ cannot be zero.

$$\delta\int_{t_1}^{t_2} L\ dt = \int_{t_1}^{t_2}\sum_j\left(\frac{\partial L}{\partial q_j}\delta q_j + \frac{\partial L}{\partial \dot{q}_j}\delta\dot{q}_j\right)dt$$

$$= \int_{t_1}^{t_2}\sum_j\left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)\delta q_j + \frac{\partial L}{\partial \dot{q}_j}\frac{d}{dt}(\delta q_j)\right]dt$$

[Since from Lagrange's equation of motion $\dfrac{\partial L}{\partial q_j} = \dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \dot{q}_j}\right)$]

$$\delta\int_{t_1}^{t_2} L\ dt \ = \ \int_{t_1}^{t_2}\sum_j\left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\delta q_j\right)\right]dt$$

Putting $\delta q_j = \Delta q_j - \dot{q}_j\,\Delta t$

$$\delta\int_{t_1}^{t_2} \mathrm{L}\ \mathrm{dt} = \int_{t_1}^{t_2}\sum_j\left[\frac{\mathrm{d}}{\mathrm{dt}}\left(\frac{\partial \mathrm{L}}{\partial \dot{\mathrm{q}}_j}\Delta \mathrm{q}_j - \frac{\partial \mathrm{L}}{\partial \dot{\mathrm{q}}_j}\dot{\mathrm{q}}_j\,\Delta \mathrm{t}\right)\right]\mathrm{dt}$$

$$= \sum_j\left(\frac{\partial L}{\partial \dot{q}_j}\Delta q_j - \frac{\partial L}{\partial \dot{q}_j}\dot{q}_j\,\Delta t\right)_{t_1}^{t_2}$$

At end points $\Delta q_j = 0$. Therefore

$$\delta\int_{t_1}^{t_2} L\,dt \ = \ -\sum_j\frac{\partial L}{\partial \dot{q}_j}\dot{q}_j\,\Delta t\,\Big|_{t_1}^{t_2}$$

$$= \ -\sum_j p_j\,\dot{q}_j\,\Delta t\,\Big|_{t_1}^{t_2}$$

Now equation (5) becomes

$$\Delta A \ = \ -\sum_j p_j\,\dot{q}_j\,\Delta t\,\Big|_{t_1}^{t_2} + L\,\Delta t\,\Big|_{t_1}^{t_2} + H\,\Delta t\,\Big|_{t_1}^{t_2}$$

$$= \ \left(H + L - \sum_j p_{j,}\,\dot{q}_j\right)\Delta t\,\Big|_{t_1}^{t_2}$$

$= 0.$

Since $\quad H = \sum_j p_j , \dot{q}_j - L$

Thus $\quad \Delta A = \Delta \int_{t_1}^{t_2} \sum p_{j,} \dot{q}_j dt = 0$

Which proves the principle of least action.

Here $\int_{t_1}^{t_2} \sum p, \dot{q}_j$ = Hamiltion's characteristic function

(i) Principle of least action in terms of arc length of the particle trajectory.

Let a system contain only one particle of mass m

Kinetic energy $T = \frac{1}{2} m \left(\frac{ds}{dt} \right)^2$

ds→ element of arc traversed in time dt

$$dt = \left(\frac{m}{2T} \right)^{\frac{1}{2}} ds$$

The principle of least action

$$\Delta \int_{t_1}^{t_2} 2T\, dt = \Delta \int_{t_1}^{t_2} 2T \left(\frac{m}{2T} \right)^{\frac{1}{2}} ds = 0$$

$$\text{ie}\, \Delta \int_{t_1}^{t_2} (2mT)^{\frac{1}{2}} ds = 0$$

$$\Delta \int_{t_1}^{t_2} [2m(E - V)]^{\frac{1}{2}} ds = 0 \qquad \text{Since } T + V = E$$

$$\Delta \int_{t_1}^{t_2} [2m(H - V)]^{\frac{1}{2}} ds = 0 \qquad \text{Since } E = H$$

$$\Delta \int_{t_1}^{t_2} [H - V]^{\frac{1}{2}} ds = 0 \qquad \text{Since m = Constant} \qquad ....(6)$$

The above equation represents the principle of least action in term of arc length of the particle trajectory.

(ii) Jacobi's form of the principle of least action:

The K.E of the system

$$T = \frac{1}{2} \sum_{j,k} a_{jk}\, \dot{q}_j\, \dot{q}_k$$

$$2T = \sum_{j,k} a_{jk}\, \dot{q}_j\, \dot{q}_k$$

$$= \sum_{j,k} a_{jk} \frac{dq_j \, dq_k}{dt^2}$$

$$= \left(\frac{d\rho}{dt} \right)^2 \qquad \text{....(7)}$$

Where $(d\rho)^2 = \sum_{j,k} a_{jk} \, d_{qj} \, dq_k$, *a differential*

From equation (7) $\mathrm{T} = \frac{1}{2}\left(\frac{\mathrm{dp}}{\mathrm{dt}}\right)^2$

$$\mathrm{dt} = \frac{d\rho}{(2T)^{\frac{1}{2}}}$$

The principle of least action

$$\Delta \int_{t_1}^{t_2} 2T \; dt = 0$$

$$\Delta \int_{t_1}^{t_2} 2T \frac{d\rho}{(2T)^{\frac{1}{2}}} = 0$$

$$\Delta \int_{t_1}^{t_2} (2T)^{\frac{1}{2}} \, d\rho = 0$$

$$\Delta \int_{t_1}^{t_2} [2(E-V)]^{\frac{1}{2}} \, d\rho = 0$$

$$\Delta \int_{t_1}^{t_2} [2(H-V)]^{\frac{1}{2}} \; d\rho = 0$$

$$\Delta \int_{t_1}^{t_2} (H-V)^{\frac{1}{2}} \, d\rho = 0 \qquad \text{....(8)}$$

This equation gives the Jacobi's form of principle of least action.

(iii) Fermat′s principle:

It states that the time taken by a light ray to travel between two points is extremum. According to principle of least action

$$\Delta \int_{t_1}^{t_2} 2\mathrm{T}\,\mathrm{dt} = 0$$

$$\Delta \int_{t_1}^{t_2} T \, dt = 0$$

If T is conserved, then

$$\Delta \int_{t_1}^{t_2} dt = 0$$

$$\Delta (t_2 - t_1) = 0$$

$$(t_2 - t_1) = \text{extremum.}$$

ie, the time taken by the light ray to travel between two points is extremum.

1.4 CANONICAL TRANSFORMATION:

Transformation is one to change one set of position and momentum coordinates into another set of position and momentum coordinates.

We assume p_j and q_j are the old momentum and position coordinates and P_j and Q_j are new one related by

$$P_j = P_j (p_j, q_j, t)$$

$$Q_j = Q_j (p_j, q_j, t) \qquad \text{....(1)}$$

Then if there exists a new Hamiltonian $\overline{H}$ in the new coordinates such that

$$\dot{P}_j = \frac{\partial \overline{H}}{\partial Q_j} \text{ and } \dot{Q}_j = \frac{\partial \overline{H}}{\partial P_j} \qquad \text{....(2)}$$

These equations are known as canonical (or) contact transformations.

Q_j, P_j are canonical coordinates.

By definition we have $H = \sum p_j q_j - L$

and $$\overline{H} = \sum p_j \dot{Q}_j - K \qquad \text{...(3)}$$

Here the position and momenta coordinates are independent.

Canonical transformations are the transformations of phase space. They are characterized by the property that they leave the form of Hamilton's equations of motion.

example : Cartesian to polar coordinate is an example of co-ordinate transformation.

The transformation of one set of position coordinates to new set of coordinates is called point transformation. They are the transformations of configuration space.

1.5 HAMILTONIAN FORMALISM:

Lagrangian equations of motion are invariant in form with respect to the set of any generalized coordinates. In the new set Q_j, Lagrange's equations will be

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{Q}_j}\right) - \frac{\partial L}{\partial Q_j} = 0$$

ie, Lagrange's equations are covariant with respect to point transformations. If we define P_j as

$$P_j = \frac{\partial L}{\partial \dot{Q}_j}\left(Q_j, \dot{Q}_j\right)$$

The Hamilton's canonical equation will also be covariant. ie,

$$\dot{Q}_j = \frac{\partial H}{\partial P_j}\left(Q_j, P_j\right)$$

$$\dot{P}_j = -\frac{\partial H}{\partial Q_j}\left(Q_j, P_j\right)$$

Therefore, this transformation is extended to Hamiltonian formulation. In Hamiltonian formulation, we admit the existence of one more independent variable called momentum. Consequently the simultaneous transformation of the independent coordinates and momenta q $_j$, p $_j$ to a new set Q $_j$, P $_j$ can be represented in the form

$$\begin{aligned} Q_j &= Q_j\left(q, p, t\right) \\ P_j &= P_j\left(q, p, t\right) \end{aligned} \qquad \text{….(1)}$$

For Q $_j$, P $_j$ to be canonical, they should be able to be expressed in Hamiltonian form of equations of motion.

ie $\dot{Q}_j = \frac{\partial K}{\partial P_j}$ $\qquad$ $\dot{P}_j = -\frac{\partial K}{\partial Q_j}$

Where K is a function of (Q, P, t) and is a substitute for H of old set in new set of coordinates. If Q $_j$, P $_j$ are to be canonical coordinates, they must satisfy the modified Hamilton's principle of the form

$$\delta\int_{t_1}^{t_2}\left[\sum P_j\,\dot{Q}_j - k\left(Q, P, t\right)\right]dt = 0 \qquad \text{....(2)}$$

The old coordinates p $_j$, q $_j$ are already canonical.

Therefore

$$\delta\int_{t_1}^{t_2}\left[\sum p_j\,\dot{q}_j - H\left(q, p, t\right)\right]dt = 0 \qquad \text{....(3)}$$

The simultaneous validity of equations (2) and (3) does not mean that the integrands of the two integrals are equal. We can therefore write

$$\delta\int_{t_1}^{t_2}\left[\left(\sum p_j\,\dot{q}_j - H\right) - \left(\sum P_j\dot{Q}_j - K\right)\right]dt = 0 \qquad \text{....(4)}$$

Equation (4) will not be affected if we add to or subtract from it a total time derivative of a function F = F(q,p,t).Now we can write equation (4) as

$$\delta\int_{t_1}^{t_2}\left\{\left(\sum p_j\,\dot{q}_j - k\right)-\left(\sum P_j\dot{Q}_j - K\right)-\frac{dF}{dt}\right\}dt = 0$$

is follows that

$$\left(\sum p_j\,\dot{q}_j - H\right)-\left(\sum P_j\dot{Q}_j - K\right)=\frac{dF}{dt} \qquad ....(5)$$

1.6 CANONICAL FORMALISM

DERIVATION OF GENERATING FUNCTIONS:

The first term in equation (5) is regarded as a function of q_j, p_j and t and the second term as a function of Q_j, P_j and t. F is in general as a function of (4n +1) variables q_j, p_j, Q_j, P_j and t. The two sets of variables are connected by the 2n transformation equations and besides t, only 2n are independent. Now F is a function of both old and new set of coordinates and four forms of F are possible. F_1(q, Q, t), F_2(q, P, t) F_3(p, Q, t) and F_4 (p, P, t) and F is termed as the generating function.

(A) <u>FIRST FORM F_1 (q, Q,t)</u>

We can write equation (5) as

$$\sum p_j\dot{q}_j - H = \sum P_j\dot{Q}_j - K + \frac{dF_1}{dt}(q,Q,t) \qquad ....(6)$$

$$F_1 = F_1\,(q, Q, t)$$

$$\frac{dF_1}{dt} = \sum_j \frac{\partial F_1}{\partial q_j}\dot{q}_j + \sum_j \frac{\partial F_1}{\partial Q_j}\dot{Q}_j + \frac{\partial F_1}{\partial t}$$

Now equation (6) becomes

$$\sum p_j\dot{q}_j - H = \sum P_j\dot{Q}_j - K + \sum\frac{\partial F_1}{\partial q_j}\dot{q}_j + \sum\frac{\partial F_1}{\partial Q_j}\dot{Q}_j + \frac{\partial F_1}{\partial t}$$

$$\sum\left(\frac{\partial F_1}{\partial q_j} - p_j\right)\dot{q}_j + \sum\left(P_j + \frac{\partial F_1}{\partial Q_j}\right)\dot{Q}_j - K + H + \frac{\partial F_1}{\partial t} = 0 \qquad .... (7)$$

Since q_j and Q_j are to be treated as independent variables, equation (7) can hold only if $\dot{q}_j$ and $\dot{Q}_j$ separately vanish.

ie $$p_j = \frac{\partial F_1}{\partial q_j}(q,Q,t) \qquad ....(8)$$

$$P_j = -\frac{\partial F_1}{\partial Q_j}(q,Q,t) \qquad ....(9)$$

and $$K = H + \frac{\partial F_1}{\partial t}(q,Q,t) \qquad ....(10)$$

Solving equation (8), we get $Q_j = Q_j(q_j, p_j, t)$

Which when substituted in (9) gives $P_j = P_j(q_j, p_j, t)$

(B) SECOND FORM $F_2(q,P,t)$

$F_2(q_j, P_j, t) = F_1(q_j, Q_j, t) + \sum P_j Q_j$

$F_1(q_j, Q_j, t) = F_2(q_j, P_j, t) - \sum P_j Q_j$ .....(11)

putting equation (13) in equation (6), we get

$$\sum p_j\dot{q}_j - H = \sum P_j\dot{Q}_j - K + \frac{d}{dt}\left[F_2\left(q_j, P_j, t\right) - \sum P_j Q_j\right]$$

$$= \sum P_j\dot{Q}_j - K + \sum\frac{\partial F_2}{\partial q_j}\dot{q}_j + \sum\frac{\partial F_2}{\partial P_j}\dot{P}_j + \frac{\partial F_2}{\partial t} - \sum\dot{P}_j Q_j - \sum P_j\dot{Q}_j$$

$$= -\sum\dot{P}_j Q_j - K + \frac{\partial F_2}{\partial t} + \sum\frac{\partial F_2}{\partial q_j}\dot{q}_j + \sum\frac{\partial F_2}{\partial P_j}\dot{P}_j$$

$$\sum\left(\frac{\partial F_2}{\partial q_j} - p_j\right)\dot{q}_j + \sum\left(\frac{\partial F_2}{\partial P_j} - Q_j\right)\dot{P}_j + H + \frac{\partial F_2}{\partial t} - K = 0 \qquad ....(12)$$

Since q_j and P_j are independent variable, equation (12) can be satisfied only when

$$p_j = \frac{\partial F_2}{\partial q_j}\left(q_j, P_j, t\right) \qquad .....(13)$$

$$Q_j = \frac{\partial F_2}{\partial P_j}\left(q_j, P_j, t\right) \qquad .....(14)$$

and $$K = H + \frac{\partial F_2}{\partial t}\left(q_j, P_j, t\right) \qquad .....(15)$$

Equation (13) can be solved to give $P_j = P_j(q_j, p_j, t)$

which when substituted in (14) gives $Q_j = Q_j(q_j, p_j, t)$

(C) THIRD FORM $F_3(p,Q,t)$

F_3 can be obtained from F_1 by replacing q_j by p_j

$F_3(p_j, Q_j, t) = F_1(q_j, Q_j, t) - \sum p_j q_j$

$F_1(q_j, Q_j, t) = F_3(p_j, Q_j, t) + \sum p_j q_j$ ....(16)

putting equation (16) in equation (6), we get

$$\sum p_j\dot{q}_j - H = \sum P_j\dot{Q}_j - K + \frac{d}{dt}\left[F_3\left(p_j, Q_j, t\right) + \sum p_j q_j\right]$$

$$= \sum P_j\dot{Q}_j - K + \sum\frac{\partial F_3}{\partial p_j}\dot{p}_j + \sum\frac{\partial F_3}{\partial Q_j}\dot{Q}_j + \frac{\partial F_3}{\partial t} + \sum\dot{p}_j q_j + \sum p_j\dot{q}_j$$

$$-H = \sum p_j\dot{Q}_j - K + \frac{\partial F_3}{\partial t} + \sum\left(\frac{\partial F_3}{\partial p_j} + q_j\right)\dot{p}_j + \sum\left(\frac{\partial F_3}{\partial Q_j} + P_j\right)\dot{Q}_j$$

$$\sum\left(\frac{\partial F_3}{\partial p_j}+q_j\right)\dot{p}_j+\sum\left(\frac{\partial F_3}{\partial Q_j}+P_j\right)\dot{Q}_j+H+\frac{\partial F_3}{\partial t}-K=0 \qquad ....(17)$$

Since p_j, Q_j are independent variables, equation (17) can be satisfied only when

$$q_j=-\frac{\partial F_3}{\partial p_j}\left(p_j,Q_j,t\right) \qquad ....(18)$$

$$P_j=-\frac{\partial F_3}{\partial Q_j}\left(p_j,Q_j,t\right) \qquad ....(19)$$

$$k=H+\frac{\partial F_3}{\partial t}\left(p_j,Q_j,t\right) \qquad ....(20)$$

equation (18) gives $Q_j = Q_j(q, p, t)$

and equation (19) gives $P_j = P_j(q, p, t)$

(D) FOURTH FORM $F_4(p, P, t)$

F_4 can be obtained from F_3 by replacing Q_j, by P_j

$F_4(p_j, P_j, t) = F_3(p_j, Q_j, t) + \sum P_j Q_j$

$= F_1(q_j, Q_j, t) - \sum p_j q_{j\,-} + \sum P_j Q_j$

$F_1(q_j, Q_j, t) = F_4(p_j, P_j, t) + \sum p_j q_j - \sum P_j Q_j$ ....(21)

putting equation (23) in equation (6) we get

$$\sum p_j\dot{q}_j-H \quad = \quad \sum P_j\dot{Q}_j-K+\frac{d}{dt}\left[F_4\left(p_j,P_j,t\right)+\sum p_jq_j-\sum P_jQ_j\right]$$

$$=\sum P_j\dot{Q}_j-K+\sum\frac{\partial F_4}{\partial p_j}\dot{p}_j+\sum\frac{\partial F_4}{\partial P_j}\dot{P}_j+\frac{\partial F_4}{\partial t}+\sum\dot{p}_jq_j+\sum p_j\dot{q}_j-\sum\dot{P}_jQ_j-\sum P_j\dot{Q}_j$$

$$-H=-K+\sum\left(\frac{\partial F_4}{\partial p_j}+q_j\right)\dot{p}_j+\sum\left(\frac{\partial F_4}{\partial P_j}-Q_j\right)\dot{P}_j+\frac{\partial F_4}{\partial t} \qquad .... (22)$$

Since p_j and P_j are independent variables, equation (22) can be satisfied only when

$$q_j=-\frac{\partial F_4}{\partial p_j}\left(p_j,P_j,t\right) \qquad ....(23)$$

$$Q_j=\frac{\partial F_4}{\partial P_j}\left(p_j,P_j,t)\right) \qquad ....(24)$$

$$K=H+\frac{\partial F_4}{\partial t}\left(p_j,P_j,t\right) \qquad ....(25)$$

Equation (23) gives $Q_j = Q_j(q, p, t)$

and equation (24) gives $P_j = P_j(q, p, t)$

(i) Condition for a transformation to be canonical:

If the expression $\Sigma\,(P_j\, dQ_j - p_j\, dq_j)$

(or) $\Sigma\,(p_j\, dq_j - P_j\, dQ_j)$

be an exact differential then the transformation from (q_j, p_j) set to (Q_j, P_j) set is canonical.

Proof:

We know that for a transformation to be canonical, equation

$$\Sigma\left(p_j \dot{q}_j - H\right) - \left(\Sigma P_j \dot{Q}_j - K\right) = \frac{dF}{dt} \qquad ….(1)$$

must be satisfied.

Suppose generating function F does not include time explicitly then

$$K = H + \frac{\partial F}{\partial t} = H$$

Now equation (1) becomes

$$\Sigma\, p_j \dot{q}_j - \Sigma\, P_j \dot{Q}_j = \frac{\partial F}{dt}$$

(or)

$$\Sigma\left(p_j\, dq_j - P_j\, dQ_j\right) = dF$$

Where dF is the exact differential of F.

Exercises:

1. Show that the transformation

$$Q = \sqrt{2q}\, e^{\alpha} \cos p$$

$$P = \sqrt{2q}\, e^{-\alpha} \sin p$$

is a canonical transformation.

Solution:

$$Q = \sqrt{2q}\, e^{\alpha} \cos p$$

$$dQ = (2q)^{-1/2} e^{\alpha} \cos p\, dq - (2q)^{1/2} e^{\alpha} \sin p dp$$

$$PdQ - pdq = (2q)^{1/2} e^{-\alpha} \sin p\, (2q)^{-1/2} e^{\alpha} \cos p\, dq - (2q)^{1/2} e^{-\alpha} \sin p\, (2q)^{1/2} e^{\alpha} \sin pdp - pdq$$

$$PdQ - pdq = \sin p\, \cos p\, dq - 2q \sin^2 p\, dp - pdq$$

$$PdQ - pdq = (\sin p\ \cos p - p)dq - 2q\sin^2\ p\,dp$$

$$= \left(\frac{1}{2}\sin 2p - p\right)dq - 2q\sin^2\ pdp$$

$$= \frac{\partial}{\partial q}\left(\frac{1}{2}q\sin 2p - pq\right)dq + \frac{\partial}{\partial p}\left(\frac{1}{2}q\sin 2p - pq\right)dp$$

$$= \frac{\partial F}{\partial q}dq + \frac{\partial F}{\partial p}dp$$

= dF

Which shows that the RHS is an exact differential of the function

$$F = \frac{1}{2}q\sin 2\,p - pq$$

and hence the transformation is canonical.

2. Show that the transformation

$$q = \sqrt{2p}\sin Q \qquad\qquad p = \sqrt{2p}\cos Q$$

(or) $P = \frac{1}{2}\left(p^2 + q^2\right) \qquad Q = \tan^{-1}\frac{q}{p} \qquad \textit{is canconical}$

Solution:

$$dq \quad = (2p)^{1/2}\cos Q\,dQ + \left(2p\right)^{-1/2}\sin Q\,dP$$

$$pdq \quad = (2p)^{1/2}\cos Q(2p)^{1/2}\cos Q\,dQ + (2p)^{1/2}\cos Q\left(2p\right)^{-1/2}\sin Q\,dP$$

pdq = 2P $\cos^2$ Q dQ + sin Q cosQ dP

pdq -PdQ = 2P $\cos^2$ Q dQ + sin Q cosQ dP-PdQ

= (2P $\cos^2$ Q - P) dQ + $\frac{1}{2}$sin 2Q dP

$$= \frac{\partial}{\partial Q}\left(\frac{1}{2}P\sin 2Q\right)dQ + \frac{\partial}{\partial P}\left(\frac{1}{2}P\sin 2Q\right)dP$$

$$= \frac{\partial F}{\partial Q}dQ + \frac{\partial F}{\partial P}dP$$

= dF where $F = \frac{1}{2}P\ \sin 2Q$

3. Show that the transformation

P = q cot p

Q = $\log\left(\frac{\sin p}{q}\right)$ is canonical. show that the generating function is

$$F = e^{-Q}\left(1 - q^2 e^{2Q}\right)^{1/2} + q\sin^{-1}(qe^{Q})$$

Solution:

$$dQ \;=\; \frac{\partial Q}{\partial q}\partial q+\frac{\partial Q}{\partial p}dp$$

$$=\frac{\partial}{\partial q}\left[\log\left(\frac{\sin p}{q}\right)\right]dq+\frac{\partial}{\partial p}\left[\log\left(\frac{\sin p}{q}\right)\right]dp$$

$$=\frac{1}{\left(\frac{\sin p}{q}\right)}\left(-\frac{\sin p}{q^2}\right)dq+\frac{1}{\left(\frac{\sin p}{q}\right)}\left(\frac{\cos p}{q}\right)dp$$

$$=-\frac{dq}{q}+\cot p\,dp$$

$$pdq-PdQ= pdq-q\cot p\left(-\frac{dq}{q}+\cot p\,dp\right)$$

$$=\left(p+\cot p\right)dq-q\,\cot^2 p\,dp$$

$$=\frac{\partial}{\partial q}\left[qp+q\cot p\right]dq+\frac{\partial}{\partial p}\left[qp+q\cot p\right]dp$$

$$=\frac{\partial F}{\partial q}\,dq+\frac{\partial F}{\partial p}dp$$

$$=dF=\text{ exact differential}$$

F = qp +q cot p

and hence the transformation is canonical.

Let us put $Q=\log\left(\frac{\sin p}{q}\right)$

$$\sin p=q\,e^{Q}\Rightarrow p=\sin^{-1}\left(qe^{Q}\right)$$

$$\cos \text{p} = \left(1-q^2e^{2Q}\right)^{1/2}$$

$$\cot \text{p} = \frac{\left(1-q^2e^{2Q}\right)^{1/2}}{qe^{Q}}$$

Now the generating function $\text{F}=q\sin^{-1}\left(q\,e^{Q}\right)+e^{-Q}\left(1-q^2e^{1}\right)^{1/2}$

1.7 HAMILTONIAN:

The quantity $\left(\sum p_j\dot{q}_j-L\right)$ is a constant of motion with the condition that L does not involve time explicitly. This constant was designated by H.

$$ie\;\; H=\sum p_j\dot{q}_j-L\left(q_j,\dot{q}_j\right)$$

H as Hamiltonian H = H (q_j, p_j)

$$= \sum p_j\dot{q}_j-L(q_j,\dot{q}_j)$$

If H does not involve time, it is said to be a constant of motion.

(i) Hamilton’s canonical equations of motion:

Hamiltonian is in general as a function of the position coordinates q $_j$, the momenta p $_j$ and the time t.

$$H = H(q_j, p_j, t)$$

$$dH = \sum \frac{\partial H}{\partial q_j} dq_j + \sum \frac{\partial H}{\partial p_j} dp_j + \frac{\partial H}{\partial t} dt \qquad \text{…(1)}$$

$$H = \sum p_j \, \dot{q}_j - L$$

So that $\delta H = \sum \dot{q}_j \, dp_j + \sum p_j d\dot{q}_j - dL$ ….(2)

But Lagrangian $L = L(q_j, \dot{q}_j, t)$

$$dL = \sum \frac{\partial L}{\partial q_j} dq_j + \sum \frac{\partial L}{\partial \dot{q}_j} d\dot{q}_j + \frac{\partial L}{\partial t} dt \qquad \text{....(3)}$$

Substituting equation (3) in equation (2) we get

$$dH = \sum \dot{q}_j dp_j + \sum p_j d\dot{q}_j - \sum \frac{\partial L}{\partial q_j} dq_j - \sum \frac{\partial L}{\partial \dot{q}_j} d\dot{q}_j - \frac{\partial L}{\partial t} dt \qquad \text{….(4)}$$

$$\frac{\partial L}{\partial \dot{q}_j} = p_j \;\; and \;\; \frac{\partial L}{\partial q_j} = \dot{p}_j$$

Now equation (4) becomes

$$dH = \sum \dot{q}_j dp_j + \sum p_j d\dot{q}_j - \sum \dot{p}_j dq_j - \sum p_j d\dot{q}_j - \frac{\partial L}{\partial t} dt$$

$$dH = \sum \dot{q}_j dp_j - \sum \dot{p}_j dq_j - \frac{\partial L}{\partial t} dt \qquad \text{….(5)}$$

Comparing coefficients in equation (5) and equation (1), we arrive

$$\left.\begin{aligned} \dot{q}_j &= \frac{\partial H}{\partial \phi_j} \\ \dot{p}_j &= -\frac{\partial H}{\partial q_j} \end{aligned}\right] \qquad \text{….(6)}$$

$$-\frac{\partial L}{\partial t} = \frac{\partial H}{\partial t}$$

Equations (6) are known as Hamilton’s canonical equations of motion and of a set of 2n first order equations of motion.

(ii) Physical Significance of H

Hamiltonian H also possesses the dimensions of energy but in all circumstances $H \neq E$

E = H equality has some restrictions. That are

1. The system be conservative one. ie. Potential energy is coordinate dependent and not velocity dependent.
2. Coordinate transformation equations be independent of time so that $\sum p_j \dot{q}_j = 2T$

Let us write H = H $(p_1, p_2, \ldots\ldots p_j, q_1, q_2, \ldots\ldots\ldots q_j, t)$

$$\frac{dH}{dt} = \sum \frac{\partial H}{\partial q_j} \dot{q}_j + \sum \frac{\partial H}{\partial p_j} \dot{p}_j + \frac{\partial H}{\partial t}$$

From Hamilton′s equations of motion

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \qquad \frac{\partial H}{\partial p_j} = \dot{q}_j$$

Therefore $\frac{dH}{dt} = -\sum \dot{p}_j \, \dot{q}_j + \sum \dot{q}_j \, \dot{p}_j + \frac{\partial H}{\partial t}$

$$= \frac{\partial H}{\partial t} \qquad \ldots.(1)$$

$$= -\frac{\partial L}{\partial t}$$

$$\therefore \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \qquad \ldots.(2)$$

If L is not an explicit function of time, $\frac{\partial L}{\partial t} = 0$

$$\therefore \frac{\partial H}{\partial t} = 0 \qquad ie \ \frac{dH}{dt} = 0$$

$$H = \text{constant} \qquad \ldots.(3)$$

Thus if L is not an explicit function of time, H is constant of motion.

For conservative systems, the Potential energy does not depend upon generalized velocity, ie

$$\frac{\partial V}{\partial \dot{q}_j} = 0 \qquad \ldots.(4)$$

We know $H = \sum p_j \dot{q}_j - L$

$$= \sum \frac{\partial L}{\partial \dot{q}_j} \dot{q}_j - L$$

$$= \sum \dot{q}_j \left\{ \frac{\partial}{\partial \dot{q}_j} (T - V) \right\} - L \qquad \text{Since } L = T - V$$

$$= \sum \dot{q}_j \left\{ \frac{\partial T}{\partial \dot{q}_j} - \frac{\partial V}{\partial \dot{q}_j} \right\} - L$$

$$= \sum \dot{q}_j \left\{ \frac{\partial T}{\partial \dot{q}_j} \right\} - L \qquad \text{since } \frac{\partial V}{\partial \dot{q}_j} = 0$$

$$H \quad = \sum \dot{q}_j \frac{\partial}{\partial \dot{q}_j} \left(\frac{1}{2} m \dot{q}_j^{\,2} \right) - L$$

$$= \sum m \dot{q}_j^{\,2} - L$$

$$= 2T - L = 2T - (T - V)$$

$$= T + V = \text{K.E} + \text{P.E} = \text{Total energy.}$$

$\Rightarrow$ H represents the total energy of the system for conservative system.

1.8 CYCLIC (OR) IGNORABLE COORDINATE:

We know that the Lagrangian L is a function of generalized coordinate q_j, generalized velocity $\dot{q}_j$ and time t. If the Lagrangian of a system does not contain a particular coordinate q_k, then $\frac{\partial L}{\partial q_k} = 0$. such a coordinate is referred to as an ignorable or cyclic coordinate.

(i) Generalised momentum: [conjugate (or) canonical momentum]

Consider a system of mass points acted upon by forces derived from potentials dependent on position only.

Now Lagrange's equations of motion are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0$$

Suppose q_j is cyclic.ie it does not occur in Lagrangian L, then for this coordinate Lagrange's equation reduces to

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j} \right) = 0$$

$$\frac{\partial L}{\partial \dot{q}_j} = \text{constant}$$

Generalized momentum = constant.

$$\frac{\partial L}{\partial \dot{x}_i} = \frac{\partial T}{\partial \dot{x}_i} - \frac{\partial V}{\partial x_i} = \frac{\partial T}{\partial \dot{x}_i}$$

$$= \frac{\partial}{\partial \dot{x}_i} \Sigma \frac{1}{2} m_1 \left(\dot{x}_i^{\,2} + \dot{y}_i^{\,2} + \dot{z}_i^{\,2} \right)$$

$$= m_i \dot{x}_i = p_{ix}$$

= x component of the linear momentum associated with the i^{th} particle.

Generalising the concept, a momentum associated with the coordinate q_j shall be

$$p_j = \frac{\partial T}{\partial \dot{q}_j} = \frac{\partial L}{\partial \dot{q}_j} = \text{generalized momentum.}$$

Thus $p_j =$ constant

The generalized momentum conjugate to a cyclic coordinate is conserved.

If we put p_j in Lagrange's equation we get $\dot{p}_j = \dfrac{\partial L}{\partial q_j}$

1.9 ROUTHIAN PROCEDURE AND EQUATIONS :

In Kepler's problem

$$L = \frac{1}{2} m\left(\dot{r}^2 + r^2 \dot{\theta}^2\right) + \frac{k}{r}$$

θ does not occur in L and is therefore an ignorable coordinate so that corresponding momentum

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2 \dot{\theta} = l = a \text{ constant}$$

It appears from the expression L that we can solve Kepler problem without considering θ which is ignorable. But this is not so in Lagrangian formation because $\dot{\theta}$ which requires how θ varies with t. Thus we consider θ. However Routhian procedure which eliminates this consideration. We want to find a function R called Routhian function such that it does not contain generalized velocities corresponding to ignorable coordinates.

$$L = L\left(q_1, q_2, \ldots\ldots q_n, \dot{q}_1, \dot{q}_2 \ldots\ldots \dot{q}_n, t\right)$$

If coordinates $q_1 \ldots\ldots q_k$ are ignorable then

$$L = L\left(q_{k+1} \ldots\ldots q_n, \dot{q}_1 \ldots\ldots \dot{q}_n, t\right)$$

$$\delta L = \sum_{j=k+1}^{n} \frac{\partial L}{\partial q_j} \delta q_j + \sum_{j=1}^{n} \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j + \frac{\partial L}{\partial t} \delta t$$

$$\text{(or)} \left[\delta L - \sum_{j=1}^{k} \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j \right] = \sum_{j=k+1}^{n} \frac{\partial L}{\partial q_j} \delta q_j + \sum_{j=k+1}^{n} \frac{\partial L}{\partial \dot{q}_j} \delta \dot{q}_j + \frac{\partial L}{\partial t} \delta t \qquad \ldots\ldots (1)$$

Routhian function R in which velocities $\dot{q}_1 \ldots\ldots \dot{q}_k$ corresponding to ignorable coordinates $q_1 \ldots\ldots q_k$ are eliminated, can be written as

$$R = R(q_{k+1} \dots q_n, \dots \dot{q}_{k+1} \dots \dot{q}_n, t)$$

so that $$\delta R = \sum_{J=k+1}^{n} \frac{\partial R}{\partial q_j}\delta q_j + \sum_{J=k+1}^{n} \frac{\partial R}{\partial \dot{q}_j}\delta q_j + \frac{\partial R}{\partial t}\delta t \qquad \dots(2)$$

We can also define the Routhian function as

$$R = L - \sum_{J=1}^{k} \dot{q}_j p_j$$

$$\delta R = \delta L - \sum_{J=1}^{k} \dot{q}_j \, \delta p_j - \sum_{J=1}^{k} \delta \dot{q}_j \, p_j$$

$$= \delta L - \sum_{J=1}^{k} p_j \delta \dot{q}_j - \sum_{J=1}^{k} \dot{q}_j \, \delta p_j$$

$$= \left[\delta L - \sum_{J=1}^{k} \frac{\partial L}{\partial \dot{q}_j} \, \delta \dot{q}_j \right] - \sum_{J=1}^{k} \dot{q}_j \, \delta p_j$$

$$= \sum_{J=k+1}^{n} \frac{\partial L}{\partial q_j}\delta q_j + \sum_{J=k+1}^{n} \frac{\partial L}{\partial \dot{q}_j}\delta \dot{q}_j + \frac{\partial L}{\partial t}\delta t - \sum_{J=1}^{k} \dot{q}_j \, \delta p_j \qquad \dots(3)$$

Comparing equations (2) and (3), we get

$$\left.\begin{aligned} \frac{\partial L}{\partial q_j} &= \frac{\partial R}{\partial q_j} \\ \frac{\partial L}{\partial \dot{q}_j} &= \frac{\partial R}{\partial \dot{q}_j} \end{aligned}\right] \quad J = k+1 \dots n \qquad \dots(4)$$

putting equation (4) in Lagrange’s equations

$$\sum_{J=1}^{n} \left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} \right] = 0$$

we get

$$\sum_{J=K+1}^{n} \left[\frac{d}{dt}\left(\frac{\partial R}{\partial \dot{q}_j} \right) - \frac{\partial R}{\partial q_j} \right] = 0 \qquad \dots(5)$$

in which Routhian function has replaced Lagranian function. These are only (n-k) second order equations in the non-ignorable variables. Thus we can eliminate the ignorable coordinates through Routhian procedure.

(i) Kepler’s problem:

we know that $p_\theta = m r^2 \dot{\theta}$

so that R $= L - p_\theta \dot{\theta}$

$$= L - m r^2 \dot{\theta}^2$$

$$=\frac{1}{2}m\left(\dot{r}^2+r^2\ \dot{\theta}^2\right)+\frac{k}{r}-mr^2\,\dot{\theta}^2$$

$$=\ \frac{1}{2}\mathrm{m}\left(\dot{\mathrm{r}}^2-\mathrm{r}^2\,\dot{\theta}^2\right)+\frac{\mathrm{k}}{\mathrm{r}}$$

$$\frac{\partial \mathrm{R}}{\partial \dot{\mathrm{r}}}\ =\ \mathrm{m}\dot{\mathrm{r}}$$

$$\frac{\partial R}{\partial r}\ =\ mr\,\dot{\theta}^2-\frac{k}{r^2}$$

Now we get the equation of motion as

$$\frac{d}{dt}\left(m\dot{r}\right)-mr\dot{\theta}^2+\frac{k}{r^2}=0 \qquad \text{[from equation (5)]}$$

$$m\ddot{r}-mr\dot{\theta}^2+\frac{k}{r^2}=0$$

$$\mathrm{m}\ddot{\mathrm{r}}\ =\ \mathrm{mr}\dot{\theta}^2-\frac{\mathrm{k}}{\mathrm{r}^2}$$

$$=\frac{\mathrm{mv}^2{}_{\theta}}{\mathrm{r}}+\mathrm{f}\,(\mathrm{r})$$

Which is the equation of motion of a particle under central force.

1.10 DERIVATION OF HAMILTON’S CANONICAL EQUATIONS FROM VARIATIONAL PRINCIPLE:

Hamilton’s principle is stated as

$$\delta I=\ \delta\int_{t_1}^{t_2}Ldt=0$$

$$H=\sum p_j\dot{q}_j-L$$

$$L=\sum p_j\dot{q}_j-H$$

and hence $\delta I=\delta\int_{t_1}^{t_2}\left[\sum p_j\dot{q}_j-H\left(q_{j,}p_{j,}t\right)\right]dt=0$ …(1)

Eqn. (1) is termed as modified Hamilton’s principle.

The δ variation can be expressed as $\delta\rightarrow d\alpha\frac{\partial}{\partial\alpha}$

$$\delta I=d\alpha\frac{\partial I}{\partial\alpha}$$

$$=d\alpha\frac{\partial}{\partial\alpha}\int_{t_1}^{t_2}\left[\Sigma p_j\dot{q}_j-H\left(q_j,p_j,t\right)\right]dt=0$$

end point's times are same for every path. Limits are independent of α and hence $\frac{\partial}{\partial\alpha}$ can be taken inside the integral.

$$\delta \mathrm{I} = \mathrm{d}\alpha \int_{t_1}^{t_2} \Sigma \left[\frac{\partial p_j}{\partial \alpha} \dot{q}_j + p_j \frac{\partial \dot{q}_j}{\partial \alpha} - \frac{\partial H}{\partial q_j} \frac{\partial q_j}{\partial \alpha} - \frac{\partial H}{\partial p_j} \frac{\partial p_j}{\partial \alpha} - \frac{\partial H}{\partial t} \frac{\partial t}{\partial \alpha} \right] dt = 0 \qquad \ldots.(2)$$

But $\frac{\partial \mathrm{t}}{\partial\alpha} = 0$ since time of travel along every path is same. Also

$$\int_{t_1}^{t_2} p_j \frac{\partial \dot{q}_j}{\partial \alpha} dt = \int_{t_1}^{t_2} p_j \frac{d}{dt}\left(\frac{\partial q_j}{\partial \alpha}\right) dt$$

$$= p_j \frac{\partial q_j}{\partial \alpha} \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \dot{p}_j \frac{\partial q_j}{\partial \alpha} dt$$

$$= -\int_{t_1}^{t_2} \dot{p}_j \frac{\partial q_j}{\partial \alpha} dt$$

$\frac{\partial \mathrm{q_j}}{\partial \alpha}$ vanishes at limits t_1 and t_2,

Now equation (2) becomes

$$\delta \mathrm{I} = \mathrm{d}\alpha \int_{t_1}^{t_2} \Sigma \left[\frac{\partial p_j}{\partial \alpha} \dot{q}_j - \dot{p}_j \frac{\partial q_j}{\partial \alpha} - \frac{\partial H}{\partial q_j} \frac{\partial q_j}{\partial \alpha} - \frac{\partial H}{\partial p_j} \frac{\partial p_j}{\partial \alpha} \right] dt = 0$$

Putting $\frac{\partial \mathrm{q_j}}{\partial \alpha} \mathrm{d}\alpha = \delta \mathrm{q_j}$

$$\frac{\partial p_j}{\partial \alpha} d\alpha = \delta p_j$$

We get $$\delta I = \int_{t_1}^{t_2} \Sigma \left[\delta p_j \, \dot{q}_j - \dot{p}_j \delta q_j - \frac{\partial H}{\partial q_j} \delta q_j - \frac{\partial H}{\partial p_j} \delta p_j \right] dt = 0$$

$$= \int_{t_1}^{t_2} \Sigma \left\{ \delta p_j \left[\dot{q}_j - \frac{\partial H}{\partial p_j} \right] - \delta q_j \left[\dot{p}_j + \frac{\partial H}{\partial q_j} \right] \right\} dt = 0$$

Since p_j and $\mathrm{q_j}$ are independent variables, the above equation can be satisfied only if

$$q_j - \frac{\partial H}{\partial p_j} = 0 \Rightarrow \dot{q}_j = \frac{\partial H}{\partial p_j}$$

$$\dot{p}_j + \frac{\partial H}{\partial q_j} = 0 \Rightarrow \dot{p}_j = -\frac{\partial H}{\partial q_j}$$

which are the desired canonical equations of motion.

1.11 APPLICATIONS OF HAMILTON’S EQUATIONS OF MOTION:

1. Simple pendulum :

The kinetic energy of the bob $T = \frac{1}{2} ml^2\dot{\theta}^2$

and the potential energy $r = mg\, l(1 - \cos\theta)$

Lagrangian $L = T - V$

$$= \frac{1}{2} ml^2 \dot{\theta}^2 - mgl(1 - \cos\theta) \qquad \text{.... (1)}$$

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = ml^2\dot{\theta}^2 \qquad \text{.... (2)}$$

Hamiltonian $H = \Sigma p_j \dot{q}_j - L$

$$= p_\theta\, \dot{\theta} - L$$

$$= ml^2\dot{\theta}^2 - \left[\frac{1}{2} ml^2\, \dot{\theta}^2 - mgl(1 - \cos\theta)\right]$$

$$= \frac{1}{2} ml^2\theta^2 + mgl(1 - \cos\theta) \qquad \text{....(3)}$$

$$= T + V$$

Then the system is conservative.

Putting equation (2) into equation (3), we get

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

giving

$$\left.\begin{aligned} \frac{\partial H}{\partial p_\theta} &= \frac{p_\theta}{ml^2} \\ \frac{\partial H}{\partial \theta} &= mgl\sin\theta \end{aligned}\right\} \qquad \text{....(4)}$$

Thus Hamilton’s equations of motion for this system will be

$$\dot{\theta} = \frac{\partial H}{\partial \theta} = \frac{p_\theta}{ml^2} \qquad \text{\_....(5)}$$

$$\dot{p}_\theta = \frac{-\partial H}{\partial \theta} = -mgl\sin\theta \qquad \text{....(6)}$$

From equation (5), we have

$$\dot{p}_\theta = ml^2\ddot{\theta}$$

and hence equation (6) becomes

$$ml^2\ddot{\theta} = -mgl\sin\theta$$

$$l\ddot{\theta} = -g\sin\theta$$

$$l\ddot{\theta} + g\sin\theta = 0$$

$$l\ddot{\theta} + g\theta = 0$$

$$\ddot{\theta} + \frac{g}{l}\theta = 0$$

which represents the equation of motion of a simple pendulum with period $2\pi\sqrt{l/g}$

2. Compound pendulum :

$$T = \frac{1}{2}I\dot{\theta}^2$$

$$V = -mgl\cos\theta$$

Now the Lagrangian L = $\frac{1}{2}I\dot{\theta}^2 + mgl\cos\theta$

Then $$p_\theta = \frac{\partial L}{\partial\dot{\theta}}$$

$$= I\dot{\theta} \qquad \text{…. (1)}$$

Hamiltonian $$H = \Sigma p_j\dot{q}_j - L$$

$$= p_\theta\dot{\theta} - L$$

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

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

$$= \frac{1}{2}I\left(\frac{p_\theta}{I}\right)^2 - mgl\cos\theta$$

$$= \frac{p_\theta{}^2}{2I} - mgl\cos\theta \qquad \text{….(2)}$$

$$= T + V$$

Then the system is conservative.

The Hamilton's equations of motion for θ and p_θ are

$$\left.\begin{aligned} \dot{\theta} &= \frac{\partial H}{\partial P_\theta} \\ \dot{p}_\theta &= \frac{-\partial H}{\partial\theta} \end{aligned}\right\} \qquad \text{….(3)}$$

From equation (2) we find

$$\frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{I}$$

$$\frac{\partial H}{\partial \theta} = mgl \sin\theta$$

Now equation (3) becomes $\dot{\theta} = \frac{p_\theta}{I}$ ….(4)

and $\dot{p}_\theta = -mgl \sin\theta$ ….(5)

From equation (4) $\dot{p}_\theta = I\ddot{\theta}$

Now equation (5) becomes

$$I\ddot{\theta} = -mgl\sin\theta$$

$$\ddot{\theta} + \frac{mgl}{I}\sin\theta = \theta$$

$$\Rightarrow \ddot{\theta} + \omega^2\theta = \theta$$

which is the equation of motion of compound pendulum with $\omega = \sqrt{\frac{mgl}{I}}$

3. Linear Harmonic Oscillator :

The system is conservative and constraint is independent of time. Hamiltonian will represent the total energy of the system. The Lagrangian

$$L = T - V$$

$$= \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2$$

$$\frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} = p = m\dot{x}$$

$$\dot{x} = \frac{p}{m}$$

giving Hamiltonian

$$H = T + V$$

$$= \frac{1}{2}m\left(\frac{p}{m}\right)^2 + \frac{1}{2}kx^2$$

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

Equations of motion are

$$\dot{p} = \frac{-\partial H}{\partial x} = -kx$$
$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}$$
$$\ddot{x} = \frac{\dot{p}}{m} = \frac{-kx}{m}$$
$$m\ddot{x} + kx = 0$$

This relation shows that motion is simple harmonic and is the desired equation.

4. Particle in a central field of force :

The system is conservative and hence the Hamiltonian represents the total energy.

$$T = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2\right)$$
$$V = V(r)$$

Lagrangian $L = T - V$

$$= \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2\right) - V(r)$$

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r} \Rightarrow \dot{r} = \frac{p_r}{m}$$

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta} \Rightarrow \dot{\theta} = \frac{p_\theta}{mr^2}$$

Hamiltonian H= T + V

$$= \frac{1}{2}m\left[\dot{r}^2 + r^2\dot{\theta}^2\right] + V(r)$$

$$= \frac{p_r{}^2}{2m} + \frac{p_\theta{}^2}{2mr^2} + V(r)$$

$$\left.\begin{aligned} \dot{p}_r &= -\frac{\partial H}{\partial r} = \frac{p_\theta{}^2}{mr^3} - \frac{\partial V}{\partial r} \\ \dot{p}_\theta &= -\frac{\partial H}{\partial \theta} = 0 \end{aligned}\right\} \quad \text{…. (1)}$$

and

$$\left.\begin{aligned} \dot{r} &= \frac{\partial H}{\partial p_r} = \frac{p_r}{m} \\ \dot{\theta} &= \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mr^2} \end{aligned}\right\} \quad \text{…. (2)}$$

Which are the desired equations of motion.

From equation (2) we can write

$$\ddot{r} = \frac{\dot{p}_r}{m} = \frac{p_\theta{}^2}{m^2 r^3} - \frac{1}{m}\frac{\partial V}{\partial r}$$

$$m\ddot{r} = \frac{p_\theta{}^2}{mr^3} - \frac{\partial V}{\partial r} \qquad \text{…. (3)}$$

We put

$$-\frac{\partial V}{\partial r} = F(r) = radial \;\; force \qquad and$$

$$\frac{p_\theta{}^2}{mr^3} = \frac{[mr^2\dot{\theta}]^2}{mr^3} = mr\dot{\theta}^2 \qquad [From\, equation\,(2)]$$

$$= \frac{m[\dot{r}\theta]^2}{r}$$

$$= \frac{m\mathrm{v}_\theta{}^2}{r} = centrifuga\, l \;\; force$$

From equation (3)

$$m\ddot{r} = \frac{m\mathrm{v}_\theta{}^2}{r} + F(r)$$

gives an equation of motion involving the actual force F(r) and a centrifugal force $\frac{m\mathrm{v}_\theta{}^2}{r}$.

5. Hamiltonian for a charged particle in an electromagnetic field :

Lagrangian $L = T - q\left(\varphi - \frac{1}{c}\vec{\mathrm{v}}\cdot\vec{A}\right)$

$$= \Sigma\frac{1}{2}\mathrm{mv_j}^2 - \mathrm{q}\left(\varphi - \Sigma\frac{\mathrm{v_j A_j}}{\mathrm{c}}\right) \qquad \text{…. (1)}$$

$$p_j = \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial L}{\partial \mathrm{v}_j}$$

$$= m\mathrm{v}_j + \frac{q}{c}A_j$$

Hamiltonian $\mathrm{H} = \Sigma\dot{\mathrm{q}}_\mathrm{j}\mathrm{p}_\mathrm{j} - \mathrm{L}$

$$= \Sigma\, \mathrm{v}_j \left(m\mathrm{v}_j + \frac{q}{c} A_j \right) - L$$

$$= \Sigma\, m\mathrm{v}_j^{\ 2} + \Sigma \frac{q}{c} \mathrm{v}_j\, A_j - L$$

$$= m\mathrm{v}^2 + \frac{q}{c}\left(\vec{\mathrm{v}} \cdot \vec{A}\right) - L$$

$$= 2T + \frac{q}{c}\left(\vec{\mathrm{v}} \cdot \vec{A}\right) - \left[T - q\left(\varphi - \frac{1}{c}\vec{\mathrm{v}} \cdot \vec{A} \right)\right]$$

$$= T + q\,\varphi$$

$$= \frac{1}{2} m\mathrm{v}^2 + q\varphi$$

such that H can be interpreted as the sum of kinetic and electrostatic potential energies of the particle.

6. Particle moving hear the surface of earth :

Let z axis be along upward vertical direction, then kinetic energy is

$$\mathrm{T} = \frac{1}{2}\mathrm{m}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$$

The applied force on the body is its weight acting in negative z direction.ie

$$F = F_z = -mg = -\frac{\partial V}{\partial \mathrm{z}}$$

$$\therefore V = mgz$$

Lagrangian

$$L = T - V$$

$$= \frac{1}{2} m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) - mgz$$

$$\frac{\partial \mathrm{L}}{\partial \dot{x}} = \frac{\partial \mathrm{T}}{\partial \dot{x}} = \mathrm{p}_x = \mathrm{m}\dot{x}$$

giving $\dot{x} = \frac{\mathrm{p}_x}{\mathrm{m}}$.

Similarly $\dot{\mathrm{y}} = \frac{\mathrm{p_y}}{\mathrm{m}}$ and $\dot{\mathrm{z}} = \frac{\mathrm{p_z}}{\mathrm{m}}$

Hamiltonian for such a system is conserved. ie

$$H = T + V$$

$$= \frac{1}{2} m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) + mg\,z$$

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

giving equations of motion

$$\left.\begin{aligned} \dot{p}_x &= -\frac{\partial H}{\partial x} = 0 \\ \dot{p}_y &= -\frac{\partial H}{\partial y} = 0 \\ \dot{p}_z &= -\frac{\partial H}{\partial z} = -mg \end{aligned}\right\} \qquad \text{…. (1)}$$

and

$$\left.\begin{aligned} \dot{x} &= \frac{\partial H}{\partial p_x} = \frac{p_x}{m} \\ \dot{y} &= \frac{\partial H}{\partial p_y} = \frac{p_y}{m} \\ \dot{z} &= \frac{\partial H}{\partial p_z} = \frac{p_z}{m} \end{aligned}\right\} \qquad \text{….(2)}$$

From equation (2) we get

$$\left.\begin{aligned} \ddot{x} &= \frac{\dot{p}_x}{m} = 0 \\ \ddot{y} &= \frac{\dot{p}_y}{m} = 0 \\ \ddot{z} &= \frac{\dot{p}_z}{m} = -g \end{aligned}\right\}$$

which shows that the acceleration along z direction is the acceleration due to gravity and is true.

UNIT 2

POISSON BRACKET AND THEORY OF SMALL OSCILLATIONS

Poisson bracket, Special cases of Poisson bracket , Poisson theorem, Poisson bracket and canonical transformation, Jacobi identity and its derivation, Lagrange bracket and its properties, the relationship between Poisson and Lagrange brackets and its derivation, the angular momenta and Poisson bracket, Liouville's theorem and its applications; Theory of small oscillations:

Formulation of the problem, Eigenvalue equation and the principle axis transformation, frequencies of free vibration and normal coordinates, free vibrations of a linear triatomic molecule

2.1 POISSON BRACKET : DEFINITION

Let F be any dynamical variable of a system.

Suppose F is function of conjugate variables q_j,p_j and t, then

$$\begin{aligned}\frac{dF}{dt} &= \frac{dF}{dt}(q_j,p_j,t) = \sum_j \frac{\partial F}{\partial q_j}\dot{q_j} + \frac{\partial F}{\partial p_j}\dot{p_j} + \frac{\partial F}{\partial t}\\ &= \sum_j \left(\frac{\partial F}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial F}{\partial p_j}\frac{\partial H}{\partial q_j}\right) + \frac{\partial F}{\partial t}\end{aligned}$$

on using Hamiltonts canonical equations of motion.

The first bracketted term is called Poisson Bracket of F with H.

In general if X and Y are two dynamical variables then

$$[X,Y]_{q,p} = \sum_j \left(\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j} - \frac{\partial X}{\partial p_j}\frac{\partial Y}{\partial q_j}\right) \tag{1}$$

2.2 SPECIAL CASES OF POISSON BRACKET

$$\begin{aligned}(a) \qquad [X,Y] &= -[Y,X]\\ (b) \qquad [X,X] &= 0\\ (c)[X,Y+Z] &= [X,Y]+[X,Z]\\ (d) \quad [X,YZ] &= Y[X,Z]+[X,Y]Z\end{aligned} \tag{2}$$

Also

$$\begin{aligned} (e) \qquad [q_i, q_j]_{q,p} &= 0 = [p_i, p_j]_{q,p} \\ (f) \qquad [q_i, p_j]_{q,p} &= \delta_{ij} = 0 \;\; if \; i \neq j \\ &= 1 \;\; if \; i = j \end{aligned} \tag{3}$$

Equation (3) are known as fundamental Poisson brackets.

Take the property

$$(c)[X, Y+Z] = [X,Y] + [X,Z]$$

Proof :

$$\begin{aligned} [X, Y+Z] &= \sum_j \left(\frac{\partial X}{\partial q_j} \, \frac{\partial (Y+Z)}{\partial p_j} - \frac{\partial X}{\partial p_j} \, \frac{\partial (Y+Z)}{\partial q_j} \right) \\ &= \sum_j \left(\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j} + \frac{\partial X}{\partial q_j}\frac{\partial Z}{\partial p_j} \right) - \sum_j \left(\frac{\partial X}{\partial p_j}\frac{\partial Y}{\partial q_j} + \frac{\partial X}{\partial p_j}\frac{\partial Z}{\partial q_j} \right) \\ &= \sum_j \left(\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j} - \frac{\partial X}{\partial p_j}\frac{\partial Y}{\partial q_j} \right) + \sum_j \left(\frac{\partial X}{\partial q_j}\frac{\partial Z}{\partial p_j} - \frac{\partial X}{\partial p_j}\frac{\partial Z}{\partial q_j} \right) \\ &= [X,Y] + [X,Z] \end{aligned}$$

Similarly

$$[q_i, q_j]_{q,p} = \sum_k \left(\frac{\partial q_i}{\partial q_k}\frac{\partial q_j}{\partial p_k} - \frac{\partial q_i}{\partial p_k}\frac{\partial q_j}{\partial q_k} \right)$$

$$\frac{\partial q_j}{\partial p_k} = \frac{\partial q_i}{\partial p_k} = 0$$

and hence

$$[q_i, q_j]_{q,p} = 0 = [p_i, p_j]_{q,p}$$

$$\begin{aligned} [q_i, p_j]_{q,p} &= \sum_k \left(\frac{\partial q_i}{\partial q_k}\frac{\partial p_j}{\partial p_k} - \frac{\partial q_i}{\partial p_k}\frac{\partial p_j}{\partial q_k} \right) \\ &= \sum_k \frac{\partial q_i}{\partial q_k}\frac{\partial p_j}{\partial p_k} \end{aligned}$$

since

$$\frac{\partial q_i}{\partial p_k} \; and \; \frac{\partial p_j}{\partial q_k} = 0$$

Also

$$\frac{\partial q_i}{\partial q_k}\ and\ \frac{\partial p_j}{\partial p_k} = 0$$

sothat

$$\begin{aligned}[q_i, p_j]_{q,p} &= \sum \delta_{ik}\delta_{jk} \\ &= \delta_{ij} \\ &= 0\ \ if i \neq j \\ &= 1\ \ if i = j\end{aligned}$$

Excercises

1.If $[\phi, \psi]$ be the Poisson bracket of ϕ and ψ prove that

$$\begin{aligned}(a)\ \frac{\partial}{\partial t}[\phi,\psi] &= \left[\frac{\partial \phi}{\partial t}, \psi\right] + \left[\phi, \frac{\partial \psi}{\partial t}\right] \\ (b)\ \frac{d}{dt}[\phi,\psi] &= \left[\frac{d\phi}{dt}, \psi\right] + \left[\phi, \frac{d\psi}{dt}\right]\end{aligned}$$

We have

$$\begin{aligned}[\phi,\psi] &= \sum_i \left(\frac{\partial \phi}{\partial q_i}\frac{\partial \psi}{\partial p_i} - \frac{\partial \psi}{\partial q_i}\frac{\partial \phi}{\partial p_i}\right) \\ \frac{\partial}{\partial t}[\phi,\psi] &= \sum_i \frac{\partial}{\partial t}\left\{\frac{\partial \phi}{\partial q_i}\frac{\partial \psi}{\partial p_i} - \frac{\partial \psi}{\partial q_i}\frac{\partial \phi}{\partial p_i}\right\}\end{aligned}$$

$$\begin{aligned}&= \sum_i \frac{\partial}{\partial q_i}\left(\frac{\partial \phi}{\partial t}\right)\frac{\partial \psi}{\partial p_i} + \sum_i \frac{\partial \phi}{\partial q_i}\ \frac{\partial}{\partial p_i}\left(\frac{\partial \psi}{\partial t}\right) \\ &- \sum_i \frac{\partial}{\partial q_i}\left(\frac{\partial \psi}{\partial t}\right)\frac{\partial \phi}{\partial p_i} - \sum_i \frac{\partial \psi}{\partial q_i}\ \frac{\partial}{\partial p_i}\left(\frac{\partial \phi}{\partial t}\right) \\ &= \sum_i \left\{\frac{\partial}{\partial q_i}\left(\frac{\partial \phi}{\partial t}\right)\frac{\partial \psi}{\partial p_i} - \frac{\partial \psi}{\partial q_i}\ \frac{\partial}{\partial p_i}\left(\frac{\partial \phi}{\partial t}\right)\right\} \\ &+ \sum_i \left\{\frac{\partial \phi}{\partial q_i}\ \frac{\partial}{\partial p_i}\left(\frac{\partial \psi}{\partial t}\right) - \frac{\partial}{\partial q_i}\left(\frac{\partial \psi}{\partial t}\right)\frac{\partial \phi}{\partial p_i}\right\}\end{aligned}$$

$$= \left[\frac{d\phi}{dt}, \psi\right] + \left[\phi, \frac{d\psi}{dt}\right]$$

2.If $\{p_l, q_i\}, \{q_l, q_i\}$ are the Lagrange's brackets and $[p_l, p_j], [q_l, p_j]$ are the Poisson brackets, then prove that

$$\sum_{i=1}^{n}\{p_l, q_i\}[p_l p_j] + \sum_{i=1}^{n}\{q_l, q_i\}[q_l, p_j] = 0$$

We have

$$\{p_l, q_i\} = -\{q_i, p_l\}$$

$$= -\delta_{il}$$

and

$$\{q_l, q_i\} = 0$$

$$[p_l, p_j] = 0$$

$$[q_l, p_j] = \delta_{lj}$$

Substituting these values we get

$$\sum_{i=1}^{n}\{p_l, q_i\}[p_l, p_j] + \{q_l, q_i\}[q_l, p_j] = -\delta_{il} \times 0 + 0 \times \delta_{lj}$$

$$= 0$$

3.If $\{q_l, q_i\}, \{p_l, q_i\}$ are the Lagrange's brackets and $[q_l, q_j], [p_l, q_j]$ are the Poisson brackets, then prove that

$$\sum_{i=1}^{n}\{q_l, q_i\}[q_l, q_j] + \sum_{i=1}^{n}\{p_l, q_i\}[p_l, q_j] = \delta_{ij}$$

We know

$$\{q_l, q_i\} = 0$$

$$[q_l, q_j] = 0$$

Also

$$\{p_l, q_i\} = -\{q_i, p_l\}$$

$$= -\delta_{il}$$

$$[p_l, q_j] = -[q_j, p_l]$$

$$= -\delta_{jl}$$

$$\begin{aligned}\sum_{i=1}^{n}\{q_l,q_i\}[q_l,q_j]+\sum_{i=1}^{n}\{p_l,q_i\}[p_l,q_j] &= 0\times 0+[-\delta_{il}\times-\delta_{jl}]\\ &=\delta_{ij}\end{aligned}$$

Hence proved.

2.3 POISSON'S THEOREM

For a dynamical variable $F(q,p,t)$

$$\frac{dF}{dt}=[F,H]+\frac{\partial F}{\partial t}$$

If F is a constant of motion so that $dF/dt=0$, then by Poisson's theorem

$$[F,H]+\frac{\partial F}{\partial t}=0$$

Furthermore if F does not contain time explicitly, that is $\partial F/\partial t=0$ then

$$[F,H]=0$$

This is the required condition for F to be a constant of motion.

2.4 POISSON BRACKET AND CANONICAL TRANSFORMATION :

Poisson brackets are invariant under a canonical transformation.That is

$$[X,Y]_{q,p}=[X,Y]_{Q,P}$$

Proof :

$$\begin{aligned}[X,Y]_{Q,P} &= \sum_i\left(\frac{\partial X}{\partial Q_i}\frac{\partial Y}{\partial P_i}-\frac{\partial X}{\partial P_i}\frac{\partial Y}{\partial Q_i}\right)\\ &= \sum_{i,j}\left\{\frac{\partial X}{\partial Q_i}\left(\frac{\partial Y}{\partial q_j}\frac{\partial q_j}{\partial P_i}+\frac{\partial Y}{\partial p_j}\frac{\partial p_j}{\partial P_i}\right)-\frac{\partial X}{\partial P_i}\left(\frac{\partial Y}{\partial q_j}\frac{\partial q_j}{\partial Q_i}+\frac{\partial Y}{\partial p_j}\frac{\partial p_j}{\partial Q_i}\right)\right\}\\ &= \sum_j\frac{\partial Y}{\partial q_j}\sum_i\left(\frac{\partial X}{\partial Q_i}\frac{\partial q_j}{\partial P_i}-\frac{\partial X}{\partial P_i}\frac{\partial q_j}{\partial Q_i}\right)+\sum_j\frac{\partial Y}{\partial p_j}\sum_i\left(\frac{\partial X}{\partial Q_i}\frac{\partial p_j}{\partial P_i}-\frac{\partial X}{\partial P_i}\frac{\partial p_j}{\partial Q_i}\right)\\ &= \sum_j\left\{\frac{\partial Y}{\partial q_j}[X,q_j]_{Q,P}+\frac{\partial Y}{\partial p_j}[X,p_j]_{Q,P}\right\}\end{aligned}$$

Further

$$\begin{aligned}
[X, q_j]_{Q,P} &= -[q_j, X]_{Q,P} \\
&= -\sum_m \left(\frac{\partial q_j}{\partial Q_m}\frac{\partial X}{\partial P_m} - \frac{\partial q_j}{\partial P_m}\frac{\partial X}{\partial Q_m} \right) \\
&= -\sum_{m,k} \left\{ \frac{\partial q_j}{\partial Q_m}\left(\frac{\partial X}{\partial q_k}\frac{\partial q_k}{\partial P_m} + \frac{\partial X}{\partial p_k}\frac{\partial p_k}{\partial P_m} \right) - \frac{\partial q_j}{\partial P_m}\left(\frac{\partial X}{\partial q_k}\frac{\partial q_k}{\partial Q_m} + \frac{\partial X}{\partial p_k}\frac{\partial p_k}{\partial Q_m} \right) \right\} \\
&= -\sum_k \frac{\partial X}{\partial q_k}\sum_m \left(\frac{\partial q_j}{\partial Q_m}\frac{\partial q_k}{\partial P_m} - \frac{\partial q_j}{\partial P_m}\frac{\partial q_k}{\partial Q_m} \right) + \sum_m \frac{\partial X}{\partial p_k}\sum_i \left(\frac{\partial q_j}{\partial Q_m}\frac{\partial p_k}{\partial P_m} - \frac{\partial q_j}{\partial P_m}\frac{\partial p_k}{\partial Q_m} \right) \\
&= -\sum_k \left\{ \frac{\partial X}{\partial q_k}[q_j, q_k]_{Q,P} + \frac{\partial X}{\partial p_k}[q_j, p_k]_{Q,P} \right\} \\
&= -\sum_k \frac{\partial X}{\partial p_k}\delta_{jk} = \frac{\partial X}{\partial p_j} \qquad (4)
\end{aligned}$$

Similarly

$$\begin{aligned}
[X, Y]_{Q,P} &= \sum_j \left(-\frac{\partial Y}{\partial q_j}\frac{\partial X}{\partial p_j} + \frac{\partial Y}{\partial p_j}\frac{\partial X}{\partial q_j} \right) \\
&= [X, Y]_{q,p}
\end{aligned}$$

Hence Poisson brackets are invariant under canonical transformation.

A canonical transformation can be generated from functions $F_1(q_j, Q_j, t)$, $F_2(q_j, P_j, t), F_3(p_j, Q_j, t)$ and $F_4(p_j, P_j, t)$.

In the case of generating function F_1, we have obtained

$$p_j = \frac{\partial F_1}{\partial q_j}$$

and

$$P_j = -\frac{\partial F_1}{\partial Q_j}$$

Using the above two relations we get

$$\frac{\partial p_j}{\partial Q_i} = \frac{\partial^2 F_1}{\partial Q_i \partial q_j} = -\frac{\partial P_i}{\partial q_j} \qquad (5)$$

Similarly in the case of generating function F_2, we have obtained

$$p_j = \frac{\partial F_2}{\partial q_j}$$

and

$$Q_j = \frac{\partial F_2}{\partial P_j}$$

Using the above two relations we get

$$\frac{\partial p_j}{\partial P_i} = \frac{\partial^2 F_2}{\partial P_i \partial q_j} = \frac{\partial Q_i}{\partial q_j} \tag{6}$$

Similarly in the case of F_3 and F_4 we have seen that

$$\frac{\partial q_j}{\partial Q_i} = -\frac{\partial^2 F_3}{\partial Q_i \partial p_j} = \frac{\partial P_i}{\partial p_j} \tag{7}$$

and

$$\frac{\partial q_j}{\partial P_i} = \frac{\partial^2 F_4}{\partial P_i \partial p_j} = -\frac{\partial Q_i}{\partial p_j} \tag{8}$$

$$[Q_i, P_j]_{q,p} = \sum_k \left(\frac{\partial Q_i}{\partial q_k}\frac{\partial P_j}{\partial p_k} - \frac{\partial Q_i}{\partial p_k}\frac{\partial P_j}{\partial q_k} \right)$$

Using eqns(5) and (7) we get

$$\begin{aligned} [Q_i, P_j]_{q,p} &= \sum_k \left(\frac{\partial Q_i}{\partial q_k}\frac{\partial q_k}{\partial Q_j} + \frac{\partial Q_i}{\partial p_k}\frac{\partial p_k}{\partial Q_j} \right) \\ &= \frac{\partial Q_i}{\partial Q_j} = \delta_{ij} = [Q_i, P_j]_{Q,P} \end{aligned}$$

and similarly

$$\begin{aligned} [Q_i, Q_j]_{q,p} &= 0 = [Q_i, Q_j]_{Q,P} \\ [P_i, P_j]_{q,p} &= 0 = [P_i, P_j]_{Q,P} \end{aligned} \tag{9}$$

Thus we have proved the affirmation for the fundamental brackets.

Excercises

1.Using Poisson bracket show that the transformation defined by
$q = \sqrt{2P} sinQ$
$p = \sqrt{2P} cosQ$ is canonical.
q,p can be rewritten as

$$\begin{aligned} tanQ &= \frac{q}{p} \\ P &= \frac{1}{2}(q^2 + p^2) \end{aligned}$$

If the transfomation is canonical, it must satisfy the conditions

$[Q, Q] = [P, P] = 0$

and

$[Q, P] = 1$ (1)

Already we know

$[Q, Q] = [P, P] = 0$

Hence we can show that

$[Q, P] = 1$ From eqn.(1)

$$\begin{aligned} sec^2Q\frac{\partial Q}{\partial q} &= \frac{1}{p} \qquad sec^2Q\frac{\partial Q}{\partial p} = \frac{-q}{p^2} \\ \frac{\partial P}{\partial q} &= q \qquad\qquad \frac{\partial P}{\partial p} = p \end{aligned}$$

Then

$$\begin{aligned} [Q, P] &= \left(\frac{\partial Q}{\partial q}\frac{\partial P}{\partial p} - \frac{\partial Q}{\partial p}\frac{\partial P}{\partial q}\right) \\ &= \left\{\left(\frac{1}{p}cos^2Q\right)p + \left(\frac{q}{p^2}cos^2Q\right)q\right\} \\ &= cos^2Q\left(1 + \frac{q^2}{\text{ﬄ}p^2}\right) \\ &= cos^2Q\left(1 + tan^2Q\right) \\ &= cos^2Q \times sec^2Q = 1 \end{aligned}$$

Hence the transformation is canonical.

2.Using Poisson bracket show that the transformation defined by

$$Q = e^{-q}(1 - p^2e^{2q})^{1/2}$$

$$P = tan^{-1}\frac{e^{-q}(1 - p^2e^{2q})^{1/2}}{p}$$

is canonical.

Q and P can be rewritten as

$$Q = e^{-q}(1 - p^2e^{2q})^{1/2}$$

$$= (e^{-2q} - p^2)^{1/2}$$

and

$$P = tan^{-1}\frac{Q}{p}$$

Now

$$\begin{aligned}
tanP &= \frac{Q}{p}\\
1+tan^2P &= 1+\frac{Q^2}{p^2}\\
1+tan^2P &= \frac{Q^2+p^2}{p^2}\\
sec^2P &= \frac{Q^2+p^2}{p^2}\\
sec\ P &= \frac{\sqrt{Q^2+p^2}}{p}\\
cos\ P &= \frac{p}{\sqrt{Q^2+p^2}}\\
&= \frac{p}{\sqrt{e^{-2q}-p^2+p^2}}\\
&= \frac{p}{\sqrt{e^{-2q}}}\\
&= \frac{p}{e^{-q}}\\
&= p\ e^q\\
P &= cos^{-1}(p\ e^q)
\end{aligned}$$

So now the transformation is

$$Q = (e^{-2q}-p^2)^{1/2}$$

$$P = cos^{-1}(p\ e^q)$$

Then

$$\begin{aligned}
\frac{\partial Q}{\partial q} &= \frac{1}{2}\frac{(-e^{-2q})(-2)}{(e^{-2q}-p^2)^{1/2}} = \frac{-e^{-2q}}{(e^{-2q}-p^2)^{1/2}}\\
\frac{\partial Q}{\partial p} &= \frac{1}{2}\frac{(-2p)}{(e^{-2q}-p^2)^{1/2}} = \frac{-p}{(e^{-2q}-p^2)^{1/2}}\\
\frac{\partial P}{\partial q} = \frac{-pe^q}{(1-p^2e^{2q})^{1/2}} &= \frac{-p}{e^{-q}(1-p^2e^{2q})^{1/2}} = \frac{-p}{(e^{-2q}-p^2)^{1/2}}\\
\frac{\partial P}{\partial p} = \frac{-e^q}{(1-p^2e^{2q})^{1/2}} &= \frac{-1}{e^{-q}(1-p^2e^{2q})^{1/2}} = \frac{-1}{(e^{-2q}-p^2)^{1/2}}
\end{aligned}$$

Therefore

$$[Q,P] = \left(\frac{\partial Q}{\partial q}\frac{\partial P}{\partial p} - \frac{\partial Q}{\partial p}\frac{\partial P}{\partial q}\right)$$

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

$$- \left\{\frac{-p}{(e^{-2q}-p^2)^{1/2}}\right\}\left\{\frac{-p}{(e^{-2q}-p^2)^{1/2}}\right\}$$

$$= \frac{e^{-2q}}{(e^{-2q}-p^2)} - \frac{p^2}{(e^{-2q}-p^2)}$$

$$= \frac{(e^{-2q}-p^2)}{(e^{-2q}-p^2)} = 1$$

Furthermore $[Q.Q] = 0$ and $[P,P] = 0$

Hence the transformation is canonical.

2.5 EQUATIONS OF MOTION IN POISSON'S BRACKET FORM :

The total time derivative of a dynamical variable $F(q_j, p_j, t)$ can be expressed as

$$\dot{F} = [F,H] + \frac{\partial F}{\partial t}$$

If F does not involve time t explicitly then

$$\dot{F} = [F,H] \qquad (1)$$

If the Poisson bracket of F with H vanishes then F=constant of motion. This requirement does not however require that H should be a constant of motion. Suppose such dynamical variables are q_j and p_j, then

$$\dot{q_j} = [q_j, H]$$

and

$$\dot{p_j} = [p_j, H] \qquad (2)$$

The above equations are identical with Hamilton's canonical equations of motion

$$[q_j, H] = \sum_i \left[\frac{\partial q_j}{\partial H}\frac{\partial H}{\partial p_i} - \frac{\partial q_j}{\partial p_i}\frac{\partial H}{\partial q_i}\right]$$

Since

$$\frac{\partial q_j}{\partial p_i} = 0$$

we get

$$[q_j, H] = \frac{\partial H}{\partial p_i}\delta_{ij}$$

$$= \frac{\partial H}{\partial p_j}(for\ i = j)$$

Therefore

$$\dot{q_j} = \frac{\partial H}{\partial p_j} = [q_j, H]$$

Similarly

$$p_j = -\frac{\partial H}{\partial q_j} = [p_j, H]$$

Equations (2) can thus be known as equations of motion inpoisson bracket form.

If Poisson bracket $[p_j, H]$ vanishes, then

$$\dot{p_j} = 0$$

$$p_j = constant$$

That is the linear momentum is conserved and hence the corresponding co-ordinate is cyclic. Thus all functions whose Poisson bracket with Hamiltonian vanish will be constants of motion and conversely Poisson brackets of all constants of motion with H must vanish.

2.6 JACOBI'S IDENTITY AND ITS DERIVATION :

$$[X, [Y, Z]] + [Y, [Z, X]] + [Z, [X, Y]] = 0$$

We have

$$[X, [Y, Z]] = \frac{\partial [X, Y]}{\partial q_j}\ \frac{\partial Z}{\partial p_j} - \frac{\partial Z}{\partial q_j}\ \frac{\partial [X, Y]}{\partial p_j}$$

$$= \frac{\partial}{\partial q_j}\left\{\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j} - \frac{\partial Y}{\partial q_j}\frac{\partial X}{\partial p_j}\right\}\ \frac{\partial Z}{\partial p_j} - \frac{\partial Z}{\partial q_j}\ \frac{\partial}{\partial p_j}\left\{\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j} - \frac{\partial Y}{\partial q_j}\frac{\partial X}{\partial p_j}\right\}$$

$$= \left\{\frac{\partial^2 X}{\partial q_{j^2}}\frac{\partial Y}{\partial p_j} + \frac{\partial X}{\partial q_j}\ \frac{\partial^2 Y}{\partial q_j \partial p_j} - \frac{\partial^2 Y}{\partial q_{j^2}}\frac{\partial X}{\partial p_j} - \frac{\partial Y}{\partial q_j}\frac{\partial^2 X}{\partial q_{j^2}}\frac{\partial Z}{\partial p_j}\right\}$$

$$-\frac{\partial Z}{\partial q_j}\left\{\frac{\partial^2 X}{\partial p_j \partial q_j}\frac{\partial Y}{\partial p_j} + \frac{\partial Y}{\partial p_j^2}\ \frac{\partial X}{\partial q_j} - \frac{\partial^2 Y}{\partial p_j \partial q_j}\frac{\partial X}{\partial p_j} - \frac{\partial^2 X}{\partial p_j^2}\frac{\partial Y}{\partial q_j}\right\}$$

$$= \frac{\partial^2 X}{\partial q_{j^2}}\ \frac{\partial Y}{\partial p_j}\ \frac{\partial Z}{\partial p_j} + \frac{\partial^2 X}{\partial p_j^2}\ \frac{\partial X}{\partial q_j}\ \frac{\partial Z}{\partial q_j} - \left\{\frac{\partial^2 Y}{\partial q_{j^2}}\frac{\partial X}{\partial p_j}\ \frac{\partial Z}{\partial p_j} + \frac{\partial^2 Y}{\partial p_{j^2}}\frac{\partial X}{\partial q_j}\ \frac{\partial Z}{\partial q_j}\right\}$$

$$-\frac{\partial^2 X}{\partial p_j \partial q_j}\left\{\frac{\partial Y}{\partial p_j}\frac{\partial Z}{\partial q_j} + \frac{\partial Y}{\partial q_j}\ \frac{\partial Z}{\partial q_j}\right\} + \frac{\partial^2 Y}{\partial p_j \partial q_j}\left\{\frac{\partial X}{\partial q_j}\frac{\partial Z}{\partial p_j} + \frac{\partial X}{\partial p_j}\frac{\partial Z}{\text{ffl}\partial q_j}\right\}$$

Similarly

$$[[Z,X],Y] = \frac{\partial^2 Z}{\partial q_{j^2}}\frac{\partial X}{\partial p_j}\frac{\partial Y}{\partial p_j} + \frac{\partial^2 Z}{\partial p_j^2}\frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial q_j} - \left\{\frac{\partial^2 X}{\partial q_{j^2}}\frac{\partial Z}{\partial p_j}\frac{\partial Y}{\partial p_j} + \frac{\partial^2 X}{\partial p_{j^2}}\frac{\partial Z}{\partial q_j}\frac{\partial Y}{\partial q_j}\right\}$$
$$-\frac{\partial^2 Z}{\partial p_j \partial q_j}\left\{\frac{\partial X}{\partial p_j}\frac{\partial Y}{\partial q_j} + \frac{\partial X}{\partial q_j}\frac{\partial Y}{\partial p_j}\right\} + \frac{\partial^2 X}{\partial p_j \partial q_j}\left\{\frac{\partial Z}{\partial q_j}\frac{\partial Y}{\partial p_j} + \frac{\partial Z}{\partial p_j}\frac{\partial Y}{\text{ﬄ}\partial q_j}\right\}$$

$$[[Y,Z],X] = \frac{\partial^2 Y}{\partial q_{j^2}}\frac{\partial Z}{\partial p_j}\frac{\partial X}{\partial p_j} + \frac{\partial^2 Y}{\partial p_j^2}\frac{\partial Z}{\partial q_j}\frac{\partial X}{\partial q_j} - \left\{\frac{\partial^2 Z}{\partial q_{j^2}}\frac{\partial Y}{\partial p_j}\frac{\partial X}{\partial p_j} + \frac{\partial^2 Z}{\partial p_{j^2}}\frac{\partial Y}{\partial q_j}\frac{\partial X}{\partial q_j}\right\}$$
$$-\frac{\partial^2 Y}{\partial p_j \partial q_j}\left\{\frac{\partial Z}{\partial p_j}\frac{\partial X}{\partial q_j} + \frac{\partial Z}{\partial q_j}\frac{\partial X}{\partial p_j}\right\} + \frac{\partial^2 Z}{\partial p_j \partial q_j}\left\{\frac{\partial Y}{\partial q_j}\frac{\partial X}{\partial p_j} + \frac{\partial Y}{\partial p_j}\frac{\partial X}{\text{ﬄ}\partial q_j}\right\}$$

Adding all we get

$$[X,[Y,Z]] + [Y,[Z,X]] + [Z,[X,Y]] = 0$$

2.7 LAGRANGE'S BRACKETS AND ITS PROPERTIES:

Lagrange's bracket u, v with respect to (q_j, p_j) is defined as

$$\{u,v\}_{q,p} = \sum_j \left(\frac{\partial q_j}{\partial u}\frac{\partial p_j}{\partial v} - \frac{\partial p_j}{\partial u}\frac{\partial q_j}{\partial v}\right) \tag{1}$$

(a) Lagrange bracket is invariant under canonical transformation :

Poincare's theorem states that the integral

$$J_1 = \int\int_S \sum_j dq_j dp_j \tag{2}$$

taken over an arbitrary two dimensional surface S of the 2n dimensional (q,p)phase space is invariant under canonical transformation.

Position of a point on any two dimensional surface is expressed as

$$q_j = q_j(u,v)$$

$$p_j = p_j(u,v)$$

$$\tag{3}$$

Transforming the integral (2) in terms of (u,v), we write

$$dq_j dp_j = \frac{\partial(q_j, p_j)}{\partial(u,v)} du dv \tag{4}$$

with

$$\frac{\partial(q_j,p_j)}{\partial(u,v)} = \begin{vmatrix} \dfrac{\partial q_j}{\partial u} & \dfrac{\partial p_j}{\partial u} \\ \\ \dfrac{\partial q_j}{\partial v} & \dfrac{\partial p_j}{\partial v} \end{vmatrix} \tag{5}$$

as the Jacobian.

Further

$$\int\int_S \sum_j dq_j dp_j = \int\int_S \sum_j dQ_j dP_j \tag{6}$$

where (Q_j, P_j) is another set of canonical co-ordinates to which the set(q_j, p_j)has been transformed.

Now relation (6) becomes

$$\int\int_S \sum_j \frac{\partial(q_j,p_j)}{\partial(u,v)} dudv = \int\int_S \sum_j \frac{\partial(Q_j,P_j)}{\partial(u,v)} dudv$$

S is arbitrary and area dudv is arbitrary. Therefore expressions on boyh the sides will be equal only when

$$\sum_j \frac{\partial(q_j,p_j)}{\partial(u,v)} = \sum_j \frac{\partial(Q_j,P_j)}{\partial(u,v)}$$

$$\sum_j \begin{vmatrix} \frac{\partial q_j}{\partial u} & \frac{\partial p_j}{\partial u} \\ \\ \frac{\partial q_j}{\partial v} & \frac{\partial p_j}{\partial v} \end{vmatrix} = \sum_j \begin{vmatrix} \frac{\partial Q_j}{\partial u} & \frac{\partial P_j}{\partial u} \\ \\ \frac{\partial Q_j}{\partial v} & \frac{\partial P_j}{\partial v} \end{vmatrix}$$

or

$$\sum_j \left(\frac{\partial q_j}{\partial u}\frac{\partial p_j}{\partial v} - \frac{\partial p_j}{\partial u}\frac{\partial q_j}{\partial v} \right) = \sum_j \left(\frac{\partial Q_j}{\partial u}\frac{\partial P_j}{\partial v} - \frac{\partial P_j}{\partial u}\frac{\partial Q_j}{\partial v} \right)$$

$$\{u,v\}_{q,p} = \{u,v\}_{Q,P} \tag{7}$$

Thus Lagrange's bracket is invariant under canonical transformation.

(b) Lagrange brackets do not obey the commutative law :

$$\begin{aligned}
\{u,v\} &= \sum_j \left(\frac{\partial q_j}{\partial u}\frac{\partial p_j}{\partial v} - \frac{\partial p_j}{\partial u}\frac{\partial q_j}{\partial v}\right) \\
&= -\sum_j \left(\frac{\partial p_j}{\partial u}\frac{\partial q_j}{\partial v} - \frac{\partial q_j}{\partial u}\frac{\partial p_j}{\partial v}\right) \\
&= -\sum_j \left(\frac{\partial q_j}{\partial v}\frac{\partial p_j}{\partial u} - \frac{\partial p_j}{\partial v}\frac{\partial q_j}{\partial u}\right) \\
&= \{v,u\} \qquad (8)
\end{aligned}$$

(c) Proof : $\{q_i,q_j\}=0$ $\{p_i,p_j\}=0$ $\{q_i,q_j\}=\delta_{ij}$ **:**

$$\{q_i,q_j\}=0$$

$$\{p_i,p_j\}=0$$

$$\{q_i,q_j\}=\delta_{ij}$$

$$\{q_i,q_j\} = \sum_k \left(\frac{\partial q_k}{\partial q_i}\frac{\partial p_k}{\partial q_j} - \frac{\partial q_k}{\partial q_j}\frac{\partial p_k}{\partial q_i}\right) \qquad (9)$$

q's and p's are independent and hence

$$\frac{\partial p_k}{\partial q_j}=0 \quad and \quad \frac{\partial p_k}{\partial q_i}=0$$

Then

$$\{q_i,q_j\}=0$$

Similarly we can prove

$$\{p_i,p_j\}=0 \qquad (10)$$

Now

$$\{q_i,p_j\} = \sum_k \left(\frac{\partial q_k}{\partial q_i}\frac{\partial p_k}{\partial p_j} - \frac{\partial q_k}{\partial p_j}\frac{\partial q_k}{\partial q_i}\right)$$

q's and p's are independent and hence

$$\frac{\partial q_k}{\partial p_j}=0$$

Then

$$\{q_i, p_j\} = \sum_k \frac{\partial q_k}{\partial q_i}\frac{\partial p_k}{\partial p_j} \tag{11}$$

We have

$$\frac{\partial q_k}{\partial q_i} = \delta_{ki} \quad and \qquad \frac{\partial p_k}{\partial p_j} = \delta_{kj}$$

Hence

$$\begin{aligned}\{q_i, p_j\} &= \sum_k \delta_{ki}\delta_{kj} \\ &= \delta_{ij} \qquad (12)\end{aligned}$$

2.8 RELATIONSHIP BETWEEN LAGRANGE AND POISSON BRACKET

We can show that

$$\sum_{i=1}^{2n} \{u_l, u_i\} \ \ [u_l, u_j] = \delta_{ij}$$

Here$\{u_l, u_i\}$ is Lagrange bracket and $[u_l, u_j]$ is Poisson bracket. Now

$$\sum_{l=1}^{2n} \{u_l, u_i\} \ \ [u_l, u_j] = \sum_{l=1}^{2n} \left\{ \sum_{k=1}^{n} \left(\frac{\partial q_k}{\partial u_l}\frac{\partial p_k}{\partial u_i} - \frac{\partial p_k}{\partial u_l}\frac{\partial q_k}{\partial u_i} \right) \right\} \left\{ \sum_{m=1}^{n} \left(\frac{\partial u_l}{\partial q_m}\frac{\partial u_j}{\partial p_m} - \frac{\partial u_l}{\partial p_m}\frac{\partial u_j}{\partial q_m} \right) \right\} \tag{1}$$

The first four terms on R.H.S on multiplication is

$$\begin{aligned}\sum_{k,m=1^n} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_m} \cdot \sum_{l=1}^{2n} \frac{\partial q_k}{\partial u_l}\frac{\partial u_l}{\partial q_m} &= \sum_{k,m} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_m} \cdot \frac{\partial q_k}{\partial q_m} \\ &= \sum_{k,m} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_m} \cdot \delta_{km}\end{aligned}$$

But

$$\delta_{km} = \frac{\partial p_m}{\partial p_k}$$

The first four terms on R.H.S on multiplication is

$$\sum_{k,m=1^n} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_m} \cdot \sum_{l=1}^{2n} \frac{\partial q_k}{\partial u_l}\frac{\partial u_l}{\partial q_m} = \sum_{k,m} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_m} \cdot \frac{\partial p_m}{\partial p_k}$$

$$= \sum_{k,m} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_k} \tag{2}$$

The last four terms will be

$$\sum_{k,m=1^n} \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_m} \cdot \sum_{l=1}^{2n} \frac{\partial p_k}{\partial u_l}\frac{\partial u_l}{\partial p_m} = \sum_{k,m} \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_m} \cdot \frac{\partial p_k}{\partial p_m}$$

$$= \sum_{k,m} \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_m} \cdot \delta_{km}$$

$$= \sum_{k,m} \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_m} \cdot \frac{\partial q_m}{\partial q_k}$$

$$= \sum_{k,m} \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_k} \tag{3}$$

The second term is

$$-\sum_{k,m=1^n} \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial q_m} \cdot \sum_{l=1}^{2n} \frac{\partial q_k}{\partial u_l}\frac{\partial u_l}{\partial p_m} = 0$$

since

$$\sum_{l=1}^{2n} \frac{\partial q_k}{\partial u_l}\frac{\partial u_l}{\partial p_m} = \frac{\partial q_k}{\partial p_m} = 0$$

Similarly the third term will be zero.

Hence R.H.S of equation (1) is

$$\sum_k \frac{\partial p_k}{\partial u_i}\frac{\partial u_j}{\partial p_k} + \sum_k \frac{\partial q_k}{\partial u_i}\frac{\partial u_j}{\partial q_k} = \sum_k \left(\frac{\partial u_j}{\partial p_k}\frac{\partial p_k}{\partial u_i} + \frac{\partial u_j}{\partial q_k}\frac{\partial q_k}{\partial u_i}\right)$$

$$= \frac{\partial u_j}{\partial u_i}(q_k, p_k)$$

$$= \frac{\partial u_j}{\partial u_i} = \delta_{ij} \tag{4}$$

Therefore

$$\sum_{i=1}^{2n} \{u_l, u_i\}\ [u_l, u_j] = \delta_{_{ij}}$$

Which gives the relation between Lagrange and Poisson brackets.

2.9 THE ANGULAR MOMENTUM AND POISSON BRACKETS :

The angular momentum **l** can be expressed in terms of linear momentum **p** and radius vector **r** as

$$\begin{aligned}\mathbf{l} &= \mathbf{r}\times\mathbf{p}\\ &= (\mathbf{i}x+\mathbf{j}y+\mathbf{k}z)\times(\mathbf{i}p_x+\mathbf{j}p_y+\mathbf{k}p_z)\\ &= \mathbf{i}(yp_z-zp_y)+\mathbf{j}(zp_x-xp_z)+\mathbf{k}(xp_y-yp_x) \qquad (1)\end{aligned}$$

giving

$$l_x = yp_z - zp_y \;\; ; \;\; l_y = zp_x - xp_z \;\; ; \;\; l_z = xp_y - yp_x$$

$$\begin{array}{ccc} \dfrac{\partial l_x}{\partial p_x} = 0 & \dfrac{\partial l_y}{\partial p_x} = z & \dfrac{\partial l_z}{\partial p_x} = -y \\ \dfrac{\partial l_x}{\partial p_y} = -z & \dfrac{\partial l_y}{\partial p_y} = 0 & \dfrac{\partial l_z}{\partial p_y} = x \\ \dfrac{\partial l_x}{\partial p_z} = y & \dfrac{\partial l_y}{\partial p_z} = -x & \dfrac{\partial l_z}{\partial p_z} = 0 \end{array} \qquad (2)$$

We know that

$$\begin{aligned}[F, p_j] &= \sum_k \left(\frac{\partial F}{\partial q_k}\frac{\partial p_j}{\partial p_k} - \frac{\partial F}{\partial p_k}\frac{\partial p_j}{\partial q_k}\right)\\ &= \frac{\partial F}{\partial q_j} \qquad (for \;\; j=k)\end{aligned}$$

so that

$$\begin{array}{ccc} [l_x,p_x] = \dfrac{\partial l_x}{\partial x} = 0 & [l_y,p_x] = \dfrac{\partial l_y}{\partial x} = -p_z & [l_z,p_x] = \dfrac{\partial l_z}{\partial x} = p_y \\ [l_x,p_y] = \dfrac{\partial l_x}{\partial y} = p_z & [l_y,p_y] = \dfrac{\partial l_y}{\partial y} = 0 & [l_z,p_y] = \dfrac{\partial l_z}{\partial y} = -p_x \\ [l_x,p_z] = \dfrac{\partial l_x}{\partial z} = -p_y & [l_y,p_z] = \dfrac{\partial l_y}{\partial z} = p_x & [l_z,p_z] = \dfrac{\partial l_z}{\partial z} = 0 \end{array} \qquad (3)$$

Equations (2) and (3) give Poisson brackets of angular and linear momentum components. We know that

$$[p_j, p_x] = 0$$

Therefore

$$[p_x, p_y] = [p_y, p_z] = [p_z, p_x] = 0 \qquad (4)$$

Now we find out the Poisson bracket of components of **l**

$$[l_x, l_y] = \sum_k \left(\frac{\partial l_x}{\partial q_k}\frac{\partial l_y}{\partial p_k} - \frac{\partial l_x}{\partial p_k}\frac{\partial l_y}{\partial q_k} \right)$$

$$= \left(\frac{\partial l_x}{\partial x}\frac{\partial l_y}{\partial p_x} - \frac{\partial l_x}{\partial p_x}\frac{\partial l_y}{\partial x} \right) + \left(\frac{\partial l_x}{\partial y}\frac{\partial l_y}{\partial p_y} - \frac{\partial l_x}{\partial p_y}\frac{\partial l_y}{\partial y} \right) + \left(\frac{\partial l_x}{\partial z}\frac{\partial l_y}{\partial p_z} - \frac{\partial l_x}{\partial p_z}\frac{\partial l_y}{\partial z} \right)$$

Using equations (2) and (3), we get

$$[l_x, l_y] = 0 - 0 + 0 - 0 + (-p_y)(-x) - (y)(p_x)$$

$$= (xp_x - yp_x) = l_z$$

Similarly we can prove

$$[l_y, l_z] = l_x$$

and

$$[l_z, l_x] = l_y$$

2.10 LIOUVILLE'S THEOREM :

The theorem consists of two parts

(1) The first part states the conservation of density in phase space

$$i.e\ \frac{d\rho}{dt} = 0$$

2) The second part states the conservation of extension in phase space

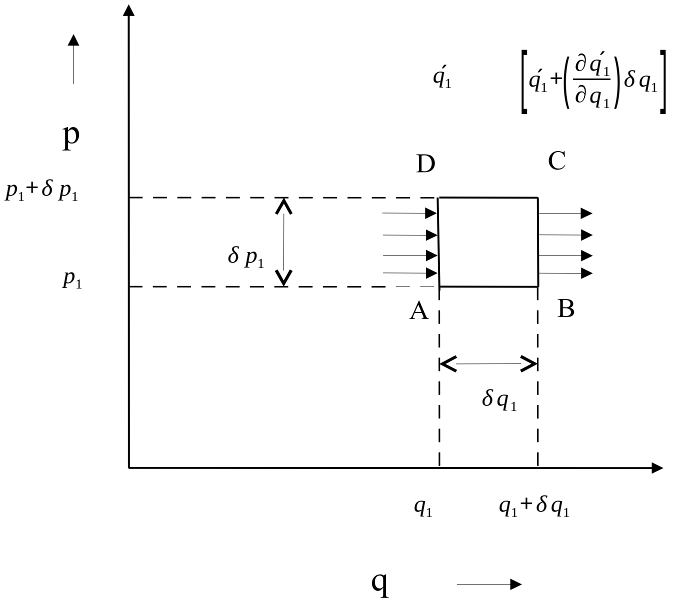
$$i.e\ \frac{d}{dt}(\delta\Gamma) = 0$$

(1) First Part :

Consider any fixed element of volume of phase space located between q_1 and $q_1 + \delta q_1, ...q_f$ and $q_f + \delta q_f, p_1$ and $p_1 + \delta p_1, ...p_f$ and $p_f + \delta p_f$.

If ρ is the density of phase points, the number of phase points in this volume element at any instant t is

$\delta N = \rho.\delta\Gamma = \rho(\delta q_1...\delta q_f \delta p_1...\delta p_f)$



The number of phase points located in the volume $(\delta q_1...\delta q_f\delta p_1...\delta p_f)$ changes as the coordinates and momenta vary. The change in the number of phase points within this volume of phase space in time dt is

$$\frac{d(\delta N)}{dt}=\frac{d(\rho.\delta\Gamma)}{dt}=\frac{d\rho}{dt}dt(\delta q_1...\delta q_f\delta p_1...\delta p_f)$$

This change is due to the number of phase points entering and leaving this volume in time dt.

Consider two faces of hypervolume normal to the q-axis with coordinates q_1 and $q_1+\delta q_1$. Number of phase points entering the first phase in time dt is

$$\rho\dot{q}_1 dt\delta q_2...\delta q_f\delta p_1...\delta p_f \tag{1}$$

ρ and $\dot{q}_1$ are the density and velocity component at $(q_1...q_f;p_1...p_f)$

Number of phase points entering the second phase in time dt is

$$\left(\rho+\frac{\partial\rho}{\partial q_1}\delta q_1\right)\left(\dot{q}_1+\frac{\partial\dot{q}_1}{\partial q_1}\delta q_1\right)dt\delta q_2...\delta q_f\delta p_1...\delta p_f \tag{2}$$

Neglecting higher order terms we have

$$\left[\rho\dot{q}_1+\left(\rho\frac{\partial\dot{q}_1}{\partial q_1}+\dot{q}_1\frac{\partial\rho}{\delta q_1}\right)\delta q_1\right]dt\delta q_2...\delta q_f\delta p_1...\delta p_f \tag{3}$$

Eqn(1)-Eqn(3) gives

$$-\left(\rho\frac{\partial\dot{q}_1}{\partial q_1}+\dot{q}_1\frac{\partial\rho}{\delta q_1}\right)dt\delta q_1...\delta q_f\delta p_1...\delta p_f \tag{4}$$

Similarly for p_1 co-ordinate

$$-\left(\rho\frac{\partial \dot{p_1}}{\partial p_1}+\dot{p_1}\frac{\partial \rho}{\delta p_1}\right)dt\delta p_1...\delta q_f\delta p_1...\delta p_f \tag{5}$$

The net increase in the number of phase points in time dt is in this volume of phase space is obtained by summing the net number of phase points entering the volume through all the faces labelled by $q_1...q_f$ and $p_1...p_f$. Hence

$$\frac{d}{dt}(\delta N)=-\sum_{j=1}^{f}\left\{\rho\left(\frac{\partial \dot{q_j}}{\partial q_j}+\frac{\partial \dot{p_j}}{\partial p_j}\right)+\left(\frac{\partial \rho}{\partial q_j}\dot{q_j}+\frac{\partial \rho}{\partial p_j}\dot{p_j}\right)\right\}dt\delta q_1...\delta q_f\delta p_1...\delta p_f \tag{6}$$

Already we have seen that

$$\frac{d}{dt}(\delta N)=\frac{\partial \rho}{\partial t}\,dt\delta q_1...\delta q_f\delta p_1...\delta p_f$$

and hence

$$\frac{\partial \rho}{\partial t}\,dt\delta q_1...\delta q_f\delta p_1...\delta p_f$$

$$=-\sum_{j=1}^{f}\left\{\rho\left(\frac{\partial \dot{q_j}}{\partial q_j}+\frac{\partial \dot{p_j}}{\partial p_j}\right)+\left(\frac{\partial \rho}{\partial q_j}\dot{q_j}+\frac{\partial \rho}{\partial p_j}\dot{p_j}\right)\right\}dt\delta q_1...\delta q_f\delta p_1...\delta p_f$$

$$\frac{\partial \rho}{\partial t}\;=\;-\sum_{j=1}^{f}\left\{\rho\left(\frac{\partial \dot{q_j}}{\partial q_j}+\frac{\partial \dot{p_j}}{\partial p_j}\right)+\left(\frac{\partial \rho}{\partial q_j}\dot{q_j}+\frac{\partial \rho}{\partial p_j}\dot{p_j}\right)\right\} \tag{7}$$

The equations of motion in canonical form are

$$\dot{q_j}=\frac{\partial H}{\partial p_j}\quad and\quad \dot{p_j}=-\frac{\partial H}{\partial q_j}$$

Now

$$\frac{\partial \dot{q_j}}{\partial q_j}=\frac{\partial^2 H}{\partial q_j\partial p_j}$$

$$\frac{\partial \dot{p_j}}{\partial p_j}=-\frac{\partial^2 H}{\partial p_j\partial q_j}$$

The order of differentian is immaterial and hence

$$\sum_{j=1}^{f}\left(\frac{\partial \dot{q_j}}{\partial q_j}+\frac{\partial \dot{p_j}}{\partial p_j}\right)=0 \tag{8}$$

Now Eqn(7) becomes

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = -\sum_{j=1}^{f}\left(\frac{\partial \rho}{\partial q_j}\dot{q}_j + \frac{\partial \rho}{\partial p_j}\dot{p}_j\right) \tag{9}$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{j=1}^{f}\left(\frac{\partial \rho}{\partial q_j}\dot{q}_j + \frac{\partial \rho}{\partial p_j}\dot{p}_j\right) = 0 \tag{10}$$

This result is known as Liouville's theorem.This equation is identical with the equation of continuity in hydrodynamics.

If ρ is a function of q, p and t and q, p are functions of t, then

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q}\frac{dq}{dt} + \frac{\partial \rho}{\partial p}\frac{dp}{dt}$$

On generalization we get

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{j}^{f}\frac{\partial \rho}{\partial q_j}\frac{dq_j}{dt} + \sum_{j}^{f}\frac{\partial \rho}{\partial p_j}\frac{dp_j}{dt} \tag{11}$$

Comparing eqns (10) and (11) we get

$$\frac{d\rho}{dt} = 0$$

This form is called the principle of the conservation of density in phase space.

(2) Second Part :

Here we have to prove that

$$\frac{d}{dt}(\delta\Gamma) = 0$$

We know

$$\delta N = \rho\, \delta\Gamma$$

Now

$$\frac{d}{dt}(\delta N) = \frac{d\rho}{dt}\, \delta\Gamma + \rho\, \frac{d}{dt}(\delta\Gamma) \tag{12}$$

The number of phase points δN in a given region must remain fixed.

$$\frac{d}{dt}(\delta N) = 0$$

$$\frac{d\rho}{dt}\,\delta\Gamma+\rho\,\frac{d}{dt}(\delta\Gamma)=0 \tag{13}$$

Already we have proved that

$$\frac{d\rho}{dt}=0$$

It follows that

$$\rho\,\frac{d}{dt}(\delta\Gamma)=0 \tag{14}$$

But $\rho \neq 0$, we get

$$\frac{d}{dt}(\delta\Gamma)=0 \tag{15}$$

This equation gives the principle of conservation of extension in phase space.

Excercises :

1.If the transformation eqations between two sets of co-ordinates are

$$P=2(1+q^{1/2}cos\ p)q^{1/2}sin\ p$$

$$Q=log\ (1+q^{1/2}cos\ p)$$

then show that (i) the transformation is canonical and (ii)the generating function of this transformation is

$$F_3=-(e^Q-1)^2tan\ p$$

Solution :

(i) For the trasformation to be canonical $(pdq-PdQ)$ must be an exact differential.

$$pdq-PdQ=pdq-2(1+q^{1/2}cos\ p)q^{1/2}sin\ p\cdot\frac{q^{1/2}(-sin\ p\ dp)+cos\ p(\frac{1}{2}q^{-1/2}dq)}{(1+q^{1/2}cos\ p)}$$

$$pdq-PdQ=pdq-2(1+q^{1/2}cos\ p)q^{1/2}sin\ p\cdot\frac{q(-sin\ p\ dp)+cos\ p(\frac{1}{2}dq)}{q^{1/2}(1+q^{1/2}cos\ p)}$$

$$=p\ dq+2qsin^2\ p\ dp-sin\ p\ cos\ p\ dq$$

$$=p\ dq+q(1-cos\ 2p)dp-(\frac{1}{2}sin\ 2p\ dq)$$

$$=(p-\frac{1}{2}sin\ 2p)\ dq+q(1-cos\ 2p)\ dp$$

$$
\begin{aligned}
&= \frac{\partial}{\partial q}[q(p-\frac{1}{2}sin\ 2p)]dq + \frac{\partial}{\partial p}[q(p-\frac{1}{2}sin\ 2p)]dp \\
&= d[q(p-\frac{1}{2}sin\ 2p)] \\
&= an\ \ exact\ \ differential
\end{aligned}
$$

(ii) We have

$$
\begin{aligned}
Q &= log\ (1+q^{1/2}cos\ p) \\
e^Q &= (1+q^{1/2}cos\ p) \\
e^Q - 1 &= q^{1/2}cos\ p \\
q^{1/2} &= \frac{e^Q-1}{cos\ p} \\
q &= \frac{(e^Q-1)^2}{(cos\ p)^2} \qquad (1)
\end{aligned}
$$

Now

$$
\begin{aligned}
P &= 2(1+q^{1/2}cos\ p)q^{1/2}sin\ p \\
&= 2e^Q\ \frac{(e^Q-1)}{cos\ p}sin\ p \\
&= 2e^Q\ (e^Q-1)tan\ p \qquad (2)
\end{aligned}
$$

We know that

$$
\begin{aligned}
q &= -\frac{\partial F_3}{\partial p} \\
P &= -\frac{\partial F_3}{\partial Q}
\end{aligned}
$$

Now

$$
\begin{aligned}
\frac{\partial F_3}{\partial p} &= -\frac{(e^Q-1)^2}{cos^2\ p} = -(e^Q-1)^2 sec^2\ p \qquad (3) \\
\frac{\partial F_3}{\partial Q} &= -2e^Q\ (e^Q-1)tan\ p \qquad (4)
\end{aligned}
$$

Integrating eqn(3) we get

$$
F_3 = -\int (e^Q-1)^2 sec^2\ p\ dp + constant
$$

Taking the constant of integration to be zero we get

$$F_3 = -(e^Q - 1)^2 tan\ p \tag{5}$$

Integrating eqn(4) we get

$$F_3 = 2\int e^Q\ (e^Q - 1) tan\ p\ dQ$$

Again taking the constant of integration to be zero we get

$$F_3 = -(e^Q - 1)^2 tan\ p \tag{6}$$

Since

$$Equation(5) = Equation(6)$$

means F_3 is the generator of the given transformation.

2.Show that the generating function for the transformation

$$p = \frac{1}{Q}, \quad p = PQ^2$$

is

$$F = \frac{q}{Q}$$

Solution :

$$p = \frac{1}{Q}, \quad p = PQ^2$$

We find

$$\begin{aligned} pdq &= \frac{1}{Q}(2PQdQ + Q^2dP) \\ &= 2PdQ + QdP \end{aligned}$$

Now

$$\begin{aligned} pdq - PdQ &= 2PdQ + QdP - PdQ \\ &= PdQ + QdP \\ &= \frac{\partial}{\partial Q}(PQ)dQ + \frac{\partial}{\partial P}(PQ)dP \\ &= \frac{\partial F}{\partial Q}dQ + \frac{\partial F}{\partial P}dP \end{aligned}$$

$$= dF$$

$$= an \;\; exact \;\; differential$$

The generating function is

$$F = PQ$$

But generating function involves both sets of co-ordinates. As

$$P = \frac{q}{Q^2}$$

we have

$$F = \frac{q}{Q^2}Q$$

$$= \frac{q}{Q}$$

Hence the result.

THEORY OF SMALL OSCILLATIONS :

2.11 FORMULATION OF THE PROBLEM :EIGEN VALUE EQUATION :

Consider a system with n degrees of freedom and whose total energy is conserved.Suppose the system is in an equilibrium stste at the point having the co-ordinates $q_{01}, q_{02}...q_{0n}$. Thus the potential energy satisfies the condition

$$\left(\frac{\partial V}{\partial q_j}\right)_{q=q_0} = 0$$

Here $q = q_0$ represents $q_j = q_{0j}$ for all values of j. let η_j denotes a small displacement in the corresponding co-ordinate q_j from the equilibrim position. Sothat

$$q_j = q_{0j} + \eta_j$$

with j=1,2,...n

Now the potential energy becomes

$$\begin{aligned} V(q_1, q_2, ...q_n) &= V(q_{01} + \eta_1, q_{02} + \eta_2, ...q_{0n} + \eta_n) \\ &= V(q_{01}, q_{02}, ...q_{0n}) + \sum_{j=1}^{n} \eta_j \left(\frac{\partial V}{\partial q_j}\right)_{q=q_0} \\ &+ \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n} \eta_j\eta_k \left(\frac{\partial^2 V}{\partial q_j \partial q_k}\right)_{q=q_0} + ... \qquad (1) \end{aligned}$$

The departure from the equilibrium position is small and we truncate the series after the first non-vanishing term in η_j.

The first term on the R.H.S is constant, the second term is zero and we consider upto the third term.

The first term gives the shift the reference of potential energy to the equilibrium point.

Thus the equation (1) becomes

$$\begin{aligned} V(q_1, q_2, ...q_n) &= \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\left(\frac{\partial^2 V}{\partial q_j \partial q_k}\right)_{q=q_0}\eta_j\eta_k \\ &= \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}V_{jk}\eta_j\eta_k \qquad (2) \end{aligned}$$

Where

$$V_{jk} = \left(\frac{\partial^2 V}{\partial q_j \partial q_k}\right)_{q=q_0}$$

Here $V_{jk} = V_{kj}$. For the stable equilibrium, the potential energy should be minimum at the equilibrium position and hence V_{jk} must be positive. The kinetic energy of the system is

$$T = \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}c_{jk}\dot{q_j}\dot{q_k} = \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}c_{jk}\dot{\eta_j}\dot{\eta_k}$$

c_{jk} be the functions of the co-ordinates q_j's and we can expand in Taylor series form about the equilibrium position :

$$\begin{aligned} c_{jk}(q_1, q_2, ...q_n) &= c_{jk}(q_{01} + \eta_1, q_{02} + \eta_2, ...q_{0n} + \eta_n) \\ &= c_{jk}(q_{01}, q_{02}, ...q_{0n}) + \sum_{j=1}^{n}\eta_j\left(\frac{\partial c_{jk}}{\partial q_j}\right)_{q=q_0} + ... \end{aligned}$$

T has the terms of second order in η's and we retain only the zeroth order term. Thus we have

$$c_{jk}(q_1, q_2, ...q_n) = c_{jk}(q_{01}, q_{02}, ...q_{0n}) = T_{jk}$$

and the kinetic energy is

$$T = \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}T_{jk}\dot{\eta_j}\dot{\eta_k} \qquad (3)$$

Here $T_{jk} = T_{kj}$.Using eqns (2) and (3) the Lagrangian of the system is

$$L = \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}T_{jk}\dot{\eta_j}\dot{\eta_k} - \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}V_{jk}\eta_j\eta_k$$

The Lagrangian equations of mtion are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\eta}_j}\right) - \frac{\partial L}{\partial \eta_j} = 0$$

where j=1,2,...n.Therefore we have

$$\sum_{k=1}^{n}(T_{jk}\ddot{\eta}_k + V_{jk}\eta_k) = 0 \tag{4}$$

where j=1,2,...n.Equation (4) can be expressed in the matrix form

$$\begin{bmatrix} T_{11} & T_{12} & ... & T_{1n} \\ T_{12} & T_{22} & ... & T_{2n} \\ ... & ... & ... & ... \\ T_{1n} & T_{2n} & ... & T_{nn} \end{bmatrix} \begin{bmatrix} \ddot{\eta}_1 \\ \ddot{\eta}_2 \\ ... \\ \ddot{\eta}_n \end{bmatrix} + \begin{bmatrix} V_{11} & V_{12} & ... & V_{1n} \\ V_{12} & V_{22} & ... & V_{2n} \\ ... & ... & ... & ... \\ V_{1n} & V_{2n} & ... & V_{nn} \end{bmatrix} \begin{bmatrix} \eta_1 \\ \eta_2 \\ ... \\ \eta_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ ... \\ 0 \end{bmatrix}$$

or

$$T\ddot{\eta} + V\eta = 0$$

Here T and V represent the square matrices of order $n \times n$.Both of these matrices are real as well as symmetric.Each of the n equations (4) involves all the n variables and can be simplified by transforming them into another set of n equations each of which involves only one variable. This is possible with the help of the normal co-ordinates and normal frequencies.Let us try the oscillatory solutions of the form

$$\eta_k = A_k e^{i\omega t} \tag{5}$$

here ω is the frequency of oscillations. The real part $A_k cos\ \omega t$ corresponds to the actual motion. Using eqn (5) in (4) we get

$$\sum_{k=1}^{n}(V_{jk} - \omega^2 T_{jk})A_k = 0 \tag{6}$$

where j=1,2,...n. Thus we have

$$\begin{bmatrix} V_{11} - \omega^2 T_{11} & V_{12} - \omega^2 T_{12} & ... & V_{1n} - \omega^2 T_{1n} \\ V_{21} - \omega^2 T_{21} & V_{22} - \omega^2 T_{22} & ... & V_{2n} - \omega^2 T_{2n} \\ ... & ... & ... & ... \\ V_{n1} - \omega^2 T_{n1} & V_{n2} - \omega^2 T_{22} & ... & V_{nn} - \omega^2 T_{2n} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ ... \\ A_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ ... \\ 0 \end{bmatrix}$$

This set of equations has anon-trivial solution when

$$\begin{vmatrix} V_{11}-\omega^2T_{11} & V_{12}-\omega^2T_{12} & ... & V_{1n}-\omega^2T_{1n} \\ V_{21}-\omega^2T_{21} & V_{22}-\omega^2T_{22} & ... & V_{2n}-\omega^2T_{2n} \\ ... & ... & ... & ... \\ V_{n1}-\omega^2T_{n1} & V_{n2}-\omega^2T_{22} & ... & V_{nn}-\omega^2T_{2n} \end{vmatrix} = 0 \tag{7}$$

This equation is known as the secular or characteristic equation.

Equation (7) may also be wrtten as

$$(VA - \omega^2 TA) = 0$$

called eigen value equation. Here A is a column matrix of n components:

$$A = \begin{bmatrix} A_1 \\ A_2 \\ ... \\ A_n \end{bmatrix}$$

Expansion of this determinant of order $n \times n$ gives a polynomial of degree n in ω^2.This polynomial has roots $\omega_1^2, \omega_2^2, ...\omega_n^2$ which are the characteristic or eigen frequencies of the system. These frequencies are known as the normal frequencies of the system. The eigen values are real as they correspond to a real symmetric matrix. For each of these frequencies equation (6) can be solved to get the eigen function A_k

To distinguish between various modes,let us put the suffix l and then the eigen function is A_{kl} and the frequency eigen value isω_l. Then a general solution for the displacement η_k consists of a linear combination of all the modes ;

$$\eta_k = A_{k1}e^{i\omega_1 t} + A_{k2}e^{i\omega_2 t} + ... + A_{kn}e^{i\omega_n t} = \sum_{l=1}^{n} A_{kl}e^{i\omega_l t}$$

Each mode associated with an eigen frequency is known as the principal or natural mode.Each of the normal frequencies must be real.The eigen functions corresponding to different eigen values must be orthogonal to each other. Thus we have

$$\sum_{k=1}^{n} A_{kl}A_{kl'} = \delta_{ll'}$$

2.12 PRINCIPAL AXES TRANSFORMATION ;

We can choose a certain system of body axes with respect to which the off-diagonal elements should disappear and only the diagonal elements remain in the expression for **I**. Such axes are called principal axes of transformation. The corresponding moments of inertia are called principal moments of inertia.
if we denote this form of inertia tensor by $\mathbf{I}'$ and I_1, I_2, I_3 stand for the principal values,

$$\mathbf{I}' = \begin{bmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{bmatrix} \tag{1}$$

where we have denoted $I_{x'x'} = I_1, I_{y'y'} = I_2, I_{z'z'} = I_3$. If $\omega_x, \omega_y, \omega_z$ are the components of angular velocity and L_x, L_y, L_z are the angular momentum about the principal axes, then

$$\begin{bmatrix} L_x \\ L_y \\ L_z \end{bmatrix} = \begin{bmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{bmatrix} \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \end{bmatrix}$$

$$= \begin{bmatrix} I_1\omega_x + 0 + 0 \\ 0 + I_2\omega_y + 0 \\ 0 + 0 + I_3\omega_z \end{bmatrix}$$

or

$$\begin{aligned} L_x &= I_1\omega_x \\ L_y &= I_2\omega_y \\ L_z &= I_3\omega_x \end{aligned} \tag{2}$$

That is each of angular momentum component along a principal axis is a function of corresponding angular velocity component only related to it through the principal moment of inertia about that direction.
Thus in general if a rigid body is rotating about a principal axis, the angular momentum **L** and ω are directed along any of the principal axes and therefore

$$\mathbf{L} = \mathbf{I}\,\omega$$

where I is the scalar, the moment of inertia about this axis.The angular momentum **L** and angular velocity ω are along the principal axes and hence

$$\mathbf{L} = L_x\widehat{\mathbf{i}} + L_y\widehat{\mathbf{j}} + L_z\widehat{\mathbf{k}} = I(\omega_x\widehat{\mathbf{i}} + \omega_y\widehat{\mathbf{j}} + \omega_z\widehat{\mathbf{k}})$$

where $\widehat{\mathbf{i}}, \widehat{\mathbf{j}}, \widehat{\mathbf{k}}$ are unit vectors along X,Y,Z axes respectively.
Thus

$$L_x = I\omega_x, L_y = I\omega_y, L_z = I\omega_z \qquad (3)$$

using the symmetry property of inertia tensor we get

$$L_x = I_{xx}\omega_x + I_{xy}\omega_y + I_{xz}\omega_z = I\omega_x$$
$$L_y = I_{yx}\omega_x + I_{yy}\omega_y + I_{yz}\omega_z = I\omega_y$$
$$L_z = I_{zx}\omega_x + I_{zy}\omega_y + I_{zz}\omega_z = I\omega_z$$

or

$$\begin{bmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} - I & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} - I \end{bmatrix} \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \end{bmatrix} = 0 \qquad (4)$$

For these equations to have non-trivial solutions, the determinant of the coefficients must vanish. That is

$$\begin{vmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} - I & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} - I \end{vmatrix} = 0 \qquad (5)$$

This is called *secular* equation of inertia and its solutions the *secular values or eigenvalues*. We solve the determinantal equation which will be cubic in **I** and therefore will furnish three values for **I** through I_1, I_2, I_3 which are desired principal moments of inertia :

The direction of any one principal axis is determined by substituting for $I = I_1$ and determine the ratios for $\omega_x : \omega_y : \omega_z$ as

$$\frac{\omega_y}{\omega_x} = \lambda_1, \quad \frac{\omega_z}{\omega_x} = \lambda_2$$

Thus

$$\omega = \omega_x\widehat{\mathbf{i}} + \omega_y\widehat{\mathbf{j}} + \omega_z\widehat{\mathbf{k}}$$

and

$$\widehat{\omega} = (\widehat{\mathbf{i}} + \lambda_1\widehat{\mathbf{j}} + \lambda_2\widehat{\mathbf{k}})/\sqrt{1+\lambda_1^2+\lambda_2^2}$$

Hence we can determine the direction of ω or the direction of principal axis corresponding to I_1.Similarly we may find the direction of the corresponding pricipal axis if we substitute I_2 or I_{13}.

Example:

If the symmetry axis of the body is taken as axis of rotation and the origin of body axes lies on this then the principal axes are the symmetry axis and any two perpendicular axes normal to the symmetry axis. In the case of a sphere, every axis through the centre is symmetry axis and hence any three orthogoal axes through the centre are principal axes.

2.13 FREQUENCIES OF FREE VIBRATIONS AND NORMAL CO-ORDINATES:

The co-ordinates in the solution of equations where only one single frequency is involved in the solution are known as the normal co-ordinates.Thus the normal co-ordinates are defined as the generalized co-ordinates wher each of them execute oscillations with a single frequency.On transformation from the co-ordinates u_j into the normal co-ordinates denotted by η_k the lagrangian as well as equations of motion are changed.

Let the new co-ordinates $\eta_k$be related to the original co-ordinates as

$$u_j = \sum_k a_{jk}\eta_k$$

In the matrix form this relation can be expressed as

$$u = a\eta \tag{1}$$

Here u and η are column matrices of order $n \times 1$ and a is a square matrix of order $n \times n$.We shall express potential and kinetic energy in terms of η.The potential energy is

$$V = \frac{1}{2}\sum_{j,k} V_{jk}u_j u_k$$

$$= \frac{1}{2}\sum_{j,k} u_j V_{jk} u_k$$

In the matrix form this relation can be expressed as

$$V = \frac{1}{2} u^T V u$$

Using eqn(1) we get

$$\begin{aligned} V &= \frac{1}{2}(a\eta)^T V a\eta \\ &= \frac{1}{2}\eta^T a^T V a\eta \\ &= \frac{1}{2}\eta^T \wedge \eta \end{aligned}$$

Where

$$\begin{aligned} A^T V A = \wedge &= diagonal\ matrix \\ &= diag({\omega_1}^2, {\omega_2}^2 ... {\omega_n}^2) \end{aligned}$$

Further the above eqn is quardratic in η so that

$$V = \frac{1}{2}\sum_l \lambda_l\ {\eta_l}^2$$

$$V = \frac{1}{2}\sum_l {\omega_l}^2\ {\eta_l}^2 \tag{2}$$

The kinetic energy is given by

$$\begin{aligned} T &= \frac{1}{2}\sum_j \sum_k T_{jk}\dot{u_j}\dot{u_k} \\ &= \frac{1}{2}\sum_j \sum_k \dot{u_j} T_{jk}\dot{u_k} \\ &= \frac{1}{2}\dot{u}^T T\dot{u} \\ &= \frac{1}{2}(a\dot{\eta})^T T(a\dot{\eta}) \\ &= \frac{1}{2}\dot{\eta}^T a^T T a\dot{\eta} \\ &= \frac{1}{2}\dot{\eta}^T\dot{\eta} \end{aligned}$$

Where

$$\begin{aligned} a^T T a &= 1 \\ &= \frac{1}{2}\sum \dot{\eta_l}^2 \end{aligned} \tag{3}$$

The Lagrangian in new co-ordinates system will be

$$L = \frac{1}{2}\text{ffl}\sum_{i=1}^{n} \dot{\eta_l}^2 - \frac{1}{2}\sum_{i=1}^{n} {\omega_l}^2\ {\eta_l}^2$$

Giving

$$\frac{\partial L}{\partial \dot{\eta_l}} = \sum_{i=1}^{n} \dot{\eta_l} \quad and \quad \frac{\partial L}{\partial \eta_l} = -\sum_{i=1}^{n} {\omega_l}^2 \dot{\eta_l}$$

Now

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\eta_l}}\right) - \frac{\partial L}{\partial \eta_l} = 0$$

gives

$$\sum_{i=1}^{n}(\ddot{\eta_l} + {\omega_l}^2 \dot{\eta_l}) = 0$$

Therefore the equations of motion in new co-ordinates are

$$\begin{gathered}
\ddot{\eta_1} + {\omega_1}^2 \dot{\eta_1} = 0 \\
\ddot{\eta_2} + {\omega_2}^2 \dot{\eta_2} = 0 \\
\dots \qquad \dots \qquad \dots \\
\ddot{\eta_l} + {\omega_l}^2 \dot{\eta_l} = 0
\end{gathered} \tag{4}$$

Thus each co-ordinate executes only one single frequency oscillation and therefore η_1, η_2 *etc* are termed as normal co-ordinates.

The solution of equation

$$\ddot{\eta_l} + {\omega_l}^2 \dot{\eta_l} = 0$$

is

$$\begin{aligned}
\eta_l &= A_l cos\ \omega_l t + B_l sin\ \omega_l t && if\ {\omega_l}^2 > 0 \\
\eta_l &= A_l t + B_l t && if\ {\omega_l}^2 = 0 \\
\eta_l &= A_l e^{\omega_l t} + B_l e^{\omega_l t} && if\ {\omega_l}^2 < 0
\end{aligned} \tag{5}$$

For ${\omega_l}^2 > 0$, all co-ordinates remain finite and the equilibrium is stable.

But for ${\omega_l}^2 = 0$ and ${\omega_l}^2 < 0$, the co-ordinates become infinite and the equilibrium is unstable.

Normal modes of vibration :

Since

$$\omega = 2\pi\nu$$

The solutions become

$$\eta_l = A_l cos\ 2\pi\nu_1 t + B_l sin\ 2\pi\nu_1 t$$

$$\eta_2 = A_l cos\ 2\pi\nu_2 t + B_l sin\ 2\pi\nu_2 t$$

$$\cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots$$

$$\eta_n = A_l cos\ 2\pi\nu_n t + B_l sin\ 2\pi\nu_n t \tag{6}$$

Here A's and B's are 2n arbitrary constants determined by the initial conditions. Suppose all constants except A_1 and B_1 are zero. Then only η_1 will vary periodically with time. This situation corresponds to a normal mode of vibration. That is the system is vibrating in a normal mode.Therefore there will be n normal modes of vibration and n normal frequencies $\nu_1, \nu_2, \nu_3 ... \nu_n$ corresponding to each normal co-ordinate $\eta_1, \eta_2, \eta_3 ... \eta_n$ Now eqn(6) will take the form

$$\eta_l = A_l cos\ (\omega_l t + \delta_l)$$

Her δ_l is the phase factor.

Now the old co-ordinates are given by

$$u_j = \sum_k a_{jk} A_k cos\ (\omega_k t + \delta_k)$$

2.14 FREE VIBRATIONS OF A LINEAR TRIATOMIC MOLECULE :

We consider a linear triatomic molecule of the type YX_2 $(e.g\ CO_2)$. Y is a central atom.There exists an elastic bond between the central atom and the end atoms with force constant k. Let the mass of each end atom be m and that of cental atom be M.Let the displacement of atoms from their equilibrium position be q_1, q_2, q_3.

The kinetic energy of the system

$$T = \frac{1}{2} m (\dot{q_1}^2 + \dot{q_3}^2) + \frac{1}{2} M \dot{q_2}^2$$

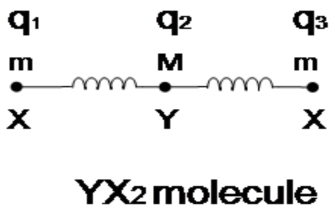


Figure 1: LINEAR TRIATOMIC MOLECULE

$$2T = \begin{bmatrix} \dot{q_1} & \dot{q_2} & \dot{q_3} \end{bmatrix} \begin{bmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{bmatrix} \begin{bmatrix} \dot{q_1} \\ \dot{q_2} \\ \dot{q_3} \end{bmatrix}$$

giving

$$T = (T_{ij}) = \begin{bmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{bmatrix}$$

The potential energy V of the system is

$$V = \frac{1}{2}\, k(q_2 - q_1)^2 + \frac{1}{2}\, k(q_3 - q_2)^2$$

$$V = \frac{1}{2}\, k({q_1}^2 + 2{q_2}^2 + {q_3}^2 - 2q_1q_2 - 2q_2q_3)$$

or

$$2V = \begin{bmatrix} q_1 & q_2 & q_3 \end{bmatrix} \begin{bmatrix} k & -k & 0 \\ -k & 2\,k & -k \\ 0 & -k & k \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix}$$

giving the matrix V as

$$V = (V_{ij}) = \begin{bmatrix} k & -k & 0 \\ -k & 2\,k & -k \\ 0 & -k & k \end{bmatrix}$$

Then write secular equation

$$|V - \omega^2 T| = 0$$

That is

$$\begin{vmatrix} k-\omega^2 m & -k & 0 \\ -k & 2\,k-\omega^2 M & -k \\ 0 & -k & k-\omega^2 m \end{vmatrix} = 0$$

After expansion we get

$$(k-\omega^2 m)[(2k-\omega^2 M)(k-\omega^2 m)-k^2]+k[-k(k-\omega^2 m)]=0$$

$$(k-\omega^2 m)[(2k-\omega^2 M)(k-\omega^2 m)-k^2]-k^2(k-\omega^2 m)=0$$

$$(k-\omega^2 m)[(2k-\omega^2 M)(k-\omega^2 m)-2k^2]=0$$

giving

$$\omega_1 = 0$$

$$\omega_2 = \sqrt{\frac{k}{m}}$$

$$\omega_3 = \sqrt{k\left(\frac{1}{m}+\frac{2}{M}\right)}$$

Now we want to express η_1, η_2 and η_3 in terms of the generalized co-ordinates q_1, q_2 and q_3 as

$$q_j = \sum_k A_{jk}\eta_k$$

giving

$$\begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \begin{bmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{bmatrix} \tag{1}$$

Our problem is to find the components of eigen vectors A_1, A_2 and A_3. For this purpose we apply the relation

$$\sum_{j=1}^{3}(V_{ij}-\omega^2 T_{ij})A_{ij}=0 \qquad\qquad i=1,2,3$$

First case :

$\omega=\omega_1=0$ and calculation of the components A_{11}, A_{21} and A_{31} of A_1. We have

$$\begin{bmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{bmatrix} \begin{bmatrix} A_{11} \\ A_{21} \\ A_{31} \end{bmatrix} = 0$$

giving

$$kA_{11} - kA_{21} = 0$$

$$-kA_{11} + 2kA_{21} - kA_{31} = 0$$

$$-kA_{21} - kA_{31} = 0$$

It gives

$$A_{11} = A_{21} = A_{31} = \alpha$$

Second case :

$\omega = \omega_2 = \sqrt{\frac{k}{m}}$ and calculation of the components A_{12}, A_{22} and A_{32} of A_2. We have

$$\begin{bmatrix} 0 & -k & 0 \\ -k & 2k - \frac{kM}{m} & -k \\ 0 & -k & 0 \end{bmatrix} \begin{bmatrix} A_{12} \\ A_{22} \\ A_{32} \end{bmatrix} = 0$$

giving

$$-kA_{22} = 0$$

$$-kA_{12} + (2k - \frac{kM}{m})A_{22} - kA_{32} = 0$$

$$-kA_{21} - kA_{31} = 0$$

It gives

$$A_{22} = 0 \qquad\qquad A_{12} = -A_{32} = \beta$$

Third case :

$\omega = \omega_3 = \sqrt{k\left(\frac{1}{m} + \frac{2}{M}\right)}$ and calculation of the components A_{13}, A_{23} and A_{33} of A_3. Then

$$\omega^2 = {\omega_3}^2 = k\left(\frac{1}{m} + \frac{2}{M}\right) = \frac{k}{m}(1 + \frac{2m}{M})$$

We have

$$\begin{bmatrix} -\frac{2mk}{M} & -km & 0 \\ -k & -\frac{kM}{m} & -k \\ 0 & -k & -\frac{2mk}{M} \end{bmatrix} \begin{bmatrix} A_{13} \\ A_{23} \\ A_{33} \end{bmatrix} = 0$$

giving

$$-\frac{2mk}{M}A_{13} - kA_{23} = 0$$

$$-kA_{13} - \frac{kM}{m}A_{23} - kA_{33} = 0$$

$$-kA_{23} - \frac{2mk}{M}A_{33} = 0$$

It leads to

$$\frac{2mk}{M}A_{13} = -kA_{23}$$

$$\frac{2m}{M}A_{13} = -A_{23} \Rightarrow A_{23} = -\frac{2m}{M}A_{13}$$

Take

$$A_{13} = \gamma$$

Then

$$A_{23} = -\frac{2m}{M}\gamma$$

Similarly

$$-kA_{23} - \frac{2mk}{M}A_{33} = 0$$

That is

$$kA_{23} + \frac{2mk}{M}A_{33} = 0$$

Which leads to

$$\frac{2mk}{M}A_{33} = -kA_{23} \Rightarrow \frac{2mk}{M}A_{33} = -k(-\frac{2m}{M}\gamma)$$

$$A_{33} = \gamma$$

It gives

$$A_{13} = A_{33} = \gamma \qquad A_{23} = -\frac{2m}{M}\gamma$$

Thus the matrix A is

$$A = A_{ij} = \begin{bmatrix} \alpha & \beta & \gamma \\ \alpha & 0 & -\frac{2m\gamma}{M} \\ \alpha & -\beta & \gamma \end{bmatrix}$$

The components can be calculated by applying

$$A^T T A = I$$

$$\begin{bmatrix} \alpha & \alpha & \alpha \\ \beta & 0 & -\beta \\ \gamma & -\frac{2m\gamma}{M} & \gamma \end{bmatrix} \begin{bmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{bmatrix} \begin{bmatrix} \alpha & \beta & \gamma \\ \alpha & 0 & -\frac{2m\gamma}{M} \\ \alpha & -\beta & \gamma \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} \alpha & \alpha & \alpha \\ \beta & 0 & -\beta \\ \gamma & -\frac{2m\gamma}{M} & \gamma \end{bmatrix} \begin{bmatrix} \alpha m & \beta m & \gamma m \\ \alpha M & 0 & -2m\gamma \\ \alpha m & -\beta m & \gamma m \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} \alpha^2(2m+M) & 0 & 0 \\ 0 & 2\beta^2 m & 0 \\ 0 & 0 & 2\gamma^2 m(1+2m/M) \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

It gives

$$\alpha^2(2m+M) = 1 \Rightarrow \alpha = \frac{1}{\sqrt{2m+M}}$$

$$2\beta^2 m = 1 \Rightarrow \beta = \frac{1}{\sqrt{2m}}$$

$$2\gamma^2 m(1+2m/M) = 1 \Rightarrow \gamma = \frac{1}{\sqrt{2m(1+2m/M)}}$$

Thus the matrix A is

$$A = A_{ij} = \begin{bmatrix} \frac{1}{\sqrt{2m+M}} & \frac{1}{\sqrt{2m}} & \frac{1}{\sqrt{2m(1+2m/M)}} \\ \frac{1}{\sqrt{2m+M}} & 0 & \frac{1}{\sqrt{2m(1+2m/M)}} \\ \frac{1}{\sqrt{2m+M}} & \frac{1}{\sqrt{2m}} & \frac{1}{\sqrt{2m(1+2m/M)}} \end{bmatrix} \tag{2}$$

The normal co-ordinates can be obtained by using equation (2) in equation (1).

Unit III - TWO - BODY CENTRAL FORCE PROBLEM AND H - J THEORY

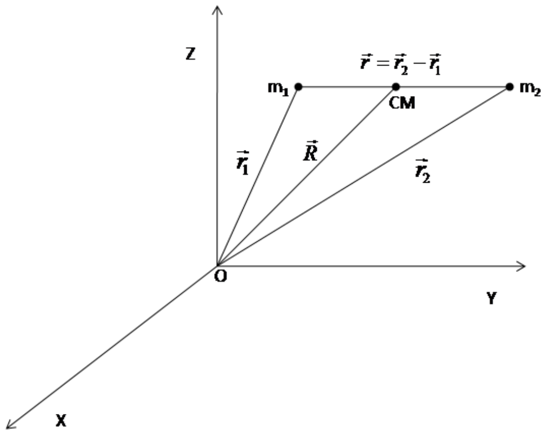
Two body central force problem: Reduction to the equivalent one body problem, the equation of motion and first integrals, classification of orbits, the virial theorem, the differential equation for the orbit, integral power law in time in the Kelper's problem, scattering in central force field;

H-J Theory: H-J equation and their solutions, use of H-J method for the solution of harmonic oscillator problem, Hamilton's principle function, Hamilton's characteristic function and their properties, Action angle variable for completely separable systems, the Kelper's problem in action angle variables

TWO - BODY CENTRAL FORCE PROBLEM :

3.1 REDUCTION TO THE EQUIVALENT ONE BODY PROBLEM:

Consider a conservative system of two mass points m_1 and m_2. Let their instantaneous position vectors in an inertial frame with origin O are $\vec{r}_1$ and $\vec{r}_2$ respectively.



Hence the vector distance of m_2 relative to m_1 is

$$\vec{r} = \vec{r}_2 - \vec{r}_1 \qquad \text{....(1)}$$

The Lagrangian for the system is

$$L = T - V$$

$$= \frac{1}{2} m_1 \dot{\vec{r}}_1^{\,2} + \frac{1}{2} m_2 \dot{\vec{r}}_2^{\,2} - V(r) \qquad \text{....(2)}$$

Let us choose the three components of the position vector of the centre of mass $\vec{R}$ and three components of the relative vector $\vec{r} = \vec{r}_2 - \vec{r}_1$ to describe the state of the system.

The position vector of the centre of mass is defined by

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \qquad \text{....(3)}$$

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 (\vec{r} + \vec{r}_1)}{m_1 + m_2}$$

$$= \frac{m_1 \vec{r}_1 + m_2 \vec{r} + m_2 \vec{r}_1}{m_1 + m_2}$$

$$= \frac{(m_1 + m_2)\vec{r}_1 + m_2\vec{r}}{m_1 + m_2}$$

$$= \vec{r}_1 + \frac{m_2\vec{r}}{m_1 + m_2}$$

$$\vec{r}_1 = \vec{R} - \frac{m_2\vec{r}}{m_1 + m_2} \qquad \text{....(4)}$$

Similarly $\vec{R} = \dfrac{m_1(\vec{r}_2 - \vec{r}) + m_2\vec{r}_2}{m_1 + m_2}$

$$= \frac{m_1\vec{r}_2 - m_1\vec{r} + m_2\vec{r}_2}{m_1 + m_2}$$

$$= \frac{(m_1 + m_2)\vec{r}_2 - m_1\vec{r}}{m_1 + m_2}$$

$$= \vec{r}_2 - \frac{m_1\vec{r}}{m_1 + m_2}$$

$$\vec{r}_2 = \vec{R} + \frac{m_1\vec{r}}{m_1 + m_2} \qquad \text{....(5)}$$

Therefore

$$\left.\begin{aligned} \dot{\vec{r}}_1 &= \dot{\vec{R}} - \frac{m_2\dot{\vec{r}}}{m_1 + m_2} \quad \text{and} \\ \dot{\vec{r}}_2 &= \dot{\vec{R}} + \frac{m_1\dot{\vec{r}}}{m_1 + m_2} \end{aligned}\right\} \qquad \text{....(6)}$$

Hence

$$L = \frac{1}{2}m_1\left[\dot{\vec{R}} - \frac{m_2\dot{\vec{r}}}{m_1 + m_2}\right]^2 + \frac{1}{2}m_2\left[\dot{\vec{R}} + \frac{m_1\dot{\vec{r}}}{m_1 + m_2}\right]^2 - V(r)$$

$$= \frac{1}{2}m_1\left[\dot{\vec{R}}^2 + \frac{m_2^{\,2}\dot{\vec{r}}^2}{(m_1 + m_2)^2} - \frac{2\dot{\vec{R}}m_2\dot{\vec{r}}}{(m_1 + m_2)}\right]$$

$$+ \frac{1}{2}m_2\left[\dot{\vec{R}}^2 + \frac{m_1^{\,2}\dot{\vec{r}}^2}{(m_1 + m_2)^2} + \frac{2\dot{\vec{R}}m_1\dot{\vec{r}}}{(m_1 + m_2)}\right] - V(r)$$

$$= \frac{1}{2}(m_1 + m_2)\dot{\vec{R}}^2 + \frac{1}{2}m_1m_2\frac{(m_1 + m_2)}{(m_1 + m_2)^2}\dot{\vec{r}}^2 - V(r)$$

$$= \frac{1}{2}(m_1 + m_2)\,\dot{\vec{R}}^2 + \frac{1}{2}\frac{m_1m_2}{(m_1 + m_2)}\dot{\vec{r}}^2 - V(r) \qquad \text{....(7)}$$

$$L = \frac{1}{2}M\dot{\vec{R}}^2 + \frac{1}{2}\mu\,\dot{\vec{r}}^2 - V(r) \qquad \text{....(8)}$$

Where $M = m_1 + m_2$ and $\mu = \frac{m_1\ m_2}{m_1 + m_2}$

Lagrangian equations of motion in terms of the two variables $\vec{R}$ and $\vec{r}$ will be

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\vec{R}}}\right) - \frac{\partial L}{\partial \vec{R}} = 0 \qquad \text{….(9)}$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\vec{r}}}\right) - \frac{\partial L}{\partial \vec{r}} = 0 \qquad \text{….(10)}$$

$$\frac{\partial L}{\partial \dot{\vec{R}}} = M\dot{\vec{R}} \text{ and } \frac{\partial L}{\partial \vec{R}} = 0$$

$$\frac{\partial L}{\partial \dot{\vec{r}}} = \mu\dot{\vec{r}} - \frac{\partial V}{\partial r}$$

Hence equations (9) and (10) become

$$\frac{d}{dt}\left(M\,\dot{\vec{R}}\right) = 0 \qquad \text{....(11)}$$

$$\frac{d}{dt}\left(\mu\dot{\vec{r}}\right) + \frac{\partial V}{\partial r} = 0 \qquad \text{....(12)}$$

Equation (11) giving $M\,\dot{\vec{R}} =$ constant

(or) $\dot{\vec{R}}$ = constant

That is velocity with which the centre of mass moves is constant.

Equation (12) giving $\mu\,\ddot{\vec{r}} = -\frac{\partial V}{\partial r} = f(r)$

representing equation of motion for the system under consideration. Consequently we can ignore the first term in equation (8) and write

$$L = \frac{1}{2}\mu\,\dot{\vec{r}}^{\,2} - V(r) \qquad \text{....(13)}$$

which is effective in describing the motion of the components of r. But L is the same as a single particle of mass μ moving at a distance r from a fixed centre of force which gives rise to the potential energy V(r). Thus two body problem can be reduced to the equivalent one body problem.

3.2 EQUATIONS OF MOTION AND FIRST INTEGRALS:

Let us describe the position of the particle in the plane poloar co-ordinates r and θ

$$T = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2\right)$$

$$V = V(r)$$

The Lagrangian $L = T - V$

$$= \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2\right) - V(r)$$

As θ is cyclic coordinate so that its conjugate angular momentum P_θ given by

$$P_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta} = l$$

$$\dot{P}_\theta = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) = \frac{d}{dt}\left(mr^2\dot{\theta}\right) = 0 \qquad \text{....(1)}$$

Integrating, $mr^2\dot{\theta} = \text{constant} = l$

$l \rightarrow$ **first integral** and represents the magnitude of angular momentum.

$$\frac{d}{dt}\left(mr^2\dot{\theta}\right) = 0$$

$$\frac{d}{dt}\left(r^2\dot{\theta}\right) = 0$$

$$\frac{d}{dt}\left(\frac{1}{2}r^2\dot{\theta}\right) = 0$$

$$\frac{1}{2}r^2\dot{\theta} = \text{constant} \qquad \text{....(2)}$$

ie, Areal velocity = constant

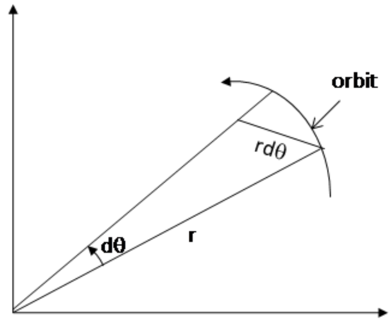
The rate at which the area swept out by the radius vector is constant which is Kepler's second law of planetory motion.

Suppose dA is the area swept out by the radius vector in time dt.

Then $dA = \frac{1}{2}r\left(rd\theta\right)$

$$= \frac{1}{2}r^2\, d\theta$$

$$\frac{dA}{dt} = \frac{1}{2}r^2\frac{d\theta}{dt} = \frac{1}{2}r^2\dot{\theta}$$



Therefore from equation (2), we write

$$\frac{1}{2}r^2\dot{\theta} = \text{constant (or)}$$

$$\frac{dA}{dt} = \text{constant} \qquad \text{....(3)}$$

Here we have two Lagrangian equations of motion. ie,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}}\right)-\frac{\partial L}{\partial r}=0 \qquad \text{....(4)}$$

and $$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right)-\frac{\partial L}{\partial \theta}=0 \qquad \text{....(5)}$$

We have $$\frac{\partial L}{\partial \dot{r}}=m\dot{r} \ and \ \frac{\partial L}{\partial r}=m\dot{r}\theta^2-\frac{dV}{dr}$$

$$\frac{\partial \mathrm{L}}{\partial \dot{\theta}}=\mathrm{mr}^2\dot{\theta} \text{ and } \frac{\partial \mathrm{L}}{\partial \theta}=0$$

Now equations (4) and (5) become

$$\frac{d}{dt}(m\dot{r})-\left(mr\dot{\theta}^2-\frac{dV}{dr}\right)=0 \qquad \text{....(6)}$$

And $$\frac{d}{dt}\left(mr^2\dot{\theta}\right)=0 \qquad \text{....(7)}$$

Equations (6) and (7) are the equations of motion

(i) Expression for r(t) and θ (t):

From equation (6) we write

$$m\ddot{r}-mr\dot{\theta}^2=-\frac{dV}{dr}$$

putting $$\dot{\theta}=\frac{l}{mr^2} we \ \ get$$

$$m\ddot{r}-mr\left(\frac{l}{mr^2}\right)^2=-\frac{dV}{dr}$$

$$m\ddot{r}-\frac{l^2}{mr^3}=-\frac{dV}{dr}$$

$$m\ddot{r}=-\frac{d}{dr}\left[V+\frac{l^2}{2mr^2}\right]$$

$$m\ddot{r}\ \dot{r}=-\frac{d}{dr}\left[V+\frac{l}{2mr^2}\right]\dot{r}$$

(or) $$\frac{d}{dt}\left(\frac{1}{2}m\dot{r}^2\right)=-\frac{d}{dr}\left[\ \mathrm{V}+\frac{l^2}{2mr^2}\right]\frac{dr}{dt}$$

$$=-\frac{d}{dt}\left[V+\frac{l^2}{2mr^2}\right]$$

So that

$$\frac{d}{dt}\left[\frac{1}{2}m\dot{r}^2+\frac{l^2}{2mr^2}+V(r)\right]=0$$

(or) $$\frac{1}{2}m\dot{r}^2+\frac{l^2}{2mr^2}+V(r) = \text{constant}$$

putting $l=\mathrm{mr}^2\dot{\theta}$, then

$$\begin{aligned}\frac{1}{2}m\dot{r}^2+\frac{l^2}{2mr^2}+V(r) &=\frac{1}{2}m\dot{r}^2+\frac{m^2r^4\dot{\theta}^2}{2mr^2}+V(r)\\ &=\frac{1}{2}m\dot{r}^2+\frac{1}{2}mr^2\dot{\theta}^2+V(r)\\ &=\frac{1}{2}m\left[\dot{r}^2+r^2\dot{\theta}^2\right]+V(r)\\ &=\mathrm{T}+\mathrm{V}=\mathrm{E}\end{aligned}$$

Thus we write

$$\frac{1}{2}m\dot{r}^2+\frac{l^2}{2mr^2}+V(r)=E \qquad \text{….(8)}$$

E is a constant of motion. This is another **first integral** of motion.

$$\dot{r}=\left[\frac{2}{m}\left(E-V-\frac{l^2}{2mr^2}\right)\right]^{\frac{1}{2}}=\frac{dr}{dt}$$

$$dt=\frac{dr}{\left[\frac{2}{m}\left(E-V-\frac{l^2}{2mr^2}\right)\right]^{\frac{1}{2}}}$$

On integration we get

$$t=\int_{r_0}^{r}\frac{dr}{\left[\frac{2}{m}\left(E-V-\frac{l^2}{2mr^2}\right)\right]^{\frac{1}{2}}} \qquad \text{….(9)}$$

where $r=r_o$ at $t=0$.

This equation gives r as a function of time. ie r (t).

We have $\dot{\theta} =\frac{l}{mr^2}$

$$\frac{d\theta}{dt} = \frac{l}{mr^2}$$

$$\theta = \frac{l}{m}\int_o^t \frac{dt}{r^2(t)} + \theta_o \qquad \text{....(10)}$$

Thus integration of equations (9) and (10) provides us r (t) and θ (t). Then we can locate the position of the particle on the path at any time t and the solution.

3.3 CLASSIFICATION OF ORBITS:

We have already derived

$$m\ddot{r} = -\frac{d}{dr}\left(V + \frac{l^2}{2mr^2}\right)$$

$$= -\frac{dV}{dr} + \frac{l^2}{mr^3}$$

$$= f(r) + \frac{l^2}{mr^3}$$

$= f'$ = effective force.

$$f' = f(r) + \frac{\left(mr^2\dot{\theta}\right)^2}{mr^3}$$

$$= f(r) + mr\dot{\theta}^2$$

$$= f(r) + \frac{m\left(r\dot{\theta}\right)^2}{r}$$

$$= f(r) + \frac{m\mathrm{v}_\theta^{\;2}}{r}$$

= Central force + Centrifugal force.

Thus equation takes the form

$$m\ddot{r} = f'$$

It is an equation of motion for a particle subjected to actual force *f* (r) and pseudo centrifugal force $\frac{l^2}{\mathrm{mr}^3}$. Also $f' = -\frac{dV'}{dr}$

V ′ = effective potential energy

$$V' = -\int f'\,dr = -\int\left[f(r) + \frac{l^2}{mr^3}\right]dr$$

$$= -\int f(r)\,dr + \frac{l^2}{2mr^2}$$

$$= V(r)+\frac{l^2}{2mr^2}$$

The second term is the potential energy related to the centrifugal force.

(i) Orbits under inverse square law of force :

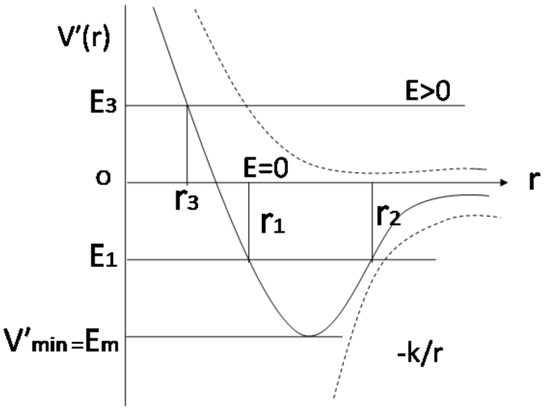
The effective potential energy

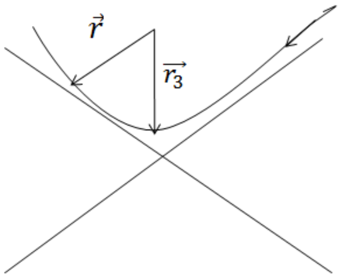
$$V'(r) = -\int \frac{k}{r^2}dr+\frac{l^2}{2mr^2}$$

$$= \frac{\mathrm{k}}{\mathrm{r}}+\frac{l^2}{2\mathrm{mr}^2}$$

as a function of r has been plotted.

(ii) Motion with different values of k:





Case (i) : E > 0:

There is a minimum radial distance r_3 but no maximum. The motion is unbounded. The particle comes in from r =∞ to a turning point and travels out to infinity again; Thus the motion is not periodic and with a single turning point.

Case (ii) : $0 > E > V'_{min} = E_m$:

corresponds to energy E_1

The radial motion is confined to the values $r = r_1 = r_{min}$ and $r = r_2 = r_{max}$

r_1 and r_2 are the turning points.

$$E_1 = \frac{1}{2}m\dot{r}^2+\frac{l^2}{2mr^2}+V(r)$$

$$= \frac{1}{2} m\dot{r}^2 + V'(r)$$

$$E_1 - V'(r) = \frac{1}{2} m\dot{r}^2 = T$$

Though $\dot{r} = 0$ at these points $\dot{\theta} \neq 0$

The particle will not be at rest at these points. The motion is confined between the areas of two circles of radii r_1 and r_2.

A possible shape for an attractive inverse square law of force is an ellipse with the focus at the centre.

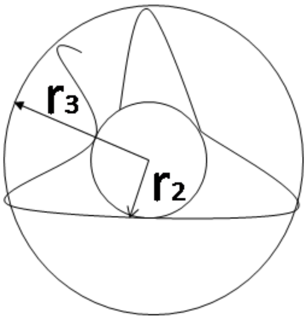
When r varies from r_1 to r_2 and back, the radius vector turns through an angle θ obtained by

$$\theta = \int \frac{l}{mr^2} dt + \theta_0$$

$$dt = \frac{dr}{\left[\frac{2}{m}\left(E - v - \frac{l^2}{2mr^2}\right)\right]^{\frac{1}{2}}}$$

$$\theta = \int \frac{\left(\frac{l}{r^2}\right) dr}{m\left[\frac{2}{m}\left(E - V - \frac{l^2}{2mr^2}\right)\right]^{\frac{1}{2}}}$$

$$= \int \frac{\left(\frac{l}{r^2}\right) dr}{\left[2m(E - V) - \frac{l^2}{r^2}\right]^{\frac{1}{2}}} + \theta_o$$



When $\theta = \frac{2\pi m}{n}$, the path is a closed orbit. When θ is not a rational fraction of 2π, the path has the shape of a rosette. Such an orbital motion is processing motion.

Case (iii) : $E = E_m = V'_{\min}$: $\dot{r} = 0$ and $\dot{\theta} = \text{finite},$ the particle moves in a circle.

Energy E_m corresponds to the minimum value of $V'(r)$

$$\frac{dV'}{dr} = \frac{d}{dr}\left[\frac{-k}{r} + \frac{l^2}{2mr^2}\right]$$

$$= \frac{k}{r^2} - \frac{l^2}{mr^3}$$

Putting r = r_o for which V′(r) is minimum.

$$\frac{k}{r_o^{\,2}} - \frac{l^2}{mr_o^{\,3}} = o \Rightarrow \frac{k}{r_o^{\,2}} = \frac{l^2}{mr_o^{\,3}}$$

$$r_o = \frac{l^2}{mk}$$

$$E_4 = V'(r)|_{\min}$$

$$= -\frac{k}{r_o} + \frac{l^2}{2mr_o^{\,2}}$$

$$= -\frac{mk^2}{l^2} + \frac{1}{2}\frac{mk^2}{l^2} = -\frac{1}{2}\,\frac{mk^2}{l^2}$$

In this case two bounds coincide

$r_3 = r_2 = r_o$

Orbit is a circle of radius $\frac{l^2}{mk}$.

Case (iv) : $E < V'_{\min}$: $\dot{r}$ will be imaginary and therefore no physically meaningful motion is possible.

(iii) Stability of orbits and conditions for closure:

(a) Stability:

The condition of stability in radial motion is given by the existence of local minimum in V′(r), the effective potential. That is we require that

$$\frac{\partial^2 V'(r)}{\partial r^2} > 0 \qquad \text{at } r = r_o$$

given by $$\frac{\partial^2 V'(r)}{\partial r} = 0$$

For any central force, the potential energy function is given by,

$$V(r) = -kr^{n+1} \text{ (for bounded motion)}$$

$$V'(r) = -k\,r^{n+1} + \frac{l^2}{2mr^2}$$

$$\frac{\partial V'(r)}{\partial r} = -k(n+1)r^{n} - \frac{l^2}{mr^3}$$

$$\left.\frac{\partial V'(r)}{\partial r}\right|_{r=r_0} = -k(n+1)r_0^{\,n} - \frac{l^2}{mr_0^{\,3}} = 0$$

$$k\,(n+1)r_0^{\,n} = -\frac{l^2}{mr_0^{\,3}}$$

$$k\,(n+1) \quad = -\frac{l^2 r_0^{\,-(3+n)}}{m}$$

$$\left.\frac{\partial^2 V'(r)}{\partial r^2}\right|_{r=r_0} = -\,kn(n+1)\,r_0^{\,n-1} + \frac{3l^2}{mr_0^{\,4}}$$

$$= n\frac{l^2}{m} r_o^{\,-(3+n)} r_o^{\,n-1} + \frac{3l^2}{m} r_o^{\,-4}$$

$$= n\frac{l^2}{m} r_0^{\,-4} + \frac{3l^2}{m} r_0^{\,-4}$$

$$= \frac{l^2}{m}(n+3)r_0^{\,-4}$$

Which is positive if $n > -3$

Therefore any circular orbit with $r = r_0$ under any central force can satisfy the stability condition if $n > -3$.

(b) Conditions for closure:

(iii) All bound orbits are closed only if for the inverse square law of force of electrostatic attraction or gravitational type and for Hooke's type linear law of force.

(iv) The condition for bound motion is that there is a bounded domain of r in which $V(r) \le E$. The condition for stability of circular orbits is $n > -3$ where $f(r) \propto r^n$. That is for $n = -1$ and $n = -2$ only closed orbits exist.

3.4 VIRIAL THEROEM:

We consider a system of mass points with position vectors $\boldsymbol{r}_i$ and applied forces $\boldsymbol{F}_i$.

Fundamental equations of motion will be

$$\dot{\boldsymbol{p}}_i \quad = \boldsymbol{F}_i \qquad \text{….(1)}$$

Let us write a quantity

$$G \quad = \sum \boldsymbol{p}_i \,.\boldsymbol{r}_i$$

$$\frac{dG}{dt} \quad = \sum \boldsymbol{p}_i.\dot{\boldsymbol{r}}_i + \sum \dot{\boldsymbol{p}}_i.\boldsymbol{r}_i \qquad \text{….(2)}$$

But $$\sum \dot{\mathbf{r}}_i.\mathbf{p}_i = \sum m_i\, \dot{\mathbf{r}}_i.\mathbf{r}_i$$

$$= \sum m_i\, \mathrm{v}_i^2$$

$$= 2\mathrm{T}$$

and $$\sum \dot{\mathbf{p}}_i.\mathbf{r}_i = \sum \mathbf{F}_i.\mathbf{r}_i$$

So that $$\frac{\partial G}{\partial t} = 2T + \sum \mathbf{F}_i.\mathbf{r}_i$$

The time average over a time interval τ will be

$$\frac{1}{\tau}\int_0^z \frac{dG}{dt}dt = \overline{2T} + \sum \overline{\mathbf{F}_i.\,\mathbf{r}_i}$$

(or) $$\overline{2T} + + \sum \overline{\mathbf{F}_i.\,\mathbf{r}_i} = \overline{\frac{dG}{dt}}$$

$$= \frac{1}{\tau}\left[G(\tau) - G(0)\right] \qquad ....(3)$$

If the motion is periodic and τ is its period then G(τ) = G(0) and hence the RHS of equation (3) is zero. If the motion is not periods but there is an upper bound to G and the co-ordinates and velocities remain finite, then τ sufficiently large, RHS again be approximated to zero. Hence

$$\overline{2T} + \sum \overline{\mathbf{F}_i.\,\mathbf{r}_i} = 0$$

$$\overline{T} = -\frac{1}{2} \sum \overline{\mathbf{F}_i.\,\mathbf{r}_i} \qquad ....(4)$$

Equation (4) is known as the virial theorem and RHS is called virial of claussius.

This theorem is used in kinetic theory of gases to prove Boyle's law and to obtain equation of state for imperfect gases etc.

It the forces are derivable from a potential, then the theorem becomes.

$$\overline{T} = \frac{1}{2}\overline{\sum \nabla_i \mathbf{V}\, \mathbf{r}_i}$$

$$= -\frac{1}{2}\overline{\left[-\frac{\partial \mathbf{V}}{\partial \mathbf{r}}\right]_i \hat{\mathbf{r}}.\mathbf{r}}$$

$$= \frac{1}{2}\overline{\frac{\partial V}{\partial r}}\, r$$

If the potential energy is

$$\overline{V} = k\, r^{\,n+1}$$

$$\frac{\partial \overline{V}}{\partial r} = (n+1)\, k r^n$$

Then $$\overline{T} = \frac{1}{2}(n+1) k\, r^n\, r = \frac{1}{2}(n+1) k\, r^{n+1} = \frac{1}{2}(n+1)\overline{V}$$

For inverse square law n = –2, hence

$$\overline{T} = -\frac{1}{2}\overline{V} \Rightarrow 2\overline{T} + \overline{V} = 0$$

3.5 DIFFERENTIAL EQUATION OF THE ORBIT:

Here we wish the obtain an equation that may provide a relation between r and θ.

i.e r = r(θ)

Such an equation will be the equation of the orbit.

It is convenient to introduce the new variable

$$u = \frac{1}{r} \ (or) \ r = \frac{1}{u}$$

so that $$\dot{r} = -\frac{1}{u^2}\frac{du}{dt} = -\frac{1}{u^2}\frac{du}{d\theta}\frac{d\theta}{dt}$$

$$= -r^2 \frac{du}{d\theta}\dot{\theta}$$

$$\dot{r} = -\frac{l}{m}\frac{du}{d\theta} \qquad \left[\text{since } \dot{\theta} = \frac{l}{mr^2}\right]$$

And $$\ddot{r} = -\frac{l}{m}\frac{d}{dt}\left(\frac{du}{d\theta}\right)$$

$$= -\frac{l}{m}\frac{d}{d\theta}\left(\frac{du}{d\theta}\right)\frac{d\theta}{dt}$$

$$= -\frac{l}{m}\frac{d^2u}{d\theta^2}\dot{\theta}$$

$$= -\frac{l^2u^2}{m^2}\frac{d^2u}{d\theta^2}$$

We know that the equation of motion of a particle is

$$m\ddot{r} = m r \dot{\theta}^2 - \frac{dV}{dr}$$

$$= \frac{l^2}{mr^3} + f(r)$$

$$m\left[-\frac{l^2u^2}{m^2}\frac{d^2u}{d\theta^2}\right]=\frac{l^2}{m}u^3+f(\frac{1}{u})$$

$$\frac{d^2u}{d\theta^2}=\frac{l^2}{m}u^3\left[\frac{-m}{l^2u^2}\right]+f\left(\frac{1}{u}\right)\left[\frac{-m}{l^2u^2}\right]$$

$$=-u-\frac{m}{l^2u^2}f\left(\frac{1}{u}\right)$$

Which is the differential equation of the orbit.

In case $l = 0$, equation is absurd but from

$$l=\mathrm{m}r^2\dot{\theta}$$

$$\mathrm{m}r^2\dot{\theta}=0$$

$$\dot{\theta}=0$$

$$\theta=\text{constant}$$

giving a straight line through the origin.

3.6 INTEGRABLE POWER LAW IN TIME IN KEPLER'S PROBLEM:

The inverse square law of force is most important of all the central force laws. It results the deduction of Kepler's laws.

1. All the planets move in an elliptical orbit with sun at one of its foci.
2. The radius vector connecting the sun and the planet sweeps at equal areas is equal intervals of time. ie, areal velocity is constant.
3. The square of the period of revolution of any planet about the sun is proportional to the cube of the semi major axis.

(i) Deduction of first law:

The central force varies inversely as the square of the distance. That is

$$f(r)=\frac{-k}{r^2} \qquad \text{k is a constant}$$

The corresponding potential energy will be

$$V(r)=\frac{-k}{r}$$

Equation of the orbit is $$\frac{d^2u}{d\theta^2}+u=\frac{-m}{l^2u^2}f\left(\frac{1}{u}\right)$$

putting $f(r)=f\left(\frac{1}{u}\right)=\frac{-k}{r^2}=-ku^2$ we get

$$\frac{d^2u}{d\theta^2}+u=\frac{mk}{l^2} \qquad \text{....(1)}$$

Let us put $y = u - \frac{mk}{l^2}$ so that

$$\frac{d^2y}{d\theta^2} = \frac{d^2u}{d\theta^2}$$

Equation of the orbit then becomes

$$\frac{d^2u}{d\theta^2}+y=0$$

The general solution of this equation is

$$y = u'\cos(\theta-\theta')$$

(or)

$$u=\frac{mk}{l^2}+u'\cos(\theta-\theta')$$

$$u=\frac{1}{r}=\frac{mk}{l^2}+u'\cos(\theta-\theta')$$

Where u' and θ' are constants.

If we orient our co-ordinate system so that $\theta'=0$, then

$$\frac{1}{r}=\frac{mk}{l^2}+u'\cos\theta$$

$$=\frac{mk}{l^2}\left[1+\frac{u'l^2}{mk}\cos\theta\right]$$

(or)

$$r=\frac{\frac{l^2}{mk}}{\left[1+\frac{u'l^2}{mk}\cos\theta\right]} \qquad \text{....(2)}$$

Thus θ' is a turning point.

We show that equation (2) represents a conic section, coincident with Kepler's first law of planetary motion. That is the orbits are conic sections with the centre at one of the foci.

We define the conic section as a curve for which the distance from a fixed point to that from a fixed line is a constant. That is

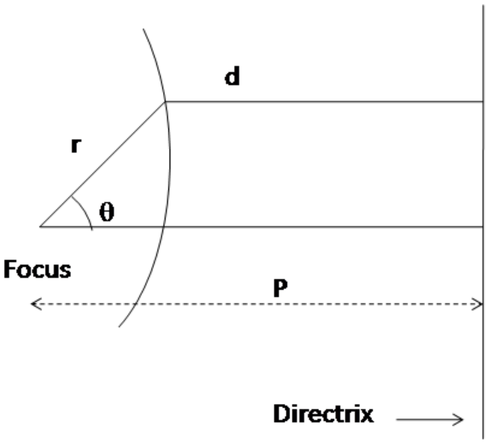
$$\frac{r}{d}=\text{constant} = \varepsilon$$

ε = eccentricity

From figure, We see that

$$P = d + r\cos\theta$$

Let $p = \varepsilon P \Rightarrow P = \dfrac{p}{\varepsilon}$



$$\frac{p}{\varepsilon} = d + r\cos\theta$$

$$= \frac{r}{\varepsilon} + r\cos\theta$$

$$p = r + r\,\varepsilon\cos\theta$$

$$= r(1+\varepsilon\cos\theta)$$

$$r = \frac{p}{1+\varepsilon\cos\theta} \qquad \text{....(3)}$$

Which represents a conic section.

Equation (2) is of the form of equation (3) orbit under an inverse square force is always a conic section.

Comparing equations (2) and (3), we get

$$p = \frac{l^2}{mk} \text{ and } \varepsilon = \frac{u'l^2}{mk}$$

Further from $\varepsilon = \dfrac{r}{d}$, we must $\varepsilon \geq 0$ or r must be positive.

(ii) To explore the shapes of orbit:

Equation (2) is the equation of the conic and consequently it should have been possible to explore the shape of orbits using this equation. Here ε involves one unknown constant u′. Hence we express ε in terms of known constants. Then we put the value of ε in one equation of the conic which yield the desired information about the shape of the conic.

Already we have E = $\dfrac{1}{2}m\dot{r}^2 + \dfrac{l^2}{2mr^2} + V(r)$

Here V (r) = $\dfrac{-k}{r}$

$$E = \frac{1}{2}m\dot{r}^2 + \frac{l^2}{2mr^2} - \frac{k}{r} \qquad \text{....(4)}$$

Suppose we take the turning point at which r is minimum say r_{min}. Then $\dot{r} = 0$. Now equation (4) becomes.

$$E = \frac{l^2}{2mr_{\min}^2} - \frac{k}{r_{\min}} \qquad ....(5)$$

From equation (3) $r_{\min} = \frac{p}{1+\varepsilon} = \frac{l^2}{mk(1+\varepsilon)}$

Now equation (5) becomes

$$E = \frac{l^2}{2m}\left[\frac{mk(1+\varepsilon)}{l^2}\right]^2 - k\left[\frac{mk(1+\varepsilon)}{l^2}\right]$$

$$= \frac{mk^2}{2l^2}(1+\varepsilon)^2 - \frac{mk^2}{l^2}(1+\varepsilon)$$

$$= \frac{mk^2}{2l^2}(1+\varepsilon)\,[1+\varepsilon-2]$$

$$= \frac{mk^2}{2l^2}(1+\varepsilon)(\varepsilon-1)$$

$$= \frac{mk^2}{2l^2}(\varepsilon^2-1)$$

giving $\varepsilon^2 - 1 = \frac{2l^2E}{mk^2} \Rightarrow \varepsilon^2 = 1 + \frac{2El^2}{mk^2}$

such that $\varepsilon = \left[1 + \frac{2El^2}{mk^2}\right]^{\frac{1}{2}}$ ….(6)

now ε is a known one. After putting the value of ε and p in equation (3) we get

$$r = \frac{\frac{l^2}{mk}}{1 + \left[1 + \frac{2El^2}{mk^2}\right]^{1/2} \cos\theta} \qquad ….(7)$$

If E > 0 giving $\varepsilon > 1$ – conic is hyperbola

If E = 0 giving $\varepsilon = 1$ – conic is parabola

If E < 0 giving $\varepsilon < 1$ – conic is ellipse

If E = $\frac{-mk^2}{2l^2}$ giving $\varepsilon = 0$ – conic is circle.

(iii) Case of elliptic orbits:

Relation between energy and semi major axis:

In the case of elliptic orbits, semi major axis is given by:-

when $\theta = 0$, $r = r_1$ = perihelion

Then $r_1 = \frac{p}{1+\varepsilon}$

$r = r_2 =$ aphelion

Then $r_2 = \frac{p}{1+\varepsilon}$

a is the sum of one half of perihelion r_1 and aphelion r_2

$$a = \frac{r_1 + r_2}{2}$$

$$= \frac{p}{2}\left[\frac{1}{1+\varepsilon} + \frac{1}{1-\varepsilon}\right]$$

$$= \frac{p}{2}\left[\frac{1-\varepsilon+1+\varepsilon}{1-\varepsilon^2}\right]$$

$$= \frac{p}{\left(1-\varepsilon^2\right)}$$

But $p = \frac{l^2}{mk}$

Hence $a = \frac{l^2}{mk\left(1-\varepsilon^2\right)}$ ….(8)

(or) $1 - \varepsilon^2 = \frac{l^2}{mka}$

Now $E = \frac{mk^2}{2l^2}\left(\varepsilon^2 - 1\right)$ becomes

$$= \frac{mk^2}{2l^2}\left[\frac{-l^2}{mka}\right] \qquad [From\,equation\ (8)]$$

$$E = \frac{-k}{2a}$$

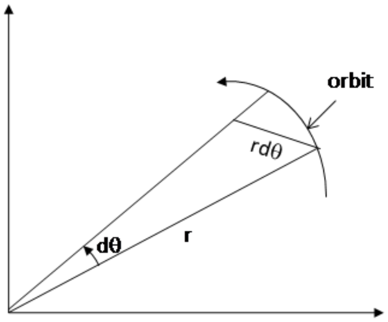
which shows that all ellipses with the same major axis have the same energy.

(iv) Deduction of Kepler's second law:

We know

$$\dot{p}_\theta = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) = \frac{d}{dt}\left(mr^2\dot{\theta}\right) = 0$$

$$\frac{d}{dt}\left(r^2\dot{\theta}\right) = 0$$



$$\frac{d}{dt}\left(\frac{1}{2}r^2\dot{\theta}\right)=0$$

$$\frac{1}{2}r^2\dot{\theta}=\text{constant}$$

ie Areal velocity = constant

The area swept out by radius vector per unit time = constant.

If r describes an angle dθ in time dt, the area swept out by r in time dt is

$$dA=\frac{1}{2}r(rd\theta)=\frac{1}{2}r^2d\theta$$

$$\frac{dA}{dt}=\frac{1}{2}r^2\frac{d\theta}{dt}$$

$$=\frac{1}{2}r^2\frac{d\theta}{dt}$$

$$=\frac{1}{2}r^2\dot{\theta}=\text{constant}$$

which is Kepler's second law.

(v) Deduction of third law : (period of elliptic motion τ)

τ is the ratio of the total area of the ellipse to the rate at which the area is swept out. Suppose dA is the area swept out by radius vector is time dt, then the rate will be dA/dt.

Hence $$\tau=\frac{area}{dA/dt}$$

Area of the ellipse = π a b

And $$\frac{dA}{dt}=\frac{1}{2}r^2\dot{\theta}=\frac{l}{2m}$$

$$\therefore\tau=\frac{\pi ab}{l/2m}=\frac{2\pi mab}{l}$$

putting $$b=a\left(1-\varepsilon^2\right)^{\frac{1}{2}}$$

Then $$\tau=\frac{2\pi ma^2}{l}\left(1-\varepsilon^2\right)^{\frac{1}{2}}$$

$$\tau^2=\frac{4\pi^2m^2a^4}{l^2}\left(1-\varepsilon^2\right)$$

$$=\frac{4\pi^2m^2a^4}{l^2}\frac{l^2}{mka}$$

$$= \left(\frac{4\pi^2 m}{k}\right) a^3$$

$$\tau^2 \alpha\ a^3$$

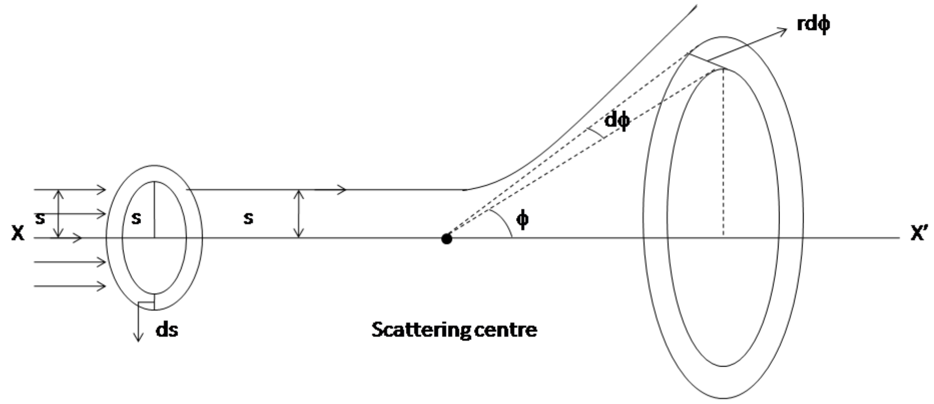
Which is Kepler's third law. It states that the square of period is proportional to cube of the semi-major axis.

3.7 SCATTERING IN CENTRAL FORCE FIELD:

(i) Rutherford scattering:

Assumptions:

1. The heavy nucleus and the positively charged particle to be point nucleus so that their dimensions are not taken into account.
2. The nucleus of the atom is so heavy that it is at rest during collision.
3. The mass of the positively charged particle may be taken as constant because the velocity is very small compared with the velocity of light.



Let a positively charged particle of charge z′e approach a heavy nucleus N of charge ze. There will be a force of repulsion between them. The force increases as the particle gets closer to the nucleus. The positively charged particle of initial velocity v_o is repelled by the heavy nucleus and changes from a straight line to a hyperbola PAQ having one focus at N. The asymptotes PO and OQ give the initial and final directions of the particle. As the initial and final directions are not the same, the particle is said to be scattered.

The perpendicular distance of PO from N =MN = s. This is the shortest distance from the nucleus to the initial direction called impact parameter.

The equation of the orbit

$$\frac{1}{r}=\frac{1}{p}\left[1+\varepsilon\cos(\theta-\theta')\right]$$

$$p=\frac{l^2}{mk} \qquad \text{and} \qquad \varepsilon=\left[1+\frac{2El^2}{mk^2}\right]^{1/2}$$

In this case k=-zz′e^2 and hence

$$\frac{1}{p}=-\frac{mzz'e^2}{l^2}$$

$$\frac{1}{r}=-\frac{mzz'e^2}{l^2}\left[1+\varepsilon\cos(\theta-\theta')\right]$$

If the initial line is set such that $\theta'=0$, then

$$\frac{1}{r}=-\frac{mzz'e^2}{l^2}\left[1+\varepsilon\cos\theta\right]$$

$$\varepsilon=\left[1+\frac{2El^2}{mk^2}\right]^{1/2}$$

$$=\left[1+\frac{2El^2}{m(-zz'e^2)^2}\right]^{1/2}$$

$$=\left[1+\frac{2El^2}{mz^2z'^2e^4}\right]^{1/2}$$

If the initial velocity is v$_o$, then

$$E=\frac{1}{2}m\mathrm{v}_o{}^2 \quad \textit{and} \quad m\mathrm{v}_o=\sqrt{2mE}$$

$$l=m\mathrm{v}_o s \quad \textit{and} \quad m\mathrm{v}_o=\frac{l}{s}$$

According to principle of conservation of angular momentum

$$m\mathrm{v}_o s=mr^2\dot{\theta}=l$$

$$m\mathrm{v}_o=\frac{l}{s}$$

$$\frac{l}{\mathrm{s}}=\sqrt{2\mathrm{mE}}$$

$$l=s\sqrt{2mE}$$

$$\varepsilon=\left[1+\frac{2E\left(s\sqrt{2mE}\right)^2}{mz^2\,z'^2\,e^4}\right]^{1/2}$$

$$=\left[1+\left(\frac{2Es}{zz'e^2}\right)^2\right]^{1/2}$$

From this equation it is clear that $\varepsilon>1$.

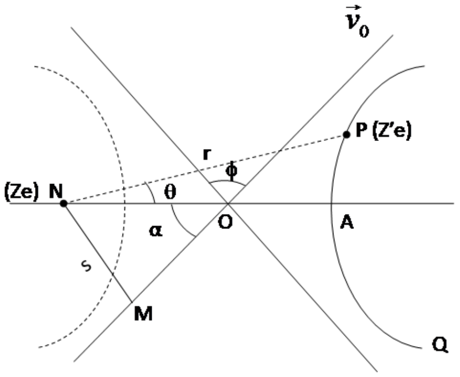
$$\therefore\frac{1}{r}=-\frac{mzz'e^2}{l^2}\left[1+\varepsilon\cos\theta\right]$$

represents a hyperbola.

(ii) Angle of scattering:

The angle between initial and final directions of the positively charged particle is called angle of scattering. That is the angle between the asymptotes is called angle of scattering. Here ϕ is the angle of scattering.

The asymptotic directions are those for which r is infinite and $\theta\rightarrow\infty$,



P=positively charged nucleus (Z'e)
N=heavy nucleus (Ze)
ϕ=angle of scattering

$$1+\varepsilon\cos\alpha=0$$

$$\cos\alpha=-\frac{1}{\varepsilon}$$

From figure $\phi+2\alpha=\pi$

$$\alpha=\frac{\pi}{2}-\frac{\phi}{2}$$

$$\therefore\cos\left(\frac{\pi}{2}-\frac{\phi}{2}\right)=-\frac{1}{\varepsilon}$$

$$\sin\frac{\phi}{2}=-\frac{1}{\varepsilon}$$

$$\cos ec\frac{\phi}{2}=-\varepsilon$$

$$\operatorname{cosec}^2\frac{\phi}{2}=\varepsilon^2$$

$$1+\cot^2\frac{\phi}{2}=\varepsilon^2=1+\left[\frac{2Es}{zz'e^2}\right]^2$$

$$\cot^2\frac{\phi}{2}=\left[\frac{2Es}{zz'e^2}\right]^2$$

$$\cot\frac{\phi}{2}=\left[\frac{2Es}{zz'e^2}\right]$$

$$\phi=2\cot^{-1}\left[\frac{2Es}{zz'e^2}\right]$$

This equation gives ϕ in terms of impact parameter s, energy E, the charge on the nucleus ze and the charge on the particle z'e.

(v) Rutherford scattering cross section:

The scattering cross section is defined as

$$\sigma(\omega)d\omega=\frac{\text{number of particles scattered into a solid angle } d\omega \text{ per unit time}}{\text{incident intensity}}$$

dω is the element of solid angle

$\sigma(\omega)$ is the differential scattering cross section.

The incident intensity is defined as the number of particles crossing unit area normal to the incident beam in unit time.

The differential of solid angle dω in the plane whose azimuth lies between θ and θ + d θ is $d\omega=2\pi\sin\phi\, d\phi$

The scattering cross section through angle ϕ in any plane is

$$\sigma(\omega)\,d\omega=\int_o^{2\pi}\sigma(\phi)\sin\phi\, d\phi\, d\theta=2\pi\ \sigma(\phi)\sin\phi\, d\phi$$

The number of particles scattered into solid angle dω per unit time $=2\pi I\sigma(\phi)\sin\phi\, d\phi$

I is the incident intensity.

The cross section for the particles having collision parameter between s and s+ds is the area of ring of radius s and width ds so that

$$\sigma(s, ds) = 2\pi s ds$$

The number of particles lying between s and s+ds $= 2\pi \, \mathrm{I} s \, ds$

Now $2\pi \, \mathrm{I} s \, ds = -2\pi \, \mathrm{I} \, \sigma(\phi) \sin\phi \, d\phi$

The negative sign is due to the decrease in $d\phi$ as the increase in ds.

$$\sigma(\phi) = -\frac{s ds}{\sin\phi d\phi}$$

$$\cot\frac{\phi}{2} = \frac{2Es}{zz'e^2}$$

$$gives\ s = \frac{zz'e^2}{2E}\cot\frac{\phi}{2}$$

$$Then\ \ ds = -\frac{zz'e^2}{2E}\cos ec^2\frac{\phi}{2}\frac{d\phi}{2}$$

$$\therefore \sigma(\phi) = \frac{-\left(\frac{zz'e^2}{2E}\right)\cot\frac{\phi}{2}\left(\frac{-zz'e^2}{2E}\right)\cos ec^2\frac{\phi}{2}\frac{d\phi}{2}}{2\sin\frac{\phi}{2}\cos\frac{\phi}{2}d\phi}$$

$$= \frac{1}{4}\left(\frac{zz'e^2}{2E}\right)^2 \cos ec^4\frac{\phi}{2}$$

This is Rutherford scattering cross section.

The scattering cross section must be proportional to i) $\cos ec^4\frac{\phi}{2}$, ii) the square of (ze), iii) the square of (z′e) and iv) inversely proportional to square of kinetic energy (E).

HAMILTON – JACOBI THEORY

In canonical transformation, the method involves the transformation of old set of coordinates (q_k) to new set of coordinates (Q_k) which are all cyclic and hence all momenta are constants provided the Hamiltonian is conserved.

In case the Hamiltonian involves time, an alternate approach is used to a canonical transformation which leads to the new Hamiltonian $H' = 0$ so that the new coordinates and momenta Q_k and P_k are constants. This procedure is due to Jacobi which is a transformation as well as a method itself and applied when Hamiltonian involves time.

3.8. HAMILTON – JACOBI EQUATION:

If we make a canonical transformation from old set of variables (q_k, p_k) to a new net of variables (Q_k, P_k), then the new equation of motion are

$$\dot{P}_k = -\frac{\partial H'}{\partial Q_k} \text{ and } \dot{Q}_k = \frac{\partial H'}{\partial P_k} \qquad \ldots(1)$$

If we require that the transformed Hamiltonian H′ =0, then equations of motion (1) assume the form

$$\dot{P}_k = 0 \text{ and } \dot{Q}_k = 0$$

$$P_k = \text{constant and } Q_k = \text{constant} \qquad \ldots(2)$$

Thus the coordinates and momenta are constants in time and they are cyclic.

The new Hamiltonian H' is related to old Hamiltonian H by

$$H' = H + \frac{\partial F}{\partial t}$$

Which will be zero when F satisfies the relation

$$H(q_k, p_k, t) + \frac{\partial F}{\partial t} = 0 \qquad ...(3)$$

Where $H(q_k, p_k, t)$ is written for $H(q_1, q_2, ...q_n, p_1, p_2, ...p_n, t)$

We take the generating function F as a function of the old coordinate q_k , the new constant momenta P_k and time t ie, $F_2(q_k, P_k, t)$. Then

$$p_k = \frac{\partial F_2}{\partial q_k} \qquad \ldots(4)$$

Therefore
$$H(q_k, \frac{\partial F_2}{\partial q_k}, t) + \frac{\partial F_2}{\partial t} = 0 \qquad \ldots(5)$$

$$F_2 = F_2(q_k, P_k, t)$$

The total time derivative of F_2 is

$$\frac{dF_2}{dt} = \sum_{k=1}^{n} \frac{\partial F_2}{\partial q_k} \dot{q}_k + \sum_{k=1}^{n} \frac{\partial F_2}{\partial P_k} \dot{P}_k + \frac{\partial F_2}{\partial t}$$

Here $\dot{P}_k = 0, \frac{\partial F_2}{\partial t} = -H$ and $\frac{\partial F_2}{\partial q_k} = p_k$

Therefore $$\frac{dF_2}{dt} = \sum_{k=1}^{n} p_k \dot{q}_k - H = L$$

(or) $$F_2 = \int L dt = S \qquad \ldots(6)$$

=Hamilton's principal function

Put $F_2 = S$ in equation (5), we get $$H(q_k, \frac{\partial S}{\partial q_k}, t) + \frac{\partial S}{\partial t} = 0 \qquad \ldots(7)$$

This is known as Hamilton – Jacobi equation. It is a partial differential equation of first order in (n+1) variables $q_1, q_2, ...q_n, t.$

Solution to Hamilton – Jacobi Equation :

Let the solution of equation (7) be of the form

$$S = S(q_1, q_2, ...q_n, \alpha_1, \alpha_2, ...\alpha_n, t) \qquad \ldots(8)$$

Where $\alpha_1, \alpha_2, ...\alpha_n$ are n independent constants of integration.

In equation (8), the solution S is a function of n co-ordinates of q_k ,time t and n independent constants. We can take these n constants of integration as the new constant momenta

ie $$P_k = \alpha_k \qquad \ldots(9)$$

Now the n transformation equation are

$$p_k = \frac{\partial S(q_1, q_2, ...q_n, \alpha_1, \alpha_2, ...\alpha_n, t)}{\partial q_k} \qquad \ldots(10)$$

These are n equations at t = t_0 give the n values of in terms of α_k in terms of q_k and p_k. The other n transformation equations are

$$Q_k = \frac{\partial s}{\partial P_k} = \beta_k$$

or
$$\beta_k = \frac{\partial S(q_1, q_2, ...q_n, \alpha_1, \alpha_2, ...\alpha_n, t)}{\partial \alpha_k} \qquad \ldots(11)$$

Similarly one can calculate the constants β_k by using initial condition at t = t_0, the known initial values of q_k. Thus α_k and β_k constants are known and equation (10) will give q_k in terms of α_k, β_k and t. that is

$$q_k = q_k\ (\alpha_1, \alpha_2, \ldots \alpha_{n,} \beta_{1,} \beta_2 \ldots \beta_n, t) \qquad \ldots(12)$$

On differentiation of equation (10), equation (12) may be substituted for q_k to obtain momenta p_k. Thus p_k will be obtained as function of constants $\alpha_{k,}\beta_k$ and t That is

$$p_k = p_k\ \ (\alpha_1, \alpha_2, \ldots \alpha_{n,} \beta_{1,} \beta_2 \ldots \beta_n, t) \qquad \ldots(13)$$

Thus we see that the Hamilton's principal function S is the generaor of a canonical transformation to constant coordinates (β_k) and momenta (q_k). Also in solving the Hamilton- Jacobi equation, we obtain simultaneously a solution to the mechanical problem.

3.9 SOLUTION OF HARMONIC OSCILLATOR PROBLEM BY HAMILTON – JACOBI METHOD:-

Consider a one - dimensional Harmonic oscillator. For such a system forces are conservative. The force acting on the oscillator at a displacement q is

$$f = -kq$$

k =Force constant.

Potential energy $V = \int_o^q -kqdq = \frac{1}{2}kq^2$

Kinetic energy $T = \frac{1}{2}\, mv^2 = \frac{p^2}{2m}$

Hamiltonian $H = T + V$

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

But $P = \frac{\partial S}{\partial q}$ and therefore

$$H = \frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2 + \frac{1}{2}\, kq^2$$

Hence the Hamilton – Jacobi equation corresponding to the Hamiltonian is

$$H + \frac{\partial S}{\partial t} = 0$$

$$\frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2 + \frac{1}{2}\, kq^2 + \frac{\partial S}{\partial t} = 0 \qquad \ldots(1)$$

Since we can separate the variables, solution will be of the form

$$S\,(q, \alpha, t) = W\,(q, \alpha) - \alpha t \qquad \ldots(2)$$

α is a constant.

$$\frac{\partial S}{\partial q} = \frac{\partial W}{\partial q} \; and \; \frac{\partial S}{\partial t} = -\alpha$$

Now equation (1) takes the form

$$\frac{1}{2m}\left(\frac{\partial W}{\partial q}\right)^2 + \frac{1}{2}\, kq^2 = \alpha \qquad \ldots(3)$$

$$\frac{1}{2m}\left(\frac{\partial W}{\partial q}\right)^2 = (\alpha - \frac{1}{2}kq^2)$$

$$\left(\frac{\partial W}{\partial q}\right)^2 = 2m\,(\alpha - \frac{1}{2}kq^2)$$

$$\frac{\partial W}{\partial q} = \sqrt{2m\,(\alpha - \frac{1}{2}\, kq^2)}$$

On integrating we get

$$\mathrm{W} = \int \sqrt{2m(\alpha - \frac{1}{2}kq^2)}\; dq + c$$

c = constant of integration

$$\text{Then S} = \int \sqrt{2m(\alpha - \frac{1}{2}kq^2)}\, dq - \alpha t + c$$

c is an additive constant and will not affect the transformation. Because to obtain the new positon coordinate $\beta = \frac{\partial S}{\partial \alpha}$ only partial derivative of S w. r. to α is required. Hence c is dropped. Thus

$$S = \int \sqrt{2m\,(\alpha - \frac{1}{2}\,kq^2)}\; dq - \alpha t \qquad \ldots(4)$$

Now α = new momentum P.

The new constant co - ordinate is obtained by the transformation.

$$\beta = \frac{\partial S}{\partial \alpha} = \frac{\sqrt{2m}}{2} \int \frac{dq}{\sqrt{\alpha - \frac{1}{2}kq^2}} - t$$

$$= \sqrt{\frac{m}{2}} \int \frac{dq}{\sqrt{\alpha - \frac{1}{2}kq^2}} - t$$

$$= \sqrt{\frac{m}{2}} \int \frac{dq}{\sqrt{\frac{k}{2}}\sqrt{\frac{2\alpha}{k} - kq^2}} - t$$

$$\beta = \sqrt{\frac{m}{k}} \int \frac{dq}{\sqrt{\frac{2\alpha}{k} - kq^2}} - t$$

$$t + \beta = \sqrt{\frac{m}{k}} \int \frac{dq}{\sqrt{\frac{2\alpha}{k} - kq^2}}$$

$$= \sqrt{\frac{m}{k}}\, \sin^{-1} q\, \sqrt{\frac{k}{2\alpha}}$$

$$\sin^{-1} \sqrt{\frac{k}{2\alpha}} = \sqrt{\frac{k}{m}}\, (t + \beta)$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$\sin^{-1} q \sqrt{\frac{k}{2\alpha}} \;\; = \omega \, (t + \; \beta)$$

$$q = \sqrt{\frac{2\alpha}{k}} \sin \omega \;\; (t + \beta) \qquad \ldots(5)$$

$$= \; q_0 \; \sin \omega \;\; (t + \beta)$$

Which is the familiar solution for the harmonic oscillator.

$$Now \; p = \frac{\partial S}{\partial q} = \frac{\partial W}{\partial q}$$

$$= \sqrt{2m(\alpha \; - \frac{1}{2} \; kq^2)}$$

$$= \; \sqrt{2m \, \alpha \; - \; m^2 \; \omega^2 \; q^2} \qquad \ldots(6)$$

$$p = \sqrt{2 \; m \, \alpha \; - \; m^2 \; \omega^2 \; \frac{2\alpha}{k} \; \sin^2 \omega \; (t + \; \beta)}$$

$$= \; \sqrt{2 \; m \; \alpha \; - \; 2 \; m \; \alpha \; \sin^2 \omega \; (t + \; \beta)}$$

$$= \; \sqrt{2 \; m \; \alpha} \; \cos \omega \;\; (t + \; \beta) \qquad \ldots(7)$$

$$= p_0 \; \cos \omega \;\; (t + \; \beta)$$

The constants α and β are to be known from initial conditions.

At t = 0 the particle is at rest

ie, p = 0 and it is at the displacement $q = \; q_0$ from the equilibrium position .

From (6) $\sqrt{2m \; \alpha \; - \; m^2\omega^2 q^2} = 0$

$$2 \; m \; \alpha \; = \; m^2\omega^2 q^2$$

$$\alpha \; = \frac{1}{2} \; m\omega^2 q^2$$

$$= \; \frac{1}{2} \; k \; q_0^2 \qquad \ldots(8)$$

$$q_0 = \sqrt{\frac{2\alpha}{m\omega^2}} = \sqrt{\frac{2\alpha}{k}}$$

and hence the solution (5) takes the form

$$q = q_0 \sin\omega \ (t + \beta) \qquad \ldots(9)$$

at $t = 0 \ q = q_0$, $\cos\omega\,\beta = 0 \ and \ \sin\omega\,\beta = 1$

$$\omega\,\beta = \frac{\pi}{2} \ (or) \ \beta = \frac{\pi}{2\omega}$$

Thus the new constant canonical coordinate measures the initial phase angle and in the present initial conditions the initial phase $\omega\beta = \frac{\pi}{2}$.

Now equation (9) become

$$q = q_0 \ \cos \ \omega t. \qquad \ldots(10)$$

Hamilton's characteristic function W (q,α) and principal function S are related by

$$S = W\ (q,\alpha) - \alpha t; \ Also \ H' = H + \frac{\partial s}{\partial t} = H - \alpha \ = 0$$

$H = \alpha$ But the system is conservative.

Hence $H = E$ Thus the new canonical momentum (P) is the total energy of the oscillator

H.J method to Harmonic oscillator :

Hamilton's principal function S can he obtained as

$$S = \int pdq - \alpha t$$

$$P = \sqrt{2\,m\,\alpha} \ \cos\omega \ (t + \beta)$$

$$q = q_0 \ \sin\omega \ (t + \beta)$$

$$= \sqrt{\frac{2\propto}{k}} \sin\omega \ (t + \beta)$$

$$dq = \omega\sqrt{\frac{2\alpha}{k}} \ \cos\omega \ (t + \beta) \ dt$$

$$S = \int \sqrt{2m\alpha} \cos\omega \ (t + \beta)\left(\omega \ \sqrt{\frac{2\alpha}{k}}\right)\cos\omega\,(t + \beta)dt - \alpha t$$

$$= \sqrt{2m\alpha}\left(\omega\sqrt{\frac{2\alpha}{k}}\right)\int cos^2\,\omega\,(t+\beta)dt - \alpha t$$

$$= +2\alpha\int cos^2\;\omega\,(t+\beta)\,dt - \alpha t$$

$$= \quad 2\alpha\int[cos^2\,\omega\,(t+\beta) - \tfrac{1}{2}]\,dt$$

The Lagrangian L is given by

$$L = \frac{p^2}{2m} - \frac{1}{2}\,kq^2$$

$$= \alpha cos^2\omega\,(t+\beta) - \frac{1}{2}\,k\,{q_0}^2 sin^2\,\omega\,(t+\beta)$$

$$= \alpha cos^2\omega\,(t+\beta) - \frac{1}{2}\,k\,\frac{2\alpha}{k}sin^2\,\omega\,(t+\beta)$$

$$= \alpha\,cos^2 w\,(t+\beta)\; - \;\alpha\,sin^2\,\omega(t+\beta)$$

$$= \alpha[cos^2\omega(t+\beta) - sin^2\,\omega\,(t+\beta)]$$

$$= \alpha[cos^2\omega(t+\beta) - \;(1 - sin^2\,\omega\,(t+\beta))]$$

$$= \alpha[2cos^2\omega(t+\beta) - \;1]$$

$$= 2\alpha[cos^2\omega\,(t+\beta) - \frac{1}{2}]$$

There fore $\quad S = \int Ldt$

Thus for Harmonic oscillator we prove that the Hamilton’s principal function is the time integral of Lagrangian.

3.10 HAMILTON’S PRINCIPAL FUNCTION :

From the solution of Hamilton Jacobi equation, we recognize S, the Hamilton’s principal function, as the generating function which gives rise to a canonical transformation involves constant momenta and constant co - ordinates.

Consider the total time derivative of

$$F_2 = F_2\,(q_k, P_k, t)$$

$$\frac{dF_2}{dt} = \sum_{k=1}^{n} \frac{\partial F_2}{\partial q_k}\dot{q}_k + \sum_{k=1}^{n} \frac{\partial F_2}{\partial P_k}\dot{P}_k + \frac{\partial F_2}{\partial t}$$

Here $\dot{P}_k = 0$, $\frac{\partial F_2}{\partial t} = -H$ and $\frac{\partial F_2}{\partial q_k} = p_k$

Therefore $$\frac{dF_2}{dt} = \sum_{k=1}^{n} p_k \dot{q}_k - H = L$$

(or) $F_2 = \int L dt = S$

S is known as the Hamilton's principal function in relation to the variational principle

3.11 HAMILTON'S CHARACTERISTIC FUNCTION:

Conservative systems:-

In a particle moving under central force in which H does not depend on time t explicitly and hence H = constant = α_1 = E. In such cases, it is Hamilton's characteristic function W. In Hamilton's principal function S, an explicit dependence on time is involved.

Hamilton – Jacobi equation for Hamilton's principal function S $(q_{k,}\alpha_{k,}t)$ becomes

$$H\left[q_{k,}\frac{\partial S}{\partial q_k}\right] + \frac{\partial S}{\partial t} = 0 \qquad \ldots(1)$$

We can assume the solution S in the form

$$S\left(q_{k,}\alpha_{k,}t\right) = W(q_{k,}\alpha_k) - \alpha_1 t \qquad \ldots(2)$$

There fore $\frac{\partial S}{\partial q_k} = \frac{\partial W}{\partial q_k}$ and $\frac{\partial S}{\partial t} = -\alpha_1$

and hence the Hamilton – Jacobi equation take the form

$$H\left[q_k, \frac{\partial W}{\partial q_k}\right] = \alpha_1 \qquad \ldots(3)$$

(or) $$\text{H}\,[q_{1,}q_{2,\ldots}q_n, \frac{\partial W}{\partial q_1}, \frac{\partial W}{\partial q_2}, \ldots \frac{\partial W}{\partial q_n}] = \alpha_1 \qquad \ldots(4)$$

This is time - independent Hamilton – Jacobi equation.

For conservative system H = α_1= E =total energy of the system. Now Hamilton – Jacobi equation is written as

$$H\left[q_{k,}\frac{\partial W}{\partial q_k}\right]=E \qquad \ldots(5)$$

Equation (4) can also be obtained directly by taking W as the generating function W (q_k, P_k) independent of time. The transformation equation are

$$p_k = \frac{\partial W}{\partial q_k}\ and\ Q_k = \frac{\partial W}{\partial P_k} \qquad \ldots(6)$$

Now if the new momenta $P_k$are all constant of motion α_k, where $\alpha_1$in particular is the constant of motion H, then $Q_k = \frac{\partial W}{\partial \alpha_k}$

The condition to determine W is that

$$H\,(q_k, p_k) = \alpha_1$$

Using $p_k = \frac{\partial W}{\partial q_k}$, we obtain

$$H\left(q_{k,}\ \frac{\partial W}{\partial q_k}\right) = \alpha_1$$

which is identical to equation (4).

Also $H^{'} = H + \frac{\partial W}{\partial t}$

But $w(q_k, p_k)$ does not involve time and hence

$$H^{'} = H = \alpha_1(= E) \qquad \ldots(7)$$

W = Hamilton's characteristic function.

It generates a canonical transformation where all new coordinates Q_k are cyclic because $H' = \alpha_{1,}$depending on one of the new momenta $P_1 = \alpha_{1,}$and does not contain any Q_k.

Now $$\dot{P}_k = -\frac{\partial H^{'}}{\partial Q_k} = 0\ (or) P_k = \alpha_k$$

and $$\dot{Q}_k = \frac{\partial H^{'}}{\partial \alpha_k} = 1\ for\ k = 1 \qquad \ldots(8)$$

$$\dot{Q}_k = \frac{\partial H'}{\partial \alpha_k} = 0 \; for \; k \; \neq 1$$

Hence the solution are

$$Q_1 = t + \beta_1 = \frac{\partial W}{\partial \alpha_1} \; for \; k = 1$$

and $$Q_k = \beta_k = \frac{\partial W}{\partial \alpha_k} \; for \; k \neq 1 \qquad \ldots(9)$$

Thus out of all the new coordinates $Q_k, \; Q_1$ is the only coordinate which is not a constant of motion. Here we observe the conjugate relationship between the time as the new coordinate and Hamiltonian as the conjugate momentum.

Physical significance of the Hamilton's characteristic function W:-

The function W has a physical significance similar to the Hamilton's principal function S. since W (q_k,P_k) does not involve time t explicitly, its total time derivative is

$$\frac{dW}{dt} = \sum_{k=1}^{n} \frac{\partial W}{\partial q_k} \dot{q}_k + \sum_{k=1}^{n} \frac{\partial W}{\partial P_k} \dot{P}_k$$

Since $P_k = \alpha_k \Rightarrow \dot{P}_k = 0$ and therefore

$$\frac{dW}{dt} = \sum_{k=1}^{n} p_k \dot{q}_k$$

$$W = \int \sum_k p_k \dot{q}_k \, dt = \int \sum_k p_k dq_k \qquad \ldots(10)$$

Which is the action.

and $S = \int L dt = \int \sum_k [p_k \dot{q}_k - H] dt$

$$= W - \int H dt$$

When H does not involve time t explicitly

$$\int H dt = \alpha_1 t$$

Now $S = W - \alpha_1 t$

$$S(q_k, \alpha_k, t) = W(q_k, \alpha_k) - \alpha_1 t$$

$$S(q_k, t) = W(q_k) - \alpha_1 t \qquad \ldots(11)$$

Here $p_k = \alpha_k$ are constants.

$\alpha_1 = \text{E} =$ total energy.

When the Hamiltonian does not involve time explicitly, one can solve a mechanical problem by using either Hamilton's principal function (or) Hamilton's characteristic function.

3.12 ACTION AND ANGLE VARIABLES:

In the motion of a system with many degrees of freedom the Hamilton- Jacobi equation is completely separable in coordinate variables. We consider conservative system in which the Hamiltonian does not involve time explicitly. The Hamilton-Jacobi equation is given by

$$H\left(q_1, q_2, \ldots\ldots\ldots q_n; \frac{\partial W}{\partial q_1}, \frac{\partial W}{\partial q_2}, \ldots\ldots\ldots \frac{\partial W}{\partial q_n}\right) = \alpha_1 \qquad \ldots.(1)$$

The variables q_k are separable, if a solution of the form

$$W = \sum_k W_k\left(q_k; \alpha_1, \alpha_2, \ldots\ldots \alpha_n\right) \qquad \ldots(2)$$

splits the equation into n equations:

$$H_k\left(q_k; \frac{\partial W_k}{\partial q_k}; \alpha_1, \alpha_2, \ldots. \alpha_n\right) = \alpha_1 \qquad \ldots(3)$$

Each of equations (3) involves only one of the coordinates q_k and the corresponding $\frac{\partial W_k}{\partial q_k}$

The equations of canonical transformation has the form

$$p_k = \frac{\partial W_k(q_k; \alpha_1, \alpha_2 \ldots\ldots \alpha_n)}{\partial q_k} \qquad \ldots(4)$$

it gives $p_k = (p_k; \alpha_1, \alpha_2, \ldots\ldots \alpha_n) \qquad \ldots(5)$

Equation (5) represents the orbit equation of the projection of the representative point of the system on the $(q_k,\ p_k)$ plane in the phase space. Now action-angle variables can be defined if the orbit equations for all the (p_k, q_k) pairs describe either closed orbits or periodic functions of q $_k$.

The action variables J $_k$ are defined as $J_k = \oint p_k\, dq_k$ …(6)

Here the integration is to be carried out over a complete period.

Suppose q $_k$ is cyclic coordinate, then p_k =constant.

If q $_k$ is angle coordinate, then integral for action variable is to be taken from 0 to 2π giving.

$$J_k = p_k \int_0^{2\pi} dq_k = 2\pi p_k \qquad \ldots(7)$$

Since *action* $A = \int_k \Sigma\, p_k\, \dot{q}_k\, dt = \int_k \Sigma\, p_k\, dq_k$

Using equation (4), we obtain

$$J_k = \oint \frac{\partial W_k}{\partial q_k}\left(q_k;\ \alpha_1, \alpha_{2,} \ldots\ldots\alpha_n\right) dq_k \qquad \ldots(8)$$

Since q $_k$ is a variable of integration and it will be out, when integration is over. Thus J $_k$ is a function of the n constants α $_k$. Thus

$$\mathrm{J_k} = \mathrm{J_k}\ (\alpha_1, \alpha_2, \ldots\ldots \alpha_n) \qquad \ldots(9)$$

(or) $$\alpha_k = \alpha_k\,(J_1, J_2, \ldots\ldots J_n) \qquad \ldots(10)$$

Thus the Hamilton’s characteristic function is

$$\left.\begin{aligned} W &= W\left(q_1, q_2, \ldots\ldots q_n;\ J_1, J_2, \ldots. J_n\right) \\ &= \sum_k W_k\,(q_k; J_{1,}\ J_{k,} \ldots\ldots J_n) \end{aligned}\right\} \qquad \ldots(11)$$

$$H = H' = \alpha_1 \qquad \text{and} \qquad \alpha_1 = \alpha_1\,(J_1, J_2, \ldots\ldots J_n)$$

$$\therefore H' = H'\,(J_1, J_2, \ldots\ldots J_n) \qquad \ldots(12)$$

The generalized coordinate ω_k conjugate to J $_k$ is defined as angle variable, given by

$$\omega_k = \frac{\partial W}{\partial J_k} = \sum_{1=1}^{n} \frac{\partial W_l}{\partial J_k}\left(q_1; J_1, J_2, \ldots\ldots.. J_n\right) \qquad (13)$$

Now the equation of motions for the angle variables are

$$\dot{\omega}_k = \frac{\partial H}{\partial J_k}\left(J_1, J_2, \ldots\ldots. J_n\right)$$

$$= \nu_k (J_1, J_2, \ldots.. J_n) \qquad \ldots(14)$$

This gives solution of the form

$$\omega_k = \nu_k\, t + \beta_k \qquad \ldots(15)$$

$\nu'_k\, s$ are constants and functions of action variables only and are frequencies of the periodic motion. Here the frequencies of the periodic motion can be obtained without complete solution of the problem.

Suppose that the change in angle variable ω_k with the completion of one cycle by q_l is $\Delta_l\, \omega_k$, then

$$\Delta_l\, \omega_k = \oint \frac{\partial \omega_k}{\partial q_l}\, dq_l$$

Using $\omega_k = \dfrac{\partial W}{\partial J_k}$ *we get*

$$\Delta_1\, \omega_k = \oint \frac{\partial^2 W_k}{\partial q_l\, \partial J_k}\, dq_l$$

$$= \frac{\partial}{\partial J_k} \oint \frac{\partial W}{\partial q_l} dq_l$$

$$= \frac{\partial}{\partial J_k} \oint p_l\, dq_l$$

$$= \frac{\partial J_l}{\partial J_k} = \delta_{kl}$$

$$\text{Thus} \quad \left.\begin{aligned} \Delta_k\, \omega_k &= 1 \quad k = l \\ &= 0 \quad k \neq l \end{aligned}\right\} \qquad \ldots(16)$$

τ_k is the period corresponding to q_k then using equation (15), $\Delta_k\,\omega_k = \nu_k\,\Delta t_k = \nu_k\,\tau_k$ …(17)

But $\Delta_k\,\omega_k = 1$ *hence*

$$\upsilon_k\,\tau_k = 1\ (or)\ \upsilon_k = \frac{1}{\tau_k} = \omega_k \qquad \ldots(18)$$

Thus $\nu_k'\,s$ are identified to the frequencies of the periodic motion.

2.13 KEPLER’S PROBLEM IN ACTION-ANGLE VARIABLES:

For a particle of mass m, moving in an inverse square force field $[V(r) = -\frac{k}{r}]$, the Hamiltonian of the system is given by

$$H = \frac{1}{2m}\left[p_r^{\,2} + \frac{p_\theta^{\,2}}{r^2}\right] - \frac{k}{r}$$

Determine the frequency by the method of action-angle variables and discuss degeneracy. Show that the period of the orbit is given by

$$\tau = \pi k\sqrt{-\frac{m}{2E^3}}$$

Solution :

The action variable J_k are given by

$$\mathrm{J_k} = \oint \mathrm{p_k\,dq_k}$$

In the case of Kepler’s problem, the action variables are given by

$$J_\theta = \oint p_\theta\,d\theta$$

and $$J_r = \oint p_r\,dr$$

$$p_\theta = \frac{\partial W}{\partial \theta} = \alpha_2$$

and therefore

$$J_\theta = \oint \frac{\partial W}{\partial \theta}\,d\theta = \oint \alpha_2\,d\theta = \int_0^{2\pi} \alpha_2\,d\theta = 2\pi\alpha_2$$

$$p_r = \frac{\partial W}{\partial r} = \sqrt{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha_2{}^2}{r^2}}$$

Where we have replaced E by α_1

$$\therefore J_r = \oint p_r \, d_r = \oint \frac{\partial W}{\partial r} \quad dr$$

$$= \oint \sqrt{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha^2{}_2}{r^2}} \; dr$$

The motion is bounded and is elliptical path for negative value of the total energy E. Further the limits are given by r_{min} and r_{max} values of r.

These values are determined by the zero of the quadratic equation in

$$\int \frac{\alpha_2 \, dr}{r^2 \sqrt{2mE + \frac{2mk}{r} - \frac{\alpha_2^2}{r^2}}} = \theta - \beta_2.$$

$$\text{ie} \sqrt{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha_2^2}{r^2}} = 0$$

$$2m\alpha_1 r^2 + 2mkr - \alpha_2^2 = 0$$

$$r^2 + \frac{k}{\alpha_1} r - \frac{\alpha_2^2}{2m\alpha_1} = 0$$

$$r = \frac{-k}{2\alpha_1} \pm \frac{1}{2\alpha_1} \sqrt{k^2 + \frac{2\alpha_1 \alpha_2^2}{m}}$$

$$= \frac{k}{2\alpha_1} \left[-1 \pm \sqrt{1 + \frac{2\alpha_1 \alpha_2^2}{mk^2}} \right]$$

$$\text{ie } r_{\min} = \frac{k}{2\alpha_1} \left[-1 - \sqrt{\frac{1 + 2\alpha_1 \alpha_2^2}{mk^2}} \right] \text{ and}$$

$$r_{\max} = \frac{k}{2\alpha_1} \left[-1 + \sqrt{\frac{1 + 2\alpha_1 \alpha_2^2}{mk^2}} \right]$$

In a complete cycle of the co-ordinate r, it varies from r_{min} to r_{max} and back to $r_{min.}$

Now

$$J_r = 2\int_{r_{min}}^{r_{max}} \sqrt{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha_2{}^2}{r^2}}\, dr$$

$$= 2\int_{r_{min}}^{r_{max}} \frac{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha_2{}^2}{r^2}}{\sqrt{2m\alpha_1 + \frac{2mk}{r} - \frac{\alpha_2{}^2}{r^2}}}\, dr$$

$$= 2\int_{r_{min}}^{r_{max}} \frac{2m\alpha_1 r + 2mk}{\sqrt{2m\alpha_1 r^2 + 2mkr - \alpha_2^2}}\, dr - 2\alpha_2^2 \int \frac{dr}{r\sqrt{2m\alpha_1 r^2 + 2mkr - \alpha_2^2}}$$

$$J_r = \frac{2\pi mk}{\sqrt{(-2m\alpha_1)}} - 2\pi\alpha_2$$

$$J_\theta + J_r = \frac{2\pi mk}{\sqrt{-2m\alpha_1}} \Rightarrow -2m\alpha_1 = \frac{(2\pi mk)^2}{(J_\theta + J_r)^2}$$

$$\alpha_1 = -\frac{2\pi^2 mk^2}{(J_\theta + J_r)^2}$$

But $H = H' = \alpha_1 = E$

Therefore $H' = E = \alpha_1 = -\dfrac{2\pi^2 mk^2}{(J_\theta + J_r)^2}$

Now the frequencies ν_θ and ν_r are given by

$$\nu_\theta = \frac{\partial H'}{\partial J_\theta} = \frac{\partial}{\partial J_\theta}\left[\frac{-2\pi^2 mk^2}{(J_\theta + J_r)^2}\right] = \frac{4\pi^2 mk^2}{(J_\theta + J_r)^3}$$

and $$\nu_r = \frac{\partial H'}{\partial J_r} = \frac{\partial}{\partial J_r}\left[\frac{-2\pi^2 mk^2}{(J_\theta + J_r)^2}\right] = \frac{4\pi^2 mk^2}{(J_\theta + J_r)^3}$$

Thus $$\nu_\theta = \nu_r = \frac{4\pi^2 mk^2}{(J_0 + J_r)^2}$$

The two frequencies are equal and the motion of the system is said to be degenerated.

The period of the orbit:

$$\tau = \frac{1}{r} = \frac{(J_\theta + J_r)^3}{4\pi^2 mk^2}$$

$$E = -\frac{2\pi^2 mk^2}{(J_\theta + J_r)^2}$$

$$(J_\theta + J_r)^2 = -\frac{2\pi^2 mk^2}{E}$$

$$(J_\theta + J_r) = \left[-\frac{2\pi^2 mk^2}{E}\right]^{\frac{1}{2}}$$

$$\tau = \frac{1}{4\pi^2 mk^2}\left[-\frac{2\pi^2 mk^2}{E}\right]^{\frac{3}{2}}$$

$$= \frac{1}{4\pi^2 mk^2}\left[\frac{2\pi^2 mk^2}{E}\right]\left[-\frac{2\pi^2 mk^2}{E}\right]^{\frac{1}{2}}$$

$$= \frac{1}{2E}\left[-\frac{2\pi^2 \mathrm{mk}^2}{\mathrm{E}}\right]^{\frac{1}{2}}$$

$$= \pi \mathrm{k}\left[-\frac{\mathrm{m}}{2\mathrm{E}^3}\right]^{\frac{1}{2}}$$

This formula agrees with Kepler’s third law that the semi-major axis $a = -\frac{k}{2E}$.

UNIT IV : CLASSICAL STATISTICAL MECHANICS

Foundations of Statistical Mechanics: The macroscopic and microscopic states, postulate of equal a priori probability, Contact between statistics and thermodynamics; Ensemble theory: Concept of ensemble, phase space, Density function, Ensemble average, Liouville's theorem, Stationary ensemble; The microcanonical ensemble, Application to the classical ideal gas; The canonical and grand canonical ensembles, Canonical and grand canonical partition functions, Calculation of statistical quantities; Thermodynamics of a system of non-interacting classical harmonic oscillators using canonical ensemble, and of classical ideal gas using grand canonical ensemble, Energy and density fluctuations; Entropy of mixing and the Gibb's paradox, Sackur-Tetrode equation.

4.1 FOUNDATIONS OF STATISTICAL MECHANICS:

- Statistical mechanics is the branch of science which gives the interpretation of the macroscopic behavior of a system in terms of its microscopic properties.
- Statistical mechanics is not concerned with the actual motion of individual particle but investigates average or most probable or statistical properties of the system.
- *The larger is the number of particles in the physical system considered, the more nearly correct are the statistical predictions. The smaller is the number of particles in the mechanical system, statistical mechanics cease to have meaning.*
- Statistical mechanics is applicable for a system consisting large number of particles.
- There are two statistical methods known as classical statistics and Quantum statistics.
- Classical statistics explained many observed physical phenomenon like temperature , pressure ,energy etc., but could not explain several experimentally observed phenomenon like black body radiation, specific heat at low temperature etc.
- For explaining such phenomenon Bose-Einstein and Fermi-Dirac made new approach known as quantum statistics.
- Quantum statistic can be classified as,
    i. Bose-Einstein statistics
    ii. Fermi-Dirac statistics

4.2 MICROSTATE AND MACROSTATE:

Microstate:

- The specification of individual position of phase points for each system or molecule of the ensemble.

Macrostate:

- The specification of the number of phase points in each cell of phase space. Many different microstates may corresponds to same macrostate.
- Consider a system consists of four particles a,b,c, and d and two cells A and B. The distribution of 4 particles in two cells can be illustrated here.

Cell A	Cell B
4	0
3	1
2	2
1	3
0	4

(2,2)-macrostate

ab	cd
bc	da
cd	ab
da	bc

(3,1 macrostate)

abc	d
bcd	a
cda	b
dab	c

- If we interchange any two phase points from different cells we have different microstates but the same macrostate.
- If we interchange any two phase points in the same cell , we have same microstate and same macrostate.
- The number of microstates corresponding to a given macrostate in called the thermodynamic probability of the macrostate.
- The probability that the ensemble possessing energy E is proportional to Ω(E).

$$P(E) = c\,\Omega(E)$$

c→proportionality constant

Ω(E)→thermodynamic probability

4.3 POSTULATE OF EQUAL A PRIORI PROBABILITY:

Statement:

- *The probability of finding the phase point for a given system in any one region of phase space is identical with that for any other region of equal volume.*
- The necessity of this postulate arises due to incompleteness of our knowledge concerning the system of interest.
- This postulate appears to be reasonable in character with the principles of statistical mechanics derived from Liouville's theorem.
- According to the principle of conservation of density, the density of a group of phase points remains constant.
- At any time the phase points are distributed uniformly in the phase space.
- There is no crowding of phase points in any particular region of phase space.
- Any arbitrary element of volume in the phase space bounded by a moving surface and containing a definite number of phase points does not change with time.
- The property of no crowding of phase points in any particular region of phase space and the constancy of volume element of phase space with time indicate the validity of the postulate.
- That is *the probability of finding a phase point in any particular region of phase space is directly proportional to the volume of that region*.
- The postulate replaces the postulate of equal priori probability when different volumes in the phase space are considered.

4.4 CONTACT BETWEEN STATISTICS AND THERMODYNAMICS : (BOLTZMANN RELATION BETWEEN ENTROPY AND PROBABILITY)

- Boltzmann used the idea that the probability of the system in equilibrium state is maximum.
- Thus in equilibrium state both the entropy and thermodynamical probability have their maximum values.
- Boltzmann concluded that the entropy 'S' is a function of thermodynamic probability Ω.

ie, $S = f(\Omega)$ ….(1)

- Consider two independent systems A and B having entropies S_1 and S_2 and thermodynamic probabilities Ω_1 and Ω_2.

- Entropy is an additive quantity and hence the entropy of systems together must be equal to the sum of their individual entropies.

$$S = S_1 + S_2 \qquad \text{….(2)}$$

- The probability Ω of finding both systems will be the product of the two probabilities Ω_1 and Ω_2.

ie $$\Omega = \Omega_1\Omega_2 \qquad \text{….(3)}$$

Substituting equations (2) and (3) in equation (1) we get,

$$S = f(\Omega) = f(\Omega_1\Omega_2) \qquad \text{….(4)}$$

$$S = S_1 + S_2$$

$$f(\Omega_1\Omega_2) = f(\Omega_1)(\Omega_2) \qquad \text{.....(5)}$$

- Differentiating with respect to Ω_1 we get,

$$\Omega_2 f'(\Omega_1\Omega_2)\, f'(\Omega_1) \qquad \text{….(6)}$$

- Differentiating with respect to Ω_2 we get,

$$\Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2) \qquad \text{….(7)}$$

- Divide equation (7)/(6), we get

$$\frac{\Omega_1}{\Omega_2} = f'(\Omega_2)/f'(\Omega_1)$$

$$\Omega_1\, f'(\Omega_1) = \Omega_2\, f'(\Omega_2)$$

$$\Omega\, f'(\Omega) = constant = k$$

$$f'(\Omega_1) = \frac{k}{\Omega}$$

Integrating, $$f(\Omega) = k\log\Omega + c$$

$$S = k\log\Omega + c \qquad \text{….(8)}$$

- For a thermo dynamical system at absolute zero Ω=1 and S=0 so that c=0.

$$S = k\log\Omega.$$

- This gives the Boltzmann's relation between entropy and probability.

(a) Identification of constant 'k':

- Consider the expansion of one mole of an ideal gas at pressure p_1 and volume V_1 into an evacuated chamber of volume V_2.
- The find pressure is p_2 and the final volume is $V_1 + V_2$.
- The probability of finding one molecule in the first container with volume V_1 is,

$$\frac{V_1}{V_1 + V_2}$$

- There are N molecules and hence the probability of finding one mole of the gas in the first container with volume V_1 is,

$$\Omega_1 = \left[\frac{V_1}{V_1+V_2}\right]^N \qquad ....(10)$$

- The probability of finding one mole of the gas in the container has volume V_1+V_2 is

$$\Omega_2 = \left[\frac{V_1+V_2}{V_1+V_2}\right]^N = [1]^N \qquad ....(11)$$

From Boltzmann relation

$$\Delta S = S_2 - S_1$$

$$= k\, log\, \Omega_2 - k\, log\, \Omega_1$$

$$= k\, log\, (\frac{\Omega_2}{\Omega_1})$$

$$= k\, log\, \left[\frac{1}{\frac{V_1}{V_1+V_2}}\right]^N$$

$$\Delta S = k\, log\, \left[\frac{V_1+V_2}{V_1}\right]^N$$

$$= log\, \left[\frac{V_1+V_2}{V_1}\right]^{Nk} \qquad ....(12)$$

- The change in entropy when the gas changes from one state with volume V_1 and temperature T_1 to another state with volume V_2 and temperature T_2 is given by,

$$\Delta S = C_v\, log\, \frac{T_2}{T_1} + R\, log\, [\frac{V_1+V_2}{V_1}]$$

For isothermal change $T_2 = T_1$ and hence $C_v\, log\, \frac{T_2}{T_1} = 0$

$$\Delta S = R\, log\, [\frac{V_1+V_2}{V_1}]$$

$$= log\, \left[\frac{V_1+V_2}{V_1}\right]^R \qquad ....(13)$$

Comparing equation (12) and (13), we get

$$Nk = R$$

$$k = R/N$$

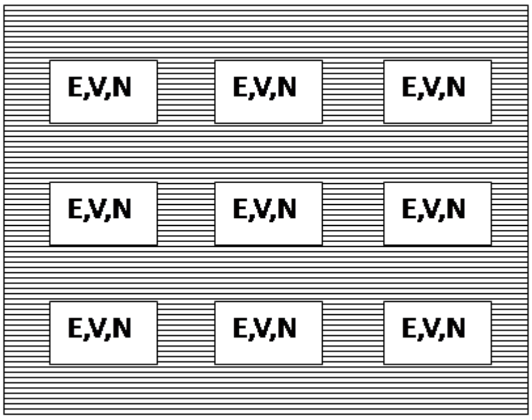
$= 1.03 \times 10^{-23}\, J/K$ = Boltzmann's constant

4.5 ENSEMBLE THEORY: CONCEPT OF ENSEMBLES:

- A system is defined as a collection of identical particles.
- An ensemble is defined as a collection of macroscopically identical, but essentially independent systems.

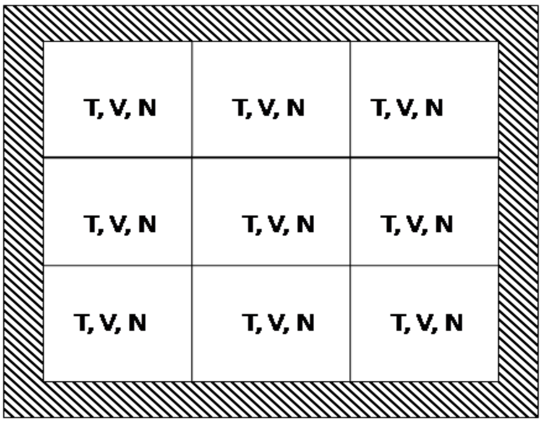
- Macroscopically identical means each system satisfies the same macroscopic conditions ex: volume, energy, pressure etc.
- Independent systems mean the systems are non interacting.
- There are three most commonly used ensembles namely,
  - (i) micro canonical ensemble
  - (ii) canonical ensemble
  - (iii) grand canonical ensemble.

Micro canonical ensemble:



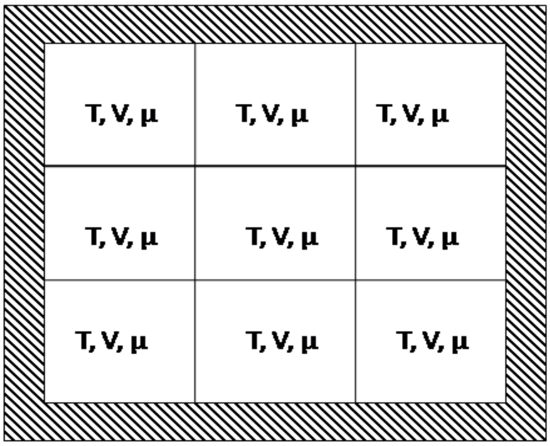
- Collection of large number of essentially independent systems with same energy E, volume V, and the number of particles N.
- All the particles are identical.
- The individual systems are separated by rigid , impermeable and well insulated walls.
- No exchange of heat energy as well as the number of particles between the systems takes place.

Canonical ensemble:



- Collection of large number of essentially independent systems with same temperature T, volume V and the number of particles N.
- All the particles are identical.
- The individual systems are separated by rigid, impermeable but conducting walls.
- Exchange of heat energy between the system takes place. But not the particles.

Grand canonical ensemble:



- Collection of large number of essentially independent systems with same temperature T, volume V, and the chemical potential μ.
- All the particles are identical.
- The individual systems are separated by rigid, permeable and conducting walls.
- Exchange of heat energy as well as the particles between the system takes place.
- The state of any ensemble can be completely specified by a large number of phase points in the phase space called ***dust cloud***.
- Thus the behavior of an ensemble can be represented by a large number of trajectories (or) phase lines (or) streaming motion of the dust cloud.

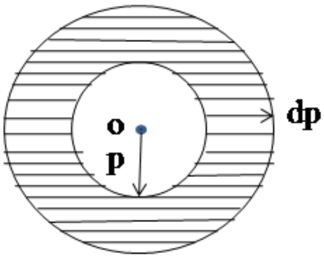
4.6 PHASE SPACE:

- The instantaneous position of a single particle is described by three independent co-ordinates $x, y\ and\ z$.
- The instantaneous motion of a particle is described by momentum co- ordinates $p_x\ , p_y\ , p_z$.
- Thus the state of a single particle is completely specified by position co-ordinates x, y, z and momentum co-ordinates $p_x\ , p_y\ , p_z$
- We may imagine a six dimensional space with volume $d_x\ d_y\ d_z\ dp_x dp_y\ dp_z$.
- The position of a point particle in this space can be described by a set of 6 co-ordinates $x\ y\ z\ p_x\ , p_y\ , p_z$.
- This 6 dimensional space for a single particle is damped as phase space.(μ=space)
- If the system contains a large number of particles such that f independent position co-ordinates $q_1, q_2, \dots \dots \dots, q_f$ and f momentum co-ordinates $p_1, p_2, \dots \dots, p_f$, then 2f combined position, momentum co-ordinates may be allowed to define 2f-dimensional space called phase space(Γ-space)
- The Γ-space is considered to be a conceptual Euclidean space having 2f rectangular axes and an element of volume represented by $dq_1, dq_2, \dots \dots, dq_f\ \ dp_1, dp_2, \dots \dots, dp_f$

- The instantaneous state of a particle in the phase-space is represented by a point known as phase point (or) representative point.
- The number of phase points per unit volume is known as phase density.

4.7 COUNTING THE NUMBER OF MICROSTATES IN THE ENERGY RANGE ε TO ε+dε:

- For a single particle we have six dimensional phase space.
- Three position co-ordinates (x, y, z) and three momentum co-ordinates (p_x, p_y, p_z) specify the microstate of a particle in the phase space.



- An element of volume in phase space is,

$$\delta_x \delta_y \delta_z \delta_{p_x} \delta_{p_y} \delta_{p_z} = h^3$$

- The total volume of phase space is $\iiint \iiint d_x d_y d_z d_{p_x} d_{p_y} d_{p_z}$
- We have $\iiint \iiint d_x d_y d_z = V$
- So the volume in phase space $= V \int \int \int d_{p_x} d_{p_y} d_{p_z}$
- Volume of momentum space containing momentum between p and $p + dp$ will be given by the volume of a spherical cell with radius p and thickness dp.
- Therefore,

$$\int \int \int d_{p_x} d_{p_y} d_{p_z} = 4\pi p^2 dp$$

$$\varepsilon = \frac{p^2}{2m} \rightarrow p^2 = 2m\varepsilon$$

$$2pdp = 2md\varepsilon$$

$$dp = \frac{m}{\varphi} d\varepsilon$$

$$= \frac{m}{\sqrt{2m\varepsilon}} d\varepsilon \quad = \sqrt{\frac{m}{2\varepsilon}} d\varepsilon$$

- Now volume of phase space

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

$$= V \times 4\pi(2m\varepsilon)\sqrt{\frac{m}{2\varepsilon}} d\varepsilon$$

$$= 4\pi V\sqrt{2}\, m^{3/2}\, \varepsilon^{1/2} d\varepsilon$$

- The number of cells within the phase space.

ie, $\Omega(\varepsilon) d\,\varepsilon = \frac{4\pi V\sqrt{2}}{h^3}\ m^{3/2} \varepsilon^{1/2} d\varepsilon$

- For a single particle the number of accessible microstates will be equal to the number of cells in phase space.
- Hence the number of microstates in this energy range ε to ε+dε is given by,

$$\Omega(\varepsilon)d\,\varepsilon = \frac{4\pi V\sqrt{2}}{h^3}\, m^{3/2}\varepsilon^{1/2}d\varepsilon$$

4.8 TIME AND ENSEMBLE AVERAGE:

- An ensemble consists of a large number of independent systems.
- It may be represented by a particular point in phase space.
- A gas containing a large number of molecules forming a system.
- The gas molecules move constantly and hence they change the position and momentum with time.
- The entire gas shows a time independent property (eg: temperature , energy etc.) which may be considered as the average of the specified property of the constituent gas molecules .
- Here, we discuss this type of average property of the ensemble.
- Let the state of the ensemble changes with time.
- Let u be the property of the ensemble.
- u takes values $u_1, u_2, \dots \dots .., u_m$ having probabilities $P_1, P_2, \dots \dots ., P_m$.

$$\bar{u} = \frac{P_1u_1 + P_2u_2 + \cdots \dots \dots + P_iu_i + \cdots \dots \dots P_mu_m}{P_1 + P_2 + \cdots \dots \dots + P_i + \cdots \dots \dots \dots P_m}$$

$$= \frac{\sum_{i=1}^{m} P_iu_i}{\sum_{i=1}^{m} P_i} \qquad \dots.(1)$$

- The sum of the probabilities of the all possible state must be equal to one.

ie, $P_1 + P_2 + \cdots \dots ..+P_i + \cdots \dots \dots .+P_m = \sum_{i=1}^{m} P_i = 1$ $\qquad \dots.(2)$

- This called normalization condition.
- Now equation (1) becomes

$$\bar{u} = \sum_{i=1}^{m} P_iu_i$$

- If the ensemble consists of N systems, u can be expressed as the function of all position and momentum co-ordinates of the systems.
- If the probability distribution function is continuous , then equation(1) can be expressed as,

$$\bar{u} = \frac{\int u(q,p)P(q,p)d\Gamma}{\int P(q,p)d\Gamma}$$

$$d\Gamma = dq_1, dq_2, \dots \dots \dots, dq_f \;\; dp_1, dp_2, \dots ., dp_f$$

- According to normalization condition

$$\int P(q,p)d\Gamma = 1$$

- Hence $\bar{u} = \int u(q,p)P(q,p)d\,\Gamma$
- This gives the ensemble average.

4.9 LIOUVILLE'S THEOREM:

- Liouville's theorem gives information about the rate of change of phase density in the phase space. The theorem may be stated in two parts.
- The rate of change of density of phase points in the neighborhood of a moving phase point in the Γ space is zero. This part represents the principle of conservation of density in the phase space.

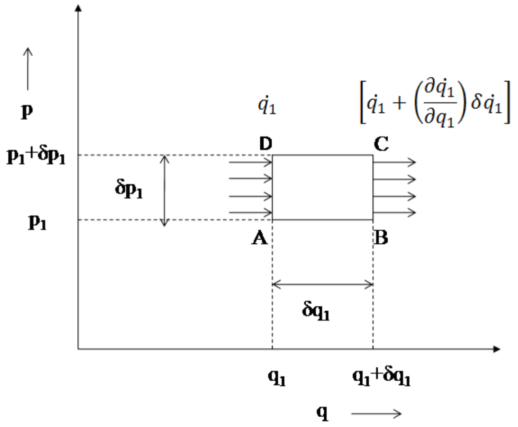
$$d\rho/dt = 0 \qquad \text{….(1)}$$

- Any arbitrary element of volume or extension in phase in the Γ space bounded by a moving surface and containing a number of phase points does not change with time. This part represents the principle of conservation of extension in the phase space.

$$\frac{d}{dt}(\delta\Gamma) = \frac{d}{dt}\left(\prod_i^f dq_i dp_i\right) = 0 \qquad \text{….(2)}$$

(i) The principle of conservation of density in the phase space:

- Consider any arbitrary hyper volume $\delta\Gamma = \delta q_1\, \delta q_2 \dots\dots..\delta q_f\;\; \delta p_1\, \delta p_2 \dots\dots..\delta p_f$ in the phase space located between q_1 and $q_1 + \delta q_1 \dots\dots\dots..q_f$ and $q_f + \delta q_f$, p_1 and $p_1 + \delta p_1, \dots\dots\dots.p_f$ and $p_f + \delta p_f$. The number of phase points in this volume element changes with time due to the motion of phase points.



- If ρ is the density of phase points, the number of phase points in this volume element at any instant t is ,

$$\delta N = \rho.\delta\Gamma = \rho\delta q_1\, \delta q_2\, \dots\dots.\delta q_f\, \delta p_1 \delta p_2\, \dots\dots\dots\delta p_f \qquad \text{….(3)}$$

- The change in number of phase points in volume element per unit time,

$$\frac{d(\delta N)}{dt} = \frac{d}{dt}(\rho.\delta\Gamma) = \dot{\rho}\delta\Gamma = \dot{\rho}\,\delta q_1\,\delta q_2 \,\dots\dots\delta q_f \delta p_1 \delta p_2 \,\dots\dots\dots\delta p_f \qquad \dots(4)$$

- This change in the number of phase points in the given hyper volume is due to the difference between the number of phase points entering the hyper volume through any face and the number of those leaving the opposite face per second.
- Consider two faces of hyper volume with co-ordinates $q_1$and $q_1 + \delta q_1$. If $\dot{q}_1$ is the component of velocity of phase point at $q_1, q_2, \dots\dots q_f, p_1, p_2, \dots\dots\dots p_f$,then the number of phase points entering the first face AD per second

$$= \rho\dot{q}_1\,\delta q_2 \dots\dots\delta q_f\;\;\delta p_1 \dots\dots\delta p_f \qquad \dots.(5)$$

- As density ρ changes with change in position and momentum co-ordinates and at the opposite face BC the co-ordinate q_1 changes to $q_1 + \delta q_1$and the density ρ changes to $(\rho + \frac{\partial\rho}{\partial q_1}\delta q_1)$ at the face BC. The velocity $\dot{q}_1$ changes to $(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\,\delta q_1)$. Therefore the number of phase points leaving the opposite face BC at $q_1+\delta q_1$ per second.

$$= (\rho + \frac{\partial\rho}{\partial q_1}\delta q_1)\,(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\,\delta q_1)\,\delta q_2 \dots\dots\delta q_f\;\delta p_1, \dots\dots\dots\delta p_f$$

- Neglecting higher order differentials, we get

$$= \left[\rho\dot{q}_1 \;+ (\rho\,\frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1\frac{\partial\rho}{\partial q_1})\delta q_1\right]\,\delta q_2 \dots\dots\delta q_f\;\delta p_1, \dots\dots\dots\delta p_f \qquad \dots.(6)$$

- Subtracting (6) from (5) we get the expression for change in the number of phase points per second corresponding to q_1.

$$= -(\rho\,\frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1\frac{\partial\rho}{\partial q_1})\delta q_1\delta q_2 \dots\dots\delta q_f\;\delta p_1, \dots\dots\dots\delta p_f \qquad \dots.(7)$$

- Similarly, the expression for the change into the number of phase points per second corresponding to p_1 is

$$= -(\rho\,\frac{\partial \dot{p}_1}{\partial p_1} + \dot{p}_1\frac{\partial\rho}{\partial p_1})\delta q_1\delta q_2 \dots\dots\delta q_f\;\delta p_1, \dots\dots\dots\delta p_f \qquad \dots.(8)$$

- Since the change in number of phase points per second corresponding to all position and momentum coordinates are like equation (7) and (8), then they are summed up.

- The net increase in the number of phase points in the given hyper volume per second is given by,

$$\frac{d(\delta N)}{dt} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + (\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i})\right] \delta q_1 \ldots \delta q_f\ \delta p_1, \ldots \delta p_f \qquad \ldots..(9)$$

- using equation (4)we get,

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + (\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i})\right] \qquad \ldots.(10)$$

- From canonical equation,

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}\ and\ \frac{\partial \dot{p}_i}{\partial p_i} = \frac{-\partial^2 H}{\partial p_i \partial q_i}$$

- Since the order of differentiation is immaterial i.e,

$$\frac{\partial^2 H}{\partial q_i \partial p_i} = \frac{\partial^2 H}{\partial p_i \partial q_i}$$

We get $\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$

$$\sum_{i=1}^{f}\left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right] = 0 \qquad \ldots.(11)$$

- Now equation (10) becomes

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = -\sum_{i=1}^{f}\left[\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i}\right]$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f}\left[\frac{\partial \rho}{\partial q_i}\dot{q}_1 + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] = 0 \qquad \ldots.(12)$$

- This equation represents Liouville's theorem.

$$\frac{d\rho}{dt}(q_1, \ldots., q_f, p_1, \ldots\ldots., p_f, t) = 0$$

ie, $\frac{d\rho}{dt} = 0$ ….(13)

- This expression represents the principle of conservation of density in phase space.

(ii) The principle of conservation of extension in phase space:

- Consider a very small region of hyper volume δΓ in the Γ space, so that the density of phase points ρ can be taken as uniform throughout the hyper volume.

  The number of phase points in this hyper volume, $\delta N = \rho . \delta\Gamma$

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho . \delta\Gamma)$$

$$= \frac{d\rho}{dt}\delta\Gamma + \rho\,\frac{d(\delta\Gamma)}{dt} \qquad \text{....(14)}$$

- As each phase point represents a definite system and systems can neither be created nor destroyed, the number of phase points δN must remain fixed.

  i.e $\frac{d}{dt}(\delta N) = 0$

$$\frac{d\rho}{dt}\delta\Gamma + \rho\,\frac{d(\delta\Gamma)}{dt} = 0$$

- from equation (14) $\frac{d\rho}{dt} = 0$

$$\rho\frac{d(\delta\Gamma)}{dt} = 0$$

$$\frac{d(\delta\Gamma)}{dt} = 0$$

$$\delta\Gamma = constant \qquad \text{....(15)}$$

- This expression represents the principle of conservation of extension in the phase space.

STATIONARY ENSEMBLE:

4.10 MICRO CANONICAL ENSEMBLE (ISOLATED SYSTEM):

- An ensemble in which each system has the same fixed energy as well as the same number of particles is called micro canonical ensemble.
- In this ensemble, density ρ, for a closed isolated thermo dynamical system is a function of energy and we take

ρ(E) = constant between the energy shells E and E+δE of phase space.

= 0 outside the region of phase space.

- We call this region in which ρ(E) = constant as accessible region dΓ of phase space.
- The above choice of ρ(E) being constant in dΓ and zero outside dΓ indicating accessibility can be justified as follows:
- Suppose we consider a gas of volume V, separated into smaller volumes V_1 and V_2 by a thin perfectly conducting wall of negligible heat capacity through which the particles of the gas can diffuse very slowly, hut through which energy can be exchange freely.
- Let at a particular instant, we determine the pressure in the two volumes, and let at this instant n out of total n' particles be in volume V_1. The particles in volume V_2 will be then $(n'-n)$. Now,
- (i) For an experiment of short duration, it would not be appropriate to take all particles could be found with equal probability anywhere within the volume V and therefore accessible region is the region of phase space in which all the first n particles are in V_1 and remaining $(n'-n)$ are in V_2.
- (ii) For an experiment of long duration in which a considerable amount of diffusion could occur, the whole of phase space is accessible.
- Thus for short duration experiments dΓ is accessible and it is inappropriate to include in the ensemble, the assembly lying outside this region dΓ, which means ρ(E) = constant for dΓ while zero outside dΓ.
- In general, *all accessible regions of phase space are given equal weightage in averaging over a microcanonical ensemble*. This is known as the 'Principle of equal a priori probabilities'.

(i) Partition Function:

- Consider an assembly of ideal gas obeying classical statistics.
- Let the distribution of gas molecules be such that n_i molecules occupy the i^{th} state with energy between ε_i and $\varepsilon_i + d\varepsilon_i$
- Let g_i be the degeneracy of the i^{th} state.
- According to M-B distribution law,

$$n_i = g_i e^{-\alpha} e^{-\beta\varepsilon i}$$

$$= g_i e^{-\alpha} e^{-\varepsilon_i/kT} \qquad [\beta=1/kT]$$

$$e^{-\alpha} = A$$

Then $n_i = Ag_i e^{-\varepsilon_i/kT}$

- Let the total number of gas molecules be N.

$$N = \sum_i n_i.$$
$$= \sum_i A\ g_i e^{-\varepsilon_i/kT}.$$
$$= A \sum_i\ g_i e^{-\varepsilon_i/kT}$$
$$\frac{N}{A} = \sum_i\ g_i e^{-\varepsilon_i/kT}$$
$$Z = \sum_i\ g_i e^{-\varepsilon_i/kT}$$

- Z is known as partition function and Z indicates how the gas molecules of an assembly are distributed (or) partitioned among the various energy levels.
- If the energy of the i^{th} level is ε_i then the weight of an individual level is unity.

ie, $g_i = 1$

$$Z = \sum_i\ e^{-\varepsilon_i/kT}$$

- Here the energy term may contain the rotational, vibrational and electronic components in addition to translational component.
- 'Z' can be used for calculating the various thermodynamic properties of ensembles.
- In classical treatment the energy distribution is continuous.
- The number of energy levels of the momentum interval p and $p + dp$ is given by,

$$g(p)dp = \frac{V\ 4\pi p^2 dp}{h^3}$$
$$p^2 = 2m\varepsilon$$
$$2pdp = 2md\varepsilon.$$
$$dp = \frac{m}{p}\ d\varepsilon.$$
$$= \frac{m}{\sqrt{2m\varepsilon}} d\varepsilon \quad = \sqrt{\frac{m}{2\varepsilon}} d\varepsilon$$

- Now the number of energy levels in the energy range ε and $\varepsilon + d\varepsilon$ is obtained as,

$$g(\varepsilon)d\varepsilon = \frac{V}{h^3}\ 4\pi(2m\varepsilon)\sqrt{\frac{m}{2\varepsilon}} d\varepsilon$$
$$= \frac{2\pi V}{h^3}\ (2m)^{3/2}\ \varepsilon^{1/2} d\varepsilon$$
$$Z = \sum_i\ g_i e^{-\varepsilon_i/kT}.$$
$$= \int_0^\infty g(\varepsilon)\ e^{-\varepsilon/kT}\ d\varepsilon$$
$$= \int_0^\infty \frac{2\pi V}{h^3}\ (2m)^{3/2}\ \varepsilon^{1/2}\ e^{-\varepsilon/kT} d\varepsilon$$

$$= \frac{2\pi V}{h^3}\ (2m)^{3/2}\ \int_0^\infty \varepsilon^{1/2}\ e^{-\varepsilon/kT} d\varepsilon$$

$$= \frac{2\pi V}{h^3}\ (2m)^{3/2}\ \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}}$$

$$= \frac{2\pi V}{h^3}\ (2m)^{3/2}\ \frac{1}{2}\sqrt{\pi(kT)^3}$$

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

- This is the translational *partition function* for a gas molecule.

4.11 CLASSICAL IDEAL GAS USING MICRO CANONICAL ENSEMBLE:

- Consider a micro canonical ensemble of a perfect gas.
- Let there be n point particles with mass m confined in a volume V with total energy u within the energy range δu.
- The corresponding volume

$$\Delta\Gamma = \int d\, q_1 \ldots\ldots\ldots . dq_{3n} \int d\, p_1 \ldots\ldots\ldots . dp_{3n}$$

$\int d\, q_1 \ldots\ldots\ldots dq_{3n} = V^n.$

Hence $\quad \Delta\Gamma = V^n \int d\, q_1 \ldots\ldots\ldots\ldots dq_{3n}$

- The momentum space integral is to be evaluated subject to the constraint of the ensemble

$$u - \delta u \leq u_r \leq u.$$

$$u_r = \sum_{i=1}^{n} {p_i}^2 / 2m\ .$$

$$u - \delta u \leq \frac{1}{2m}\sum_{i=1}^{n} {p_i}^2 \leq u.$$

- The accessible volume in momentum space is the volume of a spherical shell of radius $(2mu)^{1/2}$ and thickness $(\frac{m}{2u})^{\frac{1}{2}}\ \delta u.$
- The volume of three dimensional sphere of radius 'R' is,

$$V_3(R) = \frac{4}{3}\pi R^3 = \frac{\pi^{3/2}}{\Gamma(\frac{3}{2}+1)} R^3 = \frac{\pi^{3/2}}{\left(\frac{3}{2}\right)!}\ R^3 = C_3 R^3$$

$$V_f(R) = \frac{\pi^{f/2}}{(f/2)!}\ \ R^f \ \ = c_f R^3$$

where $C_f = \frac{\pi^{f/2}}{(f/2)!}$

- Therefore for 3n dimensional hyper-sphere of radius $(2mu)^{1/2}$, the volume is,

$$V_{3n}(R) = \frac{\pi^{3n/2}}{(3n/2)!}\ \ (2mu)^{3n/2}$$

- The volume coupled between hyper spheres of radii $(2mu)^{1/2}$ to $[2m(u - \delta u]1/2$ is

$$\int dp_1 \dots\dots\dots\dots dp_{3n} = \frac{\pi^{3n/2}}{(3n/2)!}[(2mu)^{3n/2} - \{2m(u-\delta u)\}^{3n/2}]$$

$$= \frac{\pi^{3n/2}}{(3n/2)!}\,(2mu)^{3n/2}\,[1-(1-\frac{\delta u}{u})^{3n/2}]$$

$$= \frac{\pi^{3n/2}}{(3n/2)!}(2mu)^{3n/2}\,[1-\ exp(-\frac{3n}{2}.\frac{\delta u}{u})]$$

- For a macroscopic system 3n=10^{23} ; $\frac{3n}{2}\frac{\delta u}{u}$ >>u.
- And hence we can drop the exponential term.

$$\int dp_1 \dots\dots\dots\dots\dots\dots dp_n = \frac{\pi^{3n/2}}{(3n/2)!}\ (2mu)^{3n/2}$$

$$\Delta\Gamma = V^n \int dp_1 \dots\dots\dots\dots\dots\dots\dots..dp_{3n}$$

$$= V^n \frac{\pi^{3n/2}}{(3n/2)!}\ (2mu)^{3n/2}$$

- According to classical statistical mechanics , the entropy σ in statistical equilibrium is given by,

$$\sigma = log\,\Delta\Gamma$$

$$= log\,[V^n \frac{\pi^{3n/2}}{(3n/2)!}\,(2mu)^{3n/2}\,]$$

$$= n\,log[V\,\pi^{3/2}\,(2mu)^{3/2}] - log\,(3n/2)!$$

$$= n\,log[V\,\pi^{3/2}\,(2mu)^{3/2}] - (3n/2)\,log\,(3n/2)\ + 3n/2$$

$$=\ n\,log\,[V\,\pi^{3/2}\,(2mu)^{3/2}] - n\,log\,(3n/2)^{3/2} + 3n/2$$

$$= n\,log\,\left[\frac{V\,\pi^{3/2}(2mu)^{3/2}}{(3n/2)^{3/2}}\right] +\ 3n/2$$

$$\sigma =\ n\,log\,[V\left(\frac{4\pi m}{3}\right)^{3/2}\ \left(\frac{u}{n}\right)^{3/2}] + \frac{3n}{2}$$

- We know that the entropy should not depend on the unit of hyper volume ΔΓ. To make it dimensionless we divide it by h^{3n}.

$$\sigma = log[\Delta\Gamma/h^{3n}]$$

$$= n\,log\left[V\frac{\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{3n}{2}$$

- The above equation does not satisfy the additive property and hence to satisfy the additive property we must divide by n!

$$\sigma = \ log\left[\frac{\Delta\Gamma}{h^{3n}\ n!}\right]$$

$$= \ n\ log\left[V\frac{\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{3n}{2} - logn!$$

$$= \ n\ log\left[V\frac{\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{3n}{2} - n\ log\ n + n$$

$$\sigma = \ n\ log\ \left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2}\mathrm{n}$$

- This expression satisfies the additive property because instead of V and u we have V/n and u/n.
- We shall now establish the connection of statistical quantities with corresponding thermodynamic quantities.

(a) Internal energy(U):

By the definition of statistical temperature τ,

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial u}\right)_{T,n}$$

$$= \frac{\partial}{\partial u}\left\{nlog\left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2}\mathrm{n}\right\}_{T,n}$$

$$= \frac{\partial}{\partial u}\left[n\ log\ v - n\ log\ n\ +\ n\ log\left(\frac{4\pi m}{3}\right)^{3/2} + n\ log\left(\frac{u}{n}\right)^{3/2} - nlog\ h^3\right] + \frac{\partial}{\partial u}\left(\frac{5}{2}n\right)$$

$$= \frac{\partial}{\partial u}\left[n\ log\ v - n\ log\ n\ +\ n\ log\left(\frac{4\pi m}{3}\right)^{3/2} + \frac{3}{2}\ n\ log\ u - \frac{3}{2}\ n\ log\ n - \ nlog\ h^3\right] + \frac{\partial}{\partial u}\left(\frac{5}{2}n\right)$$

$$= \frac{\partial}{\partial u}\left(\frac{3}{2}\ n\ log\ u\right)$$

$$\frac{1}{\tau} = \frac{3}{2}\ n\ \frac{1}{u}$$

$$u = \frac{3}{2}n\tau \qquad \text{(or)} \qquad u = \frac{3}{2}n\ kT$$

- Which is the well known result for the *internal energy* of a perfect mono atomic gas.

(b) Relation between τ and T:

The statistical temperature

$$\tau = k \times thermodynamic\ temperature.$$

$$\tau = kT$$

(c) Relation between τ and p:

We have $\frac{p}{\tau} = \left(\frac{\partial\sigma}{\partial V}\right)_{n.u}$

$$= \left(\frac{\partial}{\partial V}\right)\left[\left\{n\ log\ v - n\ log\ n + n\ log\ \left(\frac{4\pi m}{3}\right)^{\frac{3}{2}} + \frac{3}{2}\ n\ log\ u - \frac{3}{2} n\ log\ n - \right.\right.$$

$$n\ log\ h3 + \partial\partial V(52n)\ n,u$$

$$= \left(\frac{\partial}{\partial V}\right)\ [\,n\ log\ V]$$

$$= n/V$$

$PV = n\,\tau$ (or) $PV = nkT$

- Which is well known ideal gas equation for a perfect mono atomic gas.

(d) Thermodynamic entropy (S): ***(Sackur - Tetrode equation)***

The relation between thermodynamic entropy and statistical entropy is given by,

$$S = k\sigma$$

$$= nk\ log\left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2}nk$$

$$= nk\ log\left[\left(\frac{V}{nh^3}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\ (\frac{3}{2}kT)^{3/2}\right] + \frac{5}{2}nk$$

Since $u = \frac{3}{2}nkT$

$$= nk\,log\left[\frac{V}{nh^3}\,(2\pi mkT)^{3/2}\right] + \frac{5}{2}nk$$

$$= nk\,log\left[\frac{V}{n}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + \frac{5}{2}nk$$

$$= nk\,log\left[\frac{V}{n}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{5/2}\right]$$

- This is the famous ***Sackur - Tetrode* equation** for the entropy of a perfect gas. This formula is valid for the mono atomic gas of atoms with zero total angular momentum.
- The thermal de-broglie wavelength associated with a molecule may be defined as,

$$\lambda = h/average\ thermal\ momentum\ of\ a\ molecule.$$

$$\lambda = h/(2\pi mkT)^{1/2}$$

$$\lambda^3 = h^3/(2\pi mkT)^{3/2}$$

$$\frac{1}{\lambda^3} = (2\pi mkT/h^2)^{3/2}$$

Now $$\sigma = n\,log\left[\frac{V}{n}\frac{1}{\lambda^3}\right] + \frac{5}{2}n$$

$$S = nk\,log\left[\frac{V}{n}\frac{1}{\lambda^3}\right] + \frac{5}{2}nk$$

- Thus the entropy of a perfect gas is determined essentially by the ratio of the volume per particle to the volume λ^3 associated with de-Broglie wavelength.

(e) Chemical potential of a perfect gas:

The chemical potential of a perfect gas is given by,

$$\frac{-\mu}{\tau} = \left(\frac{\partial\sigma}{\partial n}\right)_{u,V}$$

$$= \frac{\partial}{\partial n}\left[n\,log\left[\frac{V}{n}\frac{1}{\lambda^3}\right] + \frac{5}{2}n\right]_{u,V}$$

$$= \frac{\partial}{\partial n}\,[n\,log\,V - n\,log\,n - n\,log\,\lambda^3]_{u,v} + \frac{\partial}{\partial n}\left(\frac{5}{2}n\right)_{u,v}$$

$$= log\, V\ - 1 - log n - log\, \lambda^3\ + \frac{5}{2}$$

$$= log\left(\frac{V}{n\lambda^3}\right) + \frac{3}{2}$$

$$\frac{\mu}{\tau}\ = log\left(\frac{n\lambda^3}{V}\right) - \frac{3}{2}$$

$$\frac{n}{V} = \frac{p}{\tau}$$

$$\frac{\mu}{\tau}\ = log\left(\frac{p\lambda^3}{\tau}\right) - \frac{3}{2}$$

$$\mu = \ \tau\, log\, p + \ \tau\, log(\frac{\lambda^3}{\tau}) - \frac{3\tau}{2}.$$

$$= \ \tau\, log\, p + f(\tau)$$

- Where $f(\tau)$ is the function of the temperature alone.

4.12 GIBB'S CANONICAL ENSEMBLE:

(i) System in contact with heat reservoir:

- The micro canonical ensemble describes the systems which are perfectly insulated and have given energy.
- In thermodynamics we do not know the exact value of energy as we usually deal with systems kept in thermal contact with a heat reservoir at a given temperature. Thus we know only its temperature i.e its average energy.
- The energy varies from instant to instant but the time average is known.
- On the other hand *the canonical ensemble describes those systems which are not isolated, but are in thermal contact with a heat reservoir*.
- In this situation the system of interest together with a heat reservoir forms a large closed system and the system of interest is treated as a subsystem.
- If the energy of the large closed system is constant, then it would represent a *microcanonical system* where as the subsystem which can exchange energy with a heat reservoir would represent *canonical system*.
- Thus *any part of sub system of an isolated system in thermal equilibrium can be represented by a canonical ensemble*.

- Consider a micro canonical ensemble representing a very large isolated system. Imagine that each system of the ensemble is made up of large number of subsystems which are in mutual thermal contact and can exchange energy.
- Choose a sub system s. The rest of the subsystem is denoted by r called heat reservoir. The total sub system is denoted by t. As the total system is a member of the microcanonical ensemble, it is isolated and E_t is constant.
- Let the energies of the sub system and heat reservoir be E_s and E_r so

$$E_t = E_r + E_s$$

- As s can exchange energy but not the particles, it is a member of the canonical ensemble. s is comparatively small but usually macroscopic containing 10^{24} particles. In the case of a gas, the sub system may be a single molecule.

r **heat reservoir**

S **sub system**

(ii) Thermodynamical functions and partition function:

- We shall calculate the entropy, energy, Helmholtz free energy and partition function of the canonical ensemble.
- Consider an isolated system with total energy E_0. This system is a part of a micro canonical ensemble.
- The micro canonical ensemble minus system is heat reservoir. Our system is in thermal equilibrium with the heat reservoir in such a way that $\bar{E}$=E_0.
- Let our system in the microcanonical ensemble be defined in the energy range between E_0 and E_0+δE. But in microcanonical ensemble δE is unimportant.
- Then we may choose δE to be equal to the range of reasonably probable values of the energy in the canonical ensemble.
- Therefore we define the entropy of the canonical ensemble with the mean energy E to be equal to the entropy of a microcanonical ensemble with energy $\bar{E}$.
- Consider the volume δΓ of the phase space corresponding to the energies between $\bar{E}$ and $\bar{E}$+δE

$$\Delta\Gamma == \left[\frac{\partial \Gamma(E)}{\partial E}\right]_{E} \delta E$$

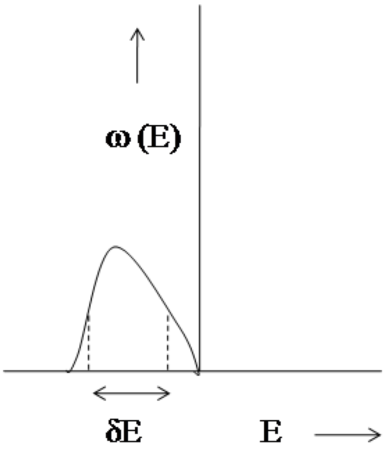
To estimate δE:

- Let ω(E) dE represent the canonical ensemble probability for a system to have energy in the range E and E+dE.
- ρ(E) is the probability density of unit volume of the phase space at energy E, then the probability of volume ΔΓ in the range E and E+dE will be ρ(E) ΔΓ(E).

So that,

$$\omega(E)dE = \rho(E)\Delta\Gamma(E) \qquad \ldots.(1)$$

$$= \rho(E)\left[\frac{\partial\Gamma(E)}{\partial E}\right]_E dE$$



- Figure represents the variation ω(t) as a function of E.
- The normalization condition is,

$$\int \omega(E)\, dE = 1 \qquad \ldots.(2)$$

- The simply means that the area under the curve ω= ω (E) is equal to unity.
- Since the mean energy of the canonical ensemble is $\bar{E}$ the function ω(E) will have an extremely sharp maximum at E=$\bar{E}$ differing appreciably from zero only in the immediate neighbourhood of this point.
- So on normalizing the plot we can introduce the width δE of the curve of ω= ω(E) defining it as the width of the rectangle whose height is equal to the value of the function ω(E) at its maximum and whose area is equal to unity.
- Thus the width δE is determined by the normalization condition.

$$\int \omega(\bar{E})\, \delta E = 1$$

- Comparing equations (1) and (2) with E = $\bar{E}$, we get

$$\text{Now, } \rho(\bar{E})\Delta\Gamma = 1$$

$$\Delta\Gamma = \frac{1}{\rho(\bar{E})}$$

- But we have, $\rho(\bar{E}) = Ae^{-\bar{E}/\tau}$

$$\Delta\Gamma = A^{-1}e^{\bar{E}/\tau}$$

$$= A^{-1}e^{U/kT} \qquad \ldots.(3)$$

- where $\bar{E}$=U=energy of the system and τ=kT
- So that the statistical entropy σ is given by,

$$\sigma = log\ \Delta\Gamma$$

$$= log[A^{-1}. e^{U/kT}]$$

$$= -\ log\ A + \frac{U}{kT}$$

$$log\ A = \frac{U}{kT} - \sigma$$

$$= \frac{U - k\sigma T}{kT}$$

$$= \frac{U - ST}{kT} \qquad ....(4)$$

- where $S = k\sigma$ = thermodynamic entropy.

Helmholtz free energy:

$$F = U - T\sigma = U - ST$$

$$log\ A = \frac{F}{kT}$$

$$A = e^{F/kT}$$

- So that the canonical distribution function takes form,

$$\rho(E) = Ae^{-E/\tau}$$

$$= e^{F/kT}e^{-E/kT}$$

$$= e^{(F-E)/kT}$$

- Now applying the normalization condition

$$\int \rho(E) d\Gamma = 1$$

$$\int e^{(F-E)/kT} d\Gamma = 1$$

$$e^{-F/kT} = \int e^{-E(p,q)/kT} d\Gamma$$

- Now the partition function is defined as,

$$Z = \int e^{-E(p,q)/kT}\, d\Gamma \text{ (classical)}$$

$$Z = \sum_i e^{-Ei/kT} \text{ (quantum)}$$

So, $e^{-F/kT} = Z$

$$-F/kT = log\ Z$$

$$-F = kT\ log\ Z$$

$$-F = \tau\ log\ Z \rightarrow F = -\tau\ log\ Z. \qquad \text{….(5)}$$

- This equation represents the expression for the Helmholtz free energy in terms of Z.
- Suppose N independent identical spinless particles, we must correct the classical partition function dimensionally and take into account the indistinguishability of the particles so that the correct expression is,

$$Z = \frac{1}{N!h^{3N}} \int e^{-E(p,q)/kT}\, d\Gamma \text{ (classical)} \qquad \text{….(6)}$$

Entropy of a system:

- The statistical entropy of a system in canonical ensemble is given by,

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

$$= \frac{\partial}{\partial \tau}(\tau \log Z)$$

$$= \log Z + \tau \frac{\partial}{\partial \tau}(\log Z) \qquad \text{….(7)}$$

- If E_i is the i th energy eigen value of a system, we have

$$Z = \sum_i e^{-E_i/\tau}$$

$$\log Z = \log(\sum_i e^{-E_i/\tau})$$

$$\frac{\partial}{\partial \tau}(\log Z) = \frac{\partial}{\partial \tau}\left[\log\left(\sum_i e^{-E_i/\tau}\right)\right]$$

$$= \frac{\sum e^{-E_i/\tau}\left(\frac{E_i}{\tau^2}\right))}{\sum_i e^{-Ei/\tau}}$$

$$= \frac{1}{\tau^2}\frac{\sum E_i e^{-Ei/\tau}}{\sum e^{-Ei/\tau}}$$

$$= \frac{1}{\tau^2}\bar{E} = \frac{U}{\tau^2} \qquad \ldots.(8)$$

- Now statistical entropy $\sigma = \log Z + \frac{U}{\tau}$ ….(9)
- The thermo dynamic entropy $S = k\sigma = k\left[\log z + \frac{U}{\tau}\right]$

$$S = k\log Z + \frac{U}{T} \qquad \ldots.(10)$$

4.13 A SYSTEM OF NON-INTERACTING CLASSICAL HARMONIC OSCILLATORS USING CANONICAL ENSEMBLE:

- We now take up the quantum-mechanical situation, according to which the energy eigenvalues of a one-dimensional harmonic oscillator are given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega; \; n = 0,1,2,.... \qquad \ldots.(1)$$

- Accordingly, we have for the single-oscillator partition function

$$Q_1(\beta) = \sum_{n=0}^{n=\infty}\exp(-\beta\varepsilon_n)$$

$$= \sum_{n=0}^{n=\infty}\exp\left[-\beta\left(n+\frac{1}{2}\right)\hbar\omega\right]$$

$$= \frac{\exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1-\exp(-\beta\hbar\omega)}$$

$$= \left\{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right\}^{-1} \qquad \ldots(2)$$

- The N – oscillator partition function is then given by

$$Q_N(\beta) = |Q_1(\beta)|^N = \left[\frac{\exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1-\exp(-\beta\hbar\omega)}\right]^N$$

$$= \frac{\exp\left(-\frac{N}{2}\beta\hbar\omega\right)}{[1-\exp(-\beta\hbar\omega)]^N} = e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N} \qquad \ldots.(3)$$

- For the Helmholtz free energy of the system, we get

$$A = -kT\ln Q_N$$

$$A = -kT\ln\left\{e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}\right\}$$

$$= NkT\ln[e^{1/2\beta\hbar\omega}] + NkT\ln[1-e^{-\beta\hbar\omega}]$$

$$= N\left[\frac{1}{2}\hbar\omega + kT\ln\left(1-e^{-\beta\hbar\omega}\right)\right] \qquad \text{….(4)}$$

- whereby

μ = A/N. …. (5)

P = 0 …. (6)

$$S = \beta kU + k\ln Q_N$$

$$S = \beta kN\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)}\right] + k\ln\left\{e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}\right\}$$

$$S = \beta kN\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)}\right] + k\ln\left(e^{-(N/2)\beta\hbar\omega}\right) + k\ln\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

$$S = \beta kN\frac{\hbar\omega}{2} + \beta kN\frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)} - \beta kN\frac{\hbar\omega}{2} + k\ln\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

- $$S = kN\left\{\frac{\beta\hbar\omega}{(e^{\beta\hbar\omega}-1)} - \ln\left[1-e^{-\beta\hbar\omega}\right]\right\}$$

- Then

$$S = kN\left\{\frac{\beta\hbar\omega}{(e^{\beta\hbar\omega}-1)} - \ln\left[1-e^{-\beta\hbar\omega}\right]\right\} \qquad \text{….(7)}$$

Also

$$S = Nk\left[\frac{1}{2}\beta\hbar\omega\coth\left(\frac{1}{2}\beta\hbar\omega\right) - \ln\left\{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right\}\right]$$

$$U = -\frac{\partial}{\partial\beta}\ln Q_N$$

$$= -\frac{\partial}{\partial\beta}\ln\left\{e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}\right\}$$

$$= -\frac{\partial}{\partial\beta}\ln\left(e^{-(N/2)\beta\hbar\omega}\right) - \frac{\partial}{\partial\beta}\ln\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

$$= -\left[\frac{e^{-(N/2)\beta\hbar\omega}\left(-N/2\hbar\omega\right)}{e^{-(N/2)\beta\hbar\omega}}\right] - \left[\frac{-N\left(1-e^{-\beta\hbar\omega}\right)^{-N-1}e^{-\beta\hbar\omega}(-\hbar\omega)}{\left(1-e^{-\beta\hbar\omega}\right)^{-N}}\right]$$

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

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

$$U = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)}\right] = \frac{1}{2} N\hbar\omega \coth\left(\frac{1}{2}\beta\hbar\omega\right) \qquad \ldots.\ (8)$$

and $$C_p = C_v = \frac{dU}{dT}$$

$$= \frac{d}{dT} N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)}\right]$$

$$= \frac{d}{dT} N\left[\frac{\hbar\omega}{(e^{\hbar\omega/kT} - 1)}\right]$$

$$= N\hbar\omega\left[-\frac{e^{\frac{\hbar\omega}{kT}}\left(\frac{-\hbar\omega}{kT^2}\right)}{(e^{\hbar\omega/kT} - 1)^2}\right]$$

$$= Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

- Then

$$C_p = C_v = Nk\left(\beta\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} \qquad \ldots.\ (9)$$

- Also

$$\mathrm{C_p} = \mathrm{C_v} = \mathrm{Nk}\left(\frac{1}{2}\beta\hbar\omega\right)^2 \operatorname{cosech}^2\left(\frac{1}{2}\beta\hbar\omega\right)$$

$\left\langle \Delta U \right\rangle$ = standard deviation in energy distribution

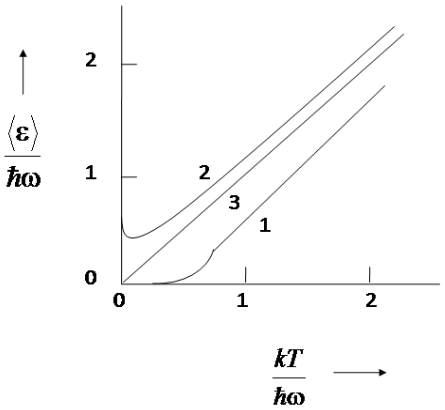
$$\left\langle \Delta U \right\rangle^2 = kT^2\left(\frac{\partial U}{\partial T}\right)_V$$

$$= kT^2 Nk\left(\beta\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} \qquad \text{[From equation (9)]}$$

$$= Nk^2T^2 \frac{1}{k^2T^2} \left(\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

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

- Now $\langle \Delta U \rangle = \sqrt{N}\ \hbar\omega \frac{e^{\beta\hbar\omega/2}}{\left(e^{\beta\hbar\omega}-1\right)}$ …. (10)
- Thus $\langle \Delta U \rangle \propto \sqrt{N}$



- Formula (8) is especially significant, for it shows that the quantum-mechanical oscillators do not obey the equipartition theorem.
- The mean energy per oscillator is different from the equipartition value kT; actually, it is always greater than kT; see curve 2 in figure.
- Only in the limit of high temperatures, where the thermal energy kT is much larger than the energy quantum $\hbar\omega$, does the mean energy per oscillator tend to the equipartition value.
- It should be noted here that if the zero-point energy $1/2\hbar\omega$ were not present, the limiting value of the mean energy would be $(kT - 1/2\hbar\omega)$, and not kT- we may call such an oscillator the Planck oscillator, see curve 1 in figure .
- In passing, we observe that the specific heat which is the same for the Planck oscillator as for the Schrodinger oscillator, is temperature dependent; moreover, it is always less than, and at high temperatures tends to, the classical value.
- Indeed, for kT>>$\hbar\omega$, formulae (2) through (9) go over to their classical counterparts, respectively.

4.14 Grand Canonical Ensemble:

(i) System in contact with a particle reservoir:

- In microcanonical ensemble each system contains same fixed energy as well as same number of particles.
- The microcanonical ensemble would not be applied to thermodynamics because we deal with systems kept in contact with heat reservoir. Then we know only the time average of energy.
- In canonical ensemble we relaxed the condition of constant energy and allowed the subsystem to exchange energy with heat reservoir. But this model could not be

applied to processes where not of particle varies. e.g. *chemical processes* and *quantum processes*.

- Therefore, we seek an ensemble which allows the subsystem to exchange energy as well as the particles with reservoir.
- Such an ensemble which allows the subsystem to exchange energy as well as the number of particles with the heat reservoir is called *grand Canonical Ensemble*.
- In grand canonical ensemble the independent variables are T,V and µ. Then we have the grand potential.

$$\Omega = U - TS - \mu n$$

which is minimal when T,V and µ are held fixed.

- Consider a microcanonical ensemble representing very large isolated system.
- Each system is made up of large number of sub system which are in mutual thermal contact and can exchange energy as well as particles with each other.
- Choose a sub system s, heat reservoir r and the total system t.
- E_s and E_r represent the energies of the sub system and the reservoir.
- n_s and n_r represent the number of particles in the sub system and the reservoir.
- Then the subsystem and the reservoir may exchange energy and particles subject to the conditions

$$E_s + E_r = E_t \text{ and } n_s + n_r = n_t$$

- Now we find the probability $d\omega_s(n_s)$ of finding the sub systems in a state in which sub system S contains n particles and is found in the element $d\Gamma(n_s)$ of its phase space.
- $d\Gamma(n_s)$ indicates that the nature of the phase space of the subsystem changes with n_s.
- For grand canonical ensemble

$$d\omega(n) = A \exp[(n\mu - E)/\tau] d\Gamma(n)$$

- Normalization constant $A = \exp\left(\frac{\Omega}{\tau}\right)$
- Ω is called grand potential or thermodynamic potential.

$$d\omega(n) = \exp[(\Omega + n\mu - E)/\tau]\, d\Gamma(n)$$

$$\int d\omega(n) = 1$$

$$\int \exp[(\Omega + n\mu - E)/\tau]\, d\Gamma(n) = 1$$

- From the normalization condition $\int \rho(n) d\Gamma(n) = 1$
- $\rho(n)$ is the density of distribution of phase points in the phase space.
- Now we get $\rho(n) = \exp[(\Omega + n\mu - E)/\tau]$
- An ensemble characterized by the probability distribution $\rho(n)$ given by the above equation is called grand canonical ensemble.

(ii) Partition function and thermodynamic function for grand canonical ensemble :

- In grand canonical ensemble sub system is allowed to exchange energy and the particles with the heat reservoir under the condition,

$$E_s + E_r = E_t \; and \; n_s + n_r = n_t \qquad \text{….(1)}$$

E_s, n_s→ the energy and the number of particles of the sub system.

E_r, n_r→the energy and the number of particles of the heat reservoir.

E_t, n_t→the energy and the number of particles of the total system.

- The probability distribution $\rho(n)$ is given by,

$$\rho(n) = \exp[(\Omega + n\mu - E)/\tau] \qquad \text{….(2)}$$

Ω→grand potential

μ→chemical potential

- The grand partition function is defined as,

$$\mathcal{Z} = \exp(-\Omega/\tau) \qquad \text{….(3)}$$

$$= \sum e^{\mu n/\tau} \int e^{E/\tau}\, d\Gamma(n) \text{ (classical)}$$

$$= \sum_n \sum_i \exp\left(\mu_n - E_{n,i}\right)/\tau \quad \text{(quantum)}$$

$$\mathcal{Z} = \sum_n e^{\mu n} Z_n$$

$$Z_n = \sum_i e^{-E/\tau}\, d\Gamma(n) \text{ (classical)}$$

$$= \sum e^{-E_{n,i}/\tau} \text{(quantum)}$$

is the canonical partition function .

- i.e *the grand partition function $\mathcal{Z}$ is the sum of canonical partition functions Z $_i$ for ensemble with different n' s with weighing factor $e^{-\mu n/\tau}$.*
- From equation (3) the partition function is given by,

$$\mathcal{Z} = \exp(-\Omega/\tau)$$

$$\Omega = -\tau \log \mathcal{Z} \qquad \text{….(4)}$$

- The entropy σ may be written as,

$$\sigma = \log \Delta\Gamma$$

$$= \log\left[\frac{1}{\rho(\bar{n}, \bar{E})}\right]$$

$$= -(\Omega + \bar{n}\mu - \bar{E})/\tau$$

$$= -(\Omega + \bar{n}\mu - U)/\tau \qquad \text{….(5)}$$

$$\tau\sigma = -(\Omega + \bar{n}\mu - U)$$

$$U - \tau\sigma = (\Omega + \bar{n}\mu)$$

Helmholtz free energy $F = U - \tau\sigma$ ….(6)

$$= \Omega + \bar{n}\mu \qquad \text{….(7)}$$

$$G = F + pV \qquad \text{….(8)}$$

$$= U - \tau\sigma + pV \qquad \text{….(9)}$$

$$dG = dU - \tau d\sigma - \sigma d\tau + pdV + Vdp$$

But $dU = \tau d\sigma - pdV + \mu dn$

Hence $dG = \tau d\sigma - pdV + \mu dn - \tau d\sigma - \sigma d\tau + pdV + Vdp$

$$= \mu dn - \sigma d\tau + Vdp$$

$$\left(\frac{dG}{dn}\right)_{\tau,p} = \mu \qquad \text{....(10)}$$

Hence $G = \mu n$ for fixed p and τ.

In this case $G = \mu\bar{n}$

$$\Omega + \bar{n}\mu + pV = \bar{n}\,\mu$$

$$\Omega = -pV$$

$$F + pV = \mu\bar{n} \qquad \text{....(11)}$$

$$U - \tau\sigma + pV = \mu\bar{n}$$

$$U - \tau\sigma - \Omega = \mu\bar{n}$$

$$U - \tau\sigma - \mu\bar{n} = \Omega \qquad \text{....(12)}$$

$$d\Omega = dU - \tau d\sigma - \sigma d\tau - \mu d\bar{n} - \bar{n} d\mu$$

$$= \tau d\sigma - pdV + \mu d\bar{n} - \tau d\sigma - \sigma d\tau - \mu d\bar{n} - \bar{n} d\mu$$

$$= -pdV - \sigma d\tau - \bar{n} d\mu \qquad \text{....(13)}$$

Then $p = -\left(\frac{\partial\Omega}{\partial V}\right)_{\tau,\mu}$

$$\sigma = -\left(\frac{\partial\Omega}{\partial \tau}\right)_{V,\mu}$$

$$\bar{n} = -\left(\frac{\partial\Omega}{\partial \mu}\right)_{V,\tau}$$

- From the above three relations we can evaluate thermodynamic quantities for the grand canonical ensemble.

4.15 CLASSICAL IDEAL GAS USING GRAND CANONICAL ENSEMBLE:

- The grand partition function is given by,

$$\mathcal{Z} = \sum_n e^{\mu n/\tau}\, Z_n \qquad \text{....(1)}$$

- Canonical partition function

$$Z_n = \frac{1}{n! h^{3n}} \int e^{-E(n)/\tau} d\Gamma(n) = \frac{f^N}{n!} \qquad \text{….(2)}$$

$$\text{where } f = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V$$

- ∴ The grand partition function

$$\mathcal{Z} = \sum_n e^{\mu n/\tau} \frac{f^n}{n!} = \sum_n \frac{\left(e^{\mu/\tau} f\right)^n}{n!} \qquad \text{….(3)}$$

- From the series expansion $\sum_n \frac{x^n}{n!} = e^x$

$$\mathcal{Z} = \exp\left(e^{\mu/\tau} f\right) \qquad \text{….(4)}$$

$$\Omega = -\tau \log \mathcal{Z} = -\tau e^{\mu/\tau} f$$

$$\Omega = \tau e^{\mu/\tau} \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V \qquad \text{….(5)}$$

(a) Chemical potential per particle ($\boldsymbol{\mu}$):

$$\bar{n} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,\tau}$$

$$= -\frac{\partial}{\partial \mu}\left[-\tau e^{\mu/\tau} \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\right]_{V,\tau}$$

$$= \frac{\partial}{\partial \mu}\left[\tau e^{\mu/\tau} \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\right]_{V,\tau}$$

$$= \tau \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, e^{\mu/\tau} \frac{1}{\tau}$$

$$\bar{n} = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V e^{\mu/\tau} \qquad \text{….(6)}$$

$$= -\frac{\Omega}{\tau}$$

$$\Omega = -\tau \bar{n} \qquad \text{….(7)}$$

$$\Omega = -\,\tau \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V e^{\mu/\tau} \qquad \text{….(8)}$$

$$-\tau \bar{n} = -\tau \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V e^{\mu/\tau}$$

This gives $e^{-\mu/\tau} = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} \frac{V}{\bar{n}} = \frac{f}{\bar{n}}$

$$-\frac{\mu}{\tau} = \log\left(\frac{f}{\bar{n}}\right)$$

$$\mu = -\tau \log\left(\frac{f}{\bar{n}}\right) \qquad \text{....(9)}$$

(b) Entropy: (*Sackur-Tetrode* equation)

- The statistical entropy σ is given by,

$$\sigma = -\left(\frac{\partial \Omega}{\partial \tau}\right)_{V,\mu}$$

$$= \frac{\partial}{\partial \tau}\left[\tau e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\right]$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2} V \frac{\partial}{\partial \tau}\left[\tau^{5/2} e^{\mu/\tau}\right]$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2} V \left[\frac{5}{2}\tau^{3/2} e^{\mu/\tau} + \tau^{5/2} e^{\mu/\tau}(-\mu/\tau^2)\right]$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2} V \tau^{3/2} e^{\mu/\tau} \left[\frac{5}{2} - \frac{\mu}{\tau}\right]$$

$$\sigma = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V e^{\mu/\tau}\left[\frac{5}{2} - \frac{\mu}{\tau}\right] \qquad \text{....(10)}$$

$$\sigma = \bar{n}\left[\frac{5}{2} - \frac{\mu}{\tau}\right] \qquad \text{....(11)}$$

- From equation (9) we have $\frac{\mu}{\tau} = -\log\left(\frac{f}{\bar{n}}\right) \rightarrow \mu = -\tau \log\left(\frac{f}{\bar{n}}\right)$
- Now equation (10) becomes $\sigma = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, e^{log\left(\frac{\bar{n}}{f}\right)} \left[\frac{5}{2} + \log\left(\frac{f}{\bar{n}}\right)\right]$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V \left(\frac{\bar{n}}{f}\right) \left[\frac{5}{2} + \log\left(\frac{f}{\bar{n}}\right)\right]$$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, \bar{n} \left(\frac{2\pi m\tau}{h^2}\right)^{-3/2} \frac{1}{V}\left[\frac{5}{2} + \log\left(\frac{f}{\bar{n}}\right)\right]$$

$$= \bar{n}\left[\frac{5}{2} + \log\left(\frac{f}{\bar{n}}\right)\right]$$

$$\sigma = \bar{n}\left[\frac{5}{2} +\right.$$

$log2\pi m\tau h23/2Vn$ ….(12)

- Thermodynamic entropy $\quad \mathrm{S} = k\sigma$

$$= \bar{n}k\left[\frac{5}{2} + log\left\{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\frac{V}{\bar{n}}\right\}\right]$$

$$= \bar{n}klog\left[\left\{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\frac{V}{\bar{n}}\right\}e^{5/2}\right] \qquad \text{….(13)}$$

- This gives the famous ***Sackur-Tetrode*** **equation** for the entropy of a perfect gas and this is in agreement with the equation for microcanonical ensemble and canonical ensemble.

(c) Internal energy:

We have $\quad \Omega = U - \tau\sigma - \mu\bar{n}$

$$U = \Omega + \tau\sigma + \mu\bar{n}$$

$\Omega = -\bar{n}\tau \quad$ [from equation (7)]

$\sigma = \bar{n}\left[\frac{5}{2} - \frac{\mu}{\tau}\right]$ [from equation (11)]

Now $\quad U = -\bar{n}\tau \ +\tau\,\bar{n}\,\left[\frac{5}{2} - \frac{\mu}{\tau}\right] + \mu\bar{n}$

$$= -\bar{n}\tau + \frac{5}{2}\bar{n}\tau - \mu\bar{n} + \mu\bar{n}$$

$$= \frac{3}{2}\bar{n}\tau.$$

$$U = \frac{3}{2}nkT.$$

- which is well known relation for the internal energy of a perfect gas.

4.16 ENERGY AND DENSITY FLUCTUATIONS IN ENSEMBLES:

(a) Canonical ensemble:

- In canonical ensemble the systems are in thermal equilibrium with the heat reservoir and so energy fluctuations take place.

- For canonical ensemble partition function,

$$Z = \sum_i e^{-\beta E_i} \qquad \text{….(1)}$$

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

$$\frac{\partial Z}{\partial \beta} = \sum_i e^{-\beta E_i}\,(-E_i)$$

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

$$\sum_i E_i e^{-\beta E_i} = -\frac{\partial z}{\partial \beta}\,.$$

- Mean energy $\bar{E} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}.$

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

$$\bar{E} = -\frac{1}{z}\frac{\partial z}{\partial \beta} \qquad \text{….(2)}$$

$$\frac{\partial^2 z}{\partial \beta^2} = \sum_i {E_i}^2 e^{-\beta E_i}$$

$$\sum {E_i}^2 e^{-\beta E_i} = \frac{\partial^2 z}{\partial \beta^2}$$

$$\bar{E}^2 = \frac{\sum_i {E_i}^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$= \frac{\sum_i {E_i}^2 e^{-\beta E_i}}{Z}.$$

$$\bar{E}^2 = \frac{1}{z}\,\frac{\partial^2 z}{\partial \beta^2} \qquad \text{….(3)}$$

- Using equation (2) $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{1}{z}\frac{\partial z}{\partial \beta}\right)$

$$= -\frac{\partial}{\partial \beta}\left(\frac{1}{z}\frac{\partial z}{\partial \beta}\right) = -\left[\frac{1}{z}\,\frac{\partial^2 z}{\partial \beta^2} - \frac{1}{z^2}\left(\frac{\partial z}{\partial \beta}\right)^2\right]$$

$$= -[\bar{E}^2 - (\bar{E})^2]$$

$$= -\left(\overline{\delta E}\right)^2 \qquad \text{….(4)}$$

- The molar heat at constant volume

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V$$

$$= \left(\frac{\partial \bar{E}}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

$$= -\left(\overline{\delta E}\right)^2\left(-\frac{1}{kT^2}\right)$$

$$C_V = \left(\frac{1}{kT^2}\right)\left(\overline{\delta E}\right)^2 \qquad \text{....(5)}$$

$$\left(\overline{\delta E}\right)^2 = kT^2 C_V$$

$$\sqrt{\left(\overline{\delta E}\right)^2} = T(kC_V)^{1/2} \qquad \text{....(6)}$$

◆ The energy fluctuation is measured by the ratio

$$\frac{\Delta E}{E} = \frac{\sqrt{\left(\overline{\delta E}\right)^2}}{\bar{E}}$$

$$= \frac{T(kC_V)^{1/2}}{\bar{E}} \qquad \text{....(7)}$$

◆ For large values of T, C $_v$ and $\bar{E}$ are proportional to the number of molecules N and hence fluctuation is proportional to $N^{-1/2}$.

◆ For an ideal gas $\bar{E} = NkT$ and $C_V = Nk$

$$\frac{\Delta E}{E} = \frac{T}{NkT}[kNk]^{1/2}$$

$$= \frac{N^{1/2}}{N} = N^{-1/2} \qquad \text{....(8)}$$

◆ For a macroscopic system N=10^{22}.

◆ So the fluctuations are very small in the order 10^{-11}.

◆ Therefore in canonical ensemble the distribution of energies is so peaked about the ensemble average energy that in practice regarded as a microcanonical ensemble.

(b) Grand canonical ensemble:

- In ground canonical ensemble the fluctuations take place in concentration as well as energy.
- The energy fluctuation can be calculated as for canonical ensemble.
- For Grand canonical ensemble the partition function,

$$\mathcal{Z} = \sum_{n,i} e^{(n\mu - E_{n,i})/\tau} \qquad \text{….(9)}$$

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_{n,i} e^{(n\mu - E_{n,i})/\tau}\ \frac{n}{\tau}$$

$$= \frac{1}{\tau} \sum_{n,i} n\, e^{(n\mu - E_{n,i})/\tau}$$

$$\sum n e^{(\mu n - E_{n,i})/\tau} = \tau\, \frac{\partial \mathcal{Z}}{\partial \mu}$$

- Mean concentration $\bar{n} = \dfrac{\sum_{n,i} n e^{(n\mu - E_{n,i})/\tau}}{\sum_{n,i} e^{(n\mu - E_{n,i})/\tau}}$

$$= \frac{\sum_{n,i} e^{(n\mu - E_{n,i})/\tau}}{\mathcal{Z}}$$

$$\bar{n} = \frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \qquad \text{….(10)}$$

$$\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \frac{1}{\tau^2} \sum_{n,i} n^2 e^{(n\mu - E_{n,i})/\tau}$$

$$\sum_{n,i} n^2 e^{(n\mu - E_{n,i})/\tau} = \tau^2 \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$\overline{n}^2 = \frac{\sum_{n,i} n^2 e^{(n\mu - E_{n,i})/\tau}}{\sum_{n,i} e^{(n\mu - E_{n,i})/\tau}}$$

$$= \frac{\sum_{n,i} n^2 e^{(n\mu - E_{n,i})/\tau}}{Z}$$

$$\overline{n}^2 = \frac{\tau^2}{z} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \qquad \text{….(11)}$$

$$\frac{\partial \bar{n}}{\partial \mu} = \frac{\partial}{\partial \mu} \left[\frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}\right]$$

$$= \frac{\tau}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{\tau}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2$$

$$\tau\frac{\partial\bar{n}}{\partial\mu} = \frac{\tau^2}{Z}\frac{\partial^2 Z}{\partial\mu^2} - \frac{\tau^2}{Z^2}\left(\frac{\partial Z}{\partial\mu}\right)^2$$

$$\tau\frac{\partial\bar{n}}{\partial\mu} = \left(\overline{\delta n}\right)^2 \qquad \ldots.(12)$$

- For an ideal classical gas $\bar{n} = e^{\mu/\tau}V\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}$

$$\frac{\partial\bar{n}}{\partial\mu} = \frac{1}{\tau}e^{\mu/\tau}V\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}$$

$$\frac{\partial\bar{n}}{\partial\mu} = \frac{1}{\tau}\,\bar{n}$$

$$\tau\frac{\partial\bar{n}}{\partial\mu} = \bar{n}$$

$$\left(\overline{\delta n}\right)^2 = \bar{n}$$

$$\sqrt{\left(\overline{\delta n}\right)^2} = \sqrt{\bar{n}}$$

- The concentration fluctuation is measured by the ratio

$$\frac{\Delta n}{n} = \frac{\sqrt{\left(\overline{\delta n}\right)^2}}{\bar{n}} = \frac{\sqrt{\bar{n}}}{\bar{n}} = \frac{1}{\sqrt{\bar{n}}}$$

$$pV = \bar{n}\,kT$$

$$\bar{n} = \frac{pV}{kT}$$

$$\frac{\Delta n}{n} = \left[\frac{kT}{pV}\right]^{1/2}$$

- Smaller of the volume greater is the fractional fluctuation.

4.17 ENTROPY OF MIXING AND THE GIBB’S PARADOX:

- The partition function of a perfect gas is given by,

$$Z = \frac{V}{h^3}(2\pi mkT)^{3/2} \qquad \ldots.(1)$$

- The entropy of a perfect gas is given by,

$$S = Nk\log Z + \frac{3}{2}Nk \qquad \ldots.(2)$$

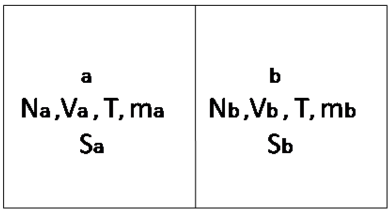
$$= Nk\,log\left[\frac{V}{h^3}\,(2\pi mKT)^{3/2}\right] + \frac{3}{2}Nk$$

$$= Nk\left[\,log\,V + \frac{3}{2}log\,m + \frac{3}{2}logT + C\right] \qquad \ldots.(3)$$

C is a constant term including h,k

- The entropy given by equation (3) does not satisfy the additive property and giving paradoxial results.

  Explanation:



- Consider two systems a and b at the same temperature T_a=T_b=T
- a and b are partitioned by a barrier as shown in figure.
- The particles of the two system are identical and distinguishable.
- The entropies of a and b are given by,

$$\left.\begin{aligned} S_a &= N_a k[log\,V_a + \frac{3}{2}\,log\,m_a + \frac{3}{2}\,logT + C] \\ S_b &= N_b k[log\,V_b\, + \frac{3}{2}\,log\,m_b + \frac{3}{2}\,logT + C] \end{aligned}\right\} \qquad \ldots.(4)$$

- Here N_a , m_a and V_a represent the number of particles, the mass of each particle and volume of system a.
- Here N_b , m_b and V_b represent the number of particles, the mass of each particle and volume of system b.
- Entropy is an extensive quantity and satisfy the additive property.
- If the entropy given by equation (3) had satisfied the additive property , then by removing partition and allowing the gas molecules to mix freely, the entropy of the joint system would be

$$S_{ab}\, = S_a + S_b$$

$$= N_a k[log\,V_a + \frac{3}{2}\,log\,m_a + \frac{3}{2}\,logT + C]\, + N_b k[log\,V_b\, + \frac{3}{2}\,log\,m_b + \frac{3}{2}\,logT + C] \qquad \ldots.(5)$$

- If the particles of the two system are the same and for convenience we take $V_a = V_b = V, N_a\, = N_b = N$ and $m_a = m_b = m$,then the entropy of the individual system be,

$$S_a\, = S_b$$

$$= Nk\left[log\,V\, + \frac{3}{2}\,log\,m + \frac{3}{2}\,logT + C\right] \qquad \ldots.(6)$$

- Now the entropy of the combined system be,

$$S_{ab} = 2Nk\left[log\, V + \frac{3}{2}\, log\, m + \frac{3}{2}\, logT + C\right] \qquad ....(7)$$

- Now we shall find actual entropy. Let the partition is removed.
- Allow the molecules of the gas to mix freely.
- Now we have a system with 2N particles and volume 2V.
- Then the entropy of the joint system ab is given by,

$$S_{ab} = 2Nk[log\, 2V + \frac{3}{2}\, log\, m + \frac{3}{2}\, logT + C]$$

$$= 2Nk[log\, V + \frac{3}{2}\, log\, m + \frac{3}{2}\, logT + C] \quad + 2NK\, log\, 2$$

$$= S_a + S_b + 2NK\, log\, 2 \qquad ....(8)$$

- Equation (8) is not equal to equation (7), but has an additional factor 2Nk log 2.
- Thus by mixing of two gases with each containing N molecules and by removing a partition between them , then the entropy of the joint system increases by 2Nk log 2.
- This additional entropy is called entropy of mixing.
- Thus if we use equation (3) for entropy we got the paradoxial results.
- This peculiar behavior of the entropy is called *Gibb's paradox*.

To resolve Gibb's paradox:

- Gibb's solved this paradox by considering the two systems with the molecules are identical and distinguishable.
- If two systems containing same number N are mixed by removing the partition then the diffusion takes place unnoticeably.
- In this situation N molecules of each system cannot be distinguished in N! ways.
- Hence the weight of the configuration $W = N! \prod \frac{g_i^{ni}}{n_i!}$

can be replaced by $W = \prod \frac{g_i^{ni}}{n_i!}$

$$log\, W = \Sigma n_i\, log\, g_i - \Sigma\, log\, n_i!$$

$$= \Sigma n_i\, log g_i - \Sigma\, n_i log n_i + \Sigma n_i$$

$$= \Sigma n_i log\, g_i - \Sigma\, n_i\, log\, n_i + N$$

- From Maxwell- Boltzmann law,

$$n_i = g_i e^{-\alpha} e^{-\beta \varepsilon i}$$

$$log\, W_{max} = \Sigma n_i\, log g_i - \Sigma\, n_i log[g_i e^{-\alpha} e^{-\beta \varepsilon i}] + N$$

$$= \Sigma n_i\, log\, g_i - \Sigma n_i log g_i + \Sigma\, n_i\, \alpha + \Sigma n_i\, \beta \varepsilon_i + N$$

$$log\, W_{\,max} = \alpha N + \beta E + N$$

Let us substitute $A = e^{-\alpha};\ ie, \alpha = -\log A$

$$\log W_{max} = -N \log A + \beta E + N$$

$$= N - N \log A + \beta E$$

$$= N[1 - \log A] + \beta E$$

$$S = k \log W_{max}$$

$$= Nk[1 - \log A] + \beta E k$$

$$= Nk[1 - \log A] + \frac{1}{kT}\frac{3}{2} NkT\, k$$

$$= Nk[1 - \log A] + \frac{3}{2} Nk\ .$$

$$= Nk - Nk \log A + \frac{3}{2} Nk\ .$$

$$= -Nk \log A + \frac{5}{2} Nk$$

$$= -Nk \log \frac{N}{Z} + \frac{5}{2} Nk$$

$$= Nk \log \frac{Z}{N} + \frac{5}{2} Nk$$

$$S = Nk \log \left[\frac{V}{h^3}\frac{(2\pi mKT)^{3/2}}{N}\right] + \frac{5}{2} Nk$$

$$= Nk \log \left[\left(\frac{V}{N}\right)\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right] + \frac{5}{2} Nk. \qquad ....(9)$$

- The entropy given by this equation satisfies the additive property since here in the argument of logarithm we have V/N in place of V.
- In equation (9) replacing N by 2N and V by 2V , the entropy of the combined system be given by,

$$S_{ab} = 2Nk \log \left[\left(\frac{2V}{2N}\right)\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right] + \frac{5}{2} 2Nk\ .$$

$$= 2\left\{Nk \log \left[\left(\frac{V}{N}\right)\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right] + \frac{5}{2} Nk\right\}$$

$$= 2S = S_a + S_b \qquad ....(10)$$

- Thus Gibb’s paradox is resolved .The resolution of Gibb’s paradox is an example of the success of the quantum theory.

UNIT V : QUANTUM STATISTICAL MECHANICS

Quantum-mechanical ensemble theory: Density matrix, Equation of motion for density matrix, Quantum- mechanical ensemble average; Statistics of indistinguishable particles, Two types of quantum statistics- Fermi-Dirac and Bose-Einstein statistics, Fermi-Dirac and Bose-Einstein distribution functions using microcanonical and grand canonical ensembles (ideal gas only), Statistics of occupation numbers; Ideal Bose gas: Internal energy, Equation state, Bose-Einstein Condensation and its critical conditions; Bose-Einstein condensation in ultra-cold atomic gases: its detection and thermodynamic properties: Ideal Fermi gas: Internal energy, Equation of state, Completely degenerate Fermi gas.

QUANTUM MECHANICAL ENSEMBLE THEORY

5.1 THE DENSITY MATRIX :

- A pure quantum state of a system is represented by a single eigenvector ψ_α.
- When the system is described by non-negative probabilities $p_\alpha, p_\beta, ...$ for being in states $\psi_\alpha, \psi_\beta ....$, a statistical approach is necessary.
- A pure classical state is represented by a single moving point in phase space, that have definite value of coordinates $q_1, q_2, ...q_f$ and canonical momenta $p_1, p_2, ...p_f$ at each instant of time.
- The statistical state can be described by a non-negative density function

  $$f\,(q_1,\ldots q_f,\ p_1\ldots..p_f,t)$$
- The probability that the system is found in the interval $dq_1,,...dq_f... \ dp_1...dp_f$ at time *t* is

  $$\rho\left(dq_1....dq_f, dp_1.....dp_f\right)$$
- The quantum analogue of the classical density function is known as density operator.
- We know that operators can be expressed by matrices and hence the density operator expressed as matrix is known as density matrix.
- The density matrix expresses the result of taking quantum mechanical matrix elements and ensemble averages in the same operation.
- Consider an ensemble consisting of *N* systems in the normalized states $\psi_i, i = 1,2,3.....N.$ Let ω_i be the probability that an assembly will be in the state ψ_i.
- We then define the density matrix in the $\{\psi_i\}$ representation as

  $$\rho_{ij} = \omega_i \ \delta_{ij} \qquad \ldots(1)$$

- Suppose now we wish to calculate the probability that if a measurement is made on an observable whose operator is $\hat{A}$ having Eigen functions ϕ_i, the result will be the Eigen value a_n corresponding to the Eigen function ϕ_n.
- If the assembly is in the state ψ_i and we express ψ_i as a linear combination of the ϕ_i we obtain

$$\psi_i = \sum_j c_{ij}\,\phi_j \qquad \ldots(2)$$

  - The probability that a measurement of $\hat{A}$ will give a_n is then simply $c_{in}{*}c_{in}$.
  - But the probability that the assembly is in the state ψ_i is ω_i. Therefore the probability that the measurement of A will yield a_n is just

$$\Sigma\omega_i\, c_{in}{*}c_{in} = \sum_i\sum_j \omega_i \delta_{ij} c_{in}{*}c_{in}$$

$$= \sum_i\sum_j \rho_{ij}\, c_{in} c_{in}{*}$$

$$= \sum_i\sum_j c_{in}\, c_{in}{*} \int \psi_i{*}\hat{\rho}\psi_j\, dq$$

$$= \int\left(\sum_i c_{in}\psi{*}\right)\hat{\rho}\left(\sum c_{in}{*}\psi_j\right)dq$$

$$= \int \psi_n{*}\hat{\rho}\psi_n\, dq \qquad \ldots(3)$$

- Therefore the probability that the measurement on $\hat{A}$ will give a_n is just

$$\int \phi_n{*}\hat{\rho}\phi_n\, dq = \rho_{nn}{}' \qquad \ldots(4)$$

- Now suppose we wish to calculate the average value of A. This will be simply

$$\overline{\left\langle \hat{A} \right\rangle} = \Sigma\, a_n\, \rho_{nn}{}'$$

$$= \sum_n \int \phi_n{*}\hat{\rho}\, a_n \phi_n\, dq$$

$$= \sum \int \phi_n{*}\hat{\rho}\hat{A}_n\, \phi_n\, dp$$

$$= \mathrm{Trace}\left[\hat{\rho}\hat{A}\right].$$

We note that the average $\left\langle \hat{A} \right\rangle$ is a double average, quantum mechanical average and a statistical mechanical average.

5.2 EQUATION OF MOTION FOR DENSITY MATRIX

(A QUANTUM MECHANICAL VERSION OF THE LIOUVILLE'S THEOREM):

- From the definition of ρ in {φ_k} representation, we write

$$\rho_{mn} = \frac{1}{N}\sum_{i=1}^{N} c_{in}^{*}\, c_{im} \qquad \text{….(1)}$$

- Again $$\frac{\partial \rho_{mn}}{\partial t} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\partial c_{in}^{*}}{\partial t} c_{im} + c_{im}^{*}\,\frac{\partial c_{im}}{\partial t}\right) \qquad \text{….(2)}$$
- The schroedinger time dependent wave equation is

$$i\frac{\text{ħ}}{2\pi}\frac{\partial}{\partial t}\Psi_i = \hat{H}\Psi_i$$

$$i\frac{\text{ħ}}{2\pi}\sum_k \frac{\partial}{\partial t} c_{ik}\phi_k = \sum_k c_{ik}\hat{H}\phi_k \qquad \text{….(3)}$$

- Multiplying equation (3) by φ_j^* and integration over q.

$$i\frac{\text{ħ}}{2\pi}\sum_k \frac{\partial}{\partial t}\int c_{ij}\phi_j * \phi_k dq = \sum_k c_{ik}\int \phi_j * \hat{H}\phi_k dq$$

$$i\frac{\text{ħ}}{2\pi}\frac{\partial}{\partial t} c_{ij} = \sum_k c_{ik} H_{jk} \qquad [H_{jk} = \int \phi_j * \hat{H}\phi_k dq] \qquad \text{….(4)}$$

- Taking complex conjugate we have

$$-i\frac{\text{ħ}}{2\pi}\frac{\partial}{\partial t} c_{ij} * = \sum_k c_{ik} * H_{jk} * \qquad \text{….(5)}$$

- Substituting equations (4) and (5) in equation (2) and taking $H_{ij}=H_{ji}^*$

$$i\frac{\text{ħ}}{2\pi}\frac{\partial \rho_{mn}}{\partial t} = i\frac{\text{ħ}}{2\pi}\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\partial c_{in}*}{\partial t} c_{im} + c_{in} * \frac{\partial c_{im}}{\partial t}\right)$$

$$= -\frac{1}{N}\sum_k c_{ik} * H_{nk} * \; c_{im} + \frac{1}{N}\sum_k c_{in} * c_{ik} H_{mk}$$

$$= -(\rho_{mk} H_{nk} * - \rho_{kn} H_{mk})$$

$$= -(\rho_{mk} H_{kn} - H_{mk}\rho_{kn})$$

$$= -[\rho, H]_{mn}$$

Thus the time development of density matrix is given by

$$i\frac{\hbar}{2\pi}\frac{\partial\rho}{\partial t} = -[\hat{\rho},\hat{H}]$$

This equation is analogous to the Liouville’s theorem in classical mechanics.

5.3 QUANTUM MECHANICAL ENSEMBLE AVERAGE :

- An ensemble in quantum statistical mechanics is assumed to be a collection of a very large number of perfectly isolated (conservative) and hence independent systems in a variety of quantum mechanical state $\Psi(q, t)$.
- Now the quantum mechanical version of *Liouville's theorem* is

$$i\hbar\frac{\partial\rho_{mn}}{\partial t} = \left[\hat{H}\hat{\rho}\right]_{mn}$$

- and for the element ρ_{mn} to be independent of time, $\frac{\partial\rho_{mn}}{\partial t} = 0$, so that $[H,\rho] = 0$, this means $\hat{\rho}$ and $\hat{H}$ commute.
- Therefore, ρ is a matrix associated with some constant of the motion of the system.
- $\hat{\rho}$ is some function of H, $\hat{\rho} = \hat{\rho}(\hat{H})$ where $\rho(\hat{H})$ can be expanded in a power series in $\hat{H}$.
- Taking ϕ_k’s as the basic set of eigenvectors, the matrix element of ρ can be written as

$$\rho_{mn} = \int \phi_n{}^{*}\rho\left(\hat{H}\right)\phi_n \, dq \qquad \ldots(1)$$

- In the special case that the energy eigenfunctions ψ_n's are chosen as basic vectors, equation (1) becomes

$$\rho_{mn} = \int \psi_n{}^{*}\rho(H)\psi_m \, dq \qquad \ldots(2)$$

- If we consider $\rho(\hat{H})$as a power series in $\hat{H}$,then

$$\rho(H) = a_0 + a_1 H + a_2 H^2 + \ldots\ldots..$$

$$\therefore \rho_{mn} = a_0\,\delta_{mn} + a_1 E_m \delta_{mn} + a_2 E_m{}^2\delta_{mn} + \ldots\ldots..$$

$(as\ H_{mn} = E_m\,\delta_{mn})$

$$= \left(a_0 + a_1 E_m + a_2 E_m{}^2 + \ldots..\right)\delta_{mn}$$

$$=\rho(E_m)\delta_{mn}$$

- and $\rho(H)\psi_m = \rho(E_m)\psi_m$ …(3)
- Thus any $\rho\,(\hat{H})$ is a diagonal matrix. Also, $\rho(E_n)$ is the probability of observing the eigenvalue E_n:

$$\rho(E_n) = \omega_n \quad ...(4)$$

- From this equation it follows that in case of degenerate level, all the basic states ψ_m have the same probability ω_n *i.e.*

$$\omega_{m1} = \omega_{m2} = \omega_{m3}... = \rho(E_{m1}). \quad ...(5)$$

- Now the state of a system known to have the energy E, within a range δE very small compared to L, must be represented by a superposition of basic states ψ_m belonging to eigen values E_m in the range $E \le E_m \le E + \delta E$.
- Let Ω be the number of basic states ψ_m belonging to eigen values E_m in the range $E \le E_m \le E + \delta E$, then from equation (5), we have

$$\omega_{m_1} = \omega_{m_1+1} = \omega_{m_1+2} = ...\omega_{m_1+\Omega-1} = \rho(E) \quad ... (6)$$

- Thus the probability of observing the eigen value E_n in the range E and $E+\delta E$ is proportional to $1/\Omega$.

(a) MICRO-CANONICAL ENSEMBLE

- For a closed, isolated thermodynamic system i.e. a system with assigned values for the independent variables E; $n_1, n_2 ... n_r$; $x_1, x_2 ... x_s$, using energy eigen functions as basic vectors, we write

$$\rho_{mn} = \delta_{mn}\,\omega_n, \quad …(7)$$

- Where $$\omega_n = \frac{1}{\Omega} \text{ for } E \le E_n \le E + \delta E \quad ...(8)$$

$$= 0 \text{ otherwise,}$$

- where δE is a very small range in E, and Ω is the number of basic states ψ_n belonging to eigen values E_n in the range $E \le E_n \le E + \delta E$. The constant $1/\Omega$ result from the normalization

$$\sum_n \omega_n = 1 \quad ...(9)$$

- From equation (8) it is clear that for a system known to have an energy between E and $E + \delta E$, all basic states ψ_n belonging to an eigen value E_n in this range have the same probability ω_n. This is usually called the postulate of "*equal a priori probabilities*".

(b) CANONICAL ENSEMBLE:

- For a closed, isothermal thermodynamic system i.e., a system with assigned values for independents variables T, ... n_1 ... n_r, x_1... x_s using arbitrary basic vectors ϕ_k

$$\rho = \text{constant} \times e^{-\beta \hat{H}} \qquad ...(10)$$

- Where β = constant = $\frac{1}{kT}$. From equation (1) we can write

$$\rho_{mn} = \text{constant} \times \int \phi_n^* e^{-\beta \hat{H}} \phi_m \, dq \qquad ....(11)$$

- In general, $\rho_{mn} = \omega_n$ is the probability of observing an eigen value a_n.
- Hence we can write

$$\sum_n \rho_{nk} = 1 = \text{constant} \times \sum_n \int \phi_n^* e^{\beta \hat{H}} \phi_m \, dq$$

- or constant = $\dfrac{1}{\sum_n \int \phi_n^* e^{-\beta \hat{H}} \phi_m \, dq}$

$$= \frac{1}{Z} \; where \; Z = \sum_n \int \phi_n^* e^{-\beta \hat{H}} \phi_m \, dq \qquad ...(12)$$

- and $\hat{\rho} = \dfrac{e^{-\beta \hat{H}}}{Z}$ ...(13)
- where Z (β, x_1,… x_s, n_1…n_r) is called the partition function.
- The classical partition function is $\int e^{-\beta \hat{H}(p,q)} \, dp \, dq$ ...(14)
- Comparing equations (12) and (14), the integration over ρ in classical mechanics is replaced by a summation over quantum states.
- Z may be written in alternative ways

$$Z = \sum_n \left(e^{-\beta \hat{H}} \right)_{nn} = trace \; e^{-\beta \hat{H}}$$

$$= \text{sum of eign values of } e^{-\beta \hat{H}}$$

- Z is obviously invariant under a change of basic vectors.
- The most invariant special choice of basic vectors is the set of energy eigen function Ψ_n.

- Therefore we can write

$$\rho_{mn} = \frac{1}{Z}\int \psi_n^{*} e^{-\beta\hat{H}}\psi_m \, dq$$

$$= \frac{1}{Z}\int \psi_n^{*}\psi_m e^{-\beta E_m}\, dq \qquad ...(15)$$

- Because $e^{-\beta\hat{H}} = 1-\beta\hat{H}+\frac{1}{2!}(\beta\hat{H})^{2}$

  and $\hat{H}\psi_m = E_m\psi_m$

- Now we obtain

$$\int \psi_n^{*} e^{-\beta H}\psi_m\, dq = \int \psi_n^{*}\psi_m e^{-\beta E_m}\, dq$$

$$= \frac{1}{Z}\delta_{mn} e^{-\beta E_n}$$

$$= \delta_{mn}\omega_n$$

- Where ω_n is the probability that a system, chosen at random from canonical ensemble, will be found in the energy state E_n
- The partition function is written as

$$Z = \int \psi_n^{*} e^{-\beta\hat{H}}\psi_n\, dq$$

$$= \sum_n |\psi_n|^2 e^{-\beta E_n}\, dq$$

$$= \sum_n e^{-\beta E_n} \qquad ....(16)$$

(c) GRAND CANONICAL ENSEMBLE:

- Now we consider the case of an ensemble composed of members which can differ not only in the state but also in the amounts of material of various kinds which they contain. Such an ensemble is called the grand canonical ensemble.
- Let us suppose that a system is composed of *r* independent kinds of components and n_1, $n_2 ... n_r$ be the number of molecules in any member system of grand ensemble.
- For an open, isothermal thermodynamic system i.e, a system with assigned values for the independent variables T; (μ_1-μ_r; x_1-x_s) we can define the grand canonical ensemble corresponding to such a system by the formula,

$$\rho = \text{constant} \times e^{-\beta\hat{H}} \times e^{-\beta\mu n} \qquad \ldots(1)$$

- where $\mu n = \mu_1 n_1 + \mu_2 n_2 + ... + \mu_r n_r$

$$\therefore \qquad \rho_{mn} = \text{constant} \times e^{-\beta\mu n} \int \psi_n^{*} e^{-\beta\hat{H}} \phi_m dq \qquad \ldots(2)$$

- The total probability of finding a system in one or another state *N* will be taken as normalized to unity. Thus we can write,

$$\sum_{N,n} \rho_{nn} = 1 \qquad \ldots(3)$$

- Now from equation (2), we have

$$\text{Constant} = \frac{1}{e^{-\beta\mu n} \int \phi_n^{*} e^{-\beta\hat{H}} \phi_m dq}$$

$$= \frac{1}{Z} \qquad \ldots(4)$$

- where Z is called the ‘grand partition function’. Therefore

$$\rho = \frac{e^{-\beta\hat{H}} e^{-\beta\mu n}}{Z} \qquad \ldots(5)$$

- From equation (5), we get

$$\Sigma \rho_{nn} = \frac{e^{-\beta\mu n}}{Z} \int \phi_n^{*} e^{-\beta\hat{H}} \phi_n dq$$

$$= \frac{e^{-\beta\mu n}}{Z} Z(n)$$

$$= \gamma\ (n) \text{ say.} \qquad \ldots(6)$$

- Combining equations (5) and (6), we get

$$\rho = \frac{\gamma(n) e^{-\beta\hat{H}(n)}}{Z(n)} \qquad \ldots(7)$$

- If the basis vectors are a set of energy eigen functions, then, the probability of observing the state ψ_n (N, *x*) is

$$\omega_n(N) = \rho_{nn} = \frac{e^{-\beta\mu_n} e^{-\beta E_n}}{\sum e^{-\beta\mu_n} e^{-\beta E_n}} \qquad \ldots(8)$$

(d) CONDITION FOR STATISTICL EQUILIBRIUM:

- When a system is in equilibrium, its corresponding ensemble must be stationary.i.e

$\rho_{mn} = 0$ .This is possible, when

i. the density matrix is constant, or

ii. the density matrix is a function of a constant of motion

(i) If the density matrix is constant, its element will be given by

$$\rho_{mn} = \rho_0 \delta_{mn} \qquad \ldots(1)$$

- i.e., all the non-diagonal elements of the matrix will be zero and all the diagonal elements will be equal to a constant ρ_0
- In the energy representation, the basic function ϕ_n are the eigen functions of the Hamiltonian $\hat{H}$ .So, the matrices H and ρ are diagonal. Thus

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \ldots(2)$$

- In the representation, the density operator $\hat{\rho}$ may be written as

$$\hat{\rho} = \sum_n \int \phi_n^* \rho_n \phi_n dq = \left[\hat{H}, \hat{\rho}\right] \qquad \ldots(3)$$

- To verify this, consider an element ρ_{kl} . Now

$$\rho_{kl} = \int \phi_k \hat{\rho} \phi_l \, dq = \sum_n \left(\int \psi_k^* \psi_n dq \right) \rho_n \left(\psi_n^* \psi_l dq \right)$$

$$= \sum_n \delta_{kn} \rho_n \delta_{nl} = \rho_k \delta_{kl} \qquad \ldots(4)$$

- This agrees with equation (2)
- Therefore $i\hbar \dot{\rho}_{mn} = \sum_l \left[\hat{H}, \hat{\rho} \right]$

$$= \sum_l \left[H_{ml} \rho_{ln} - \rho_{ml} H_{ln} \right]$$

$$= \sum_l \left[\rho_0 H_{ml} \delta_{ln} - \rho_0 \delta_{ml} H_{ln} \right]$$

$$= \rho_0 \left[H_{mn} - H_{mn} \right] = 0 \qquad \ldots(5)$$

- The distribution does not change with time. So, the system under consideration is in equilibrium.

(ii) From eq. (5), it is obvious that $\hat{\rho}$ commutes with $\hat{H}$. Therefore, ρ must be a function of

a constant of motion.

5.4 INDISTINGUISHABILITY AND QUANTUM STATISTICS:

- By indistinguishable particles we mean that if the position and spin coordinates of two of them are interchanged, there is no physical way of measuring that a change has been made.
- In classical mechanics identical particles do not lose their individuality despite the identity of their physical properties.
- If a pair of particles is completely equivalent even then it is possible to identify them by the continuity of their trajectories because this property enables an observer to follow each particle.
- This is due to the fact that their wave packets do not overlap, and the particles move in separate, distinguishable continuous orbits.
- As an example, consider the molecules in a gas at N.T.P.

  Molecular density = 10^{19} mole./cm.^{2}
  Volume available to each molecule = 10^{-19} cm.^{3}
  Molecular radius = 10^{-8} cm.
  Molecular volume = 10^{-24} cm.^{3}

- Because the molecule is smaller than the volume available, we can identify every molecule of the gas. The molecules are thus *distinguishable*.
- The situation is quite different in quantum mechanics as follows at once from the uncertainty principle.
- Due to the uncertainty principle, the concept of the path ceases to have any meaning. If the path of an electron is exactly known at a given instant, its coordinates have no definite values even at an infinitely close subsequent instant.
- By localising and numbering the identical particles at some instant, at some other instant we cannot say which of particle arrived at that point.
- In quantum mechanics there is no way of keeping track of each particle separately when the wave functions of two identical particles overlap.
- Thus in quantum mechanics there is, in principle, no possibility of separately following each of a number of similar particles and thereby distinguishing them.
- As an example, we consider the conduction electrons of a metal:

  Density of electrons = 10^{22} per cm^{3}
  Volume available to each electron = 10^{-22} cm^{3}
  Momentum $p_x = (2mE)^{1/2}$ for 1 eV. = 0.5×10^{-19} erg-sec cm^{-1}
  Uncertainty in position $\Delta x = h/p_x$ = 13×10^{-8} cm.

Volume of conduction electron $= (13 \times 10^{-8})^3\ \text{cm}^3$

$= 2 \times 10^{-21}\ \text{cm}^3$.

- Comparing the volume of conduction electron to the volume available, we conclude that the electron wave functions overlap considerably and hence they are *indistinguishable.*
- Thus we have two categories of particles:
  (i) Classical, which are identical but distinguishable.
  (ii) Quantum, which are identical and indistinguishable.
- When quantum particle density is low, *i.e.,* uncertainty is small in comparison to the volume available, the particles obey classical statistics otherwise we use quantum statistics.

5.5 ILLUSTRATION OF CLASSICAL AND QUANTUM STATISTICS

- Consider a gas consists of only two particles a and b.
- Assume that each particle can be in one of the possible quantum states S = 1,2,3.
- Let us calculate the possible states of the whole gas.

Maxwell –Boltzmann statistics:

- The particles are considered distinguishable and any number of particle can be any one state.

1	2	3
ab	-	-
-	ab	-
-	-	ab
a	b	-
b	a	-
a	-	b
b	-	a
-	a	b
-	b	a

- Total states $3^2 = 9$ possible states for the whole gas.

Bose-Einstein statistics:

- Particles are indistinguishable , i.e b=a

1	2	3
aa	-	-

-	aa	-
-	-	aa
a	a	-
a	-	a
-	a	a

- 3+3=6 possible states for the whole gas.

Fermi-Dirac statistics:

- Particles are indistinguishable and no more than one particle can be in any one state.

1	**2**	**3**
a	a	-
a	-	a
-	a	a

- 3 possible states for the whole gas.

$$\text{Let } \varepsilon = \frac{probability\ \ that\ the\ two\ partcles\ \ are\ found\ \ in\ the\ same\ \ state}{probability\ \ that\ the\ two\ particle\ \ are\ found\ \ in\ different\ \ states}$$

- Thus for the three cases,

$$\varepsilon_{M-B} = \frac{3}{6} = 1/2$$

$$\varepsilon_{B-E} = \frac{3}{3} = 1$$

$$\varepsilon_{F-D} = \frac{0}{3} = 0$$

- Thus in B-E statistics, there is a greater tendency for the particles to bunch together in the same states in comparison to M-B statistics.
- On the other hand, in the F-D statistics, there is a greater relative tendency to particles to remain apart in different states than there is in classical statistics.

5.6 BOSE-EINSTEIN STATISTICS:

- Consider a system having n identical and indistinguishable particles.
- These particles be divided into quantum groups such that there are $n_{1,}n_{2,} \dots, n_i, \dots$

number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.

- g_i be the number of eigen states in the i th level.

Conditions:

- Particles are identical and indistinguishable.
- Particles do not obey Pauli's exclusion principle.
- The total number of particles in the system is constant.

$$N = \sum n_i = constant$$

- The total energy of the system is constant.

$$E = \sum n_i \varepsilon_i = constant$$

Bose-Einstein distribution function:

- Consider the i th level
- g_i cells and n_i particles. Here we have to find out how n_i particles can be divided into g_i cells.
- First the choice that which cell will head the sequence can be found as g_i ways.
- Then the total number of permutations among n_i particles and the remaining $(g_i - 1)$ cells is $(n_i + g_i - 1)!$
- Now the total number of possible ways in which n_i particles can be distributed in g_i cells is

$$g_i(n_i + g_i 1)! \qquad \ldots.(1)$$

- Since the particles are indistinguishable the permutations of the particles among themselves will not give rise to different arrangements. Hence equation (1) must be divided by $n_i!$

$$\frac{g_i(n_i + g_i - 1)!}{n_i!}$$

- Similarly the permutations of cells among themselves will not give rise to different arrangements. Hence equation (1) must also be divided by $g_i!$

$$\frac{g_i(n_i + g_i - 1)!}{n_i!\, g_i!} = \frac{(n_i + g_i - 1)!}{n_i!\ (g_i - 1)!}$$

- Considering all the available groups such that n$_1$ particles with energy ε_1, n$_2$ particles with energy ε_2 and so on. Then the total number of possible arrangements is given by,

$$G$$

$$= \prod \frac{(n_i + g_i - 1)!}{n_i!\ (g_i - 1)!} \qquad \text{.... (2)}$$

n_i and $g_i >> 1$, hence one may be neglected.

$$G = \prod \frac{(n_i + g_i)!}{n_i!\ g_i!}$$

- The probability Ω of the system is proportional to the total number of eigen states.

$$\Omega = G \times constant$$

$\Omega = \prod \frac{(n_i+g_i)!}{n_i! g_i!} \times constant$ .... (3)

$$\log \Omega = \sum [\log(n_i + g_i)! - \log n! - \log g_i!] + constant$$

- Using stirling′s approximation, we get

$$\log \Omega = \sum [(n_i + g_i) \log(n_i + g_i) - (n_i + g_i) - n_i \ \log n_i + n_i - g_i \log g_i + g_i]$$
$$+ constant$$

$= \sum[(n_i + g_i) \log(n_i + g_i) - n_i \ \log n_i - g_i \log g_i] + constant$ .... (4)

$\delta[\log \Omega] = \sum \Big[(n_i + g_i) \frac{1}{(n_i+g_i)} \delta n_i + \log(n_i + g_i)\delta n_i - n_i \ \frac{1}{n_i} \delta n_i -$

log$ni\ \delta ni+0$

$$= \sum[\delta n_i + \log(n_i + g_i)\delta n_i - \delta n_i - \log n_i \delta n_i]$$

$$= \sum[log(n_i + g_i) - \log n_i]\delta n_i$$

$$= \sum \left[log \left(\frac{n_i+g_i}{n_i}\right)\right] \delta n_i$$

$$=$$

$$-\sum \left[log \left(\frac{n_i}{n_i+g_i}\right)\right] \delta n_i \qquad \text{.... (5)}$$

$\delta(\log \Omega) = 0.$

$$-\sum \left[log \left(\frac{n_i}{n_i+g_i}\right)\right] \delta n_i = 0$$

$$\sum \left[log \left(\frac{n_i}{n_i+g_i}\right)\right] \delta n_i = 0 \qquad \text{.... (6)}$$

$$\sum n_i = constant$$

$$\sum \delta n_i = 0 \qquad \text{....(7)}$$

$$\sum \varepsilon_i n_i = constant$$

$$\sum \varepsilon_i \delta n_i = 0 \qquad \text{.... (8)}$$

- Multiply the equation (7) by α and (8) by β and then adding to equation (6),we get,

$$\sum \left[\log \left(\frac{n_i}{n_i+g_i}\right) + \alpha + \beta \varepsilon_i\right] \delta n_i = 0 \qquad \text{....(9)}$$

$$\delta n_i \neq 0$$

$$\therefore \sum \left[\log \left(\frac{n_i}{n_i+g_i}\right) + \alpha + \beta \varepsilon_i\right] = 0$$

$$\log \left(\frac{n_i}{n_i+g_i}\right) + \alpha + \beta \varepsilon_i = 0$$

$$\log \left(\frac{n_i}{n_i+g_i}\right) = -(\alpha + \beta \varepsilon_i)$$

$$\frac{n_i}{n_i+g_i} = e^{-(\alpha+\beta \varepsilon_i)}$$

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

$$1 + \frac{g_i}{n_i} = e^{\alpha+\beta \varepsilon_i}$$

$$\frac{g_i}{n_i} = e^{\alpha+\beta\varepsilon_i} - 1$$

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1} \qquad \text{....(10)}$$

- This equation represents the most probable distribution for a system obeying Bose - Einstein statistics and known as ***Bose - Einstein distribution law***.

5.7 FERMI-DIRAC STATISTICS:

- Consider a system having n identical and indistinguishable particles.
- These particles be divided into quantum groups such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.
- g_i be the number of eigen states in the i^{th} level.

Conditions:

- Particles are identical and indistinguishable
- Particles obey Pauli's exclusion principle. Hence each cell contains 0 (or) 1 particle. Obviously $g_i \geq n_i$.
- The total number of particles in the system is constant.

$$N = \sum n_i = constant$$

- The total energy of the system is constant.

$$E = \sum n_i \varepsilon_i = constant$$

Fermi-Dirac distribution function:

- Consider the i th level.
- There are g_i cells and n_i particles.
- Each cell must be occupied by zero or one particle.
- Among g_i cells, only n_i cells are occupied by one particle and the remaining $(g_i - n_i)$ cells are empty.
- The possible number of such a distribution is given by $g_i!$ ....(1)
- Since the particles are indistinguishable the permutation of the particles among themselves will not give rise to different arrangements. Hence equation (1) must be divided by $n_i!$

$$\frac{g_i!}{n_i!}$$

◆ $(g_i - n_i)!$ permutations of empty cells among themselves will not give rise to different arrangements. Hence equation(1) must also be divided by $(g_i - n_i)!$

$$\frac{g_i!}{n_i!\,(g_i - n_i)!}$$

◆ Considering all the available groups such that n_1 particles with energy ε_1, n_2 particles with energy ε_2 and so on. Then the total number of possible arrangements is given by

$$G = \prod \frac{g_i!}{n_i!(g_i - n_i)!} \qquad \ldots.(2)$$

◆ The probability Ω of the system is proportional to the total number of eigen states.

$$\Omega = G \times constant$$

$$\Omega = \prod \frac{g_i!}{n_i!(g_i - n_i)!} \times constant \qquad \ldots.(3)$$

$$log\Omega = \sum [\log g_i! - \log n_i! - \log(g_i - n_i)\,!] + constant$$

◆ Using stirling′ approximation, we get

$$log\Omega = \sum [g_i \log g_i - g_i - n_i \log n_i + n_i - (g_i - n_i)\log(g_i - n_i) + (g_i - n_i)] + constant$$

$$= \sum [g_i \log g_i - n_i \log n_i - (g_i - n_i)\log(\,g_i - n_i)] + constant$$

$$\delta(\log \Omega) = \sum \left[-n_i \frac{1}{n_i}\delta n_i - \log n_i \delta n_i - \frac{(g_i - n_i)}{(g_i - n_i)}(-\delta n_i) - \log(g_i - n_i)\,(-\delta n_i)\right]$$

$$= \sum [-\delta n_i - logn_i \delta n_i + \delta n_i + \log(g_i - n_i)\delta n_i].$$

$$= \sum [logn_i \delta n_i + \log(g_i - n_i)\delta n_i].$$

$$= \sum \left[\log\left(\frac{g_i - n_i}{n_i}\right)\delta n_i\right].$$

$$= -\sum \left[\log\left(\frac{n_i}{g_i - n_i}\right)\delta n_i\right] \qquad \text{.... (5)}$$

$$\delta(\log \Omega) = 0$$

$$-\sum \left[\log\left(\frac{n_i}{g_i - n_i}\right)\delta n_i\right] = 0.$$

$$\sum \left[\log\left(\frac{n_i}{g_i - n_i}\right)\delta n_i\right] = 0 \qquad \text{.... (6)}$$

$$\sum n_i = constant$$

$$\sum \delta n_i = 0 \qquad \text{.... (7)}$$

$$\sum \varepsilon n_i = constant.$$

$$\sum \varepsilon \delta n_i = 0 \qquad \text{.... (8)}$$

- Multiplying equation (7) by α and (8) by β and then adding to equation (6), we get

$$\sum \left[\log\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta\varepsilon_i\right]\delta n_i = 0$$

$$\sum \left[\log\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta\varepsilon_i\right] = 0$$

$$\left[\log\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta\varepsilon_i\right] = 0$$

$$\log\left(\frac{n_i}{g_i - n_i}\right) = -(\alpha + \beta\varepsilon_i)$$

$$\frac{n_i}{g_i - n_i} = e^{-(\alpha + \beta\varepsilon_i)}$$

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

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta\varepsilon_i}$$

$$\frac{g_i}{n_i} = e^{\alpha+\beta\varepsilon_i} + 1$$

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} + 1}$$

- This equation represents the most probable distribution for a system obeying Fermi-Dirac statistics and known as ***Fermi-Dirac distribution law***.

5.8 AN IDEAL GAS IN A QUANTUM MECHANICAL MICRO CANONICAL ENSEMBLE:

- We consider a gaseous system of N non-interacting, indistinguishable particles confined to a space of volume V and energy E.
- Let $\Omega(N,V,E)$ be the number of distinct microstates accessible to the system under the macro state $\Omega(N,V,E)$.
- Let ε_i denote the average energy of a level and g_i be the number of levels in the i^{th} cell.$g_i \gg 1$.
- We have n_1 particles in the first cell, n_2 particles in the second cell and so on. The distribution set n_i must confirm to the conditions,

$$\textstyle\sum_i n_i = N \qquad \text{….(1)}$$

$$\textstyle\sum_i n_i\varepsilon_i = E \qquad \text{….(2)}$$

- Then $\Omega(N,V,E) = \Sigma' W\{n_i\}$ ….(3)
- $W\{n_i\}$ is the number of distinct microstates associated with the distribution set$\{n_i\}$. The primed summation goes over all distribution sets that confirm to conditions (1) and (2),
- $W\{n_i\} = \prod_i w(i)$ ….(4)
- $w(i)$is the number of distinct ways in which the n_i identical and indistinguishable particles can be distributed among the g_i levels of the i^{th} cell.
- In B-E case $w_{BE}(i) = \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$

  and hence $W_{BE}(n_i) = \prod \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$ ….(5)
- In the F-D case, no single level can accommodate more than one particle.

$$w_{FD}(i) = \frac{g_i!}{n_i!(g_i-1)!}$$

and hence $W_{FD}(n_i) = \frac{g_i!}{n_i!(g_i-1)!}$ ....(6)

- In M-B case the particle are distinguishable.
- $$W_{MB}(n_i) = \prod \frac{(g_i)^{n_i}}{n_i!} \qquad \text{....(7)}$$
- Now the entropy of the system would be given by,

$$S(N,V,E) = k \ln \Omega(N,V,E)$$

$$= k \ln\left[\sum\nolimits_{n_i}' W(n_i)\right]$$

$$\approx k \ln W(n_i^*) \qquad \text{....(8)}$$

- (n_i^{*}) is the distribution set that maximizes the number $W\{n_i\}$. n_i^* is the most probable value of the distribution number n_i .
- Our condition for determining the most probable distribution set $\{n_i^*\}$ now turns out to be,

$$\delta lnW(n_i) - [\alpha \sum_i \delta n_i + \beta \sum_i \varepsilon_i \delta n_i] = 0 \qquad \text{....(9)}$$

$$lnW(n_i) = \sum_i \ln w(i)$$

- In B-E case,

$$W_{BE}(n_i) = \prod \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$$

$$\approx \prod \frac{(n_i+g_i)!}{n_i! g_i\,!}$$

$$\ln W_{BE}(n_i) = \sum[\ln(n_i+g_i)! - \ln n_i! - \ln g_i!]$$

$$= \sum[(n_i+g_i)ln(n_i+g_i) - (n_i+g_i) - n_i \ln n_i + n_i -$$

$$g_i \ln g_i + g_i$$

$$= \sum[(n_i+g_i)ln(n_i+g_i) - n_i ln\, n_i -$$

$$g_i \ln g_i$$

$$= \sum[n_i \ln(n_i+g_i) - n_i \ln n_i + g_i \ln(n_i+g_i) - g_i \ln g_i]$$

$$= \sum\left\{n_i \ln\left[\frac{n_i+g_i}{n_i}\right] + g_i \ln\left[\frac{n_i+g_i}{g_i}\right]\right\}$$

$$= \sum\left\{n_i \ln\left(\frac{g_i}{n_i}+1\right) + g_i \ln\left(1 - a\,\frac{n_i}{g_i}\right)\right\}$$

- In general,

$$\ln W(n_i) = \sum\left\{n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a\,\frac{n_i}{g_i}\right)\right\} \qquad \text{....(10)}$$

a= -1	BE case
a=+1	FD case
a=0	MB case

$$\delta \ln W_{BE}(n_i) = \sum\left[(n_i + g_i)\frac{\delta n_i}{(n_i+g_i)} + \ln(n_i + g_i)\delta n_i - n_i\frac{\delta n_i}{n_i} -\right.$$

$$\ln n_i \delta n_i$$

$$= \sum[\ln(n_i + g_i) - \ln n_i]\delta n_i$$

$$= \sum\left[\ln\left(\frac{n_i+g_i}{n_i}\right)\delta n_i\right]$$

$$= \sum\left[\ln\left(\frac{g_i}{n_i} + 1\right)\delta n_i\right]$$

- In F-D case,

$$W_{FD} = \prod \frac{g_i!}{n_i!(g_i-n_i)!}$$

$$\ln W_{FD} = \sum[\ln g_i! - \ln n_i! - \ln\ (g_i - n_i)!]$$

$$= \sum[g_i \ln g_i - g_i - n_i ln\, n_i + n_i - (g_i - n_i)\ln(g_i - n_i) +$$

$$g_i - n_i$$

$$= \sum(g_i \ln n_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i))$$

$$\delta \ln W_{FD} = \sum\left[-n_i\frac{\delta n_i}{n_i} - \ln n_i \delta n_i - (g_i - n_i)\frac{(-\delta n_i)}{g_i - n_i} - \ln(g_i -\right.$$

$$n_i - \delta n_i$$

$$= \sum[(-\delta n_i) - \ln n_i \delta n_i + \delta n_i + \ln(g_i - n_i)\,\delta n_i\ ]$$

$$= \sum\left[\ln\left(\frac{g_i-n_i}{n_i}\right)\delta n_i\right] = \sum\left[\ln\left(\frac{g_i}{n_i} - 1\right)\delta n_i\right]$$

- In M-B case

$$W_{MB}(n_i) = \prod \frac{(g_i)^{n_i}}{n_i!}$$

$$\ln W_{MB} = \sum[n_i \ln g_i - \ln n_i!]$$

$$= \sum[n_i \ln g_i - n_i ln\, n_i + n_i]$$

$$\delta \ln W_{MB} = \sum\left[n_i.0 + \ln g_i \delta n_i - n_i\frac{\delta n_i}{n_i} - \ln n_i \delta n_i + \delta n_i\right]$$

$$= \sum[\ln g_i \delta n_i - \delta n_i - \ln n_i \delta n_i + \delta n_i\ ]$$

$$= \sum\left[\ln\left(\frac{g_i}{n_i}\right)\delta n_i\right] = \sum\left[\ln\left(\frac{g_i}{n_i} - a\right)\delta n_i\right]$$

- Now equation (9) becomes,

$$\sum_i \left[\ln\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta\varepsilon_i\right]_{n=n^*} \delta n_i = 0$$

$$\ln\left(\frac{g_i}{{n_i}^*} - a\right) - \alpha - \beta\varepsilon_i = 0$$

$$\ln\left(\frac{g_i}{{n_i}^*} - a\right) = \alpha + \beta\varepsilon_i$$

$$\frac{g_i}{{n_i}^*} - a = e^{\alpha+\beta\varepsilon_i}$$

$$\frac{g_i}{n_i^*} = e^{\alpha+\beta\varepsilon_i} + a$$

$$\frac{n_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i}+a} \qquad ....(11)$$

$$n_i^* = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+a} \qquad ....(12)$$

$$\frac{S}{k} \approx \ln W(n_i^*) = \sum_i \left[n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a}\ln\left(1 - a\frac{n_i^*}{g_i}\right)\right]$$

$$= \sum_i \left[n_i^*(\alpha+\beta\varepsilon_i) - \frac{g_i}{a}\ln\left(1 - \frac{a}{e^{\alpha+\beta\varepsilon_i}+a}\right)\right]$$

$$= \sum_i \left[n_i^*(\alpha+\beta\varepsilon_i) - \frac{g_i}{a}\ln\left(\frac{e^{\alpha+\beta\varepsilon_i}}{e^{\alpha+\beta\varepsilon_i}+a}\right)\right]$$

$$= \sum_i \left[n_i^*(\alpha+\beta\varepsilon_i) - \frac{g_i}{a}\ln\left(\frac{1}{1+ae^{-(\alpha+\beta\varepsilon_i)}}\right)\right]$$

$$= \sum \left[n_i^*(\alpha+\beta\varepsilon_i) + \frac{g_i}{a}\ln\left[1+ae^{-\alpha-\beta\varepsilon_i}\right]\right] \qquad ....(13)$$

- The first sum on RHS of (13) is αN while the second sum is βE. For the third sum, we have

$$\frac{1}{a}\sum g_i \ln\left[1+ae^{\alpha+\beta\varepsilon_i}\right] = \frac{S}{k} - \alpha N - \beta E \qquad ....(14)$$

$$\alpha = -\frac{\mu}{kT} \text{ and } \beta = \frac{1}{kT}$$

- The RHS of equation (14) is equal to,

$$\frac{S}{k} + \frac{\mu N}{kT} - \frac{E}{kT} = \frac{G-(E-TS)}{kT} = \frac{PV}{kT}$$

- The thermodynamic pressure of the system is given by

$$PV = \frac{kT}{a}\sum_i\left[g_i \ln\left[1+ae^{-\alpha-\beta\varepsilon_i}\right]\right] \qquad ....(15)$$

$$\frac{PV}{kT} = a^{-1}\sum_i\left[g_i \ln\left[1+ae^{-\alpha-\beta\varepsilon_i}\right]\right] \qquad ....(16)$$

- In M-B case (a→0), equation (15) takes the form

$$PV = kT\sum g_i e^{-\alpha-\beta\varepsilon_i}$$

$$= kT\sum_i n_i^*$$

$$= NkT \qquad ....(17)$$

- Which is the familiar equation of state of the *classical ideal gas*. Equation (17) for the M-B case holds irrespective of ε_i. The RHS of equation (16) is to be identical to the q-potential of the ideal gas.

5.9 AN IDEAL GAS IN A QUANTUM MECHANICAL GRAND CANONICAL ENSEMBLE:

- In canonical ensemble, the thermodynamics of a given system is derived from its partition function

$$Q_N(V,T) = \sum_E e^{-\beta E} \qquad \text{....(1)}$$

E → energy eigen values of the system.

and $\beta = 1/kT$

- E can be expressed in terms of the single-particle energies ε. For instance

$$E = \sum_\varepsilon n_\varepsilon \varepsilon \qquad \text{....(2)}$$

n_ε= number of particles in the single-particle energy state ε.

Also $\sum_\varepsilon n_\varepsilon = N$ ....(3)

- Now equation (1) can be written as,

$$Q_N(V,T) = \sum\nolimits'_{\{n_\varepsilon\}} g\{n_\varepsilon\} e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon} \qquad \text{....(4)}$$

$g\{n_\varepsilon\}$ = statistical weight factor appropriate to the distribution set $\{n_\varepsilon\}$

$\sum'$→goes over all distribution sets that conform to the restrictive condition(3).

- The statistical weight factor is given by

$$g_{B-E}\{n_\varepsilon\} = 1 \qquad \text{....(5)}$$

$$g_{F-D}\{n_\varepsilon\} = \begin{cases} 1 & \text{if all } n_\varepsilon\text{=0 (or) 1.} \\ 0 & \text{otherwise} \end{cases} \qquad \text{....(6)}$$

and

$$g_{M-B}\{n_\varepsilon\} = \prod_\varepsilon \frac{1}{n_\varepsilon!} \qquad \text{....(7)}$$

- Here we are dealing with single-particle states as individual states without requiring them to be grouped into cells.
- Take M-B case and substituting equation (7) into (4) we get

$$Q_N(V,T) = \sum\nolimits'_{\{n_\varepsilon\}} \left[\left(\prod_\varepsilon \frac{1}{n_\varepsilon!}\right) \prod_\varepsilon \left(e^{-\beta\varepsilon}\right)^{n_\varepsilon}\right]$$

$$= \frac{1}{N!} \sum\nolimits'_{\{n_\varepsilon\}} \left[\frac{N!}{\prod_\varepsilon n_\varepsilon!} \prod_\varepsilon \left(e^{-\beta\varepsilon}\right)^{n_\varepsilon}\right] \qquad \text{....(8)}$$

- Evaluated with the help of the multinomial theorem

$$Q_N(V,T) = \frac{1}{N!}\left[\sum_\varepsilon e^{-\beta\varepsilon}\right]^N$$

$$= \frac{1}{N!}[Q_1(V,T)]^N \qquad \text{....(9)}$$

- The number of single particle states with energies lying between ε and ε+dε is,

$$Q_1(V,T) = \sum_\varepsilon e^{-\beta\varepsilon}$$

$$\approx \frac{2\pi V}{h^3}(2m)^{3/2} \int_0^\infty e^{-\beta\varepsilon} \varepsilon^{1/2} d\varepsilon \qquad \text{....(10)}$$

$$= \frac{2\pi V}{h^3}(2m)^{3/2} \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}}$$

$$= V \frac{(2\pi mkT)^{3/2}}{h^3} = \frac{V}{\lambda^3}$$

where $\lambda = h/(2\pi mkT)^{1/2}$

= mean thermal wavelength of the particles.

- Hence, $Q_N(V,T) = \frac{V^N}{N!\lambda^{3N}}$ ….(11)
- From which complete thermodynamics of this system can be derived.
- We obtain for the grand partition function of this system,

$$\mathbf{Q}(z,V,T) = \sum_{N=0}^{\infty} Z^N Q_N(V,T)$$

$$= \sum_{N=0}^{\infty} z^N \frac{1}{N!}\frac{V^N}{\lambda^{3N}} = \frac{1}{N!}\sum_{N=0}^{\infty}\left(\frac{ZV}{\lambda^3}\right)^N$$

$$= \exp(zV/\lambda^3) \qquad \text{….(12)}$$

- B-E and F-D cases:

$$Q_N(V,T) = \sum_{\{n_\varepsilon\}}{}' \left(e^{-\beta\sum_\varepsilon n_\varepsilon \varepsilon}\right) \qquad \text{….(13)}$$

- Now complete thermodynamics of this system can be derived.
- The Grand partition function **Q** turns out to be

$$\mathbf{Q}(z,V,T) = \sum_{N=o}^{\infty}\left[z^N \sum_{\{n_\varepsilon\}}{}' \left(e^{-\beta\sum_\varepsilon n_\varepsilon \varepsilon}\right)\right]$$

$$= \sum_{N=0}^{\infty}\left[\sum_{\{n_\varepsilon\}}{}' \prod_\varepsilon \left(ze^{-\beta\varepsilon}\right)^{n_\varepsilon}\right] \qquad \text{….(14)}$$

- The double summation in (14) over the number n_ε constrained by a fixed value of the total number N and then over all possible values of N, which is equivalent to a summation over all possible values of n_ε independently of one another.
- Hence,

$$\mathbf{Q}(z,V,T) = \sum_{n_0,n_1,\ldots\ldots}\left[\left(ze^{-\beta\varepsilon_0}\right)^{n_0}\left(ze^{-\beta\varepsilon_1}\right)^{n_1}\ldots\right]$$

$$= \left[\sum_{n_0}\left(ze^{-\beta\varepsilon_0}\right)^{n_0}\right]\left[\sum_{n_1}\left(ze^{-\beta\varepsilon_1}\right)^{n_1}\right] \qquad \text{….(15)}$$

- In B-E case n_ε can be either 0 or 1 or 2 or ……
- In F-D case n_ε can be only 0 or 1.

$$\mathbf{Q}(z,V,T) = \begin{cases} \prod_\varepsilon \frac{1}{(1-ze^{-\beta\varepsilon})} & \text{in B-E case with } ze^{-\beta\varepsilon}<1. \\ \prod_\varepsilon (1+ze^{-\beta\varepsilon}) & \text{in F-D case} \end{cases} \qquad \text{….(16)}$$

The q potential of the system is thus given by,

$$q(z,V,T) = \frac{PV}{kT} = lnQ(z,V,T)$$

$$= \mp\sum_\varepsilon \ln(1 \mp ze^{-\beta\varepsilon}) \qquad \text{….(17)}$$

with $g_i = 1$

- The identification of the fugacity z with the quantity $e^{-\alpha}$ is quite natural. $\alpha = -\frac{\mu}{kT}$
- The upper sign in equation (17) corresponds to Bose case.
- The lower sign in equation (17) corresponds to Fermi case.
- Now in general,

$$q(z,V,T) = \frac{PV}{kT} = \frac{1}{a}\sum_{\varepsilon} \ln(1 + aze^{-\beta\varepsilon}) \qquad \text{….(18)}$$

- Where $a = -1, +1 \; or \; 0$ depending on the statistics governing the system.
- In classical case a → 0 gives,

$$q_{M-B} = z \sum_{\varepsilon} e^{-\beta\varepsilon} = zQ_1 \qquad \text{….(19)}$$

$$\bar{N} \equiv z\left(\frac{\partial q}{\partial z}\right)_{V,T}$$

$$= z\frac{1}{a}\sum \frac{ae^{-\beta\varepsilon}}{1+aze^{-\beta\varepsilon}}$$

$$= \sum \frac{z}{e^{\beta\varepsilon}+az}$$

$$= \sum \frac{1}{z^{-1}e^{\beta\varepsilon}+a} \qquad \text{….(20)}$$

$$\bar{E} \equiv -\left(\frac{\partial q}{\partial \beta}\right)_{z,V}$$

$$= -\frac{1}{a}\sum \frac{\left(aze^{-\beta\varepsilon}\right)(-\varepsilon)}{1+aze^{-\beta\varepsilon}}$$

$$= \sum \frac{\varepsilon}{z^{-1}e^{\beta\varepsilon}+a} \qquad \text{….(21)}$$

- At the same time, the mean occupation number $\langle n_\varepsilon \rangle$ of level ε turns out to be,

$$\langle n_\varepsilon \rangle = \frac{1}{\mathbf{Q}}\left[-\frac{1}{\beta}\left(\frac{\partial \mathbf{Q}}{\partial \varepsilon}\right)_{z,T,all\ other\ \varepsilon}\right]$$

$$= -\frac{1}{\beta}\left(\frac{\partial q}{\partial \varepsilon}\right)_{z,T,all\ other\ \varepsilon}$$

$$= -\frac{1}{\beta}\frac{1}{a}\frac{aze^{-\beta\varepsilon}(-\beta)}{1+aze^{-\beta\varepsilon}}$$

$$= \frac{ze^{-\beta\varepsilon}}{1+aze^{-\beta\varepsilon}}$$

$$= \frac{1}{z^{-1}e^{\beta\varepsilon}+a} \qquad \text{….(22)}$$

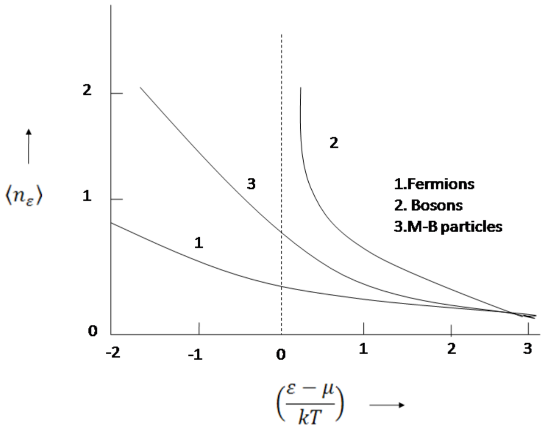
Thus the mean value <n> and the most probable value n^* of the occupation number n of a single particle state are identical.

5.10 STATISTICS OF THE OCCUPATION NUMBERS :

- The mean occupation number of a single particle with energy ε as an explicit function of the quantity $(\varepsilon-\mu)/kT$:

$$\langle n_\varepsilon \rangle = \frac{1}{e^{(\varepsilon-\mu)/kT}+a} \qquad \text{….(1)}$$

- The functional behaviour of this number is shown in figure.



- In the Fermi-Dirac case (a= +1), the mean occupation number never exceeds unity, for the variable n_ε, itself cannot have a value other than 0 or 1.

- Moreover ε < μ and $|\varepsilon-\mu| >> kT$, the mean occupation number tends to its maximum possible value 1.

- In the Bose-Einstein case (a= -1) we must have μ < all ε. When μ becomes equal to the lowest value of ε (ε_0), the occupancy level becomes high which leads to Bose-Einstein condensation.

- For $\mu < \varepsilon_0$ all $(\varepsilon-\mu)$ are positive and the behaviour of all $\langle n_\varepsilon \rangle$ is nonsingular. Finally in Maxwell-Boltzmann case (a= 0), the mean occupation number takes the form

$$\langle n_\varepsilon \rangle_{MB} = \exp\{(\mu-\varepsilon)/kT\} \propto \exp(-\varepsilon/kT) \qquad \text{….(2)}$$

- We note here that the distinction between the quantum statistics and the classical statistics becomes imperceptible when for all values of ε ,

$$\exp\{(\mu-\varepsilon)/kT\} >> 1. \qquad \text{….(3)}$$

- Now equation (1) reduces to (2) and we may write $\langle n_\varepsilon \rangle << 1$. ….(4)

- Condition (4) implies that the probability of any of the n_ε being greater than unity is quite negligible.

- The distinction between the classical treatment and the quantum-mechanical treatment then becomes rather insignificant.

- Correspondingly for large values of $(\varepsilon-\mu)/kT$ the quantum curves 1 and 2 essentially merge into the classical curve 3.

- Condition (3) also implies that μ, the chemical potential of the system must be negative and large in magnitude. This means that the fugacity $z\big| \equiv \exp(\mu/kT)$ of the system must be much smaller than unity.
- This is further equivalent to $\frac{N\lambda^3}{V} << 1$ ….(5)
- Now we examine statistical fluctuations in the variable n_ε. We have

$$\left\langle n_\varepsilon^2 \right\rangle = \frac{1}{Q}\left[\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon}\right)^2 Q\right]_{z,T,all\ \ other\ \ \varepsilon} \quad \text{….(6)}$$

- It follows that

$$\left\langle n_\varepsilon^2 \right\rangle - \left\langle n_\varepsilon \right\rangle^2 = \left[\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon}\right)^2 \ln Q\right]_{z,T,all\ \ other\ \ \varepsilon}$$

$$= \left[\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon}\right)\left\langle n_\varepsilon \right\rangle\right]_{z,T} \quad \text{….(7)}$$

- For the relative mean-square fluctuation we obtain

$$\frac{\left\langle n_\varepsilon^2 \right\rangle - \left\langle n_\varepsilon \right\rangle^2}{\left\langle n_\varepsilon \right\rangle^2} = \left(\frac{1}{\beta}\frac{\partial}{\partial\varepsilon}\right)\left\{\frac{1}{\left\langle n_\varepsilon \right\rangle}\right\} = z^{-1}e^{\beta\varepsilon} \quad \text{….(8)}$$

- The actual value of this quantity will depend on the statistics of the particles because for a given particle density (N/V) and a given temperature T, the value of z will be different for different statistics.
- Equation (8) can be written in the form

$$\frac{\left\langle n_\varepsilon^2 \right\rangle - \left\langle n_\varepsilon \right\rangle^2}{\left\langle n_\varepsilon \right\rangle^2} = \frac{1}{\left\langle n_\varepsilon \right\rangle} - a \quad \text{….(9)}$$

- In the classical case (a= 0), the relative fluctuation is normal.
- In the Fermi-Dirac case it is given by $1/\left\langle n_\varepsilon \right\rangle - 1$, which is below normal and tends to vanish as $\left\langle n_\varepsilon \right\rangle \to 1$.
- In the Bose-Einstein case , the fluctuation is above normal .
- This result would apply to a gas of photons and hence to the oscillators states in the black-body radiation.
- To understand the statistics of the occupation numbers, we evaluate the quantity $p_\varepsilon(n)$, the probability that there are exactly n particles in a state of energy ε.

- We know that $p_\varepsilon(n) \propto (ze^{-\beta\varepsilon})^n$. On normalization, it becomes in the Bose-Einstein case

$$p_\varepsilon(n)\big|_{B.E} = (ze^{-\beta\varepsilon})^n \left[1 - ze^{-\beta\varepsilon}\right]$$

$$= \left(\frac{\langle n_\varepsilon\rangle}{\langle n_\varepsilon\rangle + 1}\right)^n \frac{1}{\langle n_\varepsilon\rangle + 1} = \frac{(\langle n_\varepsilon\rangle)^n}{(\langle n_\varepsilon\rangle + 1)^{n+1}} \qquad \text{....(10)}$$

- In the Fermi-Dirac case, we get

$$p_\varepsilon(n)\big|_{F.D} = (ze^{-\beta\varepsilon})^n \left[1 + ze^{-\beta\varepsilon}\right]^{-1}$$

$$= \begin{cases} 1 - \langle n_\varepsilon\rangle & for \quad n = 0 \\ \langle n_\varepsilon\rangle & for \quad n = 1 \end{cases} \qquad \text{....(11)}$$

- In the Maxwell-Boltzmann case, we have $p_\varepsilon(n) \propto (ze^{-\beta\varepsilon})^n / n!$
- On normalization we get

$$p_\varepsilon(n)\big|_{M.B} = \frac{(ze^{-\beta\varepsilon})^n / n!}{\exp(ze^{-\beta\varepsilon})} = \frac{(\langle n_\varepsilon\rangle)^n}{n!} e^{-\langle n_\varepsilon\rangle} \qquad \text{....(12)}$$

- Equation (12) is clearly a Poisson distribution for which the mean square deviation of the variable is equal to the mean value itself.
- It also resembles the distribution of the total particle number N in a grand canonical ensemble consisting of ideal, classical systems.
- Here we seen that the ratio $p_\varepsilon(n)/p_\varepsilon(n-1)$ varies inversely with n, which is a "normal" statistical behaviour of uncorrelated events.
- The distribution in the Bose-Einstein case is geometric with a common ratio $\langle n_\varepsilon\rangle / (\langle n_\varepsilon\rangle + 1)$.
- This means that the probability of a state ε acquiring one more particle for itself is independent of the number of particles already occupying the state.
- In comparison with "normal" statistical behaviour, bosons exhibit a special tendency of "bunching" together. That is a *positive* statistical correlation among them. Fermions exhibit *negative* statistical correlation.

5.11 IDEAL BOSE-EINSTEIN GAS:

- Consider a perfect Bose-Einstein gas of n bosons.

- These particles be divided into quantum groups such that there are $n_1, n_2, \dots, n_i, \dots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_i, \dots$ respectively.
- g_i be the number of eigen states in the i th level.
- For the most probable distribution

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i - 1}} \quad \text{here } \alpha = \frac{-\mu}{kT} \text{ and } \beta = \frac{1}{kT}$$

$$= \frac{g_i}{\frac{1}{A}e^{\beta\varepsilon_i - 1}} \quad \text{where, } A = e^{-\alpha}$$

- Since the number of particles cannot be negative, we must always have

$$n_i \geq 0 \qquad \frac{1}{A}e^{\beta\varepsilon_i} \geq 0.$$

- The constant α can be determined by the condition

$$n = \sum n_i = \sum \frac{g_i}{e^{\alpha+\beta\varepsilon_i - 1}}$$

$$= \sum \frac{g_i}{\frac{1}{A}e^{\beta\varepsilon_i - 1}} \qquad \dots (1)$$

- Since the particles in a box are normal size and the translational levels are closely spaced and hence now the summation is replaced by integration.
- The number of particles states $g(p)dp$ between momentum p and p+dp is given by

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

- g_s = degenaracy factor = 1

$$\text{Now } g(p)dp = \frac{4\pi V p^2 dp}{h^3} \qquad \dots (2)$$

- Then equation (1) can be rewritten as

$$n(p)dp = \frac{g(p)dp}{e^{\alpha+\beta\varepsilon_i - 1}}$$

$$= \frac{4\pi V p^2 dp}{h^3} \frac{1}{e^{\alpha+\beta\varepsilon_i - 1}} \qquad \dots (3)$$

$$\varepsilon = \varepsilon_i = \frac{p^2}{2m}$$

$$p^2 = 2m\varepsilon$$

$$2pdp = 2md\varepsilon$$

$$dp = \frac{m}{p} d\varepsilon$$

$$= \frac{m}{\sqrt{2m\varepsilon}} d\varepsilon$$

$$= \left(\frac{m}{2\varepsilon}\right)^{1/2} \; d\varepsilon$$

- Now equation (3) becomes

$$n(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3}(2m\varepsilon)\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon \frac{1}{e^{\alpha+\varepsilon/kT}-1}$$

$$= \frac{4\pi mV}{h^3}(2m\varepsilon)^{1/2}\frac{d\varepsilon}{e^{\alpha+\varepsilon/kT}-1} \qquad \text{.... (4)}$$

$$\frac{\varepsilon}{kT} = x$$

$$\varepsilon = kTx$$

$$d\varepsilon = kTdx$$

$$n(\varepsilon)d\varepsilon = \frac{4\pi mV}{h^3}(2mkTx)^{1/2}\frac{kTdx}{e^{\alpha+x}-1}$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}\frac{2}{\sqrt{\pi}}\frac{x^{1/2}dx}{e^{\alpha+x}-1} \qquad \text{.... (5)}$$

- The total number of particles is given by

$$n = \int_0^\infty \frac{V}{h^3}(2\pi mkT)^{3/2}\frac{2}{\sqrt{\pi}}\frac{x^{1/2}dx}{e^{\alpha+x}-1}$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}-1}$$

$$n = \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha) \qquad \text{.... (6)}$$

$$\text{where } f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}-1} \qquad \text{.... (7)}$$

- The total energy is given by

$$E = \int_0^\infty \varepsilon \, n(\varepsilon)d\varepsilon$$

$$= \int_0^\infty kTx \; \frac{V}{h^3}(2\pi mkT)^{3/2}\frac{2}{\sqrt{\pi}}\frac{x^{1/2}dx}{e^{\alpha+x}-1}$$

$$= \frac{V}{h^3} kT\ (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}-1}$$

$$= \frac{3}{2}\frac{V}{h^3} kT\ (2\pi mkT)^{3/2} \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}-1}$$

$$= \frac{3}{2}\frac{V}{h^3}\ kT\ (2\pi mkT)^{3/2}\ f_2(\alpha) \qquad \ldots.(8)$$

$$f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}-1} \qquad \ldots.(9)$$

- For $A < 1, f_1(\alpha) and\ f_2(\alpha)$ may be evaluated as follows:

$$f_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}-1}$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dx}{\left(\frac{e^x}{A}-1\right)}$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{1/2} \left(\frac{e^x}{A}-1\right)^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{1/2} A e^{-x} (1 - Ae^{-x})^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{1/2} A e^{-x} [1 + Ae^{-x} + A^2 e^{-2x} + \cdots] dx$$

$$= \frac{2}{\sqrt{\pi}} \left[\int_o^\infty x^{1/2} A e^{-x} dx + \int_0^\infty x^{1/2} A^2 e^{-2x} dx + \cdots\right]$$

$$= \frac{2}{\sqrt{\pi}} \left[\sqrt{\frac{\pi}{2}}\ \left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots..\right]\right]$$

$$= A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots \ldots \ldots \ldots$$

$$f_1(\alpha) = \sum_{r=1}^{\infty} \frac{A^r}{r^{3/2}} \qquad \ldots.(10)$$

- Similarly $\qquad f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{\left(e^{-(\alpha+x)}-1\right)}$

$$= A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots$$

$$f_2(\alpha) = \sum_{r=1}^{\infty} \frac{A^r}{r^{5/2}} \qquad \ldots.(11)$$

$$\text{Now } n = \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha)$$

$$= \frac{V}{h^3}\ (2\pi mkT)^{3/2}\left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots\right] \qquad \text{.... (12)}$$

$$E = \frac{3}{2}kT\ \frac{V}{h^3}(2\pi mkT)^{3/2} f_2(\alpha).$$

$$E = \frac{3}{2}kT\ \frac{V}{h^3}(2\pi mkT)^{3/2}\left[A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots\right] \qquad \text{.... (13)}$$

$$\frac{E}{n} = \frac{3}{2}kT\ \left[A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots\right]\left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots\right]^{-1}$$

$$= \frac{3}{2}kT\ \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \cdots\right]\left[1 + \frac{A}{2^{3/2}} + \frac{A^2}{3^{3/2}} + \cdots\right]^{-1}$$

$$= \frac{3}{2}kT\left[1 - \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \cdots\right]$$

$$E = \frac{3}{2}nkT\left[1 - \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \cdots\right] \qquad \text{.... (14)}$$

- The value of α (or) A can be determined by equation (6) as

$$n = \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha)$$

$$f_1(\alpha) = \frac{n}{V}\frac{h^3}{(2\pi mkT\ )^{3/2}}$$

- Here $f_1(\alpha)$ is directly proportional to particle density n/v and inversely proportional to temperature as $T^{3/2}$.
- For $A << 1,\ f_1(\alpha) = A$

$$A = \frac{n}{V}\ \frac{h^3}{(2\pi mkT\ )^{3/2}} \qquad \text{.... (15)}$$

- Obviously A would be small for high temperatures (low density).

M-B distribution as a limiting case of B-E distribution:

- For $A << 1,\ e^{\alpha+\beta\varepsilon i}$ becomes very large compared to 1.
- Now B-E distribution $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}-1}$ becomes $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}}$ which is well known M-B distribution.
- For $A << 1, f_1(\alpha) = f_2(\alpha) = A$

- Equation (12) becomes $n = \frac{V}{h^3}(2\pi mkT)^{3/2} \times A$
- Equation (13) becomes $E = \frac{3}{2}kT\ \frac{V}{h^3}(2\pi mkT)^{3/2} \times A$

$$\frac{E}{n} = \frac{3}{2}kT \Rightarrow E = \frac{3}{2}nkT$$

- Which is well known expression for energy in M-B statistics.

5.12 BOSE-EINSTEIN CONDENSATION AND ITS CRITICAL CONDITIONS:

- The degeneracy parameter A is given by,

$$A = e^{-\alpha} = \frac{n}{V}\ \frac{(2\pi mkT\ )^{3/2}}{h^3} \qquad \text{....(1)}$$

- And $n = \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha)$ ....(2)
- If the particle density is increased or the temperature is decreased then A increases.
- Now the behaviour of perfect gas departs from the classical perfect gas.
- This is due to the fact that the velocities of the particles are subjected to quantum statistics.
- The gas under this condition is said to be degenerate gas and A is called the degeneracy parameter.
- ′A′ contains three variables n/V - the particle density , m - mass of each boson and
  T -temperature of the gas.
- The degeneracy criterion will be based on the magnitude $\frac{n/V}{(mT\ )^{1/2}}$
- Thus the degree of degeneracy will be large when T is low, n/V is large and m is small.
- For low energy values A=1 and α=0.
- Then $[f_1(\alpha)]_{max} = f_1(0) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots$

  = 2.612
- Now $\left(\frac{n}{V}\right)_{max} = \frac{(2\pi\pi mkT\ )^{3/2}}{h^3}\ (2.612)$ . ... (4)
- Equation (4) corresponds to the limiting case of Bose-Einstein degeneration.
- The solution of equation (2) can exist for

$$\frac{n}{V} > \frac{(2\pi mkT\ )^{3/2}}{h^3}(2.612) \qquad \text{. ... (5)}$$

- n/v can be alternatively expressed in terms of critical temperature T_o defined as

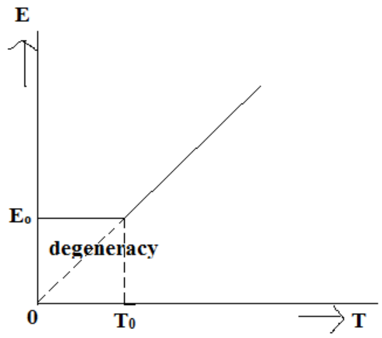
$$\frac{n}{V} = \frac{(2\pi mk\,T_0)^{3/2}}{h^3}(2.612) \qquad \ldots (6)$$

$$(2\pi mkT_0)^{3/2} = h^3\ \frac{n}{V}\ \frac{1}{2.612}$$

$$2\pi mkT_0 = h^2\left[\frac{n}{V}\ \frac{1}{2.612}\right]^{2/3}$$

$$T_0 = \frac{h^2}{2\pi mk}\ \left[\frac{n}{V}\ \frac{1}{2.612}\right]^{2/3}$$

- T_0 is the lower temperature for which a solution of equation (2) is possible.
- There is no solution for $T < T_0$
- i.e. the degeneracy starts at T_0.
- A graph is drawn between the energy E and temperature T of the gas.
- Why there is no solution $T < T_0$
- Because we have assumed continuous distribution and replaced the summation by integration.
- But at low temperature, the number of particles begin to crowd into lower energy levels.
- Hence a large number of particles may occupy the ground state $\varepsilon_0 = 0$.



- The number of particles between the energy range ε and $\varepsilon + d\varepsilon$ is given by,

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{\alpha+\varepsilon/kT}-1} \qquad \ldots (8)$$

And
$$g(\varepsilon)d\varepsilon = \frac{4\pi mv}{h^3}\ (2m\varepsilon)^{1/2}d\varepsilon \qquad \ldots (9)$$

- For ground state actually $\varepsilon_0 = 0\ and g(\varepsilon) = 1\ but\ not\ g(\varepsilon) = 0$
- For $\varepsilon \neq 0$ and $g(\varepsilon) \neq 0$, the distribution given by equation (8) is correct.
- But for $\varepsilon = 0, g(\varepsilon) = 0$ the law gives incorrect result.
- For a single state , $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}-1}$

$$\varepsilon_i = \varepsilon_0 = 0$$

$$g_i = g(\varepsilon_i) = 1$$

$$n = n_0 = \frac{1}{e^{\alpha}-1} \qquad \ldots(10)$$

- This gives the number of particles in the ground state.
- Now the total number of particles for the degenerate gas,

$$n = n_0 + \int n(\varepsilon) d\varepsilon$$

$$= n_0 + \int_0^{\infty} \frac{4\pi mV}{h^3}\ (2m)^{1/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha+\varepsilon/kT}-1}$$

$$= n_0 + n' \qquad \ldots(11)$$

$$n' = \frac{4\pi mV}{h^3}(2m)^{1/2} \int_0^{\infty} \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha+\varepsilon/kT}-1} \qquad \ldots(12)$$

$$n' = \frac{V}{h^3}\ (2\pi mkT)^{3/2}\ f_1(\alpha) \qquad \ldots(13)$$

- From equation (6) $\frac{n}{V} = \frac{(2\pi mk\,T_0)^{3/2}}{h^3}(2.612)$

$$\frac{V}{h^3}(2\pi mkT_0)^{3/2} = n\ \frac{1}{2.612}$$

- Now $\qquad n' = n\left(\frac{T}{T_0}\right)^{3/2} \frac{f_1(\alpha)}{2.612} \qquad \ldots(14)$
- As $f_1(\alpha) < f_1(0)$, n' acquires its maximum value when $\alpha = 0$.
- Hence $f_1(\alpha) = 2.612$ for maximum value.

$$n' = n\left(\frac{T}{T_0}\right)^{3/2} \qquad for\ T < T_0$$

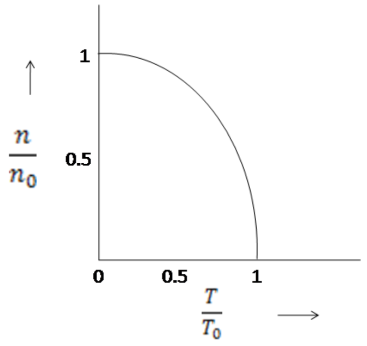
$$n = n_0 + n'$$

$$n = n_0 + n\left(\frac{T}{T_0}\right)^{3/2}$$

$$n_o = n - n\left(\frac{T}{T_0}\right)^{3/2}$$

$$n_0 = n\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] \qquad for\ T < T_0 \qquad \ldots(15)$$

- n_0 gives the number of particles condensed in the ground state.
- When the temperature is lowered below T$_0$, the number of particles in the ground state rapidly increases.
- *This rapid increase in the population of the ground state below the critical temperature T_0 for a Bose - Einstein gas is called Bose – Einstein condensation.*



- Obviously T_0 depends on the particle density n/V.
- Equation (15) is plotted in figure which represents the fraction of particles condensed in the ground state $for\ T < T_0$.
- At the ground state $\varepsilon = 0$, the particles condensed in the ground state do not contribute to the energy.
- For above T_o, $(\alpha \neq 0)$ there is negligible number of particles in the ground state and the gas is said to be classical or non - degenerate gas.
- Example: For Helium T_0 can be calculated to have the value 3.12 K.
- Therefore the degeneration and condensation of Helium must start at 3.12 K.
- But experimental observation shows that the condensation of Helium starts at 2.19 K.
- i.e. the lambda point transition observed in liquid helium at 2.19 K is essentially a Bose-Einstein condensation.

5.13 BOSE – EINSTEIN CONDENSATION IN ULTRACOLD ATOMIC GASES :

- The first demonstration of Bose- Einstein condensation in ultracold atomic gases came in 1995.
- Since 1995, many isotopes have been Bose condensed including ^{7}Li, ^{23}Na, ^{41}K, ^{52}Cr, ^{84}Sr, ^{85}Rb, ^{87}Rb, ^{133}Cs and ^{174}Yb.
- The first molecular Bose –Einstein condensates were created in 2003 by the research groups of Rudoif Grimm at the University of Innsbruck.
- The first step of the cooling of the atomic vapour uses three sets of counter-propagating laser beams oriented along cartesian axes that are tuned just below the resonant frequency of the atoms in the trap.
- Atoms that are stationary are just off resonance and so rarely absorb a photon.
- Moving atoms are Doppler shifted on resonance to the laser beam that is propagating opposite to the velocity vector of the atom.
- Those atoms preferentially absorb photons from that direction and then reemit in random directions, resulting in a net momentum kick opposite to the direction of motion.
- This results in an "optical molasses" that slows the atoms.
- This cooling method is constrained by the "recoil limit" in which the atoms have a minimum momentum of the order of the momentum of the photons used to cool the gas.

- This gives a limiting temperature of $(hf)^2/2mc^2k \approx 1\mu K$, where f is the frequency of the spectral line used for cooling and m is the mass of an atom.
- In the next step of the cooling process, the lasers are turned off and a spatially varying magnetic field creates an attractive anisotropic harmonic oscillator potential near the center of the magnetic trap

$$V(r) = \frac{1}{2}m\left(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2\right) \qquad \ldots.(1)$$

- The frequencies of the trap ω_α are controlled by the applied magnetic field. One can then lower the trap barrier using a resonant transition to remove the highest energy atoms in the trap. If the atoms in the vapor are sufficiently coupled to one other, then the remaining atoms in the trap are cooled by evaporation.
- If the interactions between the atoms in the gas can be neglected, the energy of each atom in the harmonic oscillator potential is

$$\varepsilon_{l_1,l_2,l_3} = \hbar\omega_1 l_1 + \hbar\omega_2 l_2 + \hbar\omega_3 l_3 + \frac{1}{2}\hbar\left(\omega_1 + \omega_2 + \omega_3\right) \qquad \ldots.(2)$$

- where l_α (= 0,1,2,.. .∞) are the quantum numbers of the harmonic oscillator. If the three frequencies are all the same, then the quantum degeneracy of a level with energy $\varepsilon = \hbar\omega(l + 3/2)\ is\ (l+1)(l+2)/2$
- For the general anisotropic case, the smoothed density of states as a function of energy (suppressing the zero point energy and assuming $\varepsilon >> \hbar\omega_\alpha$) is given by

$$a(\varepsilon) = \int_0^\infty\int_0^\infty\int_0^\infty \delta\left(\varepsilon - \hbar\omega_1 l_1 - \hbar\omega_2 l_2 - \hbar\omega_3 l_3\right)\, dl_1 dl_2 dl_3 = \frac{\varepsilon^2}{2\left(\hbar\omega_0\right)^3} \qquad \ldots (3)$$

- where $\omega_0 = \left(\omega_1\omega_2\omega_3\right)^{1/3}$; this assumes a single spin state per atom. The thermodynamic potential Π for bosons in the trap is then given by

$$\Pi\left(\mu, T\right) = -\frac{\left(kT\right)^4}{2\left(\hbar\omega_0\right)^3}\int_0^\infty x^2 \ln\left(1 - e^{-x}e^{\beta\mu}\right) dx = \frac{\left(kT\right)^4}{\left(\hbar\omega_0\right)^3} g_4\left(z\right) \qquad \ldots (4)$$

- where z = exp (βμ) is the fugacity. Volume is not a parameter in the thermodynamic potential since the atoms are confined by the harmonic trap. The average number of atoms in the excited states in the trap is

$$N\left(\mu T\right) = \left(\frac{\partial\Pi}{\partial\mu}\right)_T = \left(\frac{kT}{\hbar\omega_0}\right) g_3\left(z\right) \qquad \ldots. (5)$$

- For fixed N, the chemical potential monotonically increases as temperature is lowered until Bose-Einstein condensation occurs when $\mu = 0$ ($z = 1$). The critical temperature for N trapped atoms is then given by

$$\frac{kT_c}{\hbar\omega_0} = \left(\frac{N}{\varsigma(3)}\right)^{1/3} \qquad \text{…. (6)}$$

- where $\varsigma(3) = g_3(1) \approx 1.202$. While the spacing of the energy levels is of order $\hbar\omega_0$, the critical temperature for condensation is much larger than the energy spacing of the lowest levels for $N \gg 1$.
- For $T < T_c$ the number of atoms in the excited states is

$$\frac{N_{excited}}{N} = \frac{\varsigma(3)}{N}\left(\frac{kT}{\hbar\omega_0}\right)^3 = \left(\frac{T}{T_c}\right)^3 \qquad \text{…. (7)}$$

- so the fraction of atoms that condense into the ground state of the harmonic oscillator is

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^3; \qquad \text{…. (8)}$$

(a) Detection of the Bose-Einstein condensate:

- The linear size of the ground state wave function in Cartesian direction α is

$$a_\alpha = \sqrt{\frac{\hbar}{m\omega_\alpha}}, \qquad \text{….(9)}$$

- while the linear size of the thermal distribution of the noncondensed atoms in that direction is

$$a_{thermal} = \sqrt{\frac{kT}{m\omega_\alpha^2}} = a_\alpha\sqrt{\frac{kT}{\hbar\omega_\alpha}} \qquad \text{….(10)}$$

- At trap frequency $f = 100$ Hz and temperature $T = 100$ nK, these sizes are about 1 μm and 5μm, respectively.
- Instead of measuring the atoms directly in the trapping potential, experimenters usually measure the momentum distribution of the ultracold gas by a time-of-flight experiment.
- At time $t = 0$, the magnetic field is turned off suddenly, eliminating the trapping potential.

- The atomic cloud then expands according to the momentum distribution the atoms had in the harmonic trap. The cloud is allowed to expand for about 100 milliseconds.
- The speed of the atoms at this temperature is a few millimeters per second, so the cloud expands to a few hundred microns in this period of time.
- The cloud is then illuminated with a laser pulse on resonance with the atoms, leaving a shadow on a CCD in the image plane of the optics.
- The size and shape of the light intensity pattern directly measures the momentum distribution the atoms had in the trap at $t = 0$.
- The expanding cloud can be divided into two components, the N_o atoms that had been Bose-condensed into the ground state and the remaining $N - N_o$ atoms that were in the excited states of the harmonic oscillator potential.
- The Bose-condensed atoms have smaller momenta than the atoms that were in the excited states.
- After time t, the quantum evolution of the ground state has a spatial number density

$$n_0(r,t) = N_o\left|\psi_0(r,t)\right|^2 = \frac{N_0}{\pi^{3/2}}\prod_{\alpha=1}^{3}\left[\frac{1}{a_\alpha\sqrt{1+\omega_\alpha^2 t^2}}\exp\left(\frac{-r_\alpha^2}{a_\alpha^2\left(1+\omega_\alpha^2 t^2\right)}\right)\right] \quad \ldots.(11)$$

- The atoms that are not condensed into the ground state can be treated semi classically, that is, the position-momentum distribution function is treated classically while the density follows the Bose-Einstein distribution function:

$$\boldsymbol{f}(\boldsymbol{r},\boldsymbol{p},0) = \frac{1}{\exp\left(\frac{\beta p^2}{2m} + \frac{\beta m}{2}\left(\omega_1^2 \mathrm{x}^2 + \omega_2^2 y^2 + \omega_3^2 z^2\right) - \beta u\right) - 1} \quad \ldots.(12)$$

- After the potential is turned off at $t = 0$, the distribution evolves ballistically:

$$f(r,p,0) = f\left(r + \frac{pt}{m}, p, 0\right) \quad \ldots.(13)$$

- The spatial number density of atoms in the excited states is

$$n_{excited}(r,t) = \frac{1}{h^3}\int \mathrm{f}\left(r + \frac{pt}{m}, p, t\right)dp \quad \ldots.(14)$$

- which can be integrated to give

$$n_{excited}\left(r,t\right)=\frac{1}{\lambda^{3}}\sum_{j=1}^{\infty}\frac{e^{\beta\mu j}}{j^{3/2}}\left\{\prod_{\alpha=1}^{3}\left[\frac{1}{\sqrt{1+\omega_{\alpha}^{2}t^{2}}}\exp\left(\frac{-\beta jm\omega_{\alpha}^{2}r_{\alpha}^{2}}{2\left(1+\omega_{\alpha}^{2}t^{2}\right)}\right)\right]\right\} \qquad \text{….(15)}$$

- where $\lambda = h/\sqrt{2\pi mkT}$ is the thermal deBroglie wavelength. The integrals over the condensed state and the excited states correctly count all the atoms:

$$N_{0}=\int n_{o}\left(r,t\right)dr, \qquad \text{….(16a)}$$

$$N-N_{o}=\int n_{excited}(r,t)dr=N_{excited.} \qquad \text{….(16b)}$$

- Note that at early times $\omega_{\alpha}t<<1$ both the condensed and the excited distributions are anisotropic due to the anisotropic trapping potential.
- However, at late times $\omega_{\alpha}t>>1$, the atoms from the excited states form a spherically symmetric cloud because of the isotropic momentum dependence of the t = 0 distribution function.
- By contrast, the atoms that were condensed into the ground state expand anisotropically due to the different spatial extents of the ground state wavefunction at t = 0.
- The direction that has the largest ω_{0} is quantum mechanically squeezed the most at t = 0; so, according to the uncertainty principle, it expands the fastest.
- This is an important feature of the experimental data that confirms the onset of Bose-Einstein condensation.

(b) Thermodynamic properties of the Bose-Einstein condensate :

- The temperature, condensate fraction, and internal energy can all be observed using time- of-flight measurements. The internal energy can also be written in terms of the function $g_{v}(z)$:

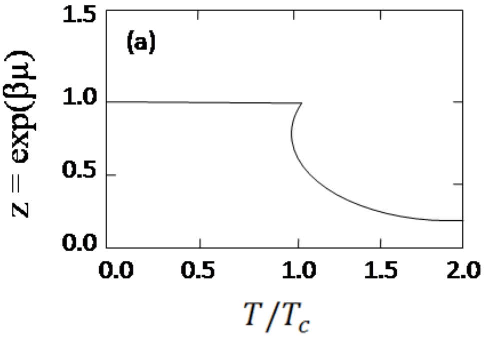
$$U\left(\mu,T\right)=\int_{0}^{\infty}\frac{\varepsilon^{3}}{2\left(\hbar\omega_{0}\right)^{3}}\frac{1}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon=3\frac{\left(kT\right)^{4}}{\left(\hbar\omega_{0}\right)^{3}}g_{4}\left(z\right) \qquad \text{….(17)}$$

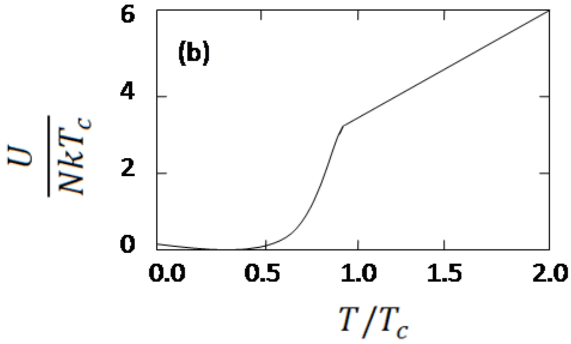
- The heat capacity at constant number can be written as

$$\mathrm{C_{N}(T)}=\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{N}}=\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mu}+\left(\frac{\partial \mathrm{U}}{\partial \mu}\right)_{\mathrm{T}}\left(\frac{\partial \mu}{\partial \mathrm{T}}\right)_{\mathrm{N}}$$

$$=\left(\frac{\partial U}{\partial T}\right)_{\mu}-\frac{\left(\frac{\partial U}{\partial T}\right)_{\mu}\left(\frac{\partial N}{\partial T}\right)_{\mu}}{\left(\frac{\partial N}{\partial \mu}\right)_{T}} \qquad \text{….(18)}$$

- Equations (5) and (6) can be used to determine the fugacity z numerically, as shown in Figure (a). The fugacity can then be used in equation (17) to obtain the scaled internal energy. [Figure (b)]





$$\frac{U}{NkT_c}=\begin{cases}3\left(\frac{T}{T_3}\right)^4\frac{\varsigma(4)}{\varsigma(3)} & \text{for } T\le T_{c,}\\ 3\left(\frac{T}{T_c}\right)^4\frac{g_4(z)}{\varsigma(3)} & \text{for } T\ge T_{c;}\end{cases}$$

….(19)

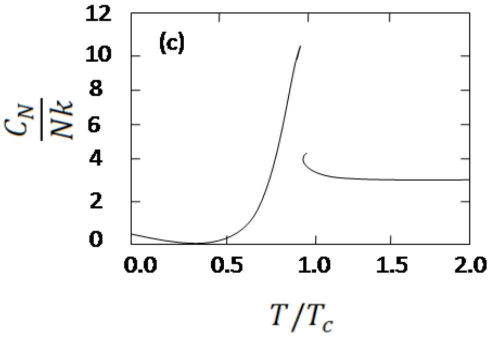
- The scaled specific heat is given by

$$\frac{C_N}{Nk}=\begin{cases}\frac{12\varsigma(4)}{\varsigma(3)}\left(\frac{T}{T_c}\right)^3 & \text{for } T<T_{c,}\\ \frac{1}{\varsigma(3)}\left(\frac{T}{T_c}\right)\left(12g_4(z)-\frac{9g_3^2(z)}{g_2(z)}\right) & \text{for } T>T_{c,}\end{cases}$$

.(20)

and shown in figure (c).

- Unlike the case of Bose-Einstein condensation of free particles in a box the specific heat of a condensate in a harmonic trap displays a discontinuity at the critical temperature.



$$\frac{C_N}{Nk} \to \begin{cases} \dfrac{12\varsigma(4)}{\varsigma(3)} \approx 10.805 & as\ T \to T_c^{\,-} \\ \dfrac{12\varsigma(4)}{\varsigma(3)} - \dfrac{9\varsigma(3)}{\varsigma(2)} \approx 4.228 & as\ T \to T_c^{\,+} \end{cases} \qquad ..(21)$$

- Equation (15) is called the Virial equation of state.
- This equation can also be written in terms of the pair correlation function and is also used in computer simulations to determine the pressure of the system.

5.14 IDEAL FERMI-DIRAC GAS:

- Consider a perfect Fermi-Dirac gas of n Fermions.
- These particles be divided into quantum groups such that there are $n_1, n_2, \dots, n_i, \dots$ number of particles with energy is $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_i, \dots$ respectively.
- g_i be the number of eigen states in the i th level.
- For the most probable distribution

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1} \quad \text{here } \alpha = \frac{-\mu}{kT} \text{ and } \beta = \frac{1}{kT}$$

$$= \frac{g_i}{\frac{1}{A}e^{\beta\varepsilon_i}+1} \quad \text{where, } A = e^{-\alpha}$$

α may be positive or negative.

- The constant α can be determined by the condition

$$n = \sum n_i = \sum \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1}$$

$$= \sum \frac{g_i}{\frac{1}{A}e^{\beta\varepsilon_i}+1} \qquad \dots (1)$$

- Since the particles in a box are normal size and the translational levels are closely spaced and hence now the summation is replaced by integration.
- The number of particle states $g(p)dp$ between momentum p and p+dp is given by

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

- g_s = degenaracy factor = $(2s+1)$

$$\text{Now } g(p)dp = g_s \frac{4\pi V p^2 dp}{h^3} \qquad \dots(2)$$

- Then equation (1) can be rewritten as

$$n(p)dp = \frac{g(p)dp}{e^{\alpha+\beta\varepsilon_i}+1}$$

$$= g_s \frac{4\pi V p^2 dp}{h^3} \frac{1}{e^{\alpha+\beta\varepsilon_i}+1} \qquad ....(3)$$

$$\varepsilon = \varepsilon_i = \frac{p^2}{2m}$$

$$p^2 = 2m\varepsilon$$

$$2pdp = 2md\varepsilon$$

$$dp = \frac{m}{p} d\varepsilon$$

$$= \frac{m}{\sqrt{2m\varepsilon}} d\varepsilon$$

$$= \left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon$$

- Now equation (3) becomes

$$n(\varepsilon)d\varepsilon = g_s \frac{4\pi V}{h^3} (2m\varepsilon) \left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon \frac{1}{e^{\alpha+\varepsilon/kT}+1}$$

$$= g_s \frac{4\pi m V}{h^3} (2m\varepsilon)^{1/2} \frac{d\varepsilon}{e^{\alpha+\varepsilon/kT}+1} \qquad ....(4)$$

$$\frac{\varepsilon}{kT} = x$$

$$\varepsilon = kTx$$

$$d\varepsilon = kTdx$$

$$n(\varepsilon)d\varepsilon = g_s \frac{4\pi m V}{h^3} (2mkTx)^{1/2} \frac{kTdx}{e^{\alpha+x}+1}$$

$$= g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2}dx}{e^{\alpha+x}+1} \qquad ....(5)$$

- The total number of particles is given by

$$n = \int_0^\infty g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2}dx}{e^{\alpha+x}+1}$$

$$= g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}+1}$$

$$n = g_s \frac{V}{h^3} (2\pi mkT)^{3/2} f_1(\alpha) \qquad ....(6)$$

where $f_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}+1}$ .... (7)

- The total energy is given by

$$E = \int_0^\infty \varepsilon\, n(\varepsilon) d\varepsilon$$

$$= \int_0^\infty kTx\, g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2}dx}{e^{\alpha+x}+1}$$

$$= g_s \frac{V}{h^3} kT\ (2\pi mkT)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}+1}$$

$$= \frac{3}{2} g_s \frac{V}{h^3} kT\ (2\pi mkT)^{3/2} \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}+1}$$

$$= \frac{3}{2} g_s \frac{V}{h^3}\ kT\ (2\pi mkT)^{3/2}\ f_2(\alpha) \quad \text{.... (8)}$$

$$f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+x}+1} \quad \text{.... (9)}$$

- $f_1(\alpha)$ and $f_2(\alpha)$ must be evaluated for both positive and negative values of α.
- Now we introduce the Fermi-Dirac distribution function $f(\varepsilon)$ defined by,

$$f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)}$$

$$= \frac{1}{e^{\alpha+\varepsilon/kT}+1}$$

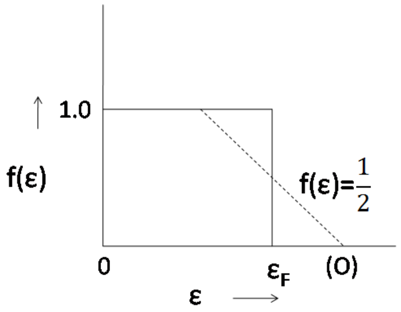
$$= \frac{1}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \quad \text{.... (10)}$$

- Where $\alpha = -\frac{\mu}{kT} = -\frac{\varepsilon_F}{kT}$
- At T=0 K, $f(\varepsilon) = 1\ for\ \varepsilon < \varepsilon_F(0)$

$= 0\ for\ \varepsilon > \varepsilon_F(0)$

$= \frac{1}{2}\ for\ \varepsilon = \varepsilon_F$

- This is shown in the figure.



- ε_F is determined by the condition that the total number of particles is constant at a given temperature T.
- The number of fermions in the energy range between ε and $\varepsilon + d\varepsilon$ is given by,

$$n(\varepsilon)d\varepsilon = \int f(\varepsilon)g(\varepsilon)d\varepsilon$$

$$= g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(11)$$

- At absolute zero, all states with $0 < \varepsilon < \varepsilon_F(0)$ are completely filled and all states with $\varepsilon > \varepsilon_F(0)$ are empty.
- ε_F at T=0 K i.e. $\varepsilon_F(0)$ is determined by,

$$n = \int_0^{\varepsilon_F(0)} n(\varepsilon) d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} f(\varepsilon) g(\varepsilon) d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} g(\varepsilon) d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \varepsilon^{1/2} d\varepsilon$$

$$= g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \int_0^{\varepsilon_F(0)} \varepsilon^{1/2} d\varepsilon$$

$$n = g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \left[\frac{2}{3} \varepsilon_F(0)^{3/2}\right]$$

$$[\varepsilon_F(0)\,]^{3/2} = \frac{3n}{4\pi V g_s} \frac{h^3}{(2m)^{3/2}}$$

$$\varepsilon_F(0) = \frac{h^2}{2m} \left[\frac{3n}{4\pi V g_s}\right]^{2/3} \qquad \ldots.(12)$$

- This gives the Fermi-energy at T=0K.
- For particles with spin equal to 1/2, g_s=2 ie, one particle with spin up and another with spin down.
- Now we define Fermi temperature T_F as,

$$T_F = \frac{\varepsilon_F(0)}{k}$$

$$= \frac{h^2}{2mk} \left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

$$\rho = \frac{mn}{V} \Rightarrow \frac{n}{V} = \frac{\rho}{m}$$

$$T_F = \frac{h^2}{2mk} \left(\frac{3\rho}{4\pi m g_s}\right)^{2/3}$$

$$\boxed{T_F = \frac{h^2}{2m^{5/3}k} \left[\frac{3\rho}{4\pi g_s}\right]^{2/3}} \qquad \ldots.(13)$$

◆ $T << T_F$	strong degeneracy	α is negative
◆ $T > T_F$	weak degeneracy	α is positive
◆ $T >> T_F$	non degeneracy	α is positive

(A) Degeneracy:

i. Weak degeneracy: (High temperature and low density)

$T > T_F$; ε_F is negative ; α is positive and hence $A < 1$.

For $A < 1$, we can write

$$\frac{1}{\frac{1}{A}e^x+1} = \left(\frac{1}{A}\, e^x + 1\right)^{-1}$$

$$= Ae^{-x}[1 + Ae^{-x}]^{-1}$$

$$= Ae^{-x}[1 - Ae^{-x} + A^2e^{-2x} + \cdots]$$

$$f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{e^{\alpha+x}+1}$$

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{\left(\frac{1}{A}e^x+1\right)}$$

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty x^{1/2}dx\, Ae^{-x}\,[1 - Ae^{-x} + A^2e^{-2x} + \cdots]$$

$$= \frac{2}{\sqrt{\pi}}\left[A\int_0^\infty x^{1/2}e^{-x}dx - A^2\int_0^\infty x^{1/2}\,e^{-2x}dx + A^3\int_0^\infty x^{1/2}e^{-3x}dx + \cdots\right]$$

$$= A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots \qquad \ldots(1)$$

- Similarly $$f_2(\alpha) = \frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{3/2}dx}{\left(\frac{1}{A}\,e^x+1\right)}$$

$$= A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots \qquad \ldots(2)$$

- Now $$n = g_s\frac{V}{h^3}(2\pi mkT)^{3/2}f_1(\alpha)$$

$$= g_s\frac{V}{h^3}(2\pi mkT)^{3/2}\left[A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots\right] \qquad \ldots.(3)$$

$$E = \frac{3}{2}g_s\frac{v}{h^3}(2\pi mkT)^{3/2}\,kT\,f_2(\alpha)$$

$$= \frac{3}{2}g_s\frac{v}{h^3}(2\pi mkT)^{3/2}\left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots\right] \qquad \ldots.(4)$$

$$\frac{E}{n} = \frac{3}{2}kT\left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \cdots\right]\left[A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \cdots\right]^{-1}$$

$$= \frac{3}{2}kT\left[1 + \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} + \cdots\right] \qquad \ldots.(5)$$

- To find first approximation we can get,

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

$$E = \frac{3}{2}nkT \qquad \ldots.(6)$$

- which is well known relation for E in classical statistics.
- Comparison of equations (5) and (6) shows that the ideal Fermi-Dirac gas deviates from a classical perfect gas and this deviation is known as degeneracy.
- A is the degeneracy function and greater the value of A, more will be the degeneracy.

ii. Strong degeneracy: (low temperature and high density)

- Here we discuss the degeneracy case in two temperature ranges.
- (a) At absolute zero(T=0 K)
- (b) Above absolute zero

(a) <u>At absolute zero(T=0 K):</u>

- In this case the Fermi-dirac gas is completely degenerate.
- At T=0 K, $f(\varepsilon) = \frac{1}{\frac{1}{A}e^{\varepsilon/kT}+1}$

$$= \frac{1}{\frac{1}{A}e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$= 1 \quad for \qquad 0 \le \varepsilon \le \varepsilon_F(0)$$

$$= 0 \quad for \qquad \varepsilon > \varepsilon_F$$

- So that $n(\varepsilon)d\varepsilon = g_s\left(\frac{4\pi mV}{h^3}\right)(2m)^{1/2}\varepsilon^{1/2}d\varepsilon \qquad for\ 0 \le \varepsilon \le \varepsilon_F(0)$

$$= 0 \qquad\qquad for\ \varepsilon > \varepsilon_F(0)$$

- The total internal energy of Fermi-Dirac gas at T=0 K gives zero point energy.

$$E_0 = \int_0^{\varepsilon_F(0)} \varepsilon\, n(\varepsilon)d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} g_s\left(\frac{4\pi mV}{h^3}\right)(2m)^{1/2}\varepsilon^{1/2}d\varepsilon$$

$$= g_s\left(\frac{4\pi mV}{h^3}\right)(2m)^{1/2}\int_0^{\varepsilon_F(0)} \varepsilon^{3/2}d\varepsilon$$

$$= g_s\left(\frac{4\pi mV}{h^3}\right)(2m)^{1/2}\ \frac{[\varepsilon_F(0)]^{5/2}}{5/2}$$

$$= \frac{2}{5}\ g_s\left(\frac{4\pi mV}{h^3}\right)\ (2m)^{1/2}\ [\varepsilon_F(0)]^{5/2}$$

$$= \frac{2}{5} g_s \left(\frac{4\pi mV}{h^3}\right) (2m)^{1/2} \left[\frac{h^2}{2m} \left(\frac{3n}{4\pi v g_s}\right)^{2/3}\right]^{5/2}$$

$$= \frac{3n}{5} \left(\frac{4\pi V g_s}{3n}\right) \left(\frac{2m}{h^2}\right)^{3/2} \frac{h^5}{(2m)^{5/2}} \left(\frac{3n}{4\pi v g_s}\right)^{5/3}$$

$$= \frac{3n}{5} \frac{h^2}{2m} \left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

$$E_0 = \frac{3n}{5} \varepsilon_F(0) \qquad \ldots.(7)$$

- Zero point pressure $p_0 = \frac{2}{3} \frac{E_0}{V}$

$$= \frac{2}{3} \frac{1}{V} \frac{3n}{5} \varepsilon_F(0)$$

$$p_0 = \frac{2}{5} \frac{n}{V} \varepsilon_F(0) \qquad \ldots.(8)$$

- Thus a strongly degenerate Fermi-Dirac gas possesses energy and pressure even at absolute zero.

(b) <u>Above absolute zero</u>: $\boldsymbol{A} >> 1 \; and \; T << \boldsymbol{T_F}$

- The Fermi gas is strongly degenerate and ε is still positive.
- The number of particles in the energy range between ε and $\varepsilon + d\varepsilon$ is given by,

$$n(\varepsilon)d\varepsilon = g_s \left(\frac{4\pi mV}{h^3}\right) (2m)^{\frac{1}{2}} \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(9)$$

$$= 3n \left(\frac{4\pi V g_s}{3n}\right) \left(\frac{2m^3}{h^6}\right)^{1/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

- We have Fermi energy

$$\varepsilon_F(0) = \frac{h^2}{2m} \left(\frac{3n}{4\pi v g_s}\right)^{2/3}$$

$$\left(\frac{3n}{4\pi v g_s}\right)^{2/3} = \left[\frac{2m\varepsilon_F(0)}{h^2}\right]$$

$$\left(\frac{3n}{4\pi v g_s}\right) = \left[\frac{2m\varepsilon_F(0)}{h^2}\right]^{3/2}$$

$$\left(\frac{4\pi v g_s}{3n}\right) = \left[\frac{2m\varepsilon_F(0)}{h^2}\right]^{-3/2}$$

$$= \left[\frac{h^2}{2m\varepsilon_F(0)}\right]^{3/2}$$

$$n(\varepsilon)d\varepsilon = 3n\left[\frac{h^2}{2m\varepsilon_F(0)}\right]^{3/2}\left(\frac{2m^3}{h^6}\right)^{1/2}\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$= \frac{3}{2}\,\frac{n}{[\varepsilon_F(0)]^{3/2}}\,\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(10)$$

$$n = \int_0^\infty n(\varepsilon)d\varepsilon$$

$$= \frac{3}{2}\,\frac{n}{[\varepsilon_F(0)]^{3/2}}\int_0^\infty\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(11)$$

$$E = \int_0^\infty \varepsilon\, n(\varepsilon)d\varepsilon$$

$$= \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}}\int_0^\infty\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(12)$$

- To solve the integrals in equation (11) and (12), we consider the general integral

$$I = \int_0^\infty\frac{\varphi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \ldots.(13)$$

- Here, $\varphi(\varepsilon)$ is a function of ε such that $\varphi(\varepsilon) = 0\ at\ \varepsilon = 0$.
- By Taylor series expansion,

$$\int_0^\infty\frac{\varphi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} = \int_0^{\varepsilon_F}\varphi(\varepsilon)d\varepsilon + \frac{(\pi kT)^2}{6}[\varphi']_{\varepsilon=\varepsilon_F} + \frac{7}{360}\,(\pi kT)^4(\varphi''')_{\varepsilon=\varepsilon_F} + \cdots$$

Take $\varphi(\varepsilon) = \varepsilon^{1/2}$

$$\varphi'\big|_{\varepsilon=\varepsilon_F} = \frac{1}{2}\,{\varepsilon_F}^{-1/2}$$

$$\varphi''\big|_{\varepsilon=\varepsilon_F} = -\frac{1}{4}{\varepsilon_F}^{-3/2}$$

$$\varphi'''\big|_{\varepsilon=\varepsilon_F} = \frac{3}{8}{\varepsilon_F}^{-5/2}$$

$$n = \frac{3}{2}\,\frac{n}{[\varepsilon_F(0)]^{3/2}}\int_0^\infty\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$= \frac{3}{2}\,\frac{n}{[\varepsilon_F(0)]^{3/2}}\left[\frac{2}{3}\,{\varepsilon_F}^{3/2} + \frac{(\pi kT)^2}{6}\frac{1}{2}\,{\varepsilon_F}^{-1/2} + \frac{7}{360}\,(\pi kT)^4\frac{3}{8}\,{\varepsilon_F}^{-5/2} + \cdots\right]$$

$$n = n\left[\frac{\varepsilon_F}{\varepsilon_F(0)}\right]^{3/2}\left[1+\frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2+\frac{7}{640}\left(\frac{\pi kT}{\varepsilon_F}\right)^4+\cdots\ldots\ldots\right]$$

$$\left[\frac{\varepsilon_F}{\varepsilon_F(0)}\right]^{3/2} = \left[1+\frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2+\frac{7}{640}\left(\frac{\pi kT}{\varepsilon_F}\right)^4+\cdots\ldots\ldots\right]$$

- To the first approximation we get ,

$$\left[\frac{\varepsilon_F}{\varepsilon_F(0)}\right]^{-3/2} = \left[1+\frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]$$

$$\left[\frac{\varepsilon_F}{\varepsilon_F(0)}\right] = \left[1+\frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]^{-2/3}$$

$$= \left[1-\frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right] \qquad \ldots.(14)$$

$$\varepsilon_F = \varepsilon_F(0)\left[1-\frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right] \qquad \ldots.(15)$$

- By applying Crude approximation we get,

$$\varepsilon_F = \varepsilon_F(0)\left[1-\frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \ldots.(16)$$

Take $\varphi(\varepsilon) = \varepsilon^{3/2}$

$$\int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon = \frac{2}{5}\,(\varepsilon_F)^{5/2}$$

$$\varphi'(\varepsilon)\Big|_{\varepsilon=\varepsilon_F} = \frac{3}{2}\,{\varepsilon_F}^{1/2}$$

$$\varphi''(\varepsilon)\Big|_{\varepsilon=\varepsilon_F} = \frac{3}{4}{\varepsilon_F}^{-1/2}$$

$$\varphi'''(\varepsilon)\Big|_{\varepsilon=\varepsilon_F} = -\frac{3}{8}{\varepsilon_F}^{-3/2}$$

$$E = \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}}\int_0^{\infty}\frac{\varepsilon^{3/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$= \frac{3}{2}\,\frac{n}{[\varepsilon_F(0)]^{3/2}}\left[\frac{2}{5}\,{\varepsilon_F}^{5/2}+\frac{(\pi kT)^2}{6}\frac{3}{2}\,{\varepsilon_F}^{1/2}-\frac{7}{360}\,(\pi kT)^4\frac{3}{8}\,{\varepsilon_F}^{-3/2}+\cdots\right]$$

$$= \frac{3}{5}\,n\,\frac{{\varepsilon_F}^{5/2}}{[\varepsilon_F(0)]^{3/2}}\left[1+\frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2-\frac{7}{384}\left(\frac{\pi kT}{\varepsilon_F}\right)^4+\cdots\right]$$

$$= \frac{3}{5}\, n\varepsilon_F(0) \left(\frac{\varepsilon_F}{\varepsilon_F(0)}\right)^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2 - \frac{7}{384}\left(\frac{\pi kT}{\varepsilon_F}\right)^4 + \cdots\right]$$

- To the first approximation we get,

$$E = \frac{3}{5} n\varepsilon_F(0) \left(\frac{\varepsilon_F}{\varepsilon_F(0)}\right)^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right] \qquad \ldots.(17)$$

- By applying Crude approximation we get,

$$E = \frac{3}{5} n\varepsilon_F(0) \left(\frac{\varepsilon_F}{\varepsilon_F(0)}\right)^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \ldots.(18)$$

- Using equation (16) we get,

$$= \frac{3}{5} n\varepsilon_F(0) \left[1 - \frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$$

$$= \frac{3}{5} n\varepsilon_F(0) \left[1 - \frac{5}{24}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \left[1 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$$

$$= \frac{3}{5} n\varepsilon_F(0) \left[1 - \frac{5}{24}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2 + \frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$$

$$E = \frac{3}{5}\, n\varepsilon_F(0) \left[1 + \frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \ldots.(19)$$

- The corresponding pressure is

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

$$= \frac{2}{5}\,\frac{n\varepsilon_F(0)}{V} \left[1 + \frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad (20)$$

- Equations (19) and (20) give the approximate energy and pressure of a strongly degenerate Fermi gas and also known as equation of state of an ideal Fermi gas.

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