SRIMAAN

PG-TRB

PHYSICS

UNIT-IV-STUDY MATERIAL

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SRIMAAN COACHING CENTRE-TRICHY.
TO CONTACT:8072230063.
PG-TRB: PHYSICS
UNIT-IV

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.

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, $$S = f(\Omega)$$
- 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.

$$S = S_1 + S_2$$

- The probability Ω of finding both systems will be the product of the two probabilities Ω_1 and Ω_2.

ie $$\Omega = \Omega_1\Omega_2$$

Substituting equations (2) and (3) in equation (1) we get,

$$S = f(\Omega) = f(\Omega_1\Omega_2)$$

$$S = S_1 + S_2$$

$$f(\Omega_1\Omega_2) = f(\Omega_1)(\Omega_2)$$

- Differentiating with respect to Ω_1 we get,

$$\Omega_2 f'(\Omega_1\Omega_2)\, f'(\Omega_1)$$

- Differentiating with respect to Ω_2 we get,

$$\Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2)$$

Divide equation 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, $$f(\Omega) = k \log \Omega + c$$

$$S = k \log \Omega + c$$

- 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,

$$\Omega_1 = \left[\frac{V_1}{V_1+V_2}\right]^N$$

- The probability of finding one mole of the gas in the container has volume V_1+V_2 is

$$\Omega_2 = \left[\frac{V_1+V_2}{V_1+V_2}\right]^N = [1]^N$$

From Boltzmann relation

$$\Delta S = S_2 - S_1$$

$$= k\, log\, \Omega_2 - k\, log\, \Omega_1$$

$$= k\, log\, \left(\frac{\Omega_2}{\Omega_1}\right)$$

$$= k\, log\, \left[\frac{1}{\frac{V_1}{V_1+V_2}}\right]^N$$

$$\Delta S = k\, log\, \left[\frac{V_1+V_2}{V_1}\right]^N$$

$$= log\, \left[\frac{V_1+V_2}{V_1}\right]^{Nk}$$

- 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 $C_v\, log\, \frac{T_2}{T_1} = 0$

$$\Delta S = R\, log\, [\frac{V_1+V_2}{V_1}]$$

$$= log\, \left[\frac{V_1+V_2}{V_1}\right]^R$$

Comparing equation , we get

$$Nk = R$$

$$k = R/N$$

$$= 1.03 \times 10^{-23}\, J/K$$ = Boltzmann's constant

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.

- 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.

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.

$$\text{ie, } \Omega(\varepsilon) d\,\varepsilon = \frac{4\pi V\sqrt{2}}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon$$

- 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,

$$\Omega(\varepsilon)d\,\varepsilon = \frac{4\pi V\sqrt{2}}{h^3}\, m^{3/2}\varepsilon^{1/2}d\varepsilon$$

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 $u_1, u_2, \ldots\ldots.., u_m$ having probabilities $P_1, P_2, \ldots \ldots., P_m$.

$$\bar{u} = \frac{P_1u_1 + P_2u_2 + \cdots \ldots\ldots + P_iu_i + \cdots \ldots\ldots P_mu_m}{P_1 + P_2 + \cdots \ldots\ldots + P_i + \cdots \ldots\ldots\ldots P_m}$$

$$= \frac{\sum_{i=1}^{m} P_iu_i}{\sum_{i=1}^{m} P_i}$$

- The sum of the probabilities of the all possible state must be equal to one.

$$\text{ie, } P_1 + P_2 + \cdots \ldots\ldots + P_i + \cdots \ldots\ldots + P_m = \sum_{i=1}^{m} P_i = 1$$

- 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,

$$\bar{u} = \frac{\int u(q,p)P(q,p)d\Gamma}{\int P(q,p)d\Gamma}$$

$$d\Gamma = dq_1, dq_2, \ldots\ldots\ldots, dq_f \;\; dp_1, dp_2, \ldots.., dp_f$$

- 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.

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.

$$d\rho/dt = 0$$

- 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.

$$\frac{d}{dt}(\delta\Gamma) = \frac{d}{dt}\left(\prod_i^f dq_i dp_i\right) = 0$$

(i) The principle of conservation of density in the phase space:

- Consider any arbitrary hyper volume $\delta\Gamma = \delta q_1\, \delta q_2 \ldots\ldots \delta q_f\ \ \delta p_1\, \delta p_2 \ldots\ldots \delta p_f$ in the phase space located between q_1 and $q_1 + \delta q_1 \ldots\ldots\ldots q_f$ and $q_f + \delta q_f$, p_1 and $p_1 + \delta p_1, \ldots\ldots\ldots p_f$ 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 ,

$$\delta N = \rho.\delta\Gamma = \rho\delta q_1\, \delta q_2\ \ldots\ldots \delta q_f\ \delta p_1 \delta p_2\ \ldots\ldots\ldots \delta p_f$$

- The change in number of phase points in volume element per unit time,

$$\frac{d(\delta N)}{dt} = \frac{d}{dt}(\rho.\delta\Gamma) = \dot{\rho}\delta\Gamma = \dot{\rho}\ \delta q_1\ \delta q_2\ \ldots\ldots\delta q_f \delta p_1 \delta p_2\ \ldots\ldots\ldots\delta p_f$$

- 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 $q_1, q_2, \ldots\ldots q_f, p_1, p_2, \ldots\ldots\ldots p_f$,then the number of phase points entering the first face AD per second

$$= \rho\dot{q}_1\ \delta q_2 \ldots\ldots\delta q_f\ \ \delta p_1 \ldots\ldots\delta p_f$$

- 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.

$$= (\rho + \frac{\partial\rho}{\partial q_1}\delta q_1)\ (\dot{q}_1 + \frac{\partial\dot{q}_1}{\partial q_1}\delta q_1)\ \delta q_2 \ldots\ldots\delta q_f\ \delta p_1, \ldots\ldots\ldots\delta p_f$$

- Neglecting higher order differentials, we get

$$= \left[\rho\dot{q}_1\ + (\rho\ \frac{\partial\dot{q}_1}{\partial q_1} + \dot{q}_1\frac{\partial\rho}{\partial q_1})\delta q_1\right]\ \delta q_2 \ldots\ldots\delta q_f\ \delta p_1, \ldots\ldots\ldots\delta p_f$$

- Subtracting (6) from (5) we get the expression for change in the number of phase points per second corresponding to q_1.

$$= -(\rho\ \frac{\partial\dot{q}_1}{\partial q_1} + \dot{q}_1\frac{\partial\rho}{\partial q_1})\delta q_1\delta q_2 \ldots\ldots\delta q_f\ \delta p_1, \ldots\ldots\ldots\delta p_f$$

- Similarly, the expression for the change into the number of phase points per second corresponding to p_1 is

$$= -(\rho\ \frac{\partial\dot{p}_1}{\partial p_1} + \dot{p}_1\frac{\partial\rho}{\partial p_1})\delta q_1\delta q_2 \ldots\ldots\delta q_f\ \delta p_1, \ldots\ldots\ldots\delta p_f$$

- 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,

$$\frac{d(\delta N)}{dt} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + (\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i})\right] \delta q_1 \ldots \delta q_f\ \delta p_1, \ldots \delta p_f$$

- using equation we get,

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + (\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i})\right]$$

- 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 $\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$

$$\sum_{i=1}^{f}\left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right] = 0$$

- Now equation (10) becomes

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = -\sum_{i=1}^{f}\left[\dot{q}_1\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i}\right]$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f}\left[\frac{\partial \rho}{\partial q_i}\dot{q}_1 + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] = 0$$

- This equation represents Liouville's theorem.

$$\frac{d\rho}{dt}(q_1, \ldots, q_f, p_1, \ldots \ldots, p_f, t) = 0$$

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

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

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho.\delta\Gamma)$$

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

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

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

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

$$\delta\Gamma = constant$$

- This expression represents the principle of conservation of extension in the phase space.

STATIONARY ENSEMBLE:

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 $n_i = A g_i e^{-\varepsilon_i/kT}$

- 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.

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

$$\Delta\Gamma = \int d\,q_1 \dots\dots\dots.dq_{3n} \int d\,p_1 \dots\dots\dots.dp_{3n}$$

$$\int d\,q_1 \dots\dots\dots dq_{3n} = V^n.$$

Hence $\Delta\Gamma = V^n \int d\,q_1 \dots\dots\dots\dots dq_{3n}$

- The momentum space integral is to be evaluated subject to the constraint of the ensemble

$$u - \delta u \le u_r \le u.$$

$$u_r = \sum_{i=1}^{n} {p_i}^2 /2m\ .$$

$$u - \delta u \le \frac{1}{2m}\sum_{i=1}^{n} {p_i}^2 \le u.$$

- 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,

$$V_3(R) = \frac{4}{3}\pi R^3 = \frac{\pi^{3/2}}{\Gamma(\frac{3}{2}+1)}R^3 = \frac{\pi^{3/2}}{(\frac{3}{2})!}\,R^3 = C_3R^3$$

$$V_f(R) = \frac{\pi^{f/2}}{(f/2)!}\,R^f = c_f R^3$$

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

$$\int dp_1 \ldots\ldots\ldots\ldots dp_{3n} = \frac{\pi^{3n/2}}{(3n/2)!}[(2mu)^{3n/2} - \{2m(u-\delta u)\}^{3n/2}]$$

$$= \frac{\pi^{3n/2}}{(3n/2)!}(2mu)^{3n/2}\,[1-(1-\frac{\delta u}{u})^{3n/2}]$$

$$= \frac{\pi^{3n/2}}{(3n/2)!}(2mu)^{3n/2}\,[1-\,exp(-\frac{3n}{2}.\frac{\delta u}{u})]$$

- For a macroscopic system 3n=10^{23} ; $\frac{3n}{2}\frac{\delta u}{u}$ >>u.
- And hence we can drop the exponential term.

$$\int dp_1 \ldots\ldots\ldots\ldots\ldots\ldots dp_n = \frac{\pi^{3n/2}}{(3n/2)!}\,(2mu)^{3n/2}$$

$$\Delta\Gamma = V^n \int dp_1 \ldots\ldots\ldots\ldots\ldots\ldots.. dp_{3n}$$

$$= V^n \frac{\pi^{3n/2}}{(3n/2)!}\,(2mu)^{3n/2}$$

- 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!

$$\sigma = \log\left[\frac{\Delta\Gamma}{h^{3n}\, n!}\right]$$

$$= n\log\left[V\frac{\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{3n}{2} - \log n!$$

$$= n\log\left[V\frac{\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{3n}{2} - n\log n + n$$

$$\sigma = n\log\left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2}\mathrm{n}$$

- 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,

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial u}\right)_{T,n}$$

$$= \frac{\partial}{\partial u}\left\{n\log\left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2}\mathrm{n}\right\}_{T,n}$$

$$= \frac{\partial}{\partial u}\left[n\log v - n\log n + n\log\left(\frac{4\pi m}{3}\right)^{3/2} + n\log\left(\frac{u}{n}\right)^{3/2} - n\log h^3\right] + \frac{\partial}{\partial u}\left(\frac{5}{2}n\right)$$

$$= \frac{\partial}{\partial u}\left[n\log v - n\log n + n\log\left(\frac{4\pi m}{3}\right)^{3/2} + \frac{3}{2}n\log u - \frac{3}{2}n\log n - n\log h^3\right] + \frac{\partial}{\partial u}\left(\frac{5}{2}n\right)$$

$$= \frac{\partial}{\partial u}\left(\frac{3}{2}n\log u\right)$$

$$\frac{1}{\tau} = \frac{3}{2}n\frac{1}{u}$$

$$u = \frac{3}{2}n\tau \qquad \text{(or)} \qquad u = \frac{3}{2}n\,kT$$

- 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 $\frac{p}{\tau} = \left(\frac{\partial \sigma}{\partial V}\right)_{n.u}$

$$= \left(\frac{\partial}{\partial V}\right)\left[\left\{n \log v - n \log n + n \log \left(\frac{4\pi m}{3}\right)^{\frac{3}{2}} + \frac{3}{2} n \log u - \frac{3}{2} n \log n - \right.\right.$$

$n \log h3+ \partial\partial V(52n)\ n,u$

$$= \left(\frac{\partial}{\partial V}\right)[n \log V]$$

$$= n/V$$

$$PV = n\,\tau \quad \text{(or)} \quad PV = nkT$$

- 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,

$$S = k\sigma$$

$$= nk \log \left[\frac{\left(\frac{V}{n}\right)\left(\frac{4\pi m}{3}\right)^{3/2}\left(\frac{u}{n}\right)^{3/2}}{h^3}\right] + \frac{5}{2} nk$$

$$= nk \log \left[\left(\frac{V}{nh^3}\right)\left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{3}{2} kT\right)^{3/2}\right] + \frac{5}{2} nk$$

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,

$$\frac{-\mu}{\tau} = \left(\frac{\partial\sigma}{\partial n}\right)_{u,V}$$

$$= \frac{\partial}{\partial n}\left[n\ log \left[\frac{V}{n}\frac{1}{\lambda^3}\right] + \frac{5}{2} n\right]_{u,V}$$

$$= \frac{\partial}{\partial n}\left[n\ log\ V - n\ log\ n - n\ log\ \lambda^3\right]_{u,v} + \frac{\partial}{\partial n}\left(\frac{5}{2} n\right)_{u,v}$$

$$= \log V - 1 - \log n - \log \lambda^3 + \frac{5}{2}$$

$$= \log\left(\frac{V}{n\lambda^3}\right) + \frac{3}{2}$$

$$\frac{\mu}{\tau} = \log\left(\frac{n\lambda^3}{V}\right) - \frac{3}{2}$$

$$\frac{n}{V} = \frac{p}{\tau}$$

$$\frac{\mu}{\tau} = \log\left(\frac{p\lambda^3}{\tau}\right) - \frac{3}{2}$$

$$\mu = \tau \log p + \tau \log\left(\frac{\lambda^3}{\tau}\right) - \frac{3\tau}{2}.$$

$$= \tau \log p + f(\tau)$$

- Where $f(\tau)$ is the function of the temperature alone.

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.

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- ENGLISH STUDY MATERIAL with Question Bank.
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- CHEMISTRY STUDY MATERIAL with Question Bank.
- MODERN OFFICE PRACTICE STUDY MATERIAL with Q.B.
- COMPUTER SCIENCE STUDY MATERIAL with Question Bank.
- INFORMATION TECHNOLOGY STUDY MATERIAL with Q.Bank.
- ECE STUDY MATERIAL with Question Bank.
- EEE STUDY MATERIAL With Question Bank.
- MECHANICAL STUDY MATERIAL With Question Bank.
- CIVIL STUDY MATERIAL With Question Bank.
- EIE STUDY MATERIAL with Question Bank.
- ICE STUDY MATERIAL with Question Bank.

UG-TRB MATERIALS

- UG TRB: TAMIL MATERIAL WITH QUESTION BANK.
- UG TRB: ENGLISH STUDY MATERIAL +Q. BANK (T/M)

- UG-TRB: MATHEMATICS MATERIAL WITH Q. BANK (E/M)
- UG TRB: PHYSICS MATERIAL WITH QUESTION BANK (E/M)
- UG TRB: CHEMISTRY MATERIAL + QUESTION BANK (E/M)
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SCERT/DIET/GTTI (LECTURER) STUDY MATERIAL AVAILABLE.

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- PG TRB: PHYSICS MATERIAL WITH QUESTION BANK (E/M)
- PG TRB: CHEMISTRY MATERIAL + QUESTION BANK (E/M)
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- PG TRB:ECONOMICS MATERIAL+Q. BANK (T/M & E/M)