Probability distribution for grand Canonical ensemble :-

Consider a sub-system A in a system A' with a difference that the walls of the sub-systems are such that A and A' can exchange both energy and particles. Such systems are known as open systems. A' is microcanonical ensemble.

If E_0, N_0 are the energy and no. of particles of the entire system.

$$E_0 = E_\alpha + E' \qquad (1)$$
$$N_0 = N_\alpha + N'$$

Where; E_α, E' and N_α, N' are the energies and no. of particles in A and A' respectively, and is ~~are~~ never constant.

The probability that the sub-system A is in a state A is in a state with energy E_α and no. of particles N_α, is given by

$$P_\alpha = C\Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha) \qquad (2)$$

Here, C is constant.

On expanding $\ln \Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha)$ in a power series

$$\ln \Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha) = \ln \Omega_\alpha (E_0, N_0) - \frac{\partial(\ln \Omega_\alpha)}{\partial E_0} E_\alpha - \frac{\partial(\ln \Omega_\alpha)}{\partial N_0} N_\alpha + \cdots$$

$$= \ln \Omega_\alpha (E_0, N_0) - \beta E_\alpha + \mu N_\alpha \qquad (3)$$

On putting $\beta = \dfrac{\partial(\ln \Omega_\alpha)}{\partial E_0}$, $-\mu = \dfrac{\partial(\ln \Omega_\alpha)}{\partial N_0}$ (4)

Hence,

$$\Omega_\alpha(E_0 - E_\alpha, N_0 - N_\alpha) = \Omega_\alpha(E_0, N_0)\, e^{-\beta E_\alpha + \mu N_\alpha}$$

$$P_\alpha = C e^{-\beta E_\alpha + \mu N_\alpha} \quad \text{—— (5)}$$

The normalization condition gives

$$C = \frac{1}{\sum_\alpha e^{-\beta E_\alpha - \mu N_\alpha \beta}} \quad \text{—— (6)}$$

and hence,

$$P_\alpha = \frac{e^{-\beta E_\alpha - \mu N_\alpha \beta}}{\sum_\alpha e^{-\beta E_\alpha - \mu N_\alpha \beta}} \quad \text{—— (7)}$$

This distribution is called the grand canonical distribution.

On introducing a quantity

$$z = e^{-\beta \mu} \quad \text{—— (8)}$$

is generally known as the ~~ga~~ fugacity of the system.

In terms of fugacity the relation (8) becomes

$$P_\alpha = \frac{z^{N_\alpha} e^{-\beta E_\alpha}}{\sum_\alpha z^{N_\alpha} e^{-\beta E_\alpha}} \quad \text{—— (9)}$$

The denominator is eq^n (9) is called the grand partition function.

Liouville's Theorem :→

In 1838, Liouville inquire the rate of change of phase point density in a classical system.

We have to prove that.

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

Here, ρ is the density function and p_i and q_i are the ~~positi~~ position and momentum coordinates of the system.

Proof:- Consider a small volume element in the hyperspace, bounded by q_1 and $q_1+\delta q_1$, p_1 and $p_1+\delta p_1$ etc. The no. of systems in the element is given by.

$$\delta N = \rho\, d\Gamma = \rho(q, p, t)\,\delta q_1 \cdots \delta p_f$$

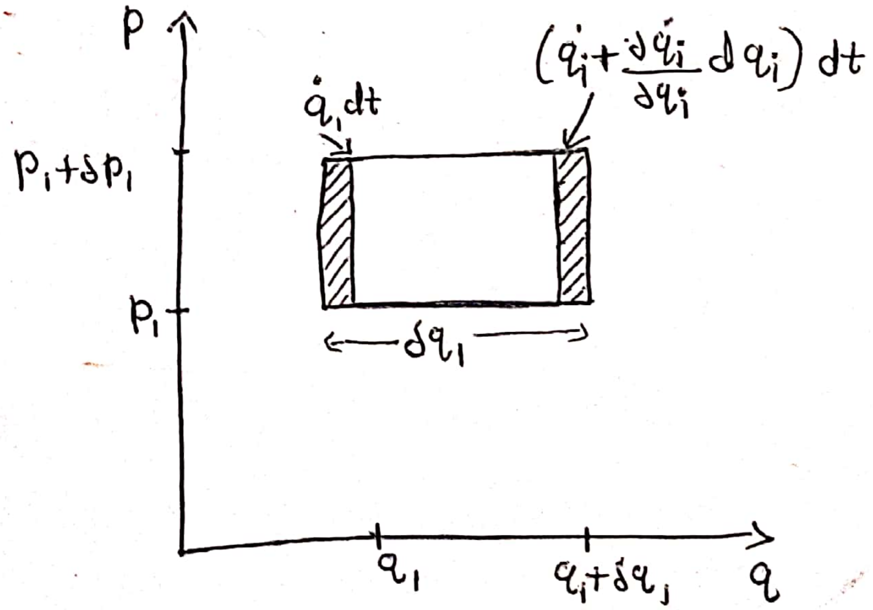

Fig. 1

A fixed volume of (2-D) phase Space

Consider two faces perpendicular to the q_1-axis which are located at q_1 and $q_1+\delta q_1$. The no. of phase points entering the element in time dt through the face q_1 = constant is

$$= \rho(q,p,t)\,\dot{q}_1\,dt\,\delta q_2 \dots \delta p_f \quad (1)$$

where, $\dot{q}_1$ is the velocity in the direction q_1.

The no. leaving the element through the face $q_1+\delta q_1$ = Constant is

$$= \left[\rho\dot{q}_1 + \frac{\partial}{\partial q_1}(\rho\dot{q}_1)\,\delta q_1\right] dt\,\delta q_2 \dots \delta p_f \quad (2)$$

Hence, the effective no. of systems entering the element in the direction q_1 is

$$= \rho\dot{q}_1\,dt\,\delta q_2 \dots \delta p_f - \left[\rho\dot{q}_1 + \frac{\partial}{\partial q_i}(\rho\dot{q}_1)\delta q_1\right] dt\,\delta q_2 \dots \delta p_f$$

$$= -\frac{\partial}{\partial q_i}(\rho\dot{q}_1)\,dt\,\delta q_1\,\delta q_2 \dots \delta p_f \quad (3)$$

Therefore, the net no. entering the volume element through all its faces is given by

$$\frac{\partial \rho}{\partial t}\,dt\,\delta q_1 \dots \delta p_f = \left[-\sum_{i=1}^{f}\frac{\partial}{\partial q_i}(\rho\dot{q}_i) - \sum_{i=1}^{f}\frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right] dt\,\delta q_i \dots \delta p_f$$

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f}\left[\frac{\partial}{\partial q_i}(\rho\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right] \quad (4)$$

On simplifying

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f}\left[\rho\left\{\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right\} + \left\{\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right\}\right] \quad (5)$$

From Hamilton's eqn of motion

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} = \frac{\partial^2 H}{\partial q_i\,\partial p_i}$$

$$\frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial}{\partial p_i}\frac{\partial H}{\partial q_i} = -\frac{\partial^2 H}{\partial q_i\,\partial p_i}$$

Therefore, the first term in the bracket vanishes and

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = -\sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i} p_i\right) \quad \text{—— (6)}$$

The symbol of partial differentiation indicates that $\left(\frac{\partial \rho}{\partial t}\right)_{q,p}$ gives the rate of the change in density at the point of interest. This is known as Liouville's eq^n and is of fundamental importance in statistical mechanics.

This eq^n may be written in any of the following form—

(1) $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = 0 \quad \text{—— (7)}$$

(2) $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = 0 \quad \text{—— (8)}$$

(3) $$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \quad \text{—— (9)}$$

Here, $\{\rho, H\} = \sum_{i}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right)$

is known as the Poisson bracket of the functions ρ and H.

The total time derivative of $\rho(q, p, t)$ is given by

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = 0 \quad \text{—— (10)}$$

In other words, the density of phase points is an integral of motion. This is Liouville's theorem in classical presentation.