Group A : Statistical Physics

Liouville's theorem

In the phase space, distribution of phase points is expressed by the probability density $\rho(q,p,t)$.

The ~~fun~~ probability density $\rho(q,p,t)$, in general, dependent upon time 't' due to the motion of phase points in the phase space.

Liouville's theorem states that the probability density $\rho(q,p,t)$ is constant along the phase trajectories of the phase points.

It is also known as the ~~principle of~~ principle of conservation of the probability density in phase space and can be mathematically expressed as

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

Proof:

Let number of identical particles $= N$

Position coordinates $= q_1, q_2 \ldots q_{3N}$

Momentum coordinates $= p_1, p_2 \ldots p_{3N}$

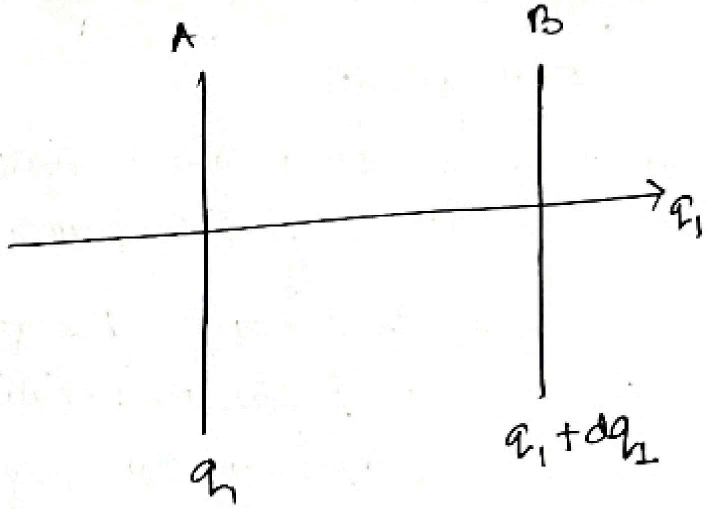
volume element $dq\,dp$ around a point (p,q) in phase space $\Big\} = dq_1\, dq_2 \ldots dq_{3N}\, dp_1\, dp_2 \ldots dp_{3N}$

The number dN of phase points in the volume element is given by ~~dM~~ $dN = \rho(q,p,t)\,dq\,dp$

$$dN = \rho(q,p,t)\, dq\, dp$$

The above equation ~~of~~ gives numbers of phase points in the volume element changes with time due to motion of the phase points. The change here signifies that number of phase points entering the volume element is different from those leaving the volume element.

Now, let us consider a motion of phase points along the q_1 axis. For that we consider two faces A and B normal to the q_1-axis at the coordinates q_1 and q_1+dq_1 respectively (shown in figure).



Let us assume that phase points are entering at the face A and are leaving at the face B.

(i) At the face A:

velocity of the phase points along the q_1-axis is $\dot{q}_1$.

Let probability density be ρ

Hence the no. of phase points entering the face A per unit area in time dt $= \rho \dot{q}_1 dt$

(ii) At the face B:

velocity of the phase points along the q_1-axis is

$$= \left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} dq_1 \right)$$

The probability density

$$\left(\rho + \frac{\partial \rho}{\partial q_1} dq_1 \right)$$

Hence, the numbers of phase points leaving the face B per unit area in time dt is

$$\left(\rho + \frac{\partial \rho}{\partial q_1} dq_1 \right) \left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} dq_1 \right) dt .$$

Hence, the net numbers of phase points entering the region between the faces A and B per unit area in time ~~dt~~ dt is given by:

$$= \rho \dot{q}_1 dt - \left(\rho + \frac{\partial \rho}{\partial q_1} dq_1 \right) \left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} dq_1 \right) dt$$

$$= \rho \dot{q}_1 dt - \rho \dot{q}_1 dt - \rho \frac{\partial \dot{q}_1}{\partial q_1} dq_1 dt - \dot{q}_1 \frac{\partial \rho}{\partial q_1} dq_1 dt$$

$$- \frac{\partial \rho}{\partial q_1} dq_1 \frac{\partial \dot{q}_1}{\partial q_1} dq_1 dt$$

By Neglecting higher order term we get

$$= - \left(\rho \frac{\partial \dot{q}_1}{\partial q_1} dq_1 + \dot{q}_1 \frac{\partial \rho}{\partial q_1} dq_1 \right) \cancel{dt}\, dt$$

When ~~dq~~ $dq_1 = 1$ (separation between face A and face B is unit.)

No. of phase points entering the region between the two faces per unit volume in time dt is $= \dfrac{-\left(\rho \frac{\partial \dot{q}}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right) dq_1 dt}{dq_1}$

$$= -\left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right) dt$$

Similarly, for the motion of phase points along the P_1-axis, the net number of phase points entering the region per unit volume in time dt is

$$= -\left(\rho \frac{\partial \dot{P}_1}{\partial P_1} + \dot{P}_1 \frac{\partial \rho}{\partial P_1}\right) dt$$

After considering all 6N coordinates of phase space the net number of phase points entering the region per unit volume in time dt is

$$= -\sum_{i=1}^{3N} \left[\left(\rho \frac{\partial \dot{q}_i}{\partial q_i} + \dot{q}_i \frac{\partial \rho}{\partial q_i}\right) dt + \left(\rho \frac{\partial \dot{P}_i}{\partial P_i} + \dot{P}_i \frac{\partial \rho}{\partial P_i}\right) dt\right]$$

Simplifying

$$= -\sum_{i=1}^{3N} \left[\rho \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i\right] dt$$

Equation of motion for Hamiltonian $H(q,p)$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where $i = 1, 2, \ldots 3N$

Thus, we have

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \quad \text{and} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i}$$

From above equation we get

$$\therefore \quad \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$$

Now, net number of phase points entering the region per unit volume in time dt $\Bigg\} = -\sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] dt \quad -(1)$

The change of phase points per unit volume in time dt is

$$\frac{1}{dq\,dp} \frac{\partial}{\partial t}(\rho\, dq\, dp)\, dt = \frac{\partial \rho}{\partial t} dt \quad -(2)$$

From eqn (1) & (2)

$$\frac{\partial \rho}{\partial t} dt = -\sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] dt$$

~~Since~~

$$\Rightarrow \left\{ \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] \right\} dt = 0$$

Since $dt = 0$

$$\Rightarrow \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i} \frac{dq}{dt} + \sum_{i=1}^{3N} \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} = 0$$

$$\left[\because \dot{q}_i = \frac{dq}{dt} \text{ and } \dot{p}_i = \frac{dp}{dt} \right]$$

Hence $\cancel{\frac{\partial \rho}{\partial t} = 0}$ $\frac{d\rho}{dt} = 0$

Above prove showed that for an ensemble $\rho(q, p, t)$ is constant along the trajectory in the phase space is known as a stationary ensemble. ~~This Co~~

II This corresponds to an equilibrium situation.

Case of Steady State

For the steady state $\frac{\partial \rho}{\partial t} = 0$

So $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i \right] = 0$$

$$\Rightarrow \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i \right] = 0$$

or $$\vec{v} \cdot \text{grad}\, \rho = 0$$

Where $\vec{v}$ is velocity in the phase space.

Hence, the system moves on a surface of constant ρ.

Thus, when ρ is explicitly independent of time and space.

Hence the phase points are uniformly distributed over the relevant region of the phase space and outside the relevant region, $\rho = 0$.