Liouville's Theorem :

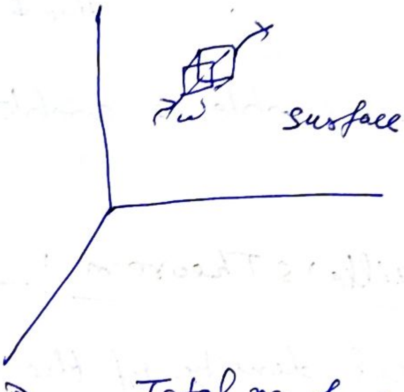
In the last lecture notes we have discussed some basic concepts & terminology of equilibrium statistical mechanics. In continuation we will discuss the Liouville's Theorem and its proof.

: Mathematical statement is given by.

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} + \frac{\partial \rho}{\partial x_i} \frac{dx_i}{dt} \right) = 0 \quad \text{—— (1)}$$

Proof:

Consider arbitrary volume ω in relevant region of phase space



No. of systems leaving ω per second → Total no. of system in ensemble → fixed
no of system entering ω per sec in Γ space
= rate of decrease of no of system in ω

$$-\frac{d}{dt}\int d\omega \cdot \rho = \int_S ds\, \hat{n} \cdot (\vec{v}\rho) \quad \text{—— (2)}$$

$\vec{v}$ → velocity vector in 6N dimensional space

$\hat{n}$ → normal vector to the surface S

$$\vec{v} \equiv (\dot{p}_1, \dot{p}_2, \ldots, \dot{p}_{3N}; \dot{q}_1, \dot{q}_2, \ldots \dot{q}_{3N}) \quad \text{—— (3)}$$

In (2) we apply divergence theorem and write

$$-\frac{d}{dt}\int d\omega\, \rho = \int_\omega d\omega\, \vec{\nabla} \cdot (\rho \vec{v}) \quad \text{—— (4)}$$

Where ∇ is 6N dimensional grad. operator

$$\vec{\nabla} \equiv \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \cdots, \frac{\partial}{\partial p_{3N}}; \frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \cdots, \frac{\partial}{\partial q_{3N}}\right) \quad \text{(5)}$$

(4) can be written as

$$\int_\omega d\omega \left[\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot(\rho\vec{v})\right] = 0$$

$\omega \rightarrow$ arbitrary volume. Thus

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot(\rho\vec{v}) = 0 \quad \text{(6)}$$

Eq (6) represents continuity equation for a fluid

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

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

or $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left[\frac{\partial \rho}{\partial p_i}\dot{p}_i + \cancel{\rho\frac{\partial}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right)} + \frac{\partial \rho}{\partial q_i}\dot{q}_i + \cancel{\rho\frac{\partial}{\partial q_i}\left(\frac{\partial H}{\partial p_i}\right)}\right] = 0$$

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

Liouville's theorem is equivalent to the statement

$$\frac{d\rho}{dt} = 0 = \frac{\partial \rho}{\partial t} + \left[\frac{\partial \rho}{\partial p_1}\frac{dp_1}{dt} + \cdots + \frac{\partial \rho}{\partial p_{3N}}\frac{dp_{3N}}{dt} + \frac{\partial \rho}{\partial q_1}\frac{dq_1}{dt} + \cdots + \frac{\partial \rho}{\partial q_{3N}}\frac{dq_{3N}}{dt}\right]$$

or $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left[\frac{\partial \rho}{\partial p_i}\frac{dp_i}{dt} + \frac{\partial \rho}{\partial q_i}\frac{dq_i}{dt}\right] = 0$$