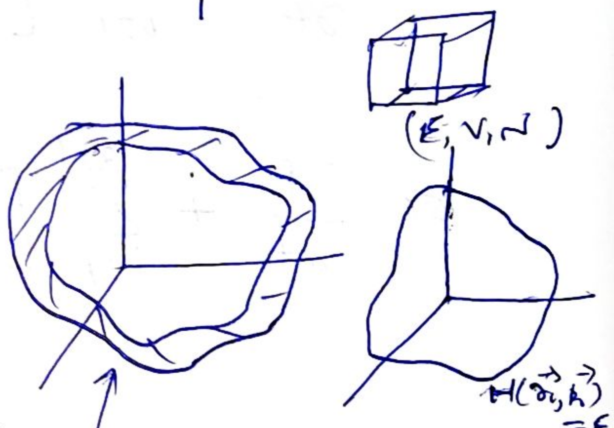
B.Sc (H) - III   Paper VI, Gp-A

Postulate of Equal à Priori Probability :—

When a macroscopic system is in thermodynamic equilibrium its state is equally ~~lq~~ likely to be any state satisfying the macroscopic conditions of the system.

In thermodynamic equilibrium we replace the time averages for a single system by an ensemble average in the 'microcanonical ensemble'.

microcanonical ensemble is a collection of systems for which the density ρ is defined by



$$\rho(\vec{r_i}, \vec{p_i}) = \begin{cases} \text{Const. if } E \le H(\vec{r_i}, \vec{p_i}) \le E+\Delta \\ 0, \text{ else} \end{cases}$$

$E \le H(\vec{r_i}, \vec{p_i}) \le E+\Delta$ 6N dimensional Phase space

To discuss further we take ensemble average of a physical ~~ensemble~~ quantity X. Since ensemble is stationary the ensemble average of X will be independent of time. Therefore

$\langle X \rangle$ = the ensemble average of X

= the time average of (the ensemble average of X)

$$\langle X \rangle = \frac{\int d\vec{r_i} \int d\vec{p_i}\, X(\vec{r_i}, \vec{p_i})\, \rho(\vec{r_i}, \vec{p_i})}{\int d\vec{r_i}\, d\vec{p_i}\, \rho(\vec{r_i}, \vec{p_i})}$$

$$= \frac{\int_{H=E} d\vec{r_i} \int_{H=E} d\vec{p_i}\, X(\vec{r_i}, \vec{p_i}) \times \rho_0}{\int_{H=E} d\vec{r_i}\, dp_i\, \rho_0}$$

we have replaced $\rho(\vec{r_i}, \vec{p_i}) = \rho_0 = \text{const}$

~~But~~

Two common averages → ① ensemble average which we have defined above

and ② most probable value → X_m

X_m → value of X that is possessed by the largest number of systems in the ensembles.

If mean square fluctuation is small, then ensemble average and the most probable value are nearly equal

$$\frac{\langle X^2 \rangle - \langle X \rangle^2}{\langle X \rangle^2} \ll 1$$

which is $O\left(\frac{1}{N}\right)$ in all physical cases

→ 0 for $N \to \infty$.