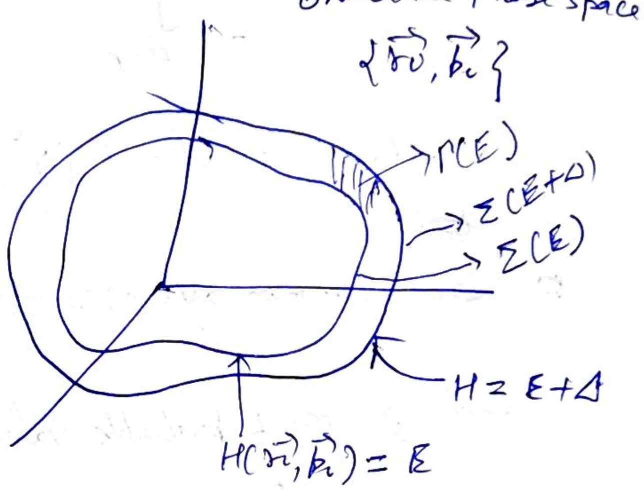
Microcanonical ensemble :- Here we discuss microcanonical ensemble in detail.

In microcanonical ensemble each system has N molecules, volume V and energy between E and E+Δ.




Let $\Gamma(E)$ denote the volume in Γ space ~~occupied by the~~ enclosed between a surface of energy E and another surface of energy E+Δ

$$\Gamma(E) \equiv \int d\vec{r_i} \int d\vec{p_i}$$

$$E \le H(\vec{r_i}, \vec{p_i}) \le E+\Delta$$

Next, let $\Sigma(E)$ denote the volume in Γ space enclosed by a surface of energy E :

$$\Sigma(E) = \int d\vec{r_i} \int d\vec{p_i}$$

$$H(\vec{r_i}, \vec{p_i}) \le E$$

Then $\Gamma(E) = \Sigma(E+\Delta) - \Sigma(E)$

$$\simeq \Delta \frac{d\Sigma}{dE} \quad \text{—— (1)}$$

or $\Gamma(E) = \Delta\,\omega(E)$ —— ②

$\omega(E) \rightarrow$ density of states of the system at energy $E$.

The entropy is defined by

$$S(E,V,N) = k_B \ln \Gamma(E) \quad \text{—③}$$

$k_B \rightarrow$ Boltzmann const.; Also equivalent to $k_B \ln \Sigma(E)$ and $k_B \ln \omega(E)$

Derivation of thermodynamics.

Entropy as a function of $S \equiv S(E,V,N)$

$$dS = \left.\frac{\partial S}{\partial E}\right|_{V,N} dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \left.\frac{\partial S}{\partial N}\right|_{E,V} dN \quad \text{—④}$$

From the first law $dE = TdS - PdV + \mu dN$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \quad \text{—⑤}$$

From ④ and ⑤

$$\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T}, \quad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}, \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = \frac{-\mu}{T}$$

Recipe to find thermodynamic functions —

i) consider the isolated system – Parameters $E, V, N$
From Hamiltonian we calculate all macroscopic quantities

i) Calculate $\Gamma(E)$, $\Sigma(E)$ and $\omega(E)$ from $H(\vec{r}, \vec{p})$

ii) Calculate $S(E,V,N) = k_B \ln \Gamma(E)$

iii) Find $T, P, \mu$ by taking potential derivatives. Other potentials are obtained by usual Legendre transformation.