Chapter 9

The Grand Canonical Ensemble (T,V,μ)

The Grand Canonical Ensemble is further generalization of the concept of ensembles in which 'N' (number of particles) and 'E'(energy) are changing and (T,V,μ) is constant.

This suits many physical and chemical systems.

I will try to explain this topic by dividing it under few points. Let us understand the concepts one by one.

1. Introduction

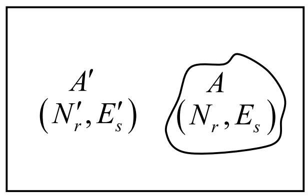
(a) N,E are variables in this ensemble.

(b) It is further generalization of canonical systems since canonical ensemble are of limited use for certain physical or chemical systems, specifically where the exchange of particles and energy is happening.

Microcanonical $\rightarrow$ Canonical $\rightarrow$ Grand Canonical Ensembles (towards more generalized ensemble).

(c) So, now the question arises what is average number of particles $\langle N \rangle = ?$ and average energy $\langle E \rangle = ?$, since both are variables in this ensemble.

System:



A statistical system immersed in a particle-energy reservoir

Equilibrium between a system and a particle-Energy reservoir

(a) Consider the given system A as immerged in a large reservoir A', with which it can exchange both energy and particles. After some both A' and A are in equilibrium.

A and $A' \rightarrow T, V, \mu \rightarrow (T, \mu)$

Any instant $\rightarrow A \rightarrow N_r, E_s$

$A' \rightarrow N'_r, E'_s \qquad (\mu, T)$

We have, $\quad 0 < \frac{E_s}{E^{(0)}} < 1 \quad$ At any point of time 't'

Also $\quad 0 < \frac{N_r}{N^{(0)}} < 1$

$$N_r + N'_r = N^{(0)} = \text{constant} \qquad (1)$$

$$E_s + E'_s = E^{(0)} = \text{constant} \qquad (2)$$

For all practical purposes,

$$\frac{N_r}{N^{(0)}} = \left(1 - \frac{N'_r}{N^{(0)}}\right) < 1 \qquad (3)$$

$\therefore$ system is much smaller than recursion.

$$\frac{E_s}{E^{(0)}} = \left(1 - \frac{E'_s}{N^{(0)}}\right) < 1 \qquad (4)$$

(b) The probability $P_{r,s}$ that at any time t the system A is found to be in an (N_r, E_s) state would be directly proportional to the number of microstates $\Omega'(N_r', E_s')$ that the reservoir can have for the corresponding microstate (N_r', E_s').

$$P_{r,s} \ \alpha \ \Omega'\left(N^{(0)} - N_r, E^{(0)} - E_s\right) \qquad (5)$$

We know that the Two-dimensional Taylor's expansion is given by,

$$T(x,y) = f(a,b) + (x-a)\left\{\frac{\partial f}{\partial x}\right\}_{a,b} + (y-b)\left\{\frac{\partial f}{\partial y}\right\}_{a,b} + \cdots$$

$a = N^{(0)}$, $b = E^{(0)}$, $x = N_r'$, $y = E_s'$, $f(N_r', E_s') = \ln \Omega'(N_r', E_s')$ (For present case)

$$\ln \Omega' = \ln \Omega'\left(N^{(0)}, E^{(0)}\right) + \left(N_r' - N^{(0)}\right)\frac{\partial \ln \Omega'}{\partial N'}\bigg|_{N'=N^{(0)}} + \left(E_s' - E^{(0)}\right)\frac{\partial \ln \Omega'}{\partial E'}\bigg|_{E'=E^{(0)}} + \cdots$$

$\because N^{(0)} = N_r + N_r', E^{(0)} = E_s + E_s'$

$$\ln \Omega' = \ln \Omega'\left(N^{(0)}, E^{(0)}\right) + (-N_r)\frac{(-\mu')}{k_B T'} + \frac{1}{k_B T'}(-E_s)$$

μ' and T' are chemical potential and Temperature of the reservoir and hence for the system.

$$\because \frac{\partial \ln \Omega'}{\partial N'} = \frac{-\mu'}{k_B T'}, \frac{\partial \ln \Omega'}{\partial E'} = \frac{1}{k_B T'}$$

$P_{r,s} \ \alpha \ e^{-\alpha N_r - \beta E_s}$ where $\alpha = \frac{-\mu}{k_B T}$, $\beta = \frac{1}{k_B T}$

$P_{r,s} = c\, e^{-\alpha N_r - \beta E_s}$ c is the proportionality constant.

$$\sum_{r,s} P_{r,s} = c \cdot \sum_{r,s} e^{-\alpha N_r - \beta E_s} \qquad 1 = c\sum_{r,s} e^{-\alpha N_r - \beta E_s} \qquad So, \qquad c = \frac{1}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} \qquad Z = \sum_{r,s} e^{-\alpha N_r - \beta E_s}$$

This is probability for a (r, s) state in a Grand Canonical Ensemble.

Note: The summation in the denominator goes for all the (N_r, E_s) States accessible to the system A. Also, final expression of $P_{r,s}$ is independent of the reservoir parameters.

A System in the Grand Canonical Ensemble

Consider an Ensemble of N identical system $(1,2,....,N)$ mutually sharing a total number of particles $N\bar{N}$ and total energy $N\bar{E}$. Where,

$\bar{N}$ - Average number of the particles in each system

$\bar{E}$ - Average Energy of each system

$n_{r,s}$ - number of systems that have at any time t the number of particles N_r and the amount of energy E_s $(r,s=0,1,2)$

$$\sum_{r,s} n_{r,s} = N \qquad \sum_{r,s} n_{r,s} N_r = N\bar{N}$$

$$\sum_{r,s} n_{r,s} E_s = N\bar{E}$$

The number of ways in which this can be done,

$$W\{n_{r,s}\} = \frac{N!}{\prod_{r,s}(n_{r,s})!}$$

Conclusions: For large N i.e. $N \to \infty$ (large)

1. $\bar{N} = \dfrac{\sum_{r,s} N_r\, e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\dfrac{\partial}{\partial \alpha}\left\{\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\}$

2. $\bar{E} = \dfrac{\sum_{r,s} E_s\, e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\dfrac{\partial}{\partial \beta}\left\{\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\}$