GRAND PARTITION FUNCTION

Ñ systems each of volume V, temperature T, chemical potential μ, and the particle number N, which is variable, whereas in microcanonical and canonical ensemble the particle number is constant. Now,

Total volume of the super system = Ñ.V

Total number of particles = $\sum n_i N_i$

Total number of systems, Ñ = $\sum n_i$

Total energy, $\bar{E} = \sum n_i \, . \, E_i$

Now, probability of having n1 systems of energy E1 and particle number N1 and so on is

$$W = \tilde{N}! / C . \prod(n_i!)$$

Here N, Ñ, and E are constants and the mostδ probable distribution is given by

$$\delta (\ln W – \alpha\tilde{N} – \beta\bar{E} – \gamma N) = 0$$

$$\ln W = \ln \tilde{N}! - \sum \ln n_i! – \ln C$$

$$= \tilde{N} \ln \tilde{N} – \tilde{N} - \sum n_i \ln n_i + \sum n_i – \ln C$$

$$= \tilde{N} \ln \tilde{N} - \sum n_i \ln n_i$$

$$\delta \ln W = \tilde{N} \, \delta\tilde{N} / \tilde{N} + \ln \tilde{N} \, \delta\tilde{N} - \sum n_i \ln n_i / n_i$$

$$- \sum \ln n_i \, \delta n_i$$

$$= \sum (\ln \tilde{N} - \ln n_i) \delta n_i = 0$$

Now,

$\alpha \delta \sum n_i = 0$, $\beta \delta \sum E_i n_i = 0$, and

$\gamma \delta \sum N_i n_i = 0$

Therefore,

$$\sum (\ln \tilde{N} - \ln n_i - \alpha - \beta E_i - \gamma N_i) = 0$$

$$\ln \tilde{N} / n_i = \alpha + \beta E_i + \gamma N_i$$

$$\tilde{N} / n_i = \exp. (\alpha + \beta E_i + \gamma N_i)$$

$$n_i / \tilde{N} = \exp. (- \alpha - \beta E_i - \gamma N_i)$$

$$\sum ni = \tilde{N} = \tilde{N} \exp.(-\alpha) \sum \exp. (- \beta E_i - \gamma N_i)$$

$$\exp. (+ \alpha) = \sum (- \beta E_i - \gamma N_i)$$

$n_i = \tilde{N} (- \beta E_i - \gamma N_i) / \sum (- \beta E_i - \gamma N_i)$,

Where $Ƶ = \sum (- \beta E_i - \gamma N_i)$, the grand partition function.

Therefore, $n_i = \tilde{N} (- \beta E_i - \gamma N_i) / Ƶ$, and

$W_i = n_i / \tilde{N} = \exp. (- \beta E_i - \gamma N_i) / Ƶ$, the probability of a chosen system having energy E_i and the number of particles $N_{i.}$

Now, $E = E (S, V, N)$ and

$$dE = (\partial E/\partial S)_{V,N}.dS + (\partial E/\partial V)_{S,N}.dV + (\partial E/\partial N)_{S,V}.dN$$

$= T.dS - P.dV + \mu.dN$, and $S = - k \sum W_i \ln W_i$

$$S = - k \sum \exp. (- E_i - \mu N_i) / kT$$

$$[(- E_i - \mu N_i)/ kT - \ln Ƶ] / Ƶ$$

$$S = \sum W_i . E_i / T - \mu \sum W_i . N_i / T + k \ln Ƶ \sum W_i$$

$$S = E / T - \mu . N / T + k \ln Ƶ$$

But from thermodynamics, it is clear that

$$S = E / T - \mu . N / T + P.V / T$$

From this we get $P.V = kT \ln Ƶ$

Now, $d(PV) = S.dT + N.d\mu + P.dV$

$$d(kT \ln Ƶ) = S.dT + N.d\mu + P.dV$$

$$S = \partial (kT \ln Ƶ)_{\mu, V} / \partial T$$

$$N = \partial (kT \ln Ƶ)_{T, V} / \partial \mu, \text{ and}$$

$$P = kT \ln Ƶ / V$$

Now, $Ƶ = \sum\sum e^{(- Ei/kT)(\mu Ni/kT)}$

$= \sum\sum e^{(\mu Ni-Ei/)kT}$

$Ƶ = = \sum\sum e^{(1/kT)\sum Nji(\mu - Eji)}$

$=\sum\prod e^{(Nji/kT)(\mu - Eji)}$

$= \prod z_i$

For Bose – Einstein Statistics n_{ji}= 0,1,2,3,.......and for Fermi Dirac Statistics n_{ji} = 0,1

For Bose – Einstein statistics,

$z_i = 1 + e^{(\mu - Ei)/kT} + e^{2(\mu - Ei)/kT} + ...$

$= [1 – e^{(\mu - Ei)/kT}]^{-1}$

Whereas for Fermi Dirac statistics

$z_i = 1 + e^{(\mu - Ei)/kT}$