

Chapter 9

The Grand Canonical Ensemble (T, V, μ)

2. Relation of statistical quantities with various thermodynamical quantity

Let us define a quantity, q -potential given by “Kramer”.

$$q \equiv \ln \left\{ \sum_{r,s} e^{-\alpha N_r - \beta E_s} \right\}$$

(\because Since all quantities will be derived from q' it is very important and will be center of all calculations)

$$q = \ln \left\{ \sum_{r,s} (\bar{e}^\alpha)^{N_r} \bar{e}^{\beta E_s} \right\} \quad \sum_{r,s} \Rightarrow \sum_r \sum_s$$

$$\xi = \bar{e}^\alpha = e^{\mu/k_B T} \rightarrow \text{fugacity}, \alpha = -\mu / k_B T$$

$$q = \ln \left\{ \sum_{r,s} (\xi)^{N_r} \bar{e}^{\beta E_s} \right\}, q = \ln Z_\mu$$

Grand canonical partition function

$$Z_\mu = \sum_{r,s} e^{-\alpha N_r} e^{-\beta E_s}$$

$$Z_\mu = \sum_{N_r=0}^{\infty} (\xi)^{N_r} Z_{N_r}$$

Following are the important results of this Ensemble.

$$\rightarrow q = \frac{PV}{k_B T} \quad \rightarrow \bar{N} = N = k_B T \left[\frac{\partial q}{\partial \mu} \right]_{V,T} \quad \rightarrow \bar{E} = U = k_B T^2 \left[\frac{\partial q}{\partial T} \right]_{\xi,V}$$

$$\rightarrow F = N\mu - PV = -k_B T \ln \left(\frac{Z_\mu}{(\xi)^N} \right) \quad G = N\mu$$

$$\rightarrow S = \frac{U - A}{T} = k_B T \left(\frac{\partial q}{\partial T} \right)_{\mu,V} - N k_c \ln \xi + k_B q$$