Chapter 9
The Grand Canonical Ensemble (T, V, μ)

3. Derivations of the above results

We define q potential

(a) $q = \ln\left\{\sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s}\right\}, \qquad q = q(\alpha, \beta, E_s)$

$$dq = \frac{\partial q}{\partial \alpha} d\alpha + \frac{\partial q}{\partial \beta} d\beta + \frac{\partial q}{\partial E_s} dE_s \Rightarrow dq = -\bar{N} d\alpha - \bar{E}\,\partial\beta + \frac{\partial q}{\partial E_s} dE_s$$

$$\frac{\partial q}{\partial E_s} = \frac{1}{\sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s}} \sum_{r,s} (-\beta) \overline{e}^{N_r - \beta E_s}$$

$$dq = -\bar{N} d\alpha - \bar{E} d\beta - \frac{\beta \sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s} dE_s}{\sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s}} = -\bar{N} d\alpha - \bar{E} d\beta - \frac{\beta}{N} \sum_{r,s} \langle n_{r,s} \rangle dE_s$$

$$\because \frac{\langle n_{r,s}\rangle}{N} = \frac{\bar{e}^{\alpha N_r - \beta E_s}}{\sum_{r,s} \bar{e}^{\alpha N_r - \beta E_s}}$$

$$d\left(q + \alpha\bar{N} + \beta\bar{E}\right) = \beta\left(\frac{\alpha}{\beta}d\bar{N} + d\bar{E} - \frac{1}{N}\sum_{r,s}\langle n_{r.s}\rangle dE_s\right)$$

Now, first law of thermodynamics

$$dQ = d\bar{E} + dW - \mu dN$$

$$\because dW = \frac{-1}{N}\sum_{r,s}\langle n_{n,s}\rangle dE_s, \mu = \frac{-\alpha}{\beta}$$

$$d\left(q + \alpha\bar{N} + \beta\bar{E}\right) = T\cdot\beta\frac{dQ}{T} = \frac{dS}{K_B} \qquad \beta = \frac{1}{k_BT}, \alpha = -\mu / k_BT$$

$$q + \alpha\bar{N} + \beta\bar{E} = \frac{S}{k_B}$$

$$q = \frac{S}{k_B} - \alpha\bar{N} - \beta\bar{E} = \frac{TS}{k_BT} - \frac{k_BT\alpha\bar{N}}{k_BT} - \frac{\bar{E}}{k_BT}$$

$$q = \frac{TS + \mu\bar{N} - \bar{E}}{k_BT} \qquad -k_BT + \alpha\bar{N} = \mu\bar{N}$$

$$q = \frac{TS + G - \bar{E}}{k_BT} \qquad \mu = \frac{-\alpha}{\beta}$$

$$q = \frac{PV}{k_BT} \qquad G = U + PV - TS$$

$$TS + G - U = PV \qquad q = \frac{PV}{k_BT}$$

(b) $q = \ln\left\{\sum_{r,s}\left(\bar{e}^{\alpha}\right)^{N_r}\bar{e}^{\beta E_s}\right\} = \ln\left\{\sum_{r.s} e^{\beta\mu N_r}\cdot\bar{e}^{\beta E_s}\right\}$

$$\frac{\partial q}{\partial\mu} = \frac{1}{\sum_{r,s} e^{\beta\mu N_r}\bar{e}^{\beta E_s}}\sum_{r,s}\left(e^{\beta\mu N_r}\cdot\beta N_r\bar{e}^{\beta E_s}\right)$$

$$\frac{\sum_{r,s} N_r e^{\beta\mu N_r} e^{-\beta E_s}}{\sum_{r,s} e^{\beta\mu N_r}\bar{e}^{\beta E_s}} = k_BT\left(\frac{\partial E}{\partial\mu}\right)_{V,T}$$

$$\bar{N} = N = k_BT\left(\frac{\partial q}{\partial\mu}\right)_{V,T}$$

(c) $q = \ln\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)$

$$\frac{\partial q}{\partial \beta} = \frac{1}{\sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s}} \sum_{r,s} (-E_s) \overline{e}^{\alpha N_r - \beta E_s}$$

$$\frac{-\partial q}{\partial \beta} = \frac{\sum_{r,s} E_s \overline{e}^{\alpha N_r - \beta E_s}}{\sum_{r,s} \overline{e}^{\alpha N_r - \beta E_s}}$$

$$U = \frac{-\partial q}{\partial \beta} \Rightarrow U = k_B T^2 \left[\frac{\partial q}{\partial T}\right]_{V,\xi}$$

(d) $F = G - PV$ $\qquad \xi = e^{\mu / k_B T} = e^{-\alpha}$

$F = N\mu - PV$ $\qquad \ln \xi = \dfrac{\mu}{k_B T}$

$F = Nk_B T \ln \xi - PV$ $\qquad \mu = k_B T \ln \xi$

$= Nk_B T \ln \xi - k_B T q$

$$F = k_B T \ln \xi^N - k_B T \ln Z_\mu = k_B T \ln \frac{\xi^N}{Z_\mu}$$

(e) $S = \dfrac{U - F}{T} = k_B T \left(\dfrac{\partial q}{\partial T}\right)_{\xi,V} - k_B T \ln \dfrac{\xi^N}{Z_\mu} = k_B T \left(\dfrac{\partial q}{\partial T}\right)_{\xi,V} - Nk_B \ln \xi + k_B q$

Illustrative Example

Classical Ideal Gas (Indistinguishable (let "Non-localized)

$$Z_n = \frac{Z_1^N}{N!} \qquad (1)$$

$$Z_1 = V f(T) \qquad (2) \quad \text{(Non localized anywhere in the space)}$$

$f(T)$ -function of temperature alone.

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

$$Z_\mu = \sum_{N_r=0}^{\infty} (\xi)^{N_r} \frac{(Z_1)^{N_r}}{N_r!} = \sum_{N_r=0}^{\infty} \frac{\{\xi V f(T)\}^{N_r}}{N_r!}$$

$$Z_\mu = e^{\xi V f(t)}$$

$$q = \xi V f(t)$$

$$\rightarrow p = \xi k_B T f(T) \qquad q = \frac{PV}{k_B T}, P = \frac{q k_B T}{V}$$

$$P = \frac{\xi V f(T) \cdot k_B T}{V}, \ \frac{P}{N} = \frac{\xi k_B T \, f(T)}{\xi V \, f(T)}, \quad PV = k_B T$$

$$\rightarrow N = \xi V f(T)$$

$$\rightarrow U = \xi V k_B T^2 \, f'(T)$$

$$\rightarrow F = N k_B T \ln \xi - \xi V \, k_B T \, f(T) \qquad PV = N k_B T$$

$$\rightarrow S = -N k_B \ln \xi + \xi V k_B \left\{ T f'(T) + f(T) \right\}$$

Also, $U = N k_B T^2 \dfrac{f'(T)}{f(T)}$

$$C_V = N k_B \frac{2T \, f(T) f'(T) + T^2 \left\{ f(T) f''(T) - \left[f'(T) \right]^2 \right\}}{\left[f(T) \right]^2}$$

In general, $C_V \ \alpha \ T^{\alpha}$

$$U = \alpha N k_B T$$

$$C_V = \alpha N k_B$$

$\alpha = 3/2$ Nor relativistic gas

$\alpha = 3$ Extreme relativistic gas

Localized particles: Distinguishable, Ex Harmonic Oscillator, Approximates a solid.

$$Z_N = Z_1^N$$

The single particle partition function due to localized nature of the particles,

Canonical partition function $Z_1 = \phi(T)$ (Function of T alone)

$$Z_\mu = \sum_{N_r=0}^{\infty} \left[\xi \varphi(T) \right]^{N_r} = 1 + \frac{\left(\xi \varphi(T) \right)^1}{1!} + \cdots = \left(1 - \xi \varphi(T) \right)^{-1} \qquad \xi \varphi(T) < 1$$

$$q = \ln\left(1 - \xi \varphi(T)\right)^{-1} = -\ln\left(1 - \xi \varphi(T)\right) \rightarrow p = \frac{-k_B T}{V} \ln\left(1 - \xi \varphi(T)\right)$$

$$V \rightarrow \infty, p \rightarrow 0 \qquad \rightarrow N = \frac{\xi \varphi(T)}{1 - \xi \varphi(T)} \qquad \rightarrow U = \frac{\xi k_B T^2 \varphi(T)}{1 - \xi \varphi(T)}$$

$$\to F = Nk_BT\ln\xi + k_BT\ln\left(1-\xi\varphi(T)\right)$$

$$\to S = -Nk_BT\ln\xi - k_B\left(1-\xi\varphi(T)\right) + \frac{\xi k_BT\varphi'(T)}{1-\xi\varphi(T)}$$

Now, $\xi\varphi(T) = N\left(1-\xi\varphi(T)\right)$

$$\frac{\xi\varphi(T)}{1-\xi\varphi(T)} = \frac{N}{1} \Rightarrow \xi\varphi(T) = N - N\xi\varphi(T) \Rightarrow \xi\varphi(T)(1+N) = N$$

$$\xi\varphi(T) = \frac{N}{N+1} = \frac{1}{1+1/N} = 1-\frac{1}{N}(N \gg 1)$$ (Case)

It follows that,

$$1-\xi\varphi(T) = \frac{1}{N+1} \sim \frac{1}{N}$$

$$\to U = \frac{\xi k_BT^2\phi(T)}{1/N}, \frac{U}{N} = k_BT^2\frac{\varphi'(T)}{\varphi(T)}$$

$$\to F = Nk_BT\ln\xi + k_BT\ln\frac{1}{N} = Nk_BT\ln\xi - k_BT\ln N$$

$$\frac{F}{N} = +k_BT\ln\xi - k_BT\frac{\ln N}{N},$$

Substituting $\varphi(T) = \left[2\sinh\frac{(\hbar\omega)}{2k_BT}\right]^{-1}$ (Quantum Mechanical H.O)

Also, $\varphi(T) = \frac{k_BT}{\hbar\omega}$ (Classical H.O (1D))

Two cases taken from precious roles.