Grand Canonical ensemble

- S system
- Reservoir, R of heat and energy
- E_0 total energy
- N_0 total number of particles

$$P_j = c\,\Omega_R(E_0 - E_j, N_0 - N_j)$$

$$\ln(P_j) = \text{constant} + \left(\frac{\partial \ln(\Omega_R)}{\partial E}\right)_{E_0,N_0}(-E_j) + \left(\frac{\partial \ln(\Omega)}{\partial N}\right)_{E_0,N_0}(-N_j) + \dots$$

$$\frac{\partial \ln(\Omega_R)}{\partial E} = \frac{1}{K_B T} \quad \text{and} \quad \frac{\partial \ln(\Omega_R)}{\partial N} = \frac{-\mu}{K_B T}$$

then,

$$\ln(p_j) = \text{constant} - \frac{E_j}{K_B T} + \frac{\mu N_j}{K_B T}$$

$$p_j = \frac{\exp(-\beta E_j + \beta \mu N_j)}{\Xi}$$

where,

$$\Xi := \sum_j \exp(-\beta E_j + \beta \mu N_j)$$

$$\Xi = \sum_N \exp(\beta \mu N) \sum_j \exp[-\beta E_j(N)]$$

j restricted to N

$$= \sum_N \exp(\beta \mu N)\, Z(\beta, N)$$

$$= \sum_N \exp(\beta \mu N + \ln(Z))$$

$$\sim \exp\left[-\beta \min_N(-K_B T \ln(Z) - \mu N)\right]$$

$$= \exp\left[-\beta \min_N \{F - \mu N\}\right]$$

$$\Xi \longrightarrow \exp(-\beta \Phi)$$

then

$$\phi(T,V,\mu) \longrightarrow -\frac{1}{\beta}\ln(\Xi(T,V,\mu))$$ Grand potential

$$\phi(T,\mu) = -\frac{1}{\beta}\lim_{V\to\infty}\frac{1}{V}\ln(\Xi(T,V,\mu))$$ Grand potential per volume

As $\Phi = U - TS - N\mu = -pV$

$$\phi = -p$$

Fluctuations

$$\langle E_j\rangle = \Xi^{-1}\sum_j E_j \exp(-\beta E_j + \beta\mu N_j)$$

$$= -\frac{\partial}{\partial\beta}\ln(\Xi) + \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\ln(\Xi)$$

$$\langle N_j\rangle = \Xi^{-1}\sum_j N_j \exp(-\beta E_j + \beta\mu N_j)$$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln(\Xi)$$

$$z := \exp(\beta\mu)$$ Fugacity

$$\Xi = \Xi(z,\beta) = \sum_j z^{N_j}\exp(-\beta E_j)$$

$$= \sum_{N=0}^{\infty} z^N Z(\beta,N)$$

then,

$$\langle E_j\rangle = \Xi^{-1}\sum_j N_j z^{N_j}\exp(-\beta E_j)$$

$$= -\frac{\partial}{\partial\beta}\ln(\Xi(z,\beta))$$

$$\langle N_j\rangle = \Xi^{-1}\sum_j N_j z^{N_j}\exp(-\beta E_j)$$

$$= z\frac{\partial}{\partial z}\ln(\Xi(z,\beta))$$

$$\langle E_j\rangle = U \quad \text{and} \quad \langle N_j\rangle = N.$$

$$\langle (\Delta N)^2 \rangle = \langle (N_j - \langle N_j \rangle)^2 \rangle = \frac{1}{\beta^2} \frac{\partial}{\partial \mu}\left[\frac{\partial}{\partial \mu} \ln(\Xi)\right]$$

$$\langle (N_j - \langle N_j \rangle)^2 \rangle = \frac{1}{\beta}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} > 0$$

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dp \qquad \text{Gibbs-Duhem relation}$$

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

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

From the Helmholtz representation, we get.

$$\left(\frac{\partial p}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N} \qquad \text{Maxwell relation}$$

then

$$\left(\frac{\partial \mu}{\partial N}\right) = -\frac{V}{N}\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = -\left(\frac{V}{N}\right)^2\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{V}{N^2 K_T}$$

$$\langle (\Delta N)^2 \rangle = \langle (N_j - \langle N_j \rangle)^2 \rangle = \frac{N k_B T K_T}{v} \geq 0$$

$$\frac{\langle (\Delta N)^2 \rangle^{1/2}}{\langle N_j \rangle} = \left(\frac{k_B T K_T}{v}\right)^{1/2} \frac{1}{\sqrt{N}}$$

Ideal gas

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} V^N$$

then,

$$\Xi = \sum_N^{\infty} z^N \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} V^N = \exp\left[z\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V\right]$$

Also,

$$\frac{1}{V}\ln(\Xi) = z\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}$$

$$\langle E_j \rangle = \Xi^{-1} \sum_j E_j z^{N_j} \exp(-\beta E_j)$$

$$= -\frac{\partial}{\partial \beta} \ln(\Xi(\beta, z)) = \frac{3z}{2}\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V \beta^{-1} = U$$

$$\langle N_j \rangle = \Xi^{-1} \sum_j N_j z^{N_j} \exp(-\beta E_j)$$

$$= z \frac{\partial}{\partial z} \ln(\Xi(\beta, z)) = z \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} V = N$$

therefore

$$U = \frac{3}{2} N k_B T$$

$$\phi = -\frac{1}{\beta} \ln(\Xi) = -V \left(\frac{2\pi m}{h^2} \right)^{3/2} (k_B T)^{5/2} \exp\left(\frac{\mu}{k_B T} \right)$$

$$d\phi = dU - TdS - SdT - \mu dN - N d\mu$$

$$= -pdV - SdT - Nd\mu,$$

then

$$\frac{\partial \phi}{\partial V} = -p \qquad \frac{\partial \phi}{\partial T} = -S \qquad \frac{\partial \phi}{\partial \mu} = -N$$

$$S = -\left(\frac{\partial \phi}{\partial T} \right)_{V,\mu}$$

$$= V \left(\frac{3}{2} - \frac{\mu}{T} \right) \left(\frac{2\pi m}{h^2} \right)^{3/2} (k_B T)^{3/2} \exp\left(\frac{\mu}{k_B T} \right)$$

$$N = -\left(\frac{\partial \phi}{\partial T} \right)_{T,V}$$

$$= V \left(\frac{2\pi m}{h^2} \right)^{3/2} (k_B T)^{3/2} \exp\left(\frac{\mu}{k_B T} \right)$$

$$p = -\left(\frac{\partial \phi}{\partial V} \right)_{T,\mu}$$

$$= \left(\frac{2\pi m}{h^2} \right)^{3/2} (k_B T)^{5/2} \exp\left(\frac{\mu}{k_B T} \right)$$

$$= \frac{N}{V} k_B T.$$