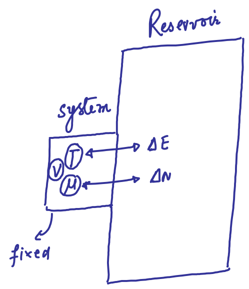
Grand Canonical Ensemble (μ, V, T) :

$\mu \rightarrow \Delta N \neq 0$

$V \rightarrow$ fixed walls

$T \rightarrow \Delta E \neq 0$



Eg. Ideal gas as a working example:

$$\nu \equiv \{\vec{q}_i, \vec{p}_i\} \qquad \vec{q}_i \in V$$

$$-\infty < \vec{p}_i < +\infty$$

$$i \in [1, N_\nu]$$

Microstate : $[\nu, N_\nu]$

probability density function (PDF) : $$p(\nu, N_\nu) = \frac{1}{N_\nu!} \cdot \frac{1}{h^{3N_\nu}} \frac{e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)} \quad (1)$$

Connection between S.M & Therm. : $$\mathcal{G} = -\frac{1}{\beta} \ln \mathcal{Z}(\mu, V, T) \quad (2)$$

$\mathcal{G} \rightarrow$ Grand potential

$$\mathcal{G} = E - TS - \mu N \quad (3)$$

Compute $\mathcal{Z}(\mu, V, T)$: $$\sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \cdot \frac{e^{\beta\mu N_\nu}}{h^{3N_\nu}} \int_{\{\vec{q}_i \in V, -\infty < \vec{p}_i < \infty\}} \cdots\cdots \int \prod_{j=1}^{N_\nu} d^3\vec{q}_j \, d^3\vec{p}_j \, e^{-\beta \sum_{i=1}^{N_\nu} p_i^2/2m}$$

$$\mathcal{Z}(\mu, V, T) = \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \frac{e^{\beta\mu N_\nu}}{h^{3N_\nu}} \left(\int_{\vec{q}_1 \in V} d^3\vec{q}_1 \right)^{N_\nu} \left(\int_{\vec{p}_1 \in [-\infty, +\infty]} d^3\vec{p}_1 \, e^{-\beta p_1^2/2m} \right)^{N_\nu}$$

$$= \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \cdot \frac{1}{h^{3N_\nu}} \cdot \underbrace{e^{\beta\mu N_\nu} \, V^{N_\nu} \left(\frac{2\pi m}{\beta}\right)^{3N_\nu/2}}_{\text{Canonical Partition function}}$$

$$= \sum_{N_\nu=0}^{\infty} \frac{V^{N_\nu}}{N_\nu!} \cdot e^{\beta\mu N_\nu} \left(\frac{2\pi m}{h^2 \beta}\right)^{3N_\nu/2}$$

Realizing that $\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} = \frac{1}{\lambda(T)^3}$

$$= \sum_{N_\nu=0}^{\infty} \left(\frac{V e^{\beta\mu}}{\lambda(T)^3}\right)^{N_\nu} \cdot \frac{1}{N_\nu!}$$

Since $\sum_{n=0}^{\infty} x^n/n! = e^x$

$$\therefore \mathcal{Z}(\mu, V, T) = \exp\left(\frac{V e^{\beta\mu}}{\lambda(T)^3}\right)$$

Grand Potential therefore is —

$$\mathcal{G} = -\frac{1}{\beta} \ln \mathcal{Z} = -k_B T \frac{V e^{\beta\mu}}{\lambda(T)^3} \quad \text{—— (4)}$$

But, $\mathcal{G} = E - TS - \mu N$

$$d\mathcal{G} = dE - Tds - sdT - \mu dN - N d\mu$$

$$= -Pdv - sdT - Nd\mu \qquad \because \text{ I}^{st} \text{ law: } Tds = dE + Pdv - \mu dN$$

Hence: $P = -\frac{\partial \mathcal{G}}{\partial V}\Big|_{\mu,T}$, $S = -\frac{\partial \mathcal{G}}{\partial T}\Big|_{V,\mu}$, $N = -\frac{\partial \mathcal{G}}{\partial \mu}\Big|_{V,T}$

$$\because\ \mathcal{G} = -\frac{k_B T V e^{\beta\mu}}{\lambda(T)^3} \quad \therefore\ P = \frac{k_B T e^{\beta\mu}}{\lambda(T)^3}$$ ...... Pressure

$$S = k_B V \frac{\partial}{\partial T}\left(\frac{T e^{\beta\mu}}{\lambda(T)^3}\right) = k_B V \left[\frac{1}{\lambda(T)^3}\cdot\frac{\partial}{\partial T}\left(T e^{\beta\mu}\right) + T e^{\beta\mu}\cdot\frac{\partial}{\partial T}\left(\frac{1}{\lambda(T)^3}\right)\right]$$

$$= k_B V\left[\frac{1}{\lambda(T)^3}\cdot\left(e^{\beta\mu} - T e^{\beta\mu}\cdot\frac{\mu}{k_B}\left(\frac{1}{T^2}\right)\right) + T e^{\beta\mu}\frac{(-3)}{\lambda(T)^4}\cdot\frac{\partial}{\partial T}\lambda(T)\right]$$

$$= \frac{k_B V e^{\beta\mu}}{\lambda(T)^3}\left[1 - \frac{\mu}{k_B T} + \frac{3\cancel{T}}{\cancel{\lambda(T)}}\cdot\frac{\cancel{h}}{\cancel{(2\pi m k_B)^{1/2}}}\cdot\frac{1}{2\cancel{T^{3/2}}}\right] \qquad \lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$S = \frac{k_B V e^{\beta\mu}}{\lambda(T)^3}\left[\frac{5}{2} - \frac{\mu}{k_B T}\right]$$ ...... Entropy

To compute $N = -\frac{\partial \mathcal{G}}{\partial \mu}\Big|_{V,T} = -\frac{\partial}{\partial\mu}\left(-\frac{k_B T V e^{\beta\mu}}{\lambda(T)^3}\right)_{V,T}$

$$= \frac{\cancel{k_B T} V}{\lambda(T)^3} e^{\beta\mu}\cdot\cancel{\beta}$$

$$N = \frac{V e^{\beta\mu}}{\lambda(T)^3}$$ ...... No. of particles