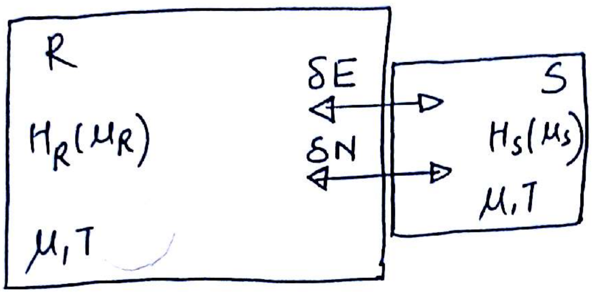
Grand Canonical Ensemble: A system at constant $(\mu, \vec{x}, T)$

Let us now generalize the previous ensembles to include chemical work as well. The chemical work here refers to the exchange of particles with the reservoir.

Macrostates are thus specified as : $M \equiv (\mu, \vec{x}, T)$

$\vec{x}$ could be volume, magnetization, etc.



" A system in contact with a reservoir through which it maintains constant μ, T. "

Note: To maintain constant T and μ, there must be exchange of E and N respectively.

Let μ_S : microstate of the system

& μ_R : microstate of the reservoir

The probability of finding the system in a microstate μ_s

$$p(\mu_s) = \frac{e^{-\beta[H(\mu_s) - \mu N(\mu_s)]}}{\mathcal{Z}} \qquad \text{——} \quad (1)$$

$N(\mu_s)$ = No. of particles in the microstate μ_s.

$\mathcal{Z} \equiv$ Grand canonical partition function.

$$\mathcal{Z} = \mathcal{Z}(\mu, \vec{x}, T) = \sum_{\mu_s} e^{-\beta[H(\mu_s) - \mu N(\mu_s)]}$$

$$= \sum_N e^{\beta \mu N} \underbrace{\sum_{\mu_s | N} e^{-\beta H_N(\mu_s)}}_{\text{Restricted sum over microstates: } Z(N, \vec{x}, T)} \qquad \text{——— (2)}$$

Thus the grand canonical partition function is :

$$p(N) = \frac{e^{\beta \mu N} Z(N, \vec{x}, T)}{\mathcal{Z}(\mu, \vec{x}, T)} \qquad \text{——— (3)}$$

the average number of particles in the system is thus:

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_{\mu_s} N(\mu_s)\, e^{-\beta[H(\mu_s) - \mu N(\mu_s)]}$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial(\beta\mu)}$$

$$= \frac{\partial}{\partial(\beta\mu)} (\ln \mathcal{Z}) \qquad \text{——— (4)}$$

Next we calculate the number fluctuations in this ensemble

The number fluctuations are related to the variance

$$\langle N^2\rangle_c = \langle N^2\rangle - \langle N\rangle^2$$

$$= \frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial(\beta\mu)^2} - \frac{1}{(\mathcal{Z})^2}\left(\frac{\partial \mathcal{Z}}{\partial(\beta\epsilon)}\right)^2$$

$$= \frac{\partial}{\partial(\beta\epsilon)}\frac{\partial}{\partial(\beta\epsilon)}(\ln \mathcal{Z})$$

$$= \frac{\partial}{\partial(\beta\epsilon)}\langle N\rangle \quad \because \text{ from eq}^n \ 4 \qquad \text{— } 5$$

this scaling of $\langle N^2\rangle_c$ gives rise to the ensemble equivalence in the thermodynamic limit: $\frac{\langle N^2\rangle_c^{1/2}}{\langle N\rangle_c} \sim N^{-1/2} \xrightarrow{N\to\infty} 0$

Since, the distribution of N becomes sharp peaked around some N^* (due to ensemble equivalence) in the large N limit, we write, using saddle point approximation:

$$\mathcal{Z}(\mu,\vec{x},T) = \lim_{N\to\infty}\sum_{N=0}^{\infty} e^{\beta\mu N}\underbrace{\sum_{\mu_s|N} e^{-\beta H_N(\mu_s)}}_{Z(N,\vec{x},T)}$$

$$= e^{\beta\mu N^*} Z(N^*,\vec{x},T)$$

$$= e^{\beta\mu N^*} e^{-\beta F(E^*)} \qquad \because Z = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{E} e^{-\beta F(E)} \simeq e^{-\beta F(E^*)}$$

$$\therefore \mathcal{Z}(\mu, \vec{X}, T) \simeq e^{-\beta(-\mu N^* + E^* - TS(E^*))}$$

$\because F(E^*) = E^* - TS(E^*)$

$$\simeq e^{-\beta \mathcal{G}} \quad \text{--- (6)}$$

where $\mathcal{G} = -\mu N + E - TS \equiv$ Grand canonical potential — 6(a)

Note: We have dropped $*$ for convenience as all quantities in above expression are thermodynamic in nature.

Equation (6) gives us:

$$\mathcal{G} = -\frac{1}{\beta} \ln \mathcal{Z} \quad \text{--- (7)}$$

This equation provides the connection between statistical mechanics $(\mathcal{Z})$ and thermodynamics $(\mathcal{G})$ in the Grand canonical ensemble

Now the grand canonical potential is

$$\mathcal{G} = E - TS - \mu N \quad \text{--- (8)}$$

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

From 1st & 2nd law: $dE = Tds + \underbrace{\vec{J}\cdot d\vec{x}}_{\text{PV work}} + \underbrace{\mu dN}_{\text{chemical work}}$ — (9)

Plugging (9) in (8) gives,

$$d\mathcal{G} = \vec{J}\cdot d\vec{x} - SdT - N d\mu \quad \text{--- (10)}$$

$$\therefore \left(\frac{\partial \mathcal{G}}{\partial T}\right)_{\mu, \vec{x}} = -S$$

$$\left(\frac{\partial \mathcal{G}}{\partial \mu}\right)_{T, \vec{x}} = -N$$

$$\left(\frac{\partial \mathcal{G}}{\partial x_i}\right)_{T, \mu} = J_i \qquad \text{——— } 10(a)$$

<u>Example:</u> Ideal gas in grand canonical ensemble.

Macrostate $M \equiv (\mu, V, T)$

Microstates $\{\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, \ldots\}$ have indefinite particle number. the grand partition function is given by

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} \int \cdots \int \frac{d^3q_1 \ldots d^3q_N \, d^3p_1 \ldots d^3p_N}{h^{3N}} e^{-\beta \sum_{i=1}^{N} p_i^2/2m}$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \cdot \frac{1}{N!} \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$= \sum_{N=0}^{\infty} \left[e^{\beta \mu} \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} \right]^N \frac{1}{N!}$$

$$= \exp\left[e^{\beta \mu} \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} \right] \qquad \text{——— } (11)$$

The grand canonical potential is

$$\mathcal{G}(\mu, V, T) = -\frac{1}{\beta} \ln \mathcal{Z} = \frac{-1}{\beta} e^{\beta\mu} \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}$$

The pressure of the gas is

$$P = -\frac{\partial \mathcal{G}}{\partial V}\bigg|_{\mu,T} \quad \ldots \text{ from } 10(a)$$

$$= \frac{1}{\beta} e^{\beta\mu} \cdot \frac{1}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{1}{\beta} e^{\beta\mu} \left(\frac{2\pi m}{\beta h^2}\right)^{3/2}$$

The particle number is

$$N = -\left(\frac{\partial \mathcal{G}}{\partial \mu}\right)_{T,V} = e^{\beta\mu} \cdot \frac{1}{h^3} \cdot \left(\frac{2\pi m}{\beta}\right)^{3/2} = e^{\beta\mu} \left(\frac{2\pi m}{\beta h^2}\right)^{3/2}$$

The chemical potential is

$$\mu = \frac{1}{\beta} \cdot \ln\left[N \left(\frac{\beta h^2}{2\pi m}\right)^{3/2}\right] = \frac{1}{\beta} \ln\left(P\beta \left(\frac{\beta h^2}{2\pi m}\right)^{3/2}\right)$$