Gibbs canonical ensemble: A system at constant $(N, \vec{J}, T)$

We will generalize the canonical ensemble to include the addition of both heat and work.

Microstates are specified as: $M \equiv (N, \vec{J}, T)$ $\vec{J}$: Generalized force.

$\vec{J}$ could be pressure, magnetic field ...

The system is maintained at:

constant T through a heat reservoir &

constant $\vec{J}$ through pistons, magnets etc.

Energy of the system is now given as: $H - \vec{J}\cdot\vec{x}$

The micro-states of this combined system occur with probabilities:

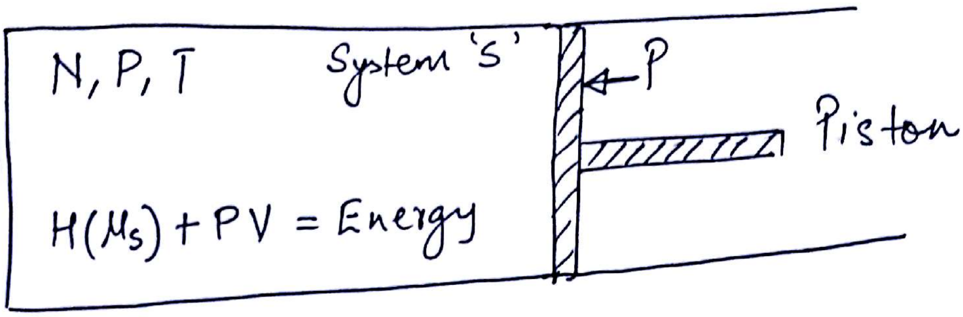
$$p(\mu_s, \vec{x}) = \frac{e^{-\beta\left[H(\mu_s) - \vec{J}\cdot\vec{x}\right]}}{Z(N, \vec{J}, T)} \quad \text{———} \; (1)$$

where the Gibbs partition function:

$$Z(N, \vec{J}, T) = \sum_{\mu_s, \vec{x}} e^{-\beta\left[H(\mu_s) - \vec{J}\cdot\vec{x}\right]} \quad \text{———} \; (2)$$

The sum of over all micro-states and $\vec{x}$.

For eg: $H - \vec{J}\cdot\vec{x} = H + PV$ for a gas compressed with a piston.



the expectation value of variable $\vec{x}$ is :

$$\langle \vec{x} \rangle = \frac{1}{\beta}\frac{\partial (\ln Z)}{\partial \vec{J}} \quad \text{——— (3)}$$

Proof: $\frac{1}{\beta}\frac{\partial}{\partial \vec{J}}(\ln Z)$

$$= \frac{1}{\beta Z}\frac{\partial Z}{\partial \vec{J}}$$

$$= \frac{1}{\beta Z}\sum_{\mu_s, \vec{x}} \beta \vec{x}\, e^{-\beta[H(\mu_s) - \vec{J}\cdot\vec{x}]}$$

$$= \langle \vec{x} \rangle$$

Now from thermodynamics:

$$T ds = dE - \vec{J}\cdot d\vec{x}$$

$$\& \quad dG = -S dT - \vec{x}\cdot d\vec{J} \quad \left[\because G = E - \vec{x}\cdot\vec{J} - TS\right.$$

$$dG = dE - \vec{x}\cdot d\vec{J} - \vec{J}\cdot d\vec{x} - Tds - SdT$$

$$= \cancel{-\vec{J}d\vec{x}} - \vec{x}\cdot d\vec{J} - SdT$$

$$\therefore \left.\frac{\partial G}{\partial \vec{J}}\right|_T = -\vec{x} \quad \text{——— (4)}$$

Comparing (3) & (4), we get

$$G = \frac{-1}{\beta}\ln Z \quad \text{——— (5)}$$

The enthalpy $E-\vec{J}\cdot\vec{x}$ is easily computed in this ensemble

$$E-\vec{J}\cdot\vec{x} = \langle H(\mu_s) - \vec{J}\cdot\vec{x}\rangle = \frac{1}{Z(N,\vec{J},T)} \sum_{\mu_s,\vec{x}} \left[H(\mu_s) - \vec{J}\cdot\vec{x}\right] e^{-\beta\left[H(\mu_s)-\vec{J}\cdot\vec{x}\right]}$$

$$= \frac{-\partial}{\partial\beta}(\ln Z) \qquad (6)$$

The heat capacity at constant force $C_{\vec{J}}$ is computed from enthalpy

$$C_{\vec{J}} = \frac{\partial}{\partial T}(E-\vec{J}\cdot\vec{x}) = \frac{-\partial}{\partial T}\frac{\partial}{\partial\beta}(\ln Z) \qquad \text{..... from } (6)$$

$$= \frac{1}{K_B T^2}\frac{\partial}{\partial\beta}\frac{\partial}{\partial\beta}(\ln Z) \qquad \because \frac{\partial}{\partial\beta} \equiv -K_B T^2 \frac{\partial}{\partial T}$$

$$= \frac{1}{K_B T^2}\frac{\partial}{\partial\beta}\left[\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta}\right]$$

$$= \frac{1}{K_B T^2}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2\right]$$

$$= \frac{1}{K_B T^2}\left[\left\langle\left(H(\mu_s)-\vec{J}\cdot\vec{x}\right)^2\right\rangle - \left\langle H(\mu_s)-\vec{J}\cdot\vec{x}\right\rangle^2\right]$$

$$= \frac{1}{K_B T^2}\left\langle\left(H(\mu_s)-\vec{J}\cdot\vec{x}\right)^2\right\rangle_c \qquad (7)$$

"Fluctuations in enthalpy are related to the heat capacity at constant force in the Gibbs ensemble"

Examples in the Gibbs canonical ensemble.

(1) Ideal gas in the isobaric ensemble:

Macrostate $M \equiv (N, P, T)$

Microstate $\mu \equiv \{\vec{q_i}, \vec{p_i}\}$ in a volume V.

Microstate probability:

$$p(\{\vec{q_i}, \vec{p_i}\}, V) = \frac{1}{Z} e^{-\beta\left[\sum_{i=1}^{N} \frac{p_i^2}{2m} + PV\right]} \qquad \{\vec{q_i}\} \in V$$

$$= 0 \qquad ; \text{ otherwise}$$

The Gibbs partition function is

$$Z(N,P,T) = \int_0^\infty e^{-\beta PV} dV \int \cdots \int \frac{d^3q_1 \cdots d^3q_N \, d^3p_1 \cdots d^3p_N}{N!\, h^{3N}} e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}}$$

$$= \int_0^\infty e^{-\beta PV} V^N dV \cdot \frac{1}{N!\, h^{3N}} \cdot \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$= \frac{1}{N!\, h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \frac{N!}{(\beta P)^{N+1}} \qquad \because \int_0^\infty e^{-x} x^{N-1} dx = (N-1)!$$

$$= \frac{1}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \frac{1}{(\beta P)^{N+1}} \qquad \text{—— (8)}$$

Now $G = -K_BT \ln Z$

$$= -K_BT\left[-3N\ln h + \frac{3N}{2}\ln\left(\frac{2\pi m}{\beta}\right) - (N+1)\ln(\beta P)\right]$$

... from (8)

Dropping the term $\ln(\beta P)$ as it is $O(N^0)$ compared to other terms which are $O(N^1)$.

$$G = K_BTN\left[\ln h^3 - \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right) + \ln(\beta P)\right]$$

$$= NK_BT\left[\frac{3}{2}\ln\left(\frac{h^2}{2\pi m}\right) + \frac{5}{2}\ln\beta + \ln P\right] \quad (9)$$

Now $dG = \mu dN + vdp - sdT$

$\because G = E + PV - TS$

$\therefore dG = dE + Pdv - vdP - sdT - Tds$

$= \mu dN + vdp - sdT$

we get: $\left(\frac{\partial G}{\partial P}\right)_{N,T} = V$

$\therefore$ we get from eq (9),

$$\frac{NK_BT}{P} = V$$

$\Rightarrow PV = NK_BT$ (Ideal gas law)

Hence Enthalpy : $E + PV = \frac{3}{2}NK_BT + K_BT = \frac{5}{2}NK_BT$