VIVEKANANDA COLLEGE THAKURPUKUR KOLKATA-700063

NAAC ACCREDITED ‘A’ GRADE

Topic: Grand Canonical Ensemble II (https://youtu.be/1uogRCJXwmM)

Course Title: Statistical Mechanics

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Grand Canonical Ensemble

$N_m \rightarrow$ identical system

$N_m \bar{E} \rightarrow$ total energy

$N_m \bar{N} \rightarrow$ total no. of particles

If $n_{r,s}$ be no. of system having N_r no. of particles & energy E_s, then

$$\sum_{r,s} n_{r,s} = N_m \quad \Rightarrow \quad \sum \delta n_{r,s} = 0$$

$$\sum_{r,s} n_{r,s} N_r = N_m \bar{N} \quad \Rightarrow \quad \sum_{r,s} \delta n_{r,s} N_r = 0 \quad - \times \alpha$$

$$\sum_{r,s} n_{rs} E_s = N_m \bar{E} \quad \Rightarrow \quad \sum_{r,s} \delta n_{r,s} E_s = 0 \quad - \times \beta$$

No. of ways $$W\{n_{rs}\} = \frac{N_m!}{\prod_{r,s} n_{r,s}!}$$

$$\delta \ln W = \delta n_{r,s} \ln \{n_{r,s} + 1\}$$

Most probable distr.

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

Grand Canonical Ensemble

$$n_{r,s} = e^{-\alpha N_r - \beta E_s} \Big/ \sum_{r,s} e^{-\alpha N_r - \beta E_s}$$

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum e^{-\alpha N_r - \beta E_s}} \quad ; \quad \bar{E} = \frac{\sum E_s e^{-\alpha N_r - \beta E_s}}{\sum e^{-\alpha N_r - \beta E_s}}$$

$$= -\frac{\partial}{\partial \alpha}\left\{\ln \sum e^{-\alpha N_r - \beta E_s}\right\} \qquad = -\frac{\partial}{\partial \beta}\{\underbrace{\ln \sum e^{-\alpha N_r - \beta E_s}}_{q}\}$$

<u>q potential:</u> $q = \ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}$

$$= q(\alpha, \beta, E_s)$$

$$dq = \frac{\partial q}{\partial \alpha} d\alpha + \frac{\partial q}{\partial \beta} d\beta + \frac{\partial q}{\partial E_s} dE_s$$

$$= -\bar{N} d\alpha - \bar{E} d\beta - \beta \frac{\sum e^{-\alpha N_r - \beta E_s} dE_s}{\sum e^{-\alpha N_r - \beta E_s}}$$

$$d(q + \bar{N}\alpha + \bar{E}\beta) = \underline{dq} + \alpha d\bar{N} + \underline{\bar{N} d\alpha} + \beta d\bar{E} + \underline{\bar{E} d\beta}$$

$$= \alpha d\bar{N} + \beta d\bar{E} - \beta \frac{\sum e^{-\alpha N_r - \beta E_s} dE_s}{\sum e^{-\alpha N_r - \beta E_s}}$$

$$d(q + \bar{N}\alpha + \beta\bar{E}) = \beta\left(d\bar{E} + \frac{\alpha}{\beta} d\bar{N} - \frac{\sum e^{-\alpha N_r - \beta E_s} dE_s}{\sum e^{-\alpha N_r - \beta E_s}}\right)$$

1st law of Th. dy.

$$\delta Q = d\bar{E} + \mu d\bar{N} + \delta W$$

$$d(q + \bar{N}\alpha + \bar{E}\beta) = \beta \delta Q$$

Grand Canonical Ensemble

$\beta = \frac{1}{kT}$; $\mu = -\frac{\alpha}{\beta}$; $\delta W = -\frac{\sum e^{-\alpha N_r - \beta E_s} dE_s}{\sum e^{-\alpha N_r - \beta E_s}}$

$\Downarrow$

$\mu = -\alpha kT$

$\alpha = -\mu / kT$

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

$$q = \frac{S}{k} + \frac{\bar{N}\mu}{kT} - \frac{\bar{E}}{kT}$$

$$= \frac{TS + \bar{N}\mu - \bar{E}}{kT} = \frac{TS - \bar{E} + G}{kT}$$

$$= \frac{\cancel{TS} - \cancel{\bar{E}} + \cancel{\bar{E}} - \cancel{TS} + PV}{kT}$$

$$\boxed{q = \frac{PV}{kT}}$$ → link between GCE & th.dy.

$$q = \ln \sum_{r,s} e^{-\alpha N_r - \beta E_s} = \ln \sum_{r,s} e^{\frac{\mu N_r}{kT}} e^{-E_s/kT}$$

let $z = e^{\mu/kT}$, $Q_{N_r} = \sum_s e^{-\beta E_s}$

$$q(z,V,T) = q = \ln \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}$$

$\Downarrow$

$q(\mu,V,T)$