VIVEKANANDA COLLEGE
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NAAC ACCREDITED ‘A’ GRADE

Topic: Grand Canonical Ensemble III (https://youtu.be/1ZyakIxHUwg)

Course Title: Statistical Mechanics

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Grand Canonical Ensemble

$\alpha = -\frac{\mu}{kT}$

$\mu = -kT\alpha$

$= +kT \ln z$

$$z = e^{-\alpha} \rightarrow \text{Fugacity}$$
$$= e^{\mu/kT}$$

q potential

$$q = \ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}$$
$$= \ln \sum_r z^r \left(\sum_s e^{-\beta E_s} \right)$$
$$= \ln \sum_r z^r \, \underbrace{Q_{N_r}(V,T)}$$

$\rightarrow$ Canonical Partition funct

$$= \ln \mathcal{Q}(z, V, T)$$

$\mathcal{Q} \rightarrow$ Grand Canonical Partition function

$$q = \ln \mathcal{Q} = \frac{PV}{kT} \Rightarrow P = \frac{kT}{V} \ln \mathcal{Q}$$

$$\Rightarrow \boxed{P(z,V,T) = \frac{kT}{V} \ln \mathcal{Q}}$$

$\mu = kT \ln z$

$\frac{\partial}{\partial \mu} = \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z}$

$1 = \frac{kT}{z} \frac{\partial z}{\partial \mu}$

$\frac{\partial z}{\partial \mu} = \frac{z}{kT}$

$\frac{\partial}{\partial \mu} = \frac{z}{kT} \frac{\partial}{\partial z}$

$$\bar{N} = -\frac{\partial}{\partial \alpha} \left(\ln \sum e^{-\alpha N_r - \beta E_s} \right)$$
$$= kT \frac{\partial q}{\partial \mu} = z \frac{\partial}{\partial z} q \Rightarrow \boxed{\bar{N}(z,V,T) = z \frac{\partial}{\partial z} \ln \mathcal{Q}}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} q = kT^2 \frac{\partial q}{\partial T} \Rightarrow \boxed{U = E(z,V,T) = kT^2 \left(\frac{\partial q}{\partial T} \right)}$$

$$A = G - PV = N\mu - PV$$
$$= NkT \ln z - kT \ln \mathcal{Q}$$
$$= -kT \ln \left(\mathcal{Q} / z^N \right)$$

$$S = \frac{U - A}{T}$$

Grand Canonical Ensemble

Classical Ideal Gas:

Single Particle Partition funct. $Q_1(V,T) = \frac{V}{h^3}(2\pi mkT)^{3/2}$

$= V f(T)$

N Particle $Q_N(V,T) = \frac{(Q_1)^N}{N!}$

$q = \ln \mathcal{Q}(z,V,T)$

Grand Canonical Partition Func $\mathcal{Q} = \sum_N z^N \frac{(Q_1)^N}{N!} = \sum_N z^N \frac{(Vf(T))^N}{N!}$

$e^x = \sum_r \frac{x^r}{r!}$

$= \sum_N \frac{(zVf(T))^N}{N!}$

$= e^{zVf(T)}$

$P = \frac{kT}{V} q = \frac{kT}{\cancel{V}} \cdot z\cancel{V} f(T)$ $\quad q = \ln \mathcal{Q} = \ln e^{zVf(T)}$

$= zVf(T)$

$P = zkTf(T)$

$N = z\frac{\partial q}{\partial z} = zVf(T)$ $\quad \frac{P}{kT} = \frac{N}{V} \Rightarrow PV = NkT$

$U = kT^2 \frac{\partial q}{\partial T} = kT^2 zVf'(T)$

$S =$

$A =$

Grand Canonical Ensemble

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

$$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta, E_s} = \frac{\sum -N_r^2 e^{-\alpha N_r - \beta E_s}}{\sum e^{-\alpha N_r - \beta E_s}} + \frac{\left(\sum N_r e^{-\alpha N_r - \beta E_s}\right)^2}{\left(\sum e^{-\alpha N_r - \beta E_s}\right)^2}$$

$$= -\overline{N^2} + (\bar{N})^2$$

$\alpha = -\frac{\mu}{kT}$

$$\left(-\frac{\partial \bar{N}}{\partial \alpha}\right)_{V,T} = \overline{N^2} - \bar{N}^2 = \overline{\Delta N}^2$$

$$\frac{\overline{\Delta N}^2}{\bar{N}^2} = -\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{V,T} = \frac{kT}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T}$$

let $v = \frac{V}{N}$ ← specific volume

$$\frac{\overline{\Delta N}^2}{\bar{N}^2} = \frac{kT}{(V/v)^2} \frac{\partial (V/v)}{\partial \mu} = \frac{kTv^2}{V^2} \cdot \left(\frac{-V}{v^2}\right)\left(\frac{\partial v}{\partial \mu}\right)_{V,T}$$

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

$$\mu N = G = A + PV$$

$$= U - TS + PV \Rightarrow dG = dU - TdS - SdT + PdV + VdP$$

$$\mu dN + N d\mu = \mu dN - SdT + VdP$$

$$d\mu = -sdT + vdP$$

T = Const

$$v = (\partial \mu / \partial P)_T \Rightarrow d\mu = v dP$$

$$\frac{\overline{\Delta N}^2}{\bar{N}^2} = \frac{-kT}{V} \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{kT}{V} k_T \rightarrow \text{Isothermal Compressibi}$$

Grand Canonical Ensemble

$$\frac{\overline{\Delta n^2}}{\bar{n}^2} = \frac{\overline{\Delta N^2}}{\bar{N}^2} = -\frac{kT}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{v,T}$$

$n = \frac{N}{V}$

$$= \frac{kT}{V} K_T \quad \text{where } K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Isothermal Compressibility

$$K_T \propto \frac{1}{N}$$

RMS fluctuations in no. density

$$\sqrt{\frac{\overline{\Delta n^2}}{\bar{n}^2}} \propto \frac{1}{\sqrt{N}} = \frac{1}{N^{0.5}}$$