in class notes 2/15/23

(I)

1) $F = \ln W - \alpha\left[\sum n_i - \tilde{N}\right]$

$- \beta\left[\sum n_i \varepsilon_i - \tilde{\varepsilon}\right]$ (II)

2) $F = \ln \tilde{N}! - \sum_i \ln(n_i!) - \text{I} - \text{II}$

Stirling approx

3) $\boxed{F = \tilde{N}\ln\tilde{N} - \cancel{\tilde{N}}\sum_{i=1} n_i - \sum_i \left[\left[n_i \ln n_i - n_i\right]\right] - \text{I} - \text{II}}$

Reif's Text pdf

(I) $\boxed{\text{indep vbls} = n_1, n_2, \ldots}$

Stir app

$\boxed{\ln x! = x\ln x - x}$

$+ \frac{1}{2}\ln(2\pi x)$ (III)

4) $\frac{\partial F}{\partial n_j} = 0 \quad j = 1, 2, 3 \ldots$

for large x III tiny

$\Rightarrow$ $\cancel{1 \ln \tilde{N} - n_j \tilde{N}\left(\frac{1}{n_j}\right) - 1}$

$\boxed{0 = -\left[\left[(1)\ln n_j + n_j \cancel{\frac{1}{n_j}} - \cancel{1}\right]\right] - \alpha - \beta\varepsilon_j}$

②

5) ∴ $\boxed{n_j = e^{-\alpha} e^{-\beta E_j}}$

6) ⇒ $\sum n_j = \tilde{N} = e^{-\alpha}\left(\sum_j e^{-\beta E_j}\right) = e^{-\alpha} Q$

7) ⇒ $\boxed{e^{-\alpha} = \tilde{N}/Q}$

this is the set of $n_1, n_2, \ldots$ that max's F

8) ∴ 7) & 5) ⇒ $n_j^* = \frac{\tilde{N}}{Q} e^{-\beta E_j}$

~~Or~~

9) ∴ $\boxed{\frac{n_j^*}{\tilde{N}} = \frac{e^{-\beta E_j}}{Q}} \equiv$

⊕ $\frac{n_j^*}{\tilde{N}} \equiv P(E_j) =$ probability of observing a system in Q state E_j

⊕ @ equilibrium

⊕ turns out, all macroscopic thermo can be gotten from Q

1) $\boxed{U = -\frac{\partial}{\partial B} \ln Q}$ * * *

internal en for our system

$\boxed{\text{1) is a \underline{general} \underline{recipe} for getting } U \text{ given } Q}$

2) $U = -\frac{\partial}{\partial \beta} \ln \Big(\overbrace{\sum_{i=1} e^{-\beta E_i}}^{(F)} \Big)$

$\Rightarrow -\frac{\partial}{\partial B}(\ln F) = -\frac{1}{F}\frac{\partial F}{\partial B}$

E_i = sum of all indiv eigen energies

$E_i = E_{trans_i} + E_{rot_i} + etc$

$= \left(-\frac{1}{Q}\right) \frac{\partial}{\partial B} \left(\sum_i e^{-B E_i} \right)$

$= -\frac{1}{Q}\left[\sum_{i=1} (-E_i) e^{-B E_i} \right]$

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3) $\therefore$ $\boxed{-\frac{\partial}{\partial B} \ln Q = \left[\sum_i P(\epsilon_i)\epsilon_i\right]}$

$$P(\epsilon_i) = \boxed{\left(\frac{e^{-B\epsilon_i}}{Q}\right)}$$

$$\equiv \langle E \rangle \equiv U$$

avg energy for each of $\tilde{N}$ replica systems

4) $\therefore$ $\boxed{-\frac{\partial}{\partial B} \ln Q = U}$

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III) Show ~~that~~ Bridge reln. (5)

(*) $\boxed{A(N,V,T) = -k_B T \ln Q(\ldots)}$

A) $\boxed{A \equiv U - TS}$

$dA) \Rightarrow$ B) $\boxed{dA = dU - TdS - SdT}$

C) $= T\cancel{d}S - PdV + \mu dN - T\cancel{d}S - SdT$

Bring in "~~Fund.~~ Fund. thermo. reln."

D) $\therefore$ $\boxed{dA = -PdV + \mu dN - SdT}$

⊙ So Let's think of $A = A(V, N, T)$

E) D) $\Rightarrow$ $\boxed{-P = \left.\frac{\partial A}{\partial V}\right|_{N,T}}$ (2*)

D) $\Rightarrow$ $\boxed{\mu = \left.\frac{\partial A}{\partial N}\right|_{V,T}}$ (3*)

D) $\Rightarrow$ $\boxed{-S = \left.\frac{\partial A}{\partial T}\right|_{N,T}}$ (4*)

(+) if we can dev. microscopic model $\Rightarrow$ $\boxed{Q}$

(+) Given (*) $\Rightarrow$ use (2*) – (4*) $\Rightarrow$ P, μ, S