in-class notes 2/20/23

(1)

I) READING

REIF — PDF ON CANVAS HOME PG.

ch. 9 — QUANTUM IDEAL GAS ~~es~~ SYSTEMS

(1) photons in a black cavity

(2) intuition ~~Electr~~ E & M

(3) statistical model

(2) conduction e's in metals

(2) physical

(3) Diatomic

~~Q~~ $Q = Q_{trans} \cdot Q_{rot} \cdot Q_{vibn} \cdot Q_{elect}$

II) All Thermo connected

to partition fn:

0) ~~system~~ ensemble of replica system = N Ideal gas ptcls (photons, e's, molecules, ...)

a) Z :

b) $Z = \sum_{R} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \dots)}$

solve stationary Q S.E.

$+ \epsilon_1 =$ 1st energy single ptcl Q

$\epsilon_2 =$ 2nd " " energy ptcl

⊛ The system = N single, non-coupled (⇒ interparticle forces weak) ptcls (in a box)

⊛ n_1 = no. of molecules in Q state 1 (ϵ_1) single ptcl.

er

(3)

(+) For example, for ~~multi atom~~ multi atom molecule

$\epsilon_j \Leftarrow \epsilon_{\text{mole}}$

j^{th} single mole Q #N

$= \epsilon^{(j)}_{trans} + \epsilon^{(j)}_{rot} + \epsilon^{(j)}_{vib} + \epsilon^{(j)}_{electron}$

(+) R = "distbn (set)" of $(n_1, n_2 \ldots \ldots)$

where for fermions

$$\boxed{n_1 = 0 \text{ or } 1}$$

And ~~for~~ bosons (e.g. photons)

$$\boxed{n_1 = 1, 2, 3 \text{ or and integer up to } N}$$

~~And~~ plus sum of n's must $= N$

$$\boxed{\sum_{j=1} n_j = N}$$

III) Hill shows that

$$Z = \sum_{R} e^{-B(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

$$Z \underset{\text{ALWAYS Be EXP'd as}}{\overset{\text{CON}}{=}} \left(\sum_{n_1=0}^{\infty} e^{-Bn_1\epsilon_1}\right) \cdot \left(\sum_{n_2=0}^{\infty} e^{-Bn_2\epsilon_2}\right) \cdot$$

(Geometric series)

LAST

$$Z = \left[\frac{1}{(1 - e^{-B\epsilon_1})}\right] \cdot \left[\frac{1}{1 - e^{-B\epsilon_2}}\right]$$

$\ln[(1-e^{-B\epsilon_1})]$

VERY LAST

$$\ln Z = \{\ln(1) - \ln(1 - e^{-B\epsilon_1})\}$$

$$\boxed{\ln Z = -\sum_{j=1} \ln(1 - e^{-B\epsilon_j})} \times$$

(5)

ASIDE: signif of
Z or Q and
how gotten

1) Given Z all macro
thermo h, u, c_v, c_p

$\Rightarrow$

2) ~~Gibbs~~ to get Z
or we have
to solve S, E
stationary
for our system
dynamics

⑥

IV) Derive: 2nd Bridge reln

MACROSCOPIC thermo

Microscopic dynamics

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

$$\boxed{Q = \sum_{j=1} e^{-\beta E_j}}$$

E_j = j^{th} QUANTUM energy for a system of N [coupled (liq or solid) or uncoupled (gas)] ptcls

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

b) $\boxed{dA = dU - T\,dS - S\,dT}$ (7.0)

c) Fund thermo reln (involves dU):

$$(7.1) \quad \boxed{dU \overset{dq}{=} T\,dS - P\,d\forall + \mu\,dN}$$

⊕ implicit defn for S

d) (7.1) ⊕ (9.0):

$$(7.2) \quad \boxed{dA = -P\,d\forall + \mu\,dN - S\,dT}$$

⊕ $(\forall, N, T)$ NAT'L VBLS A

⊕ ∴ $P = \left.\frac{\partial A}{\partial \forall}\right|_{N,T}$

$$\mu = \left.\frac{\partial A}{\partial N}\right|_{\forall,T}$$

$$\boxed{-S = \left.\frac{\partial A}{\partial T}\right|_{N,\forall}}$$

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e) PAIMRIA:

i) $\left(\frac{\partial(A/T)}{\partial(1/T)}\right)\Big|_{N,V} = A - T\left(\frac{\partial A}{\partial T}\right)\Big|_{N,V}$

ii) $U =$

iii) $U = -\frac{\partial \ln Q}{\partial \beta}\Big|_{N,V}$ Last time

$\boxed{1)}$ a) ~~∂ ∂x~~ $x = 1/T$

b) $\frac{\partial}{\partial x}(xA)\Big|_{N,V} = A + x\frac{\partial A}{\partial x}\Big|_{N,V}$ $(1/T)$

c) $\frac{\partial A}{\partial x}\Big|_{N,V} = \frac{\partial A}{\partial T}\Big|_{N,V} \cdot \frac{dT}{dx}$ $(1/x)$ $\left(-1/x^2\right) = T^2$

$= k\frac{1}{x_i}$

[iii] a) $U \equiv A + TS$

b) $= A + T\left(-\frac{\partial A}{\partial T}\right)\Big|_{N,V}$

[iii] a) $U = -\frac{\partial}{\partial \beta} \ln Q \Big|_{N,V}$

b) $= -\frac{\partial}{\partial \beta} \ln \left(\sum_{j=1}^{U} e^{-\beta E_j} \right)$

c) $= -\underbrace{\frac{1}{\sum_j e^{-\beta E_j}}}_{Q} \sum_{j=1} \left(\frac{\partial}{\partial \beta} e^{-\beta E_j} \right)$

$= \frac{1}{Q} \sum_j E_j e^{-\beta E_j}$

$= \sum_{j=} E_j P(E_j) = \bar{E}$ ||| ensemble avg energy of ensemble replica N-ptcl sys

$$\boxed{P(E_j) = \frac{e^{-\beta E_j}}{Q}}$$

$\therefore \boxed{\bar{E} = \langle E \rangle \Leftrightarrow U}$