QUANTUM IDEAL GASES

{ uses: T dep. of semiconductors ...

BACKGROUND INFO

CHEMICAL POTENTIAL (8.7)

- HAVE >1 TYPES OF MOLECULES : N_i = # TYPE i
- N_i'S CAN CHANGE!
  - ex CHEMICAL REACTIONS
  - DIFFUSION
  - PHOTONS: CAN BE CREATED / ABSORBED

Ω (& S) DEP. ON N_i !

$$S = S(E, V, N_i)$$

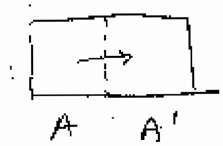
$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{E,V,\underset{\text{OTHER } N_{j\neq i}}{N}} dN_i$$

DEFINE
$$\boxed{\mu_i \equiv -\frac{1}{\beta}\left(\frac{\partial \ln \Omega}{\partial N_i}\right)_{E,V,N} = -T\left(\frac{\partial S}{\partial N_i}\right)_{E,V,N}}$$
{ expect $\mu < 0$

"CHEMICAL POT. PER MOLECULE" FOR TYPE i

~ RATE AT WHICH # AVAIL STATES CHGS AS ADD PARTICLES

IN EQUIL: (ex GAS w/ PERMEABLE WALL, 2 CHEMICALS --)



$$\boxed{\mu_i = \mu_i'}$$ FOR EACH i

should think about this more; time for one species how does it work for 2 or more chemicals in contact?

ALSO: RECALL $T\,dS = đQ = dE + p\,dV$

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}$$

$$\Rightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum_i \frac{\mu_i}{T} dN_i$$

$$\Rightarrow dE = T\,dS - p\,dV + \sum_i \mu_i\, dN_i$$

$$\Rightarrow \boxed{\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N}}$$

~ CHG IN AVE ENERGY DUE TO ADDITION OF EACH MOLECULE OF TYPE i (S FIXED)

(negative: need to drop E to keep S fixed)

ALSO

$$dF = d(E - TS) = -S\,dT - p\,dV + \sum_i \mu_i\, dN_i$$

$$\boxed{\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N}}$$

$$\left\{ \begin{array}{l} F = -kT \ln Z \\ \Rightarrow \mu_i = -kT\left(\dfrac{\partial \ln Z}{\partial N_i}\right)_{T,V,N} \end{array} \right.$$

$$dG = d(E - TS + pV) = -S\,dT + V\,dp + \sum \mu\, dN$$

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N}}$$

GRAND CANONICAL ENS:

RES.

$$E^{(0)} = E + E' \qquad A' \gg A$$
$$N^{(0)} = N + N'$$

- ASSUME A CAN BE SEPARATE FROM A' (AS BEFORE)
- ALLOW N TO VARY (1 TYPE OF MOLECULE)

$$P_r \propto \Omega'(E^{(0)} - E_r,\ N^{(0)} - N_r)$$

PROB. OF BEING IN SPECIFIC STATE r

$$\ln \Omega' \sim \ln \Omega'(E^{(0)}, N^{(0)}) - \underbrace{\frac{\partial \ln \Omega'}{\partial E}}_{\beta} E_r - \underbrace{\frac{\partial \ln \Omega'}{\partial N}}_{-\beta\mu} N_r$$

β, μ FIXED BY RES.

$$\Rightarrow \boxed{P_r \propto e^{-\beta E_r + \beta \mu N_r}}$$

(IF > 1 MOLECULE, $\mu N_r \to \sum_i \mu_i N_{ri}$

ESTIMATES FOR μ : (1 TYPE) (MINE)

HIGH-T / CLASSICAL

$$\mu = -kT \left(\frac{\partial \ln \Omega}{\partial N} \right)_{E,V}$$

- E FIXED, BUT LOTS AVAILABLE
- NEW PARTICLE CAN BE IN ANY 1-PART STATE

$$\Omega_{TOT} \sim \Omega(\text{NEW PART}) \cdot \Omega_0$$

$$\frac{\partial \ln \Omega}{\partial N} \sim \ln \Omega(1 \text{ PART})$$

$$\boxed{\mu \sim -kT \ln \Omega(1 \text{ PART})}$$

skip { CHECK:

$$\mu = \frac{\partial F}{\partial N} = -kT \frac{\partial \ln Z}{\partial N} = -kT \ln \left[\underbrace{\Sigma_r e^{-\beta E_r}} \right]$$

β SMALL $\sim \Sigma_r \cdot 1$

$\sim \Omega_r$

$\sim -kT \ln \Omega_r$ ✓

LOW T -

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} \sim \text{CHG IN } E \text{ TO KEEP } S \text{ FIXED}$$

BOSONS

GND ST: NEED TO ADD ϵ_0 FOR NEW PART JUST SO $\Omega \sim 1$ $(S \sim 0)$

$$\Rightarrow \boxed{\mu \sim +\epsilon_0}$$

FERMIONS

NEED TO ADD ϵ_F FOR NEW PART SO $\Omega \sim 1$

$$\Rightarrow \boxed{\mu \sim +\epsilon_F}$$

QUANTUM IDEAL GAS (WILL RESTRICT TO 1 PART. TYPE)

- NEED FOR LOW T / HIGH DENSITY ⇒
  SYMM. OR ANTISYMM OF WFN IMPORTANT

- WILL STILL IGNORE PARTICLE INTERACTIONS ⇒
  STATE IS GIVEN BY PROD. OF 1-PART. STATES

n_r = # PARTICLES IN (1-PART) STATE r w/ ENERGY ϵ_r

BOSONS (OBEY BOSE-EINSTEIN STATISTICS)
- INTEGER SPIN
- $n_r = 0, 1, 2, \ldots$

FERMIONS (FERMI-DIRAC STATISTICS)
- $\frac{1}{2}$ - INT. SPIN
- $n_r = 0, 1$

QM: PARTICLES ARE IDENTICAL
[n_r] COMPLETELY SPECIFY STATE R (IF KNOW 1-P STATES r)

WILL COMPUTE:

(A) $\overline{n_r}$

(B) Z (INCLUDES (A)) } haven't gotten to yet

USES:

- PLANCK BLACK BODY DISTR: PHOTONS AT T IN CAVITY IN EQUIL

: EQUIL ⇒ BB EMITS AT SAME RATE AS ABSORBS
BLACK ⇒ ABSORBS ALL LT. INCIDENT
⇒ EMISS. SPECTRUM OF BB ⇔ E DISTR. OF LT. IN BOX AT T

IG: GOOD APPROX ⇒ γ's INTERACT VERY WEAKLY

- CONDUCTION e^-'s IN METAL / SEMICOND. AS FN OF T

(A) FIND $\overline{n_r}$:

HAVE $\quad E_R = \sum_r n_r \epsilon_r \qquad$ (IG)

IF # FIXED

$$N = \sum_r n_r$$

{ FOR $m \neq 0$, TRUE UNLESS $kT \sim 2mc^2$
{ FOR γ, NOT TRUE

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta \sum_r n_r \epsilon_r}$$

$\sum_R$: SUM OVER TOTAL STATES

$\equiv$ SUM OVER SETS $[n_r] \ni N = \sum_r n_r$

$$\overline{n_s} = \frac{\sum_R n_s e^{-\beta \sum n_r \epsilon_r}}{\sum_R e^{-\beta \sum n_r \epsilon_r}} = \frac{1}{Z}\left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\right) Z$$

$$\boxed{\overline{n_s} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_s}}$$

ALSO, (AS FOR $\Delta^* E$)

$$\boxed{\left(\Delta^* n_s\right)^2 \equiv \overline{(\Delta n_s)^2} = \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial \epsilon_s^2} = -\frac{1}{\beta}\frac{\partial \overline{n_s}}{\partial \epsilon_s}}$$

(A) $\overline{n_s}$:

USING CAN. DISTR

(1) PHOTONS (m = 0 BOSONS)

- IN BOX AT T : NO RESTRICTION ON N

$$\overline{n_s} = \frac{\sum_R n_s e^{-\beta E_R}}{\sum_R e^{-\beta E_R}} = \frac{\sum_{n_1, n_2 \ldots} n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}}{\sum e^{-\beta(\;''\;)}}$$

CAN PULL OUT S - TERMS

$$= \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s} \sum_{n_1, n_2 \cdot}^{(s)} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}}{\sum_{n_s} e^{-\beta n_s \epsilon_s} \sum^{(s)} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}}$$

$$= \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln\left(\sum_{n_s} e^{-\beta n_s \epsilon_s}\right)$$

$$\sum_{n_s} e^{-\beta n_s \epsilon_s} = \sum \left(e^{-\beta \epsilon_s}\right)^{n_s} = \frac{1}{1 - e^{-\beta \epsilon_s}}$$

$$\Rightarrow \quad \overline{n_s} = \cancel{+} \frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln\left(1 - e^{-\beta \epsilon_s}\right)^{\cancel{-1}} = \frac{e^{-\beta \epsilon_s}}{1 - e^{-\beta \epsilon_s}}$$

$$\boxed{\overline{n_s} = \frac{1}{e^{\beta \epsilon_s} - 1}}$$ PLANCK DISTRIBUTION

PHOTONS: CAN USE $\omega = 2\pi\nu$ (FREQ.) OR $k = \frac{2\pi}{\lambda}$ FOR S:
$(\because \lambda\nu = c = \omega/k)$

$$\epsilon(\omega) = \hbar\omega = h\nu = \frac{hc}{\lambda}$$

$$\overline{n(\omega)} = \frac{1}{e^{\hbar\omega/kT} - 1}$$

(2) FERMIONS $(m \neq 0,\ N \text{ FIXED})$

$$\overline{n_s} = \frac{\sum_{n_1 n_2 \cdots} n_s\, e^{-\beta(n_1\epsilon_1 + \cdots)}}{\sum_{n_1 n_2 \cdots} e^{-\beta(n_1\epsilon_1 + \cdots)}}$$

BUT : $n_i = 0, 1$ ONLY

$\sum_i n_i = N$ FIXED

ex: Z (IN DEN'OM) : DO n_s SUM

$$\sum_{n_1, \cdots n_s = 0, \cdots} e^{-\beta \sum^{(s)} n_i \epsilon_i} + \sum_{n_1, \cdots n_s = 1, \cdots} e^{-\beta\epsilon_s} e^{-\beta \sum^{(s)}_i}$$

DEFINE

$$Z_s(N) \equiv \sum^{(s)}_{n_1, n_2 \cdots} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}$$

ie Z FOR N PARTICLES BUT w/ STATE s NOT ALLOWED

THEN DEN $\Rightarrow$

$$\underbrace{Z_s(N)}_{\text{SINCE } n_s = 0} + e^{-\beta\epsilon_s} \underbrace{Z_s(N-1)}_{n_s = 1}$$

AND

$$\overline{n_s} = \frac{0 + 1 \cdot e^{-\beta\epsilon_s} Z_s(N-1)}{Z_s(N) + e^{-\beta\epsilon_s} Z_s(N-1)}$$

$$= \frac{1}{[Z_s(N)/Z_s(N-1)]\, e^{\beta\epsilon_s} + 1}$$

LARGE SYSTEM: $\Delta N \ll N$

(a) $Z(N)$ INCR. RAPIDLY W/ N $\Rightarrow$ MANY MORE TERMS IN SUM
(RECALL $S = k(\ln Z + \beta \bar{E})$ SO Z GROWS AS Ω)

$$\ln Z_S(N - \Delta N) \approx \ln Z_S(N) - \underbrace{\frac{\partial \ln Z_S}{\partial N}}_{= \alpha_S} \Delta N + \cdots$$

$$Z_S(N - \Delta N) \approx Z_S(N)\, e^{-\alpha_S \Delta N}$$

$$\underbrace{\boxed{Z_S(N) / Z_S(N-1) = e^{\alpha_S}}}_{\Delta N = 1}$$

(b) α_S APPROX INDEP OF S (i.e. WHICH STATE LEFT OUT OF Z)

- PLAUSIBLE: Z INCLUDES MANY STATES
- REIF GIVES JUSTIFICATION

?

- EXPECT: $\ln Z$ (AS $S = \ln \Omega$) EXTENSIVE

$\therefore \ln Z_S \sim \mathcal{O}(N)$

$\alpha_S \equiv \dfrac{\partial \ln Z_S}{\partial N} \sim \mathcal{O}(1)$ (INTENSIVE)

$\dfrac{\partial \alpha_S}{\partial N} \sim \mathcal{O}\left(\dfrac{1}{N}\right)$ $\Rightarrow$ OK FOR N LARGE

$\Rightarrow$ $\alpha_S \approx \alpha \approx \dfrac{\partial \ln Z}{\partial N}$ (Z UNRESTRICTED)

$$\overline{n_S} = \frac{1}{e^{\alpha + \beta \epsilon_S} + 1}$$

CAN FIX α BY

$$\sum_r \overline{n_r} = \sum_r \frac{1}{e^{\alpha + \beta \epsilon_r} + 1} = N$$

(so α depends on T, V (through ϵ_r), N)

ALSO RECALL

$$F = -kT \ln Z$$

$$\Rightarrow \alpha = -\frac{1}{kT}\frac{\partial F}{\partial N} = -\frac{\mu}{kT} = -\beta\mu$$

CHEM. POTENTIAL

$$\Rightarrow \boxed{\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s-\mu)}+1}}$$

FERMI-DIRAC DISTR

NOTE: DEN ≥ 1

$$0 \leq \bar{n}_s \leq 1$$

(3) BOSONS ($m \neq 0$, N FIXED)

- SIMILAR, BUT $n_s = 0, 1, 2, \ldots$

- STILL: $\sum_r n_r = N$

$$\bar{n}_s = \frac{\sum_{n_1, n_2} n_s e^{-\beta(n_1\epsilon_1 + \cdots)}}{\sum e^{-\beta(\quad)}}$$

$$= \frac{0 + e^{-\beta\epsilon_s} Z_s(N-1) + 2e^{-2\beta\epsilon_s} Z_s(N-2) + \cdots}{Z_s(N) + e^{-\beta\epsilon_s} Z_s(N-1) + e^{-2\beta\epsilon_s} Z_s(N-2) + \cdots}$$

SAME APPROX:

$$Z_s(N-\Delta N) \approx Z_s(N) e^{-\alpha_s \Delta N}$$

$$\alpha_s \approx \alpha \approx \frac{\partial \ln Z}{\partial N}$$

$$\bar{n}_s \approx \frac{Z_s(N)\left[0 + e^{-\beta\epsilon_s} e^{-\alpha} + 2 e^{-2\beta\epsilon_s} e^{-2\alpha} + \cdots\right]}{Z_s(N)\left[1 + e^{-\beta\epsilon_s} e^{-\alpha} + e^{-2\beta\epsilon_s} e^{-2\alpha} + \cdots\right]}$$

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-n_s(\alpha+\beta\epsilon_s)}}{\sum_{n_s} e^{-n_s(\alpha+\beta\epsilon_s)}} = \frac{1}{e^{\alpha+\beta\epsilon_s}-1}$$

$$\Rightarrow \boxed{\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s-\mu)}-1}}$$

BOSE-EINSTEIN DISTR

WITH $\sum_s \bar{n}_s = N$ (FIXES μ)

NOTE $\bar{n}_s > 0 \Rightarrow \boxed{\epsilon_s - \mu > 0}$

$\bar{n}_s$ CAN GET LARGE : $\beta(\epsilon_s-\mu) \sim 0^+$

$\bar{n}_s \to \infty$

$\Rightarrow \boxed{\mu < +\epsilon_0}$ GND ST. E

LIMITS: CLASSICAL

FOR COMPARISON – DISTING. PARTICLES

- CAN LABEL PARTICLES $r_1, r_2, \cdots$
- Z INCLUDES SUM OF STATES FOR EACH PARTICLE

$$Z = \sum_{r_1, r_2, \cdots r_N} e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2} + \cdots \epsilon_{r_N})}$$

$$= \left[\sum_r e^{-\beta \epsilon_r} \right]^N$$

$$\boxed{\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = N \cdot \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}}}$$

MAXWELL – BOLTZMANN DISTR.

NOTE:

SAME RESULT WHEN TREAT 1 PARTICLE AS SMALL SYS. IN CONTACT W/ RES (= REST OF SYS)

$$\Rightarrow \quad P_s = \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}}$$

$$\bar{n}_s = N P_s$$

LIMITS

(I) $$\overline{n}_r = \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1}$$

(II) $$\sum_r \overline{n}_r = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} = N \quad \Rightarrow \text{FIXES } \alpha$$

CLASSICAL:

(a) LOW DENSITY $\Rightarrow$ N SMALL

by (II), EACH TERM IN SUM MUST BE SMALL

$$\Rightarrow e^{\alpha+\beta\epsilon_r} \gg 1$$

(b) HIGH T, $\beta \to 0$

– MANY MORE STATES w/ HIGHER ϵ_r CONTRIBUTE

– α MUST INCREASE SO EACH TERM DECREASES
(by II)

$$\Rightarrow e^{\alpha+\beta\epsilon_r} \gg 1$$

$\Rightarrow \overline{n}_r \ll 1$ FOR BOTH CASES

$$\Rightarrow \overline{n}_r \sim e^{-\alpha-\beta\epsilon_r}$$

BY (II)

$$\sum \overline{n}_r = e^{-\alpha} \sum_r e^{-\beta\epsilon_r} = N$$

$$e^{-\alpha} = \frac{N}{\sum_r e^{-\beta\epsilon_r}}$$

$$\overline{n}_r = N \frac{e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}} \quad \Rightarrow \text{MAX-BOLTZ DISTR.}$$

LOW T $\qquad \bar{n}_r = \dfrac{1}{e^{\beta(\epsilon_r-\mu)} \pm 1}$ $\qquad$ + FERM, − BOS

± 1 MAKES LARGE DIFFERENCE:

BOSONS

- EXPECT $\bar{n}_0 \sim N$ (GND STATE)

$\bar{n}_{r\neq 0} \sim 0$

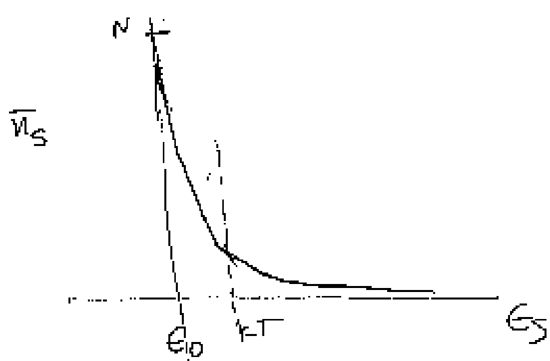
$$\Rightarrow \quad \bar{n}_0 = \frac{1}{e^{\beta(\epsilon_0-\mu)} - 1} \sim N$$

LARGE IF $\beta(\epsilon_0-\mu) \sim 0$

$$\sim \frac{1}{\beta(\epsilon_0-\mu)} = \frac{kT}{\epsilon_0-\mu} \sim N$$

$$\Rightarrow \boxed{\mu \sim \epsilon_0 - \frac{kT}{N}}$$

$\bar{n}_s$ SMALL WHEN $\dfrac{\epsilon_s-\mu}{kT} \sim \dfrac{\epsilon_s-\epsilon_0}{kT} \sim 1$



$\epsilon_s - \epsilon_0 \gtrsim kT$

(USUAL EST.)

FERMIONS

— EXPECT $\bar{n}_S \sim 1$ FOR $\epsilon_S \leq \epsilon_F$

"FERMI ENERGY"

LAST FILLED E LEVEL

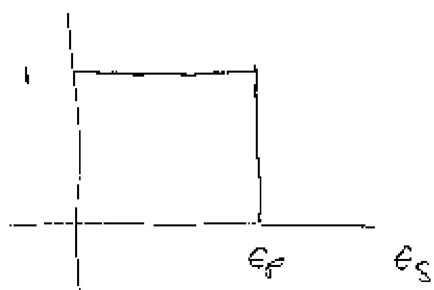
$\bar{n}_S \sim 0$ FOR $\epsilon_S > \epsilon_F$

NEED $e^{\frac{(\epsilon_S - \mu)}{kT}} \underset{T \to 0}{\sim} \infty$ FOR $\epsilon_S > \epsilon_F$

~ 0 FOR $\epsilon_S < \epsilon_F$

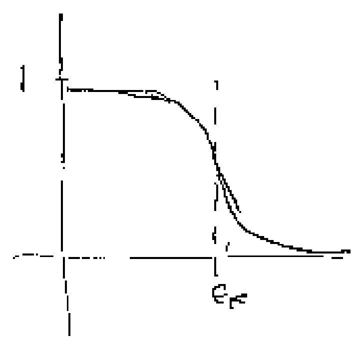
$$\Rightarrow \boxed{\mu \approx \epsilon_F}$$

$$\bar{n}_S \cong \frac{1}{e^{(\epsilon_S - \epsilon_F)/kT} + 1}$$



$T \sim 0$

$\Rightarrow$ STEP FN



$T \gtrsim 0$

$\sim e^{-\frac{(\epsilon_S - \epsilon_F)}{kT}}$

8.9.1 or
8.14

ALTERNATE DERIVATION FOR $\bar{n}_s$:

$$P_r \propto e^{-\beta E_r + \beta \mu N_r}$$ GRAND CAN. ENS

- CAN'T TAKE A TO BE SINGLE PARTICLE (AS CLASSICALLY)
- CAN TAKE A TO BE PARTICULAR STATE & ASK PROB FOR n_r IN STATE r ;

  A' THEN ALL STATES $\neq r$

$$p(n_r) \propto e^{-\beta n_r \epsilon_r + \beta \mu_r n_r} = e^{-\beta(\epsilon_r - \mu_r) n_r}$$

$$\mu_r = \frac{-1}{\beta}\left(\frac{\partial \ln \Omega^{(r)}}{\partial N}\right)_{E,V}$$. $\Omega^{(r)}$ = # STATES FOR $N - n_r$ PARTICLES NOT IN STATE r

$$\bar{n}_r = \frac{\sum_{n_r} n_r e^{-\beta(\epsilon_r - \mu_r) n_r}}{\sum_{n_r} e^{-\beta(\epsilon_r - \mu_r) n_r}}$$

FERMIONS: $n_r = 0, 1$

$$\bar{n}_r = \frac{0 + 1 \cdot e^{-\beta(\epsilon_r - \mu_r)}}{1 + e^{-\beta(\epsilon_r - \mu_r)}} = \frac{1}{e^{\beta(\epsilon_r - \mu_r)} + 1}$$

(BOSONS— SAME WAY)

CONSTRAINT: $$\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu_r)} + 1} = N.$$

- IF GET ALL μ_r RIGHT → AUTOMATIC
- APPROX: $\mu_r = \mu$ ⇒ INDEP. OF r

  ⇒ FIX VALUE BY CONSTR