CH 6 SYSTEMS AT KNOWN T OR $\bar{E}$

BACK TO STAT. METHODS (from micro description)
(will put bars back on macro qtys)

SPECIFIC CASES (IN EQUIL.)

(1) ISOLATED: ENERGY FIXED BETW. E & $E+\delta E$

ALL ACCESSIBLE STATES EQUALLY LIKELY IN ENSEMBLE

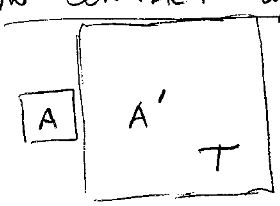
$\Rightarrow$ P_r = PROB. SYS. IN MICRO STATE r

$= C$ FOR $E < E_r < E+\delta E$ {only ever need relative probs;

$= 0$ IF NOT

"MICROCANONICAL ENSEMBLE" ($\underbrace{\text{MICRO}}_{\equiv \text{rule}}$) } most general - can always isolate system & step back far enough

(2) IN CONTACT W/ HEAT RES. ($\equiv T$ HELD FIXED (ie KNOWN))
any time sys. in equil w/ much larger system



(COMMON SITUATION; TURNS OUT TO BE MORE GENERALLY USEFUL THAN MIGHT GUESS)

$A^{(0)} = A + A'$ (ISOLATED)

STUDY A: (ie study part of case (1))

WANT PROB P_r THAT A IN PARTIC. STATE r, BUT A' IN ANY STATE

$$E^{(0)} = E_r + E' \quad \text{(FIXED)}$$

FROM FUND. POST: (ie (1))

$$P_r = C'\Omega'(E') = C'\Omega'(E^{(0)} - E_r)$$ {how many ways can A be in state r?}

(ie prop. to # states avail to A' if take out E_r; don't need to count states for A since I'm asking about a partic. state r)

skip { AS ALWAYS $\sum_r P_r = 1$ }

32 (A?)

USE $E^{(0)} >>> E_r$:

$\Omega'(E')$ GROWS QUICKLY w/ E'

$$\ln \Omega'(E^{(0)} - E_r) \approx \ln \Omega'(E^{(0)}) - \underbrace{\left[\frac{\partial \ln \Omega'}{\partial E'}\right]_{E' \approx E^{(0)}}}_{= \beta = \frac{1}{kT}} E_r + \cdots$$

FOR RESERVOIR AT $E^{(0)}$

skip { (expand in $E_r \sim 0$ ie $E_r / E^{(0)} \sim f_A / f_{A'}$)

$\Rightarrow \beta \sim$ CONST (IND. OF E_r) (this is WHAT WE MEAN BY RES: T DOESN'T CHG w/ E_r)

{note: $T \sim$ const as A pulls out more E but $\Omega'(E^{(0)} - E_r)$ decreases rapidly:}

(can use $\Omega \sim E^f$ to see reasonable from T related to $\ln \Omega$, not Ω)

$$\ln \Omega'(E^{(0)} - E_r) \approx \ln \Omega'(E^{(0)}) - \beta E_r$$

$$\Omega'(E^{(0)} - E_r) \approx \Omega'(E^{(0)}) e^{-\beta E_r}$$

$$\Rightarrow \quad P_r = C e^{-\beta E_r} = C e^{-E_r/kT}$$

FOR RES. (FIXED)

NORM: $\sum_r P_r = 1 = C \sum_r e^{-\beta E_r}$

$$\Rightarrow \boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}$$

prob. A is in r just depends on # states still access. to A'; as E_r incr., these drop exponentially; How fast? depends on β for res:

4/22/04

Large β = small T $\Rightarrow$ drops very fast
$\Rightarrow$ P very small unless A in state w/ min E_r

Small β = large T $\Rightarrow$ drops slowly w/ E_r
$\Rightarrow$ P ~ const for all states with $E_r \ll kT$, small for $E_r \gtrsim kT$

** Note: $e^{-E_r/kT}$ starts to drop quickly w/ E_r for $E_r \gtrsim kT$

"CANONICAL ENSEMBLE" $\equiv$ ENS. IN CONTACT w/ RES. AT T

DISTRIBUTION $P_r \equiv$ "CANONICAL DISTR." OR "BOLTZ. DISTR"

$e^{-\beta E_r} \equiv$ BOLTZMANN FACTOR

(again, $P_r \neq$ const as in micro. distr. because sys. is in contact w/ res $\Rightarrow$ incr. E_r robs avail states from res.)

{ FOR ME:
WHY CAN A AFFECT Ω' BUT NOT T?
CAN USE $\Omega \sim E^f$ to EST. EFFECT $\Rightarrow$ leave as exercise.

skip

$$\Omega^0 = \Omega'(E^0 - E_r)\underbrace{\Omega(E_r)}_{=1 \text{ since asking for partic. state}}$$

$$\sim (E^0 - E_r)^f = (E^0)^f (1 - E_r/E^0)^f$$

$$\ln \Omega' = f \ln E^0 + f \ln(1 - E_r/E^0)$$

$$\sim f \ln E' - f(E_r/E^0) + \mathcal{O}(E_r/E^0)$$

$$\beta = \frac{\partial \ln \Omega'}{\partial E} \simeq \frac{f}{E} \simeq \frac{f}{E^0 - E_r} \sim \frac{f}{E^0}\left(1 + \frac{E_r}{E^0} + \cdots\right)$$

$$\Rightarrow \Omega \sim C e^{[\beta E_r + \mathcal{O}(E_r/E^0)]}$$

$\Omega \sim 0$ when this can contribute }

COMPLETELY DESCRIBES A; ~~ex~~
COMPUTE AVES FOR A:

P_r = PROB IN STATE r

LET y BE SOME QTY w/ VALUE y_r IN STATE r

$$\boxed{\bar{y} = \sum_r P_r y_r = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}}}$$

skip

RELATED PROB:

$P(E) \equiv$ PROB A HAS E TO $E + \delta E$

— LESS SPECIFIC BUT USEFUL

$$P(E) = \sum_{r \atop (E < E_r < E + \delta E)} C e^{-\beta E_r}$$

IF $\delta E \ll E_r$

$$\approx C e^{-\beta E} \underbrace{\sum_{r \atop (E \ldots \delta E)} 1}_{\equiv \Omega(E) \text{ FOR } A}$$

$$\Rightarrow \boxed{P(E) = C\,\Omega(E)\, e^{-\beta E}}$$

ACCTS. FOR RES

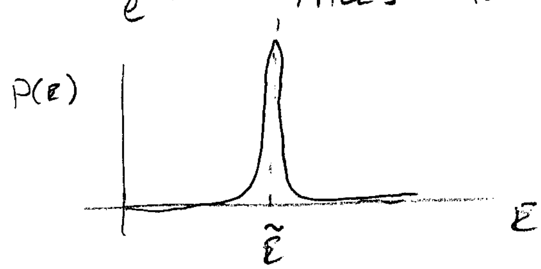
STATES IN A AT E

CONNECT TO PREVIOUS PICTURE:

NOTE: P_r HOLDS FOR ANY SYS A IF $A \ll A'$
(EVEN SINGLE ATOM)

BUT IF A MACROSCOPIC:

$\Omega(E)$ GROWS EXPON. w/ E
$e^{-\beta E}$ FALLS " "

$\Rightarrow$ 

AS BEFORE

(larger A is, more sharply peaked)

ex 1 PARAMAGNETISM IN SPIN SYS

$\Rightarrow$ MAGN. $\vec{M}$ INDUCED BY EXT. $\vec{H}$

SYS : N SPIN-$\frac{1}{2}$ ATOMS IN SOLID (FROM UNPAIRED e^-)

EXT $\vec{H} = H\hat{z}$

MOMENT (EACH ATOM) ALONG $\vec{H}$: $\mu_z = \pm\mu$

ISOLATED w/ FIXED E, T

FIND $\bar{\mu}_z$ FOR SINGLE ATOM

TRICK 1: ATOM LOCATED AT PARTIC. SITE

$\Rightarrow$ CAN TREAT AS ISOLATED SYS FROM REST

MAIN INT. IS w/ $\vec{H}$ (ie IGNORE INTS w/ OTHER ATOMS)

$\Rightarrow$ $E^{(0)} = E_{ATOM} + E_{REST}$

$N \gg 1$

$\Rightarrow$ $E_{REST} \gg E_{ATOM}$ $\left\} \begin{array}{l} \text{ATOM} = A \\ \text{REST} = A' \quad \text{(RESERVOIR)} \end{array} \right.$

FOR A: SINGLE ATOM

	STATE r	μ_z	E_r
(MAGN MOM)	$\uparrow$	$+\mu$	$-\mu H$
	$\downarrow$	$-\mu$	$+\mu H$

$$P_\uparrow = C e^{-\beta E_\uparrow} = C e^{+\beta\mu H}$$

$$P_\downarrow = C e^{-\beta E_\downarrow} = C e^{-\beta\mu H}$$

$$P_\uparrow + P_\downarrow = 1 \Rightarrow C = \frac{1}{e^{\beta\mu H} + e^{-\beta\mu H}}$$

$$\bar{\mu}_z(T,H) = \Sigma_r P_r \mu_r = P_\uparrow \cdot (\mu) + P_\downarrow(-\mu) = \mu \underbrace{\left[\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{'' + ''}\right]}_{\tanh(\beta\mu H)}$$

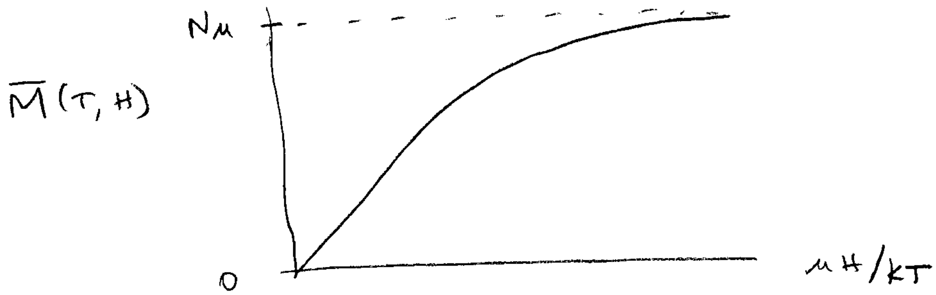
$$\boxed{\bar{\mu}_z(T,H) = \mu \tanh\left(\mu H/kT\right)} \quad 1 \text{ ATOM}$$

11/27/02

TRICK 2: ALL ATOMS SAME

MAGNETIZATION $\boxed{\bar{M}(T,H) = N\bar{\mu}_z(T,H) = N\mu \tanh(\mu H/kT)}$

(recall: worked hard to get this in HW 3.2) NOTE: EOS FOR M, H, T



LOW T: $\mu H/kT \to \infty$ $\quad \bar{M} \to N\mu$ $\left.\right\}$ GND STATE ALL LINE UP w/ $\vec{H}$

HIGH T: $\mu H/kT$ SMALL

$$\tanh(\mu H/kT) \sim \frac{\mu H}{kT} + \cdots$$

$$\bar{M} \sim \left(\frac{N\mu^2}{kT}\right) H \qquad (\propto H)$$

PER VOL: $M_0 \equiv M/V \qquad N_0 \equiv N/V$

$$\bar{M}_0 \sim \underbrace{\left(\frac{N_0\mu^2}{kT}\right)}_{\equiv \chi(T)} H$$

$\equiv \chi(T) =$ MAGNETIC SUSCEPTIBILITY

$\sim$ SIZE OF MAGN. RESPONSE TO $\vec{H}$

NOTE: BOOTSTRAPPED TO ANSWER

(1) 1 ATOM IS A, REST IS A′ (RES)

→ ONLY NEED A′ >> A & ABILITY TO TRANSF Q (DON'T HAVE TO BE PHYS. SEPARATE)

→ GIVES P_r (1 ATOM)

(2) ALL ATOMS SAME → P_r SAME FOR ALL

LOW T: ONE SPIN IN WRONG DIR COSTS LOTS OF E FOR REST → SEVERELY LIMITS Ω

HIGH T: LOTS OF E AVAIL, SPIN FLIP HAS SMALL EFFECT → $P_\downarrow \sim P_\uparrow \sim \frac{1}{2}$

DIVIDING LINE: $kT \sim \Delta E \sim \mu H$

ex 2 IDEAL GAS AT KNOWN T

- DIFFUSE: CAN ISOLATE 1 MOLECULE ≡ SYS A
  (IF NOT - SEE QM EFFECTS LIKE PAULI EXCL. PRINC.
  (ie IDENT. PARTS.) ⇒ CAN'T ISOLATE 1
  ⇒ MORE SUBTLE REASONING)

- IGNORE INTS.

$$E = \frac{p^2}{2m}$$

- CONTINUOUS PHASE SPACE (FOR 1 PARTICLE)
  ⇒ STATE r ⟺ LOCATION IN $\vec{r}$ & $\vec{p}$
  ⇒ USE CELLS OF VOL $d^3r\, d^3p$
  ⇒ ASSIGN BOLTZMANN FACTOR TO EACH CELL

GEN'L RESULT

$$P(\vec{r},\vec{p}) \equiv \mathcal{P}(\vec{r},\vec{p})\, d^3r\, d^3p = C\, d^3r\, d^3p\, e^{-\beta(p^2/2m)}$$

(ie PROB OF BEING IN PARTIC. CELL $\propto e^{-\beta E_R}$ E FOR THAT CELL)

- NORM: $\int d^3r\, d^3p\, \mathcal{P}(\vec{r},\vec{p}) = 1$

⇒ CAN USE RULES FOR PROB TO APPLY TO MORE SPECIFIC CASES:
- PROB. IN FINITE REGION OF $\vec{r}$ & $\vec{p}$?
  ⇒ INTEGRAL OVER ALLOWED "

- PROB AT $\vec{p}$ BUT ANY $\vec{r}$

$$P(\vec{p}) \equiv \mathcal{P}(\vec{p})\, d^3p = \Big[\int d^3r\, \underbrace{\mathcal{P}(\vec{r},\vec{p})}_{\text{IG: IND. OF } \vec{r}}\Big]\, d^3p$$

$$= C\, d^3p\, e^{-\beta p^2/2m}$$

note: C just means norm const

- IN TERMS OF $\vec{v}$: CHG VARS:

$$\mathcal{P}(\vec{v})\, d^3v = C\, e^{-\beta(mv^2/2)}\, d^3v$$

- IN TERMS OF SPEED v (NOT $\vec{v}$): ALLOW ANY θ, φ

$$d^3v = v^2 dv \sin\theta \, d\theta \, d\varphi$$

$$P(v)\,dv = \left[\int \sin\theta \, d\theta \, d\varphi\right] v^2 dv \, e^{-\beta m v^2/2}$$

$$= c \, dv \, v^2 e^{-\beta m v^2/2}$$

"MAXWELL DISTR." (NOTE 0 PROB OF $v=0$ $\Rightarrow$ ZERO VOL. IN PHASE SP.)

IG w/ GRAVITY: (FIXED T)

$$E = p^2/2m + mgz$$

$$P(\vec{r}, \vec{p})\, d^3r\, d^3p = C\, d^3r\, d^3p\, e^{-\beta\left[\frac{p^2}{2m} + mgz\right]}$$

NOTE: IT FACTORS $\left[P(\vec{r})\,d^3r\right]\left[P(\vec{p})\,d^3p\right]$ $\Rightarrow$ INDEP. PROBS.

SPECIAL CASES:

ANY $\vec{r}$: $P(\vec{p})\,d^3p = \left[\int d^3r \, P(\vec{r},\vec{p})\right] d^3p$

$$= c\left[\int d^3r\, e^{-\beta mgz}\right] d^3p\, e^{-\beta p^2/2m}$$

$$= c\, d^3p\, e^{-\beta p^2/2m}$$ SAME AS w/ NO GRAV

NOTE: CAN BOOTSTRAP THIS TO GIVE DENSITY OF MOLS. VS $\vec{r}$: $\rho(\vec{r}) = N P(\vec{r})$

ANY $\vec{p}$: $P(\vec{r})\,d^3r = \left[\int d^3p\, P(\vec{r},\vec{p})\right] d^3r$

$$= c\left[\int d^3p\, e^{-\beta p^2/2m}\right] e^{-\beta mgz}\, d^3r$$

$$= c\, d^3r\, e^{-\beta mgz}$$

ANY x, y: $P(z)\,dz = \left[\int dx\,dy\, P(\vec{r})\right] dz = c\,dz\,e^{-\beta mgz}$

$$= c\,dz\,e^{-mgz/kT}$$ (cf HW 5.25)

APPLY: AVE HT: (FROM GND)

$$\bar{z} = \frac{\int_0^\infty dz\, e^{-mgz/kT}\, z}{\int_0^\infty dz\, e^{-mgz/kT}}$$

$$= kT/mg$$

AVE p^2:

$$\overline{p^2} = \frac{\int d^3p\, e^{-\frac{p^2}{2mkT}}\, p^2}{\int \text{''} \quad \text{''}}$$

$$= mkT$$

(will discuss later)

skip: just mention result

CAN APPLY TO BRICK IN ROOM IN THERMAL CONTACT w/ AIR AT TEMP T

- IGNORE POTENTIAL BETW. BRICK & MOLS:

$$E = \frac{p^2}{2M} + Mgz$$

⇒ SAME AS FOR MOL. EXCEPT M NOT m

⇒ PROB OF FINDING BRICK AT HT z w/ MOM $\vec{p}$:

$$\mathcal{P}(z, \vec{p}) \propto e^{-p^2/2MkT} e^{-Mgz/kT}$$

NOTE:

- $kT \sim E$ PER MOLECULE ~ ATOMIC SIZE E'S
- $\mathcal{P}$ SMALL WHEN $Mgz > kT$
  ⇒ RARE FOR Mgz ~ MACROSCOPIC
- EQUIV TO PROB 5.25

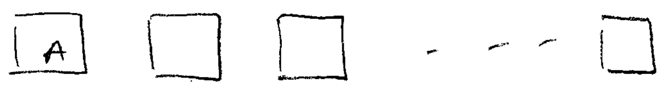
(3) ISOLATED SYS A w/ $\bar{E}$ KNOWN (BUT E NOT FIXED)

$\Rightarrow$ FOR A w/ $\bar{E}$ WHAT IS P_r FOR BEING IN MICROST r?

(NOTE: KNOWING $\bar{E}$ MORE COMMON THAN EXACT E; E NOT EXACT ONCE IN CONTACT w/ OTHER SYS)

TO SEE BOLTZMANN DISTR. APPLIES (SUBTLE):

1. $\bar{E}$ KNOWN $\Rightarrow$ IMPLIES AVERAGE ENS.



$\rightarrow$ a COPIES (LARGE)

$a_r \equiv$ # SYS IN r

$P_r = \frac{a_r}{a} \Rightarrow \bar{E} = \frac{1}{a}\sum_r a_r E_r$ KNOWN

subtle: will need to work backwards from $\bar{E}$ to get P_r

28 → 1/10

→ 4/27/04

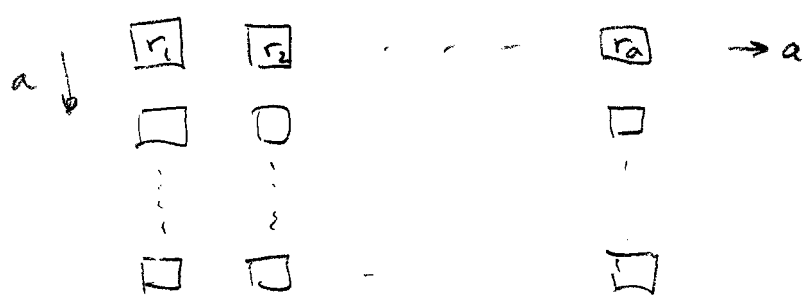
$\Rightarrow \sum a_r E_r = a\bar{E} = E_{TOT}$ IN ENS $\Rightarrow$ FIXED

41 28

2. DIFFICULT TO APPLY FUND. POST w/ OVER-ALL CONSTRAINT

- USUAL CONSTR. APPLIES TO EACH SYS: EVERY ALLOWED r APPEARS IN ENS. IN SAME #
- IF INCL. ALL " " HERE (INCL. r w/ DIFF E_r's) WON'T IN GEN'L SATISFY $E_{TOT} = a\bar{E}$

CAN APPLY TO ENS. OF ENSEMBLES:



$\Rightarrow$ POSTULATE: EACH ALLOWED ENS. OF MICROSTATES w/ $\sum_{i=1}^{a} E_{r_i} = a\bar{E}$ APPEARS EQ. # TIMES

(ie satisfies constr. on the ens.)

27 ⇒

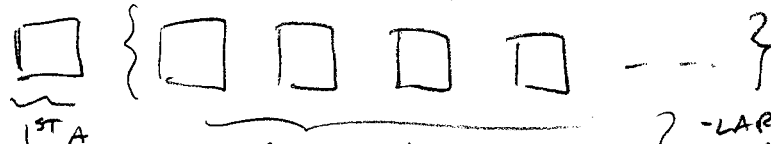
⇒ CAN USE 1ST COLMN TO DETERMINE

$$P_r = a_r / a$$

FOR SINGLE SYS. (OR ANY OTHER COLMN)

3. TRICK: MATH. IDENTICAL TO  w/ FIXED $E_{TOT} \equiv a\bar{E}$

A RES.

w/ 

1ST A

$(a-1)$ A's ≡ RES. } - LARGE (EVEN IF A SMALL)
- SHARES TOT, $a\bar{E} \gg \mathcal{E}_r$ w/ A

$\mathcal{E}_r$ $\quad E_{TOT} - \mathcal{E}_r = a\bar{E} - \mathcal{E}_r$

⇒ $P_r \propto$ # TIMES r APPEARS IN 1ST COLMN {1st column is an ens.

$\propto$ # STATES POSSIBLE FOR OTHER $(a-1)$ A's IF 1ST IS IN r } FUND POST

$\equiv \Omega_{RES}(\mathcal{E}_{RES})$ w/ $\mathcal{E}_{RES} \equiv a\bar{E} - \mathcal{E}_r$

(= PROD OF $(a-1)$ Ω_A's) {so unlikely to find $\mathcal{E}_r$ large, since not many possibilities for other $(a-1)$ A's w/ little remaining $\mathcal{E}_{RES}$}

AS BEFORE: Ω_{RES} GROWS RAP. w/ $\mathcal{E}_{RES}$

$$\beta \equiv \frac{\partial \ln \Omega_{RES}}{\partial \mathcal{E}_{RES}}$$

APPROX $\ln \Omega_{RES}$ AGAIN ⇒ $P_r \propto e^{-\beta \mathcal{E}_r}$

WHAT IS β? (OR T?)

⇒ NOT REAL TEMP (its associated w/ fake system)

VALUE: $\bar{E} = \dfrac{\sum_r e^{-\beta \mathcal{E}_r} \mathcal{E}_r}{\sum_r e^{-\beta \mathcal{E}_r}}$ KNOWN

⇒ DETERMINES β (or T) ⇒ work backwards

MEANING: WHAT TEMP RES. WOULD NEED TO PUT SYS IN CONTACT w/ TO HAVE RIGHT $\bar{E}$? (even if A is 1 atom)

SUMMARY CANON DISTR. APPLIES IF (a) T KNOWN (RES)
(b) $\bar{\mathcal{E}}$ KNOWN

MICROCANON $\rightarrow \Omega$
CANON $\rightarrow Z$

how much goes to which state

just as could incorp all info in S, similar for here where mean do sense

PARTITION FN:

$$\boxed{Z \equiv \sum_r e^{-\beta E_r}}$$

- $\Rightarrow$ FN OF β (OR T) & EXT. PARAMS (VIA E_r)
- $\Rightarrow$ CONTAINS ALL INFO IN CANON. DISTR.
- $\Rightarrow$ CAN EXTRACT MACRO PROPERTIES VIA DERIVS: * so mostly useful for A macro (otherwise just use P_r directly)

similar to Ω but useful when T const. or $\bar{E}$ known, and easier, since E not restricted to particular value

COMPUTING AVES: ENERGY

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$$

NUM:
$$\sum_r e^{-\beta E_r} E_r = -\frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} = -\frac{\partial}{\partial \beta} Z$$

$$\therefore \quad \bar{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z$$

$$\boxed{\bar{E} = -\frac{\partial}{\partial \beta}(\ln Z)}$$

2ND DERIV:

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \frac{\partial}{\partial \beta}\left[\frac{\partial}{\partial \beta} \ln Z\right]$$

$$= \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$= \underbrace{-\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2}_{-\bar{E}^2} + \underbrace{\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}_{\underbrace{\frac{\sum e^{-\beta E_r} E_r^2}{\sum e^{-\beta E_r}}}_{\overline{E^2}}}$$

$$\therefore \quad \boxed{\frac{\partial^2}{\partial \beta^2} \ln Z = \overline{E^2} - \bar{E}^2 = (\Delta^* E)^2}$$

GENERALIZED FORCES

- IF SYS. DEPENDS ON EXT PARAM x, THEN $E_r = E_r(x)$
- RECALL: GEN FORCE $X_r \equiv -\frac{\partial E_r}{\partial x}$ (FOR SYS. IN r)

FOR $\underset{\sim}{\text{Q-S}}$ CHG. IN x: $\bar{X} = \dfrac{\sum_r e^{-\beta E_r}\left(-\frac{\partial E_r}{\partial x}\right)}{\sum e^{-\beta E_r}}$

(so Boltz distr applies during chg)

FROM CHAIN RULE: $\frac{\partial}{\partial x}\sum_r e^{-\beta E_r(x)} = \sum_r e^{-\beta E_r(x)}\left(-\beta\frac{\partial E_r}{\partial x}\right)$

THEN

$$\boxed{\bar{X}_\alpha = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x_\alpha}}$$

ALLOW FOR >1 PARAM

skip

$đW$ = (AVE CHG IN E DUE TO dx) $= \bar{X}\,dx$

$$\boxed{đW = \bar{X}\,dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}\,dx}$$

ex IF EXT PARAM IS V:

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

skip

$$đW = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}\,dV$$

ENTROPY

- CAN GET ALL MACRO QTYS FROM S (ie Ω) } for combined isolated sys incl res.
- FOR THESE CASES (T CONST OR $\bar{E}$ KNOWN) CAN GET FROM Z

$\Rightarrow$ SHOULD BE RELATED

RELATE $d \ln Z$ TO $đW$ & $d\bar{E}$ (1 PARAM)

$$Z(\beta, x) = \sum_r e^{-\beta E_r(x)}$$

(or $Z(T, x)$)

$$d(\ln Z) = \underbrace{\overset{\beta \bar{X}}{\overset{\shortparallel}{\frac{\partial \ln Z}{\partial x}}} dx}_{\beta\, đW} + \underbrace{\frac{\partial \ln Z}{\partial \beta} d\beta}_{-\bar{E}\, d\beta}$$

TO RELATE TO $đQ$ (& $\therefore dS$) NEED IN FORM $d\bar{E}$

CH 5 TRICK

$\Rightarrow$

$$d \ln Z = \beta\, đW - d(\beta \bar{E}) + \beta\, d\bar{E}$$

for me: this is true if A is macro }

$$d(\ln Z + \beta \bar{E}) = \beta(đW + d\bar{E}) = \underbrace{\beta\, đQ}$$

$$\frac{đQ}{kT} = \frac{1}{k} dS$$

$$\Rightarrow S = k(\ln Z + \beta \bar{E}) + \text{CONST}$$

FIX CONST:

$T \to 0$ KNOW $S \to 0$

ALSO

$$Z = \sum_r e^{-\beta E_r} \to e^{-\beta E_0} \qquad \bar{E} \to E_0$$

$$\Rightarrow \ln Z + \beta \bar{E} \to -\beta E_0 + \beta E_0 = 0 \quad \Rightarrow \text{CONST} = 0$$

$$\Rightarrow \boxed{S = k(\ln Z + \beta \bar{E})}$$