CH 6 MICRO 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

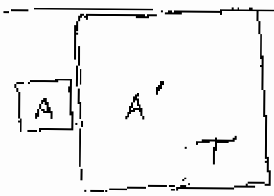
$= C$ FOR $E < E_r < E + \delta E$ { only ever need relative probs;

$= 0$ IF NOT

"MICROCANONICAL ENSEMBLE" } most general – can always isolate system & step back far enough

$\underbrace{\text{MICRO}}_{= \text{rule}}$

(2) IN CONTACT W/ HEAT RES. (ie T HELD FIXED)



(COMMON SITUATION; any time sys. in equil w/ much larg system 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

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

~~P_r (PROB A IN SINGLE DEFINITE STATE r)~~

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

(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 $\sum_r P_r = 1$ }

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

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

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

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

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

$\Rightarrow \beta \sim$ 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 $\Omega \sim E^f$ & see reasonable

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

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

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

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:

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."

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

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

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

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

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

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

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

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

COMPLETELY DESCRIBES A; $\therefore$ COMPUTE AVES FOR A:

P_r = PROB IN STATE r

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

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

LESS SPECIFIC DISTR:

- OFTEN CONVENIENT TO HAVE $P(E)$ RATHER THAN P_r

PROB. THAT A HAS ENERGY FROM E TO $E+\delta E$:

$$P(E) = {\sum_r}' C e^{-\beta E_r} \quad \text{w/} \quad E < E_r < E+\delta E$$

SUM RESTRICTED TO

$$\approx C e^{-\beta E} \underbrace{{\sum_r}' 1}_{\Omega(E)} \qquad \text{IF } \delta E \ll E_r$$

$\Omega(E) \equiv$ # STATES FOR A w/ E TO $E+\delta E$

$$\boxed{P(E) = C\, \underbrace{\Omega(E)}_{\#\text{ states in A}}\, \underbrace{e^{-\beta E}}_{\text{accts for res.}}}$$

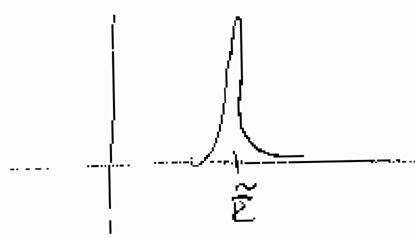
CONNECT TO PREVIOUS PICTURE:

NOTE: P_r HOLDS FOR ANY SYS. A AS LONG AS $A \ll A'$ (EVEN SINGLE ATOM IF CAN ISOLATE IT) (only treating reserv. statistically)

BUT IF A ALSO MACROSCOPIC:

$\Omega(E)$ GROWS EXP. w/ E

$e^{-\beta E}$ FALLS

$\Rightarrow$ $P(E)$ ~ 

(as before)

(larger A is, sharper P is)

skip - same for eg

BOLTZ. DISTR:

EXTREMELY USEFUL, GENERAL:

eg ISOLATE SMALL PART OF LARGE SYS AT T

P_r GIVES PROB SUBSYS IS IN PARTIC. STATE

(more restrictive than ch 3 → not allowing T to chg)

<u>ex</u> 1 <u>SPIN SYSTEM</u>: PARAMAGNETISM {ext. $\vec{H}$ induces $\vec{M}$}

↑ I'll use Reif's notation for mag. field so don't confuse w/ β

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

EXT. FIELD $\vec{H}$

MAGN. MOM. ALONG $\vec{H}$: $\pm\mu$

WHAT IS $\bar{\mu}$ FOR SINGLE ATOM?

(can treat atom as separate system if atoms localized, interactions weak so $E^{(0)} = E_{ATOM} + \underbrace{E_{REST}}_{\text{AT TEMP } T}$)

<u>A</u>: SINGLE ATOM (rest of system is "reservoir")

STATES:	<u>SPIN</u>	<u>ENERGY</u>
	$+$	$\epsilon_+ = -\mu H$
	$-$	$\epsilon_- = +\mu H$

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

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

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

$$\bar{\mu}(T,H) = \sum_r P_r \mu_r = P_+ \cdot (\mu) + P_- \cdot (-\mu)$$

$$= \mu \underbrace{\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}}_{\tanh(\beta\mu H)}$$

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

along axis of $\vec{H}$

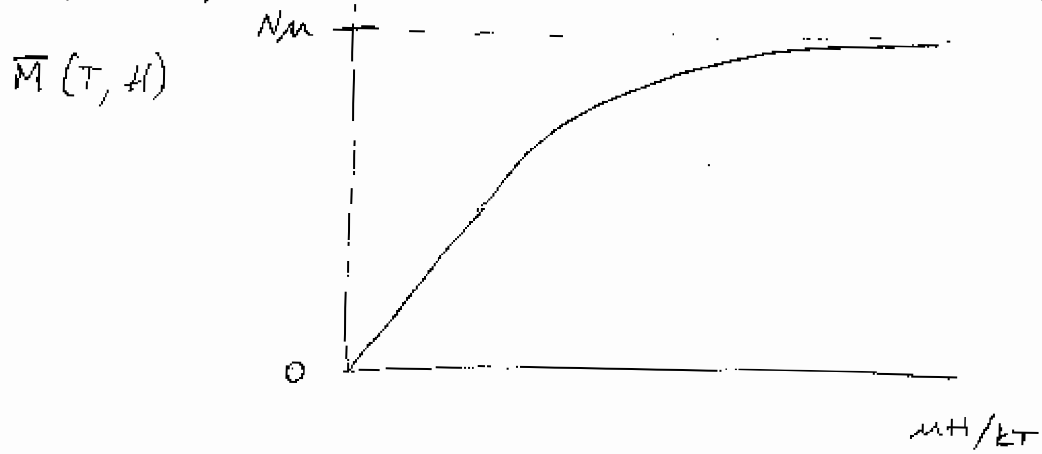
{ by treating each atom as small sys. in contact w/ res. made of rest, can say someth about entire system

MAGNETIZATION (AVE MOMENT)

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

ave (not vect)

worked very hard to get this in prob 3.2



LOW T $\quad (\mu H/kT \to \infty) \qquad \overline{M} \to N\mu$

(END ST : ALL LINE UP)

HIGH T $\quad \mu H/kT$ SMALL

$$\tanh\left(\frac{\mu H}{kT}\right) \sim \frac{\mu H}{kT} + \dots$$

$$\overline{M} \cong \left(\frac{N\mu^2}{kT}\right) H \qquad \text{(prop. to } H\text{)(cf plot)}$$

PER VOLUME:

$M_0 = M/V$

$N_0 = N/V$

$$\overline{M}_0 \cong \underbrace{\left(\frac{N_0\mu^2}{kT}\right)}_{\equiv\, \chi(T)\, \equiv \text{ MAGNETIC SUSCEPTIBILITY}} H$$

$\Rightarrow$ how magnetized sys. becomes w/ H

- Bootstrapped way to answer:
  - (a) consider 1 atom as interacting w/ res. ≡ rest of system & get P_+, P_-
  - (b) all atoms are same ⇒ get $\overline{M}$ for whole system
- Low T: one atom having spin opp → costs lots of E from rest of system; severely limits Ω
- High T: lots of E avail; taking small amount out for 1 doesn't limit rest of sys. Dividing line: $kT \sim \Delta E$ } ~ what's a lot of E for 1 dof

ex 2 <u>IDEAL GAS</u> AT KNOWN T :

- DIFFUSE ⇒ CAN ISOLATE SINGLE MOLECULE ≡ SYS A
(trickier if not diffuse ⇒ have to treat as qm system; ex can't put 2 e^-'s in same space; need to talk about qm states for all; can still do, but talk about A being partic qm state)

- IGNORE INTERACTIONS

$$E = \tfrac{1}{2} m v^2 = \frac{p^2}{2m} \qquad \big\}\ \text{3-vector sqd}$$

- PROB AT POSITION $\vec{r}$ w/ $\vec{p}$: (WITHIN d^3r, d^3p)

$$\Rightarrow P(\vec{r},\vec{p}) \equiv \underbrace{\mathcal{P}(\vec{r},\vec{p})}_{\text{density}}\, d^3r\, d^3p \ \propto\ d^3r\, d^3p\, e^{-\beta p^2/2m}$$

- PROB IN SOME FINITE REGION OF $\vec{p}$ OR $\vec{r}$? INTEGRATE OVER THAT REGION.
- ALLOW ANY $\vec{r}$ (ie IGNORE)? SUM PROB. ⇒

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

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

- IN TERMS OF $\vec{v}$: $\mathcal{P}(\vec{v})\, d^3v \ \propto\ e^{-\beta m v^2/2}\, d^3v$ (MAXWELL DISTR (famous))

skip

COMPUTE AVES : $\bar{f}(\vec{p}) = \dfrac{\int d^3p\ f(\vec{p})\, e^{-\beta p^2/2m}}{\int d^3p\ e^{-\beta p^2/2m}}$ ← takes care of norm.

ex : $\bar{p}_x$ $(= 0)$

$\bar{E} = \overline{\dfrac{p^2}{2m}}$ $(\sim kT)$

IDEAL GAS W/ GRAVITY: (FIXED T) (won't work to very large $z \Rightarrow T$ drops)

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

$$\mathcal{P}(\vec{r},\vec{p})\, d^3r\, d^3p \;\propto\; d^3r\, d^3p\, e^{-\beta[p^2/2m + mgz]}$$

it factors: $\mathcal{P}(\vec{r})d^3r\,\mathcal{P}(\vec{p})d^3p \Rightarrow$ indep prob

FOR ANY $\vec{r}$, SPECIFIC $\vec{p}$

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

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

$$\propto d^3p\, e^{-\beta p^2/2m}$$ (SAME AS BEFORE)

FOR ANY $\vec{p}$, SPECIFIC $\vec{r}$

(EASY BECAUSE $P(\vec{r},\vec{p})$ FACTORS TO $P(\vec{r})P(\vec{p})$ $\Rightarrow$ PROBS. INDEP.

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

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

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

AT ANY x, y:

$$\mathcal{P}(z)dz \propto dz\, e^{-\beta mgz} = dz\, e^{-mgz/kT}$$

{ note you obtained this for atmosphere at const. T in prob 5.7 }

(next pg is 6.4)

(1) LHS ...
(2) best vs.

(3) SYS A WITH $\bar{E}$ KNOWN (BUT E NOT FIXED)

say

- MORE COMMON THAN E FIXED EXACTLY

ex: MACRO SYS: W, Q GIVE $\Delta \bar{E}$

IF START w/ E EXACT,
AFTER W, Q, ONLY KNOW $\bar{E}$
(all calcs. in ch 5 were for $\bar{E}$)

⇒ FOR SYS A w/ $\bar{E}$, WHAT IS PROB. P_r OF BEING IN STATE r (w/ E_r)?

replace

Several ways to do; text gives one ingenious method where think of systems in ensemble as part of single super system. Simpler:

not sure this is rigorous, tho I think it's right, (maybe only for large A) use regular proof instead (following)

(a) SYS IN EQUIL w/ $\bar{E}$ ⇒ SHOULD HAVE WELL-DEFD T

(b) PUT IN CONTACT w/ RES. AT SAME T: NOTHING HAPPENS

(c) NOW SAME AS ABOVE: $P_r \propto e^{-\beta E_r}$

PROB: DON'T KNOW T

SOLN: DO KNOW $\bar{E} = \sum_r P_r E_r = \dfrac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$

⇒ KNOW LHS → DETERMINES T (or β) ON RHS
(i.e. solving T self-consistently. Example that this distribution can be used in cases where didn't expect.)

SKIP

<u>SUMMARY:</u> (I) MICROCANONICAL: ISOLATED, E FIXED
(most general)

(II) CANONICAL DISTR:

(a) T KNOWN (≡ IN CONTACT w/ RES)

or (b) $\bar{E}$ KNOWN
- FOR <u>MACRO</u> SYS: $\Delta^* E$ SMALL; NOT VERY DIFF FROM KNOWING E EXACTLY. CAN OFTEN USE CANON
- DISTR TO APPROX MICROCAN. TO COMPUTE MACRO AVES. (CAN BE OFF LITTLE ON STD DEVS; $\Delta^* E$ for ex.)

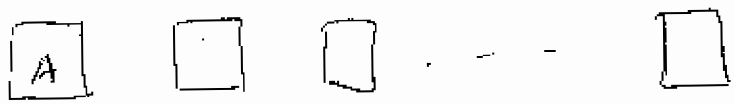
VALID? USE $\Omega \sim E^f$

⇒ VERY GENERAL, EASY TO USE;
STAT MECH REDUCED TO FINDING E_r's

4

FOR ISOLATED SYS $\boxed{A}$ w/ $\bar{E}$, WHAT IS PROB P_r OF BEING IN STATE w/ E_r

1. $\bar{E}$ KNOWN: HAVE ENS. IN MIND:



→ a COPIES (large #)

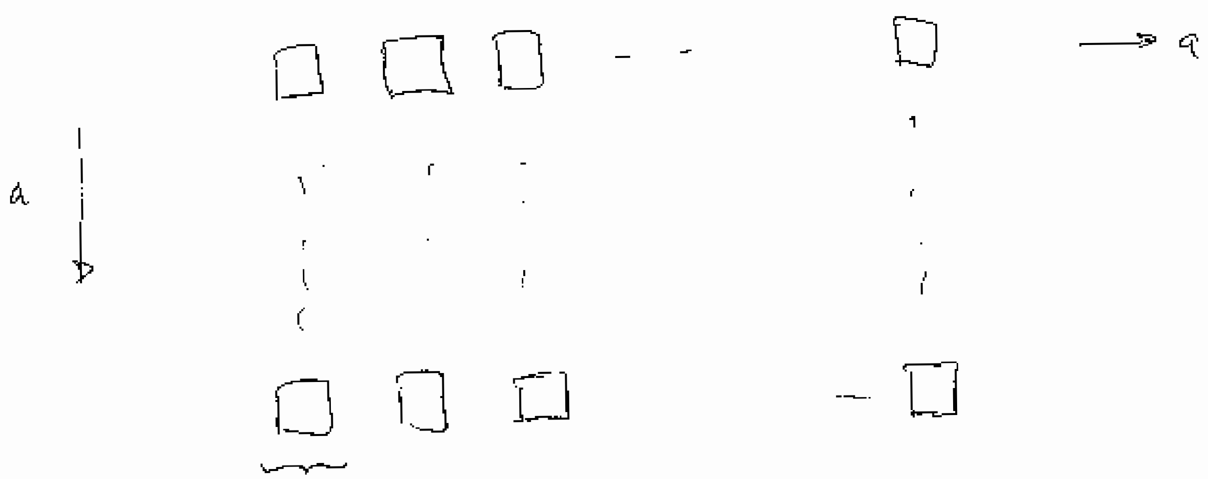
$a_r \equiv$ # SYSTEMS IN STATE r

$$P_r = \frac{a_r}{a} \quad \text{(FUND POST)}$$

$$\bar{E} = \frac{1}{a}\sum_r a_r E_r \quad \underline{\text{KNOWN}}$$

OR $\sum a_r E_r = a\bar{E} = E_{TOT}$ IN ENS. ⇒ <u>FIXED</u>

2. MAKE SUPER. ENS.: a INDEP COPIES {ens. of ens.'s}



THEN P_r ALSO $\propto$ # TIMES r APPEARS IN <u>1ST SYS</u>

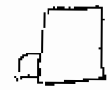
3. TRICK:

TREAT EACH ENS. AS SINGLE ISOLATED (MACRO) SYSTEM WITH $E_{TOT} = a\bar{E}$.

⇒ FOCUS ON 1ST SYS. TO <u>GET P_r.</u>

$\underset{E_r}{\boxed{A}}\ \underbrace{\{\square \ \cdots \ \square\}}_{\text{RES. w/ } E_{RES} = E_{TOT} - E_r}$ } MACRO, EVEN IF $\square$ IS NOT

(MATHEMATICALLY)

$\Rightarrow$ IDENTICAL TO PREVIOUS CASE (ENS. FOR)  ISOLATED w/ FIXED E_{TOT}

$\Omega_{RES}(E_{RES}) \equiv$ # STATES FOR $(a-1)$ A's (= prod. of indiv. Ω_A's)

GROWS RAPIDLY w/ $E_{RES} = E_{TOT} - E_r = a\bar{E} - E_r$

$$\beta \equiv \frac{\partial \ln \Omega_{RES}}{\partial E_{RES}}$$

APPROX $\ln \Omega_{RES}$

FIND AGAIN: $P_r \propto e^{-\beta E_r}$

same reason; how often r (w/ E_r) appears is $\propto$ # diff things rest of sys. in ensemble could be doing

WHAT IS β (OR T)?

$\Rightarrow$ NOT REAL TEMP (associated w/ fake system)

$\Rightarrow$ VALUE:

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

KNOWN

DETERMINES β (or T) (work backwards)

PHYSICAL MEANING:

WHAT TEMP RES. WOULD NEED TO PUT SYS IN CONTACT w/ SO GET RIGHT $\bar{E}$?

(even if A is 1 atom)

SUMMARY VERY GENERAL:

CANON DISTR. APPLIES IF (a) T KNOWN (RES.)

(b) $\bar{E}$ KNOWN

USEFUL APPROX: MACRO SYS: $\Delta^* E$ SMALL — NOT TOO DIFF FROM E KNOWN EXACTLY $\Rightarrow$ CAN USE CANON DISTR. AS APPROX FOR MICROCANONICAL TO COMPUTE AVE'S (CAN BE OFF FOR STD DEV'S $\to$ EX $\Delta^* E$)

ESSENTIALLY SAME IF $\Delta^* E \leq \delta E$.

skip?

{ For me:

For system to be at ave $\bar{E} \neq \infty$, there has to be

(1) contact w/ some other system so E can be exchanged (otherwise E is exact)

(2) some reason E is limited.

If any E were possible, the # states Ω grows so rapidly that $\bar{E}$ would be dominated by larger values of E, driving $\bar{E}$ to ∞. Because of the exponential growth in Ω, for each E, the prob. of having that E must fall exponentially for $\bar{E}$ to be finite. Hence the $e^{-\beta E_r}$ distribution. }

→ how much goes to which state

just as could incorp all inf in S, similar for here where mean do some

PARTITION FN:

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

(β OR T CONST)

⇒ FN OF β (OR T), & EXT. PARAMS (VIA E_r)
⇒ CONTAINS ALL INFO IN CANON. DISTR.
⇒ 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 val

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

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

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

MORE PARAMS; ONE EQN

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 THESE CASES (T CONST OR $\bar{E}$ KNOWN) CAN GET FROM Z

$\Rightarrow$ SHOULD BE RELATED

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

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

(or $Z(T, x)$)

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

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

CH 5 TRICK

$\Rightarrow$

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

for me: this is true if A is macro

$$d(\ln Z + \beta\bar{E}) = \beta(\text{đ}W + d\bar{E}) = \underbrace{\beta\, \text{đ}Q}_{\frac{\text{đ}Q}{kT} = \frac{1}{k} dS}$$

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

FIX CONST:

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

ALSO

$Z \to e^{-\beta E_0}$, $\bar{E} \to E_0$

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

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

MULT BY T:

$$TS = kT\ln Z + \bar{E}$$

$$\Rightarrow \quad \underbrace{\bar{E} - TS}_{\equiv F} = -kT\ln Z$$

$\equiv F$ (HELM. FREE ENERGY)

$$\boxed{F = -kT\ln Z \quad \text{or} \quad Z(T,x) = e^{-F(T,x)/kT}}$$

{ RECALL NATURAL VARIABLES FOR F ARE (T,V) (or (T,x)) }

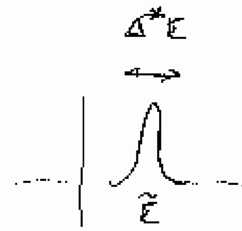
---

skip

KNOW $S = k\ln\Omega(\bar{E})$

CONSISTENT ?

$$Z = \sum_r e^{-\beta E_r} = \sum_E \underbrace{\Omega(E)}_{\text{GROWS w/ } E}\, \underbrace{e^{-\beta E}}_{\text{DROPS w/ } E}$$



PEAKED AT $\tilde{E} \approx \bar{E}$

$$\approx \underbrace{\frac{\Omega(\bar{E})}{\delta E}}_{\text{DENSITY}} e^{-\beta\bar{E}}\, \underbrace{\Delta^* E}_{\text{WIDTH}}$$

$$\ln Z = \underbrace{\ln\Omega(\bar{E}) - \beta\bar{E}}_{\approx f} + \underbrace{\ln\left(\frac{\Delta^* E}{\delta E}\right)}_{\text{small}} \quad (\approx \ln f)$$

$$\Rightarrow k\ln Z \approx \underbrace{k\ln\Omega(\bar{E})}_{S} - \beta\bar{E} \quad \checkmark$$

LOW T LIMIT:

$T \to 0 \quad \beta \to \infty \qquad Z = \sum_E \Omega(E) e^{-\beta E}$

$\sim \Omega(E_0) e^{-\beta E_0}$

(next contrib is exponentially smaller)

THEN

$\bar{E} \to E_0$

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

$\to k(\ln \Omega(E_0) - \beta E_0 + \beta E_0) = k \ln \Omega(E_0)$

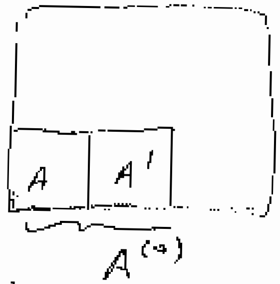
$S \to k \ln \underbrace{\Omega(E_0)}_{\substack{\#\ \text{states} \\ \text{at lowest } E_0}}$ AS BEFORE

(shows we got the const. right)

$\to 0$ IF ONE GND ST.

skip 9 — Mention good approx to microcanonical ensemble for macro systems (if not done already) summary of short term

$\ln Z$ IS ADDITIVE: (ie EXTENSIVE)



(1) A & A' PARTS OF SYS. IN EQUIL. W/ TEMP T

(2) IF ENERGY IS ADDITIVE

$$E^{(0)} \simeq E + E'$$

(WILL BE TRUE IF SYSTEMS are macro & INTERACT WEAKLY AT EDGES)

$$Z = \sum_r e^{-\beta E_r} \qquad Z' = \sum_s e^{-\beta E'_s}$$

$$Z Z' = \underbrace{\sum_{r,s}}_{\text{SUMS OVER ALL POSSIBLE } E^{(0)}} e^{-\beta(E_r + E'_s)}$$

$$= \sum_t e^{-\beta E^{(0)}_t} = Z^{(0)}$$

$$\boxed{\begin{aligned} Z^{(0)} &= Z Z' \\ \ln Z^{(0)} &= \ln Z + \ln Z' \end{aligned}} \qquad (\text{LIKE } S)$$

THEN $\ln Z^{\text{TOTAL}} = \sum_i \ln Z_i$

↑ SUBSYSTEMS