CH 3 HEAT, TEMP, ENTROPY

(i) mech ints: have seen can make direct connection to ave'd gen. F's and W; therm ints: can I find params which govern Q?

HEAT FLOW

- WILL DEF. MACRO QTY'S TO DESCRIBE Q EXCHANGE
- ALL BASED ON PROB. (i.e. FUND. POST.) { will one system give E to another?: yes, on ave, if it's more likely; i.e, if there are many more ways for that to happen than not }

(ii) since it dep. on micro. details we're not following, could imagine it's very complicated, but will find if look at sys. in equil, it dep. on only 1 number, macro'ly accessible

ex

w/ E, E' FIXED

ISOLATED : TOTAL $E^{(0)} = E + E'$ CONST

INSULATED : E, E' CONST

$\Rightarrow$ MACRO CONSTRAINTS : $E^{(0)}$, E (Then $E' = E^{(0)} - E$)
(choose these rather than E & E' since $E^{(0)}$ will remain a const.)

KEEP ALL X_α FIXED (NO W)

$\Rightarrow$ ALL SYS. IN ENS. SATISFY THESE

IN EQUIL : ALL POSS. STATES EQ. LIKELY

NOW :

REMOVE INSUL :

- RELAXES CONSTRAINT :
  $E^{(0)}$ CONST. , BUT E (& E') CHG
- $\Omega_f \geq \Omega$: { # MICRO STATES POSSIBLE } { by defn of constraint }
  - HAVE ALL ORIGINAL STATES + (USUALLY MANY) MORE w/ DIFF. E, E'
  - (MANY) NEW STATES APPEAR IN ENS. (assume big enough that all still well-represented)

– NOT IMMEDIATELY IN EQUIL (USUALLY):

Q FLOWS UNTIL ALL P_r = CONST ⇒ NEW EQUIL;

IN ENS: E (& E') WILL DIFFER

** emphasize: can't use fund post. during process unless do it QS; have to study at micro level in gen'l

– CAN'T UNDO BY PUTTING INSUL. BACK IN

(would need to do more → work on system)

(won't get heat to flow back)

10/18/02

example of

IRREVERSIBLE PROCESS:

– ISOLATED SYS.

– RELAX CONSTRAINT:

say { ANYTHING RESTRICTING STATES IN ENS. (REIF: y_α – MORE GENERAL THAN x_α)

ex: $E, N, V, \bar{p}$ ...

anything known or set which can be used to exclude states from ens.

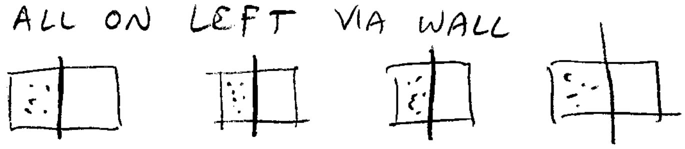
$$\Rightarrow \Omega_f > \Omega_i$$

⇒ CAN'T UNDO BY SIMPLY REVERSING ACTION (ex put back wall, insulation)

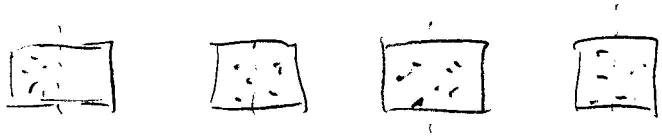
say (already covered in intro)

ex PARTICLES IN BOX:

CONSTR: ALL ON LEFT VIA WALL

ENS:  . . . .

RELAX: REMOVE WALL

ENS:  . . . .

SMALL SUBSET

$\Omega_f \gg \Omega_i$

HOW MUCH ? (twice? not even close)

IN EQUIL: $P(\text{ALL LEFT})$ NOW $= \dfrac{1}{2^N}$ $\quad N \sim 10^{24}$

FROM: $\underbrace{P(\text{LEFT}) = \dfrac{\Omega_i}{\Omega_f}}_{\text{FUND. POST}} = \dfrac{1}{2^N} \sim \dfrac{1}{2^{10^{24}}}$ (we only needed to pay attn to location, since $\vec{p}$ played no role)

$\Rightarrow$ INITIAL CONFIGS SWAMPED BY NEW CONFIGS

$\Rightarrow$ VERY UNLIKELY TO FIND IN ORIG. CONFIG AFTER NEW EQUIL

- CAN'T UNDO BY PUTTING WALL BACK
  (like Pandora's box; doesn't restore orig. configs in ens.)

- CAN IF INTERACT w/ ANOTHER SYS (but then not isolated)
  DOES WORK

4

REVERSIBLE PROCESS

skip

- RARE

- RELAX $\Rightarrow \Omega_f = \Omega_i$ (ie doesn't gain access to new state)

  $\Rightarrow$ REALLY WASN'T A CONSTRAINT

- CAN RESTORE BY REIMPOSING (no additional work) (dumb example: $0 < E < E^{(0)}$; or putting wall out & in again)

BACK TO: $\boxed{A \,|\, A'}$ $\quad E^{(0)} = E + E'$

ALL PROB. DEPENDS ON Ω (IN EQUIL)

$\Rightarrow$ WHAT'S NEW $\bar{E}$?

$\Rightarrow$ IS Q LIKELY ?

BACK TO $A+A'$: Find new $\bar{E}$ via fund post.

[Ω_{COMBINED} might be a better choice]

NEW $\bar{E}$, Q DETERMINED BY

$$\Omega(E^{(0)}, E)_{\text{TOTAL}} = \Omega(E)\,\Omega'(E') \qquad E' = E^{(0)} - E$$

(# STATES AVAIL AT VARIOUS E's)

FROM POST: $\boxed{P(E) = \dfrac{\Omega_{\text{TOT}}(E^{(0)}, E)}{\sum_E \Omega_{\text{TOT}}(\,''\,)}}$

16 ⇒ 14

BEHAVIOR:

EXPECT:

- $\Omega(E)$, $\Omega'(E')$ GROW RAPIDLY w/ E, E'
- Ω_{TOTAL} SHARPLY PEAKED AT SOME $E = \tilde{E}$ (MAX):

$$\Omega_{\text{TOTAL}} = \underbrace{\Omega(E)}\,\underbrace{\Omega'(E^{(0)} - E)}$$

AS E INCR: GROWS FAST, SHRINKS FAST (and v.v.)

(SHRINKING SETS IN WHEN E IS SIGNIFICANT FRACTION OF $E^{(0)}$)

(falls to zero when $E \geq E^{(0)}$)

FROM OUR EST:

$$\Omega(E) \sim E^f \qquad \Omega'(E') \sim (E')^{f'}$$

$$\Omega_{\text{TOTAL}} \sim E^f (E^{(0)} - E)^{f'}$$

$\Rightarrow$ SHARP PEAK FOR $f \sim 10^{24}$

ex HW PROB:

LET $f = f'$ $\qquad x \equiv \dfrac{E}{E^{(0)}}$ (fraction of E_{TOTAL} in sys A)

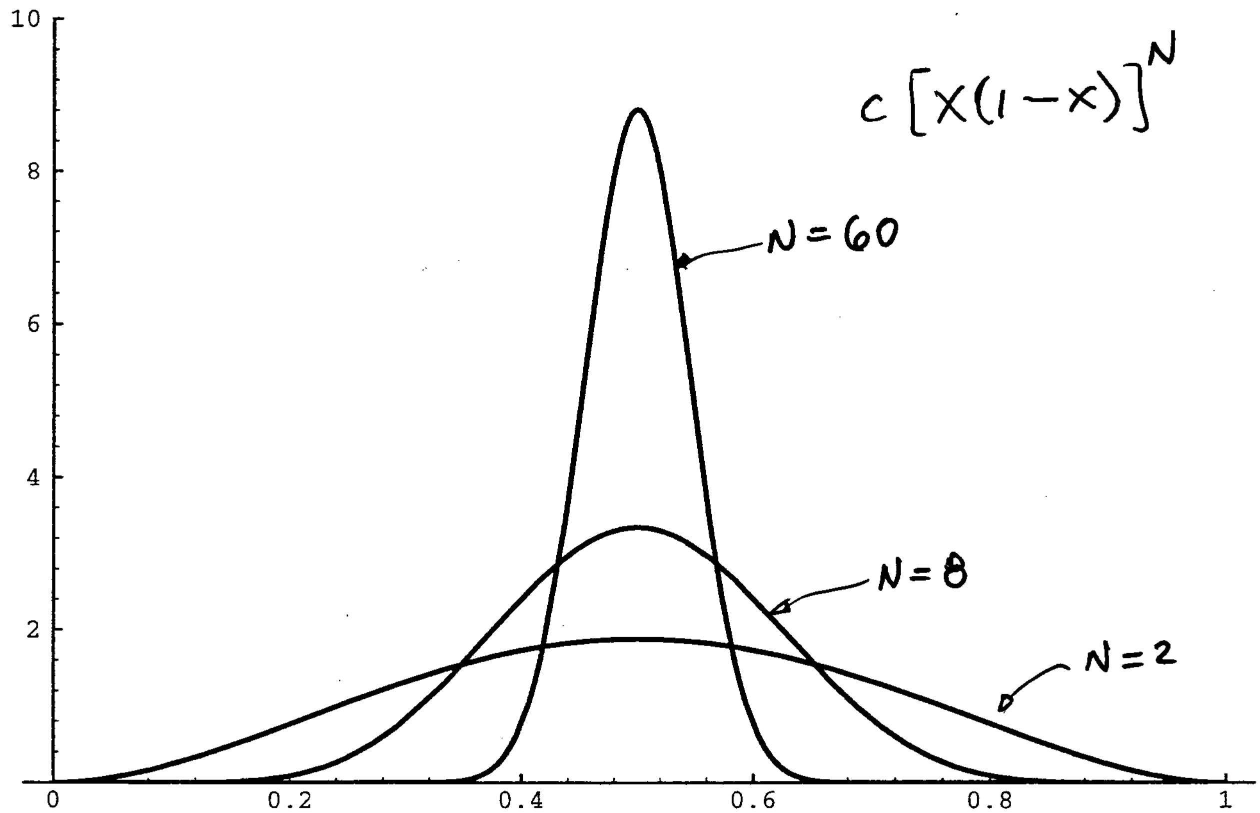
$$\Omega_{\text{TOT}} \sim E^{(0)2f} x^f (1-x)^f$$

SHARP PEAK NEAR $x \sim \frac{1}{2}$ (cf PLOT)

imagine $f = 10^{24}$

$\Rightarrow$ peak where dof share E equally: At peak

$$\frac{\partial}{\partial E}\Omega_{\text{TOT}} = 0 \Rightarrow \frac{E}{f} \approx \frac{E'}{f'}$$

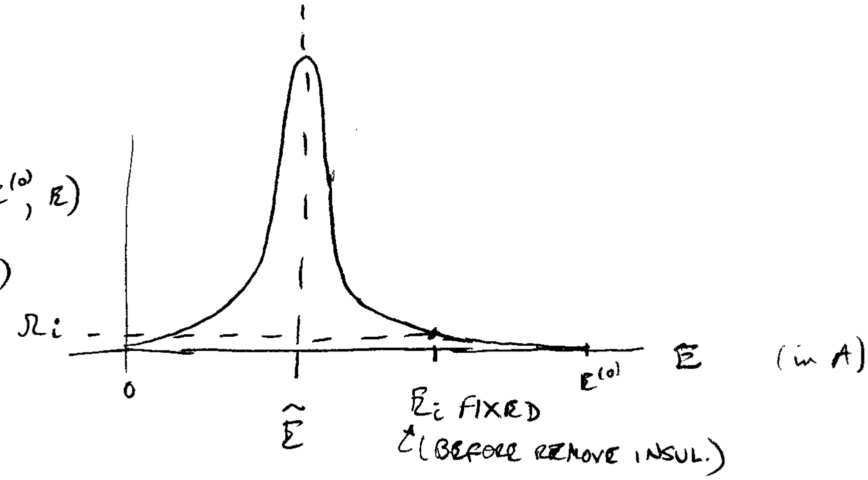


$c\left[x(1-x)\right]^N$
N=60
N=8
N=2
10
8
6
4
2
0
0.2
0.4
0.6
0.8
1

IN GENERAL:

$P(E) \propto \Omega_{TOT}(E^{(0)}, E)$

$= \Omega(E)\Omega'(E')$



REMOVE INSUL:

(1) MANY MORE STATES AVAIL, MOST NEAR $\tilde{E}$ (i.e. many more ways can have $\tilde{E}$ than E_i)

(2) MOST SYS. IN ENS. EXCHANGE ENERGY SO $E \approx \tilde{E}$

(3) NEW EQUIL

$$\bar{E} \cong \tilde{E} \quad \Rightarrow \quad \text{DETERMINES } Q \underset{= \bar{E} - E_i}{} \quad (\text{ave expectation of } E)$$

E NOT FIXED, BUT LITTLE PROB TO FIND $E \neq \bar{E} \approx \tilde{E}$

(so E near $\tilde{E}$ is most important, since that's most probable, tho any E is possible up to $E^{(0)}$)

Start emphasizing: sharpness of distributions for macro systems is what makes stat mech useful

QTYS ASSOCIATED w/ PEAK $\tilde{E}$: (i.e. w/ new equil) (i.e. what happens when bring together) (depends on 1 param)

$$P(E) = C\,\Omega_{TOTAL}(E^{(0)}, E) = C\,\Omega(E)\,\Omega'(E')$$

AT $E = \tilde{E}$ P (OR $\ln P$) IS MAX: see later

[WILL USE $\ln$ ⇒ SMOOTHER FOR RAPIDLY INCR FNS
- CONVENIENT: TURNS × TO +
- MORE CLOSELY CONNECTED TO FAMILIAR QTYS]

$$\ln P = \ln C + \ln \Omega(E) + \ln \Omega'(E')$$

MAX

$$\frac{\partial \ln P}{\partial E} = \underbrace{\frac{\partial \ln \Omega(E)}{\partial E}}_{\beta(E)} + \underbrace{\frac{\partial \ln \Omega'(E')}{\partial E'}}_{\beta'(E')}\underbrace{\frac{\partial E'}{\partial E}}_{-1} = 0$$

$\beta(E)$ (rate at which $\ln(\#)$ states grows w/ E) $\qquad (E' = E^{(0)} - E)$

MAX ⇒ $\boxed{\beta(\tilde{E}) = \beta'(\tilde{E}') = \beta'(E^{(0)} - \tilde{E})}$

AT MAX: rate at which number states gained by $\Omega(E)$ = rate lost by $\Omega'(E')$

DEFNS:

ABSOLUTE TEMP $\boxed{kT \equiv \frac{1}{\beta}}$ dim = energy

DIMENSIONLESS (T)

CONST w/ DIM OF ENERGY (depends on units) (k)

SMALL T ⟷ LARGE β ⇒ Ω GROWS QUICKLY w/ E

LARGE T ⟷ SMALL β " " SLOWLY "

⇒ $\ln \Omega_{TOT}$ GROWS BY ENERGY E MOVE. FROM SYS AT LARGE T TO SMALL T

(AS $\bar{E}$ MOVES TO $\tilde{E}$, Q FROM LARGE T TO SMALL UNTIL EQUAL)

{ ~~ave~~ note T is abstract → can't look at a single microstate & pick out its T; macro qty; have in mind ... }

ENTROPY $\boxed{S \equiv k \ln \Omega}$ (DIM: ENERGY VIA k; JUST A CONVENTION)

- $\ln$ OF AVAILABLE STATES
- MEAS OF HOW LIKELY TO FIND SYS w/ PARTIC. SET OF MACRO VARS: GIVES # WAYS THAT CAN HAPPEN (from fund post)
- MEASURE OF RANDOMNESS OR DISORDER:

$\Rightarrow$ LESS KNOWN ABOUT SYSTEM (i.e. FEWER CONSTR.), MORE STATES AVAIL, LARGER S

$\Rightarrow$ "RANDOM" STATES ARE ELEMENTS OF SETS w/ MANY POSSIBILITIES (cf LICENSE PLATES) (cf vs)

THEN $\boxed{\dfrac{1}{T} = \dfrac{\partial S}{\partial E}}$ (BY DEFN) (lower T, more S incr. with E)

$\Rightarrow$ P(E) IS MAX WHEN: (and so this is where most states are, determines Ω)

$E \equiv \tilde{E}$

$\beta(\tilde{E}) = \beta'(\tilde{E}')$

(A) $T = T'$

$S + S' = \text{MAX}$

additive

ALL PROPERTIES OF $\Omega(E)$; NOTE THESE ARE STATISTICAL QTY'S BY DEFN. CAN'T LOOK INSIDE ONE SYS. & SEE T OR S BY WATCH. PARTS; WOULDN'T DEF. FOR SMALL SYS.

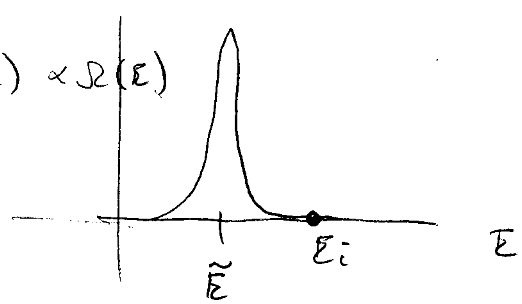
(note def. S as $\ln \Omega$ means add S's) MULT Ω's → ADD S's

skip it

SUMMARY (just say)

APPROACHING EQUIL:

skip drawing again?



AFTER REMOVE INSUL: MOST AVAIL. STATES HAVE

$E = \tilde{E}$ ∴ IN EQUIL

$\bar{E} = \tilde{E}$

~~AS OCCUPY NEWLY ALLOWED STATES:~~

~~$\bar{E}(t) \rightarrow \tilde{E} = \bar{E}_f$~~

OTHER PROPERTIES OF ABS TEMP T:

(1) SIGN $$\frac{1}{kT} \equiv \beta \equiv \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\text{more } E,\ \text{more } \Omega} > 0$$

$$\boxed{T > 0}$$

(EXCEPTION: SPIN SYSTEM – MOLECULES (say) TIED DOWN (NO KE) (somewhat artificial)
HAS MAX E → ALL ALLIGNED OPP. $\vec{B}$

AS APPROACH E_{MAX}, Ω DECREASES,
$T < 0$)

(2) RELN TO E OF PARTICLES:

$$\Omega(E) \propto E^f$$

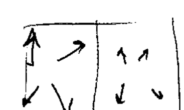
$$\ln \Omega \sim f \ln E + \text{const}$$

$$\beta = \frac{\partial \ln \Omega}{\partial E} \sim \frac{f}{E} \Rightarrow \boxed{kT \approx \frac{E}{f}}$$

$$\Rightarrow \boxed{kT \sim \text{ENERGY PER DOF}}$$ (very useful est.)

(familiar – high T, lots of E per molecule, etc)
incl KE, INTERNAL E, ETC

skip ⇒ AS GO TO EQUIL



→ Q

UNTIL ALL DOF HAVE ~ SAME E
(WE'VE SEEN IN COUNTING EXERCISES:
RARE FOR FEW PARTICLES TO HAVE LOTS of E)

GAUSS APPROX FOR Ω_{TOT}:

SHARPLY PEAKED — EXPAND $\ln \Omega_{TOT}$ AT $E = \tilde{E}$:

$$\ln \Omega_{TOT}(E) = \ln[\Omega(E)\,\Omega'(E')] = \ln\Omega + \ln\Omega'$$

NEED

$$\frac{\partial \ln \Omega_{TOT}}{\partial E} = \frac{\partial \ln \Omega}{\partial E} + \frac{\partial \ln \Omega'}{\partial E'}\underbrace{\left(\frac{\partial E'}{\partial E}\right)}_{-1}$$

$$(E' = E^{(0)} - E)$$

$$= \beta(E) - \beta'(E')$$

$$\frac{\partial^2 \ln \Omega_{TOT}}{\partial E^2} = \frac{\partial^2 \ln \Omega}{\partial E^2} + \frac{\partial^2 \ln \Omega'}{\partial E'^2}\underbrace{\left(\frac{\partial E'}{\partial E}\right)^2}_{+1}$$

$$\equiv -\left(\lambda(E) + \lambda'(E')\right)$$

since expect < 0 at max

MAX: $\left.\dfrac{\partial \ln \Omega_{TOT}}{\partial E}\right|_{E=\tilde{E}} = 0 \Rightarrow \beta(\tilde{E}) = \beta'(\tilde{E}')$

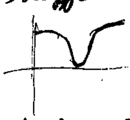
$\Rightarrow T = T'$ WHEN $E = \tilde{E} = \bar{E}$

(KNOW THIS: same T at max)

$$\Rightarrow \ln \Omega_{TOT}(E) \sim \ln \Omega_{TOT}(\tilde{E}) - \frac{1}{2}\big(\underbrace{\lambda(\tilde{E}) + \lambda'(\tilde{E}')}_{\equiv \lambda_0}\big)(E-\tilde{E})^2 + \cdots$$

$\Rightarrow \quad \lambda_0 > 0$ IF AT MAX (if not max at equal T, wouldn't be at equil; would run away)

$\Rightarrow \quad \lambda(\tilde{E})$ & $\lambda'(\tilde{E}')$ BOTH > 0

(IF for ex $\lambda(\tilde{E}) < 0$, could put two of these ident. sys. together $\Rightarrow \lambda_0 = 2\lambda(\tilde{E}) < 0$) (think what happens if $\rho \sim$ )

$$\Rightarrow \boxed{\Omega_{TOT}(E) \approx \Omega_{TOT}(\tilde{E})\, e^{-\frac{1}{2}\lambda_0 (E-\tilde{E})^2}}$$

$\Rightarrow$ one sys gets all the E
$\Rightarrow$ sloshes around
$\Rightarrow$ wildly diff T's

$$P(E) \propto \Omega_{TOT}(E) \qquad \text{(FUND POST)}$$

$$\Rightarrow \quad P(E) = P(\tilde{E})\, e^{-\frac{1}{2}\lambda_0 (E-\tilde{E})^2}$$

($\tilde{E}$ determined by 1st deriv $\beta = \frac{1}{kT}$)

GAUSSIAN:

$$\bar{E} = \tilde{E} \qquad \text{(exact in this approx)}$$

$$\sigma = \Delta^* E = \frac{1}{\sqrt{\lambda_0}}$$

all determined by Ω

HOW SHARP?

$$\Omega(E) \sim E^f \qquad \ln\Omega \sim f \ln E$$

$$-\lambda(E) = \frac{\partial^2 \ln\Omega}{\partial E^2} \sim -\frac{f}{E^2}$$

$$\text{AT } \tilde{E} = \bar{E}: \quad \lambda_0 \sim +\frac{f}{\bar{E}^2}$$

taking $f \approx f'$, $\lambda \approx \lambda'$

$$\Rightarrow \quad \frac{\Delta^* E}{\bar{E}} \sim \frac{1}{\sqrt{f}} \sim 10^{-12}$$

VERY SHARP:

$$P(E) \sim 0 \quad \text{IF} \quad |\Delta E| \gtrsim 10^{-12}\, \bar{E}$$

$\Rightarrow$ E FLUCTS, BUT RARE THAT MEAS. FLUCTUATION OF 1 PART/TRILLION

$\Rightarrow$ MOST MEAS. NOT PRECISE ENOUGH TO DETECT

SURPRISE: LARGER f

$\Rightarrow$ MORE COMPLICATED SYS

$\rightarrow$ MORE PREDICTIVE $P(E)$ BECOMES

$\Rightarrow$ SIMPLICITY IN LARGE #'s

CONSEQUENCES OF SHARP PEAK / SMALL $\Delta^* E$:

(0) GAUSS APPROX ~ EXACT: $\bar{E} = \hat{E}$ $\quad \bar{E}' = E^{(0)} - \bar{E}$

(a) FLUCTS. ARE TINY $\Rightarrow$ FEW SYS IN ENS HAVE E FAR FROM $\bar{E}$

$\Rightarrow$ E STAYS CLOSE TO $\bar{E}$ VS t FOR 1 SYS

(b) SIMILAR TO CASE WHERE E IS NOW EXACTLY $\bar{E}$

E' " " $E^{(0)} - \bar{E}$

AND SEPARATELY ISOLATED

(c) IF $\Delta^* E < \delta E$ (ABILITY TO MEAS.) THEN IDENTICAL TO "

(d) BY OUR DEFN, $T(\bar{E})$ NOT STRICTLY THE TEMP FOR A AFTER CONTACT W/ A'

$\Rightarrow$ T DEFINED FOR SYS AT DEFINITE E (W/IN δE)

$\Rightarrow$ A CAN HAVE $0 < E < E^{(0)}$

BUT CAN IF (b) & (c) TRUE

(NOTE: T NOT USEFUL FOR SMALL SYS W/ WIDE RANGE IN E's

$\Rightarrow$ HAS WIDE RANGE OF VALUES)

SINGLE SYSTEM:

(e) Q, T DEF'D VIA Ω FOR ENS., NOT 1 SYS $\Rightarrow$ GIVE AVES

IF NARROW: KNOW (W/ REL ERR 10^{-12})

$E_f = \bar{E} \qquad \Delta E = \bar{E} - E_i = Q$ FOR SINGLE SYS

WHAT MAKES STATMECH USEFUL :

say ↓ USUALLY STUDYING 1 SYS ≡ SYS IN MY LAB

- ONLY MEAS FEW MACRO PROPERTIES
- WOULD LIKE TO MAKE PREDICTIONS

IN PRINCIPLE

- MANY MICRO POSSIBILITIES CONSIST. w/ FEW KNOWN MACRO PROPS
- MUST CONSIDER SETS / ENSEMBLES
- ALL QTYS PREDICTED ARE RELATED TO PROB. DISTR (AVES, # STATES, ...)

  ex $Q, \beta, T, \bar{E}, S$ ...

⇒ GIVE PREDICTIONS FOR ENS.

⇒ GIVES RANGE OF " " MY 1 SYS

MACRO SYS

- DISTR. ARE NARROW FOR LARGE f

⇒ CAN MAKE PRECISE PREDICTION FOR 1 SYS

ex HEAT EXCH: NEW $\bar{E}$ w/ $\Delta^* E \sim 10^{-12}\,\bar{E}$

⇒ IN ENS. ALMOST ALL SYS HAVE $E = \bar{E} \pm \underbrace{\Delta^* E}_{10^{-12}\bar{E}}$

⇒ MY SYS WILL HAVE $E = \bar{E} \pm \Delta^* E$ (ie ALMOST EXACTLY $\bar{E}$)

⇒ EXTREMELY UNLIKELY TO BE OFF BY $10\,\Delta^* E$

- MUST LOOK VERY HARD TO SEE FLUCTS; OFTEN TOO SMALL VS EXPTL ERROR

⇒ CAN MAKE VERY PRECISE PREDICTIONS FOR 1 SYS

(f) IN THIS SPIRIT (ie CAN TALK ABOUT SINGLE T EVEN AFTER Q) :

0^{TH} LAW OF THERMO

- ORIGINALLY FROM OBSERVATION:

IF	SYS A	IN	THERM EQ. w/	SYS	C
AND	" B	"	"	"	C
THEN	" A	"	"	"	B

ie $Q = 0$

WHY? WE SHOWED THERM EQ. REQUIRES SAME β's (OR T's).

$\Rightarrow$ $\boxed{\text{IF } \beta_A = \beta_C \text{ AND } \beta_B = \beta_C \text{ THEN } \beta_A = \beta_B}$

$\Rightarrow$ SIMPLE PROPERTY OF REAL #'s

CONTENT: THERMAL EQUIL. DEP? ON SINGLE PARAMETER

SEEMS OBVIOUS?

SUPPOSE: DON'T KNOW ABOUT Ω

" " WHAT Q IS (A FLUID?)

IF KNEW

(1) NO Q FOR GLASS OF H_2O IN CONTACT w/ ELEPHANT

(2) " SAME " " TOASTER

IS IT OBVIOUS NOTHING HAPPENS FOR TOASTER $\Leftrightarrow$ ELEPHANT?

(g) SIMPLIFIES PROPERTIES OF ENTROPY S:

(1) δE (ACC. OF MEAS.) DOESN'T MATTER MUCH:

(a) $\Omega(E) \equiv \omega(E)\,\delta E$ (ie $\Omega \propto \delta E$)

know for narrow δE, $\Omega \propto \delta E$ (cf. before)

$$\ln \Omega = \ln \omega + \ln \delta E$$

all statmech props follow from Ω; seems arbitrary if it dep on my expt'l abilities

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial \ln \omega}{\partial E}$$

$\Rightarrow$ β OR T INDEP OF δE

(b) $S = k \ln \Omega$

DIFF CHOICE FOR δE: $\delta E \to \delta E^*$

$$\Omega^* = \omega(E)\,\delta E^* = \Omega \cdot \left(\frac{\delta E^*}{\delta E}\right)$$

$$S^* = k \ln \Omega^* = k\Big[\underbrace{\ln \Omega}_{\sim f} + \underbrace{\ln\left(\frac{\delta E^*}{\delta E}\right)}_{\sim 1}\Big]$$

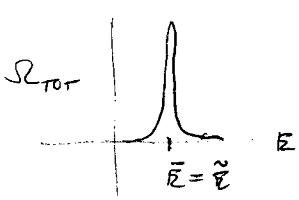
even if δE^* differs by factor of 100

stat mech: exponent matters, not factors

$\therefore$ $S^* = S$

(2) TWO SYSTEMS: can show $S_{ALL\ E} \approx S(\bar{E}) + S'(\bar{E}')$ $\boxed{A}\boxed{A'}$

(ie same as if isolated again)



- ANY E POSSIBLE

$$S_{A.E.} = k \ln \Omega_{AE}^{TOT}$$

$$\Omega_{A.E.} = \int_0^{E^{(0)}} dE\ \omega_{TOT}(E^{(0)}, E)$$

$$\omega_{TOT}(E^{(0)}, E) = \frac{\Omega_{TOT}(E^{(0)}, E)}{\delta E}$$

NARROW:

$$\int dE\, \Omega_{TOT}(E^{(0)}, E) \approx \Omega_{TOT}(E^{(0)}, \bar{E})\, \Delta^* E \qquad \text{(like } \delta \text{ fn)}$$

$$\Rightarrow \Omega_{AE} \sim \Omega_{TOT}(E^{(0)}, \bar{E}) \left(\frac{\Delta^* E}{\delta E}\right)$$

so

$$S_{AE} \sim \underbrace{\overbrace{k \ln \Omega_{TOT}(\bar{E})}^{\sim f}} + \overbrace{k \ln \left(\frac{\Delta^* E}{\delta E}\right)}^{\sim 1} \rightarrow \text{NEGLIGIBLE}$$

$$k \ln \Omega(\bar{E}) + k \ln \Omega'(\bar{E}')$$

$$= S(\bar{E}) + S'(\bar{E}') \qquad \left(\bar{E} = \tilde{E} \quad \bar{E}' = E^{(0)} - \bar{E}\right)$$

27 ~~19~~

(this is example of statement that almost same as if system were locked exactly at $E = \bar{E} = \tilde{E}$)

$\Rightarrow$ We saw this in problem 2.4: spin-½ system

$$\underset{\frac{1}{2}\text{ up } \frac{1}{2}\text{ dn}}{\ln \Omega(E=0)} \approx N \ln 2 \Rightarrow \Omega \sim 2^N = \text{Total \# possible for all spin configs}$$

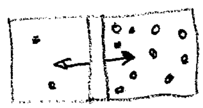
skip (* also note (if don't discuss (a)), that when compute $S = k \ln \Omega$, value of δE is irrelevant (again, cf prob 2.4)

$$\ln \Omega = \underbrace{\ln \omega}_{\sim f} + \underbrace{\ln \delta E}_{\sim 1}$$

GRN'L INTERACTIONS:

ALLOW BOTH E & X_α TO CHANGE

ex PUT GASES IN CONTACT; AFTER EQUIL, WHERE'S WALL?



cp E TRANSFER: Q FLOWS UNTIL MOST SYS. IN ENS. NEAR $\bar{E}$ WHERE Ω (OR S) IS MAX

HERE: HOW WILL WALL MOVE TO MAX Ω?

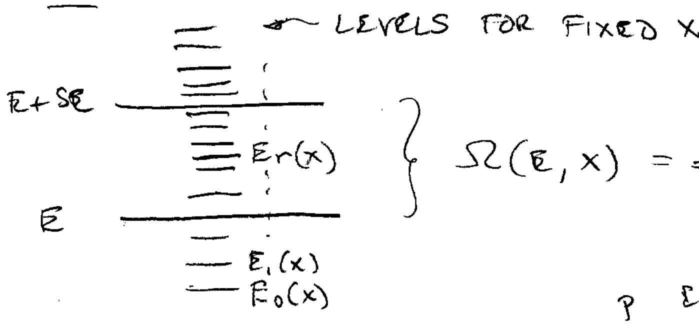
CP THERM INTS
- NEEDED TO KNOW HOW Ω CHGD w/ E
- EQUIL. WHEN RATE SAME $\Rightarrow T = T'$

NOW
- NEED TO KNOW HOW Ω CHGS w/ X_α

10/14

ASSUME 1 X FOR NOW

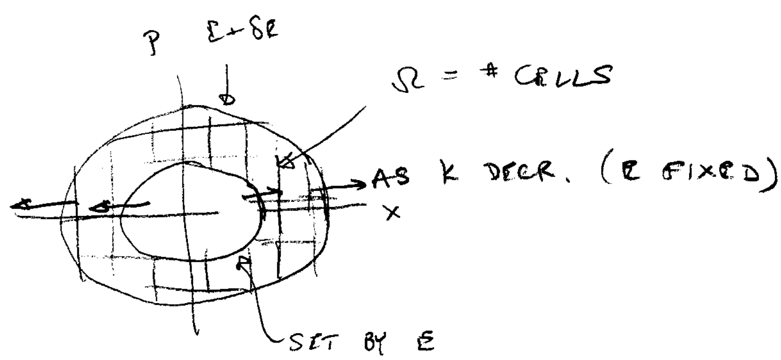
QM: E_r LEVELS ARE FNS OF X   possible energy levels for entire sys



$\Omega(E, X)$ = # MICROST. AT THIS E & X

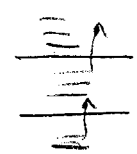
CLASSICAL (ex HARM OSC)

w/ SPRING CONST = EXT PARAM



(WILL USE QM CASE)

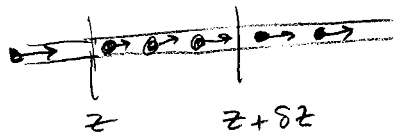
CHG X: $E_r(X)$ CHG DIFF'LY
- SOME INSIDE LEAVE
- " OUTSIDE ENTER



$\Rightarrow$ WANT NET CHG IN Ω = # INSIDE

COMMON ANALOGOUS PROBLEM: PARTICLE (OR FLUID) FLOW
– EASIER TO PICTURE

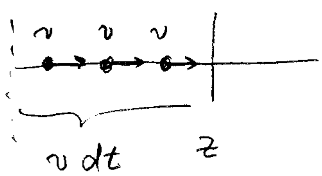
1D:



CALC CHG. IN DENSITY $\rho(z) \equiv \dfrac{N_{\text{INSIDE}}}{\delta z}$ AS FLOWS

TO GET RATE $\dfrac{d\rho}{dt} = \dfrac{dN_{\text{INS}}}{dt}\,\dfrac{1}{\delta z}$

1ST: CONSIDER RATE CROSS 1 PT.
2ND: COUNT (RATE IN) – (RATE OUT) AT z & $z+\delta z$



(1) IF ALL HAVE VEL v w/ UNIFORM DENS

RATE CROSS z

IN TIME dt, ALL IN LENGTH $v\,dt$ CROSS

$\Rightarrow dN = \#\text{ CROSSING} = \left(\dfrac{\#\text{ PARTS.}}{\text{LENGTH}}\right)\cdot\text{LENGTH} = \rho\, v\, dt$

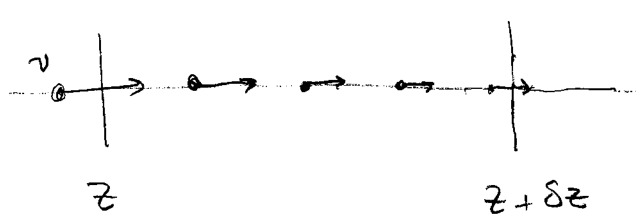
& ie CHG IN # ON RHS

$\Rightarrow$ RATE $\dfrac{dN}{dt} = \rho v = \dfrac{\#\text{ CROSS}}{\text{TIME}} \equiv$ FLUX

(SAME AT ALL z SO FAR)

(2) NOW ALLOW ρ TO DEP. ON v & z

$\rho_v(z) \equiv \dfrac{\#\text{ PARTS. w/ VEL } v \text{ AT } z}{\text{LENGTH}}$



} CAN HAVE PARTS. BUILD UP

ENTERING FROM LEFT IN dt:

(a) w/ VEL v: $\rho_v(z)\, v\, dt$

(b) w/ ALL v's: $\sum_v \rho_v(z)\, v\, dt$

could also be $\int dv$

LEAVING RIGHT:

$$\sum_v \rho_v(z+\delta z)\, v\, dt$$

CHG. INSIDE IN dt = # ENTER − # LEAVE

$$dN_{INS} = \left[\sum_v \rho_v(z) v - \sum_v \rho_v(z+\delta z) v\right] dt$$

(3) CAN SEE ρ WILL ALSO DEP. ON t ⇒ INCL AS VAR,

$$\frac{dN_{INS}}{dt} = \left[\sum_v \rho_v(z,t)\, v - \sum_v \rho_v(z+\delta z, t)\, v\right]$$

BACK TO OUR PROBLEM: DICTIONARY

PARTICLE LABEL $\longrightarrow$ r

$z \longrightarrow E_r$

$t \longrightarrow x$

$N_{INS}(z,t) \longrightarrow \Omega(E,x)$

$v = \frac{dz}{dt} \longrightarrow \frac{\partial E_r}{\partial x} \equiv -X_r$ GEN FORCE (ASSOC w/ r)

LET $\Omega_X(E,x) \equiv$ # STATES w/ E TO $E+\delta E$, X TO $X+\delta X$ } ie ORGANIZE STATES ACC. TO X VALUES

$$\rho_v(z,t) \longrightarrow \frac{\Omega_X(E,x)}{\delta E} \equiv \omega_X(E,x)$$ } DENS. OF STATES

18 ↦ 110 (28)

THEN

$$\frac{dN_{INS}}{dt} \rightarrow \frac{\partial \Omega(E,x)}{\partial x} = \sum_X \left[\frac{\Omega_X(E,x)}{\delta E}(-X) - \frac{\Omega_X(E+\delta E,x)}{\delta E}(-X) \right]$$

ENTER BOTT. LEAVE TOP

ASSUME QUASI-STATIC (CAN USE FUND POST)

$$\bar{X}(E,x) = \frac{\sum_X \Omega_X(E,x)\, X}{\Omega(E,x)}$$

PROB OF X HAVING PARTIC. VALUE $\propto$ # STATES w/ "

$$\Rightarrow \frac{\partial \Omega(E,x)}{\partial x} = \left[-\Omega(E,x)\bar{X}(E,x) + \Omega(E+\delta E,x)\bar{X}(E+\delta E,x) \right]\frac{1}{\delta E}$$

$$\sim \frac{\partial(\Omega \bar{X})}{\partial E} \quad \text{IF} \quad \delta E \ll E$$

$$= \frac{\partial \Omega}{\partial E}\bar{X} + \Omega \frac{\partial \bar{X}}{\partial E}$$

USING $\ln \Omega$:

$$\frac{\partial \ln \Omega}{\partial E} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial E}$$

$$\frac{\partial \ln \Omega}{\partial x} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial x}$$

REPLACE ABOVE w/ LHS

$$\Omega \frac{\partial \ln \Omega}{\partial x} = \Omega \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\equiv \beta} \bar{X} + \Omega \frac{\partial \bar{X}}{\partial E}$$

$$\boxed{\frac{\partial \ln \Omega}{\partial x} = \beta \bar{X} + \frac{\partial \bar{X}}{\partial E}}$$

TYPICAL MACRO SYSTEM:

$$\Omega \sim E^f \qquad \beta \bar{X} \sim \frac{f}{E} \bar{X} \quad \gg \quad \underbrace{\frac{\partial \bar{X}}{\partial E} \sim \frac{\bar{X}}{E}}$$

ROUGH EST FOR ORDER OF MAGN. (FOR WANT OF ADDITIONAL INFO

ex $f(x) = x^3$

$\frac{\partial f}{\partial x} = 3x^2$ vs $\frac{f}{x} = x^2$)

NOT BAD

MAIN RESULT FOR CH 3: (REPEAT EACH α)

$$\Rightarrow \boxed{\frac{\partial \ln \Omega (E, x_\alpha)}{\partial x_\alpha} = \beta \bar{X}_\alpha (E, x_\alpha)}$$

Q-S

IN GENERAL, COULD REPEAT EACH OF SEVERAL EXT. PARAMS

UP TO $\boxed{\frac{\partial \ln \Omega}{\partial E} \equiv \beta}$

(roughly like chain rule: $\frac{\partial \ln \Omega}{\partial x} \sim \frac{\partial \ln \Omega}{\partial E} \frac{\partial E}{\partial x}$)

NOTE: CONNECT CHGS IN $\ln \Omega$ w/ MEAS'BLE QTYS: T & $\bar{X}$ (like $\bar{p}$)

say (KNEW HOW $\ln \Omega$ VARIES IN GEN'L. WILL USE TO GET GEN'L EQUIL CONDITIONS)

MONATOMIC

EX **IDEAL GAS** (CLASSICAL)

- IF KNOW $\Omega(E, x_\alpha)$ CAN GIVE AVE FOR ALL MACRO VARS (IN EQUIL)
- " " SOMETHING ABOUT Ω, CAN OFTEN AT LEAST RELATE "

[mention that often E varies and have $\bar{E}$ here instead, but for macro sys., so sharp, it's almost same] (ie don't worry about putting $\bar{E}$ everywhere)

IDEAL GAS:

MOST USEFUL VARS: $\bar{E}$, V, T, $\bar{p}$, S (all related to $\Omega(E,V)$) (S is abstract but will see it's very useful; not really a property of a single sys., but for your sys. you can ask how big is the set it's a member of, or how random it is)

HAVE

$$\beta = \frac{\partial \ln \Omega}{\partial E} \qquad \bar{X}_\alpha = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial x_\alpha}$$

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

KNOW (since ignoring forces between)

(1) # STATES AVAIL. FOR EACH MOL. $\propto V$ (OBVIOUS) (we actually know more) { equiv. to each mol. equally likely anywhere from fund. post.

$$\Omega = V^N \chi(E)$$

"CHI"

recall:

$$\Omega_{IG} \propto \int_{SE} d^3x_1 \cdots d^3x_N \, d^3p_1 \cdots d^3p_N$$

$V^N \qquad \chi(E)$

THEN

$$\ln \Omega = N \ln V + \ln \chi(E)$$

$$\Rightarrow \quad \bar{p} = \frac{1}{\beta}\frac{N}{V} = \frac{NkT}{V}$$

$$\boxed{\bar{p}V = NkT}_{IG.}$$

IDEAL GAS LAW

{ How would this differ for diatomic IG?

OTHER VERSIONS:

IN DENSITY $n = N/V \Rightarrow \bar{p} = nkT$

IN MOLES $\nu \equiv N/N_a \Rightarrow \bar{p}V = \nu \underbrace{N_a k}_{\equiv R} T = \nu RT$ (GAS CONST)

$\Rightarrow$ **EQN OF STATE**: RELATES MACRO VARS

skip (sharply peaked $\to \bar{p}$ not very diff from p meas; 10^{-12} or so makes sense to talk singly about pressure in single system)

19 → '14

ALSO

$$\underset{\frac{1}{kT}}{\beta} = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial \ln \chi(E)}{\underbrace{\partial E}_{\text{FN OF } E \text{ ONLY}}}$$

$\Rightarrow \quad T = T(E) \quad$ OR $\quad \boxed{E = E(T)}_{IG}$

(CP TO INTERACTING MOLS: $E = E(T, V)$
SINCE SMALL $V \to$ CLOSER TOGETHER $\to$ E DROPS IF ATTRACTIVE)

CONTENT: $\boxed{\Omega \propto V^N}$ FOR IG } like magic how much follows from so little input
(for both relns)

(2) WE KNOW MORE ABOUT Ω

$$\Omega = \underset{\text{CONST}}{B} V^N E^{3N/2} \qquad (N \text{ LARGE; } \underline{\text{MONATOMIC}} \text{ IG})$$

(will see in HW that diatomic is slightly diff)

$$\underset{\frac{1}{kT}}{\beta} = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial}{\partial E}\left(\frac{3N}{2} \ln E\right) = \frac{3}{2}\frac{N}{E}$$

$$\Rightarrow \quad \boxed{E = \frac{3}{2} NkT}_{\text{MON IG}}$$

(RECALL EST: $kT \sim E/f$ HERE $f = 3N$ $\Rightarrow \frac{E}{3N} = \frac{1}{2} kT$ ✓)

$\Rightarrow$ CAN GIVE ALL QTYS LISTED FOR MON IG IF KNOW E & V:

$$T = \frac{2}{3}\frac{1}{Nk} E$$

$$\bar{p} = \frac{2}{3}\frac{E}{V}$$

} RECALL HW REIF 2.7
SAME FOR QM PART IN BOX

$$S = k \ln \Omega = k\left(N \ln V + \frac{3N}{2} \ln E\right) + \text{CONST}$$

{ WARNING:

- ASSUME HERE E KNOWN (W/IN δE) $\Rightarrow$ T HAS SINGLE VALUE (for ex)
- ONCE SYS IN THERMAL CONTACT, TAKES RANGE OF VALUES
  $\Rightarrow$ SHOULD USE $\bar{E}$ (NOT E)
- MACRO SYS: $P(E)$ SHARP (IN EQUIL)
  $\Rightarrow$ KNOWING $\bar{E}$ ~ SAME AS KNOWING E
  $\Rightarrow$ CAN REPLACE E W/ $\bar{E}$ IN ABOVE RELNS

} ONLY NEED TO DISTINGUISH WHEN PREDICT $\Delta^* E$, FOR EX