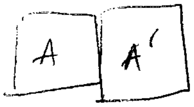
THERMAL + MECHANICAL INTERACTIONS:

quick; not much new here



ISOLATED

- DEF'D BY E, x_α & $E', x'_{\alpha'}$

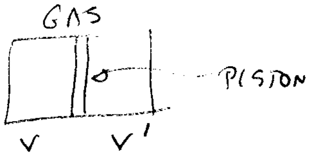
  $\uparrow \alpha = 1 \cdots n$

- PUT INTO CONTACT ⇒ ALLOW BOTH Q & CHG. IN x_α

main pt here { - $E', x'_{\alpha'}$ WILL DEPEND ON E, x_α

{ MECH. CONTACT MEANS x_α & $x'_{\alpha'}$ TIED TOGETHER IN SOME WAY

ex



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

$V + V' = V^{(0)}$

⇒ CAN USE E, x_α TO DESCRIBE ENTIRE SYS

⇒ GET $P(E, x_\alpha)$

ALLOW PISTON TO MOVE: DON'T CONTROL V NOW
WILL VARY IN ENS.

EXPECT $\Omega_{TOT}(E, x_\alpha)$ HAS SHARP PEAK AT $\tilde{E}, \tilde{x}_\alpha$

$\Rightarrow \quad \bar{E}, \bar{x}_\alpha = \tilde{E}, \tilde{x}_\alpha$

ex: $V = 0$ ⇒ NO STATES

Ω GROWS RAPIDLY AS V INCR (AS $\sim V^N$ FOR IG); Ω' DECR

SHARP PEAK FOR SOME $\tilde{V}$

29

⇒ NEW EQUIL AT $\tilde{E}, \tilde{x}_\alpha$, $\tilde{E}', \tilde{x}'_{\alpha'}$

ex $\tilde{E}$, $E^{(0)} - \tilde{E}$

$\tilde{V}$, $V^{(0)} - \tilde{V}$

TO DESCRIBE STATISTICALLY*: $P(E, x_\alpha) \propto \Omega_{TOT}(E, x_\alpha)$

WANT (I) HOW DOES $\ln \Omega_{TOT}(E, x_\alpha)$ CHANGE? (as let systems affect each other

(II) NEW EQUIL. CONDS

(everything follows from Ω)

(skip plot)

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

(I) CONSIDER CHG IN Ω FROM
INFINIT. CHGS IN E & x_α

$\Rightarrow$ ALLOWS US TO USE FUND. POST

(CP GEN'L INTS: AS SYS IN CONTACT FIND
NEW EQUIL W/ $\bar{E}$ AT $\tilde{E}$, x_α AT $\tilde{x}_\alpha$
NOT IN EQUIL, TAKES TIME TO FIND,
LIMITED TO DISCUSSING INIT & FINAL STATES ONLY)

$\Rightarrow$ MUST STAY NEAR EQUIL:

- SMALL $\text{đ}Q$ → MUST BE CLOSE IN T
- SMALL dx_α → " " " X_α

THEN PEAK AT $\bar{E}, \bar{x}_\alpha = \tilde{E}, \tilde{x}_\alpha$ CHGS TO NEW PEAK AT

$$\left.\begin{aligned} \bar{E} &\to \bar{E} + d\bar{E} \\ \bar{x}_\alpha &\to \bar{x}_\alpha + d\bar{x}_\alpha \end{aligned}\right\}$$

SMALL ON MACRO SCALE
BUT >> SIZE OF FLUCTS
(ie $\Delta^* E$, $\Delta^* x_\alpha$)

CAN USE Q-S RESULTS: FOCUS ON Ω AT PEAK

$$\underbrace{d \ln \Omega(\bar{E}, \bar{x}_\alpha)}_{} = \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\beta} d\bar{E} + \sum_\alpha \underbrace{\frac{\partial \ln \Omega}{\partial x_\alpha}}_{\beta \bar{X}_\alpha} d\bar{x}_\alpha$$

} just chain rule

(SINCE Q-S)

RECALL ALMOST ALL
OF $\ln\Omega$ COMES FROM
AMT AT PEAK

$$= \beta\left(d\bar{E} + \sum_\alpha \bar{X}_\alpha dx_\alpha\right)$$

$$\overbrace{}^{\frac{1}{k} dS} = \beta\left(\underbrace{d\bar{E} + \text{đ}W}_{\text{đ}Q}\right)$$

(Q, W def'd as ave)

$$\Rightarrow \boxed{dS = \frac{\text{đ}Q}{T}}_{QS}$$

(SMALL CHGS IN $\bar{E}$ & $\bar{X}_\alpha$)
(for any amt of W in any form)

3.18.2

Q-S CHGS OF ENTROPY:

(1) EXACT DIFF = DIFF IN FN S FOR 2 MACROSTATES

$$dS = \frac{\bar{d}Q}{T} \qquad (dS \text{ IS, } \bar{d}Q \text{ IS NOT})$$

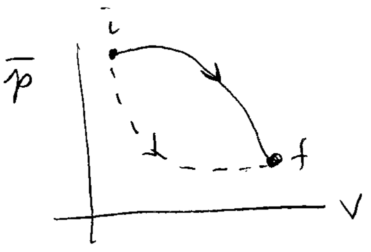
(2) FINITE DIFF

$$S_f - S_i = \underset{\text{HARD TO MEASURE}}{\int_i^f dS} = \underset{\text{EASY}}{\int_i^f \frac{\bar{d}Q}{T}}$$

⇒ INDEP OF HOW GO FROM i TO f (ANY SYSTEM) (IF Q-S)

⇒ ALREADY HAVE $\bar{E}_f - \bar{E}_i = \int_i^f [-\bar{d}W + \bar{d}Q]$

ex



$\int_i^f \bar{d}Q = Q$ DEP ON PATH

(RECALL W = AREA UNDER CURVE
SAME $\Delta\bar{E} = -W + Q$
⇒ HIGHER PATH w/ BIG W ⇒ BIG Q)

$\int_i^f \frac{\bar{d}Q}{T}$ DOES NOT

⇒ IF DIDN'T KNOW ABOUT S, COULD STUMBLE ON
IF OBSERVED THIS (ie $\int \frac{\bar{d}Q}{T}$ IND. OF PATH ⇒ MUST BE
SOME FN OF SYS S OTHER THAN $\bar{E}$
w/ $\Delta S = \int \frac{\bar{d}Q}{T}$)

10-?

WHY IS THIS AMAZING?

- NO MATTER HOW MANY DIFF MECH. THINGS DO TO SYS AS LONG AS DIV. $\bar{d}Q$ BY T AND SUM UP DURING PROCESS, ALWAYS GET SAME ANS. (IF QS); COMPLETELY INDIFF. TO $\bar{d}W$
- CAN TRACK CHGS IN VERY ABSTRACT QTY $S = \ln(\#\text{ AVAIL STATES})$ = SIZE OF SET OUR SYS IS ELEM. OF, JUST BY TRACKING Q & T
  can meas how it chgs, but unlike $\bar{E}$, can't see it
- SURPRISING NEW STATE FN (ie FN OF MACRO PARAMS) LIKE $\bar{E}$ BUT DIFFERENT

WHY IS THIS USEFUL?

- IN STATMECH, Ω (AND S) DETERMINE PROBS VIA FUND POST; THIS IS EVERYTHING
- (WILL SEE) JUST HAVING INDEP. FN OF SYS S (LIKE E BUT DIFF.) GIVES MANY USEFUL RELNS (CH 5)
- USEFUL EVEN IF DON'T GO FROM $i \to f$ QS'ly

$\Rightarrow$ I CAN CP. $\Delta\bar{E}$ & ΔS IN i (IN EQUIL) TO f (IN EQ) EVEN IF DON'T GO Q-S

$\Rightarrow$ COMPUTE USING FICTIONAL BUT Q-S PROCESS

(WILL USE THIS OFTEN; I'LL POINT OUT)

WHY IS THIS PLAUSIBLE?

- Q IS EXCH OF $\bar{E}$ NOT TRACKING (ie NOT VIA W)

  $\Rightarrow$ NOT TRACKING IS WHAT GIVES $\Omega \neq 1$
- T RELATED TO CHG IN $\ln\Omega$ $(= S/k)$ VS E:

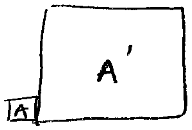
$$\beta = \frac{1}{kT} = \frac{\partial \ln\Omega}{\partial E}$$

$$\frac{đQ}{T} = đQ\,\frac{\partial(k\ln\Omega)}{\partial E} = đQ \cdot \frac{\partial S}{\partial E}$$

(ie TRACKS HOW THIS Q MIGHT AFFECT S)

10/30/02

SPECIAL CASES:



$A' \gg A$ (ie $f' \gg f$)

(1) HEAT RESERVOIR: (BATH)

(a) $T' \sim$ CONST $\quad T \to T'$

(b) $Q' \ll \bar{E}'$ → SMALL EFFECT ON A'; TREAT Q-S

$$\Delta S' = \int \frac{\bar{d}Q'}{T'} \cong \frac{1}{T'}\int \bar{d}Q' = \frac{Q'}{T'} = \frac{-Q}{T'}$$

{BUT WILL SEE IN HW: $\Delta S > \frac{Q}{T'}$, $\Rightarrow \Delta S_{TOT} > 0$} how can I raise T a finite amt but Q-S ?

30

(2) INSULATED:

$$\bar{d}Q = 0 \qquad \text{(ADIABATIC)}$$

$$\Rightarrow dS = 0$$

FINITE (Q-S) CHG IN $x_\alpha \Rightarrow \Delta S = 0$

⇒ Q-S WORK CHGS $\bar{E}$, LEAVES # ACCES. STATES FIXED

⇒ REVERSIBLE ⇒ NO $\Delta\Omega$, EQ. LIKELY TO GO EITHER DIRECTION
(ex: expanding piston and grains of sand ⇒ cf Van Ness; would run in either dir. w/ equal likelihood)

IN GENERAL:

NON Q-S PROCESS: $\Delta S > 0$

NOT REVERSIBLE

will come back to this

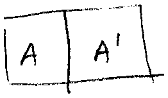
(ex: remove wall ⇒ will need to compress and then remove heat to get back to original S) f.8

3.20

(II) GEN. EQUIL CONDS

AT EQUIL: BOTH E, x_α VARY $\Rightarrow$ MAXIMIZE Ω_{TOT} FOR BOTH

ex $\quad x_\alpha = V$



$E^{(0)} = E + E'$ $\quad V^{(0)} = V + V'$

(IN GEN'L, CONNECTIONS AMONG x_α COMPLICATED)

$$\Omega_{TOT}(E, V) = \Omega(E,V)\,\Omega'(E',V')$$

$= \#$ STATES AT E, V IN A

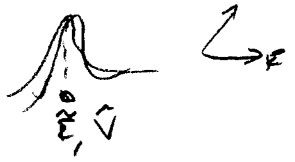
$$\ln \Omega_{TOT} = \ln \Omega + \ln \Omega'$$

$$S_{TOT} = S + S'$$

FIND PEAK AT $E = \tilde{E}$ $\quad V = \tilde{V}$

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

~



$$\frac{\partial \ln \Omega_{TOT}}{\partial E} = 0 = \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\beta} + \underbrace{\frac{\partial \ln \Omega'}{\partial E'}}_{\beta'} \underbrace{\frac{\partial E'}{\partial E}}_{-1}$$

$\Rightarrow \boxed{\beta = \beta'}$ $\quad$ THERMAL EQUIL

$$\frac{\partial \ln \Omega_{TOT}}{\partial V} = 0 = \underbrace{\frac{\partial \ln \Omega}{\partial V}}_{\beta \bar{p}} + \underbrace{\frac{\partial \ln \Omega'}{\partial V'}}_{\beta' \bar{p}'} \underbrace{\frac{\partial V'}{\partial V}}_{-1} \qquad \text{(this ex)}$$

USING $\beta = \beta'$ $\Rightarrow$ $\boxed{\bar{p} = \bar{p}'}$ $\quad$ MECH. EQUIL

AT $\quad E = \tilde{E} = \bar{E}$
$\quad\quad V = \tilde{V} = \bar{V}$

(note - don't expect p balanced exactly in any individ sys $\Rightarrow$ wiggling)

SURPRISING: $\bar{p} = \bar{p}'$ FROM COUNTING STATES.

NOTE: SPS $\bar{p}' > \bar{p}$ (BUT $\beta = \beta'$) $\Rightarrow$ $\dfrac{\partial \ln \Omega'}{\partial V'} > \dfrac{\partial \ln \Omega}{\partial V}$

$\Rightarrow$ RATE $\ln \Omega'$ GETS AVAIL STATES INTO E' TO $E' + \delta E'$ GREATER THAN FOR Ω $\Rightarrow$ MORE STATES IF V' INCR, V DECR

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NOTE :

- CONDITIONS HOLD FOR SYSTEMS IN EQUILIBRIUM, NO MATTER HOW GOT THERE ; ie EITHER Q-S'ly OR NOT.

GENERAL PROPERTIES OF S:

SHAPE OF $S(E)$:

HAVE (USUALLY) $\beta = \dfrac{\partial \ln \Omega(E)}{\partial E} > 0 \Rightarrow T > 0$

$-\lambda = \dfrac{\partial^2 \ln \Omega}{\partial E^2} < 0$ ELSE NO MAX, NO EQUIL., WHEN PUT IN CONTACT w/ ANOTHER SYS

$$\Rightarrow \boxed{\frac{\partial S}{\partial E} > 0 \qquad \frac{\partial^2 S}{\partial E^2} < 0}$$

ALSO, AT $E = E_0$ (GND ST)

$\Omega(E_0) = 1 \qquad \ln \Omega(E_0) = 0$

$$\Rightarrow \boxed{S(E_0) = 0}$$

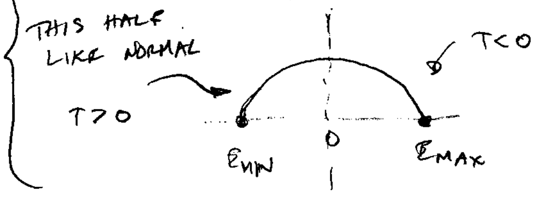
NOTE: USE QM FOR LOW E

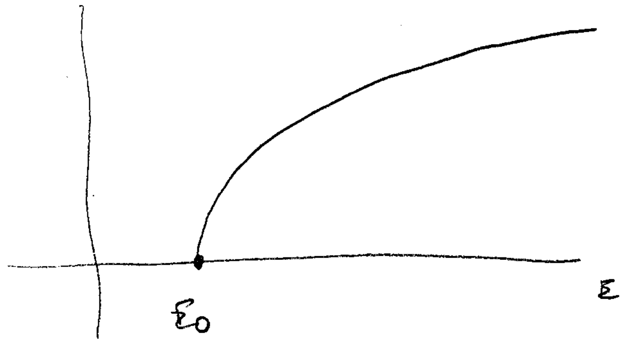
(cp CLASSICAL: WRONG → ex IG $\Omega \propto V^N$ EVEN FOR $E \sim 0$) (but $S \sim kN \ln V$ indep of type of gas) {skip

SHAPE:

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

EXCEPTION: SPIN SYS





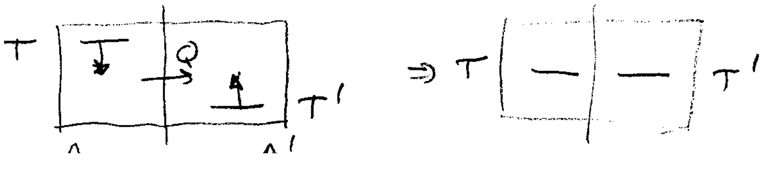
slope > 0
curvature < 0

ALSO: $-\lambda \equiv \dfrac{\partial \beta}{\partial E} < 0 \Rightarrow \dfrac{\partial \beta}{\partial E} = \dfrac{\partial}{\partial E}\left(\dfrac{1}{kT}\right) = -\dfrac{1}{kT^2}\dfrac{\partial T}{\partial E}$

$\Rightarrow \boxed{\dfrac{\partial T}{\partial E} > 0} \Rightarrow$ T INCR w/ E

SEE AGAIN HOW $\lambda > 0$ NECESS. TO REACH EQUIL

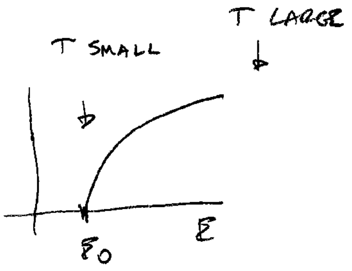
APPROACH TO EQUIL:



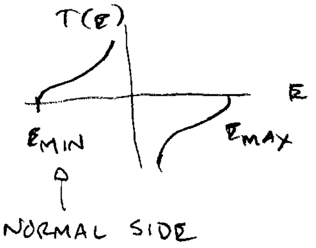
T vs S & E

$$\beta \equiv \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E} = \frac{1}{k}\frac{\partial S}{\partial E}$$

$$\Rightarrow \boxed{T = \left(\frac{\partial S}{\partial E}\right)^{-1}} = (\text{SLOPE})^{-1} \text{ OF}$$



(cp SPIN SYS:



)

EST:

LARGE E: $\Omega \sim E^f$ $\quad S \sim kf \ln E$ $\quad \frac{\partial S}{\partial E} \sim \frac{kf}{E}$ $\Rightarrow kT \sim E/f$ (AS BEFORE)

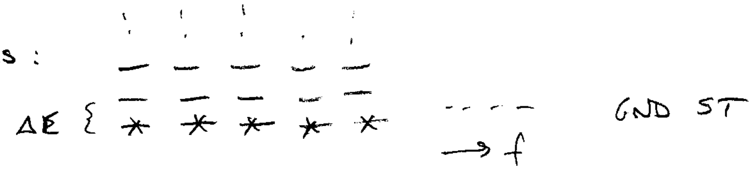
VERY SMALL E: $E \sim E_0$ (GND ST)

$\Rightarrow$ NEED TO TREAT VIA QM : $\Delta E \sim E$ (NOT ~ CONTIN.)

$\Rightarrow$ cf COUNTING ON HW

ex f DISTING. PARTS. w/ ΔE = EXCITE E FOR 1 PART

1 PART LEVELS:



$E = E_0$ $\quad \Omega = 1$ $\quad S = 0$

$E = E_0 + \Delta E$ $\quad \Omega = f$ $\quad S = k \ln f$ $\quad \frac{\partial S}{\partial E} \sim \frac{\Delta S}{\Delta E} \sim \frac{k \ln f}{\Delta E}$

$kT \sim \frac{\Delta E}{\ln f}$ $\quad \ln f \sim O(1)$ (55 FOR 10^{24})

$\Delta E \sim$ TINY (ex H-ATOM IN 1-LITER BOX:
(cf NOTES)
$kT \sim 10^{-40}$ J $\quad T \sim 10^{-24}$ °K)
essentially 0

$$\Rightarrow \boxed{T \rightarrow 0^+ \text{ AS } E \rightarrow E_0,\ S \rightarrow 0}$$

skip in '14
and mention when
do 3rd law

PRACTICAL LIMIT FOR S AS $E \to E_0$, $T \to 0$

USUALLY: $E \to E_0 \quad \Omega \to 1 \quad S \to 0$

EXCEPTION: DEGENERATE GND ST (>1 ST. w/ E_0)

COMMON EXAMPLE:

- N ATOMS w/ SPIN-S NUCLEI
- IN ATOMIC GND ST, EACH NUCLEUS HAS CHOICES

  $S_z = -s\hbar,\ (-s+1)\hbar,\ \cdots\ (s-1)\hbar,\ s\hbar$

  $\Rightarrow 2s+1$
- CHOICE HAS (ALMOST) NO EFFECT ON ATOM
- TOTAL POSSIBLE: $(2s+1)^N$

$$\Rightarrow \quad E \to E_0 \qquad \Omega \to (2s+1)^N \qquad S \to kN \ln(2s+1) \equiv S_0$$

NOTE: SAME FOR SOLID, LIQUID, ANY $\bar{p}$, V, ---

(ONLY DEP. ON TYPE & # OF ATOMS, NOT STATE OF SYS)

TECHNICAL POINT:

- NOT EXACTLY DEGENERATE: SMALL DIFFS ("SPLITTINGS") DUE TO SPIN INT. w/ $\vec{B}$ (FROM e^-'s, OTHER NUCLEI, ETC)

$$\Rightarrow \quad E_0 \ \text{——} \ \longrightarrow \ \equiv \Big\}(2s+1)^N \text{ CLOSE LEVELS}$$

- INCLUDE IN Ω (& S) ALL w/in δE
- δE USUALLY $\propto E$ (ie SOME %)

  $\Rightarrow$ δE < SPLITTINGS (SO DON'T COUNT ALL)

  REQUIRES VERY SMALL E $\Longleftrightarrow$ LOW T

TYPICAL SYS: $T \sim 0.1\,^\circ K$

$\Rightarrow$ IN ATOMIC GND ST — but enough E bouncing around that splittings ~ neglig.

$S \to S_0 = kN \ln(2s+1)$ — from nucl. spins

$T \sim 10^{-6}\,^\circ K$ — splittings no longer negl.

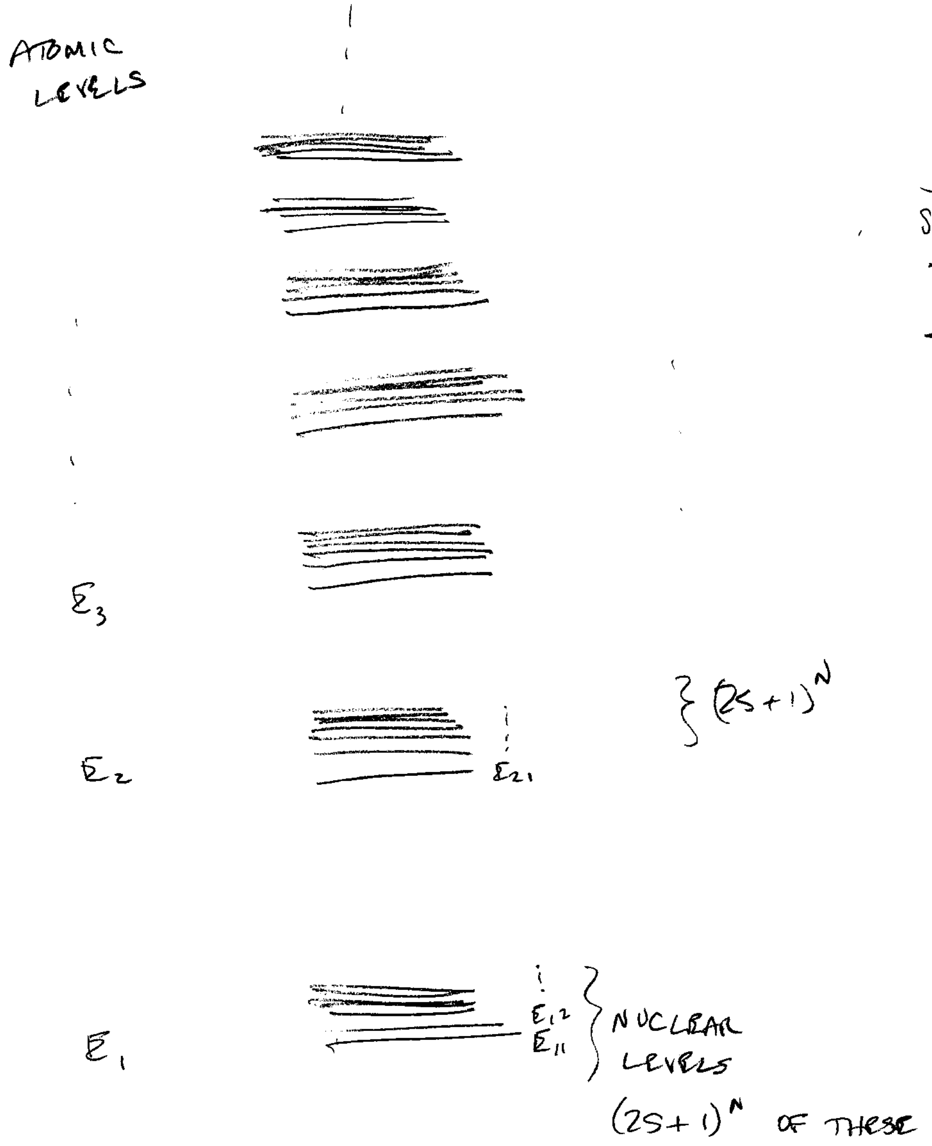
$\Rightarrow$ IN EXACT GND ST — lowest " " state

$S \to 0$

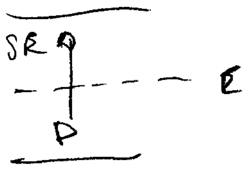
(for notes)

IN PICTURES:

$$\boxed{\Omega = \Omega_{ATOMIC}(E) \times \Omega_{NUCL\ SPIN}(E)}$$

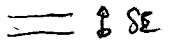


LARGE E



$$\Omega = \Omega_{ATOMIC}(E) \cdot \underbrace{(2S+1)^N}_{\Omega_{NUCL\ SP}}$$

Can think of δE as ≈ Δ*E, where $\bar{E}$ & Δ*E are determined by being in contact w/ some reservoir. For large E, there's too much E sloshing around / Δ*E is too big to restrict to single spin state; generally it will incl lots of atomic levels, each w/ 2S+1 spin state



SMALL E

$$\Omega = \underbrace{1}_{\Omega_{ATOMIC}} \cdot \Omega_{NUCL\ SPIN}(E)$$

do 3rd law 1st

3.24

MORE THERMO LAWS

FROM OBSERV, BEFORE STATISTICAL DESCR.

- NOT ALL BELIEVED IN ATOMS
- GETTING AT S WAS SUBTLE; COULD FIND VIA INDEP. OF PATH FOR $\int \frac{\text{đ}Q}{T}$; FIRST VIA CARNOT / HEAT ENGINES

2ND LAW

(a) THERM. ISOLATED (ie INSULATED) SYS FROM ONE MACRO STATE TO ANOTHER:

$$\Delta S \geq 0 \qquad (\text{EVEN IF } W \neq 0)$$

(b) NOT INSULATED BUT Q-S:

$$dS = \frac{\text{đ}Q}{T} \qquad (=0 \text{ IF INSUL.})$$

(applies to both mech. & thermal ints)

(c) NOT INSUL OR QS:

$$dS > \frac{\text{đ}Q}{T}$$

(OR SIMPLY: $dS \geq \frac{\text{đ}Q}{T}$ w/ = IF QS)

will discuss further

3RD LAW

AS $T \to 0^+$ $\quad S \to S_0$ w/ S_0 INDEP OF PARAMS OF SYS

(S_0 OFTEN 0 IN PRINCIPLE, CONST IN PRACTICE)

(If it's $S_0 \neq 0$, it's because it's something like nuclear spins, and can't get to it; can't lower E avail to restrict enough to limit ⇒ so doesn't matter what you're doing to sys.: V, $\bar{p}$, ...)

3.12.4

maybe just do the classical case

MORE ON

2^{ND} LAW:

PROVED (b) : Q-S ⇒ $dS = \frac{đQ}{T}$

ARGUE OTHER CASES: (this is a description, not a proof; don't know of proof exists; maybe proof by exhaustion: ** for specific sys, can check by cp to Q-S process for same S_i to S_f)

** really falls outside scope of stat mech since can't use fund post

(a) COMPLETELY ISOLATED (no Q or W)

$\Delta S \geq 0$ ONLY MEANS IF LEAVE SYS. ALONE, WILL MOVE FROM LESS LIKELY TO MORE LIKELY CONFIGS

ex: after remove wall 

ie naturally move from element of small set to " " large. For macro amts of ΔS (recall has units of E) this corresp. to much bigger set

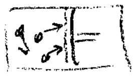
(c) $dS > \frac{đQ}{T}$ IF NON-QS:

SHOW IN HW R3.4 FOR NON-QS Q; WILL FOCUS ON W

(1) S GROWS w/ E

(2) W BY SYS IS MAX w/ ΔX WHEN GO w/ $\bar{X}$ IF Q-S:

ex CLASS. GAS ⇒ RELAX PISTON



QS: SLOW, BALANCE $\vec{p}$, ALL PARTICLES HAVE TIME TO BOUNCE, DO WORK

FASTER: CAN'T CATCH UP, $\vec{p}$ ON WALL LESS, LESS $\bar{p}$ TRANSF. DURING COLL., LESS W

EXTREME: REMOVE WALL ⇒ NO W

(ALSO, CF VAN NESS: GRAINS OF SAND ON PISTON)

(i) QS: MAX W, BIGGEST E LOSS, LEAST FINAL S; ALSO KNOW $dS = \frac{đQ}{T}$

⇒ (ii) NON-QS: $dS > \frac{đQ}{T}$ (WILL HAVE GREATER FINAL S)

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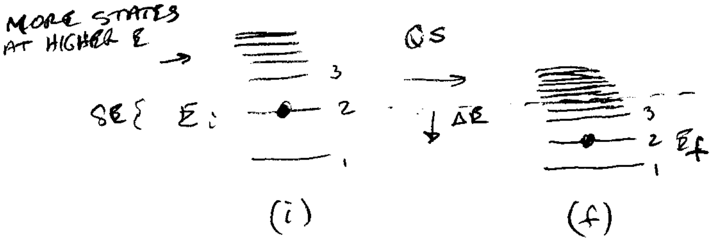
QM SYS:

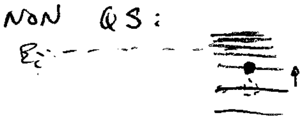
SINGLE SYSTEM



QS: E LEVELS DROP, BUT SYS STAYS IN SAME STATE (CAN'T MAKE TRANSITION: CF STURGE: NEED INT. w/ LT (FOR EX) w/ $\hbar\omega = \Delta E$ FOR TRANS, BUT SLOW ⇒ $\omega = 0$.)

(all work goes into chging levels; none left to cause a trans. dn or up)

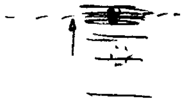
NON QS:



(f)

CAN JUMP UP AS LEVELS DROP ⇒ LESS ΔE, LESS W BY SYS

EXTREME: DROP LEVELS SUDDENLY (REMOVE WALL FOR PART. IN BOX)



$E_f = E_i$ $\Delta E = 0$

STAYS PUT AS LEVELS DROP (from E cons.)

NOTE: # STATES AVAIL LARGER

ENS: TRANSITIONS OCCUR, BUT IN EQUIL, # IN EACH r FIXED; SAME (ON AVE) AS IF ALL STAYED PUT

(3) REVERSE: W INTO SYS IS <u>MIN</u> IF Q-S

<u>ex</u> GAS:

EXPANDING: CAN AVOID CONTACT BY MOVING FASTER

CONTRACTING FAST REQUIRES MORE $\vec{F}$, GREATER W

GENTLEST = Q-S ⇒ MIN W ⇒ LEAST FINAL E IN SYS

QM: ex PART. IN BOX

EXPAND. QUICKLY ⇒ CAN LEAVE WFN INTACT

STAY AT SAME E WHILE LEVELS DROP

this is esp. obvious for gnd st: very best can do is stay in new gnd st; anything else requires transition & extra E

CONTRACT:

ADD E, FORCE WFNS TO CONTRACT

Q-S MIN W: STATE RIDES LEVEL BACK UP
(know this puts in just enough E to allow this)

NON Q-S : STATE JUMPS & RIDES HIGHER LEVEL UP

putting in E via work → E has to go up

(4) BOTH CASES:

NON-Q-S LEAVES MORE E IN SYS

Q-S: $dS = \frac{đQ}{T}$

⇒ NON-QS: $dS > \frac{đQ}{T}$

FROM M.D. STURGE 2003

4.10 Adiabatic Processes

The above reasoning—in particular, the derivation of Equation (4.13) and the consequent identification of $T\,dS$ with $đQ$ in a reversible process—is somewhat abstract, and we will now consider how it applies to the system of spin 1/2 nuclear magnets discussed in Chapter 3. In particular, we show for this model that a process that is *adiabatic* in the quantum mechanical sense (which will be explained) is necessarily isentropic.

Consider first a single isolated spin in a magnetic field B, in a particular state (say, spin up), with energy $-\mu B$. Now we *slowly* change B. In order to produce a transition (a *spin flip*) to the spin down state, whose energy is $+\mu B$, quantum mechanics tells us that we need a component of the field oscillating at the frequency corresponding to the energy separation of the states; that is, $\frac{2\mu B}{h}$. If B were to change rapidly, it could have a Fourier component at this frequency, but we will assume that B changes sufficiently slowly that no such high frequency field is present. Then the spin must stay in whatever state it began in, even though the energy of this state is changing. The energy needed is supplied (or taken up) by the electromagnetic field. Such a slow change, in which the occupation of quantum states does not change, is called an *adiabatic* change.

Now suppose that we have a collection of spins isolated from its surroundings. Although in our model we neglected the interaction between them, the spins must interact weakly if they are to come into equilibrium with each other. The interaction occurs because the motion of one spin in the field generates a high frequency magnetic field of just the right frequency to cause a neighboring spin to flip; this spin-spin interaction ensures that the whole assemblage of spins reaches its equilibrium condition of maximum Ω. However, the quantum mechanics of this interaction tells us that if one spin flips $\uparrow$ to $\downarrow$, the other has to flip from $\downarrow$ to $\uparrow$ (see Figure 4.5), so that the total spin is conserved. Although there is a change of microstate, the macrostate does not change, so that Ω (and hence S) does not change. While this is a very specific model, it illustrates the general result, which we justify in Chapter 5, that an adiabatic change is isentropic.

$$\uparrow\downarrow\ \Rightarrow\ \downarrow\uparrow$$

Figure 4.5. Mutual spin flip, conserving total spin.

In general, a process is adiabatic in the quantum mechanical sense if it does not change the average occupancy of the quantum states. Ω is unchanged, so that such a process does not change the entropy and is called an isentropic process. An adiabatic process in this sense is always possible in principle. Here we have shown this for a spin system, which has discrete energy levels; the case of continuous levels, as in a gas, will be dealt with later (see Example 9.2).

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[11] See L. R. G. Treloar, *Physics of Rubber Elasticity* (Oxford University Press, 1958) for a fuller treatment.