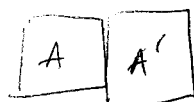


THERMAL + MECHANICAL INTERACTIONS:

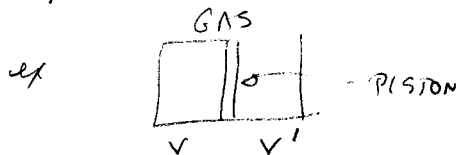


ISOLATED

- DEF'D BY $E, X_\alpha \} E', X'_\alpha$
 $\uparrow \alpha=1 \dots n$

- PUT INTO CONTACT \Rightarrow ALLOW BOTH Q & CHG. IN X_α

- E', X'_α WILL DEPEND ON E, X_α } MECH. CONTACT MEANS $X_\alpha \neq X'_\alpha$ TIED TOGETHER IN SOME WAY



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

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

\Rightarrow CAN USE E, X_α TO DESCRIBE ENTIRE SYS
 \Rightarrow 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 $\tilde{E}, \tilde{X}_\alpha$
 $\Rightarrow \bar{E}, \bar{X}_\alpha = \tilde{E}, \tilde{X}_\alpha$

ex: $V=0 \Rightarrow$ NO STATES

Ω GROWS RAPIDLY AS V INCR (AS $\sim V^N$ FOR IG); Ω' DEOR
 SHARP PEAK FOR SOME \tilde{V}

\Rightarrow 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 $\frac{\partial \ln \Omega}{\partial E} = \beta$ $\frac{\partial \ln \Omega}{\partial X_\alpha} = \beta \bar{X}_\alpha$

fixed;
not much
new here

main
pt
here

29
+

↓

(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}_α
 NOT IN EQUIL, TAKES TIME TO FIND,
 LIMITED TO DISCUSSING INIT & FINAL STATES ONLY)

\Rightarrow MUST STAY NEAR EQUIL:

- SMALL $dQ \rightarrow$ MUST BE CLOSE IN T

- SMALL $dX_\alpha \rightarrow$ " " " X_α

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

$$\begin{aligned} \bar{E} &\rightarrow \bar{E} + d\bar{E} \\ \bar{X}_\alpha &\rightarrow \bar{X}_\alpha + d\bar{X}_\alpha \end{aligned} \left. \vphantom{\begin{aligned} \bar{E} &\rightarrow \bar{E} + d\bar{E} \\ \bar{X}_\alpha &\rightarrow \bar{X}_\alpha + d\bar{X}_\alpha \end{aligned}} \right\} \begin{array}{l} \text{SMALL ON MACRO SCALE} \\ \text{BUT } \gg \text{ SIZE OF FLUCTS} \\ \text{(ie } \Delta^*E, \Delta^*X_\alpha) \end{array}$$

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

$$d \ln \Omega(\bar{E}, \bar{X}_\alpha) = \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\beta} d\bar{E} + \sum_{\alpha} \underbrace{\frac{\partial \ln \Omega}{\partial X_\alpha}}_{\beta X_\alpha} d\bar{X}_\alpha \quad \left. \vphantom{\frac{\partial \ln \Omega}{\partial X_\alpha}} \right\} \begin{array}{l} \text{just} \\ \text{chain rule} \end{array}$$

RECALL ALMOST ALL
 OF $\ln \Omega$ COMES FROM
 AMT AT PEAK (SINCE Q-S)

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

$$\frac{1}{k} dS = \underbrace{\beta (d\bar{E} + \sum_{\alpha} \bar{X}_\alpha d\bar{X}_\alpha)}_{dQ} \quad (\text{Q, W def'd as ax})$$

$$\Rightarrow \boxed{dS = \frac{dQ}{T}} \quad \text{QS (SMALL CHGS IN } \bar{E} \text{ \& } \bar{X}_\alpha)$$

(for any amt of W in any form)

Q-S CHGS OF ENTROPY:

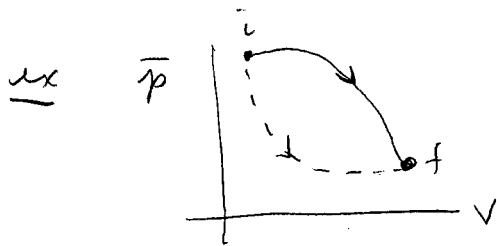
(1) EXACT DIFF = DIFF IN FN S FOR 2 MACROSTATES

$$dS = \frac{\delta Q}{T} \quad (dS \text{ IS, } \delta Q \text{ IS NOT})$$

(2) FINITE DIFF

$$S_f - S_i = \int_i^f dS = \int_i^f \frac{\delta Q}{T}$$

\uparrow HARD TO MEASURE \uparrow EASY

 \Rightarrow INDEP OF HOW GO FROM i TO f (ANY SYSTEM) (IF Q-S) \Rightarrow ALREADY HAVE $\bar{E}_f - \bar{E}_i = \int_i^f [-\delta W + \delta Q]$ 

$$\int_i^f \delta Q = Q \text{ DEP ON PATH}$$

(RECALL $W =$ AREA UNDER CURVE)

$$\text{SAME } \Delta E = -W + Q$$

 \Rightarrow HIGHER PATH \wedge BIG $W \Rightarrow$ BIG Q

$$\int_i^f \frac{\delta Q}{T} \text{ DOES NOT}$$

\Rightarrow IF DIDN'T KNOW ABOUT S , COULD STUMBLE ON
IF OBSERVED THIS (i.e. $\int \frac{\delta Q}{T}$ IND. OF PATH \Rightarrow MUST BE
SOME FN OF SYS S OTHER THAN \bar{E}
 $\wedge \Delta S = \int \frac{\delta Q}{T}$)

WHY IS THIS AMAZING?

- NO MATTER HOW MANY DIFF MECH. THINGS DO TO SYS AS LONG AS DIV. δQ BY T AND SUM UP DURING PROCESS, ALWAYS GET SAME ANS. (IF Q-S); COMPLETELY INDIFF. TO δW
- CAN TRACK CHGS IN VERY ABSTRACT QTY $S = \ln(\# \text{ AVAIL STATES})$
= SIZE OF SET OUR SYS IS ELEM. OF, JUST BY TRACKING $Q \div T$

WHY IS THIS USEFUL?

- IN STATMECH, \mathcal{R} (AND S) DETERMINE PROBS VIA FUND POST; THIS IS EVERYTHING
- (WILL SEE) JUST HAVING INDEP. FN OF SYS S (LIKE \mathcal{E} BUT DIFF.) GIVES MANY USEFUL RELNS (CH 5)
- USEFUL EVEN IF DON'T GO FROM $i \rightarrow f$ Q-S'ly
 \Rightarrow I CAN CP. $\Delta \bar{\mathcal{E}} \stackrel{?}{\approx} \Delta S$ 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 $\bar{\mathcal{E}}$ NOT TRACKING (i.e. NOT VIA W)
 \Rightarrow NOT TRACKING IS WHAT GIVES $\mathcal{R} \neq 1$
- T RELATED TO CHG IN $\ln \mathcal{R}$ ($= S/k$) VS \mathcal{E} :

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

$$\frac{\partial Q}{T} = \partial Q \frac{\partial (\ln \mathcal{R})}{\partial \mathcal{E}} = \partial Q \cdot \frac{\partial S}{\partial \mathcal{E}}$$

(i.e. TRACKS HOW THIS Q MIGHT AFFECT S)

10/30/02
7

SPECIAL CASES:



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

(1) HEAT RESERVOIR:
(BATH)

(a) $T' \sim \text{CONST}$

$$T \rightarrow T'$$

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

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

{ BUT WILL SEE IN HW: $\Delta S > \frac{Q}{T}$ } $\Rightarrow \Delta S_{\text{TOT}} > 0$ } how can I raise T a finite amt but $Q-S$?

(2) INSULATED:

$$dQ = 0 \quad (\text{ADIABATIC})$$

$$\Rightarrow dS = 0$$

$$\text{FINITE } (Q-S) \text{ CHG IN } X_\alpha \Rightarrow \Delta S = 0$$

\Rightarrow Q-S WORK CHGS E , LEAVES # ACCES. STATES FIXED

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

IN GENERAL:

$$\text{NON } Q-S \text{ PROCESS: } \Delta S > 0$$

NOT REVERSIBLE

will come back to this

(ex: remove wall \Rightarrow will need to compress and then remove heat to get back to original S)

(II) GEN. EQUIL CONDS

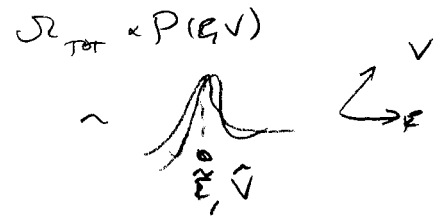
AT EQUIL: BOTH E, X_α VARY ⇒ MAXIMIZE Ω_{TOT} FOR BOTH

ex X_α = V A | A' E⁽⁰⁾ = E + E' V⁽⁰⁾ = V + V' ↗
 (IN GEN'L, CONNECTIONS AMONG X_α COMPLICATED)

Ω_{TOT}(E, V) = Ω(E, V) Ω'(E', V')
 = # STATES AT E, V IN A

ln Ω_{TOT} = ln Ω + ln Ω'
 S_{TOT} = S + S'

FIND PEAK AT E = Ẽ V = Ṽ



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

⇒ β = β' THERMAL EQUIL

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

USING β = β' ⇒ p̄ = p̄' MECH. EQUIL

AT E = Ẽ = Ẽ' V = Ṽ = Ṽ'

SURPRISING: p̄ = p̄' FROM COUNTING STATES.

NOTE: SPS p̄' > p̄ (BUT β = β') ⇒ $\frac{\partial \ln \Omega'}{\partial V'} > \frac{\partial \ln \Omega}{\partial V}$

⇒ RATE ln Ω' GETS AVAIL STATES INTO E' TO E' + SE'
 GREATER THAN FOR Ω ⇒ MORE STATES IF V' INCR,
 V DECR

(note - don't apply p balanced exactly in any individual sps → averaging)

GENERAL PROPERTIES OF S:

SHAPE OF S(E):

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

$-\lambda = \frac{\partial^2 \ln \Omega}{\partial E^2} < 0$

ELSE NO MAX,
NO EQUIL.,
WHEN PUT IN CONTACT
W/ ANOTHER SYS

$\Rightarrow \left[\begin{array}{l} \frac{\partial S}{\partial E} > 0 \\ \frac{\partial^2 S}{\partial E^2} < 0 \end{array} \right]$

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

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

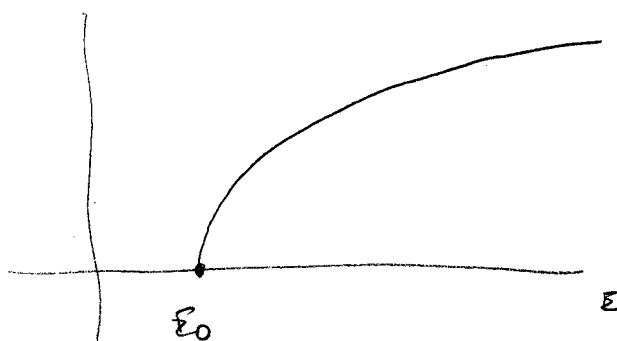
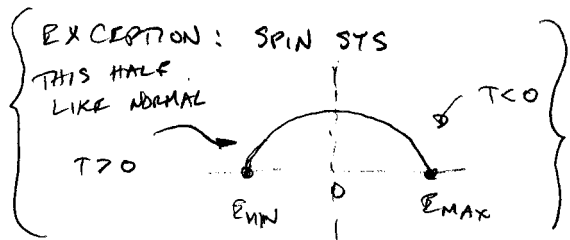
$\Rightarrow \boxed{S(E_0) = 0}$

NOTE: USE QM FOR LOW E

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

SHAPE:

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



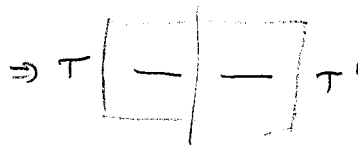
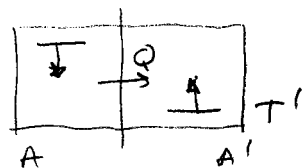
ALSO: $-\lambda \equiv \frac{\partial \beta}{\partial E} < 0 \Rightarrow \frac{\partial \beta}{\partial E} = \frac{\partial}{\partial E} \left(\frac{1}{kT} \right) = -\frac{1}{kT^2} \frac{\partial T}{\partial E}$

$\Rightarrow \boxed{\frac{\partial T}{\partial E} > 0}$

$\Rightarrow T$ INCR w/ E

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

APPROACH TO EQUIL:

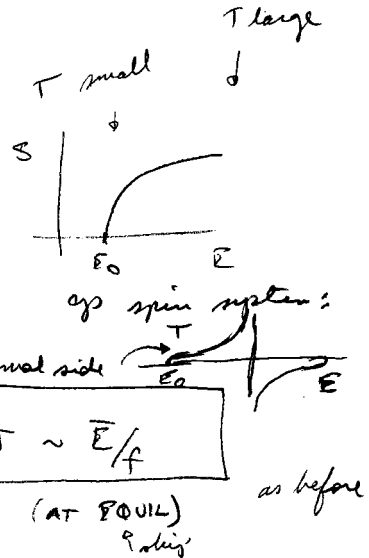


T vs S vs E

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

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

is slope⁻¹ of



ESTIMATES:

MOD - LARGE E: $\Omega \sim E^f$

$$S \sim k + \ln E$$

$$\frac{\partial S}{\partial E} \sim \frac{kf}{E}$$

slope dec. w/ E

$$\boxed{kT \sim \bar{E}/f}$$

(AT EQUIL) radius

as before

VERY SMALL E: $E \rightarrow E_0$ (NEED QM)

ship {

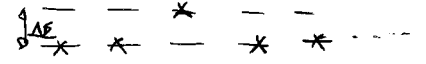
VERY ROUGHLY $\Omega \sim (E - E_0)^f$
(NOT REALLY LEGIT)

as above $\Rightarrow kT \sim \frac{\bar{E} - E_0}{f} \rightarrow 0$ AS $\bar{E} \rightarrow E_0$ {OR $kT \sim \Delta E$ per particle}

{ CRUDE: had in mind fair amt of E to go around; will do better in this }

my est.

BETTER: f DISTINGUISHABLE PARTICLES
 $\Delta E = \text{EXCITE. E FOR } \perp$



OR COULD JUST GIVE $kT \sim \Delta E$

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

$$E = E_0 + \Delta E \quad (\text{enough to excite 1})$$

$$\Rightarrow \Omega = f \quad S = k \ln f$$

$$\frac{\partial S}{\partial E} \sim \frac{\Delta S}{\Delta E} \sim \frac{k \ln f}{\Delta E}$$

$$kT \sim \frac{\Delta E}{\ln f}$$

$\ln f \sim \text{order } 1$ (or 55 or so)

H-

OX: ATOMS IN 1 LITER BOX

$$L = 10^{-1} \text{ m}$$

$$kT \sim \frac{\Delta E}{\ln f}$$

$$\sim \frac{\pi^2 \hbar^2 \perp}{L^2 m_p \ln f} \sim \pi^2 (10^{12} \text{ m}^{-2}) \frac{(1 \times 10^{-34} \text{ J-s})^2}{10^{-27} \text{ kg}} \frac{1}{50}$$

$$kT \sim 10^{-40} \text{ J}$$

$$\text{and } T \sim 10^{-24} \text{ }^\circ\text{K}$$

\Rightarrow

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

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

$E \rightarrow E_0$ GO TO GND ST $\Rightarrow \Omega \rightarrow 1, S \rightarrow 0, T \rightarrow 0$

EXCEPTION:

DEGENERATE GND ST (> 1 STATE W/ SAME E_0)

COMMON EX: N ATOMS W/ SPIN-S NUCLEI

- EVEN IF IN ATOMIC GND ST (ALL e^- 'S IN LOWEST LEVEL $\frac{1}{2}$ ATOMS NOT MOVING)
EACH NUCLEUS CAN HAVE

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

$$\underbrace{\hspace{10em}}_{2S+1}$$

- TOTAL POSSIBLE: $(2S+1)^N$

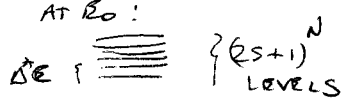
$\Rightarrow E \rightarrow E_0 \quad \Omega \rightarrow (2S+1)^N \quad S \rightarrow kN \ln(2S+1) \equiv S_0$

NOTE: SAME IF SOLID, LIQUID, ANY \bar{p}, V, \dots
(only dep. on type of atom, not what system is doing) and how many

INSERT

NOT EXACTLY DEGENERATE

- FEEL WEAK FORCE FROM \vec{B} 'S (FROM e^- 'S, OTHER NUCLEI, ETC)
" " \rightarrow SMALL SPLITTINGS AT E_0 :



- CAN ONLY SEE IF \bar{E} SMALL:

$\Rightarrow \Delta^* E$ DEGR. W/ \bar{E} ; $\Omega \sim \omega(\bar{E}) \Delta^* E \Rightarrow$ ONLY COUNT STATES W/IN $\Delta^* E$

\Rightarrow COUNT ALL UNTIL PEAK SHARP ENOUGH TO FIT W/IN SPLITTINGS
(at higher E , these all sit well w/in $\Delta^* E$ and get clumped together)

TYPICAL SYS:

$T \sim 0.1^\circ K$ (REMEMBER E DEGR W/ T)

\Rightarrow IN ATOMIC GND ST
 $S \rightarrow S_0 = kN \ln(2S+1)$

(kT small rel to atomic level spacing)

$T \sim 10^{-6}^\circ K$

\Rightarrow IN EXACT GND ST
 $S \rightarrow 0$

(" " rel to nuclear spin spacing)

reln betw $\Delta^* E$ & \bar{E} dep. on details of sys, but approx. proportional.
ex: recall Debye approx:
 $\frac{\Delta^* E}{\bar{E}} \sim \frac{1}{T}$

insert

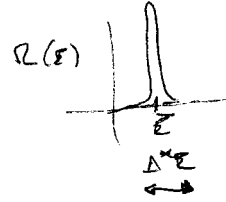
* recall that after interaction, E not precisely known; only known to w/in $\Delta^* E$ at best; should incl. all ψ in $\Rightarrow S_{width} \sim \omega \Delta^* E$

insert

RECALL:

- IF E NOT EXACT, INCLUDE ^{INS} ALL STATES
w/in ALLOWED E 's:

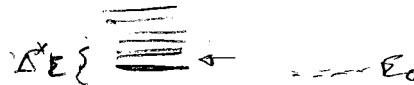
MUCH MORE COMMON SITUATION



- $\rho_{TOT} \sim \omega(\bar{E}) \Delta^* E$

- $\Delta^* E \propto \bar{E}$ USUALLY (EXACT DEPENDS ON DETAILS OF SYS; WILL LOOK AT IN CH 6-7)
- (RECALL (EST: $\frac{\Delta^* E}{\bar{E}} \sim \frac{1}{\sqrt{f}}$))

\Rightarrow COUNT ALL $(2s+1)^N$ LEVELS UNTIL $\bar{E} \uparrow \Delta^* E$ SMALL ENOUGH TO FIT w/in SPLITTINGS.



(AT HIGHER E , THESE ALL FIT WELL w/in $\Delta^* E$
 \Rightarrow GET CLUMPED TOGETHER)

do 3rd law 1st

MORE THERMO LAWS

FROM OBSERV, BEFORE STATISTICAL DESCR.

- NOT ALL BELIEVED IN ATOMS

- GETTING AT S WAS SUBTLE; VIA INDEP. OF PATH FOR $\int \frac{\delta Q}{T}$?

2ND LAW

(i.e. INSULATED)

(a) THERM. ISOLATED[^] SYS FROM ONE MACRO STATE TO ANOTHER:

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

(b) NOT INSULATED BUT Q-S:

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

(applies to both mech. } thermal ints)

(c) NOT INSUL OR QS:

$$dS > \frac{\delta Q}{T}$$

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

will discuss further

3RD LAW

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

(S_0 OFTEN 0 IN PRINCIPLE, CONST IN PRACTICE)

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

MORE ON

2ND LAW:

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

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

ARGUE OTHER CASES: (this is a description, not a proof; don't know if proof exists; maybe proof by exhaustion: for specific sys, can check by going to QS process for same S_i to S_f)

(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



R3.9

SHOWED IN HW 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 \Rightarrow RELAX PISTON



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

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

EXTREME: REMOVE WALL \Rightarrow NO W

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

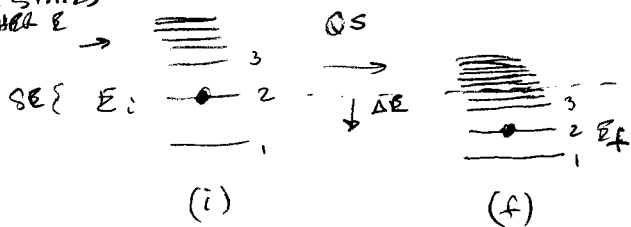
(i) QS: MAX W, BIGGEST E LOSS, BIGGEST S DROP $\Rightarrow dS = \frac{dQ}{T}$

\Rightarrow (ii) NON-QS: $dS > \frac{dQ}{T}$



QM SYS: SINGLE SYSTEM

MORE STATES AT HIGHER E



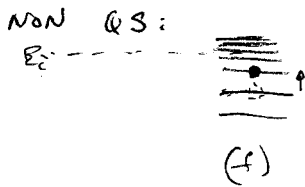
QS: E LEVELS DROP, BUT SYS STAYS IN SAME STATE

(CAN'T MAKE TRANSITION:

OR STUCK: NEED INT. w/ LT (FOR EX) w/ $\Delta W = \Delta E$ FOR TRANS, BUT SLOW $\Rightarrow W=0$.)

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

sys. naturally move to bigger sets



CAN JUMP UP AS LEVELS DROP
 DROP \Rightarrow 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 R com.)

NOTE: # STATES AVAIL LARGER

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

(3) REVERSE: W INTO SYS IS MIN IF Q-S

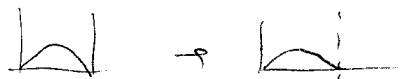
LI GAS:

EXPANDING: CAN AVOID CONTACT BY
 MOVING FASTER

CONTRACTING FAST REQUIRES MORE \bar{F} , GREATER W
 GENTLEST = Q-S \Rightarrow MIN W

QM: EX PART. IN BOX

EXPAND. QUICKLY \Rightarrow CAN LEAVE WFN INTACT



STAY AT SAME E WHILE
 LEVELS DROP

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

CONTRACT:

ADD E, FORCE WANTS 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 $\frac{1}{2}$ RIDES
 HIGHER LEVEL UP

pulling in
 E via work \rightarrow
 E has to go up

(4) BOTH CASES:

NON-Q-S LEAVES MORE E IN SYS

Q-S: $ds = \frac{dQ}{T}$

\Rightarrow NON-Q-S: $ds > \frac{dQ}{T}$

4.10 Adiabatic Processes

The above reasoning—in particular, the derivation of Equation (4.13) and the consequent identification of TdS with dQ 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,

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

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

Figure 4.5. Mutual spin flip, conserving total spin.

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.

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).