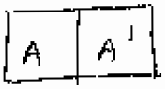
THERMAL + MECHANICAL INTERACTIONS:



ISOLATED

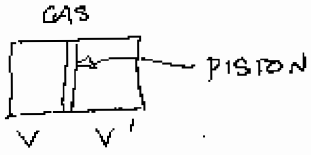
- DEFINED BY E, X_α $\&$ E', X_α'
  $\alpha = 1 \cdots n$

- BRING INTO CONTACT, ALLOW BOTH Q & ~~[illegible]~~ CHG IN X_α

  {for sure: this discussion doesn't need ~~[illegible]~~ Q-S chg in either; still know where will end up in new equ

- E', X_α' WILL DEP. ON E, X_α

ex



$$\left.\begin{array}{l} E + E' = E^{(0)} \\ V + V' = V^{(0)} \end{array}\right\} \text{FIXED}$$

WANT:

(I) HOW DOES $\ln \Omega_{TOTAL}(E, X_\alpha)$ CHG?
~~$(\Omega_{TOT} = \Omega_{TOT}(E, X_\alpha))$~~ (depends on E, x_α for sys. A)

(II) WHAT NEW EQUIL. CONDS? {COULD GUESS}

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

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

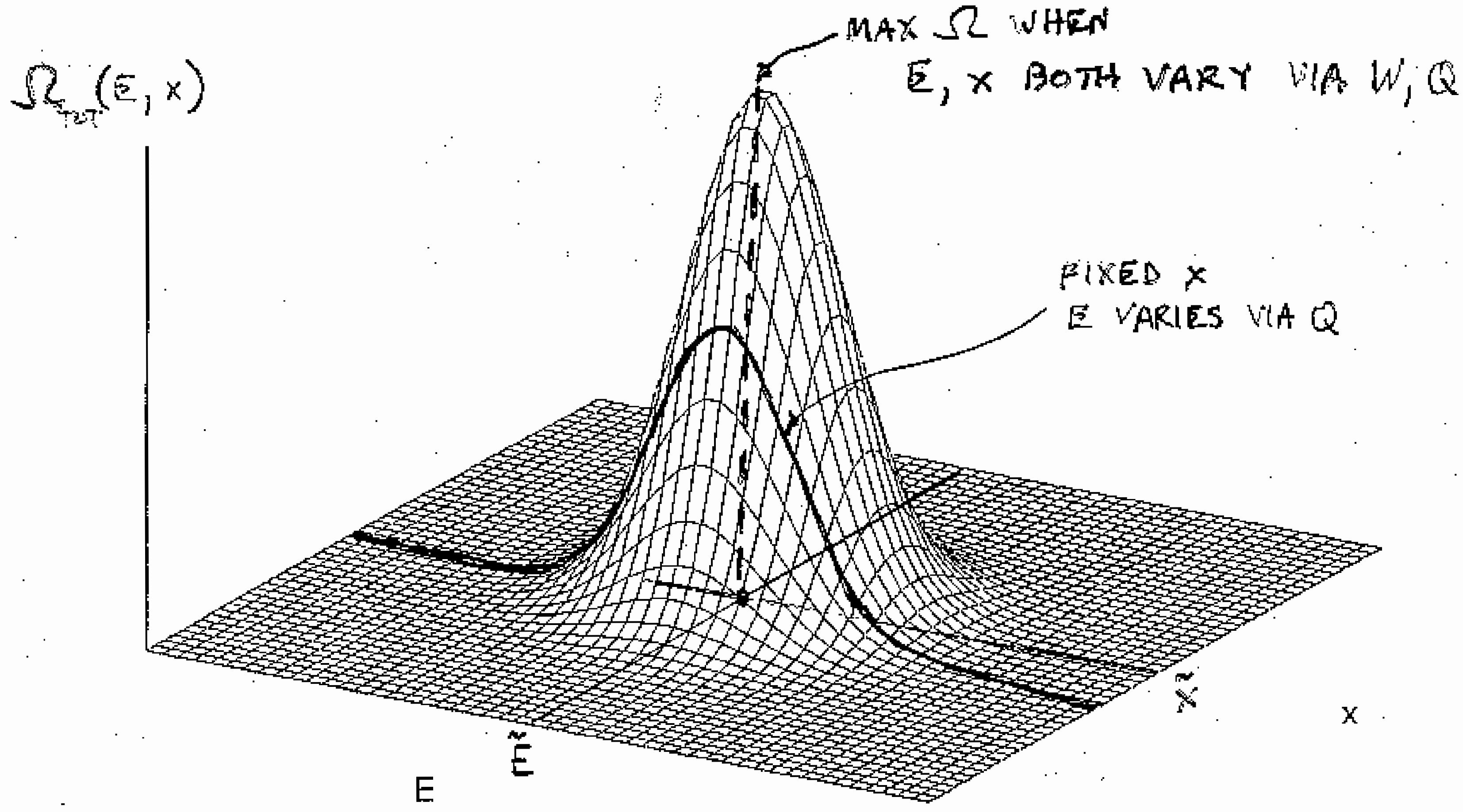
** ex: $V = 0 \rightarrow$ no states, grows rapidly as V^N **

PLOT: CP. X_α FIXED, NOT INSULATED $\Rightarrow$ Q

skip plot

skip → not obvious; (E ≠ CONST) some closed restricted curve { X_α FREE, INSULATED $\Rightarrow$ W }

X_α FREE, NOT INSULATED $\Rightarrow$ Q & W


$\Omega_{TOT}(E, x)$
MAX Ω WHEN
E, x BOTH VARY VIA W, Q
FIXED x
E VARIES VIA Q
$\tilde{x}$
x
$\tilde{E}$
E

3.18.1

(I) CHG IN $\ln \Omega$ (FOR A)

{ in general: put in contact, system moves quickly, bounces aro[und] eventually reaches new equil. [at] very diff $\tilde{E}$, $\tilde{x}_\alpha$. Can't [use] stat. reasoning to describe interim, But if move slowly from one to oth[er] (ex: slow chg in V, sequence of diff sys at diff T's), .

⇒ FOR SMALL CHG IN MACRO PARAMS:

new equil is near old → can use dS

$$\bar{E} \rightarrow \bar{E} + d\bar{E}$$

$$\bar{x}_\alpha \rightarrow \bar{x}_\alpha + d\bar{x}_\alpha$$

SMALL ON MACRO SCALE
BUT >> FLUCTUATIONS

in ensem, some more, some less, but not by much

⇒ MOVE FROM Ω_{TOT} PEAKED AT " TO "

IF QUASI-STATIC:

- STAY IN EQUIL
- USE STATISTICAL REASONING

just math

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

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

$$\underbrace{}_{\frac{1}{k} dS} = \underbrace{\beta}_{\frac{1}{kT}}\underbrace{(d\bar{E} + đW)}_{đQ}$$

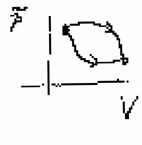
(remember, W, Q def'd for ave)

$$\Rightarrow \boxed{dS = \frac{đQ}{T}}_{\text{Q-S}}$$

- FOR SMALL CHGS IN $\bar{E}$ & $\bar{x}_\alpha$
- EXACT DIFF: $\int_A^B \frac{đQ}{T}$ INDEP. OF PATH

(classical thermo: this is how learned of existence of S)

} mention pV plot



Q not same, $\int \frac{dQ}{T}$ [i]

(skip this pg; already covered)

PROPERTIES OF ENTROPY:

(1) EXACT DIFF. : DIFF. BETWEEN FN S FOR 2 MACROSTATES

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

S hard to measure ✓ , $\bar{d}Q$, T easy to measure ✓

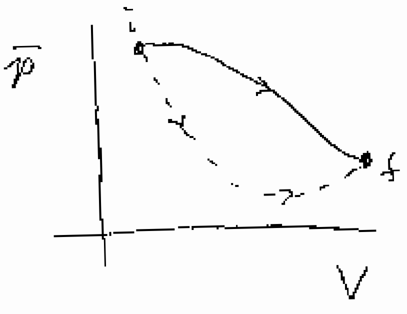
(2) FINITE DIFF:

$$S_f - S_i = \int_i^f dS = \int_i^f \frac{\bar{d}Q}{T} \quad \text{(EQUIL)}$$

- INDEP. OF HOW GO FROM INITIAL TO FINAL STATE (ANY SYSTEM)
- ~~FINAL INTEGRAL~~ PERFORM CHANGES QUASI-STATICALLY

ex

(V IS ONLY EXT PARAM)



$\int_i^f \bar{d}Q$ DEPENDS ON PATH *

$\int_i^f \frac{\bar{d}Q}{T}$ DOES NOT " } SURPRISING! **

(cf problem 2.11 $\Delta \bar{E}$, ΔS IND. OF PATH; Q NOT)

skip

TO EVALUATE:

- IN GEN. WILL BE IN CONTACT WITH OTHER SYSTEMS: $\bar{d}W, \bar{d}Q \neq 0$
- STAY IN EQUIL AT EACH STEP:
  $\Omega(E, V) \rightarrow$ DETERMINES $\bar{p}$, T FOR EACH $\bar{E}$, V UNIQUELY
  $\rightarrow$ CAN COMPUTE $\bar{d}Q = d\bar{E} + \bar{d}W$ AFTER EACH SMALL STEP
- GET SAME RESULT

** - USEFUL TOOL EVEN IF DON'T GET FROM i TO f Q-S:
  - S_i, S_f PROPERTIES OF i, f STATE, NOT HOW GOT THERE
  - CAN CALC. S_f FROM S_i FOR Q-S PROCESS ⇒ SAME RESULT

---

* from i to f $\bar{d}W$ (by sys.) = area under curve
$\Delta \bar{E} = 0$ $Q = \Delta \bar{E} + W = W$ ∴ higher path has $Q >$ lower path

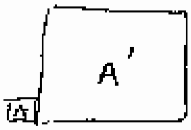
---

** even if didn't know what S was, could stumble onto its existence by this observation: if $\bar{d}Q/T$ indep of path, there must be some fn. S whose $\Delta S = \int \frac{\bar{d}Q}{T}$

⑦

SPECIAL CASES:

(1) HEAT RESERVOIR:
(BATH)



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

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

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

{ BUT WILL SEE IN HW: $\Delta S > \frac{Q}{T'}$ }

how can I raise T a finite amt but Q-S ?

(2) INSULATED:

$đQ = 0$ (ADIABATIC)

$\Rightarrow dS = 0$

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

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

⇒ REVERSIBLE (CAN UNDO VIA Q-S CHG) (no dS, no $d\Omega$)

IN GENERAL:

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

NOT REVERSIBLE

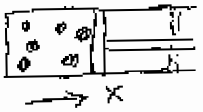
3.19.1

(my thoughts:)

IMPORTANCE OF Q-S PROCESS IN $dS = \frac{dQ}{T}$

$\Rightarrow \Delta S = 0$ IF INSULATED

CP:



Q-S: (a) LET PISTON MOVE OUT SLOWLY, UNDER EFFECT OF $\bar{p}$ (ie particles bounce off)

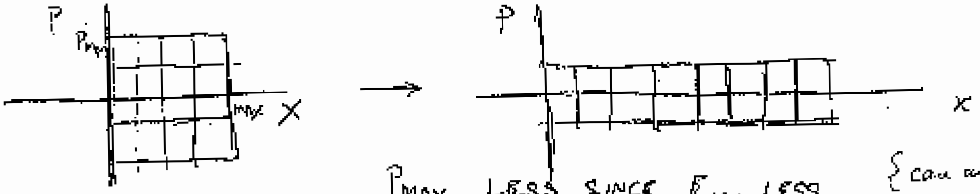
(b) EACH BOUNCE  LOSES E TO PISTON

(c) $\Delta E = -W = -\int \bar{p}\, dV$ (work by sys.)

(d) $\Delta S = 0$ ∴ NEWLY AVAIL. STATES FROM INCR. IN X COMPENSATED EXACTLY BY LESS E AVAIL. TO GET TO CERTAIN STATES

(e) ex: CLASSICAL SYS. w/ 1 DOF (NOT 3N DOF)

PHASE SPACE MIGHT LOOK LIKE



P_{MAX} LESS SINCE E_{MAX} LESS

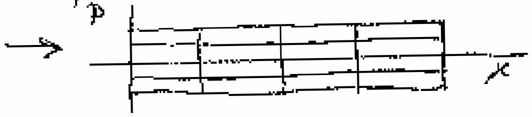
S CONST SINCE # CELLS CONST

$\Rightarrow$ REVERSIBLE

{can also picture QM: state level drop, but less E avail to get to them: ex - single state

pull E out can redo gently}

for me: {OR COULD CHGE δp & δx ∋. $h_0 = \delta p \delta x$ CONST:



SAME RESULT}

VS NOT QS! REMOVE WALL / MOVE ABRUPTLY

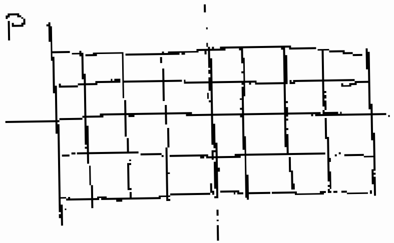
(a) NO TIME FOR MOLECULES TO BOUNCE

$\Rightarrow$ CAN'T REMOVE E $\Rightarrow \Delta E = 0$

(b) NO LOSS OF AVAIL. E, TWICE AS MANY δx's

(P_{MAX} CONST)

" →



(c) $\Delta S > 0$

simple connection; could in general be more complicated

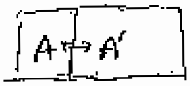
f. 8

3, 20

(II) GEN. EQUIL

EQUIL: BOTH E, X_α VARY $\rightarrow$ MAX BOTH δ

ex. $X_\alpha = V$:



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

$$\Omega_{TOT}(E, V) = \Omega(E, V)\,\Omega'(E', V') \quad \text{(for partic. } E\text{)}$$

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

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

MAX Ω_{TOT} (or S_{TOT}): $d \ln \Omega_{TOT} = d(\ln \Omega + \ln \Omega') = 0$

(equiv to req. all partial der. vanish)

ALLOW E & V TO CHG:

A: $$d \ln \Omega = \frac{\partial \ln \Omega}{\partial E} dE + \underset{\sim}{\frac{\partial \ln \Omega}{\partial V}} dV = \beta dE + \beta \bar{p}\, dV$$

(Ω chg because: (a) more E makes more states avail

(b) chg V chgs how many states are at partic. E) $\frac{\partial \ln \Omega}{\partial X_\alpha} = \beta \bar{X}_\alpha$ from before

A': $$d \ln \Omega' = \beta' dE' + \beta' \bar{p}' dV' = -\beta' dE - \beta' \bar{p}' dV$$

$$(dE' = -dE, \quad dV' = -dV)$$

MAX: $$d \ln \Omega_{TOT} = (\beta - \beta') dE + (\beta \bar{p} - \beta' \bar{p}') dV = 0$$

is $\frac{\partial \ln \Omega}{\partial E} = 0$, $\frac{\partial \ln \Omega}{\partial V} = 0$

dE, dV INDEP $\Rightarrow$ $\boxed{\begin{array}{l} \beta = \beta' \\ \bar{p} = \bar{p}' \end{array}}$ $\Rightarrow$ THERMAL EQUIL; $\Rightarrow$ MECH. EQUIL.

$$\boxed{\text{AT} \quad \begin{array}{l} E = \tilde{E} = \bar{E} \\ V = \tilde{V} = \bar{V} \end{array}}$$

in gen: T equal, $\bar{X}$ "

true $\rightarrow$? required $dV' = -dV$

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

** (surprising that $\bar{p} = \bar{p}'$ comes just by counting states:

sps $\bar{p}' > \bar{p}$ (but $\beta = \beta'$) $\Rightarrow$ $\frac{\partial \ln \Omega'}{\partial V'} > \frac{\partial \ln \Omega}{\partial V}$

$\Rightarrow$ rate at which Ω' gets avail states squeezed into $E' + dE'$ greater than for Ω $\Rightarrow$ more states avail if V' incr., V decr.)

~~but note: if $\bar{p}$'s diff, the same chg in V does work at diff rate for 2 sys.~~
~~$\Rightarrow$ one will gain E faster than other loses it~~
~~$\Rightarrow$ more avail states; also explains why β is involved~~

~~E cons?~~

GEN. PROPERTIES OF S:

SHAPE OF $\ln\Omega(E)$ OR $S(E)$ (FOR INDIV SYS :)

HAVE (USUALLY)

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E} > 0 \qquad \left(= \frac{1}{kT} \Rightarrow \boxed{T > 0}\right)$$

(else no max when put in contact, no equil position)

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

(ignore = possibility)

(for me: need this true at all E can always put 2 ident sys. together w/ any amt of E — NOT TRUE IF

CLASSICAL: ex IDEAL GAS $\Omega \propto V^N$ EVEN IF $E \sim 0$

BUT $S = k\ln\Omega \propto N\ln V$ indep of type of gas

*

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

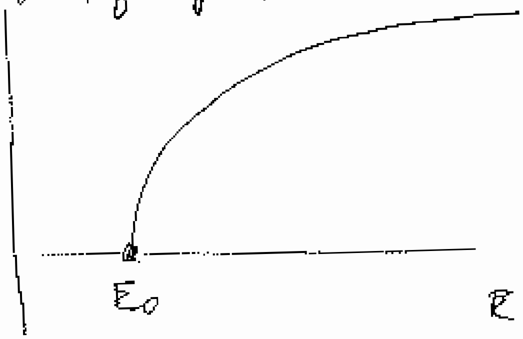
ALSO, AT $E = E_0$ (GND ST)

$\Omega(E_0) = 1$ (~~or few~~)

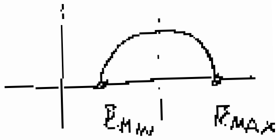
$\ln\Omega(E_0) = 0$ (~~or small #~~)

$\boxed{S(E_0) = 0}$ (~~or few # of degen~~)

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



EXCEPTION: (spin systems:



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* ALSO: $-\lambda = +\dfrac{\partial\beta}{\partial E} < 0$

$$\frac{\partial\beta}{\partial E} = \frac{\partial}{\partial E}\left(\frac{1}{kT}\right) = -\frac{1}{kT^2}\frac{\partial T}{\partial E}$$

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

ie T incr. w/ E

TO EQUIL

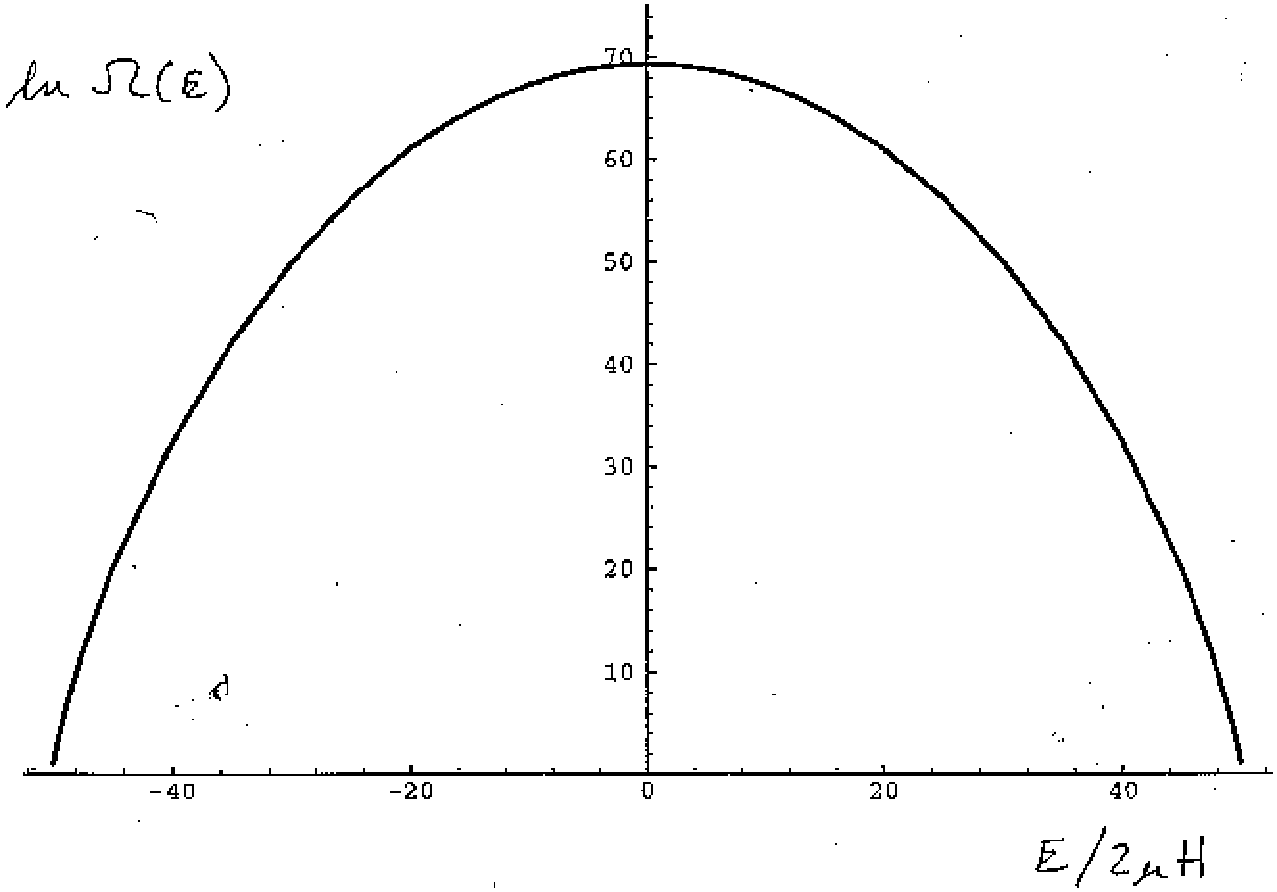
(ANOTHER WAY TO SEE NECESSARY FOR REACHING NEW EQUIL)

3.21.1

skip

SPIN SYSTEM (REIF 2.4)
$\ln \Omega(E)$

$N = 100$



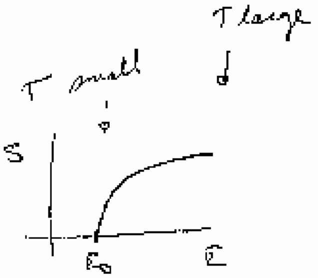
3.22

T VS S $\&$ E

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

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

ie slope^{-1} of



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

$S \sim kf \ln E$ $\frac{\partial S}{\partial E} \sim \frac{kf}{E}$ $\boxed{kT \sim \bar{E}/f}$ as before

slope decr. w/ E (AT EQUIL)

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

VERY ROUGHLY $\Omega \sim (E - E_0)^f$ {we were assuming E large when did est; ignored gnd st E_0; if kept in would find this

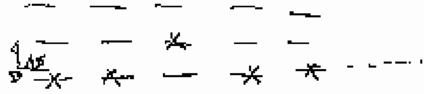
$\xrightarrow{\text{as above}}$ $kT \sim \frac{\bar{E} - E_0}{f} \to 0$ AS $\bar{E} \to E_0$ {or $kT \sim \Delta E$ per particle}

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

$\downarrow$ my est.

BETTER: f DISTINGUISHABLE PARTICLES

ΔE = EXCITE. E FOR 1 "



JUST GIVE $kT \sim \Delta E$

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

$E = E_0 + \Delta E$ (enough to excite 1)

$\Rightarrow \Omega = f$

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

$kT \sim \frac{\Delta E}{\ln f}$ $\ln f \sim$ order 1 (or 55 or 100)

ex: ATOM IN 1 LITER BOX

$L = 10^{-1}\,m$ $kT \sim \frac{\Delta E}{\ln f} \sim \frac{\pi^2}{L^2}\frac{\hbar^2}{m_p}\frac{1}{\ln f} \sim \pi^2 (10^{2}\,m^{-2}) \frac{(1 \times 10^{-34}\,J\text{-}s)^2}{10^{-27}\,kg}\frac{1}{5}$

$\sim 10^{-40}\,J$

(or 10^{-24} °K)

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

{ for me :

even better:

f indisting. particles

n units of ΔE $\Rightarrow$ $E = E_0 + n\Delta E$

n units in f slots

$$\Omega \sim \binom{f}{n} = \frac{f!}{n!(f-n)!}$$

$$\ln \Omega \sim \ln f! - \ln n! - \ln(f-n)!$$

$$\sim f \ln f - n \ln n - (f-n)\ln(f-n)$$

$$\ln \Omega \sim n \ln f \quad \text{if } n \ll f$$

$$S = k \ln \Omega \sim k n \ln f = \frac{k E \ln f}{\Delta E}$$

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

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

}

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

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

EXCEPTION:

DEGENERATE GND ST ($\overset{\text{ie}}{>1}$ 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) + AND ATOMS NOT MOVING, EACH NUCLEUS CAN HAVE

$$s_z = \underbrace{-s\hbar, (-s+1)\hbar, \cdots (s-1)\hbar, s\hbar}_{2s+1}$$

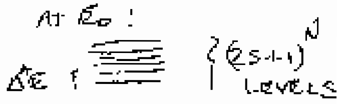
- TOTAL POSSIBLE: $(2s+1)^N$

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

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

NOT EXACTLY DEGENERATE

- FEEL WEAK FORCE FROM $\vec{B}$'s (FROM e^-'s, OTHER NUCLEI, ETC.)
- " " $\to$ SMALL SPLITTINGS



- CAN ONLY SEE IF $\bar{E}$ SMALL:
  - $\Rightarrow \Delta^* E$ DECR. w/ $\bar{E}$; $\Omega \sim \omega(E)\Delta^* E$ $\Rightarrow$ ONLY COUNT STATES w/in $\Delta^* E$
  - $\to$ COUNT ALL UNTIL PEAK SHARP ENOUGH TO SIT w/in SPLITTINGS

recall Gauss approx: $\frac{\Delta^* E}{E} \sim \frac{1}{\sqrt{f}}$

TYPICAL SYS:

$T \sim .1\,°K$ (REMEMBER E DECR w/ T)

$\Rightarrow$ IN ATOMIC GND ST

$S \to S_0 = kN\ln(2s+1)$

(kT small rel to atomic level spacings)

$T \sim 10^{-6}\,°K$

$\Rightarrow$ IN EXACT GND ST

$S \to 0$

(" " rel to nuclear spin spacings)

3.12.3

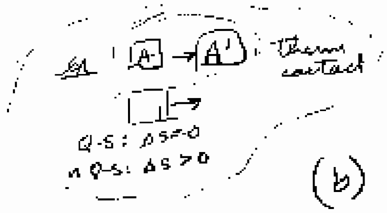
MORE THERMO LAWS

(FORMULATED BEFORE MICRO (STATISTICAL) DESCRIPTION)

* **2ND** (a) THERMALLY ISOLATED (INSULATED) SYSTEM GOES FROM ONE MACRO STATE TO ANOTHER (ie macro params chg)

$$\Delta S \geq 0$$

(even if do work on it or let it do work)



(b) NOT INSULATED BUT Q-S:

$$dS = \frac{đQ}{T} \qquad (=0 \text{ IF INSULATED})$$

(NOTE: Q-S ALSO MEANS SLOW CHG IN TEMP, SLOW FLOW OF Q; SLOW CHG IN EXT. PARAMS)

(c) NOT INSUL. OR Q-S: $dS > \frac{đQ}{T}$ {could say simply $dS \geq \frac{đQ}{T}$, w/ = when Q-S?}

3RD AS $T \to 0_+$ $S \to S_0$

INDEP. OF PARAMS OF PARTICULAR SYSTEM

(S_0 OFTEN 0 IN PRINCIPLE CONST IN PRACTICE)

{if its $S_0 \neq 0$, its because its something like nuclear spin, and can't get to it (ie can't nature E avail. to be small enough to limit): doesn't matter what you're doing system: V, P, ---

→ LAWS FORMULATED BY OBSERVATION, BEFORE STATISTICAL DESCRIPTION (S WAS SUBTLE) (presumably detected its existence by noting $\int \frac{đQ}{T}$ was indep of path ∴ had to be some fn S ⇒ $\Delta S = \int đQ/T$. Then can always meas relative S

* COULD ALSO MENTION

0TH: A IN THERM. EQ. W/ C
B " " " " C ⇒ A W/ B

1ST: $\Delta E = -W + Q$ (E CONS.)

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 efforts; maybe proof by exhaustion; for specific sys, can check by eq to Q-S 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 

(c) $dS > \frac{đQ}{T}$ (but more diff of W:)

SHOWED 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 $\bar{p}$, ALL PARTICLES HAVE TIME TO BOUNCE, DO WORK

FASTER: CAN'T CATCH UP, $\bar{p}$ LESS, LESS W

EXTREME: REMOVE WALL ⇒ NO W

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

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

⇒ (ii) NON-QS: $dS > \frac{đQ}{T}$

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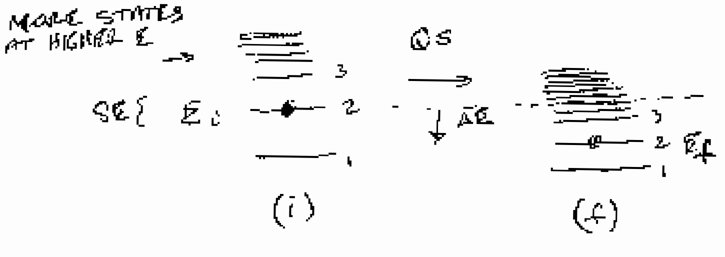
QM SYS:

SINGLE SYSTEM

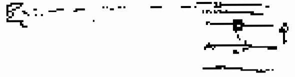


QS: E LEVELS DROP, BUT SYS STAYS IN SAME STATE (CAN'T MAKE TRANSITION: CF STURGE: NEED INT. W/ LT (FOR E W/ $\hbar\omega = \Delta E$ FOR TRANS BUT SLOW ⇒ $W = 0$.)

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

3.12.5

NON QS:



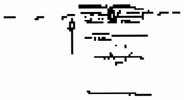
(4)

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 AVG) AS IF ALL STAYED PUT

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

ex GAS:

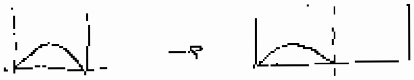
EXPANDING: CAN AVOID CONTACT BY MOVING FASTER

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

GENTLEST ≡ Q-S ⇒ MIN W

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

(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 $\bar{d}Q$ 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, $\frac{2\mu B}{\hbar}$. 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 ↑ to ↓, the other has to flip from ↓ to ↑ (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.