Consider TWO EINSTEIN SOLIDS

$\longrightarrow$ BOTH HAVE N OSCILLATORS

$\hookrightarrow$ PUT THEM in thermal Contact

SOLID A $\longrightarrow$ q_A quanta $\quad E = q_A \cdot \hbar\omega$

Solid B $\rightarrow$ q_B quanta

TOTAL MULTIPLICITY

$$\Omega(q_A, q_B; N, N) \approx \left(\frac{e q_A}{N}\right)^N \left(\frac{e q_B}{N}\right)^N$$

ASSUME $q_{A,B} \gg N$

A	B
$q_A = \frac{q}{2} + x$	$q_B = \frac{q}{2} - x$

Total energy $q(\hbar\omega)$ constant

$x \rightarrow$ CAN change

$$\Omega_{TOTAL} \approx \left(\frac{e^2}{N^2}\right)^N \left(\frac{q}{2} - x\right)^N \left(\frac{q}{2} + x\right)^N$$

use "difference of 2 squares"

$$\Omega_{TOTAL}(\overset{E}{q}; \overset{imb}{X}; \overset{A}{N}; \overset{B}{N}) \approx \left(\frac{e^2}{N^2}\right)^N \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$

$$= \left(\frac{e^2}{N^2}\right)^N \left(\frac{q^2}{4}\right)^N \left(1 - \left[\frac{2x}{q}\right]^2\right)^N$$

now put $X = 0$

$$\Omega_{TOTAL}(q; 0; N; N) \approx \left(\frac{e^2}{N^2}\right)^N \left(\frac{q^2}{4}\right)^N$$

so $\Omega_{TOTAL}(q; x) \approx \Omega_{TOT}(q, 0) \left[1 - \left(\frac{2x}{q}\right)^2\right]^N$

$$\left(\frac{e^2}{N^2}\right)^N \left(\frac{q^2}{4}\right)^N \rightarrow$$ MAX VALUE of Ω WHICH OCCURS AT $X = 0$

Define $\Omega_{TOT}(q, 0; N; N) \equiv \Omega_{MAX}$

$$\frac{\Omega(q, x; N; N)}{\Omega_{MAX}} \approx \left[1 - \left(\frac{2x}{q}\right)^2\right]^N$$

or

$$\ln\left[\frac{\Omega_{TOTAL}(q, x; N; N)}{\Omega_{MAX}}\right] \approx N \ln\left[1 - \left(\frac{2x}{q}\right)^2\right]$$

Take case $x \ll q$

imbalance

TOTAL energy.

Then $\frac{2x}{q} \ll 1$

USE TAYLOR EXPANSION FOR Ln

$$\ln\left(1 - \left(\frac{2x}{q}\right)^2\right) \approx -\left(\frac{2x}{q}\right)^2$$

so $$\ln\left\{\frac{\Omega_{TOTAL}(q, x, N)}{\Omega_{MAX}}\right\} \approx -N\left(\frac{2x}{q}\right)^2$$

exponentiate:

$$\frac{\Omega_{TOT}(q, X, N; N)}{\Omega_{MAX}} = e^{-N\left(\frac{2x}{q}\right)^2}$$

This is VALID FOR

→ $N \gg 1$ Requirement of Stat Mech.

→ $\frac{q}{2} \pm x \gg N$ many q per oscillator

↳ high T limit

→ $x \ll \frac{q}{2}$ → SMALL energy imbalance A ↔ B

STAT MECH POSTULATE

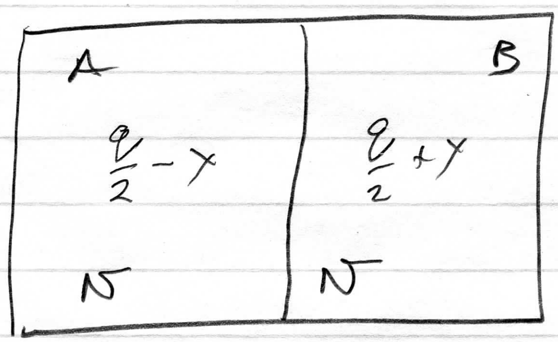
PROB OF X ∝ to NUMBER of μSTATES

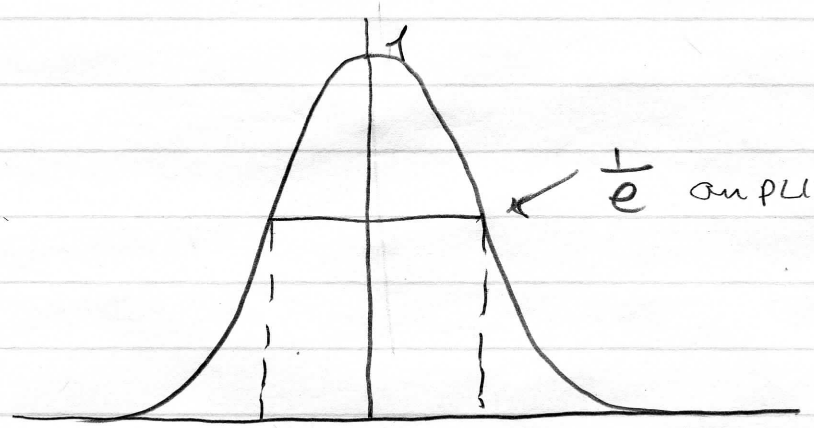
WITH THAT X

↳ $\Omega_{TOTAL}(q, x; N; N)$

$$\frac{\text{PROBABILITY of } X \neq 0}{\text{PROBABILITY } X = 0} = e^{-N\left(\frac{2x}{q}\right)^2}$$

THIS IS A GAUSSIAN DISTRIBUTION





$\frac{1}{e}$ amplitude.

$x^{-} = \frac{-q}{2\sqrt{N}}$ $\quad$ $x^{+} = \frac{q}{2\sqrt{N}}$

WIDTH OF GAUSSIAN = $|x|$

Point WHEN PROB = $\frac{1}{e}$

$\frac{2x}{q} = \frac{x}{q/2}$ → Fractional energy imbalance between A & B.

$\frac{X}{q/2} \rightarrow$ fractional energy imbalance.

$\hookrightarrow$ for $N \sim 10^{23}$, $\frac{2X}{q} = 10^{-5}$

$$\frac{\text{Prob}\left(\frac{2X}{q} \sim 10^{-5}\right)}{P(0)} \approx e^{-10^{23}(2\times10^{-5})}$$

$$\approx e^{-10^{13}}$$

VANISHINGLY SMALL

ONLY values of $|X| < X^{\pm}$ HAVE

Substantial non zero probability.

$X^{\pm} = \frac{q}{2\sqrt{N}}$ as $N \rightarrow \infty$

$\frac{1}{\sqrt{N}} \rightarrow 0$

We considered $N_B = N_A = N$

IN $q_A, q_B >> N$ limit $\rightarrow$ SIMPLICITY

— AS $N \rightarrow \infty$ MULTIPLICITY FN A + B
PEAKS AT $\underline{\underline{x = 0}}$

$$\frac{q_A}{N} = \frac{q_B}{N} \longrightarrow \text{EQUIPARTITION.}$$

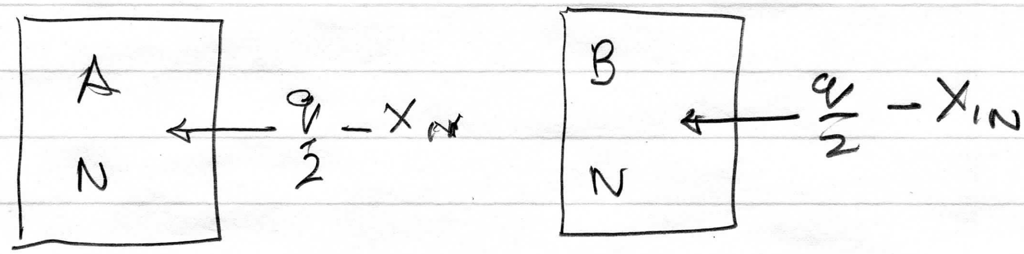
WITH Essentially ZERO WIDTH

PROB$\left(\begin{matrix}\text{NON ZERO}\\ \text{IMBALANCE}\end{matrix}\right)$ vanishes as $\frac{1}{\sqrt{N}}$
as $N \rightarrow \infty$.

We looked at Einstein Solid in hi-T limit
$\frac{q}{N} >> 1$

BUT THIS is $\underline{\text{TRUE}}$ for any 2 large N systems in THERMAL CONTACT.

GENERalize scen for Einstein Solid



INitially isolated.

↳ brought together → energy exchange.

According to STAT MECH postulate

X_{IN} will change in such a way

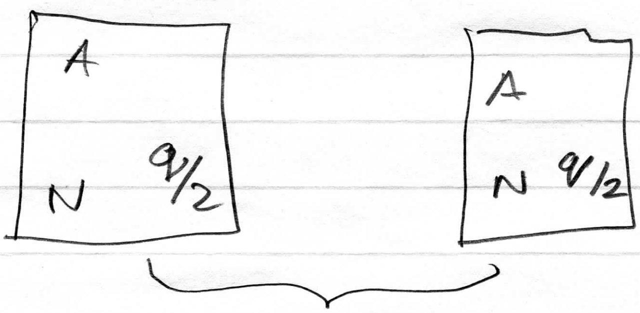
that TOTAL MULTIPLICITY (= ENTROPY)

will be MAXIMIZED (since PROB ~ MULT)

— X_{IN} EVOLVES → value corresponding

to MAX MULT → MAX ENTROPY

$X_{IN} \to 0$



SAME MACROSTATE — MAX ENTROPY

→ CLOSED system in thermoDynamic

Equilibrium → MOST likely to be in

STAT of MAX ENTROPY

→ In limit $N \to \infty$, STATE of HIGHEST

ENTROPY → VIRTUALLY CERTAIN

the entropy of a closed system always

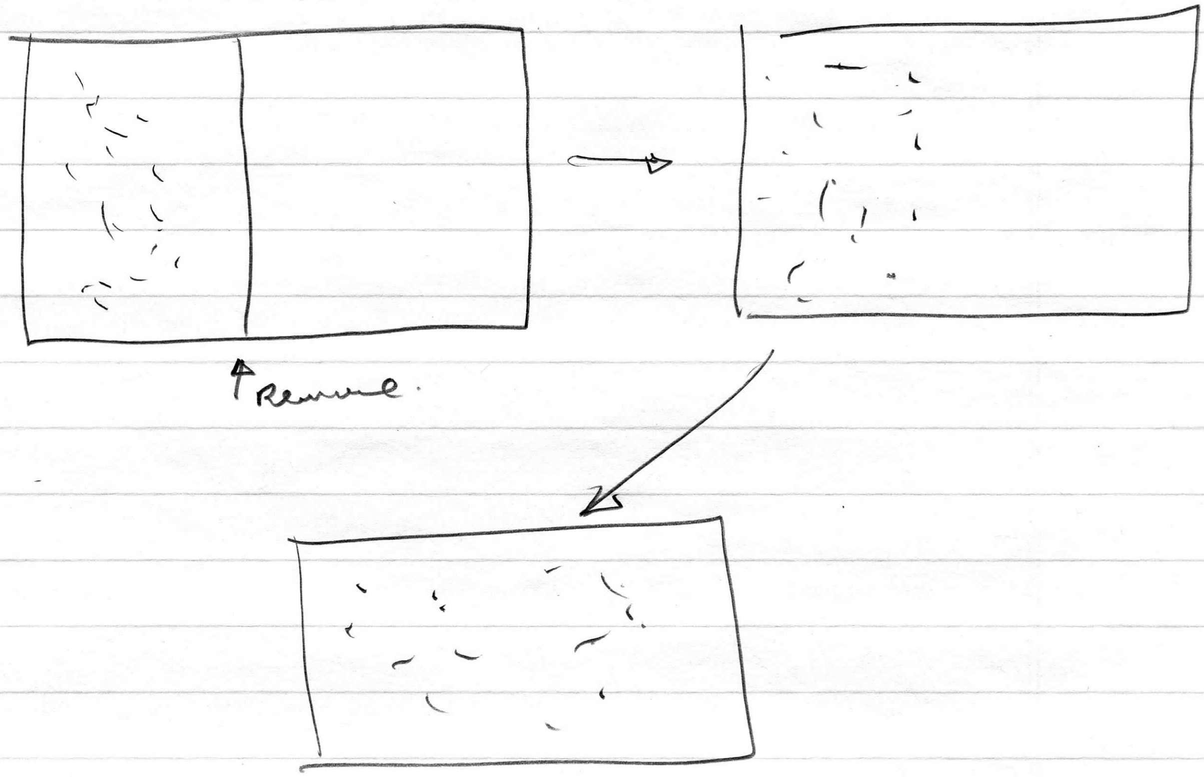
increases until it reaches

maximum possible value

2ND LAW of THERMODYNAMICS.

Many Examples — Just look Around You!

eg DIFFUSION



— multiplicity of macrostate where gas fills volume is LARGE

↓ more re-arrangement of positions / velocities possible in larger volume.

↓ Hence ENTROPY of final uniform state is VASTLY larger than entropy of state where gas is confined in LHS

↓ lets move on to gases

= picture from JPH441

= Feynman note

Some MORE ON ENTROPY & TEMP

Defined $\frac{1}{T} = \frac{\partial}{\partial E} k \ln \Omega(E)$

$$= \frac{\partial S(E)}{\partial E}$$

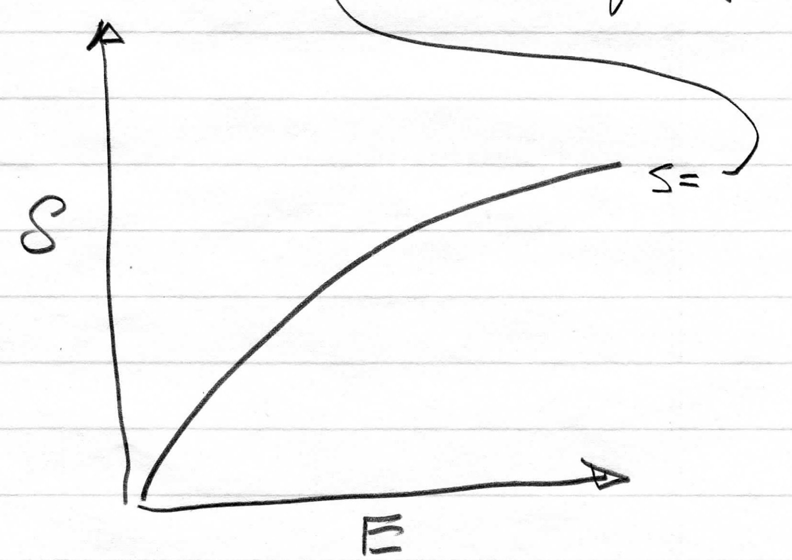
Behavior of S as fn E ?

In Einstein Solid — $\left.\begin{matrix} N \to \infty \\ q >> N \end{matrix}\right\}$ limit

Found $S = kN \ln\left(\frac{qe}{N}\right)$ $\quad \left(q = \frac{E}{\hbar\omega}\right)$

$S = kN \ln\left(\frac{Ee}{\hbar\omega N}\right)$ $\quad \Big| \quad E >> \hbar\omega N$, $q >> N$

AS $E\uparrow$, $S\uparrow$



AS E↑ expect number of μSTATE ↑

└ CLEARLY FOR Einstein Solid

└→ eventually will show it for GAS.

→ E↑ → S↑

└→ $\frac{\partial S}{\partial E} > 0$

$\frac{1}{T} = \frac{\partial S}{\partial E}$

$\Big\} \; T > 0$

this is true for normal system in thermodynamic Equilibrium

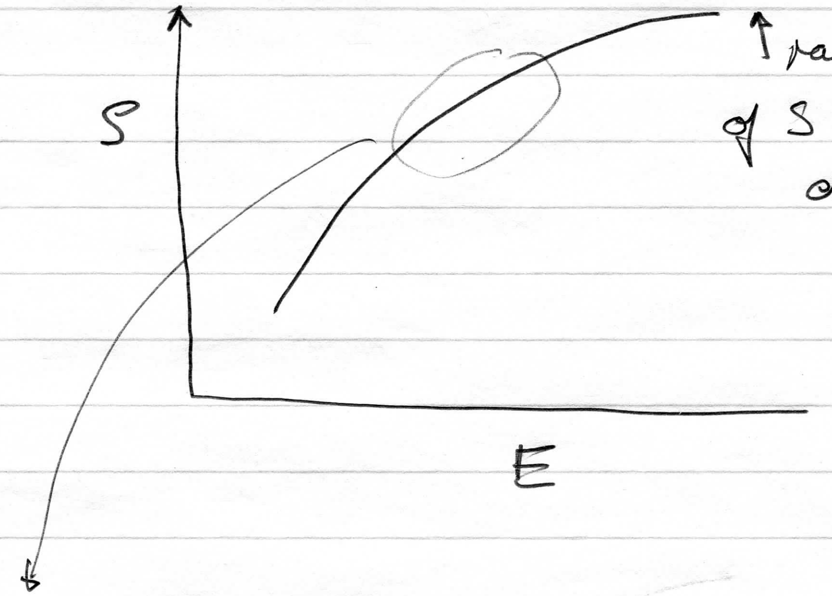
Also $S(E) \sim \ln E$

$$\frac{\partial S(E)}{\partial E} \sim \frac{1}{E}$$

$$\frac{\partial^2 S(E)}{\partial E} \sim -\frac{1}{E^2}$$

NEGATIVE

So $\frac{\partial^2 S(E)}{\partial E^2}$ → generally −ve



↑ rate of change of S wrt E decreasing

This looks like

→ Physics of CONCAVE SHAPE

1ST derivate gets smaller as E↑

ie $\frac{1}{T}$ get smaller.

⇒ E↑ T↑ $\frac{1}{T}$↓

Heat system — add energy

— NOT remove it.

SAME as GENERAL STATEMENT about HEAT CAPACITIES

$C_V > 0$ FOR stable systems.

Remember $C_V = \left(\frac{\partial U}{\partial T}\right)$ energy

So $C_V > 0 \Rightarrow T\uparrow\ U\uparrow$

PARAMAGNET does NOT behave like this

energy $= U = -\mu_0 B S$

NOT ENTROPY → SPIN

$$U = -\mu_0 B(2N_\uparrow - N)$$

$N_\uparrow$ can be $(0, 1, \ldots\ldots N)$

$U_{MAX} = \mu_0 B N \rightarrow N_\uparrow = 0$

All spins OPPOSITE B-field.

$U_{MIN} = -\mu_0 B N \longrightarrow N_\uparrow = N$

All spins $\parallel$el to B-field

? ENTROPY of spin system as fn of $\mathcal{U}$?

↳ entropy as fn of $N_\uparrow$

$$\left\{ \begin{array}{ll} N_\uparrow = 0 ; & U_{MAX} \\ N_\uparrow = N ; & U_{MIN} \end{array} \right\}$$

$$S = k \ln \Omega (N, N_\uparrow)$$

and $\Omega = \binom{N}{N_\uparrow} = \dfrac{N!}{N_\uparrow! \, (N - N_\uparrow)!}$

$\Omega = 1$ at $N_\uparrow = N$ $(U = U_{MIN})$

$0! = 1$

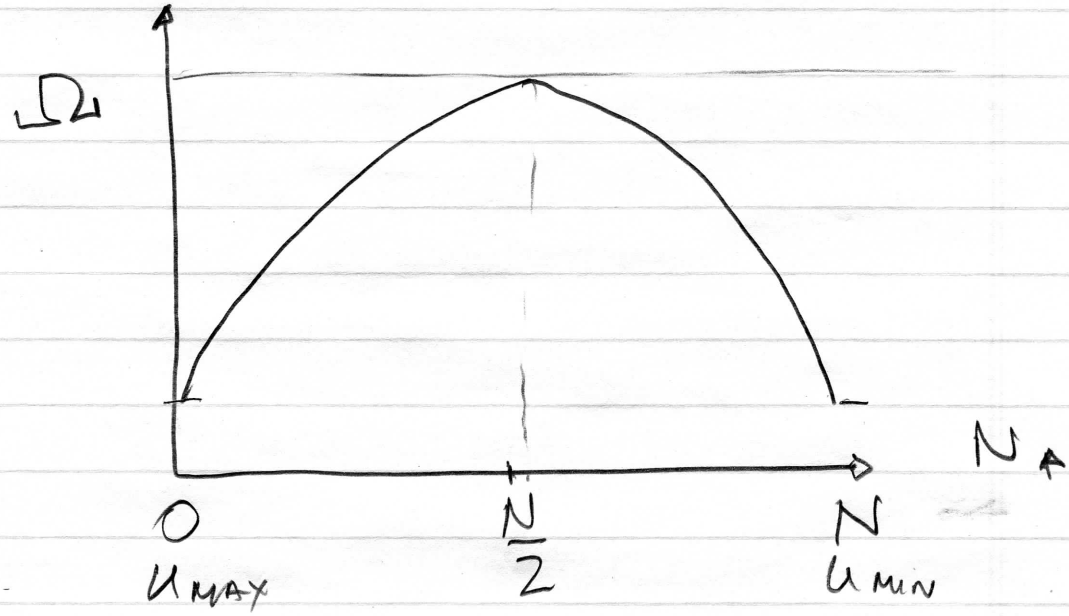
$\Omega = 1$ at $N_\uparrow = 0$ $(U = U_{MAX})$

$\Omega = \text{MAX}$ at $N_\uparrow = \dfrac{N}{2}$ $\qquad \mu_0 B \left(2 \times \dfrac{N}{2} - N\right) = 0$

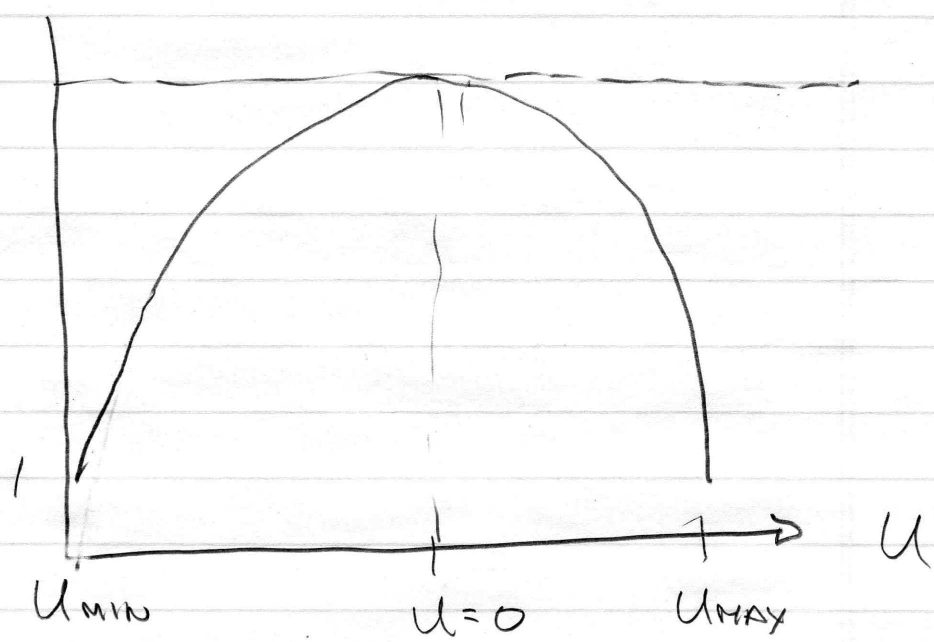
STATE $S = 0$ CLEARLY HAS HIGHEST MULTIPLICITY

(see text)

COULD DRAW THIS like

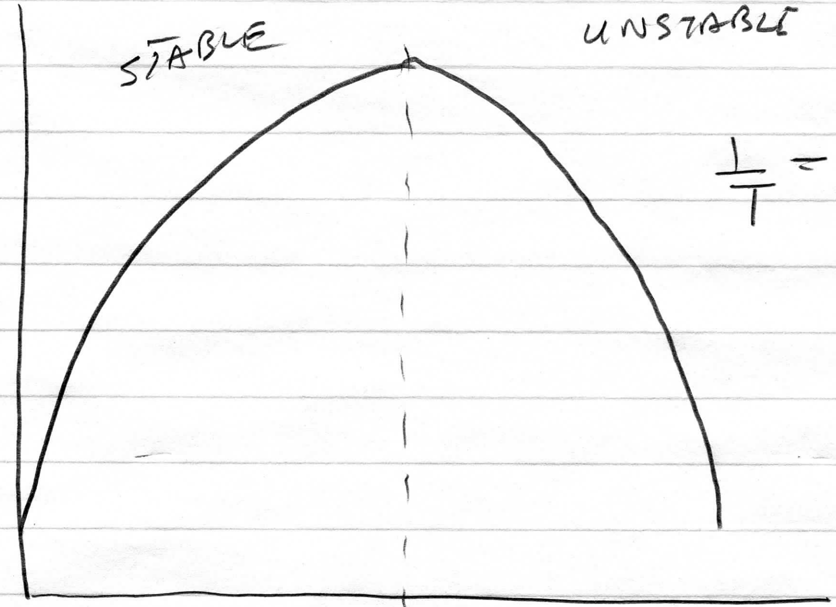


In terms of U



$S = k \ln \Omega$

$\longrightarrow \infty$



POSITIVE T

$\frac{1}{T} = \frac{\partial S}{\partial U} > 0$

$T > 0$

$\frac{1}{T} = \frac{\partial S}{\partial U} < 0$

↑

Negative T

$U_{MIN} = -\mu_0 BN$ $\quad U = 0 \quad$ $U_{MAX} = +\mu_0 BN$

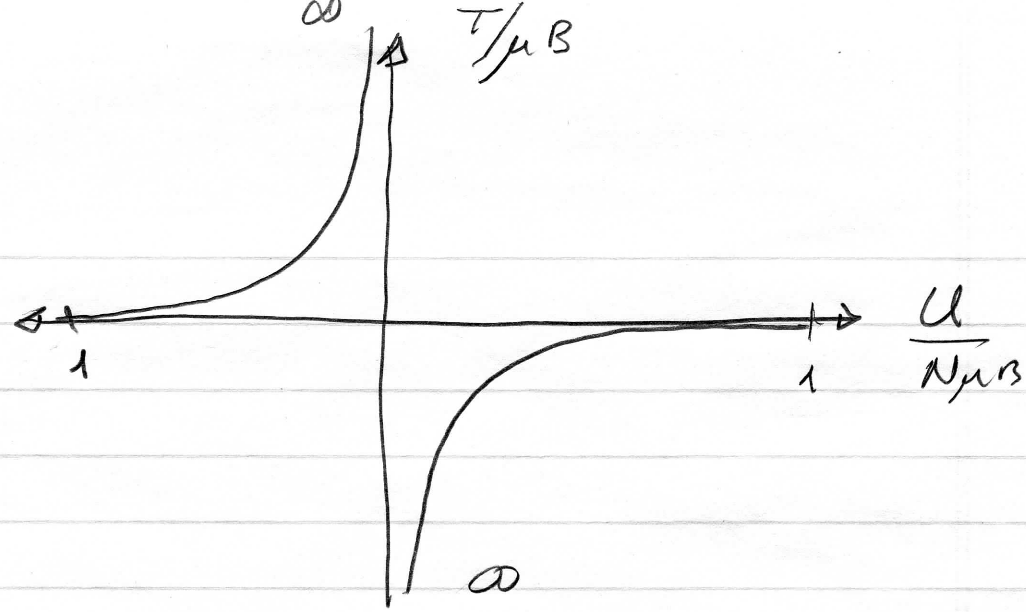
FOR $-\mu_0 BN < U < 0$

PARAMAGNET is NORMAL behaviour $T > 0$

as $U \to 0$ $\left(N_\uparrow - \frac{N}{2}\right)$ $\frac{1}{T} = 0$

$\hookrightarrow -\infty$

$T \to \infty$



As U changes from $0 \to U_{MAX}$

$$U_{MA} = +\mu_0 B N$$

$\frac{1}{T}$ STARTS at $-\infty$ → increases.

- $U > 0$, $T < 0$ is NOT A STABLE thermodynamic state of para magnet. it is unstable state at -ve T.

- SYSTEM with $T<0$ cannot exist in thermodynamic equilibrium with another system

  ↳ Quickly Loses energy to system place in con~~tact~~ TO

  ↳ this increases Ω

$T<0$ is Hotter than $T>0$.

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ENTROPY → DISORDER

UNIVERSE ORDER → DISORDER

ORDER → Number of ways it can be arranged internally and still look the same from the outside

$t - r/c$, $t + r/c$

in enclosure advanced and retarded potentials give the same result

why is everyday life always out of equilibrium

After a long time box of mixed black and white balls will separate

↳ universe had such a fluctuation in the past → things got separated and are now running back together again.

↳ this says irreversibility is just one of the accidents of life

past ← ○ → future → looks same, either way gas mixes if universe came from fluctuation

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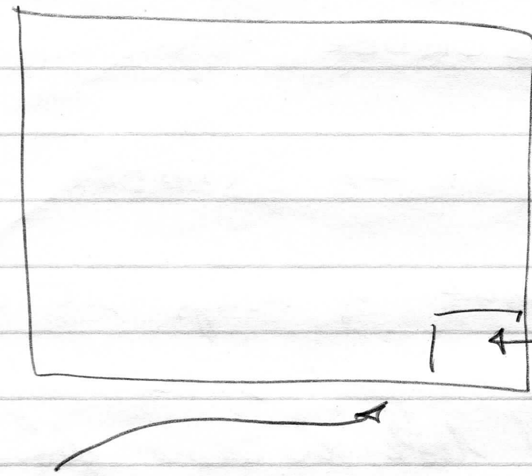

just look into small part of box

→ order in here

→ if we believe order arose from fluctuation

in disorder → most likely rest of box is DISORDERED

even if our part is ordered → everywhere else we look is disordered

Assume separation is because of part of universe
↳ really was ordered

predicts order in other places → stars galaxies

order is memory of conditions when things started.