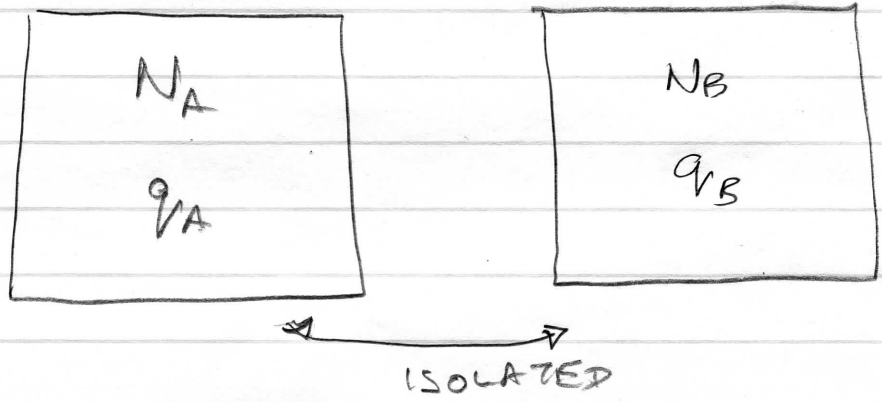


Consider TWO SYSTEMS

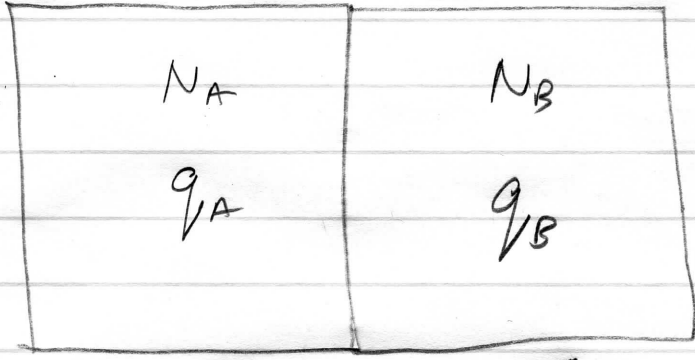
↳ ISOLATED from EACH OTHER
INITIALLY

↳ ISOLATED FROM environment.

↳ MACROSCOPIC

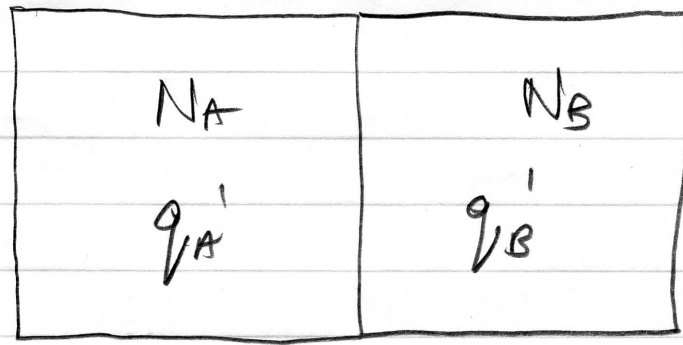


Thermal Contact



do not allow EXCHANGE of particles = oscillators

$$q_A + q_B = \text{Constant}$$



Energy flow?

What are values of q_A' q_B'
when Thermodynamic Equilibrium
established

$$q_A' + q_B' = q_A + q_B$$

Total number of energy
quanta do not change



SYSTEMS ISOLATED

STAT MECH POSTULATE

↳ every microstate of the combined system is equally likely.

For given $q \rightarrow q = q_A' + q_B'$

↑ many different

? which values of q_A', q_B' most likely.

↳ it will be q_A', q_B' which have

HIGHEST MULTIPLICITY

→ A & B are both MACROSCOPIC

↳ makes sense to speak

of how $q = q_A' + q_B'$

distributed

$q_A', q_B' \rightarrow$ BOTH MACROSCOPIC

Numerically $N_A = 300$, $N_B = 200$

$$q = 100 = q_{A'} + q_{B'}$$

$$\Omega_A(N_A, q_{A'}) = \frac{(N_A - 1 + q_{A'})!}{(N_A - 1)! q_{A'}!}$$

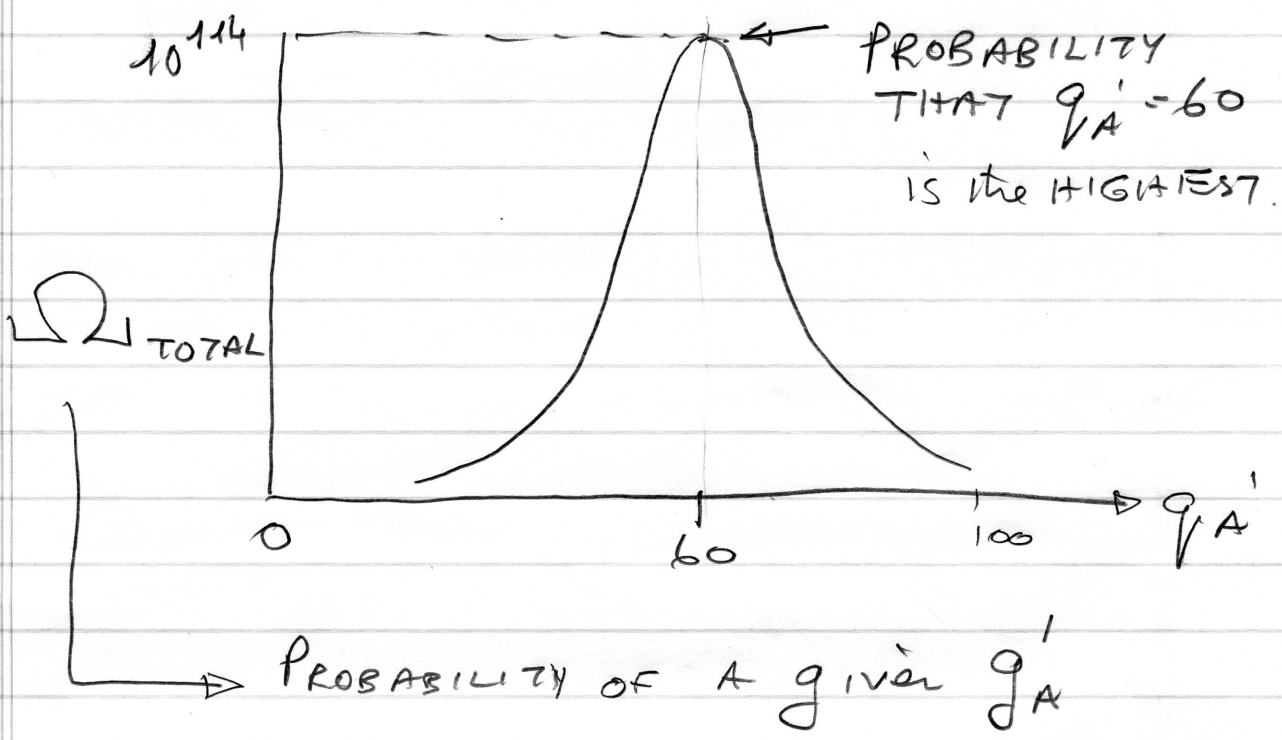
$$\overset{\text{TOTAL}}{\Omega}(N_A + N_B, q = q_{A'} + q_{B'}) = \underset{\text{each system}}{\Omega}(N_A, q_{A'}) \Omega(N_B, q_{B'})$$

$q_{A'}$	Ω_A	$q_{B'}$	Ω_B	Ω_{TOT}
0	1	100	2.8×10^{81}	2.8×10^{81}
1	300	99	9.3×10^{80}	2.8×10^{83}
2	45150	98	3.1×10^{80}	1.4×10^{85}
⋮				
59	2.2×10^{68}	41	3.1×10^{46}	6.8×10^{114}
60	1.3×10^{69}	40	5.3×10^{45}	6.9×10^{114}
61	7.7×10^{69}	39	8.8×10^{44}	6.8×10^{114}
⋮				
100	1.7×10^{96}	0	1	1.7×10^{96}

MULTIPLICITY OF μ STATES

(5)
14

FOR 3 VALUES of q_A' in BOX $\Omega_{TOTAL} \sim 10^{114}$



\sim NO OF μ STATES ACCESSIBLE at this q_A'

$N_A = 300, N_B = 200$ \leftarrow small number

BUT STILL enormous preponderance of μ states where ENERGY IS DISTRIBUTED EQUALLY between oscillations

$$1.5 = \frac{60}{40} \quad \Leftrightarrow \quad \frac{q_A'}{q_B'} = \frac{N_A}{N_B} \quad \Rightarrow \quad \frac{300}{200} = 1.5$$

(6)
15

EQUIPARTITION for $N \approx 100$

Jim limit $N_{A,B} \rightarrow \infty$ (or 10^{23})

\hookrightarrow Distribution VERY SHARPLY peaked.

\Rightarrow IT IS POSSIBLE that energy per

oscillator is zero in A

$\propto \frac{q}{N_B}$ in B \rightarrow ZERO PROBABILITY

IN OUR example RELATIVE PROBABILITIES

$$\frac{10^{81}}{10^{114}} = 10^{-31} \rightarrow \text{SMALL!}$$

AS $N \rightarrow \infty$

$\rightarrow 0$

In Thermo Dynamic Equilibrium of

LARGE SYSTEM

↳ VALUES of q_A' , q_B' are ones
with HIGHEST COMBINED (A+B) MULTIPLICITY

— IF START WITH $\frac{q_A}{N_A} \neq \frac{q_B}{N_B}$

↳ PUT SYSTEMS IN CONTACT, THEN THIS
WILL MAXIMIZE Ω_{TOTAL} ← MULTIPLICITY OF μ STATES

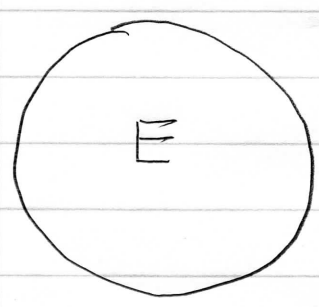
and leads to

$$\frac{q_A'}{N_A} = \frac{q_B'}{N_B} \rightarrow \text{Equal Temp.}$$

2ND LAW
of
TD

Maximize Ω = Maximize Entropy

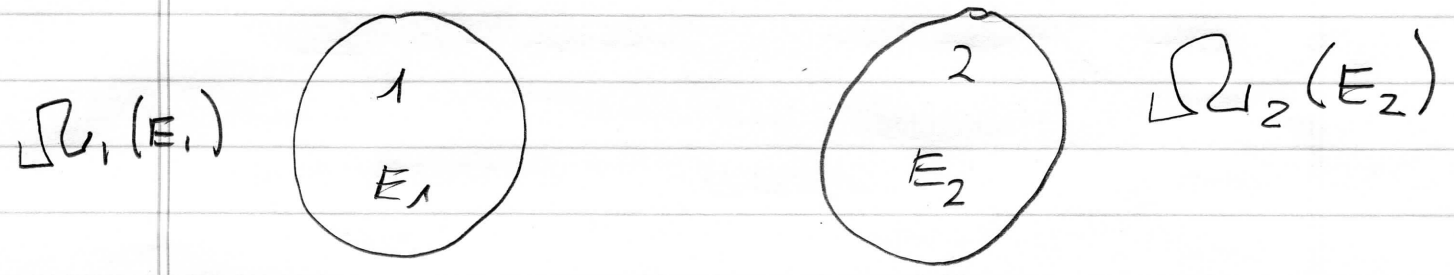
GENERALIZE EINSTEIN SOLID



- Closed system energy E
- multiplicity $\Omega(E)$
- Prob (any μ STATE with $E = \frac{1}{\Omega(E)}$)

POSTULATE
of
STAT
MECH

Use the Postulate of STAT Mech.

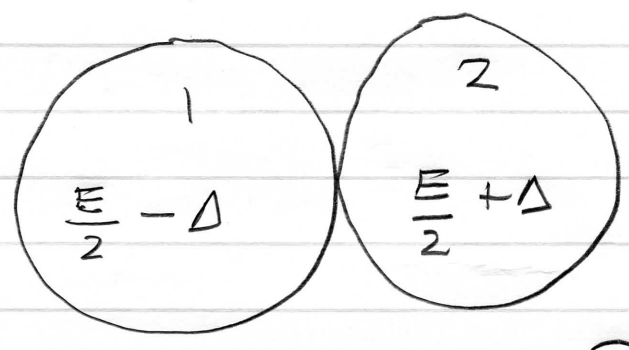


initially isolated

put in THERMAL CONTACT

$$E = E_1 + E_2 = \text{CONSTANT}$$

When TD Equilibrium Established



How to determine Δ ?

↳ maximize PROBABILITY

Prob of given $\Delta \propto \Omega_{1+2}(E, \Delta) = \Omega_1\left(\frac{E}{2} - \Delta\right) \Omega_2\left(\frac{E}{2} + \Delta\right)$

↳ this TRUE for All systems in THERMODYNAMIC LIMIT.

$N \rightarrow \infty$

$V \rightarrow \infty$

$U \rightarrow \infty$
(E)

But $\frac{N}{V}$ & $\frac{N}{E}$ fixed.

↳ All systems, not just Spin
EINSTEIN SOLID

$$\Omega_{1+2} = \Omega_1 \times \Omega_2$$

means!

for EVERY μ STATE OF (1) $\begin{matrix} \nearrow \\ \searrow \end{matrix}$ Can have ANY μ STATE of (2)

\rightarrow TRUE even if interactions between 1 \leftrightarrow 2 NON-negligible

\hookrightarrow REASON

\hookrightarrow interactions between, say,

spins only occur close to Boundary

As $V \rightarrow \infty$ relevance of Boundary

goes as area $\propto V^{2/3}$

$V^{2/3}$ grows much slower

than V , as $V \rightarrow \infty$

In TERMS of PROBABILITIES

$$P(E, \Delta) = \frac{\Omega_1\left(\frac{E}{2} - \Delta\right) \Omega_2\left(\frac{E}{2} + \Delta\right)}{\Omega_{1+2}(E)}$$

↑
 PROBABILITY THAT
 COMBINED SYSTEM
 will have

↑
 TOTAL NUMBER of
 μ STATES of 1+2
 with energy E

$$\frac{E}{2} - \Delta \text{ in } \textcircled{1}$$

$$\frac{E}{2} + \Delta \text{ in } \textcircled{2}$$

$$\Omega_{1+2}(E) = \sum_{\Delta'} \Omega_1\left(\frac{E}{2} - \Delta'\right) \times \Omega_2\left(\frac{E}{2} + \Delta'\right)$$

Σ → over ALL energy distⁿs.

DENOMINATOR → INDEPENDENT OF Δ

↳ TO MAXIMIZE P(E, Δ) w.r.t Δ

Simply MAXIMIZE NUMERATOR

$$\frac{\partial \ln \Omega_1 (E_1')}{\partial E_1'} = \frac{\partial \ln \Omega_2 (E_2')}{\partial E_2'}$$

Depends on

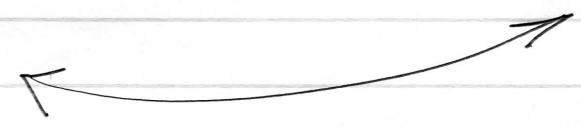
Depends on

- 1) Nature of system
↳ Ω_1

- 1) Nature of system 2

- 2) Total energy of system

- 2) TOTAL Energy E_2



This MAXIMIZES PROBABILITY

↳ E_1', E_2' will SPONTANEOUSLY ADJUST until these 2 quantities become EQUAL

Define $\frac{1}{T_1} = \frac{\partial}{\partial E_1} (k \ln \Omega_1 (E_1))$

defines SCALE!

lets make up a word for this
? TEMPERATURE?

$$\frac{1}{T_2} = \frac{\partial}{\partial E_2} (k \ln \Omega_2 (E_2))$$

$$\frac{1}{T_1} = \frac{\partial}{\partial E_1} (k \ln \Omega_1(E_1))$$

$$\frac{1}{T_2} = \frac{\partial}{\partial E_2} (k \ln \Omega_2(E_2))$$

In TD Equilibrium

↳ MOST PROBABLE STATE $T_1 = T_2$

Have derived QUANTITY \rightarrow DIMENSIONS $\frac{1}{E}$

that tends to equality

mult by $k \rightarrow$ call it TEMPERATURE

STATISTICAL DEFINITION OF TEMPERATURE

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

ENTROPY \rightarrow

\uparrow
BOLTZMAN
CONST.

\uparrow
 $\ln(\# \text{ of ACCESSIBLE } \mu \text{ STATES})$

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

RETURN to EINSTEIN SOLID

Apply understanding of ENTROPY TEMP

MULTIPLICITY function of EINSTEIN SOLID

$$\Omega(N, q) = \frac{(q + N - 1)!}{q! (N - 1)!}$$

$$\approx \frac{(q + N)!}{q! N!} \quad \begin{matrix} N \approx N - 1 \\ \text{for } N = 10^{23} \end{matrix}$$

$$\ln \Omega(N, q) \approx \ln (q + N)! - \ln q! - \ln N!$$

STERLING'S APPROXIMATION

$$\ln n! \Big|_{n \rightarrow \infty} \approx \ln \left(n^n e^{-n} \sqrt{2\pi n} \right)$$

$\ln = \log_e$
 $\log_e e = 1$

$$\ln(n^n e^{-n} \sqrt{2\pi n})$$

$$= \ln(n^n) + \ln(e^{-n}) + \ln(\sqrt{2\pi n})$$

$$= n \ln(n) - n + \frac{1}{2} \ln 2\pi n$$

$$= n(\ln n - 1) + \frac{1}{2} \ln 2\pi n$$

OR

USE THIS →

$$= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi$$

Now we assume N large, q large

AND $q \gg N$

→ this is a MACROSTATE where, on average, there is a large number of

quanta of energy in EACH OSCILLATOR

$$\frac{q}{N} \gg 1$$

$$N \gg 1, q \gg N$$

had

$$\ln \Omega(N, q) = \ln (q+N)! - \ln q! - \ln N!$$

→ 1st term using STERLING

$$(q+N) \ln (q+N) = (q+N) \left[\ln (q+N) + 1 \right]$$

NEGLIGIBLE

$$+ \frac{1}{2} \ln (q+N)$$

$$+ \frac{1}{2} \ln \pi$$

NEGLIGIBLE

$$= (q+N) \ln (q+N) + \frac{1}{2} \ln (q+N)$$

But $(q+N) \ln (q+N) \gg \ln (q+N)$
LARGE NUMBERS

→ So $\ln (q+N)! = (q+N) \ln (q+N)$

by same logic

$$\ln q! = q \ln q$$

$$\ln N! = N \ln N$$

$$\begin{aligned}
\text{So } \ln \Omega(N, q) &= (q+N) \ln(q+N) - q \ln q - N \ln N \\
&= (q+N) \ln \left[q \left(1 + \frac{N}{q} \right) \right] - q \ln q - N \ln N \\
&= (q+N) \ln q + (q+N) \ln \left(1 + \frac{N}{q} \right) - q \ln q - N \ln N
\end{aligned}$$

↑
≪ 1

Taylor EXPANSION $\ln(1+\epsilon) = \epsilon + \frac{1}{2} \epsilon^2$

IF $\left(\frac{N}{q}\right) \ll 1$, $\left(\frac{N}{q}\right)^2 \ll \ll 1$

$$\text{so } \ln \left(1 + \frac{N}{q} \right) \approx \frac{N}{q}$$

$$\begin{aligned}
&\rightarrow (q+N) \ln q + (q+N) \cdot \frac{N}{q} - q \ln q - N \ln N \\
&= \cancel{q \ln q} + N \ln q + (q+N) \frac{N}{q} - \cancel{q \ln q} - N \ln N \\
&= N \ln q - N \ln N + \left(1 + \frac{N}{q} \right) \cdot \cancel{q} \frac{N}{\cancel{q}} \xrightarrow{\text{NEGLECT}} \\
&= N \ln q - N \ln N + N
\end{aligned}$$

$$= N \ln q - N \ln N + N$$

$$= \ln q^N - \ln N^N + \ln e^N$$

i.e.

$$\ln \Omega(N, q) = \ln \left(\frac{q e}{N} \right)^N$$

so $\Omega(N, q) \Big|_{\substack{N \gg 1 \\ q \gg N}} = \left(\frac{q e}{N} \right)^N \leftarrow *$

Recall $S = k \ln \Omega$

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



$q \times \omega h$

↑
number of quanta

What are S , and $\frac{1}{T}$ for

EINSTEIN SOLID

$N \gg 1, q \gg N$

$E \gg N h \omega$ — many quanta per oscillator

$$S = k \ln \Omega \approx kN \ln \left(\frac{q^e}{N} \right)$$

$N \gg 1$
 $q \gg N$

$k \ln(\)^N$

Remember $\frac{\partial \ln q}{\partial q} = \frac{1}{q}$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial (\hbar \omega q)}$$

↑ const

$$\Rightarrow \frac{1}{T} = \frac{1}{\hbar \omega} \frac{\partial S}{\partial q} = \frac{1}{\hbar \omega} \frac{\partial}{\partial q} \left\{ kN \ln \left(\frac{q^e}{N} \right) \right\}$$

↑ const

$$\frac{1}{T} = \frac{1}{\hbar \omega} \cdot \frac{kN}{q}$$

So $kT \approx \frac{q \hbar \omega}{N}$

TOTAL ENERGY

TOTAL NUMBER OF OSCILLATOR

average of kT per OSCILLATOR

VIBRATOR



NB
 $S = k \ln \left(\frac{e q^e}{N} \right)^N = Nk \ln \left(\frac{e q^e}{N} \right)$
 $\frac{\partial}{\partial q} = 0$
 $N \gg 1$
 $q \gg N$

$kT \approx$ average energy per oscillator

EQUIPARTITION OF ENERGY

kT per vibrator

for $q \gg N \rightarrow kT \gg \hbar\omega$

this is HIGH-T LIMIT OF EINSTEIN SOLID

— Equipartition HOLDS IN HIGH-T LIMIT.