2/10

(1)

Goal's For Today's Lecture

study multiplicity for big Einstein solid containing two macroscopic <u>interacting</u> Einstein solids

introduce fundamental assumption of statistical physics: all accessible microstates of isolated system are equally likely

show how fundamental assumption leads to several conclusions:

- Ω spontaneously evolves to maximum # of microstates
- heat transfer is irreversible
- heat transfer is not a law of nature but a consequence of probabilities

how to handle large factorials by Stirling's formula

show that width of multiplicity is $1/\sqrt{N}$ so exceedingly narrow for $N \sim 10^{23}$

Key discovery of last lecture

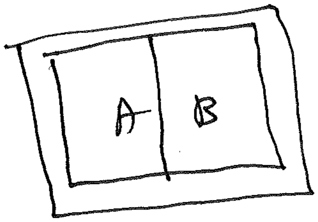
$$\Omega(N,q) = \binom{N-1+q}{q}$$

N = # of identical independent quantum harmonic oscillators

q = total energy of all N oscillators, $q = q_1 + \cdots + q_N$

Einstein Solid With Two Interacting Subsystems

To understand why entropy evolves to maximum, why there is "spontaneous" irreversible transfer of heat from high temp to low temp subsystems, look at isolated Einstein solid consisting of two macroscopic interacting subsystem



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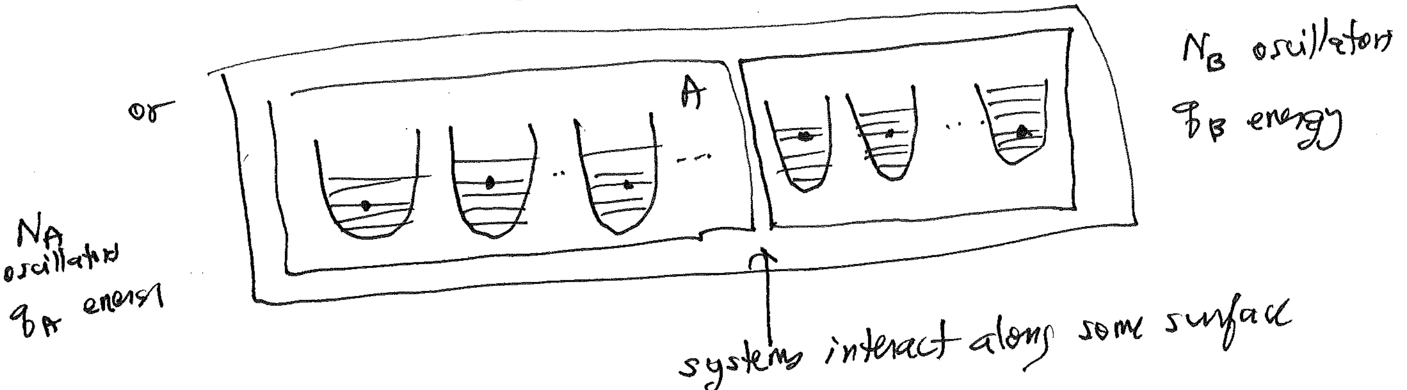


$$\# \text{ of atoms in surface} \propto L^2$$

$$\# \text{ of atoms in volume} \propto L^3$$

$$\frac{\text{energy of interaction}}{\text{energy of subsystem}} \sim \frac{A}{V} = \frac{1}{L}$$

so for local interactions, just between nearby atoms and oscillators, interaction is weak, transfer of energy is slow

For weakly interacting subsystems, energy of each subsystem changes slowly over time, of order L^2/K where K is thermal diffusivity ($\sim 10^{-5}\ m^2/s$ for many solids).

So over short time intervals $< L^2/K$, can consider energies q_A and q_B of two subsystems constant

so can define macrostate of two subsystems by value of q_A since q_B known by energy conservation

$$q_A + q_B = q \quad = \text{total energy}$$

q_A, q_B, q non-negative integers

multiplicity of A: $\Omega_A = \Omega(N_A, q_A) = \binom{N_A - 1 + q_A}{q_A}$

multiplicity of B: $\Omega_B = \Omega(N_B, q_B) = \binom{N_A - 1 + q - q_A}{q - q_A}$ since $q_B = q - q_A$

multiplicity of entire isolated solid

$$\boxed{\Omega_{total} \approx \Omega_A \times \Omega_B}$$

since, for weakly interacting subsystems, A and B are statistically independent so # microstates in A independent of # microstates in B

Ω is multiplicative over subsystems!

Discuss Fig. 2.5 on page 57 of Schroeder

Show Mathematica code coupled-einstein-solids.nb on projector

assume $N_A = 300$ oscillators

$N_B = 200$ oscillators

$q = 100$ energy units (actual $U = \hbar\omega q$) ← harmonic oscillator frequency

total number of macrostates is 101

$q_A = 0, 1, \ldots, 99, 100$

total number of microstates is $\binom{N_A + N_B - 1 + q}{q}$ } pool all oscillators together to get this #

$$= \binom{499 + 100}{100} \sim 10^{116}$$

an enormous number compared to # of macrostates

If we put A together with B and wait, we expect uniform distribution of energy so expect equilibrium solid to have

$$q_A \text{ in equilibrium} = \frac{300}{300+200} \times \overset{q}{100} = 60$$

$$q_B \text{ in equilibrium} = \frac{200}{300+200} \times 100 = 40$$

Work out multiplicity $\Omega_{total}(q_A)$

q_A	$\Omega_A = \binom{N_A-1+q_A}{q_A}$	q_B	$\Omega_B = \binom{N_B-1+q-q_B}{q-q_B}$	$\Omega_{total} = \Omega_A \Omega_B$
0	1	100	$2.8 \cdot 10^{81}$	$3 \cdot 10^{81}$
1	300	99	$9.3\ 10^{81}$	$2.8 \cdot 10^{83}$
2	45150	98	$3.1 \cdot 10^{80}$	$1.4 \cdot 10^{85}$
⋮		⋮		
100	$1.7 \cdot 10^{96}$	0	1	$1.7 \cdot 10^{96}$
				Σ

sum of Ω_{total} column $= \binom{N_A+N_B-1+q}{q} \simeq 10^{116}$

see Schroeder p. 59 and Mathematica code

$\max(\Omega_{total}) = \Omega_{total}(60) \simeq 6.9 \cdot 10^{114}$

$\min(\Omega_{total}) = \Omega_{total}(0) \simeq 2.8 \cdot 10^{81}$ ← huge # even for smallest multiplicity

$\frac{\max(\Omega_{total})}{\min(\Omega_{total})} \simeq 10^{33}$

some macrostates enormously more likely than other macrostates because # of accessible microstates differ by so much

Connection of multiplicities to physics made by fundamental assumption of statistical physics

"all accessible microstates of isolated system are equally likely"

Bit tricky how to interpret words "equally likely"

① if you take a snapshot of system at any time, each microstate equally likely to be observed at that time, in which requires sense of rapid random evolution, macroscopic system fluctuates or flitters or transitions endlessly from one consistent microstate to another consistent microstate

② Or consider an ensemble of K identical isolated Einstein solids, each with $N_A + N_B$ oscillators, each with total energy q. Then we can look at all K solids at one time and see many different accessible microstates

Fundamental assumption allows us to convert multiplicities $\Omega_{total}(q_A)$ into probability of observing Einstein solid with energy q_A in A, energy $q - q_A$ in B

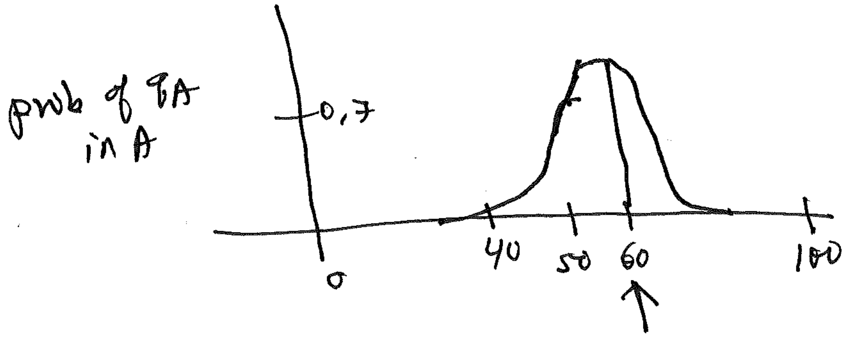
$$\text{prob}(q_A \text{ in } A) = \frac{\Omega_{total}(q_A)}{\Omega_{total}}$$

} total # of microstates for A+B

Look at Mathematica code

coupled-einstein-solids.nb

and calculation of probalities. Get plot



prob hits peak at $q_A = 60$, exactly as we expect based on uniform distribution of energy

prob decreases rapidly away from $q_A = 60$

$\text{prob}(q_A < 30)$, $\text{prob}(q_A > 90) \sim 10^{-6}$

$\text{prob}(q_A < 10) \sim 10^{-20}$

↖ unobservable over age of universe

$10^9\,\text{y} \times 10^7\,\frac{\text{s}}{\text{y}} \simeq 10^{16}\,\text{s}$

Conclude: if all microstates of Einstein solid equally likely, only energy partitions with q_A close to 60 likely

(1) system evolves spontaneously toward max of Ω_{total}

(2) transfer of heat is irreversible, very probable

Have discovered entropy: $S = k\ln\Omega$

Ω is multiplicative over weakly interacting subsystem

$$\Omega_{total} \approx \Omega_A \times \Omega_B$$

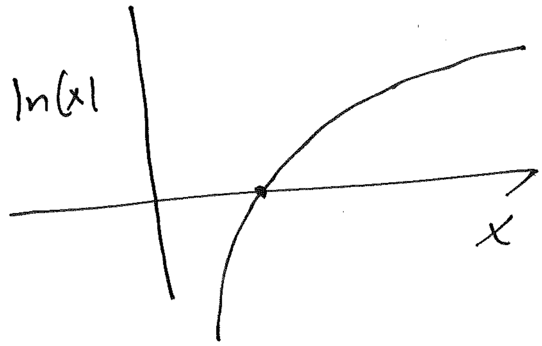
so $$S_{total} = k\ln[\Omega_A \Omega_B] = k\ln\Omega_A + k\ln\Omega_B$$
$$= S_A + S_B$$

entropy is additive since Ω multiplicative

Further: $\frac{dS}{dt} > 0$ for nonequilibrium isolated system

reason is that Ω steadily increases towards Ω_{max} as macrostates with most accessible microstates are much more likely

S = k ln Ω also increases to maximum since ln(x) is monotone increasing: $\frac{d\ln(x)}{dx} = \frac{1}{x} > 0$ for $x > 0$

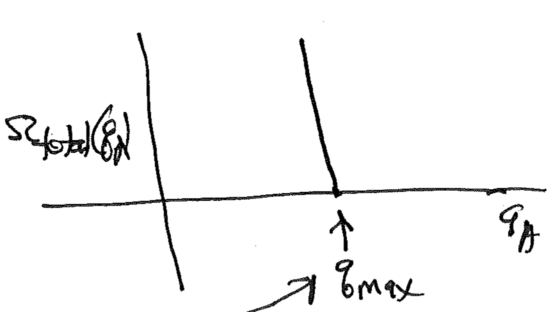


Next Big Insight:

Width of $\Omega_{total}(q_A) \propto \frac{1}{\sqrt{N}}$ where

N = total # of oscillators

In English: as # of oscillators approaches big #s of order $N_A \sim 10^{23}$, multiplicity of Einstein solid becomes fantastically narrow, $1/\sqrt{N} \simeq 10^{-10}$



what curve looks like for $N_A \sim N_B \simeq 10^{23}$,

essentially never see any arrangement of energy between two subsystems except for uniform distribution

$$q_A = \left(\frac{N_A}{N_A + N_B}\right) q = q_{max}$$

$$q_B = \left(\frac{N_B}{N_A + N_B}\right) q$$

can only observe one state (to 10 digits) with maximum number of microstates.

To derive this result, need to learn how to approximate binomial coefficients $\binom{N}{k}$ when $N \sim 10^{23}$, $k \sim 10^{23}$

surprisingly, this is not so hard to do

Working With Big Numbers

To understand Einstein solids for $N \sim 10^{23}$ need to find ways to approximate $\Omega(N, q) = \binom{N-1+q}{q}$ for $N, q \gg 1$

Useful to think about different sizes of #s:

small or human #s: 1–1,000 can count comfortably
money you would notice missing

large #s: $\underset{\text{large \#}}{\underset{\uparrow}{l}} = 10^{\overset{\text{small \#}}{\overset{\downarrow}{s}}}$

Avogadro 10^{23}

#stars in galaxy 10^{11} = # neurons in human brain = # galaxies in universe

googol 10^{100}

moves in chess game $\sim 10^{120}$

10^{36} years time for proton to decay

machine precision $\frac{1}{10^{16}}$

note: $70! \simeq 10^{100}$

large #'s have unusual property that

$$\boxed{s + l = l}$$

small number added to large # same as large #

e.g. $10 + 10^{23} \simeq 10^{23}$

$10^{-17} + 1 = 1$ on computer

implies that one should add power series backwards, smallest terms first

$$\underrightarrow{x^{100} + x^{99} + \dots + x + 1}$$

Very Large Numbers

$V = 10^l$

examples $\Omega \sim 10^{10^{23}}$

googolplex $10^{10^{100}}$

Very large numbers have property

$\boxed{l \cdot V = V}$ large × very large = very large

E.g. $10^{23} \cdot 10^{10^{100}} = 10^{23+10^{100}} = 10^{10^{100}}$

Biggest number used in serious way in science or mathematics is Graham's #, extremely difficult to grasp

hint is to understand g_1, first of 64 recursions of exponentiation

algorithm:

tower 1 = 3 $3^{27} = 7625597484987$

tower 2 = 3^(3^3) height of tower given by tower 1

tower 3 = 3^3^...3 ← # of 3's is 3^3^3

tower 4 = 3^3...^3 # of 3's given by tower 3

⋮

tower n = 3^3^...3 } # of 3's given by tower $n-1$

when n = value of 3rd tower

g_1 is starting point for constructing Graham's #

Stirling's Formula

Back to problem of how to estimate $\binom{N}{k} = \frac{N!}{k!(N-k)!}$ for N, k large numbers, 10^5 eg, say 10^{23}

Use gift of 17^{th} and 18^{th} century mathematics from de Moivre and Stirling called Stirling's formula

$$n! = 1 \cdot 2 \cdot \cdots \cdot n \simeq \sqrt{2\pi n}\left(\frac{n}{e}\right)^n = St(N)$$

already accurate for $n \gtrsim 5$

see Mathematica plot of relative error

$$\frac{n! - St(n)}{n!} \quad \text{vs } n$$

Note: for n large, $\left(\frac{n}{e}\right)^n$ is a very large #

$\sqrt{2\pi n}$ is just a large #

so $\quad n! \simeq \left(\frac{n}{e}\right)^n$ for $N \sim 10^{23}$

$$\Longrightarrow \boxed{\ln(n!) = n\ln n - n}$$

widely used form of Stirling's formula

$$n! \simeq e^{n\ln n - n} = e^{n(\ln n - 1)}$$

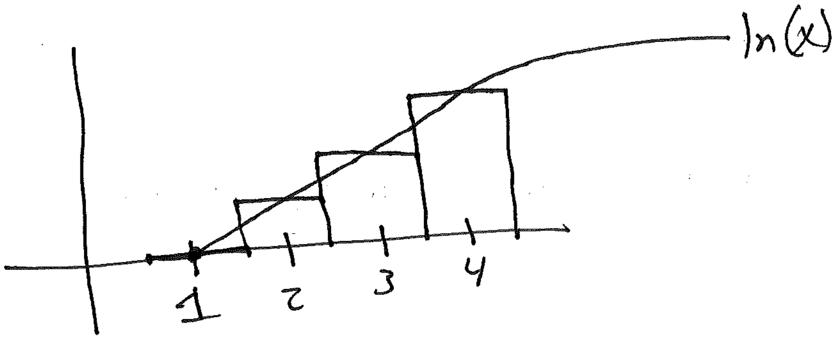
grows a bit faster than exponentially with n

$$70! \simeq 10^{100} = 1 \text{ googol}$$

Origin Of Stirling's Formula

Look at $\ln(n!) = \ln(1 \cdot 2 \cdot 3 \cdots n)$

$= \ln(1) + \ln(2) + \cdots + \ln(n)$



can guess that $\ln(1) + \ln(2) + \ln(3) + ..$ is roughly area under $\ln(x)$ from 1 to n

$$\ln(n!) = \sum_{i=1}^{n} \ln(i) \simeq \int_{1}^{n} \ln(x)\,dx = x\ln(x) - x \Big|_{1}^{n} \simeq n\ln(n) - n$$

This was discovered by de Moivre

Stirling discovered the $\sqrt{2\pi n}$ factor

Euler using Euler-Maclaurin formula showed how to develop systematic corrections to this area formula

Schroeder gives another derivation on pages 390-391 that I will guide you through on homework problem.

Outline of analyzing Einstein solid for many ($\mathcal{O}(N_A)$) oscillators

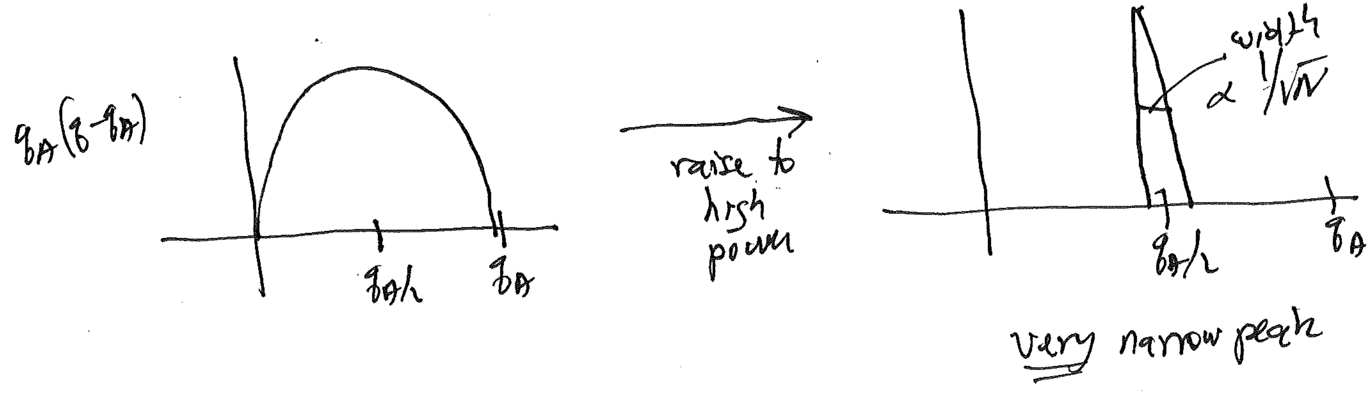
show that $$\Omega(N,q) = \binom{N-1+q}{q} \simeq \left(\frac{eq}{N}\right)^N$$

when $q \gg N \gg 1$ "high temperature" limit for which a lot of energy over "few" oscillators

then $$\Omega_{total} \simeq \Omega_A(q_A)\,\Omega_B(q_B) = \Omega(N,q_A)\,\Omega(N,q_B) \simeq \left(\frac{e}{N}\right)^{2N}\left[q_A(q-q_A)\right]^N$$

assume equal # of oscillators for simplicity $N_A = N_B = N$

will then show that $[q_A(q-q_A)]^N$ is extremely narrow peak with width $1/\sqrt{N}$ for N large



High temperature approximation to $\Omega(N,q)$, $q \gg N \gg 1$

Use Stirling and Taylor series, nice application

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

The minus ones in $N+q-1$, $N-1$ you would guess can be dropped if $q \gg N \gg 1$ since 1 small compared to N and $N+q$

so guess that

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

can justify this using our rule that "large # × very large # = very large #", For example, observe that

$$\frac{1}{(N-1)!} = \frac{N}{N!} \quad \text{and} \quad (N+q-1)! = \frac{(N+q)!}{N+q}$$

so

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

$\approx \frac{N}{q}$, large # (or reciprocal of large #) compared to $q!$, $N!$ so ignore good mathematical strategy: convert

(1) very large # to large # by log, simplify, then exponentiate to recover original expression

(2) look for opportunity to identify tiny ratio $\frac{N}{q} \ll 1$ and use Taylor expansion

$$\ln \Omega(N,q) \cong \ln\left[\frac{(N+q)!}{N!\,q!}\right] = \ln[(N+q)!] - \ln N! - \ln q!$$

$$\simeq \left((N+q)\ln(N+q) - (N+q)\right) - (N\ln N - N) - (q\ln q - q)$$

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

Observe that $\ln(N+q) = \ln\left[q\left(1+\frac{N}{q}\right)\right] = \ln q + \ln\left(1+\frac{N}{q}\right)$

$$\simeq \ln q + \frac{N}{q} \qquad \text{since } N/q \ll 1$$

where I used Taylor series approx $\boxed{\ln(1+x) \simeq x}$ $\quad |x| \ll 1$

So:

$$\ln \Omega(N,q) = (N+q)\left[\ln q + \frac{N}{q}\right] - N\ln N - q\ln q$$

$$= \left(N\ln q + q\ln q + \frac{N^2}{q} + N\right) - N\ln N - q\ln q$$

$$\cong N[\ln q - \ln N + 1] + \underbrace{N\cdot\left(\frac{N}{q}\right)}_{\text{drop as tiny compared with } N}$$

$\ln(e) = 1$ by defn

$$\simeq N[\ln q - \ln N + \ln(e)]$$

$$\simeq N\ln\left[\frac{qe}{N}\right] \implies \boxed{\Omega = \left(\frac{qe}{N}\right)^N} \quad \text{qed}$$