

Chapter 2 - 2nd Law of Thermodynamics

↳ heat spontaneously flows from high temp to low temp

Einstein Solid

Ideal Gas

↳ Entropy

→ Anacanda python
install language
Monty Python

Combinatorics

one coin
 $P(\text{heads}) = \frac{1}{2}$

multiple coins

$$P(n) = \frac{n}{N}$$

$$P(3 \text{ heads}) = \frac{\Omega(3)}{\Omega(\text{all})}$$
$$= \frac{\Omega(3)}{\sum_{n=0}^n \Omega(n)}$$

← microstate in the macrostate of 3
← all of the microstates

5 coins

microstates { H H T T H — 3 H } macrostates
 T H H H H — 4 H }

how many microstates are in a macrostate?
↳ multiplicity

$$\Omega(n) = \frac{5!}{n!(5-n)!}$$

↑
number of heads

$$\begin{aligned} \Omega(0) &= 1 \\ \Omega(1) &= 5 \\ \Omega(2) &= 10 \\ \Omega(3) &= 10 \\ \Omega(4) &= 5 \\ \Omega(5) &= 1 \end{aligned}$$


$$\Omega(1) = \frac{5!}{1!(5-1)!} = \frac{5!}{1!4!}$$
$$= \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{1 \cdot 4 \cdot 3 \cdot 2 \cdot 1}$$
$$= 5$$
$$\Omega(2) = \frac{5!}{2!3!} = 10$$

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} \leftarrow \text{Notation: } \binom{N}{n}$$

\uparrow
 # of coins

10 atoms each w/ 0 or 1 packets of energy (energy unit)

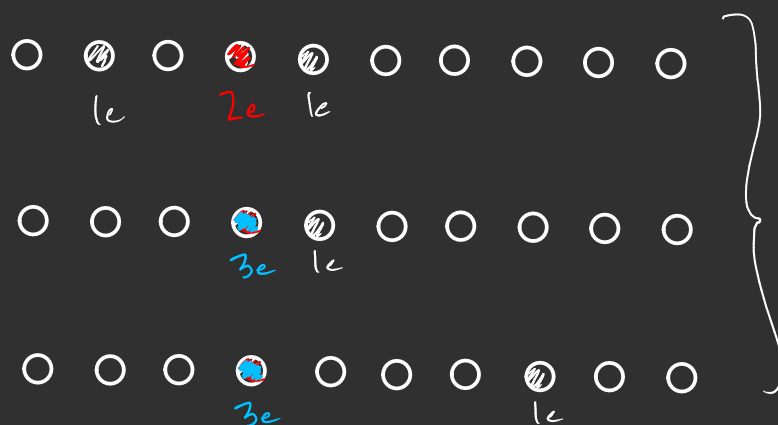
How many possible ways are there to distribute 4 energy units


 \leftarrow microstate

4 energy packets \leftarrow macrostate

$$\Omega(10, 4) = \frac{10!}{4!6!} = 210$$

What if an atom can have more than one energy packet at a time?

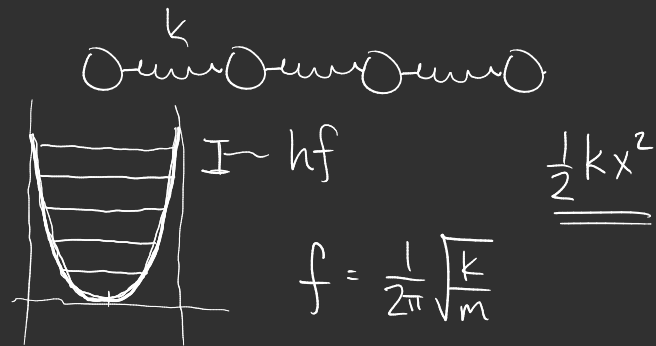

 \leftarrow microstates

4 energy packets \leftarrow macrostate

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

\uparrow # of atoms \uparrow # of energy packets
 $q = \text{macrostate}$

This model of a collection of atoms w/ equal size energy quanta distributed among them is the Einstein Solid.



→ Debye Model

• Large Number → addition of small numbers is not important

$$10^{23} + 23 = 10^{23}$$

• Very Large Number

$$10^{10^{23}} \times 10^{23} = 10^{10^{23} + 23} \approx 10^{10^{23}}$$

Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

↓

$$\ln N! \approx N \ln N - N$$

very large numbers
we leave this off

Two Systems



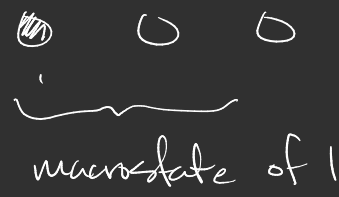
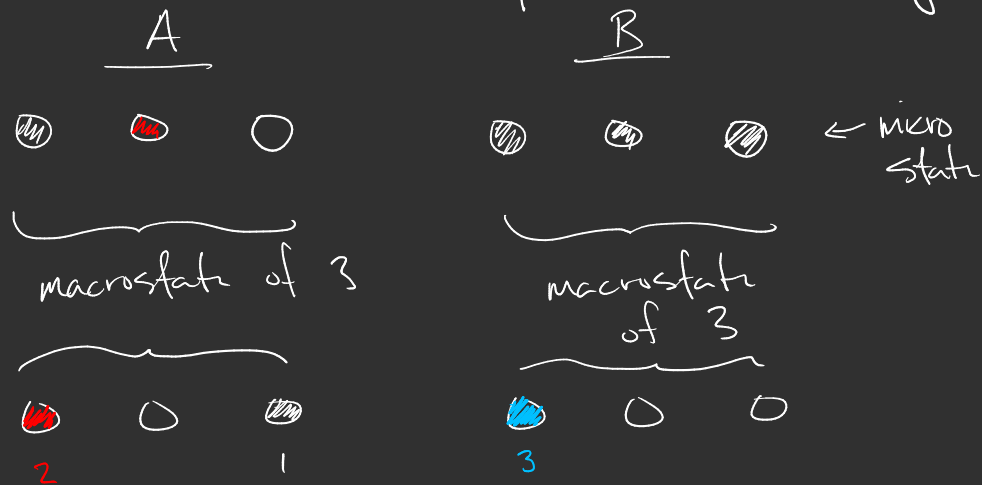
q_A	mult_A	q_B	mult_B	$\text{mult}_{\text{total}}$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

macrostate w/
the most microstates

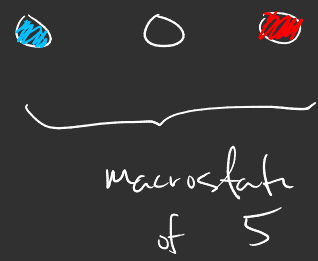
total number
of microstates

(462)

Ex. Each system has 3 particles
and 6 total quanta of energy



$$\Omega(3, 1) = 3$$



$$\Omega(3, 5)$$

$$= \frac{7!}{5!2!} = 21$$

Fundamental Assumption of Stat Mech:

all microstates are possible and equally probable

But that does not mean that every microstate will occur.

Not all macrostates are equally probable.

$$P_A(q) = \frac{\Omega_{\text{total}}(q_A)}{\sum_{q_A} \Omega_{\text{total}}(q_A)}$$

We could find the total # of microstates:

$$\Omega(6, 6) = \frac{(6+6-1)!}{6! (6-1)!} = 462$$

$\uparrow \quad \uparrow$
 $N \quad q$

So let's apply Stirling's Approx to Multiplicity $[\ln N! = N \ln N - N]$

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

very large number

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

$\underbrace{\ln(q+N)!}_{\ln(q+N)! = (q+N) \ln(q+N) - (q+N)}$ $\underbrace{\ln q!}_{q \ln q - q}$ $\underbrace{\ln N!}_{N \ln N - N}$

$$\ln \Omega = (q+N) \ln(q+N) - \cancel{q} - \cancel{N} - q \ln q + \cancel{q} - N \ln N + \cancel{N}$$

$$\boxed{\ln \Omega = (q+N) \ln(q+N) - q \ln q - N \ln N}$$

high temperature limit $\rightarrow q \gg N$

$$\begin{aligned}
 \ln \Omega &= (q+N) \ln(q+N) - q \ln q - N \ln N \\
 &= \underbrace{q \ln(q+N)} + \underbrace{N \ln(q+N)} - q \ln q - N \ln N \\
 &= \ln \left[q \cdot \left(1 + \frac{N}{q} \right) \right] \\
 &= \ln q + \ln \left(1 + \frac{N}{q} \right) \\
 &\quad \downarrow \quad \quad \quad \begin{array}{l} \ln(1+x) \approx x \text{ for small } x \\ \rightarrow \frac{N}{q} \end{array} \\
 &= \ln q + \frac{N}{q} \approx \ln(q+N)
 \end{aligned}$$

$$\begin{aligned}
 \ln \Omega &= \cancel{q \ln q} + N + \underbrace{N \ln q} + \frac{N^2}{q} - \cancel{q \ln q} - \underbrace{N \ln N}_{\text{small}} \\
 &= N \ln \left(\frac{q}{N} \right) + N + \frac{N^2}{q}
 \end{aligned}$$

$$\ln \Omega(q \gg N) \approx N \ln \left(\frac{q}{N} \right) + N$$

$$\Omega(q \gg N) = e^{N \ln \left(\frac{q}{N} \right) + N} = e^{N \ln \left(\frac{q}{N} \right)} \cdot e^N = \underbrace{\left(e^{\ln \left(\frac{q}{N} \right)} \right)^N} \cdot e^N$$

$$\Omega(q \gg N) = \left(\frac{q}{N} \right)^N e^N = \left| \left(\frac{eq}{N} \right)^N \right|$$

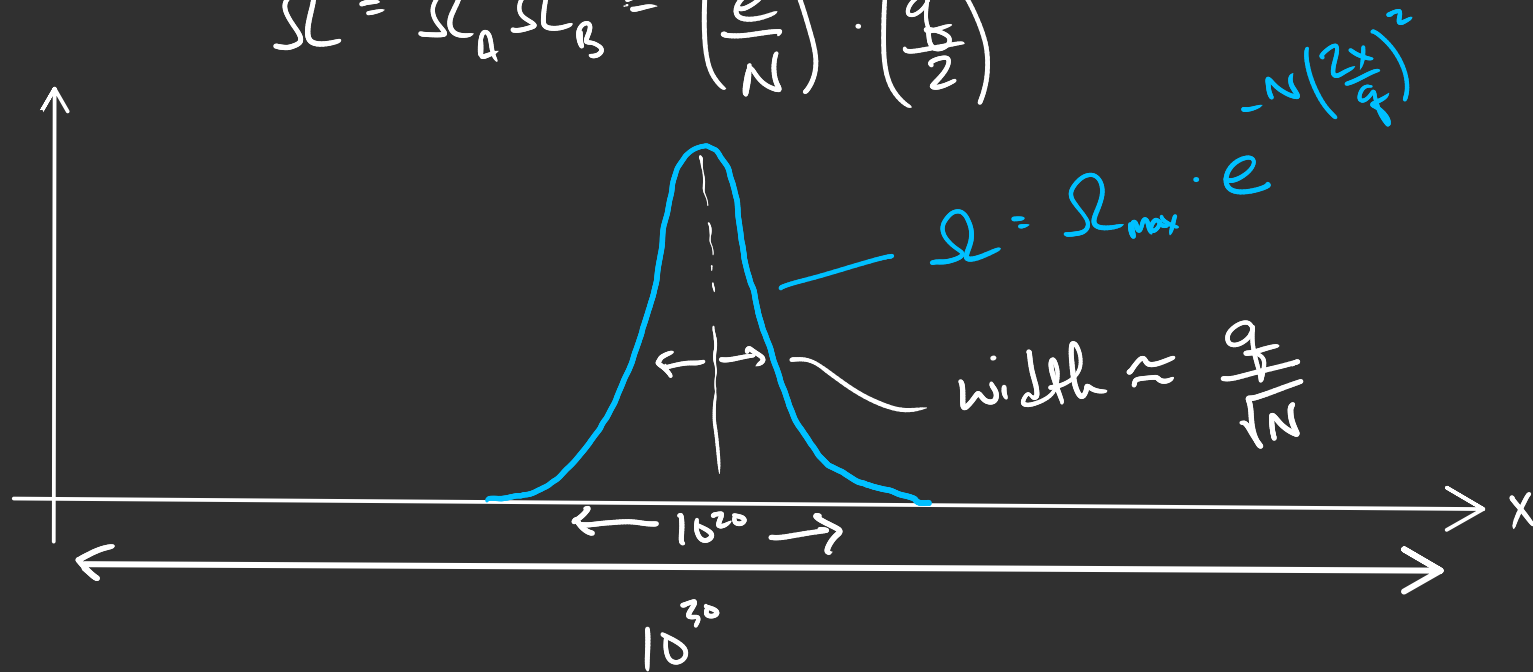
- 2 Einstein solids (high temperature limit) ($q \gg N$)

$$\Omega_A = \left(\frac{eq_A}{N_A} \right)^{N_A} \quad \Omega_B = \left(\frac{eq_B}{N_B} \right)^{N_B}$$

$$q = q_A + q_B$$

if $N_A = N_B$, multiplicity max will occur $\frac{q}{2} = q_A = q_B$

$$\Omega = \Omega_A \Omega_B = \left(\frac{e}{N} \right)^{2N} \cdot \left(\frac{q}{2} \right)^{2N}$$



$$q = 10^{30}$$

$$N = 10^{20}$$

$$\frac{q}{\sqrt{N}} = 10^{20}$$

Entropy + the 2nd Law:

Any large system in equilibrium will be found in the macrostate with the greatest ~~multiplicity~~
entropy

2nd Law of Thermodynamics

~~Multiplicity~~ tends to increase.
Entropy

Multiplicities are very large! Take the natural log of them.

$$\text{entropy} \rightarrow S = k_B \ln \Omega$$

$$\frac{S}{k_B} = \ln \Omega$$

Ex: Entropy of an Einstein solid

$$\Omega = \left(\frac{eq}{N}\right)^N \quad q \gg N \text{ Einstein solid}$$

$$N = 10^{23} \quad q = 10^{25}$$

$$S = k_B \ln \left(\left(\frac{eq}{N} \right)^N \right) = N \cdot k_B \ln \left(\frac{eq}{N} \right) = N k_B \left(1 + \ln \left(\frac{q}{N} \right) \right)$$

\uparrow
 $10^{23} \cdot 1.38 \cdot 10^{-23}$

$$= 1.38 \left(1 + \ln(10^2) \right)$$

$$S = 7.7 \text{ J/K} \quad \underbrace{\quad}_{4.6}$$

Entropy of a composite system

$$\Omega_{\text{total}} = \Omega_A \Omega_B$$

$$S = k_B \ln \Omega_A \Omega_B = k_B \ln \Omega_A + k_B \ln \Omega_B$$

$$S_{\text{t}} = S_A + S_B$$

Chapter 3

Thermal equilibrium

For the Einstein solid

$$\frac{\partial S_{\text{total}}}{\partial q_A} = 0$$

↓ generalize

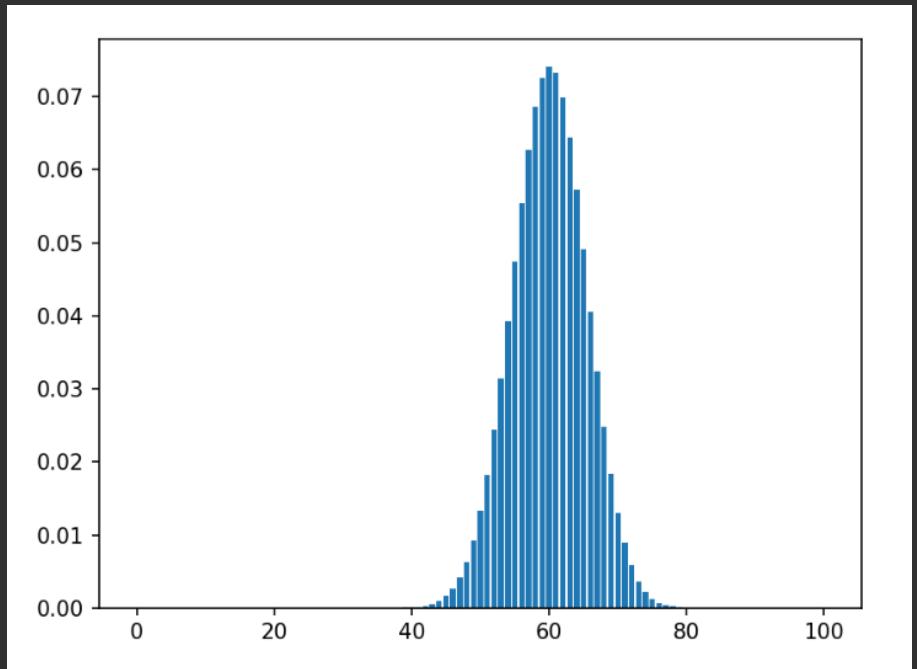
$$\frac{\partial S_{\text{total}}}{\partial U_A} = 0$$

$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

$$U_B = U - U_A$$

$$\left\{ \begin{array}{l} dU_B = -dU_A \end{array} \right.$$



$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

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

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1}_{N,N}$$

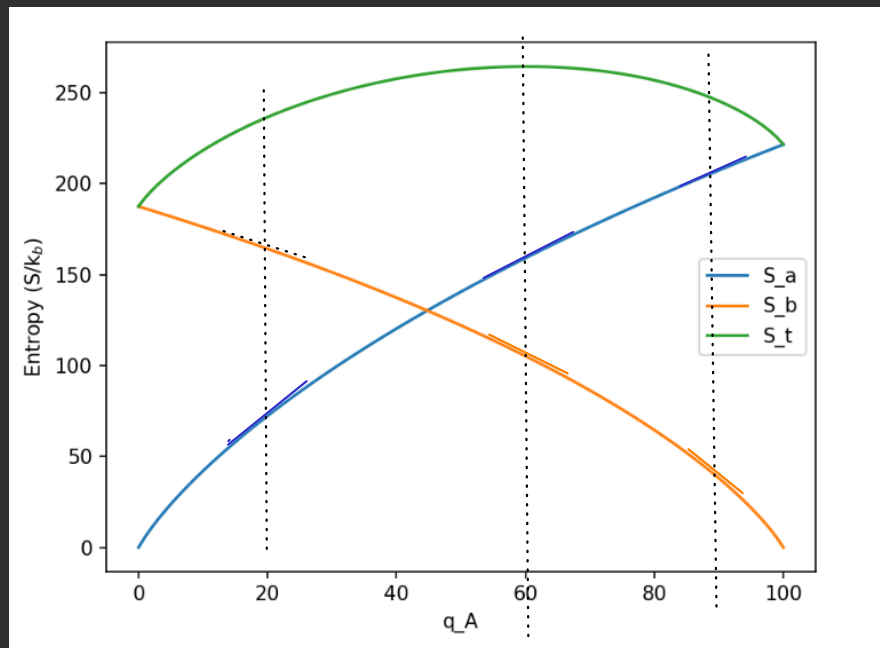
Now apply to our Einstein Solid ($q \gg N$)

$$U = q \cdot \epsilon \Rightarrow q = \frac{U}{\epsilon}$$

↑
of energy packets

↑ energy in one packet

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



$$S = k_B \ln \Omega$$

$$S = k_B \ln \left(\left(\frac{eg}{N} \right)^N \right) = N \cdot k_B \ln \left(\frac{eg}{N} \right) = N k_B \left(1 + \ln \left(\frac{g}{N} \right) \right)$$

$$S = N k_B \left(1 + \ln \left(\frac{U}{N \epsilon} \right) \right)$$

$$S = N k_B + N k_B \ln U - N k_B \ln (N \epsilon)$$

$$\underbrace{\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,V} = \frac{\partial (N k_B \ln U)}{\partial U} = \frac{N k_B}{U}}$$

$$U = N k_B T \leftrightarrow U = \frac{f}{2} N k_B T$$

Heat Capacity of Einstein solid: $f = 2$ } Einstein solid

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{V,N} = N k_B \leftarrow \begin{array}{l} \text{experimentally} \\ \text{testable} \\ \text{quantity} \end{array}$$

↳ 1D kinetic energy

↳ 1D spring pot. energy

Review our process so far:

1. Used combinatorics and QM to find Ω in terms of N, V, U etc. } could be impossible!

2. $S = k_B \ln \Omega$ to get entropy

3. $T = \left(\frac{\partial S}{\partial U} \right)^{-1}_{N, V, \text{etc}}$

4. Solve step #3 for U as a function of T

5. $C_v = \frac{\partial U}{\partial T}$

stat mech
give an alternative
to arriving
at #4

But, going backward to measure the entropy is easy

$$dS = \underbrace{\frac{\partial S}{\partial U}}_{\text{mp}} \cdot dU$$

$$dS = \frac{dU}{T}$$

→ use constant volume process (isochoric)

$$\left. \begin{array}{l} dV = 0 \\ \pm W = 0 \end{array} \right\} dU = \pm Q + \pm W$$

$$dU = \pm Q$$

$$dS = \frac{\pm Q}{T}$$

→ important! used to be the definition of entropy!

→ T does not change much w/ a small addition of heat!

$$dS = \frac{C_v \cdot dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T} dT \rightarrow C_v \text{ can be constant, or a function of temperature}$$

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_v}{T} dT$$

$$S(T) - S(0) = \int_0^T \frac{C_v}{T} dT$$

but you need to know this function all the way to zero kelvin!
 $C_v \rightarrow 0 \text{ as } T \rightarrow 0$

could be 0 or residual entropy but some constant

much experimental data has gone into this for many substances

3rd Law of Thermodynamics

①

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

② ②

③ ④
⑤ ⑥

⑦ ⑧

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

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

⑨ ⑩ ⑪

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