Chapter 2 - 2^{nd} Law of Thermodynamics

↳ heat spontaneously flows from high temp to low temp

Einstein Solid → $\boxed{\text{Entropy}}$ ← Ideal Gas

→ $\boxed{\text{Anaconda}}$ python language

install

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

$$\text{microstates}\begin{cases} H\,H\,T\,T\,H & - \quad 3H \\ T\,H\,H\,H\,H & - \quad 4H \end{cases}\text{macrostates}$$

how many microstates are in a macrostate?

↳ multiplicity

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

number of heads

$\Omega(0) = 1$

$\Omega(1) = 5$

$\Omega(2) = 10$

$\Omega(3) = 10$

$\Omega(4) = 5$

$\Omega(5) = 1$

$$\Omega(1) = \frac{5!}{1!(5-1)!} = \frac{5!}{1!4!}$$

$$= \frac{5 \cdot \cancel{4} \cdot \cancel{3} \cdot \cancel{2} \cdot \cancel{1}}{1 \cdot \cancel{4} \cdot \cancel{3} \cdot \cancel{2} \cdot \cancel{1}}$$

$$= 5$$

$$\Omega(2) = \frac{5!}{2!3!} = 10$$

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

# 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

← microstate

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

4 energy packets ← macrostate

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

microstates

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

# of atoms

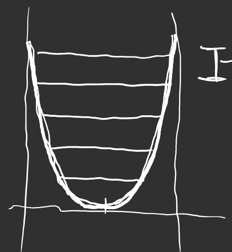
# of energy packets

q = macrostate

4 energy packets ← macrostate

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

$\hookrightarrow$ Debye Model



$\text{I} \sim hf$

$\frac{1}{2}kx^2$

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

- Large Number $\rightarrow$ 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

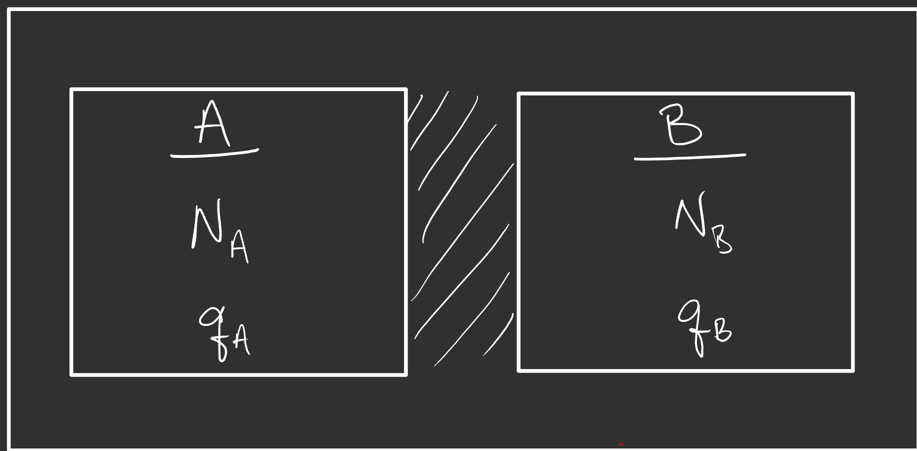
$$N! \approx N^N e^{-N} \sqrt{2\pi N} = \frac{N^N}{e^N} \underbrace{\sqrt{2\pi N}}$$

very large numbers
we leave this off

$$\downarrow$$

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

Two Systems



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

$\Omega(3,1) = 3$

$$\Omega(3,5) = \frac{7!}{5!\,2!} = 21$$

q_A	mult_A	q_B	mult_B	mult_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

462

total number of microstates

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.

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

We could find the total # of microstates:

$$\Omega(\underset{\substack{\uparrow \\ N}}{6}, \underset{\substack{\uparrow \\ q}}{6}) = \frac{(6+6-1)}{6!\,(6-1)!} = \underline{\underline{462}}$$

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

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!} \approx \underbrace{\frac{(q+N)!}{q!\,N!}}_{\text{very large number}}$$

$$\ln \Omega = \underline{\ln(q+N)!} - \underset{\rightarrow\, q \ln q - q}{\ln q!} - \ln N! \longrightarrow N \ln N - N$$

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

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

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

high temperature limit $\rightarrow q \gg N$

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

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

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

$$= \ln q + \underbrace{\ln\left(1+\frac{N}{q}\right)}$$

$\ln(1+x) \approx x$ for small x

$$\frac{N}{q}$$

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

$$\ln\Omega = \cancel{q\ln q} + N + N\ln q + \frac{N^2}{q} \cancel{- q\ln q} - N\ln N$$

$$= N\ln\left(\frac{q}{N}\right) + N + \underbrace{\frac{N^2}{q}}_{\text{small}}$$

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

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

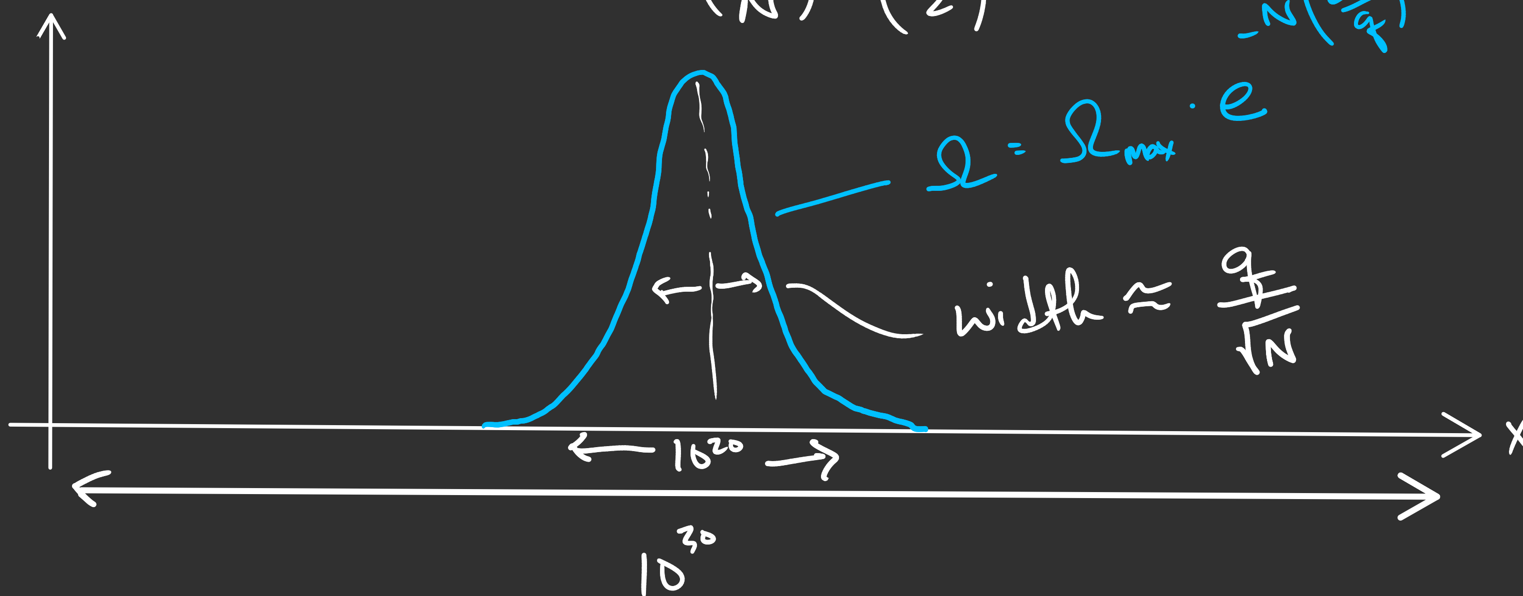
$$\Omega(q>>N) = \left(\frac{q}{N}\right)^{N} e^{N} = \boxed{\left(\frac{eq}{N}\right)^{N}}$$

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

$$\Omega_A = \left(\frac{e q_A}{N_A}\right)^{N_A} \qquad \Omega_B = \left(\frac{e q_B}{N_B}\right)^{N_B} \qquad q = q_A + q_B$$

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

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



$$\Omega = \Omega_{max} \cdot e^{-N\left(\frac{2x}{q}\right)^2}$$

width $\approx \frac{q}{\sqrt{N}}$

$q = 10^{30}$

$N = 10^{20}$

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

Entropy + the 2nd Law:

$$\underbrace{\text{Any large system in equilibrium will be found in the macrostate with the greatest } \cancel{\text{multiplicity}} \text{ entropy}}$$

2nd Law of Thermodynamics

~~Multiplicity~~ Entropy tends to increase.

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

entropy $\rightarrow S = k_B \ln \Omega$

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

Ex: Entropy of an Einstein solid

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

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

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

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

$$= 1.38\left(1 + \underbrace{\ln(10^2)}_{4.6}\right)$$

$$S = 7.7 \text{ J/K}$$

Entropy of a composite system

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

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

$$S_t = S_A + S_B$$

Chapter 3

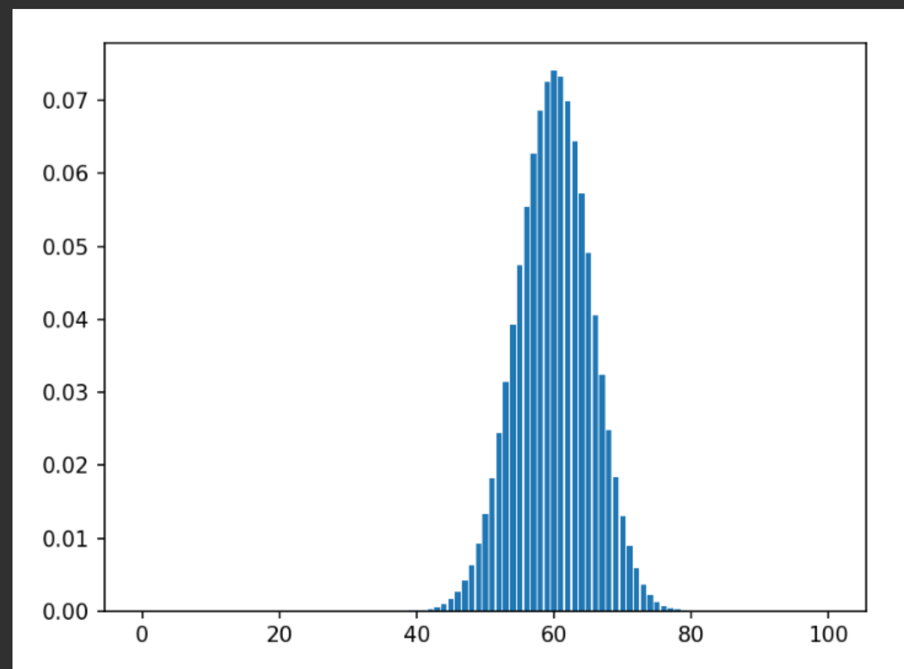
Thermal equilibrium

For the Einstein solid

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

generalize

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



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

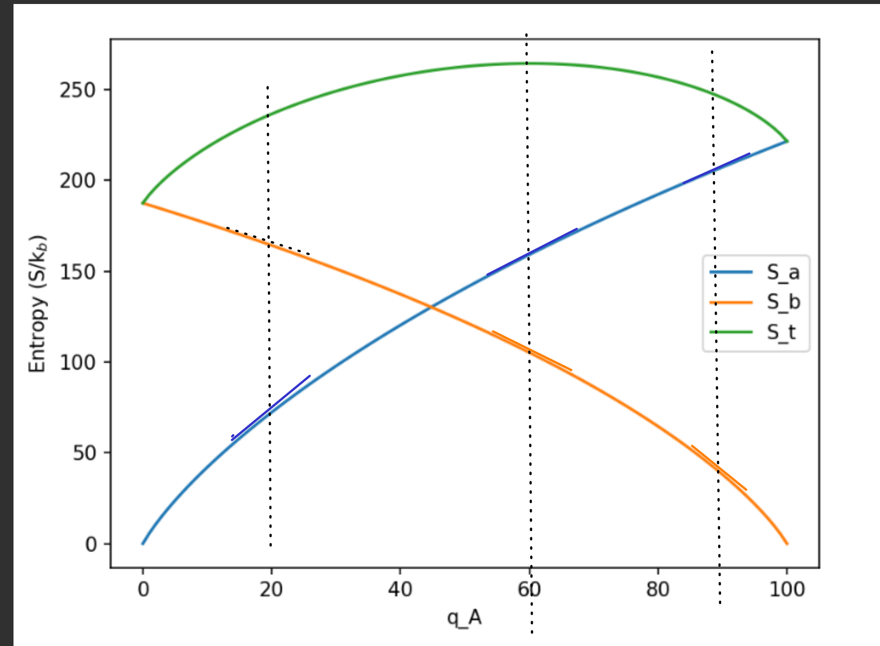
$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

$U_B = U - U_A$

$\{ dU_B = -dU_A$

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

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



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

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

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

$$U = q \cdot \epsilon$$

energy in one packet

# of energy packets

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