# Chapter 2 → $2^{nd}$ Law → Entropy

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

## Combinatorics

Coin flips → 5 coins

H H T T H ← microstate

T H H H H

3 heads ← macrostate

4 heads

$$P(3\text{ heads}) = \frac{\Omega(3)}{\Omega(\text{all})}$$

$$\sum_{n=0}^{n} \Omega(n)$$

How many microstates are in a macrostate?

↳ multiplicity

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

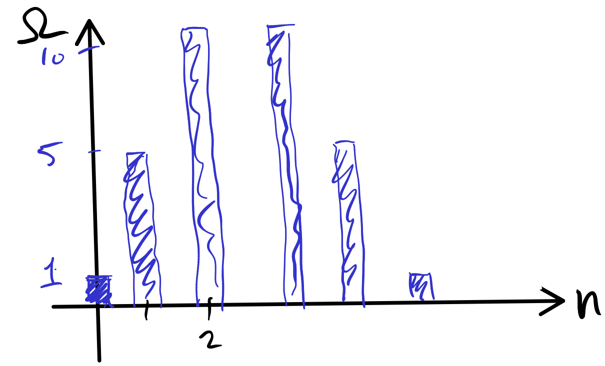
# of heads

$$\frac{5!}{3!\,2!} =$$

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

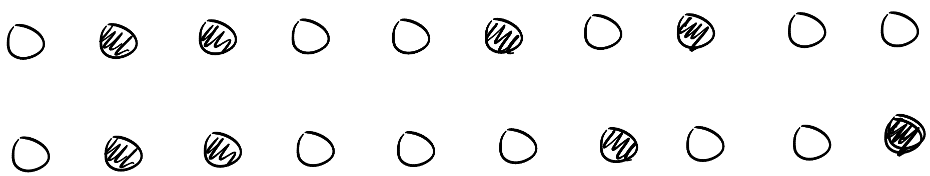
# of coins

# of heads



10 atoms → each one can have 0 or 1 energy units.

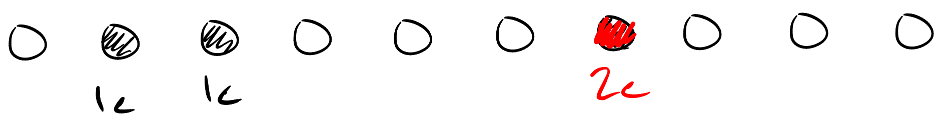
So how many ways are there of arranging 4 units of energy? (10 units of energy)



← microstate

4 energies vs. 10 energies ← macrostate

What if an atom can have more than 1?

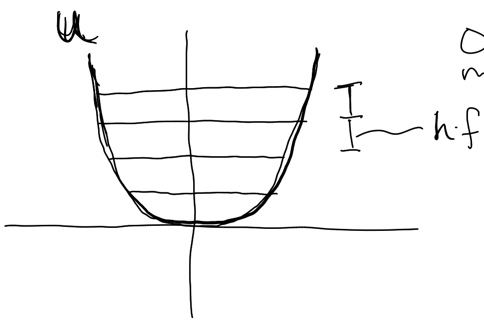


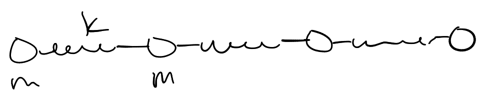

→ need to update the formula

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

This idea of treating a solid like

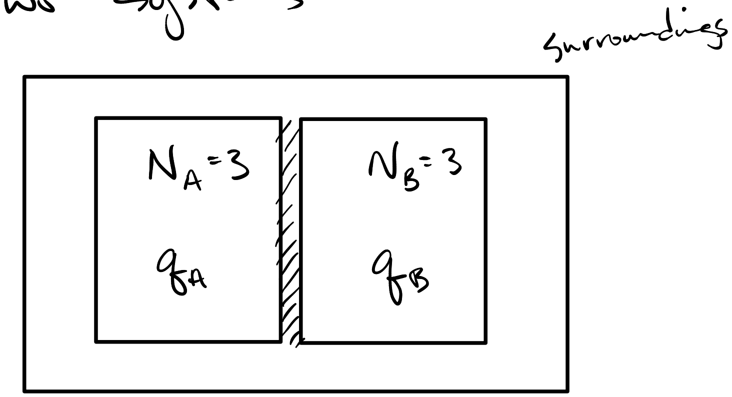
this is known as an Einstein solid ← Debye model




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

Two systems




$q = 6$ ← six quanta of energies that can be shared

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- Large Number → addition of small #s does not matter

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

- Very Large Number

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

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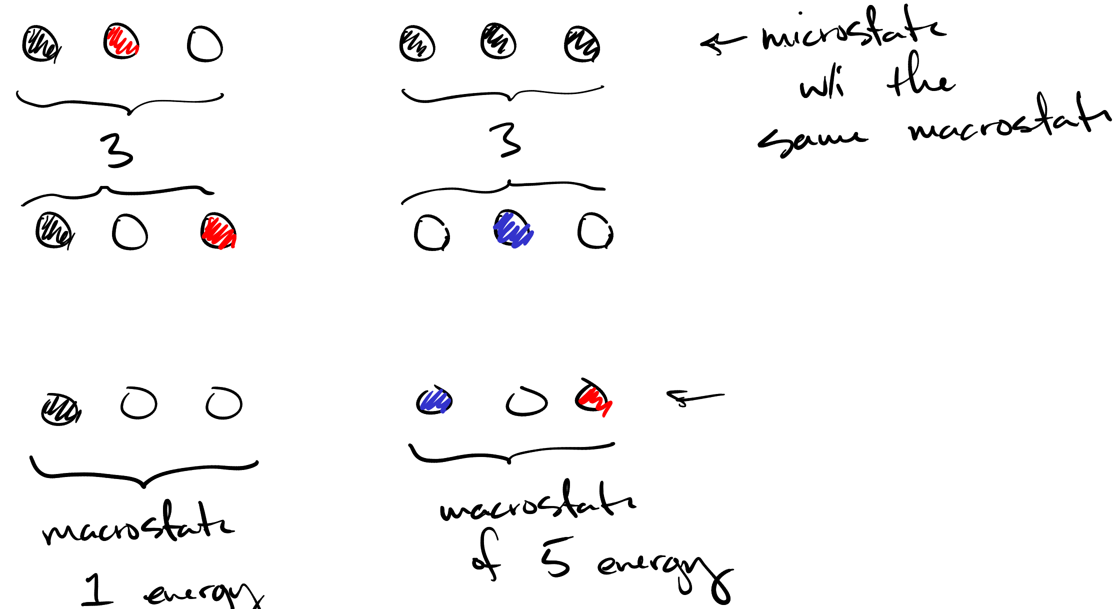
Stirling's Approximation

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

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




$\Omega_A(1) = 3$

$\Omega_B(5) = 21$

$$\Omega_{total} = \Omega_A \cdot \Omega_B = 63$$

Anaconda → jupyter lab

Fundamental Assumption of Statistical Mechanics

↳ all microstates are possible and equally probable.

But, that does not mean that every microstate will occur.

Not all macrostates are equally probable.

```
[1]: %matplotlib widget
```

```
[2]: import numpy as np
     import pandas as pd
     import matplotlib.pyplot as plt
     import scipy.special as sp
```

```
[3]: pd.set_option('display.max_colwidth', None)
     pd.set_option('display.max_columns', None)
     pd.set_option('display.max_rows', None)
```

```
[12]: def factorial(x):
          return sp.factorial(x, exact=True)

      def multiplicity(N, q):
          return factorial(q+N-1)//factorial(q)//factorial(N-1)

      def logArray(array):
          import math
          return [math.log(x) for x in array]
```

## two einstein solids

### 3 particles each and 6 energy units

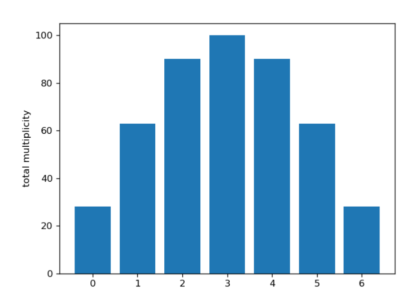
```
[24]: table0 = pd.DataFrame()
      table0['q_A'] = range(0,6+1, 1)
      table0['q_B'] = range(6, 0-1, -1)
      table0['mult_A'] = [multiplicity(3, i) for i in table0['q_A']]
      table0['mult_B'] = [multiplicity(3, i) for i in table0['q_B']]
      table0['mult_total'] = table0['mult_A']*table0['mult_B']
```

```
[25]: table0
```

[25]:

| | q_A | q_B | mult_A | mult_B | mult_total |
|---|---|---|---|---|---|
| 0 | 0 | 6 | 1 | 28 | 28 |
| 1 | 1 | 5 | 3 | 21 | 63 |
| 2 | 2 | 4 | 6 | 15 | 90 |
| 3 | 3 | 3 | 10 | 10 | 100 |
| 4 | 4 | 2 | 15 | 6 | 90 |
| 5 | 5 | 1 | 21 | 3 | 63 |
| 6 | 6 | 0 | 28 | 1 | 28 |

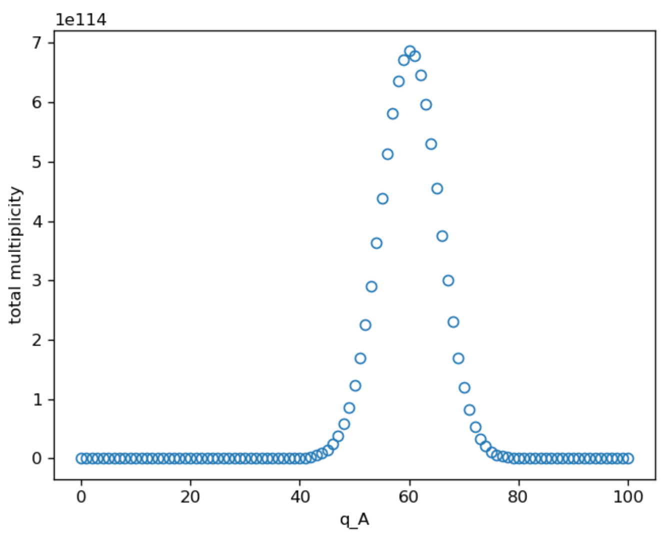
Figure 1




increase to

$N_A = 300,\ N_B = 200$

$q = 100$



So, now lets apply Stirlings Approximation to the Multiplicity

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

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

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

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

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

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

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

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

high temperature limit $\rightarrow$ $q \gg N$

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

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

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

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

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

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

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

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

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

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

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

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

$$\boxed{\Omega(q \gg N) = \left(\frac{eq}{N}\right)^N}$$ ← Einstein solid at high temps

## - problem 2.18

High temperature 2 solids in thermal contact

$$\Omega = \left(\frac{e q_A}{N_A}\right)^{N_A} \cdot \left(\frac{e q_B}{N_B}\right)^{N_B} \qquad N_A = N_B = N$$

$$\Omega = \left(\frac{e}{N}\right)^{2N} \cdot (q_A \cdot q_B)^N$$

$$q_A = q_B = \frac{q}{2}$$

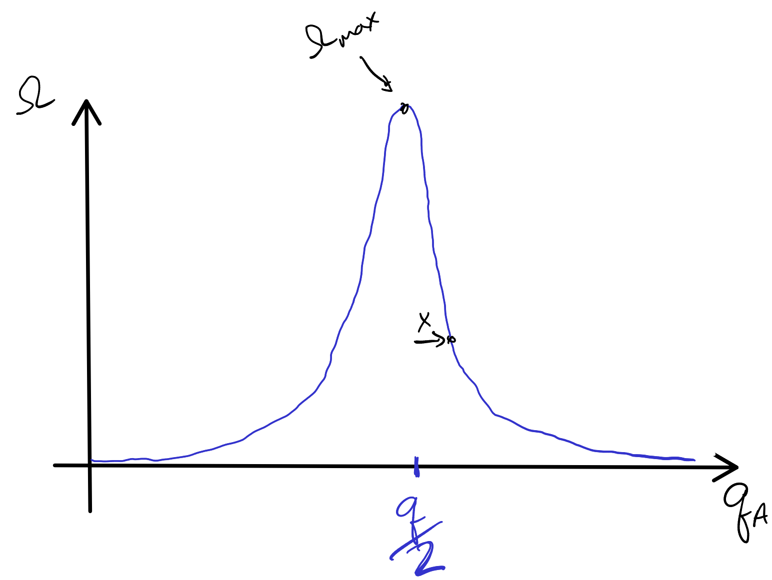
$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

$$q_A = \frac{q}{2} + x$$

$$q_B = \frac{q}{2} - x$$

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

$$\ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]^N = N \cdot \ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]$$




back to the graph:

$q_A = 10^{28}$

width $= 10^{16}$

$$\frac{0.6\,m}{10^{28}} \cdot 10^{16} = 0.6 \cdot 10^{-12}$$

$$= \underbrace{6 \cdot 10^{-13}\,m}_{\text{sharp peak!}}$$

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

$$= N\left(\ln\left(\frac{q}{2}\right)^2 + \underbrace{\ln\left(1 - \frac{x^2}{(q/2)^2}\right)}\right)$$

Takeaway! There is one macrostate where we will ever measure this system to be in.

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

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

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

$$\Omega = \left(\frac{e}{N}\right)^{2N} \underbrace{e^{N \cdot \ln\left(\frac{q}{2}\right)^2}}_{\left(\frac{q}{2}\right)^{2N}} e^{-N\left(\frac{2x}{q}\right)^2}$$

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

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

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

$$\frac{1}{e} = e^{-1}$$

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

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

$$\frac{1}{N} = \left(\frac{2x}{q}\right)^2$$

how far from the central peak we go to have a value of 37% of max $\rightarrow$ $x = \frac{q}{2\sqrt{N}}$

suppose $N = 10^{22}$, $q = 10^{28}$ $\Bigg\}$ width $= 2x = \frac{q}{\sqrt{N}} = \frac{10^{28}}{\sqrt{10^{22}}} = \frac{10^{28}}{10^{11}} = \underline{\underline{10^{17}}}$

2.18 + 2.22

2.18 show: $\Omega = \dfrac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}}$

Stirling's Approximation

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

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

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

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

$$\Omega = \frac{(q+N)^{q+N} \cdot \cancel{e^{-q-N}} \sqrt{\cancel{2\pi}(q+N)}}{q^q \cancel{e^{-q}} \sqrt{\cancel{2\pi} q} \cdot N^N \cdot \cancel{e^{-N}} \cdot \sqrt{2\pi N}}$$

$$N! = N \underbrace{(N-1)(N-2)\ldots\ldots}_{(N-1)!}$$

$$\Omega = \frac{(q+N)^q \cdot (q+N)^N \cdot \sqrt{(q+N)}}{q^q \cdot N^N \cdot \sqrt{2\pi q N}}$$

$$N-1! = \frac{N!}{N}$$

$$\frac{\left(\frac{q+N}{q}\right)^q \cdot \left(\frac{q+N}{N}\right)^N}{\sqrt{\frac{2\pi q N}{q+N}}}$$

# Entropy and the Second Law of Thermodynamics

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

2nd Law of Thermodynamics

$\downarrow$

Multiplicity tends to increase

Multiplicities are large numbers! Take the natural log of them

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

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

**Ex:** entropy of an Einstein solid.

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

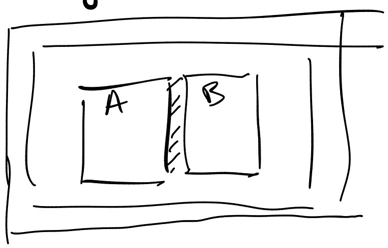
$$N = 10^{23} \qquad q = 10^{25}$$

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

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

$$S = N k_B \left(1 + \ln(10^2)\right) = 1.38(1 + 4.6) = 7.7 \text{ J/K}$$

Entropy of a composite system




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

$$S_{total} = k_B \ln \Omega_{total} = k_B \ln(\Omega_A \cdot \Omega_B) = k_B \ln \Omega_A + k_B \ln \Omega_B$$

$$S_{total} = S_A + S_B$$

Chapter 3 - temperature -> thermal equilibrium

For an Einstein solid:

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

generalize

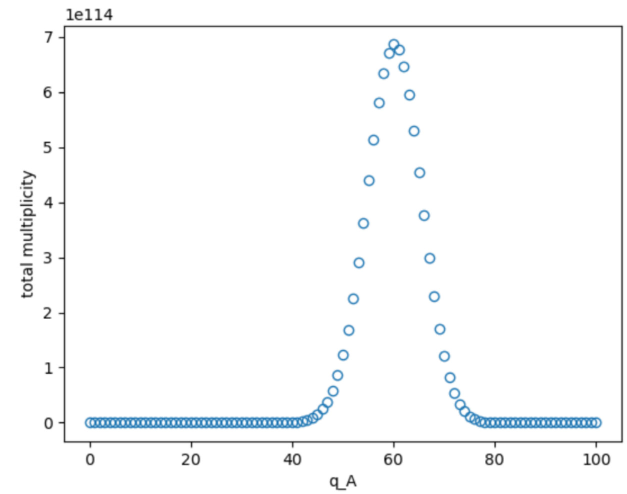
$$\frac{\partial S_{total}}{\partial U_A} = 0$$

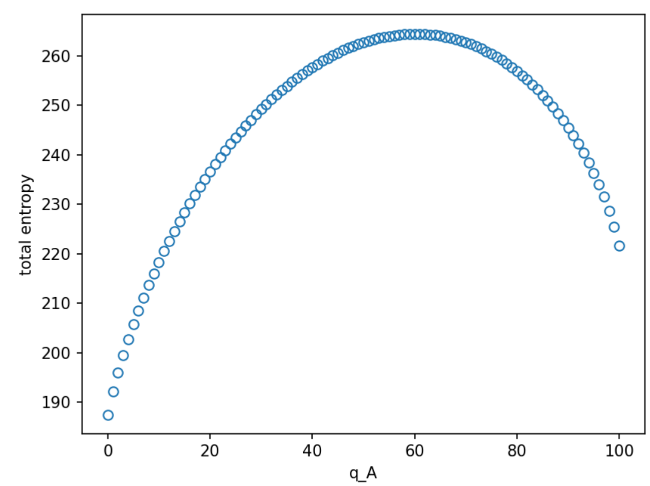
$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

$$U_B = U - U_A$$

$$dU_B = -dU_A$$

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



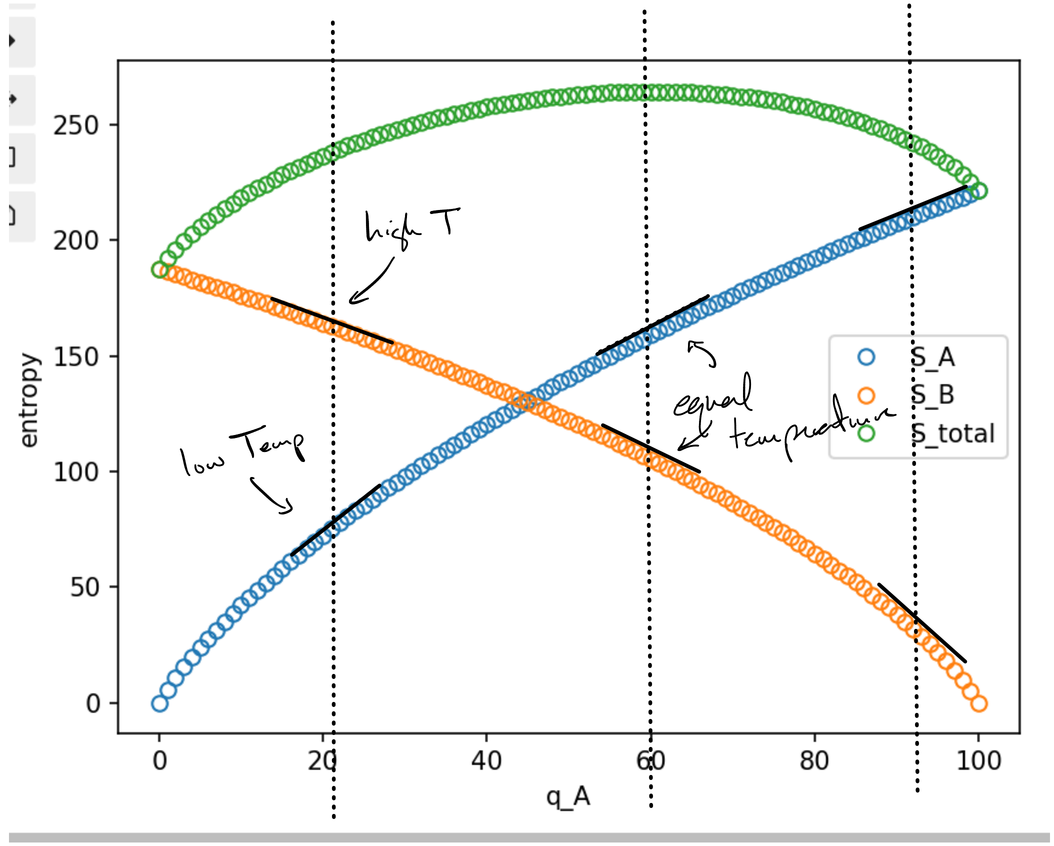



$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

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

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

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




HW: 2.29 & 2.30 → look at 3.1