Chapter 2 → 2^{nd} Law → Entropy

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

Combinatorics

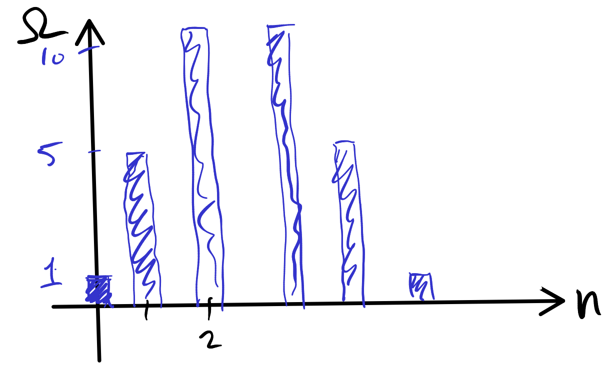
Coin flips → 5 coins

H H T T H ← microstate → 3 heads ← macrostate

T H H H H → 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

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

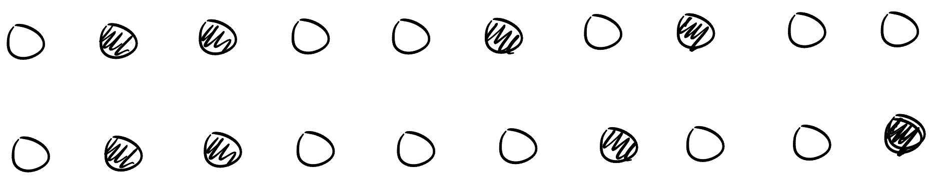
$$\Omega(N,n) = \frac{N!}{n!(N-n)!} \leftarrow \binom{N}{n}$$

# 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?

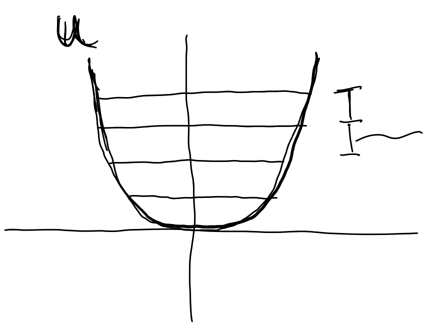
1e 1e 2e

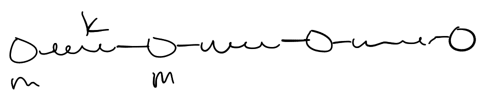
→ need to update the formula

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

This idea of treating a solid like

this is known as an Einstein solid ← Debye model

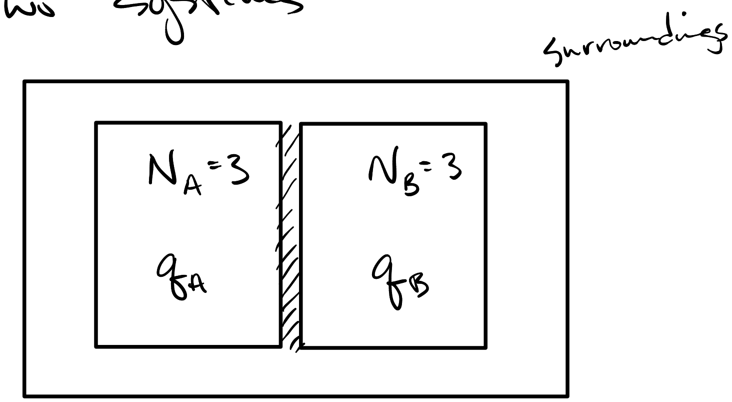




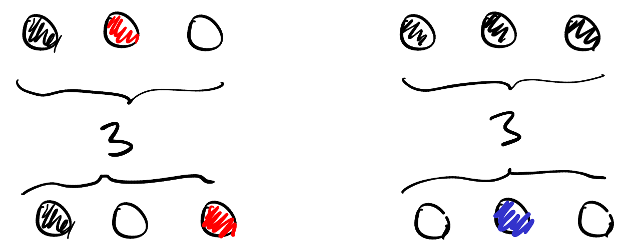
$h \cdot f$

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

Two systems



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



← microstate w/i the same macrostate

macrostate 1 energy

$\Omega_A(1)=3$

macrostate of 5 energy

$\Omega_B(5)=21$

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

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

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

- Very Large Number

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

Anaconda → jupyter lab

Stirling's Approximation

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

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

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

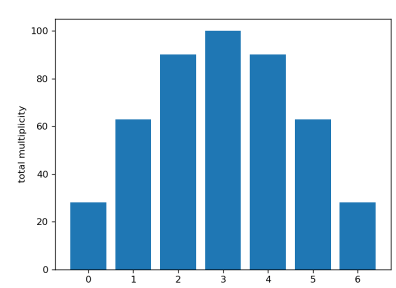
[24]:
```
table0 = pd.DataFrame()
table0['q_A'] = range(0,6+1, 1)
table0['q_B'] = range(6, 0-1, -1)
table0['mult_A'] = [multiplicity(3, i) for i in table0['q_A']]
table0['mult_B'] = [multiplicity(3, i) for i in table0['q_B']]
table0['mult_total'] = table0['mult_A']*table0['mult_B']
```

[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

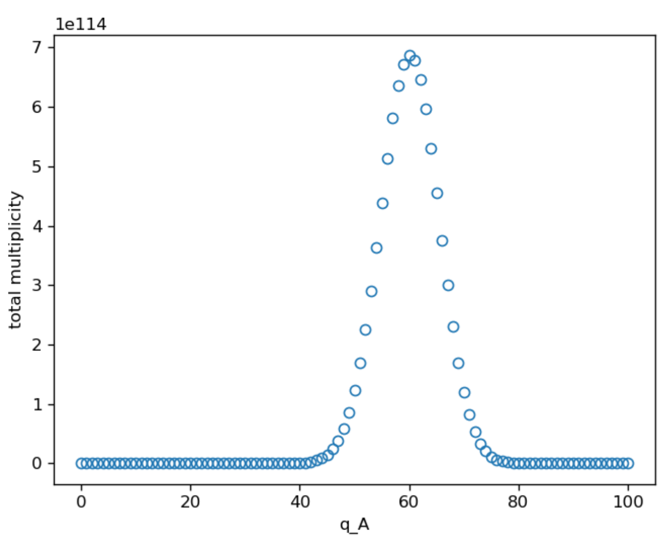
Figure 1



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

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

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

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

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

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

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

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

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

- problem 2.18

High temperature 2 solids in thermal contact

$$\Omega = \left(\frac{eq_A}{N_A}\right)^{N_A} \cdot \left(\frac{eq_B}{N_B}\right)^{N_B} \qquad N_A = N_B = N$$

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

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

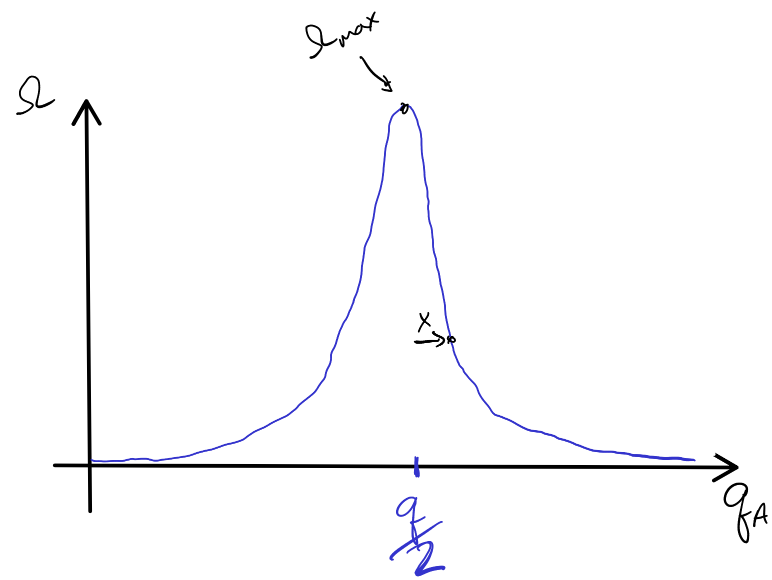
$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

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

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

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

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



back to the graph:

$q_A = 10^{28}$

width $= 10^{16}$

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

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

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

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

Takaway! 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 $N = 10^{22}$, $q = 10^{28}$ $\Big\}$ 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

Stirling's Approximation

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

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

2.18

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

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

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

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

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

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

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