Chapter 2 → 2nd 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

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

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

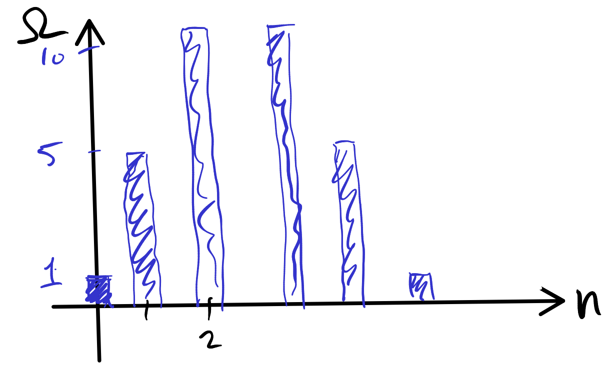
How many microstates are in a macrostate?

↳ multiplicity

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

\# of heads

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



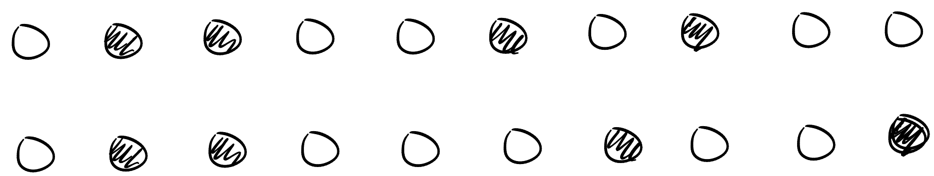
$$\Omega(N,n) = \frac{N!}{n!(N-n)!} \leftarrow \binom{N}{n}$$

\# of coins

\# of heads

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

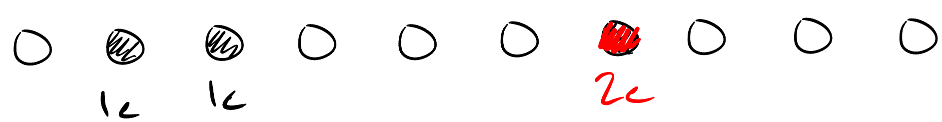
So how many ways are there of arranging 4 units of energy? (10 units of energy)



← microstate

4 energies vs. 10 energies ← macrostate

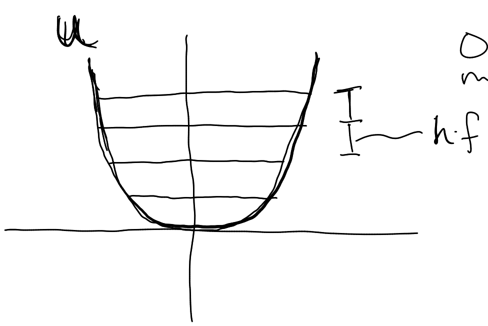
What if an atom can have more than 1?

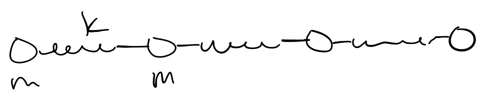


→ need to update the formula

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

This idea of treating a solid like this is known as an Einstein solid ← Debye model

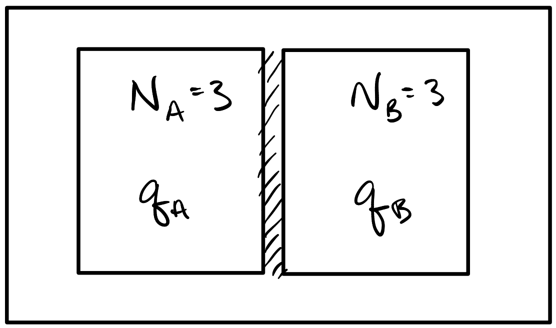




$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

Two systems

surroundings



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

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

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

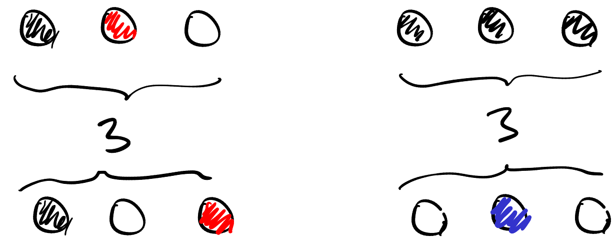
- Very Large Number

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

Stirling's Approximation

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

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



← microstate w/i the same macrostate

macrostate 1 energy

$\Omega_A(1) = 3$

macrostate of 5 energy

$\Omega_B(5) = 21$

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

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

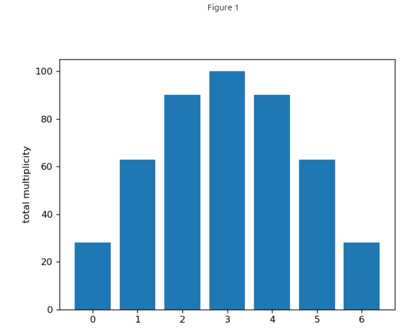
[24]:
```
table0 = pd.DataFrame()
table0['q_A'] = range(0,6+1, 1)
table0['q_B'] = range(6, 0-1, -1)
table0['mult_A'] = [multiplicity(3, i) for i in table0['q_A']]
table0['mult_B'] = [multiplicity(3, i) for i in table0['q_B']]
table0['mult_total'] = table0['mult_A']*table0['mult_B']
```

[25]:
```
table0
```

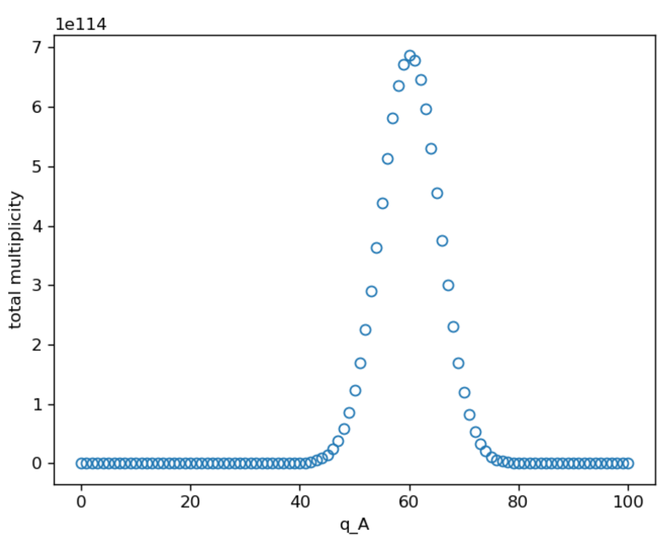
[25]:

	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

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

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

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

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

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

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

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

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

- problem 2.18

High temperature 2 solids in thermal contact

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

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

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

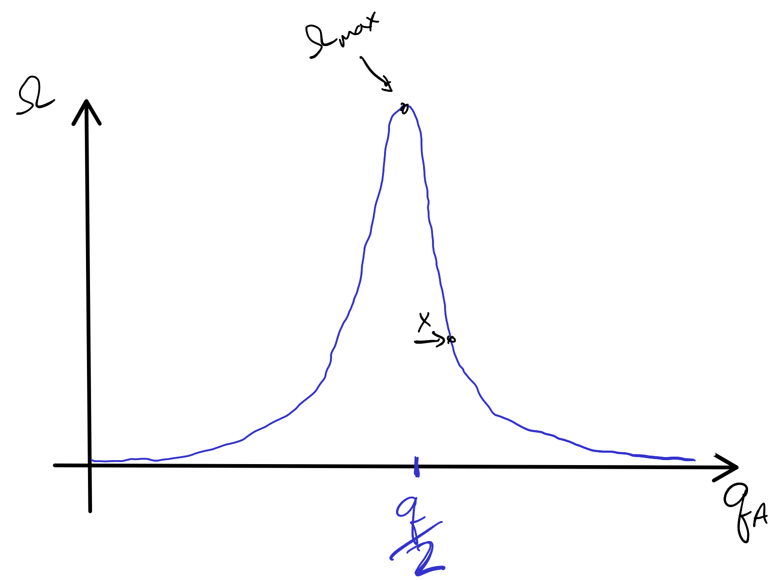
$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

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

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

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

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



back to the graph:

$$q_A = 10^{28}$$

$$\text{width} = 10^{16}$$

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

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

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

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

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 $N = 10^{22}$, $q = 10^{28}$ } 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: $\Omega = \dfrac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}}$

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

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

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

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

← not working

Stirling's Approximation

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

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

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

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

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

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

Entropy and the Second Law of Thermodynamics

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.

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

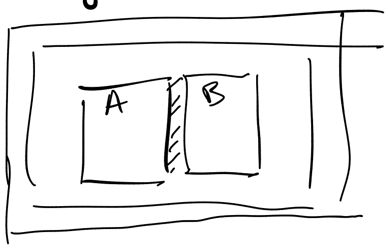
$$N = 10^{23} \qquad q = 10^{25}$$

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

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

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

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

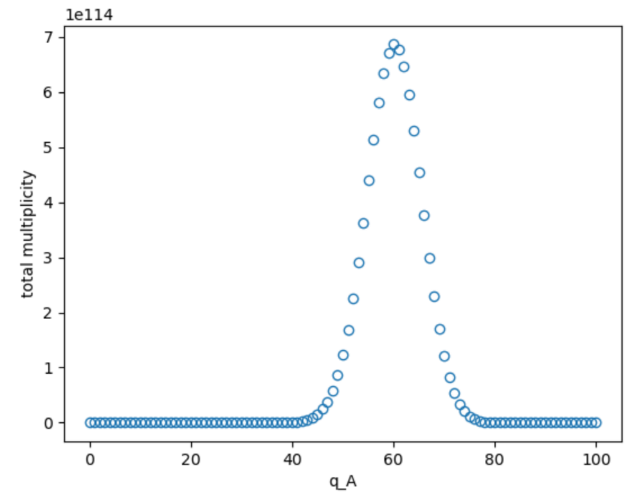
$$\frac{\partial S_{total}}{\partial U_A} = 0$$

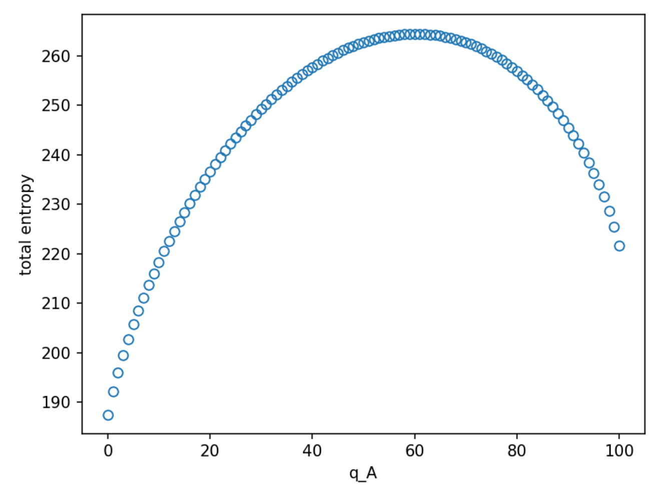
$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

$$U_B = U - U_A$$

$$dU_B = -dU_A$$

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



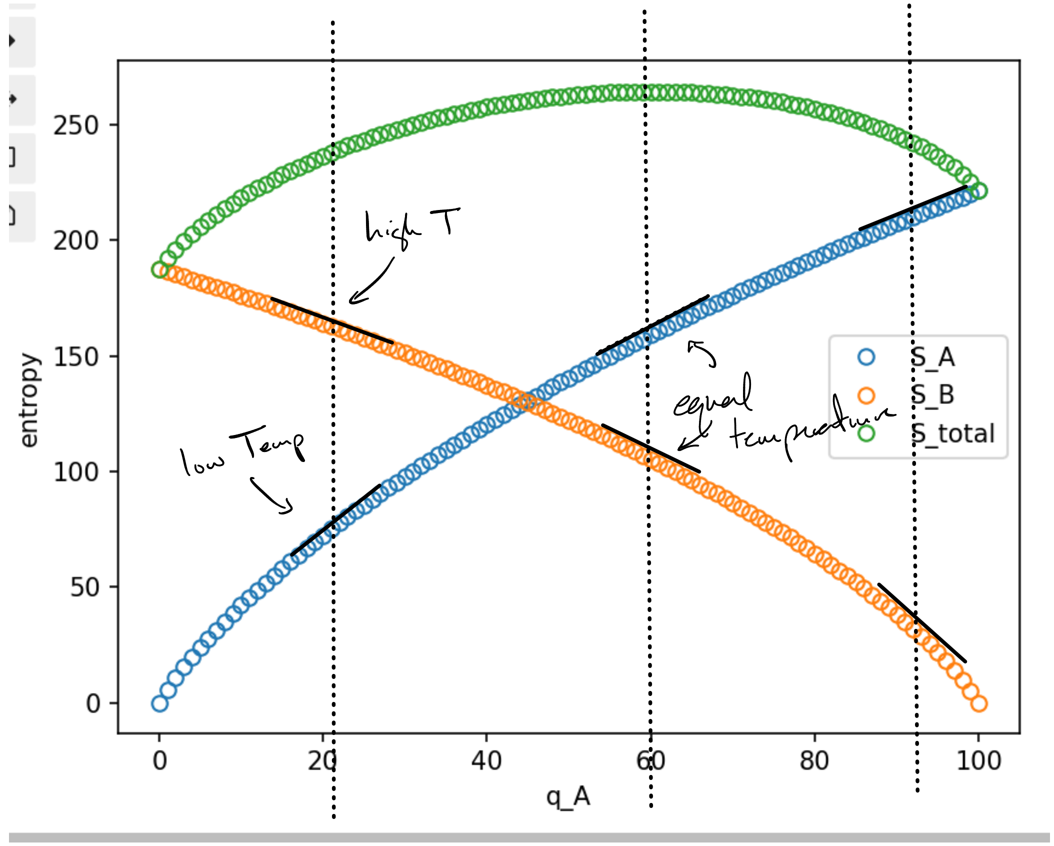


$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

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

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

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



HW: 2.29 & 2.30 → look at 3.1

Total HW: 2.18, 22, 29, 30, 3.1

Let's apply this to an Einstein solid at high temp: $\Omega = \left(\frac{eq}{N}\right)^N$

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

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

# of energy packets

energy of one packet

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

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

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

$$S = N k_B + \underline{N k_B \ln U} - N k_B \ln N\epsilon$$

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

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

$f = 2$ } Einstein → 1D kinetic energy → 1D spring potential energy

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = N k_B$$ ← experimentally testable quantity

Review our process so far:

1. Used combinatorics + 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 *

statistical mechanics gives an alternative approach to arriving at step #4.

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

<u>But</u>, going backwards to measure entropy is easy

$$dS = \underbrace{\frac{\partial S}{\partial U}}_{\frac{1}{T}} dU$$

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

→ use constant volume process (isochoric)

$$\left.\begin{array}{l} dV = 0 \\ đW = 0 \end{array}\right\} \quad \begin{array}{l} dU = đQ + \cancel{đW}^{\,0} \\ dU = đQ \end{array}$$

$$\boxed{dS = \frac{đQ}{T}}$$

→ important! used to be the definition of entropy

→ T does not change very much w/ a đQ amount of heat!

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

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T}\, dT$$

→ C_v can be constant, or can be a function of temp

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

→ but, you need to know this function all the way to zero Kelvin!

$C_v \to 0$ as $T \to 0$

→ could be 0 or residual entropy but it is a constant

much experimental data has been gathered for many substances new problems: 3.10, 3.14

+ Total HW: 2.18, 22, 29, 30, 3.1

$\underbrace{\hphantom{xxxxxxxxxxxxxxxxxxxx}}$

New total HW:

$\overbrace{\hphantom{xxxxxxxxxxxxxxxxxxxx}}$

3rd Law of Thermodynamics

2.22 a) $q \to 2N$

$N_A = N_B = N$

macrostates $= q + 1 = \underline{\underline{2N+1}}$

b) $$\Omega(N,q) = \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}}$$

$$\Omega_{total} = \Omega_A \cdot \Omega_B = \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}} \cdot \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}}$$

$q = 2N$

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

Let's go back to section 2.5

2.5 | Ideal Gas Multiplicity

$\hookrightarrow$ the number of microstates in a macrostate.

$\hookrightarrow$ $\underbrace{\text{total energy, volume}}_{\text{what defines a macrostate for an ideal gas}}$

$$\Omega = \text{distribution of particles in space} \cdot \text{distribution of energy among particles}$$

For a single particle

$$\Omega_1 \propto \mathbb{V} \cdot \underbrace{\text{combinations of momentums that has some energy}}_{\text{volume of momentum space}}$$

$$\Omega_1 \propto \mathbb{V} \cdot \mathbb{V}_p$$

$$\Omega_1 = \frac{L_x \cdot L_y \cdot L_z}{\Delta x \, \Delta y \, \Delta z} \cdot \frac{L_{p_x} \cdot L_{p_y} \cdot L_{p_z}}{\Delta p_x \cdot \Delta p_y \cdot \Delta p_z}$$

Heisenburg Uncertainty Principle

$$\Delta x \cdot \Delta p_x \approx h \leftarrow \text{Plank constant}$$

uncertainty in position

uncertainty in momentum

inversely proportional

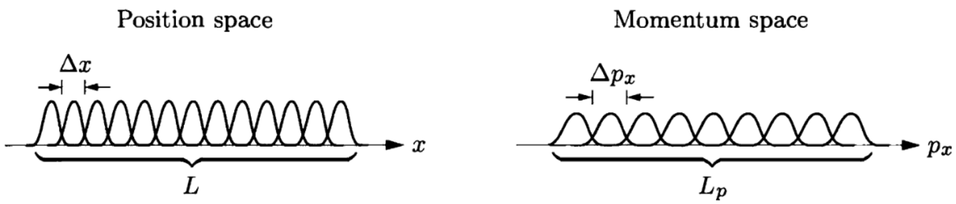


Figure 2.9. A number of "independent" position states and momentum states for a quantum-mechanical particle moving in one dimension. If we make the wavefunctions narrower in position space, they become wider in momentum space, and vice versa.

$$\Omega_1 = \frac{V \cdot V_p}{h^3}$$

So, what about two particles?

$$\Omega_2 = \Omega_A \cdot \Omega_B$$

cannot distinguish the particles

$$\Omega_2 = \frac{V^2 \cdot V_p^2}{(h^3)^2} \cdot \frac{1}{2}$$

So, what about N particles?

$$\Omega_N = \frac{1}{N!} \frac{V^N V_p^N}{(h^3)^N}$$

Let's go back to one particle that has all of the energy of the system, U.

$$U = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)\left(\frac{m}{m}\right)^2$$

$$U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$\underbrace{p_x^2 + p_y^2 + p_z^2 = \underbrace{\left(\sqrt{2mU}\right)^2}_{\text{if this is constant}}}_{\text{equation of a sphere in momentum space}}$$

equation of a sphere in momentum space that has a radius $r_p = \sqrt{2mU}$

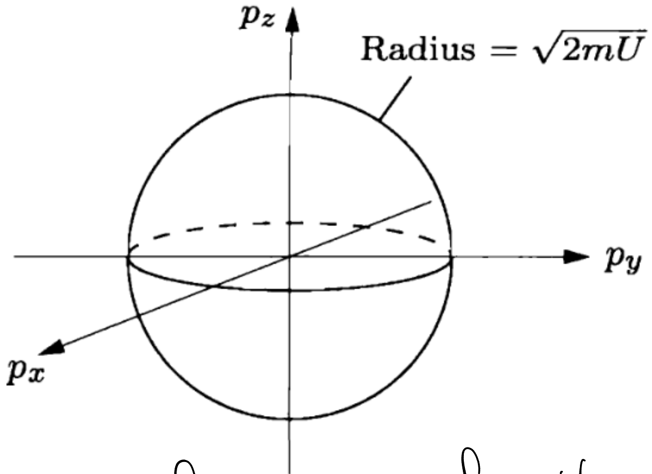


Figure 2.8. A sphere in momentum space with radius $\sqrt{2mU}$. If a molecule has energy U, its momentum vector must lie somewhere on the surface of this sphere.

So the energy is really the surface area of this sphere

$\hookrightarrow 4\pi r^2 \rightsquigarrow 4\pi\left(\sqrt{2mU}\right)^2$

So, for two particles constrained to having U total energy.

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = \left(\sqrt{2mU}\right)^2$$

6 dimensional sphere? → hypersphere!

$$\text{"surface area"} = \frac{2\pi^{d/2} \cdot r^{d-1}}{\left(\frac{d}{2}-1\right)!}$$

TEST: $d=2$

$$2\pi r \overset{?}{=} \frac{2 \cdot \pi^{2/2} \cdot r^{2-1}}{\left(\frac{2}{2}-1\right)!}$$

$$= 2 \cdot \pi r \checkmark$$

Now go to N particles

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \cdot \frac{2\pi^{3N/2} \cdot (2mU)^{\frac{3N-1}{2}}}{\left(\frac{3N}{2}-1\right)!}$$

let's throw away what does not matter!

$$\boxed{\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \cdot \frac{\pi^{3N/2} \cdot (2mU)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}}$$

$$\Omega_N = f(N) \cdot V^N \cdot U^{\frac{3N}{2}}$$

Put two ideal gases in thermal contact
(barrier exchange energy + volume)

$$\underline{\Omega_{total}} = f(N) V_A^N U_A^{3N/2} \cdot f(N) V_B^N U_B^{3N/2}$$

$$= (f(N))^2 \cdot (V_A V_B)^N \cdot (U_A \cdot U_B)^{3N/2}$$

TEST: $d = 3$

$$4\pi r^2 = \frac{2\pi^{3/2} r^{3-1}}{\left(\frac{3}{2}-1\right)!}$$

$$= 2\underbrace{\left[\frac{\pi^{3/2}}{\left(\frac{1}{2}\right)!}\right]}_{2\pi} r^2$$

need to dig in!

$$\frac{1}{2}! = \Gamma\left(\frac{1}{2}+1\right)$$

$$\frac{1}{\left(\frac{1}{2}\right)!} = \frac{2}{\sqrt{\pi}} \quad \checkmark\checkmark$$

$$= 4\pi r^2$$

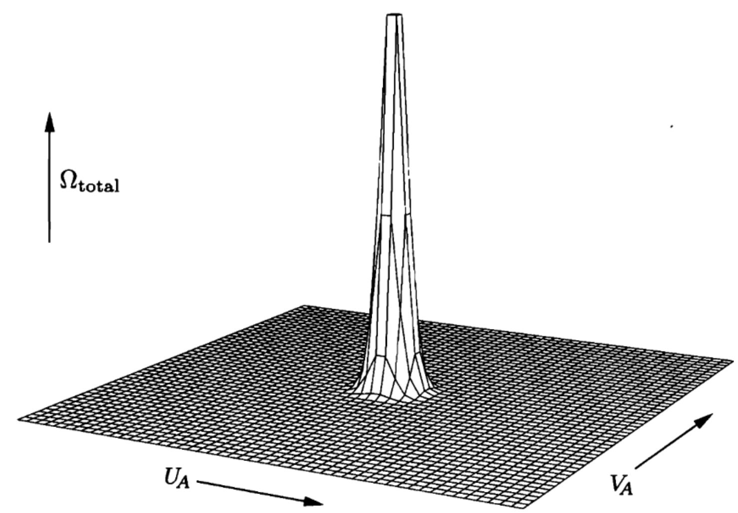


Figure 2.12. Multiplicity of a system of two ideal gases, as a function of the energy and volume of gas A (with the total energy and total volume held fixed). If the number of molecules in each gas is large, the full horizontal scale would stretch far beyond the edge of the page.

Entropy of an ideal gas: