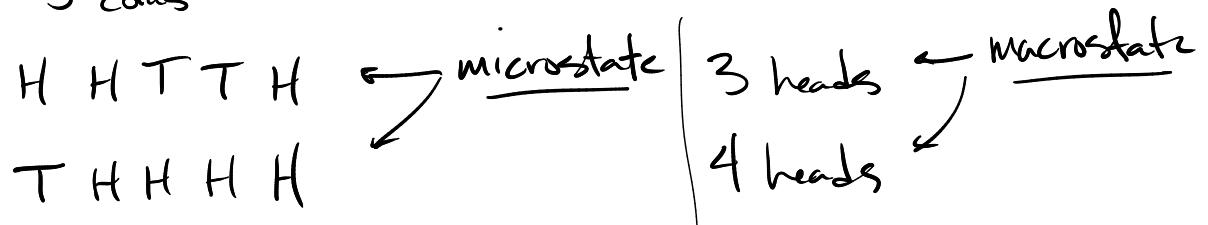


Chapter 2  $\rightarrow$  2<sup>nd</sup> Law  $\rightarrow$  Entropy

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

### Combinatorics

Coin flips  $\rightarrow$  5 coins



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

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

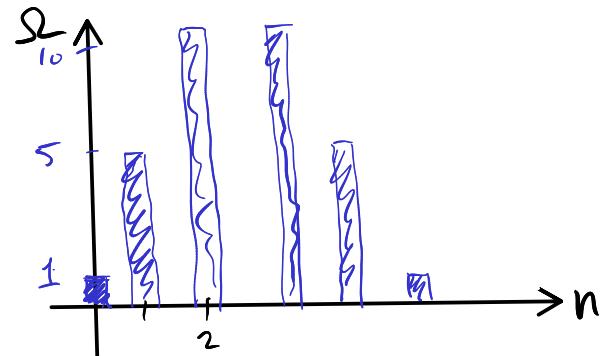
How many microstates are in a macrostate?  
 ↳ multiplicity

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

$$\begin{array}{c} \# \text{ of} \\ \text{heads} \end{array} \quad \begin{array}{c} 5! \\ \hline 3! \cdot 2! \end{array}$$

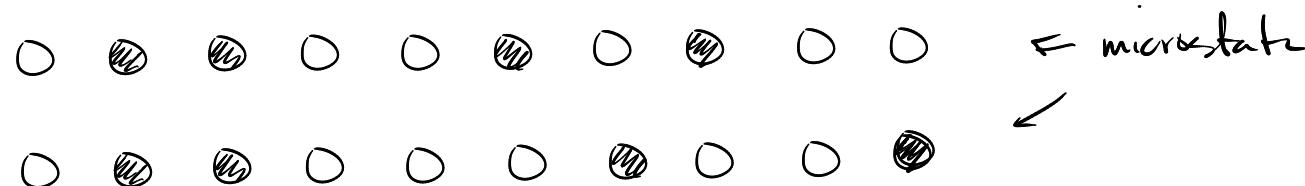
$$\Omega(N, n) = \frac{N!}{n!(N-n)!} \leftarrow \binom{N}{n}$$

$$\begin{array}{c} \# \text{ of} \\ \text{coins} \end{array} \quad \begin{array}{c} \# \text{ of} \\ \text{heads} \end{array}$$



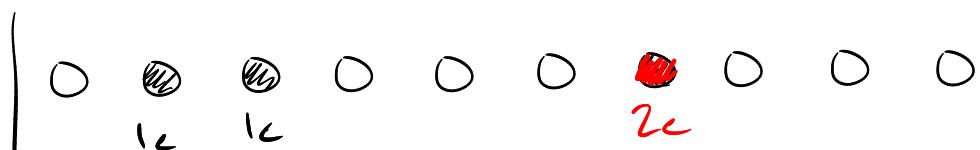
10 atoms  $\rightarrow$  each one can have 0 or 1 energy units.

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



4 energies vs. 10 energies ← macrostate

What if an atom can have more than 1?

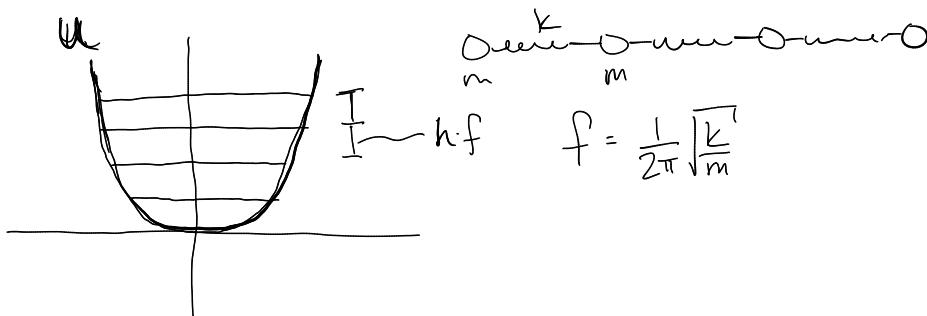


→ need to update the formula

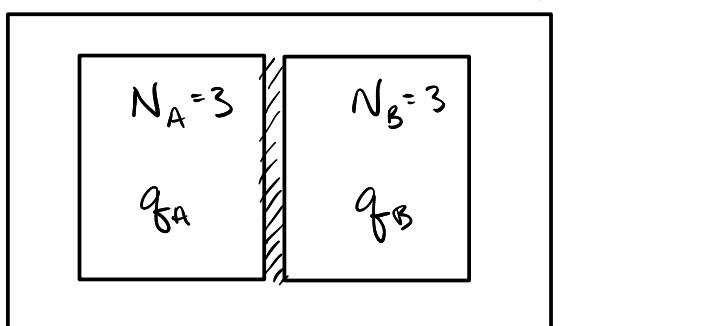
$$\Omega(N, q) = \frac{(q + N - 1)!}{q! (N - 1)!}$$

This idea of treating a solid like

this is known as an Einstein solid ← Debye model



Two systems



$g = 6 \leftarrow$  six quanta of energies that can be shared

- Large Number  $\rightarrow$  addition of small #s does not matter

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

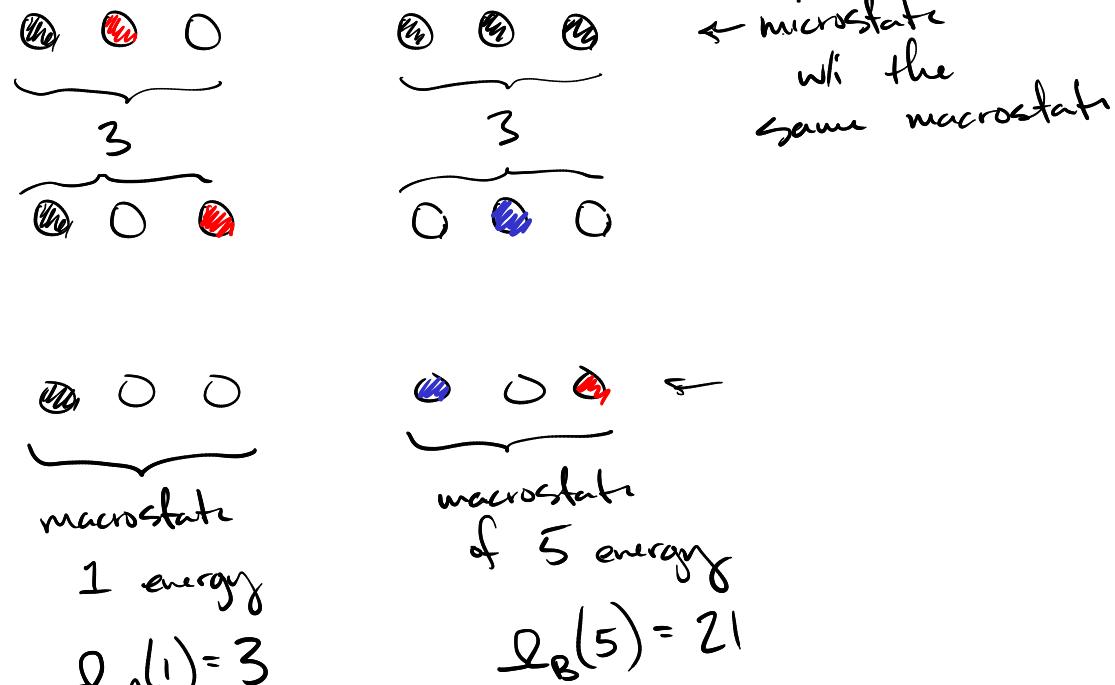
- Very Large Number

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

Stirling's Approximation

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

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



$$\mathcal{L}_{\text{total}} = \mathcal{L}_A \cdot \mathcal{L}_B = 63$$

Anaconda  $\rightarrow$  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

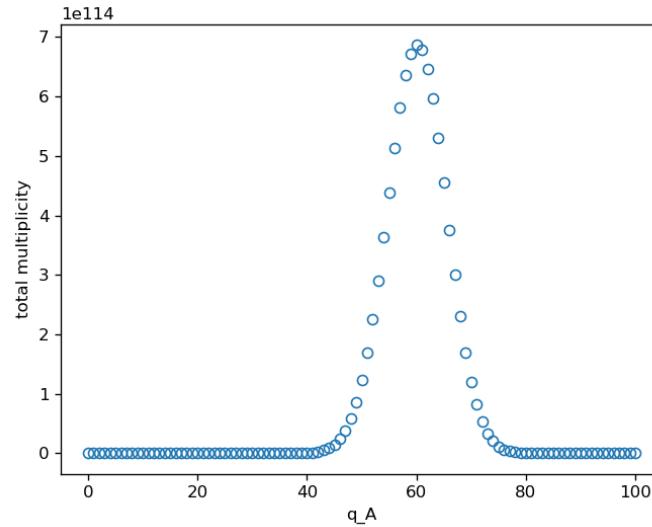
3 particles each and 6 energy units

```
[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']
```

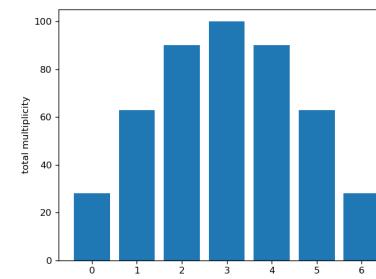
```
[25]: table0
```

	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  
 $n_A = 300, n_B = 200$   
 $q_f = 100$



So, now lets apply Stirlings Approximation to the Multiplicity

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

$$\begin{aligned}\ln \Omega &= \ln(q+N)! - \ln q! - \ln N! \rightarrow \ln N! = N \ln N - N \\ &\rightarrow \ln q! = q \ln q - q \\ &\rightarrow \ln(q+N)! = (q+N) \ln(q+N) - (q+N)\end{aligned}$$

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

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

high temperature limit  $\rightarrow q \gg N$

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

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

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

$$= \ln q + \underbrace{\ln \left( 1 + \frac{N}{q} \right)}_{\substack{\hookrightarrow \ln(1+x) \approx x \text{ for small } x \\ \Rightarrow \frac{N}{q}}}$$

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

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

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

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

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

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

$$\Omega(g \gg N) = \left(\frac{e g}{N}\right)^N \quad \leftarrow \text{Einstein solid at high temps}$$

- problem 2.18 |

High temperature 2 solids in thermal contact

$$\Omega = \left(\frac{e g_A}{N_A}\right)^{N_A} \cdot \left(\frac{e g_B}{N_B}\right)^{N_B} \quad N_A = N_B = N$$

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

$$g_A = g_B = \frac{g}{2}$$

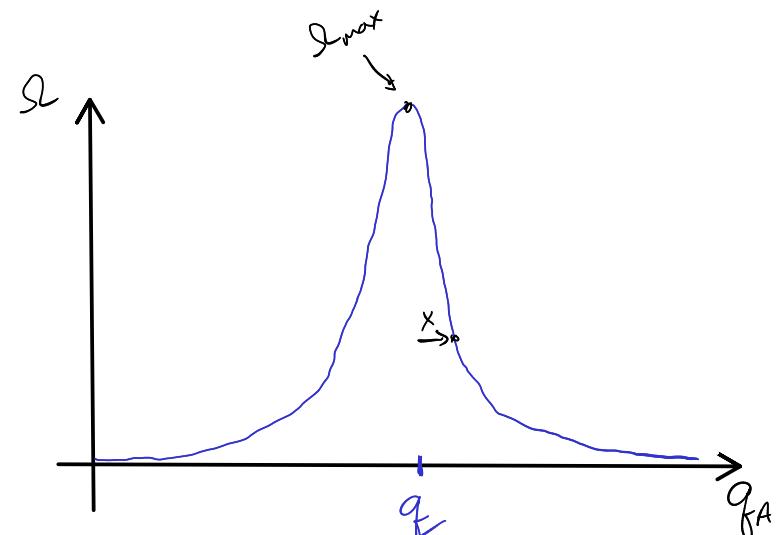
$$\Omega_{\max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{g}{2}\right)^{2N}$$

$$g_A = \frac{g}{2} + x$$

$$g_B = \frac{g}{2} - x$$

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

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



back to the graph:

$$g_A = 10^{28}$$

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

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

$$= \underbrace{6 \cdot 10^{-13} \text{ m}}$$

sharp peak!

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

$$= N \left( \ln \left( \frac{q}{2} \right)^2 + \underbrace{\ln \left( 1 - \frac{x^2}{\left( \frac{q}{2} \right)^2} \right)}_{\text{Takaway! There is one macrostate where we will ever measure this system to be in.}} \right)$$

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

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

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

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

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

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

Gaussian function

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

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

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

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

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

how far  
from the  
central peak →  $x = \frac{q}{2\sqrt{N}}$

suppose  $N = 10^{22}$   
 $q = 10^{28}$

} width =  $2x = \frac{q}{\sqrt{N}} = \frac{10^{28}}{\sqrt{10^{22}}} = \frac{10^8}{10^1} = 10^7$

2.18 + 2.22

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

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

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

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

$$\Omega = \frac{\left(\frac{q+N}{q}\right)^q \cdot \left(\frac{q+N}{N}\right)^N}{\sqrt{\frac{2\pi q N}{q+N}}} \quad \leftarrow \text{not working}$$

Stirling's Approximation

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

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

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

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

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

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

## Entropy and the Second Law of Thermodynamics

Any large system in equilibrium will be found in the macrostate with the largest multiplicity

2<sup>nd</sup> Law of Thermodynamics  
↓

Multiplicity tends to increase

Multiplicities are large numbers! 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.

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

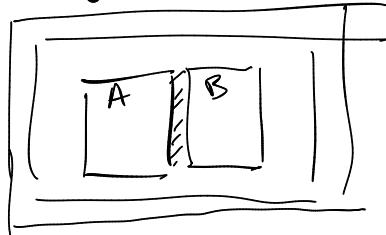
$$N = 10^{23} \quad q = 10^{25}$$

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

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

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

# Entropy of a composite system



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

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

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

Chapter 3 - temperature  $\rightarrow$  thermal equilibrium

For an Einstein solid:

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

(generalize)

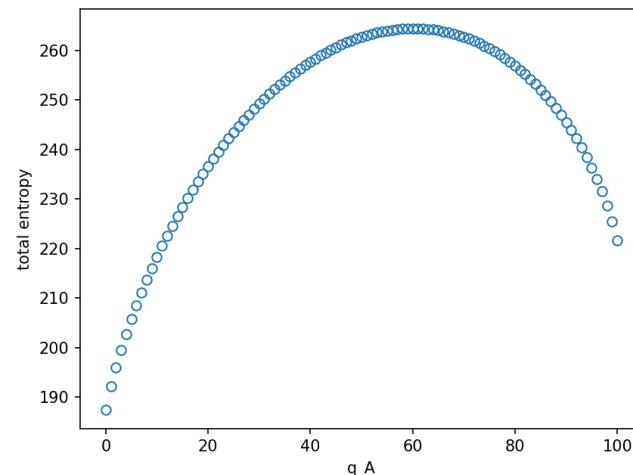
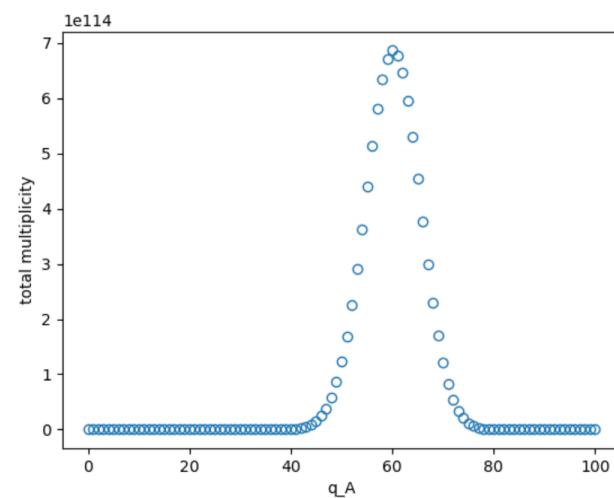
$$\frac{\partial S_{\text{total}}}{\partial U_A} = 0$$

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

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

$$U_B = U - U_A$$

$$dU_B = -dU_A$$



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

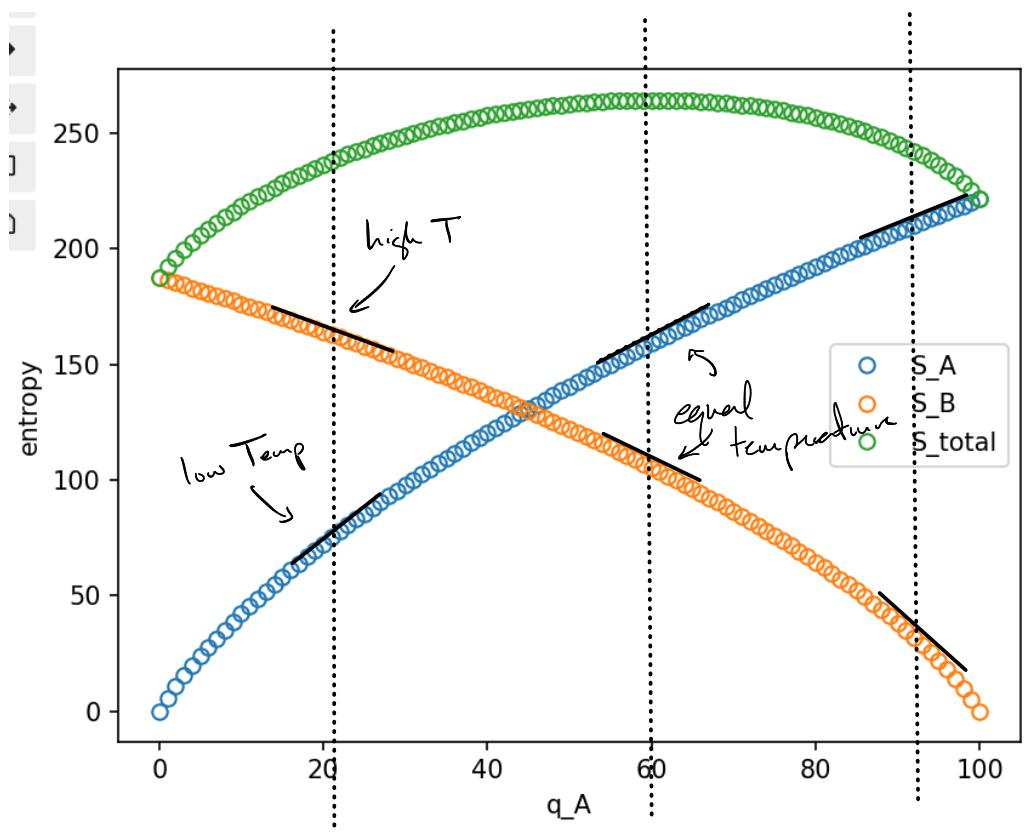
$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

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

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

HW: 2.29 + 2.30  $\rightarrow$  look at 3.1

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



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

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

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

↓  
 # of energy packets  
 ↓  
 energy of one packet

$$S = k_B \ln \mathcal{Q} = k_B \ln \left( \frac{e\epsilon}{N} \right)^N = N k_B \ln \left( \frac{e\epsilon}{N} \right) = N k_B \left( 1 + \ln \left( \frac{\epsilon}{N} \right) \right)$$

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

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

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

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

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

↗ 1D kinetic energy

$f=2 \quad \left. \begin{array}{l} \{ \text{Einstein} \rightarrow 1D \text{ spring potential energy} \end{array} \right.$

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

Review our process so far:

1. Used combinatorics + QM to find  $\Omega$  in terms of  $N, V, U$  etc. } could be impossible!

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

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

4. solve step 3 for  $U$  as a function of  $T$

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

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

But, going backwards to measure entropy is easy

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

$$\frac{1}{T}$$

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

→ use constant volume process (isochoric)

$$\begin{aligned} dV &= 0 \\ dW &= 0 \end{aligned} \quad \left. \begin{array}{l} \{ \\ \} \end{array} \right. \quad \begin{aligned} dU &= dQ + dW \\ dU &= dQ \end{aligned}$$

$$\boxed{dS = \frac{dQ}{T}} \rightarrow \text{important! need to be the definition of entropy}$$

→ T does not change very much w/ a  $\pm Q$  amount of heat!

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

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T} dT \quad \begin{array}{l} \nearrow C_v \text{ can be constant, or} \\ \nearrow \text{can be a function of temp} \end{array}$$

$$S(T) - S(0) = \int_0^T \frac{C_v}{T} dT \quad \begin{array}{l} \nearrow \text{but, you need to know} \\ \nearrow \text{this function all the} \\ \nearrow \text{way to zero Kelvin!} \\ \nearrow C_v \rightarrow 0 \text{ as } T \rightarrow 0 \end{array}$$

much experimental data  
has been gathered for  
many substances

could be 0 or residual entropy  
but it is a constant

3<sup>rd</sup> Law of  
Thermodynamics

2.22] a)  $g \rightarrow 2N$

$$N_A = N_B = N$$

$$\underline{\text{macrostates}} = g + 1 = \underline{\underline{2N+1}}$$

$$\text{b) } \mathcal{Q}(N, g) = \frac{\left(\frac{g+N}{g}\right)^g \left(\frac{g+N}{N}\right)^N}{\sqrt{2\pi g(g+N)/N}}$$

$$\mathcal{Q}_{\text{total}} = \mathcal{Q}_A \cdot \mathcal{Q}_B = \frac{\left(\frac{g+N}{g}\right)^g \left(\frac{g+N}{N}\right)^N}{\sqrt{2\pi g(g+N)/N}} \cdot \frac{\left(\frac{g+N}{g}\right)^g \left(\frac{g+N}{N}\right)^N}{\sqrt{2\pi g(g+N)/N}}$$

$$g = 2N$$

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

Let's go back to section 2.5

## 2.5] Ideal Gas Multiplicity

↳ the number of microstates in a macrostate.

↳ total energy, volume

which defines a macrostate  
for an ideal gas

$\Omega$  = distribution of particles in space . distribution of energy among particles

For a single particle

$\Omega_1 \propto V \cdot$  combinations of momentums that has some energy  
volume of momentum space

$$\Omega_1 \propto V \cdot V_p$$

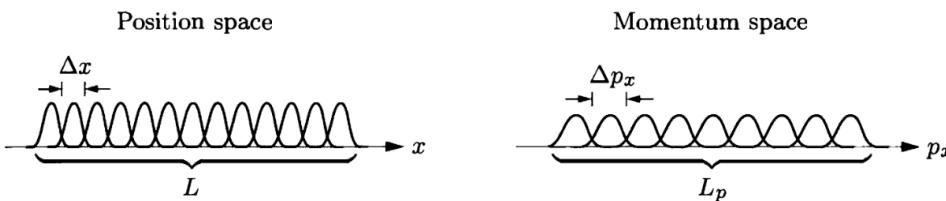
$$\Omega_1 = \frac{L_x \cdot L_y \cdot L_z}{\Delta x \cdot \Delta y \cdot \Delta z} \cdot \frac{L_{p_x} \cdot L_{p_y} \cdot L_{p_z}}{\Delta p_x \cdot \Delta p_y \cdot \Delta p_z}$$

# Heisenberg 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.

Let's go back to one particle - as all of the energy of the system,  $U$ .

$$U = \frac{1}{2}mv^2 = \frac{1}{2}m(V_x^2 + V_y^2 + V_z^2) \left(\frac{m}{\cancel{m}}\right)^2$$

$$U = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2)$$

$$\mathcal{D}_1 = \frac{\sqrt{V} \cdot \sqrt{V_p}}{h^3}$$

So, what about two particles?

$$\mathcal{D}_2 = \mathcal{D}_A \cdot \mathcal{D}_B$$

$$\mathcal{D}_2 = \frac{\sqrt{V} \cdot \sqrt{V_p}}{(h^3)^2} \cdot \frac{1}{2}$$

So, what about  $N$  particles?

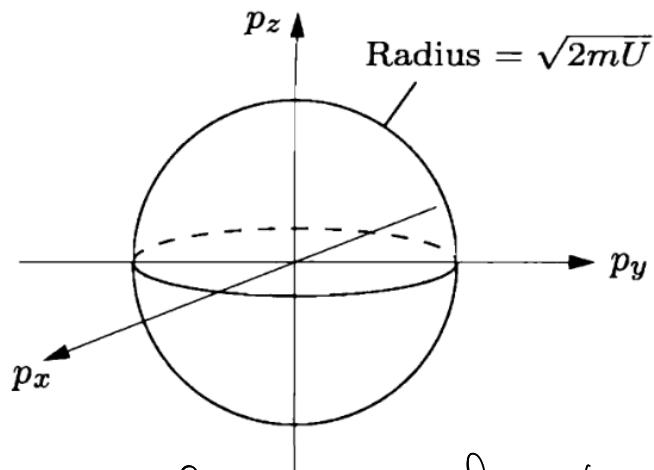
$$\mathcal{D}_N = \frac{1}{N!} \frac{\sqrt{V}^N \sqrt{V_p}^N}{(h^3)^N}$$

$$P_x^2 + P_y^2 + P_z^2 = \underbrace{(\sqrt{2mU})^2}_{\text{if this is constant}}$$

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  
 $\rightarrow 4\pi r^2 \rightsquigarrow 4\pi(\sqrt{2mU})^2$

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

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

6 dimensional sphere?  $\rightarrow$  hypersphere!

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

TEST:  $d=2$

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

Now go to  $N$  particles

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

Let's throw away what does not matter!

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

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


---

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

$$\begin{aligned} \underline{\Omega_{\text{total}}} &= f(N) V_A^N U_A^{\frac{3N}{2}} \cdot f(N) V_B^N U_B^{\frac{3N}{2}} \\ &= (f(N))^2 \cdot (V_A V_B)^N \cdot (U_A \cdot U_B)^{\frac{3N}{2}} \end{aligned}$$

TEST:  $d = 3$

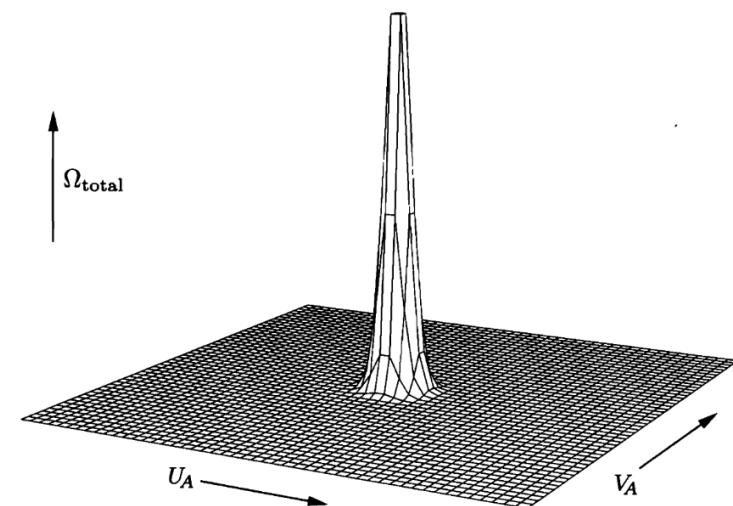
$$4\pi r^2 = \frac{2\pi^{\frac{3}{2}} r^{3-1}}{\left(\frac{3}{2} - 1\right)!} = 2 \left[ \frac{\pi^{\frac{3}{2}}}{\left(\frac{1}{2}\right)!} \right] r^2$$

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:

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

$$S = k_B \ln \Omega = k_B \ln \left( \frac{1}{N!} \frac{\nabla^N}{h^{3N}} \cdot \frac{\pi^{\frac{3N}{2}} \cdot (2mU)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \right)$$

$$S = k_B \left[ -\ln N! - \ln \left(\frac{3N}{2}\right)! + N \ln \nabla + \frac{3N}{2} \ln \left(2\pi mU\right) - \frac{3N}{2} \ln (h^2) \right]$$

$\xrightarrow{-\ln N! = -N \ln N + N}$        $\xrightarrow{-\frac{3N}{2} \ln \left(\frac{3N}{2}\right)! + \frac{3N}{2}}$   
 $= N \ln \frac{1}{N} + N$        $\frac{3N}{2} \ln \left(\frac{2}{3N}\right) + \frac{3N}{2}$

$$S = k_B N \left( \ln \left[ \frac{\nabla}{N} \cdot \left( \frac{2\pi mU}{h^2} \cdot \frac{2}{3N} \right)^{3/2} \right] + \frac{3}{2} + 1 \right)$$

$$S = k_B N \left( \ln \left[ \frac{\nabla}{N} \left( \frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right) \quad \xrightarrow{\text{Sackur-Tetrode Equation}}$$

$\frac{\nabla}{N} \xrightarrow{\text{volume per particle}} V \xrightarrow{\text{little red}} \underline{V}$        $\frac{U}{N} \xrightarrow{\text{energy per particle}} \underline{U} \xrightarrow{\text{little blue (new)}}$

apply to one mole of  $N_2$  gas at room temp and atmospheric pressure.

$$n_m = 1 \quad \text{or} \quad N = N_A \quad N_2 \rightarrow \text{diatomic} \rightarrow f = 5$$

$$\bullet U = \frac{5}{2} N k_B T = \frac{5}{2} n_m R T = \frac{5}{2} P V$$

$$\bullet \langle V \rangle = \frac{N k_B T}{P} = \frac{n_m R T}{P}$$

$$m_{N_2} = 28 \frac{\text{g}}{\text{mol}} = 0.028 \frac{\text{kg}}{\text{mol}} \cdot \frac{1 \text{ mol}}{6.022 \cdot 10^{23} \text{ part.}} = 4.65 \cdot 10^{26} \frac{\text{kg}}{\text{part}}$$

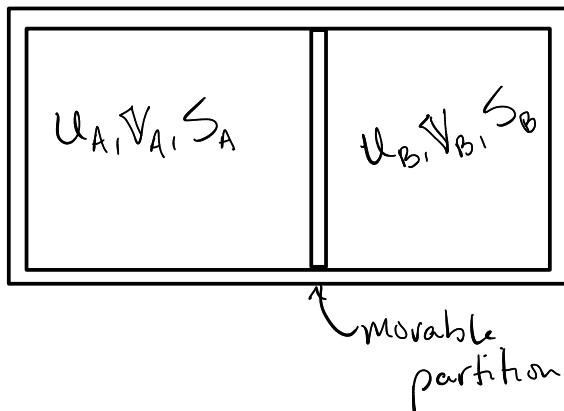
$$S = k_B N \left( \ln \left[ \frac{\langle V \rangle}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right)$$

$$S = \underbrace{k_B N_A}_{R} \left( \ln \left[ \frac{N_A k_B T}{N A P} \left( \frac{4\pi (4.65 \cdot 10^{26} \text{ kg}) \cdot \frac{5}{2} \cdot 8.31 \cdot 293}{3 \cdot 1 \text{ mol} \cdot (6.626 \cdot 10^{34})^2} \right)^{3/2} \right] + \frac{5}{2} \right) = ?$$

### 3.4] Mechanical Equilibrium + Pressure

- Exchange of energy is governed by temperature.
- Exchange of volume is governed by pressure difference.

know:  $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$  ← is pressure related to entropy also?



equilibrium  $\left\{ \begin{array}{l} \frac{\partial S_{\text{total}}}{\partial U} = 0 \\ \text{this is the definition} \\ \text{of the same temp} \\ \text{for } A + B \end{array} \right.$

propose:  $\frac{\partial S_{\text{total}}}{\partial V_A} = 0$        $S_{\text{total}} = S_A + S_B$

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

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

$$dV_A = -dV_B$$

$$\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0$$

↖

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

At equilibrium, pressure is the same, b/c otherwise the partition would move

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

units?

$$\frac{J}{K m^3} = \frac{Nm}{K m^3 2} = \frac{Pa}{K} \quad \text{units work!}$$

is this right?

$$\Omega = f(N) \cdot V^N \cdot U^{\frac{3N}{2}} \quad \leftarrow \text{multiplicity of an ideal gas}$$

$$S = k_B \left( \ln f(N) + N \ln V + \frac{3N}{2} \ln U \right)$$

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

$$\boxed{P = \frac{N k_B T}{V}} \quad \leftarrow \text{ideal gas law!}$$

$$\Delta S = (\Delta S)_u + (\Delta S)_v$$

$$\underline{\Delta S} = \underbrace{\left( \frac{\partial S}{\partial U} \right)_V dU}_{\frac{1}{T}} + \underbrace{\left( \frac{\partial S}{\partial V} \right)_U dV}_{\frac{P}{T}}$$

$$\underline{dS} = \frac{1}{T} dU + \frac{P}{T} dV$$

$$T \underline{dS} = dU + P dV$$

$$dU = T \underline{dS} - P dV$$

Thermodynamic Identity } true for any infinitesimal  
 changes as long as  $T + P$  are the same throughout the system

new problems: 3.10, 3.14 ←  
 + Total HW: 2.18, 22, 29, 30, 3.1

New total HW:

2.26, 32

New New total HW (totally new)

3.24 + 3.25

↓ compare this to the first law:

$$W = \vec{F} \cdot \vec{\Delta x}$$

$$dU = dQ + dW$$

$$dQ ?= TdS \quad dW ?= -pdV$$

- $dV$  happens quasistatically
- no non-compressive work (like electric fields)
- no other relevant variable change (like  $N$ )

$$dQ = TdS \quad dW = -pdV$$

- 
- ① an adiabatic and quasistatic process  
is now: isentropic (no change in entropy)  
→  $dQ = 0 = dS$

- ② even if the volume is changing

$$dQ = TdS \rightsquigarrow dS = \frac{dQ}{T} \rightsquigarrow dS = \frac{Q}{T}$$

1 L of water boils:  
→ 2260 kJ heat added  
 $dS = \frac{2260,000 \text{ J}}{373 \text{ K}} = 6060 \frac{\text{J}}{\text{K}}$

$$(3) (\Delta S)_p = \int_{T_i}^{T_f} \frac{C_p}{T} dT \quad \leftarrow \text{much more practical than the constant volume version.}$$

What about a non-quasistatic process?



$$dW > p dV$$

will not change much for a small  $dV$

I will have to do more work to move aside the molecules that pile up quickly.

greater than

$$dW + dQ = dU = TdS - pdV$$

must be less than

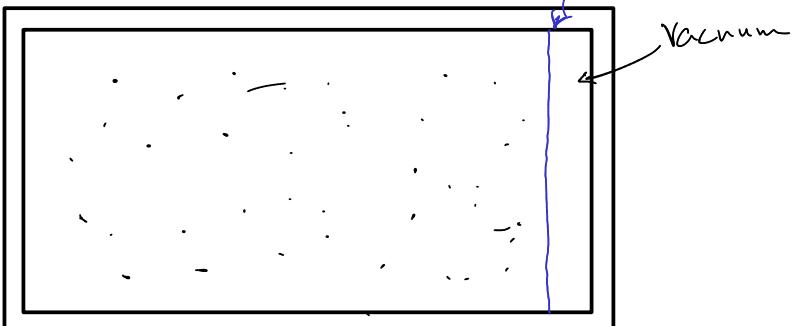
$$dQ \leq TdS \quad \text{when} \quad dW \geq pdV$$

$$TdS \geq dQ$$

$$dS \geq \frac{dQ}{T}$$

$\left. \begin{array}{l} \text{extra entropy was created since} \\ \text{more work was done to change the volume} \end{array} \right\}$

Alternative:



$$\delta W = 0$$

$$\delta Q = 0$$

$$\therefore \delta U = 0$$

but,  $\delta U = T \delta S - p \delta V$

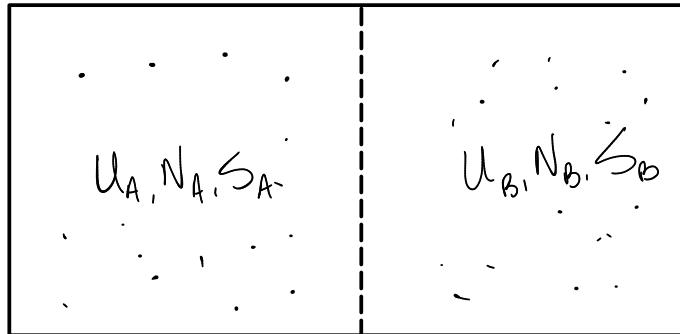
$$0 = T \delta S - p \delta V$$

$$\underbrace{T \delta S}_{> 0} = p \delta V > 0$$

$\hookrightarrow$  entropy was created, even though  
no heat flowed in.

### 3.5 Chemical Potential

So thermal equilibrium  $\rightarrow$  temperature stays the same  
 mechanical equilibrium  $\rightarrow$  pressure stays the same  
 diffusive equilibrium  $\rightarrow$  ?



can exchange  
energy + particles  
 same kind of particle  
 (indistinguishable)

$$\left( \frac{\partial S_{\text{total}}}{\partial N_A} \right)_{U,V} = 0 \quad \leftarrow \text{at equilibrium}$$

$$\underbrace{\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}}_{\text{diffusive equilibrium}} \Rightarrow \underbrace{-T \frac{\partial S_A}{\partial N_A} = -T \frac{\partial S_B}{\partial N_B}}_{\hookrightarrow \text{chemical potential}}$$

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

↳ particles move from  
 } higher  $\mu$  to lower  $\mu$ ,  
 But, be careful w/ the sign.

modify the thermodynamic identity,

$$dS(U,V,N) = \underbrace{\left( \frac{\partial S}{\partial U} \right)_{V,N} dU}_{\frac{1}{T}} + \underbrace{\left( \frac{\partial S}{\partial V} \right)_{U,N} dV}_{\frac{P}{T}} + \underbrace{\left( \frac{\partial S}{\partial N} \right)_{U,V} dN}_{-\frac{\mu}{T}}$$

$$TdS = dU + PdV - \mu dN$$

$$\rightarrow dU = TdS - PdV + \mu dN$$

associated w/  
 the "chemical work"

new problems: 3.10, 3.14 ←  
 + Total HW: 2.18, 22, 29, 30, 3.1

New total HW:

2.26, 32

New New total HW (totally new)

3.24 + 3.25

New New New in a totally new way  
 3.31 + 3.32

# 3.24

$$\frac{kT}{e}$$

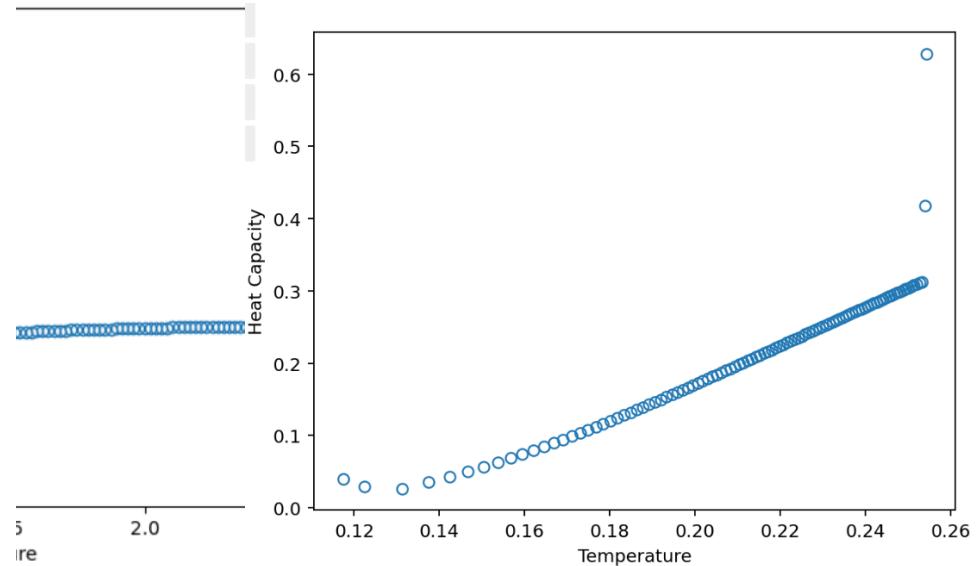
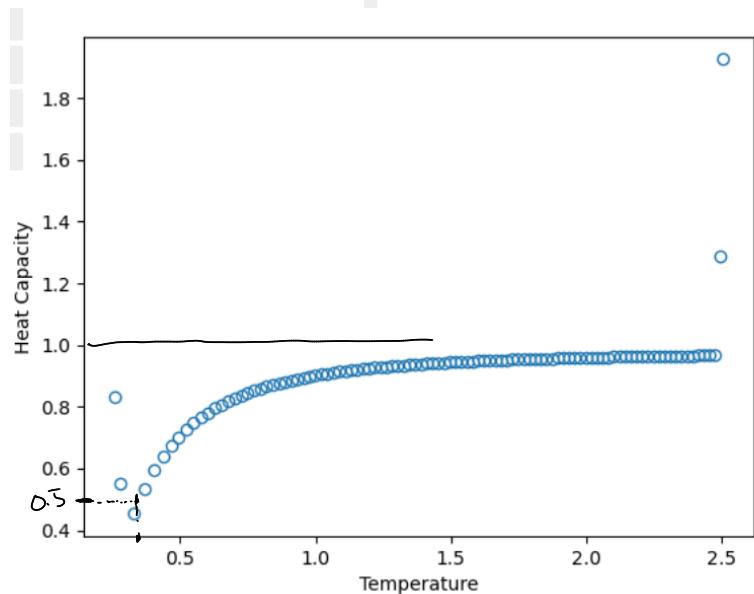
$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

$$U = g e$$

$$T = \left( \frac{\partial S}{\partial U} \right)_{N,V}^{-1} \Rightarrow \left[ \frac{\partial \left( \frac{S}{k_B} \right)}{\partial (g e)} \right]^{-1} = \left[ \frac{\partial S}{k_B e \partial g} \right]^{-1}$$

$$\frac{T}{k_B e} = \left[ \frac{\partial S}{\partial g} \right]^{-1} = \left[ \frac{S_f - S_0}{g_f - g_0} \right]^{-1}$$

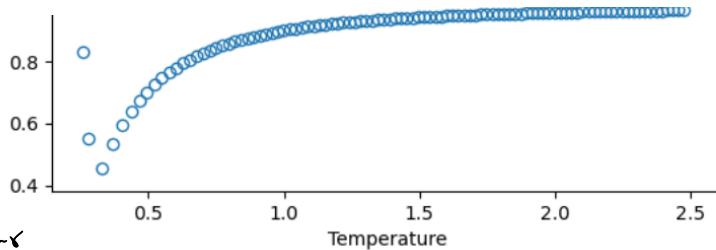
	$g$	$S$	$T$
0	0	0	0
1	3.9	3.9	13.9
2	7.15	7.15	27.15
3	10	10	50



$$\frac{k_B T}{E}$$

$$\frac{T_{1/2} k_B}{E} = \frac{1}{3}$$

$E = 3k_B T_{1/2}$  for this particular temperature  $C$  is approximately  $\frac{1}{2}$  of its high temp. value



for Pb:

$$\frac{T_{1/2}}{T_{1/2}} = 25 \text{ K}$$

$$E = 3 \cdot \left(8.62 \cdot 10^{-5} \frac{\text{eV}}{\text{K}}\right) 25 \text{ K}$$

$$E = 0.0064 \text{ eV}$$

$$k_B = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \cdot \frac{1 \text{ eV}}{1.6 \cdot 10^{-19} \text{ J}}$$

$$k_B = 8.62 \cdot 10^{-5} \frac{\text{eV}}{\text{K}}$$

Back to chemical potential:

$$dU = TdS - pdV + \mu dN$$

→ First, constant energy & constant volume:

$$\cancel{dU}^0 = TdS - \cancel{pdV}^0 + \mu dN$$

$$0 = TdS + \mu dN \quad \leftarrow \text{solve for } \mu$$

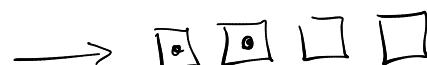
$$\mu = -T \left( \frac{dS}{dN} \right)_{U,V}$$

→ Next, let's assume constant  $S$  and  $V$

$$dU = \cancel{TdS}^0 - \cancel{pdV}^0 + \mu dN$$

$$\mu = \left( \frac{dU}{dN} \right)_{S,V} \quad \leftarrow \text{a useful formula!}$$

Examine a small Einstein solid:



one  
particular  
microstate

$$\Omega = 10$$

$$S = k_B \ln 10$$

$$\mu = \left( \frac{dU}{dN} \right)_{S,V} = \frac{-E}{1} = -E$$

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

$$\begin{aligned} \Omega(3, 3) &= \frac{(3+3-1)!}{3!(3-1)!} = \frac{5!}{3! \cdot 2!} \\ &= \frac{5 \cdot 4 \cdot (3 \cdot 2 \cdot 1)}{3! \cdot 2!} \\ &= 10 \quad \checkmark \end{aligned}$$

$$\begin{aligned} \Omega(4, q) &= 10 = \frac{(2+4-1)!}{2!(4-1)!} = \frac{5!}{2! \cdot 3!} \\ &\downarrow \text{try } 2! \\ \therefore q &= 2 \end{aligned}$$

Now for an ideal gas:  $\mu$  for a monoatomic ideal gas

$$\mu = -T \left( \frac{dS}{dN} \right)_{U,V}$$

$$S = k_B N \left( \ln \left[ \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right) \quad \text{← Sackur-Tetrode}$$

$$\mu = -T \frac{d}{dN} \left[ k_B N \left( \ln \left[ \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right) \right]_{U,V}$$

$$\mu = -T k_B \left( \ln \left[ \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right) + -T k_B N \left[ \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right]^{-1} \cdot \left[ -1 \cdot \frac{V}{N^2} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{V}{N^2} \frac{3}{2} \cdot \left( \frac{4\pi m U}{3N h^2} \right)^{1/2} \right]$$

$$\mu = -T k_B \ln \left[ \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right] - T k_B \frac{5}{2}$$

$$U = \frac{3}{2} N k_B T \quad \text{monoatomic}$$

$$\mu = -T k_B \ln \left[ \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]$$

Now that we have a thing, we need to test it!

$$\begin{aligned} &+ \cancel{T k_B} \left[ \frac{N^2}{V} \right] \left[ -\frac{V}{N^2} - \frac{3}{2} \frac{V}{N^2} \right] \\ &+ T k_B \left( 1 + \frac{3}{2} \right) \\ &+ \frac{5}{2} T k_B \end{aligned}$$

$$\bullet -1 \cdot \frac{\left( \frac{4\pi m U}{3N h^2} \right)^{3/2}}{N}$$

1 mol of He, room temp., atmospheric pressure  $\rightarrow -5.12 \cdot 10^{-20} \rightarrow -0.32 \text{ eV}$

So if we increase the N while everything else is fixed  $\rightarrow \mu$  becomes less negative

Multiple types of particles

$$\mu_i = -T \left( \frac{\partial S}{\partial N_i} \right)_{U,V,N_1, N_2} \quad \mu_2 = -T \left( \frac{\partial S}{\partial N_2} \right)_{U,V,N_1}$$

first law

$$dU = T dS - P dV + \sum_i \mu_i dN_i$$

In chemistry

$$\mu_{\text{chem}} = -T \left( \frac{\partial S}{\partial n} \right)$$

↑ number of moles  
not number of particles

$$n = \frac{N}{N_A}$$