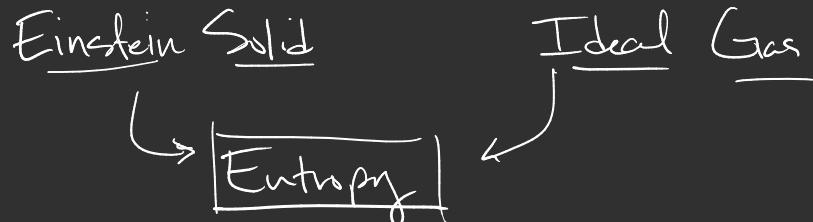


Chapter 2 - 2nd Law of Thermodynamics

↳ heat spontaneously flows from high temp to low temp



→ Anaconda python
install language
Monty Python

Combinatorics

$$\frac{\text{one coin}}{P(\text{heads})} = \frac{1}{2}$$

multiple coins

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

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

$$= \frac{\Omega(3)}{\sum_{n=0}^5 \Omega(n)}$$

$$\begin{array}{c} \xrightarrow{5 \text{ coins}} \\ \text{microstates} \left\{ \begin{array}{l} \text{HHTTH} - 3H \\ \text{THHHH} - 4H \end{array} \right. \end{array} \quad \text{macrostates}$$

how many microstates are in a macrostate?
 ↗ multiplicity

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

number of heads
$\Omega(0) = 1$
$\Omega(1) = 5$
$\Omega(2) = 10$
$\Omega(3) = 10$
$\Omega(4) = 5$
$\Omega(5) = 1$

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

$$= 5$$

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

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

↑
 # of coins

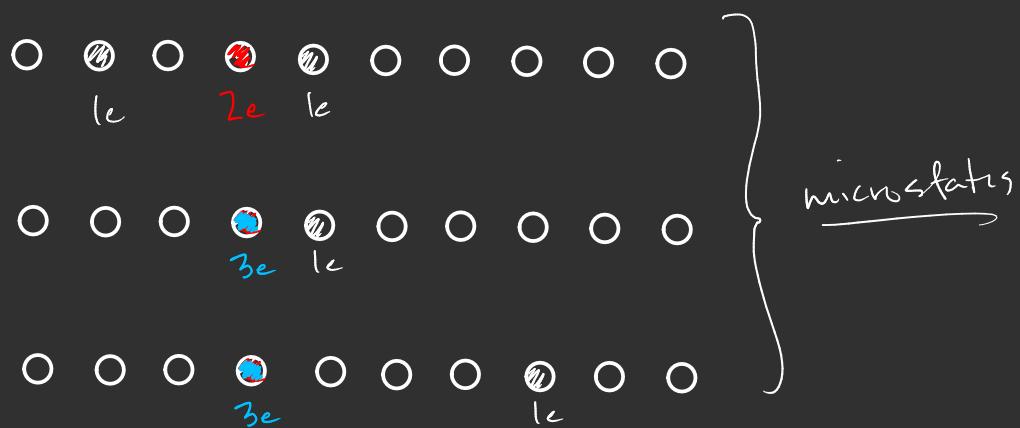
10 atoms each w/ 0 or 1 packets of energy (energy unit)

How many possible ways are there to distribute 4 energy units

$$0 \otimes 0 \otimes 0 \otimes 0 \otimes 0 \otimes 0 \leftarrow \text{microstate} \quad \Omega(10, 4) = \frac{10!}{4! 6!} = 210$$

4 energy packets \leftarrow macrostate

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



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

↑
 # of atoms
 ↑
 # of energy packets
 $q_f = \text{macrostate}$

4 energy packets \leftarrow macrostate

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



Debye Model

- Large Number → addition of small numbers is not important

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

- Very Large Number

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

Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N} = \underbrace{\frac{N^N}{e^N}}_{\substack{\text{very large numbers} \\ \downarrow \\ \ln N! \approx N \ln N - N}} \sqrt{2\pi N}$$

we leave this off

Two Systems

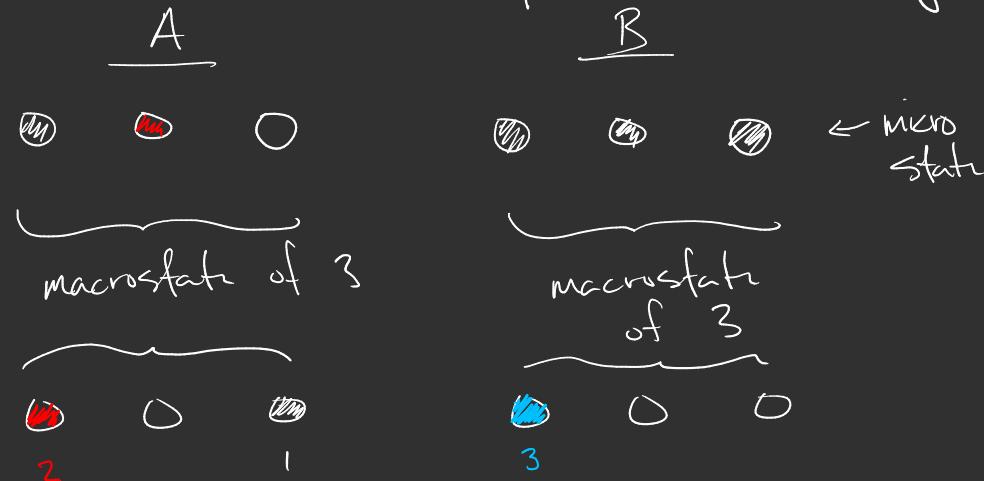


q_A	mult_A	q_B	mult_B	mult_total
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

(462) ← total number of microstates

macrostate of the most w/ microstates

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



macrostate of 1

$$\Omega(3,1) = 3$$

macrostate of 5

$$\Omega(3,5)$$

$$= \frac{7!}{5!2!} = 21$$

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.

$$P_A(q_f) = \frac{\Omega_{\text{total}}(q_f)}{\sum_{q_f} \Omega_{\text{total}}(q_f)}$$

We could find the total # of microstates:

$$\mathcal{L}(6, 6) = \frac{(6+6-1)}{6! (6-1)!} = 462$$

$\uparrow \quad \uparrow$
 $N \quad q$

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

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

$$\ln \mathcal{L} = \underbrace{\ln(q+N)!}_{\rightarrow q \ln q - q} - \underbrace{\ln q!}_{\rightarrow q \ln q - q} - \underbrace{\ln N!}_{\rightarrow N \ln N - N} \rightarrow N \ln N - N$$

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

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

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

high temperature limit $\rightarrow q \gg N$

$$\begin{aligned}
 \ln Q &= (q_f + N) \ln(q_f + N) - q_f \ln q_f - N \ln N \\
 &= q_f \underbrace{\ln(q_f + N)}_{\ln q_f + \ln(1 + \frac{N}{q_f})} + N \underbrace{\ln(q_f + N)}_{\ln(1 + \frac{N}{q_f})} - q_f \ln q_f - N \ln N \\
 &= \ln \left[q_f \cdot \left(1 + \frac{N}{q_f} \right) \right] \\
 &= \ln q_f + \underbrace{\ln \left(1 + \frac{N}{q_f} \right)}_{\ln(1+x) \approx x \text{ for small } x} \\
 &\quad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\
 &= \ln q_f + \frac{N}{q_f} \approx \ln(q_f + N)
 \end{aligned}$$

$$\begin{aligned}
 \ln Q &= \cancel{q_f \ln q_f} + N + N \cancel{\ln q_f} + \cancel{\frac{N^2}{q_f}} - \cancel{q_f \ln q_f} - \cancel{N \ln N} \\
 &= N \ln \left(\frac{q_f}{N} \right) + N + \underbrace{\frac{N^2}{q_f}}_{\text{small}}
 \end{aligned}$$

$$\ln Q(q_f \gg N) \approx N \ln \left(\frac{q_f}{N} \right) + N$$

$$\begin{aligned}
 Q(q_f \gg N) &= e^{N \ln \left(\frac{q_f}{N} \right) + N} = e^{N \ln \left(\frac{q_f}{N} \right)} \cdot e^N = \underbrace{\left(e^{\ln \left(\frac{q_f}{N} \right)} \right)^N}_{\left(\frac{q_f}{N} \right)^N} \cdot e^N \\
 Q(q_f \gg N) &= \left(\frac{q_f}{N} \right)^N e^N = \boxed{\left(\frac{e^{q_f}}{N} \right)^N}
 \end{aligned}$$

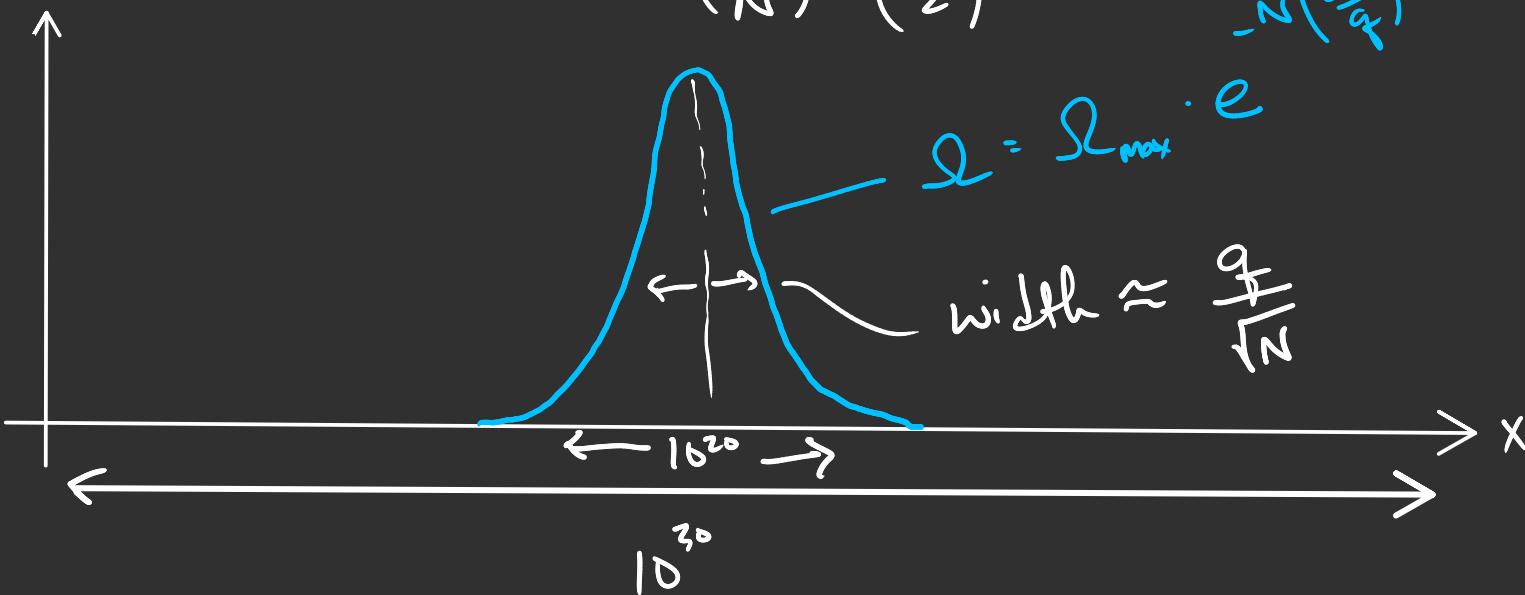
- 2 Einstein solids (high temperature limit) ($g \gg N$)

$$\mathcal{L}_A = \left(\frac{e g_f}{N_A} \right)^{N_A} \quad \mathcal{L}_B = \left(\frac{e g_f}{N_B} \right)^{N_B}$$

$$g_f = g_{fA} + g_{fB}$$

if $N_A = N_B$, multiplicity max will occur $\frac{g_f}{2} = g_{fA} = g_{fB}$

$$\mathcal{L} = \mathcal{L}_A \mathcal{L}_B = \left(\frac{e}{N} \right)^{2N} \cdot \left(\frac{g_f}{2} \right)^{2N}$$



$$g_f = 10^{30}$$

$$N = 10^{20}$$

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

Entropy + the 2nd Law:

Any large system in equilibrium will be found in the macrostate with the greatest ~~multiplicity~~ entropy

2nd Law of Thermodynamics

~~Multiplicity~~ tends to increase.
Entropy

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

$$\text{entropy} \rightarrow S = k_B \cdot \ln \Omega$$

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

Ex: Entropy of an Einstein solid

$$\mathcal{I} = \left(\frac{eq}{N}\right)^N \quad q \gg N \quad \text{Einstein solid}$$

homework

$$(q \approx N)$$

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

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

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

$$= 1.38 \left(1 + \ln(10^2) \right)$$

$$S = 7.7 \text{ J/K} \quad \underbrace{4.6}_{\text{4.6}}$$

Entropy of a composite system

$$\mathcal{I}_{\text{total}} = \mathcal{I}_A \mathcal{I}_B$$

$$S = k_B \ln \mathcal{I}_A \cdot \mathcal{I}_B = k_B \ln \mathcal{I}_A + k_B \ln \mathcal{I}_B$$

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

Chapter 3

Thermal equilibrium

For the Einstein solid

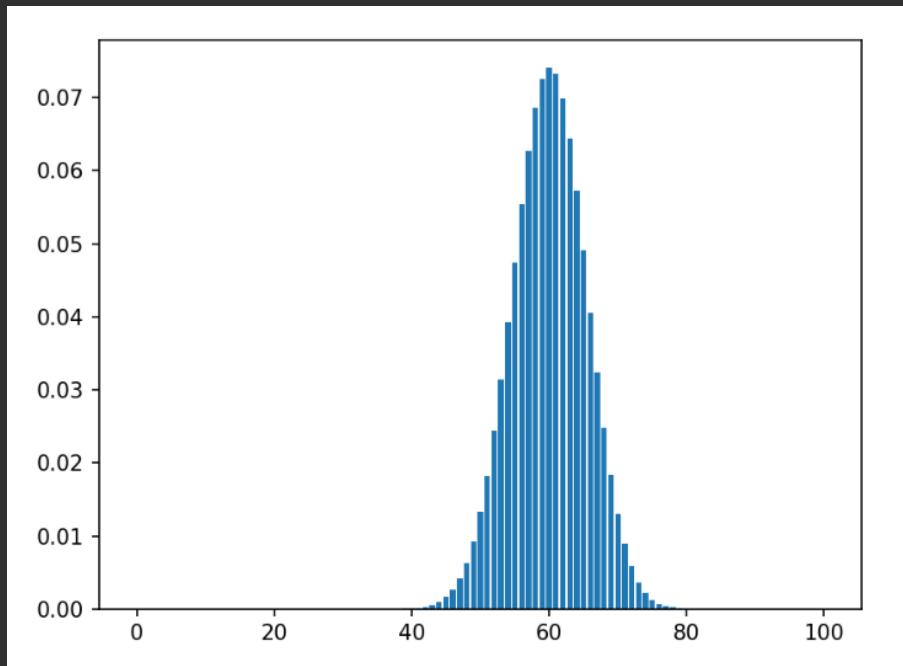
$$\frac{\delta S_{\text{total}}}{\delta q_A} = 0$$

↓ generalize

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

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

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



$$U_B = U - U_A$$

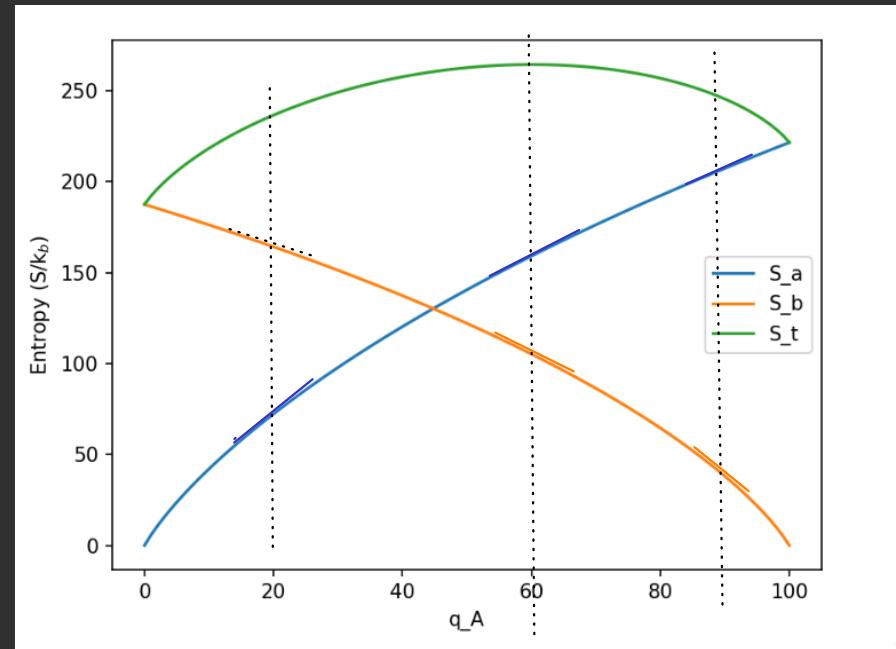
$$\left\{ \begin{array}{l} dU_B = -dU_A \end{array} \right.$$

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

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

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

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



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

$$U = q \cdot E \Rightarrow q = \frac{U}{E}$$

of energy packets in one packet

energy packets

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

$$S = k_B \ln \Omega$$

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

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

$$S = N k_B + N k_B \ln U - N k_B \ln (N\epsilon)$$

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

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

$$f = 2 \quad \} \text{ Einstein solid}$$

Heat Capacity of Einstein solid:

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

↳ 1D kinetic energy

↳ 1D spring pot. energy

Review our process so far:

1. Used combinatorics and QM to find Ω in terms of N, V, U etc.

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

} could be impossible!
Stat mech
give an alternative
to arriving
at #4

But, going backward to measure the entropy is

easy

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

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

→ Use constant volume process (isochoric)

$$\left. \begin{array}{l} dV = 0 \\ dW = 0 \end{array} \right\} dU = \pm Q + \pm W$$

$$dU = \pm Q$$

$$dS = \frac{\pm Q}{T}$$

important! used to be
the definition of entropy!

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

$\Rightarrow T$ does not change much w/
a small addition of heat!

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

\$\Rightarrow C_v\$ can be constant, or a function of temperature

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_v}{T} dT$$

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

\Rightarrow but you need to know this function all the way to zero kelvin!

$C_v \rightarrow 0$ as $T \rightarrow 0$

\Rightarrow could be 0 or residual entropy but some constant

\Rightarrow much experimental data has gone into this for many substances

3rd Law
of Thermodynamics

$$L = \frac{N!}{q!(N-q)!}$$

$$\begin{aligned}
 L(1000, 500) &= \frac{1000!}{(500!)^2} \approx \frac{1000^{1000} e^{-1000} \sqrt{2\pi 1000}}{(500^{500} e^{-500} \sqrt{2\pi 500})^2} = \frac{1000^{1000} \sqrt{2\pi 1000}}{500^{1000} (\sqrt{2\pi 500})^2} \\
 &= \left(\frac{1000}{500}\right)^{1000} \frac{\sqrt{2\pi 1000}}{\sqrt{2^2 \pi^2 500^2}} \\
 &= 2^{1000} \cdot \sqrt{\frac{2 \cdot 1000}{(2 \cdot 500)^2 \pi}} \\
 &= 2^{1000} \cdot \sqrt{\frac{2}{1000 \pi}} \\
 &= \frac{2^{1000}}{\sqrt{500 \pi}}
 \end{aligned}$$

2^{1000}
 $\sum_{q=1}^{1000} \frac{1000!}{q!(1000-q)!}$??

2.5 Ideal Gas Multiplicity

Multiplicity is the number of microstates in a macrostate.

total energy, volume
what defines macrostate
for ideal gas

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

For a single particle,

$\Omega_1 \propto V$. combination of momentums that has some energy
volume of momentum space

$$I_1 \propto V \cdot V_p$$

Heisenberg Uncertainty Principle

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

uncertainty in position uncertainty in momentum
inversely proportional

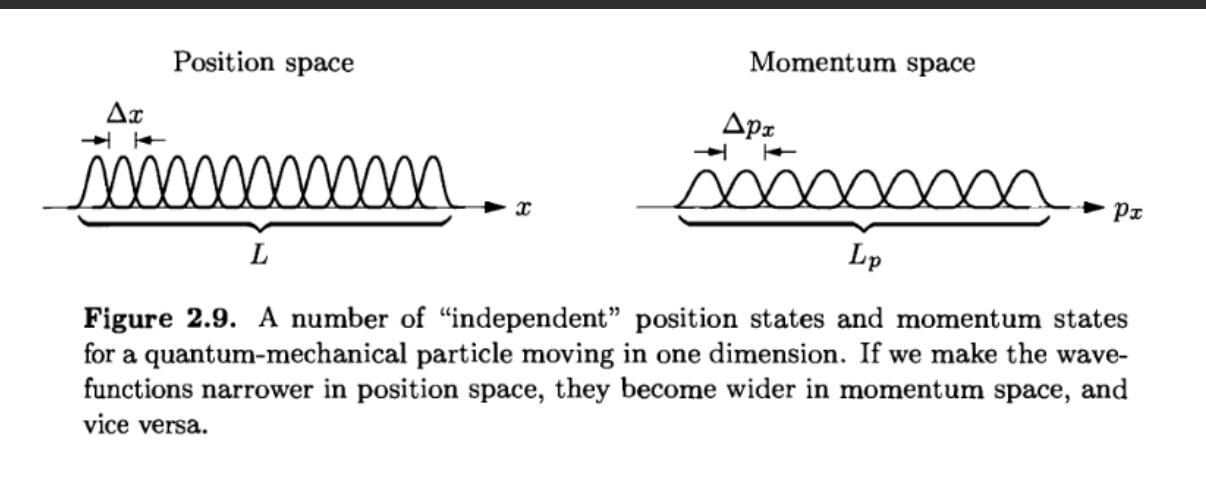


Figure 2.9. A number of “independent” position states and momentum states for a quantum-mechanical particle moving in one dimension. If we make the wavefunctions narrower in position space, they become wider in momentum space, and vice versa.

$$I_1 = \frac{L_x L_y L_z}{\Delta x \Delta y \Delta z} \cdot \frac{L_{p_x} L_{p_y} L_{p_z}}{\Delta p_x \Delta p_y \Delta p_z}$$

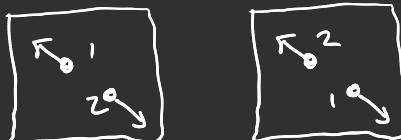
$$I_1 = \frac{V \cdot V_p}{h \cdot h \cdot h} = \frac{V \cdot V_p}{h^3}$$

So what about two particles?

$$I_2 = I_A \cdot I_B$$

cannot distinguish
the particles

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



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

So lets go back to one particle that has all of the energy of the system, U ,

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

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

$$p_x^2 + p_y^2 + p_z^2 = 2mU = (\sqrt{2mU})^2$$

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

So the "volume" of momentum space that represents all of the possible momenta that the particle can have and still have U amount of energy is really the surface area of the sphere in momentum space $\sim 4\pi r^2 \sim 4\pi(\sqrt{2mU})^2$

For two particles constrained to U total energy,

then

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

6 dimensional sphere? hypersphere!

"Surface area" = $\frac{2\pi^{d/2} r^{d-1}}{(\frac{d}{2}-1)!}$

3N dimensional sphere

"Surface area" = $\frac{2\pi^{\frac{3N}{2}} r^{\frac{3N-1}{2}}}{(\frac{3N}{2}-1)!}$

$$\sqrt{2mU} = (2mU)^{\frac{1}{2}}$$

TEST: d=2

$$2\pi r \stackrel{?}{=} \frac{2\pi^{\frac{2}{2}} r^{2-1}}{(\frac{2}{2}-1)!}$$

$$= 2\pi r \checkmark$$

TEST: d=3

$$4\pi r^2 \stackrel{?}{=} \frac{2\pi^{\frac{3}{2}} r^{\frac{3-1}{2}}}{(\frac{3}{2}-1)!}$$

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

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

$$\frac{1}{(\frac{1}{2})!} = \frac{2}{\sqrt{\pi}}$$

$$= 4\pi r^2 \checkmark$$

so let's throw away what does not matter for large numbers

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

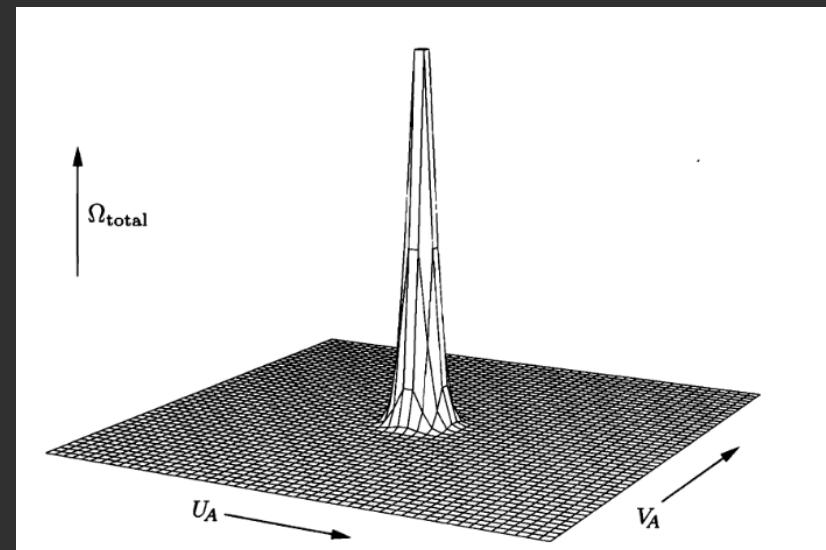
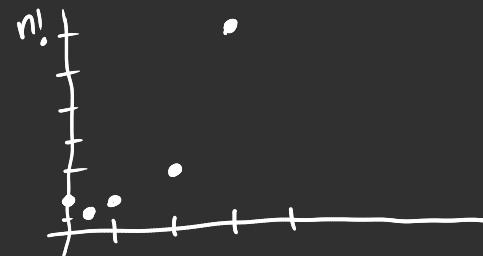
$$\Omega_N = f(N) \cdot V^N \cdot U^{\frac{3N}{2}}$$

Put two ideal gasses in thermal contact
(barrier exchanges energy + volume)

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

$$2! = 2 \cdot 1$$

$$\frac{1}{2}! = \frac{\sqrt{\pi}}{2} = 0.8862$$



Entropy of an ideal gas

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

$$S = k_B \ln \Omega = k_B \ln \left[\frac{1}{N!} \frac{V^N}{h^{3N}} \cdot \frac{(2\pi m u)^{\frac{3N}{2}}}{(\frac{3N}{2})!} \right]$$

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

\$-\ln(N!)\$ \$\ln\left(\frac{3N}{2}!\right)\$ \$N \ln V\$ \$\frac{3N}{2} \ln(2\pi m u)\$ \$-\frac{3N}{2} \ln(h^2)\$
\$N \ln \frac{1}{N} + N\$ \$-\frac{3N}{2} \ln\left(\frac{3N}{2}\right) + \frac{3N}{2}\$
\$\frac{3N}{2} \ln\left(\frac{2}{3N}\right) + \frac{3N}{2}\$

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

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

$\frac{V}{N} \rightarrow$ volume
per particle

$\frac{U}{N} \rightarrow$ energy
per particle

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

Find entropy: $n_m = 1$, or $N = N_A = n_m$

$$U = \frac{5}{2} n_m RT = \frac{5}{2} N k_B T$$

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

$$\hookrightarrow V = \frac{RT}{P} = \frac{N_A k_B T}{P}$$

$$N_2 = 28 \frac{\text{g}}{\text{mol}} = 0.028 \frac{\text{kg}}{\text{mol}} = \frac{0.028 \text{ kg}}{6.022 \cdot 10^{23} \text{ atoms}} = 4.65 \cdot 10^{-26} \text{ kg}$$

$$\begin{aligned} S &= k_B N \left(\ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right) \\ &= k_B N_A \left(\ln \left[\frac{N_A k_B T}{N_A \cdot P} \left(\frac{4\pi (4.65 \cdot 10^{-26}) \cdot \frac{5}{2} N_A k_B \cdot 293 K}{3 N_A h^2} \right)^{3/2} \right] + \frac{5}{2} \right) \\ &= 8.31 \left(\ln \left[\frac{1.38 \cdot 10^{-23} \cdot 293 K}{10^5 P_a} \left(\frac{4\pi (4.65 \cdot 10^{-26}) \cdot \frac{5}{2} \cdot 1.38 \cdot 10^{-23} \cdot 293}{3 (6.626 \cdot 10^{-34})^2} \right)^{3/2} \right] + \frac{5}{2} \right) = 135.5 \text{ J/K} \end{aligned}$$

HW: Ch 2.26, 32

$$\mathcal{L}(\text{all}) = \sum_{n=0}^N \frac{N!}{n!(N-n)!} = \cancel{\text{N}} \cdot 2^N$$

HW: Ch 3.1, 10, 14 ←

2.26] $\mathcal{L} = \frac{A \cdot A_p}{h^2}$

so how
do you adapt for
2D gas

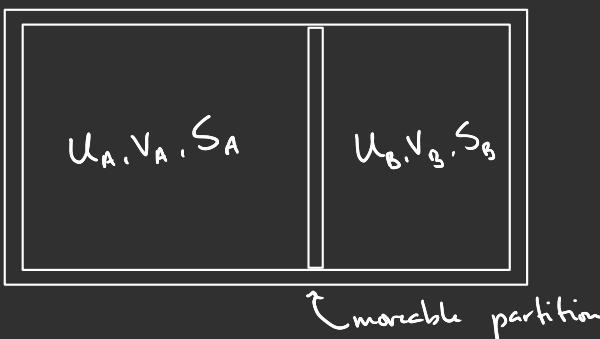
$$\mathcal{L}_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times (\text{area of the momentum hypersphere})$$

3.4 Mechanical Equilibrium + Pressure

Exchange of energy is governed by temperature difference

Exchange of volume is governed by pressure difference.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,V} \quad \leftarrow \text{is the pressure related to entropy too?}$$



equilibrium { $\frac{\delta S_{\text{total}}}{\delta U_A} = 0$

this is defined
for same temperature
for A & B

$$\underbrace{\frac{\delta S_{\text{total}}}{\delta V_A} = 0}_{\text{new}}$$

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

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

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

$$dV_A = -dV_B$$

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

at equilibrium
constant U, N

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

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

$$\underbrace{\frac{J}{Km^3}}_{\text{units?}} = \frac{N \cdot m}{K \cdot m^{3/2}} = \frac{Pa}{K}$$

is this right?

CHECK

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

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

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

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

$$P = \frac{N k_B T}{V}$$

$$\underline{PV = N k_B T} \quad \checkmark \checkmark$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

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

$$dU = TdS - PdV$$

thermodynamic identity

} true for any infinitesimal change
as long as T & P are the
same throughout the system

Compare this to 1st Law

$$dU = \delta Q + \delta W$$

$$\delta Q \stackrel{?}{=} TdS \quad \delta W \stackrel{?}{=} -PdV$$

- dV happen quasistatically
w/ no friction

- no non-compressive sources of work \rightarrow like electric fields
- no other relevant variables change \rightarrow like N

if these are true,

$$\delta Q = T \delta S$$

Examples:

so an adiabatic and quasistatic process, is called isentropic

$$\delta Q = D = T \delta S$$

$$D = \delta S$$

Example: even when the volume of a system is changing

$$\delta Q = T \delta S$$

$$\delta S = \frac{\delta Q}{T} \quad \left. \right\} \begin{array}{l} 1 \text{ L of water boils} \rightarrow 2260 \text{ kJ} \\ \text{are added} \end{array}$$

$$\Delta S = \frac{Q}{T} = \frac{2260 \text{ kJ}}{373 \text{ K}} = \frac{2,260,000 \text{ J}}{373 \text{ K}}$$

$$\Delta S = 6060 \text{ J/K}$$

Exampk: $(\Delta S)_p = \int_{T_i}^{T_f} \frac{C_p}{T} dT \} = \pm Q$



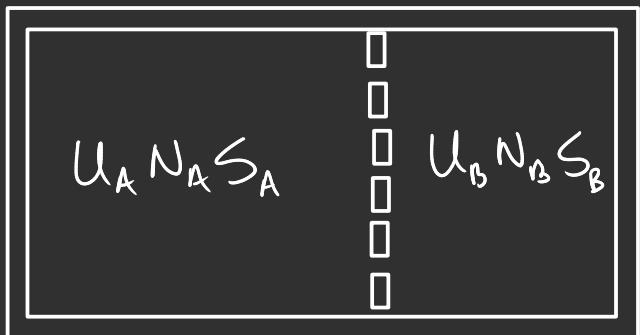
much more practical
than the constant
volume version

3.5] Diffusive Equilibrium + Chemical Potential

thermal equilibrium \rightarrow temperature is the same

mechanical equilibrium \rightarrow pressure is the same

diffusive equilibrium ?



can exchange
energy and particles
(can not exchange volume)
same kind of particle
(indistinguishable)

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

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

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$-T \frac{\partial S_A}{\partial N_A} = -T \frac{\partial S_B}{\partial N_B}$$

$$\mu_A = \mu_B$$

chemical potential $\leftarrow \mu = -T \frac{\partial S_A}{\partial N_A}$

modify thermodynamic identity

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

$$TdS = \underbrace{dU + PdV - \mu dN}_{=}$$

$$\boxed{dU = TdS - PdV + \underbrace{\mu dN}_{\text{associated w/ "chemical work"}}$$

if we hold S and V constant

$$dU = \mu dN$$

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

$\rightarrow \mu$ is the energy add/removed to add a particle & keep entropy constant
(Usually you have to remove energy, so μ is negative)

