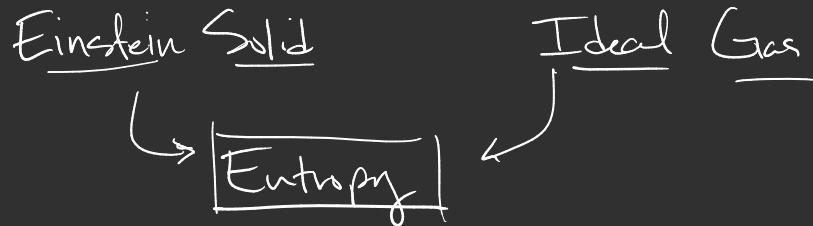


## Chapter 2 - 2<sup>nd</sup> Law of Thermodynamics

↳ 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

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

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

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

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

$$= 5$$

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

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

↑  
 # 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?

$$\begin{array}{ccccccccc}
 0 & \otimes & 0 & \otimes & \textcolor{red}{\otimes} & \otimes & 0 & 0 & 0 \\
 & 1e & & 2e & & 1e & & & \\
 \\ 
 0 & 0 & 0 & \textcolor{red}{\otimes} & \otimes & 0 & 0 & 0 & 0 \\
 & 3e & & 1e & & & & & \\
 \\ 
 0 & 0 & 0 & \textcolor{red}{\otimes} & 0 & 0 & 0 & \otimes & 0
 \end{array}
 \left\{
 \begin{array}{l}
 \text{microstates} \\
 \text{of atoms} \\
 \text{\# of} \\
 \text{energy} \\
 \text{packets}
 \end{array}
 \right.$$

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

$q_f = \text{macrostate}$

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  $\rightarrow$  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

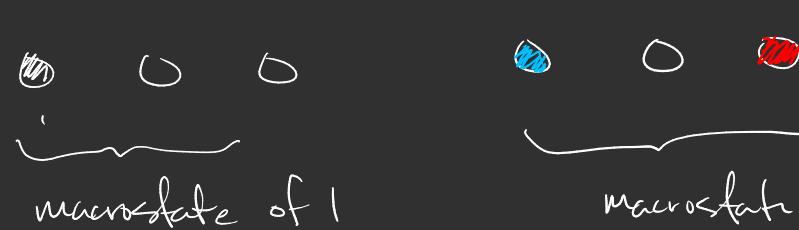
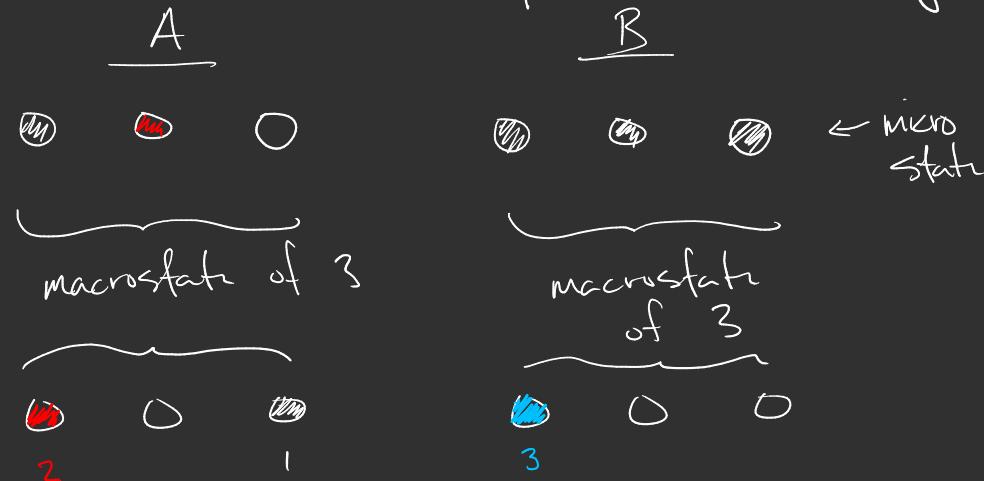


q_A	mult_A	q_B	mult_B	mult_total
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

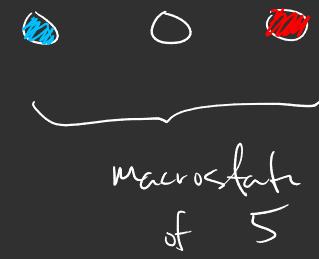
(462) ← total number of microstates

macrostate of the most w/ microstates

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



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



$$\Omega(3,5)$$

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

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  $\left[ \ln N! = N \ln N - N \right]$

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

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

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

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

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

high temperature limit  $\rightarrow q \gg N$

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

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

$$= N \ln \left( \frac{q}{N} \right) + N + \frac{N^2}{\cancel{q}}$$

$\brace{}$   
small

$$W \mathcal{L}(q \gg N) \approx N \ln\left(\frac{q}{N}\right) + N$$

$$\sum_{f \geq N} (q_f) = e^{N \ln \left( \frac{q}{N} \right) + N} = e^{\overbrace{N \ln \left( \frac{q}{N} \right)}^N} \cdot e^N = \underbrace{\left( e^{\ln \left( \frac{q}{N} \right)} \right)^N}_{e^N} \cdot e^N$$

$$L(q \gg N) = \left( \frac{q}{N} \right)^N e^{-N} = \left\lceil \left( \frac{e^q}{N!} \right)^N \right\rceil$$

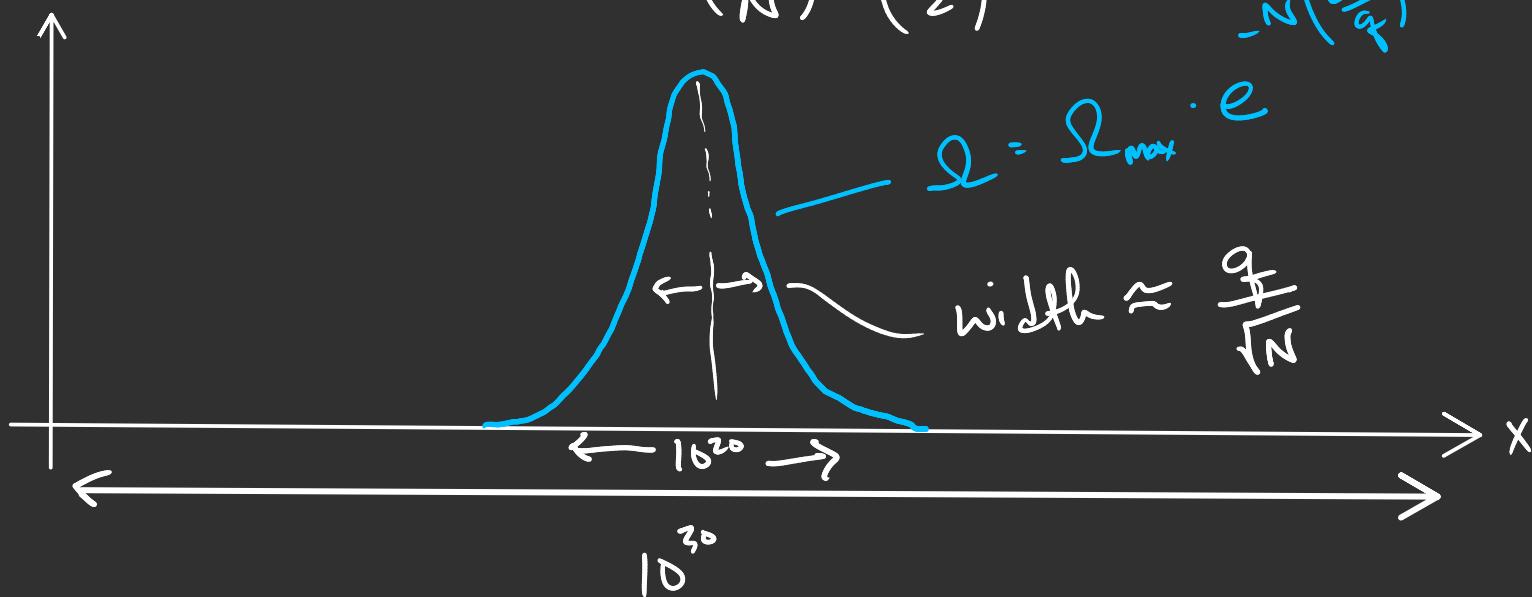
- 2 Einstein solids (high temperature limit) ( $g \gg N$ )

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

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

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 2<sup>nd</sup> Law:

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

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

~~Multiplicity~~ tends to increase.  
Entropy

Multiplicities are very large! 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

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

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

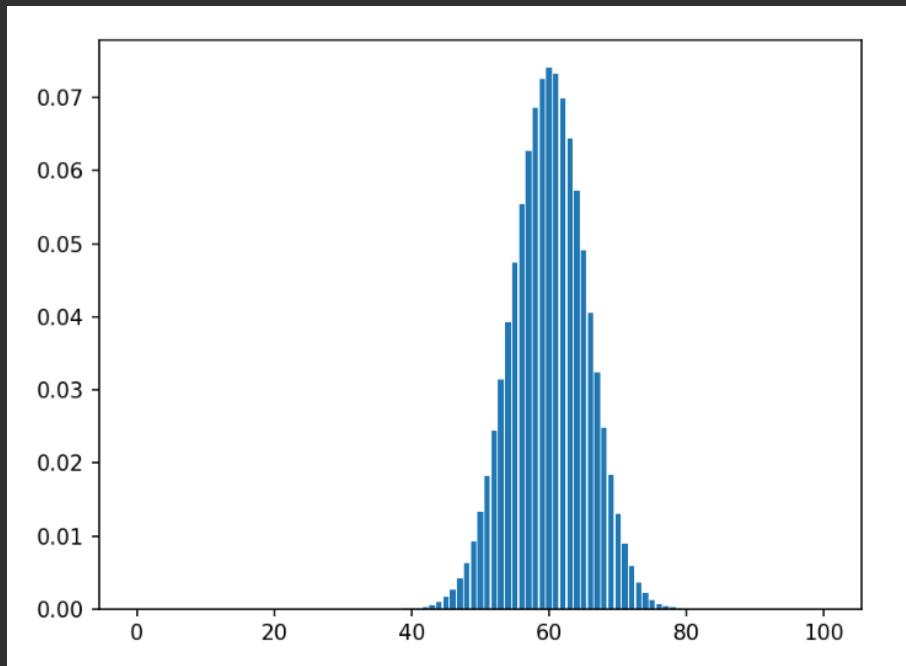
$$\frac{\delta S_{\text{total}}}{\delta q_A} = 0$$

↓ generalize

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

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

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



$$U_B = U - U_A$$

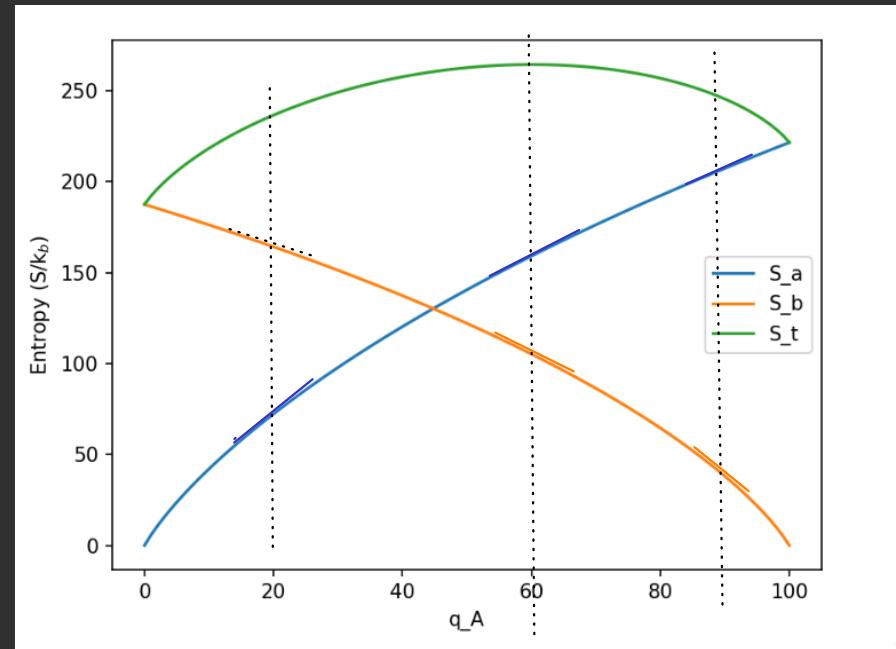
$$\left\{ \begin{array}{l} dU_B = -dU_A \end{array} \right.$$

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

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

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

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



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  $\Omega$  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.  $C_v = \frac{\partial U}{\partial T}$
- 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!

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

→  $C_v$  can be constant, or a function of temperature

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

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

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

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

→ could be 0 or residual entropy  
but some constant

→ 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,

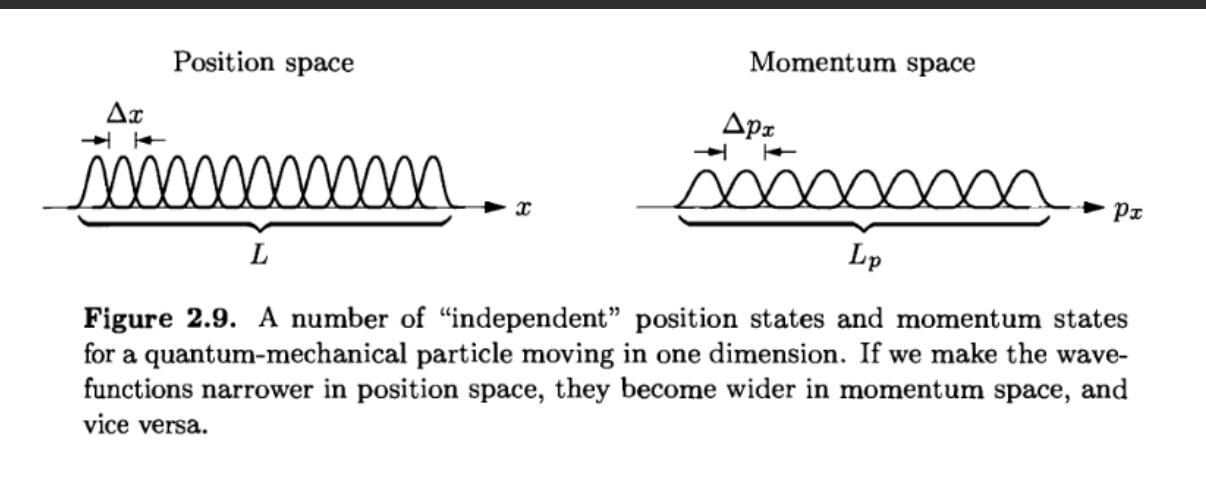
$\Omega_1 \propto V$ . combination of momentums that has some energy  
volume of momentum space

$$I_1 \propto V \cdot V_p$$

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.

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

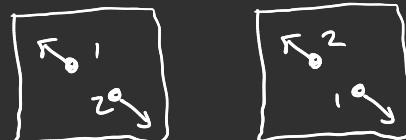
$$I_1 = \frac{V \cdot V_p}{h \cdot h \cdot h} = \frac{V \cdot V_p}{h^3}$$

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

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

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

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

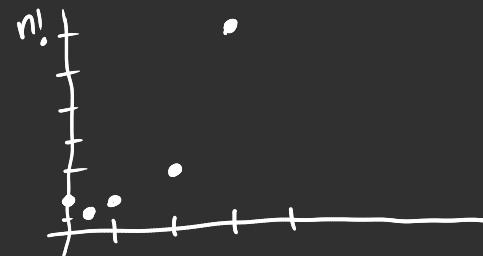
$$\frac{1}{(\frac{1}{2})!} = \frac{2}{\sqrt{\pi}}$$

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

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

$$2! = 2 \cdot 1$$

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

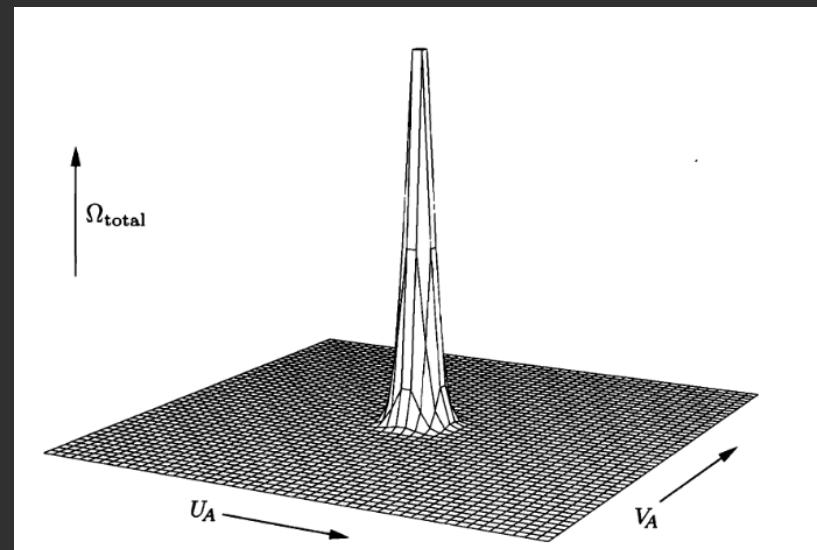


$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \cdot \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} (2mU)^{\frac{3N}{2}}$$

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

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

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



Entropy of an ideal gas

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

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

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

$\rightarrow -N \ln N + N$        $\rightarrow -\frac{3N}{2} \ln\left(\frac{3N}{2}\right) + \frac{3N}{2}$

$N \ln \frac{1}{N} + N$        $\frac{3N}{2} \ln\left(\frac{2}{3N}\right) + \frac{3N}{2}$

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

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

$\frac{V}{N} \rightarrow$  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

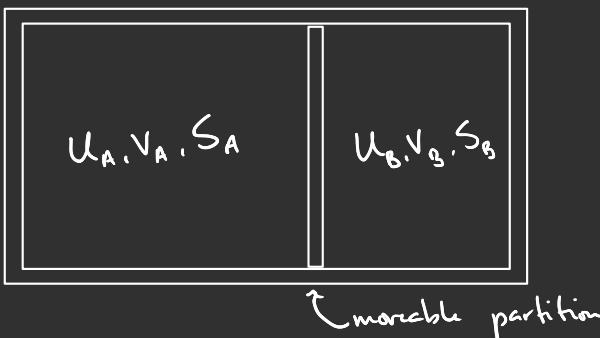
$$\mathcal{L}_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times (\text{area of the momentum hypersphere})$$

### 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.

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

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

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

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

$$\underbrace{\delta Q \stackrel{?}{=} TdS}_{\text{and}} \quad \underbrace{\delta W \stackrel{?}{=} -PdV}_{\text{and}}$$

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



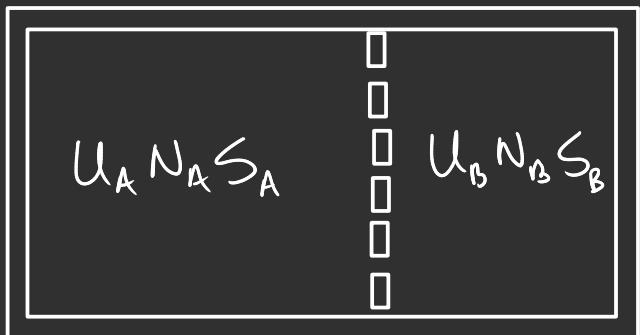
much more practical  
than the constant  
volume version

### 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  $\mu$  is negative)

Use ideal gas multiplicity to find the internal energy as a function of temperature.

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

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

$$\underbrace{\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_N}_{=} = \frac{3}{2} N k_B \frac{1}{U}$$

Solve for  $U$

$$\underbrace{U = \frac{3}{2} N k_B T}_{\text{equipartition theorem}} \quad \checkmark$$

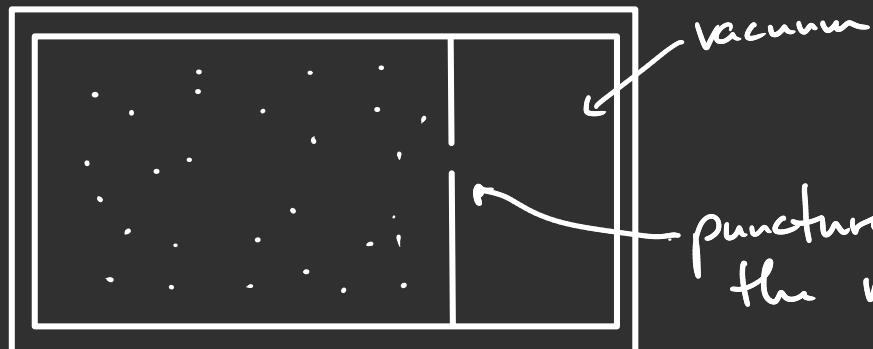
equipartition  
theorem

$$\begin{aligned}\Delta U &= \underbrace{\frac{3}{2} N k_B \Delta T}_{=} \\ &= \Delta P \cdot V \\ &= P \cdot \Delta V \\ &\neq \cancel{\Delta P \cdot V}\end{aligned}$$

Now for all the weird cases:

## Joule Expansion (Free Expansion)

↳ new process



$\dot{W} = ?$  no push/pull

$\dot{W} = 0$

$\dot{Q} = ?$  isolated/insulated

$\dot{Q} = 0$

put these together

$\Delta U = ? \rightarrow$  no change in temperature

$\Delta U = 0$

$$\underset{\downarrow}{P} V = \underset{\uparrow}{n R T}$$

But!  $\Delta S = S_f - S_i$

$$= k_B \ln\left(\frac{S_f}{S_i}\right)$$

$$\left( S = f(N) \cdot V^N \cdot U^{3N/2} \right)$$

$$\Delta S = k_B N \ln\left(\frac{V_f}{V_i}\right)$$

(remove the partition) (move it very fast)

So what if the volume change was small?  $dV$

$$dU = 0$$

$$dU = \cancel{\delta Q} + \cancel{\delta W}$$

$$dU = T dS - p dV$$

$$T dS = p dV > 0$$

Compare to below ↴

If I draw back the partition I do  $\ominus$  work, and I add heat to keep energy the same.

$$\Delta S = k_B N \ln\left(\frac{V_f}{V_i}\right)$$

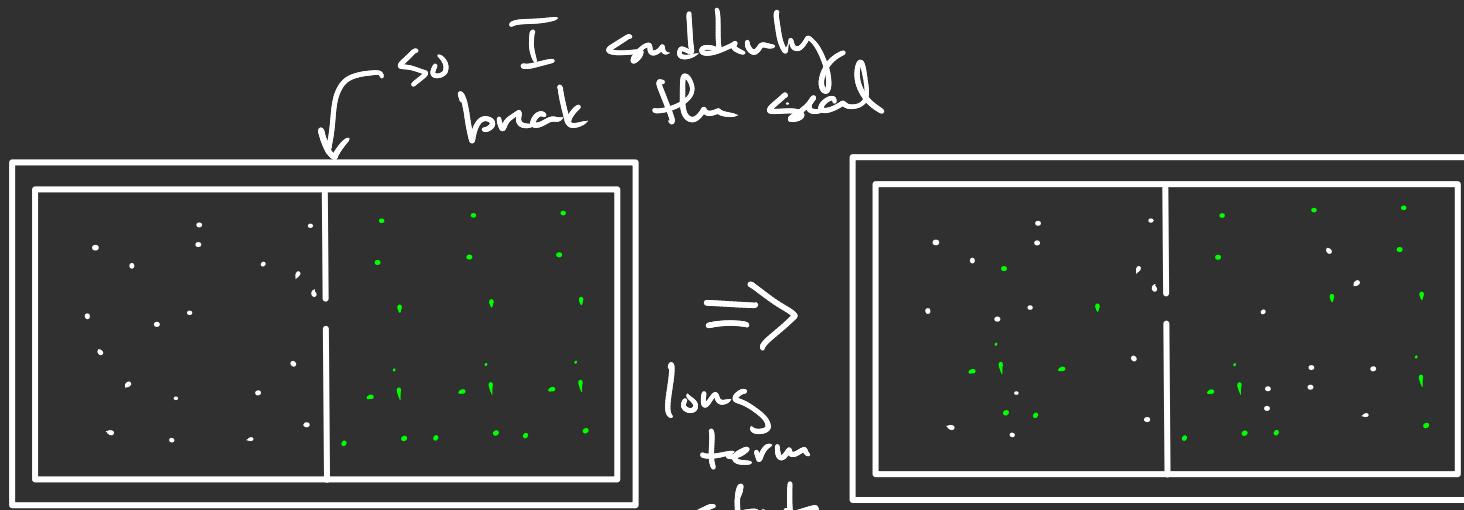
} . Constant  $N + U$  process  
} . Isothermal expansion

$$\Delta U = 0$$

$$Q = -W$$

↑  
putting into the system  
always causes an increase  
in entropy

Now what if instead of vacuum, there was another gas



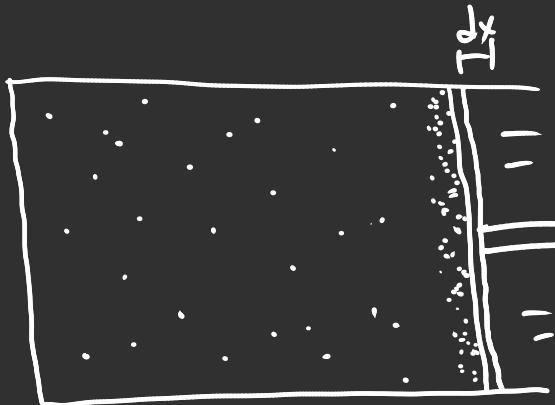
is that they are equally mixed  
But the volume has changed!

$$\Delta S_A = k_B N \ln \underbrace{\left( \frac{V_f}{V_i} \right)}_{2 \text{ for equally sized containers}}$$

$$\left. \begin{array}{l} \Delta S_A = k_B N \ln 2 \\ \Delta S_B = k_B N \ln 2 \end{array} \right\} \Delta S_{\text{total}} = 2 k_B N \ln 2$$

$\hookrightarrow$  entropy of mixing

What about another non-quasistatic process?



$$\delta W > p\delta V$$

I have to do  
more work to move  
aside all the molecules  
quickly

greater than

$$\delta W + \delta Q = \delta U = T\delta S - p\delta V$$

must be less than

$$\delta Q \leq T\delta S \text{ when } \delta W \geq p\delta V$$

$$\delta S \geq \frac{\delta Q}{T}$$

extra entropy that was created  
since more work was done to  
change the volume

will not change much  
for a small  $\delta V$  change.

3.32] a)  $W = F \cdot \Delta x$

$$= 2000 \text{ N} \cdot 0.001 \text{ m} = 2 \text{ J}$$

} work done by me.  
done on the gas

b)  $Q = 0$  (suddenly)

c)  $\Delta U = \xi Q + \xi W$

$$\Delta U = 2 \text{ J}$$

} from the perspective of the gas

d)  $\Delta S = ?$

$$\Delta U = T \Delta S - P \Delta V$$

$$\downarrow 300 \text{ K}$$

$$\downarrow 10^5 \text{ Pa}$$

$$\downarrow \Delta x \cdot A$$

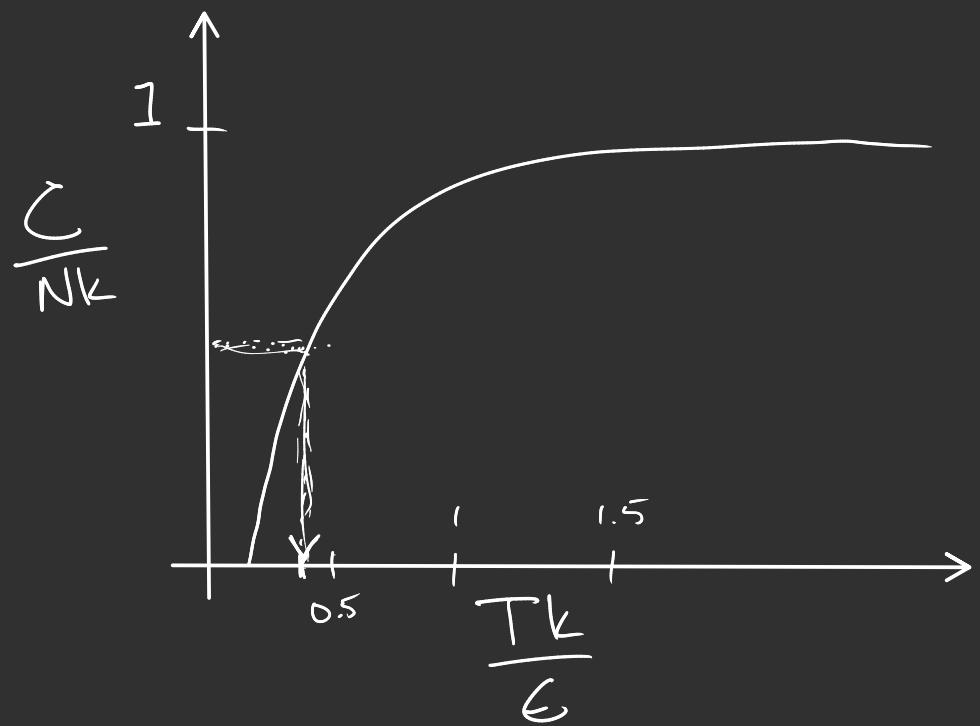
$$\downarrow -0.001 \text{ m} \times 0.01 \text{ m}^2$$

$$\downarrow 10^{-3} \quad 10^{-2}$$

$$= -0.00001 \text{ m}^3 = -10^{-5} \text{ m}^3$$

$$\Delta S = \frac{2 \text{ J} - 1 \text{ J}}{300 \text{ K}} = 0.0033 \frac{\text{J}}{\text{K}}$$

3.24]



$$\frac{Tk_B}{E} = \frac{1}{3}$$

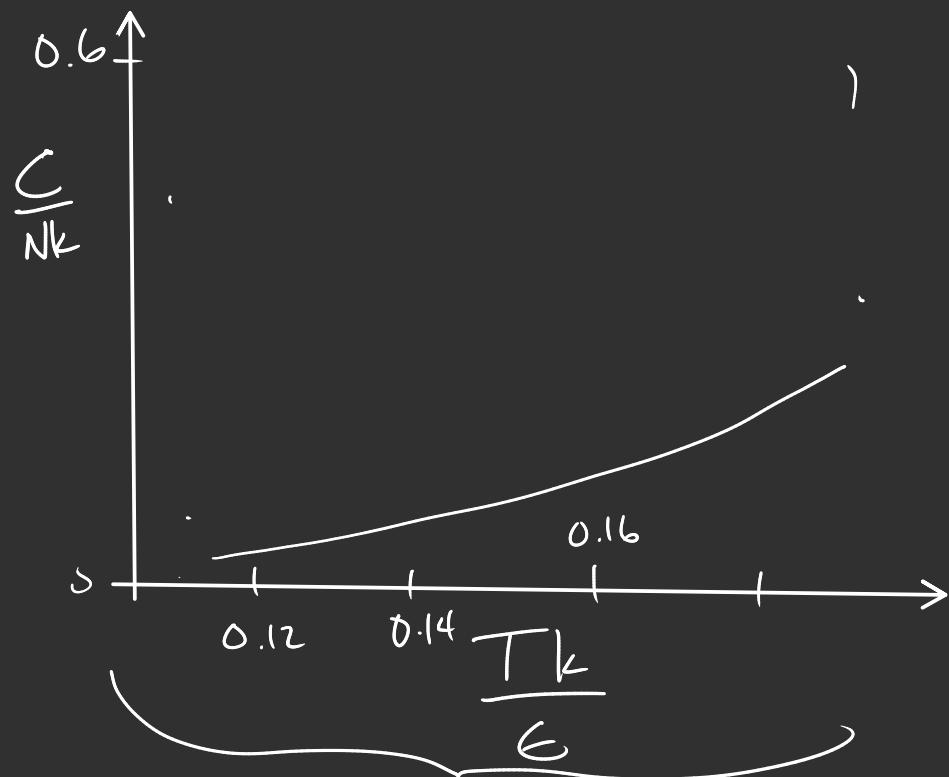
$E = 3Tk_B$  for the particular temperatures where  $C$  is approx  $1/2$  its total value

for Pb:

$$T_h = 25\text{ K}$$

$$E = 3 \cdot 25\text{ K} \cdot 8.6 \cdot 10^{-5} \frac{\text{eV}}{\text{K}}$$

$$= 0.0664 \text{ eV}$$



plot on the same vertical + horizontal axis

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

$$= 8.6 \cdot 10^{-5} \frac{\text{eV}}{\text{K}}$$

for Al:

$$T_{y_2} = 100K, \quad \epsilon = 3 \cdot 100K \cdot 8.6 \cdot 10^{-5}$$
$$= 0.026 \text{ eV}$$

for C:

$$T_{y_2} = 425K, \quad \epsilon = 3 \cdot 425K \cdot 8.6 \cdot 10^{-5}$$
$$= 0.109 \text{ eV}$$

Why?

$$U = q \cdot \epsilon$$

$$\text{qc: } U \approx \frac{1}{2} kx^2 + \frac{1}{2} mv^2$$