

Microstates of an ideal gas contained
within volume V with energy E :

$$\Omega = \frac{1}{(2\pi\hbar)^{3N}} \frac{V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{N! \Gamma(\frac{3N}{2})}$$

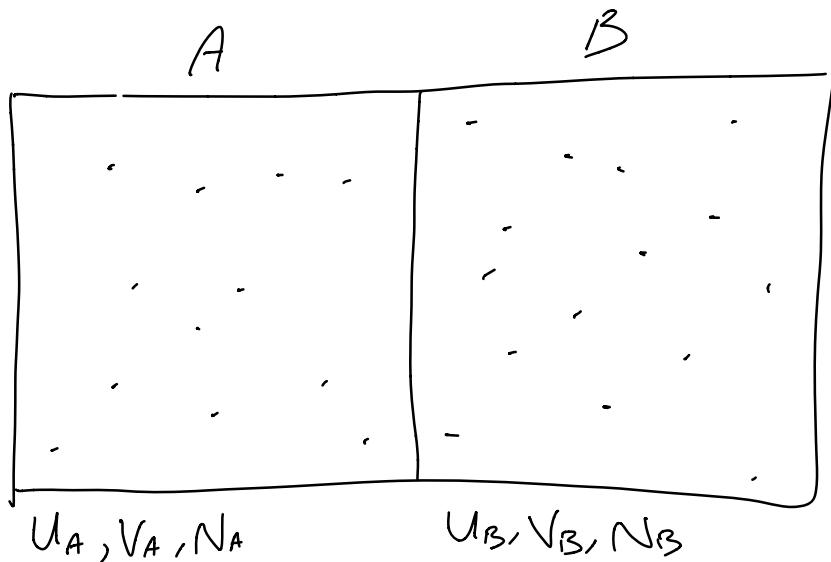
This is why it's unlikely to find all of our gas
in a small corner of the room

$$\Omega(v) \propto V^N$$

$$\frac{\Omega(10\%V)}{\Omega(100\%V)} = (0.1)^N,$$

$$\text{if } N \sim 100 \quad \text{if } N \sim 10^{23}$$

$$P \sim 10^{-100} \quad P \sim 0$$



- Can exchange energy + volume

Ex: Constant volume, N

Macrostates specified by energy distribution U_A, U_B

$$U_A + U_B = U_{\text{tot}}$$

$$0 \leq U_A \leq U_{\text{tot}}$$

$$U_B = U_{\text{tot}} - U_A$$

$$N_A = N_B = N$$

$$\sigma = \sigma_A \sigma_B$$

$$\sigma = \frac{1}{(\hbar)^{3N}} \frac{V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{N! \Gamma(\frac{3N}{2})}$$

$$\sigma = \frac{1}{(\hbar)^{6N}} \frac{(V_A V_B)^N \pi^{3N} (2m)^{3N} (U_A - U_B)^{\frac{3N}{2}}}{(N!)^2 (\Gamma(\frac{3N}{2}))^2}$$

const V, N

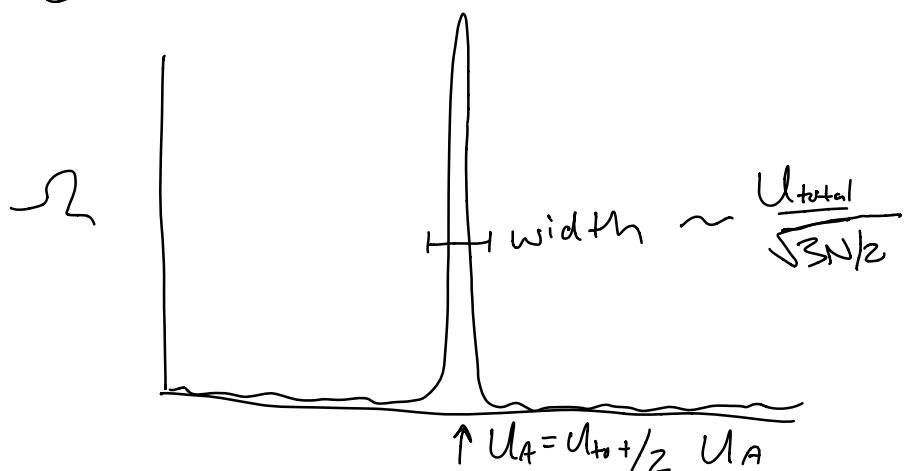
$$\sigma \propto (U_A U_B)^{\frac{3N}{2}}$$

$$\sigma \propto [U_A (U_{\text{tot}} - U_A)]^{\frac{3N}{2}}$$

Similar to the Einstein solids

$$\sigma \approx \left(\frac{e}{N}\right)^{2N} (q_A (q - q_A))^N \quad \text{width } \sim \frac{2}{\sqrt{3N}}$$

$$q \rightarrow U$$



width as a frac of total energy

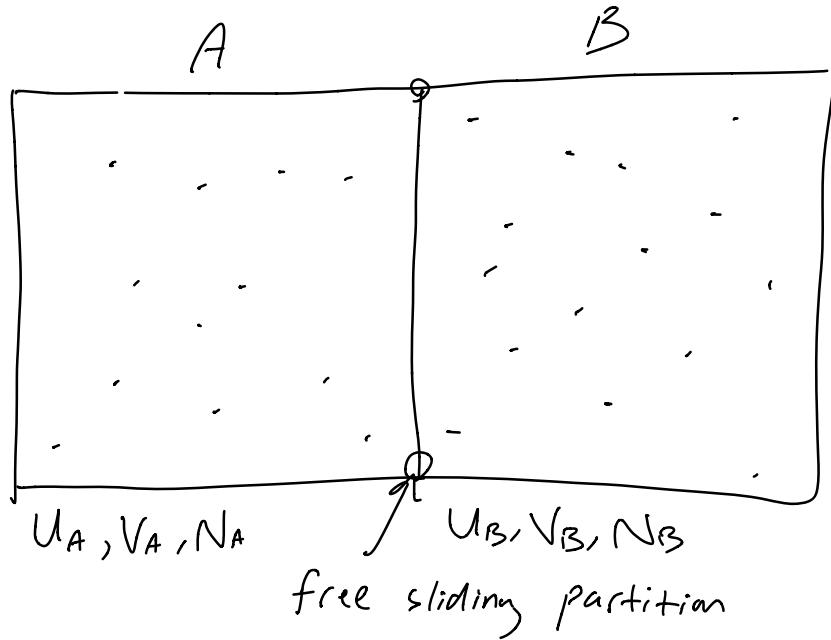
$$\sim \frac{1}{\sqrt{N}} \quad \text{if } N \sim 10^{23}$$

$$\text{relative width} \sim 10^{-12}$$

If $U_{tot} \sim 10^7 \text{ J}$

The energy of each gas will fluctuate
by $\sim 10^{-5} \text{ J}$

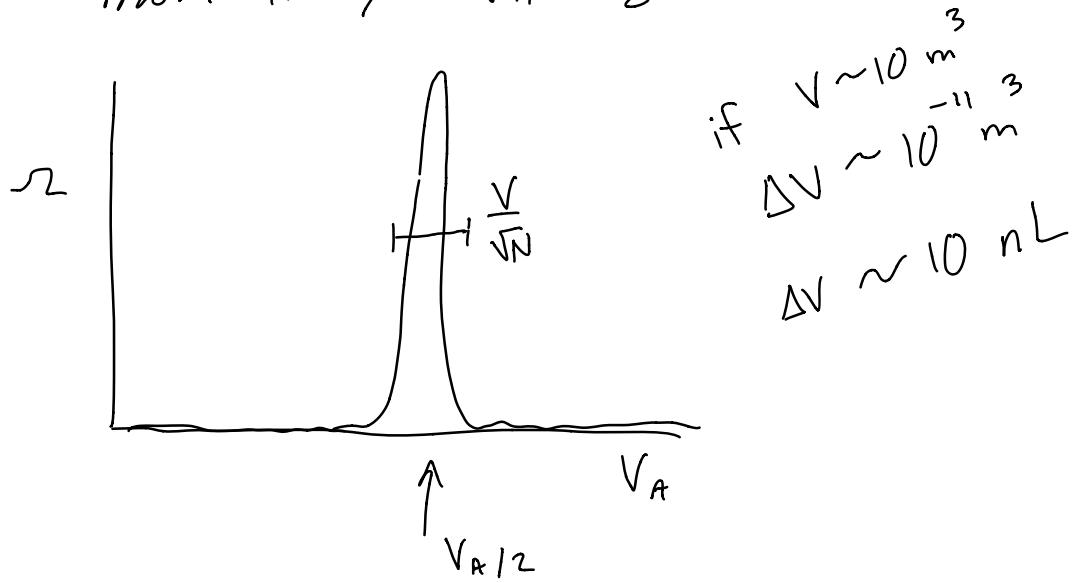
Gases can also exchange volume



$$\sim \propto (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$$

$$\sim \propto [V_A(V - V_A)]^N [U_A(U_{\text{tot}} - U_A)]^{\frac{3N}{2}}$$

most likely: $V_A = \frac{1}{2} V$



For both Einstein solids + ideal gases

The system will tend to evolve toward the macrostate with the greatest multiplicity Ω

- If I start an ideal gas in a tiny corner of the room, it will almost certainly spread out to fill the whole volume

The reverse will essentially never happen

The macrostate can fluctuate, but at levels so small it's essentially unmeasurable

"Multiplicity tends to increase"

2nd Law of Thermodynamics

Multiplicity is connected to entropy

$$S \propto \ln(\Omega)$$

$$S = k_B \ln \Omega$$

Will see why next chapter

What is entropy

- Macroscopic property, like energy or pressure
- Ignore units + log: entropy is the number of microstates of a macroscopic system

More microstates \longrightarrow higher entropy

This is why entropy is sometimes equated to "disorder"

- A shuffled deck of cards has higher entropy than a sorted

why? more possibilities

- Clothes in your room

only a few different ways to arrange them that are neat and folded

many more microstates for a "messy"

- Password entropy^{room}

- Can't take this too far:

- glass of crushed ice \ominus lower entropy than equal amount of liquid water

The Second Law*

- The entropy of an isolated system tends to increase, or stay the same

* Note a "fundamental" law like energy conservation
or $\vec{F} = \frac{d\vec{p}}{dt}$

Still, one of the most reliable principles in all of physics

The entropy of an isolated system tends to increase, or stay the same

Ex: Einstein Solids

$$N_A = N_B = 50 \quad q_A + q_B = 100$$



$$\text{Initially: } q_A = 90$$

$$q_B = 10$$

$$\text{Later: } q_A = 50 \quad q_B = 50$$

Didn't entropy of A decrease?

$$\mathcal{S}_{A,i} = \frac{(g_A + N_A - 1)!}{g_A! (N_A - 1)!} \approx 10^{38}$$

$$S_{A,i} \approx k \ln 10^{38} = 38k \ln 10 \approx 87.5 \text{ K}$$

$$\mathcal{S}_{A,F} = \frac{(50 + 50 - 1)!}{50! (50 - 1)!} \approx 5 \times 10^{28}$$

$$S_{A,F} \approx 66.1 \text{ K}$$

$\Delta S_A < 0$, 2nd Law over!

A is not isolated!

What about ΔS for the whole system

$$S = k \ln \mathcal{S} = k \ln (\mathcal{S}_A \mathcal{S}_B) = k (\ln \mathcal{S}_A + \ln \mathcal{S}_B)$$

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

$$\Delta S_{\text{tot}} = \Delta S_A + \Delta S_B$$

$$\Delta S_A \approx -21.4 \text{ K}$$

$$\mathcal{S}_{B,i} = \frac{(10 + 50 - 1)!}{10! (50 - 1)!} \approx 6.3 \times 10^{10}$$

$$S_{B,i} \approx 24.9 \text{ K}$$

$$S_{Bf} = \frac{(50+50-1)!}{50! (50-1)!} \approx 5 \times 10^{28}$$

$$S_{Bf} \approx 66.1 \text{ K}$$

$$\Delta S_B \approx 41.2 \text{ K}$$

$$\begin{aligned}\Delta S_{\text{tot}} &\approx \Delta S_A + \Delta S_B \\ &\approx -21.4 \text{ K} + 41.2 \text{ K}\end{aligned}$$

$$\Delta S_{\text{tot}} \approx 19.8 \text{ K}$$

In the whole universe

$$\Delta E = 0$$

$$\Delta S \geq 0$$

$\Delta S = 0$; system was already in most likely state

Entropy of the ideal gas

$$\Omega = \frac{1}{(\frac{h}{k})^{3N}} \frac{V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{N! \Gamma(\frac{3N}{2})}$$

$$S = k \ln \Omega$$

$$\begin{aligned} \ln \Omega &= \ln \left(V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}} \right) - \ln \left(\frac{h^{3N}}{k^N N! \Gamma(\frac{3N}{2})} \right) \\ &= N \ln \left(V (2\pi m E)^{\frac{3}{2}} \right) - N \ln \frac{h^3}{k} - \ln N! - \ln \Gamma\left(\frac{3N}{2}\right) \end{aligned}$$

Stirlings:

$$\ln(N!) \approx N \ln N - N$$

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

$$\ln \left(\Gamma\left(\frac{3N}{2}\right) \right) \approx \left(\frac{3N}{2} - 1\right) \ln \left(\frac{3N}{2} - 1\right) - \left(\frac{3N}{2} - 1\right)$$

End result:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3Nk^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$

$$S = S(E, V, N)$$

Ex: Isothermal Expansion/compression
(gas pushing on a piston)

From $V_i \rightarrow V_f$

$$S_i = NK \left[\ln \left(\frac{V_i}{N} \left(\frac{4\pi m E}{3Nk^2} \right)^{3/2} \right) + \frac{S}{2} \right]$$

$$S_f = NK \left[\ln \left(\frac{V_f}{N} \left(\frac{4\pi m E}{3Nk^2} \right)^{3/2} \right) + \frac{S}{2} \right]$$

$$\Delta S = S_f - S_i = NK \ln \left(\frac{V_f}{V_i} \right)$$

Expansion increase ΔS

Compression : $\Delta S < 0$

(but we create more entropy in the process of doing work on the gas)

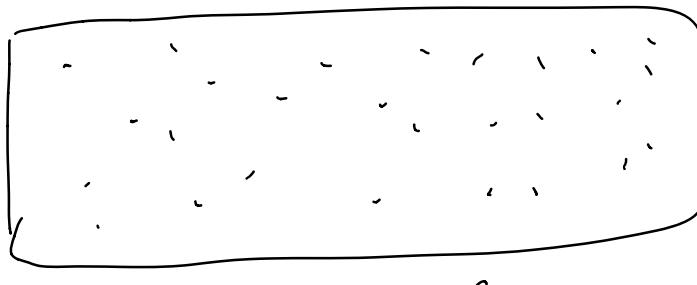
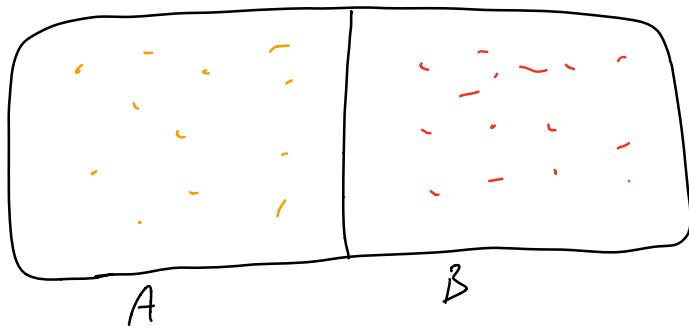
Free expansion

gas expands into vacuum

$$\Delta E = 0 \quad \text{no work}$$

$$\Delta Q = \Delta W = 0$$

Entropy of mixing



A+B

$$\Delta S = \Delta S_A + \Delta S_B$$

Each gas ~ doubles in volume

$$\Delta S_A = \Delta S_B = Nk \ln 2$$

$$\Delta S = 2Nk \ln 2$$

If a process increases ΔS of the universe, that process cannot happen in reverse

If $\Delta S = 0$, it can

Reversible vs Irreversible processes

$$\Delta S > 0 \rightarrow \text{irreversible}$$

$$\Delta S = 0 \rightarrow \text{reversible}$$

Ex: Interacting Einstein Solids

$$N_A = N_B = 50 \quad q_A + q_B = 100$$

$$\text{Initially: } q_A = 90$$



$$q_B = 10$$

$$\text{Later: } q_A = 50 \quad q_B = 50$$

Heat flow from $A \rightarrow B$

$$\frac{P(g_A = 90)}{P(g_A = 50)} \approx 10^{-9}$$

Even for $N, g \sim 10^6$, reverse is very rare

For $N, g \sim 10^{20}$ reverse is effectively impossible

Gas expanding from small corner to full volume

Only happens one way

- I can force it to reverse, that's not what we mean. Can it spontaneously reverse?

if ΔS of the universe > 0 , irreversible

if $\Delta S = 0$, reversible

Most interactions are irreversible

- Combustion of gasoline
- Breaking an egg
- digestion of food
- stirring cream into coffee
- a glass cup falls & shatters

Thus, entropy tells us which things can happen,
+ in what order

- If I see a collection of spilled water + shattered glass, I can guess what it used to be: a glass of water on a table. I know that it can never again be a glass of water on a table
- Most processes only happen one direction in time

This is worth pausing on

- Each individual molecule is governed by the laws of physics

$$\frac{d\vec{p}}{dt} = \vec{F}, \Delta E = 0, \text{ etc}$$

The laws of physics are time reversible!

Imagine a video of two balls colliding + bouncing or a projectile flying through a vacuum

Could you tell if the video was being played in reverse? No!

$$m \frac{d^2x}{dt^2} = \vec{F}$$
$$t \rightarrow -t$$

$$m \left(-\frac{d}{dt} \right) \left(-\frac{d}{dt} \right) x = \vec{F} = \frac{d^2}{dt^2} x$$

But if I showed you a video of a glass of water falling off + breaking, you would know if the video was going backward

- A bunch ($\sim 10^{20}$) of time reversible interactions result in a time irreversible process

Nothing in Newton's Law prevents the process from spontaneously rejoining, but we know it won't happen. At least, probably not

Our experience of time is deeply connected to the second law

- If you could reverse the second law:

Shattered glasses spontaneously
reforming

- Thermal energy in the air focuses it's off at exhaust from a car engine to form liquid gasoline
- Cream would miraculously separate itself from coffee and arrange neatly in the container

etc ..

would be indistinguishable from time running backwards!