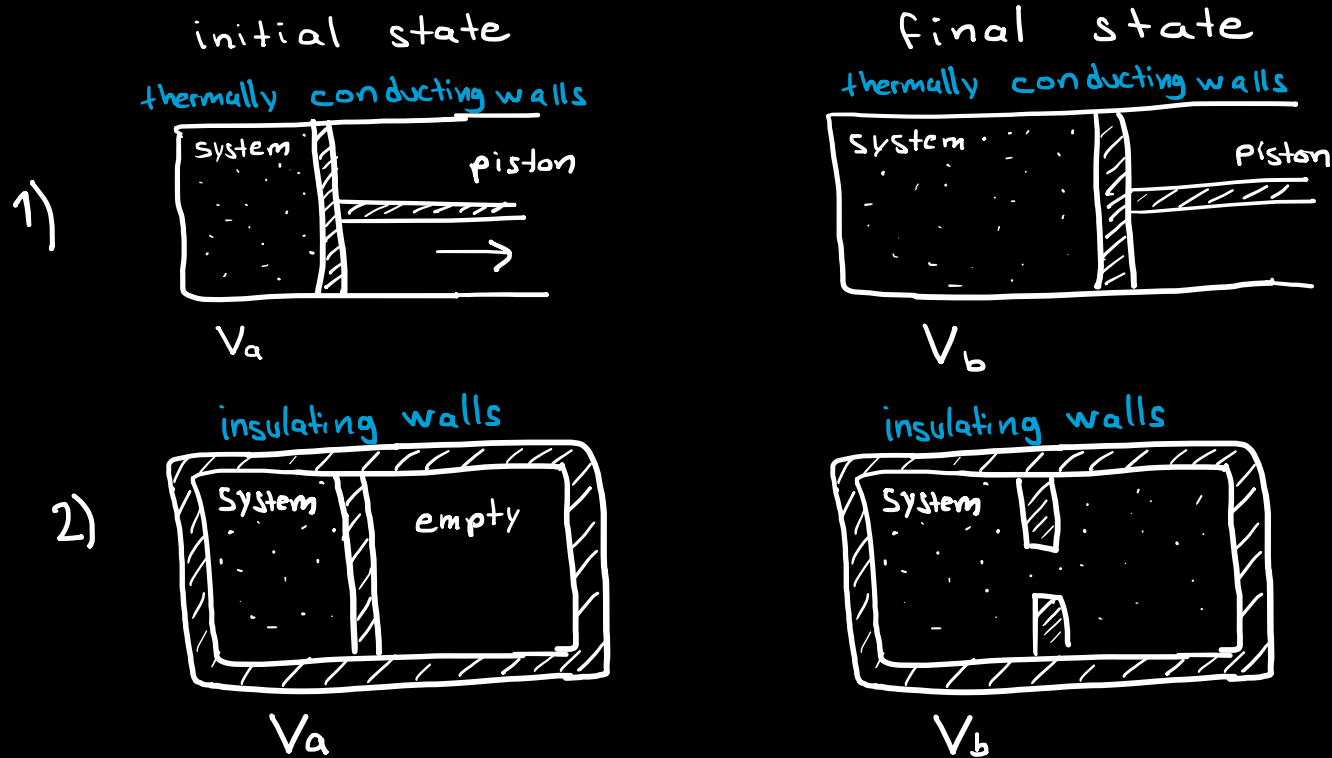


# Summary previous class

## (30.10: the 2<sup>nd</sup> law of thermodynamics)

### Reversible vs Irreversible processes in Thermodynamics

Full-cycle: system goes back to initial state



Isothermal expansion  
 $T_a = T_b$   
 $V_b > V_a$

**REVERSIBLE**

In a full-cycle, the surroundings go back to their initial state as well

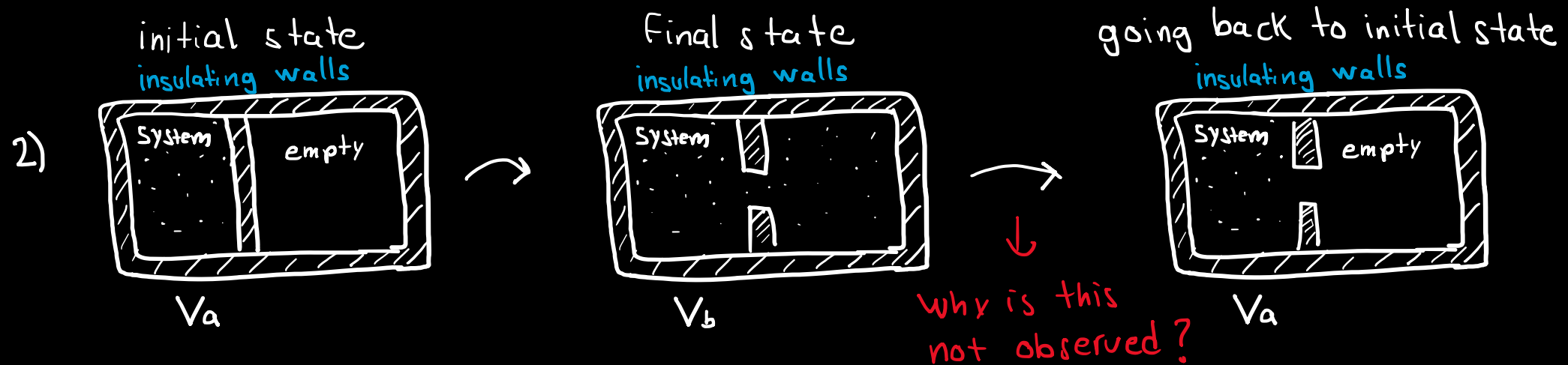
Isothermal  
"Free expansion"  
 $T_a = T_b$   
 $V_b > V_a$

**IRREVERSIBLE**

In a full-cycle, the surroundings do change

# Entropy and the 2<sup>nd</sup> law of thermodynamics

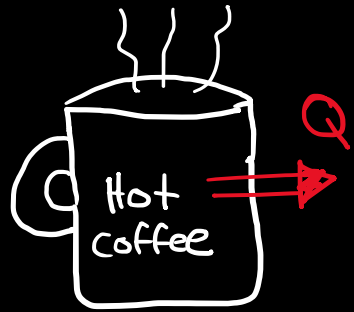
The concept of irreversibility is connected to something fundamental:  
Why is it not observed in nature that the gas in the free expansion case spontaneously moves back to the left of the container to occupy its initial state?



- There is nothing in the 1<sup>st</sup> law of thermodynamics forbidding this from happening
- There is nothing in the particle mechanics (Newton's laws) of the individual particles forbidding this from happening
- This is simply something we know from experience (or doing experiments) that doesn't occur!!

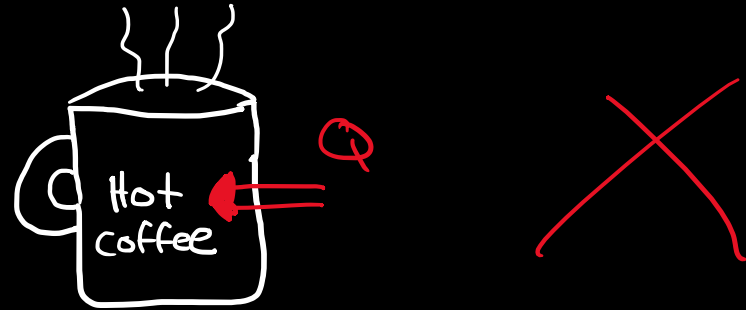
# Entropy and the 2<sup>nd</sup> law of thermodynamics

→ Another example of an irreversible process: when a hot system is put into contact with cold surroundings, the heat exchange occurs from hot to cold, never viceversa



$$T > T_{\text{room}}$$

Hot coffee in a cup will eventually cool down to room temperature



$$T > T_{\text{room}}$$

Spontaneously a cup of hot coffee will not be observed to become even hotter absorbing heat from the air around making the room temperature colder!

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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

For every system in thermal equilibrium, there exists a thermodynamic quantity called entropy 'S'.

For a reversible process, the entropy change is given by:

$$\Delta S = \left( \frac{\Delta Q}{T} \right)_{\text{reversible}} \quad \text{Clausius 1865}$$

The total entropy change of the system AND the surroundings (considered together) is equal to zero if the process is reversible and positive otherwise.

$$\Delta S (\text{system} + \text{surroundings}) \geq 0 \quad \rightarrow \text{2<sup>nd</sup> law of Thermodynamics}$$

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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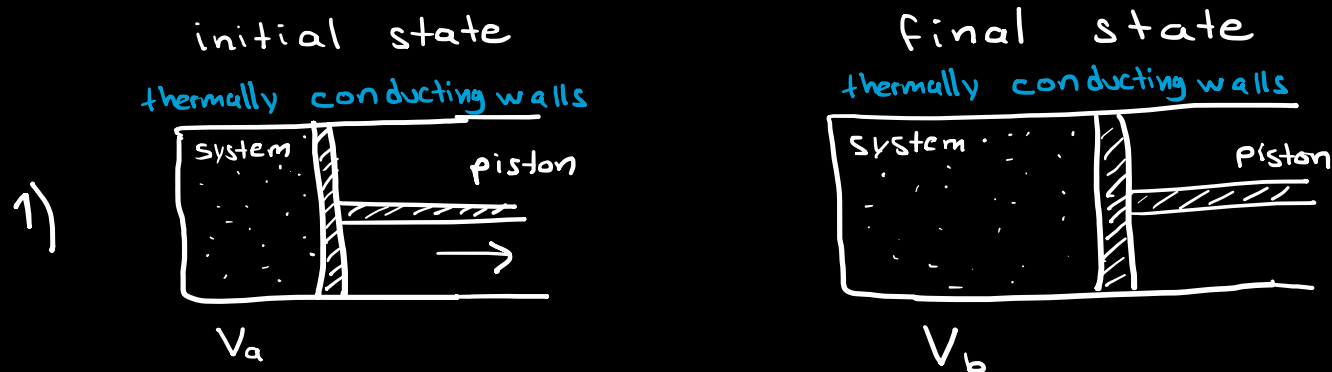
Notes: i)  $\Delta S$  (system) or  $\Delta S$  (surroundings) might decrease or increase

ii)  $\Delta S$  (full cycle) for a system is equal to zero

iii) To compute  $\Delta S$  for irreversible processes, we must imagine/invent a reversible process between the initial and final states. We can do this because entropy is a thermodynamic state variable (like pressure, temperature) and thus, it is path-independent

# Entropy and the 2<sup>nd</sup> law of thermodynamics

→ Isothermal expansion (Boyle's law) is reversible



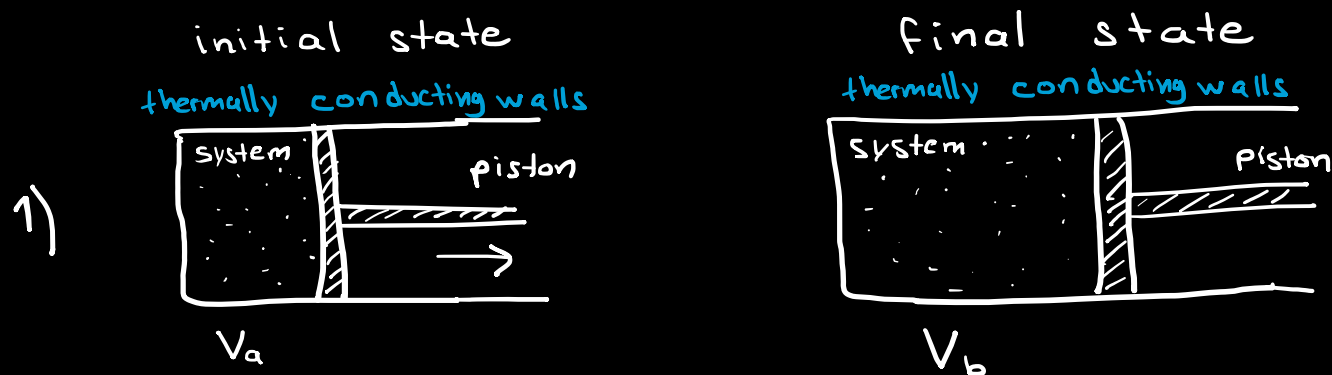
Isothermal expansion  
 $T_a = T_b$   
 $V_b > V_a$

$$\Delta S(\text{system}) = \int_a^b \left( \frac{dQ}{T} \right)_{\text{rev}}$$

≡ definition of entropy change for reversible processes

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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Isothermal expansion  
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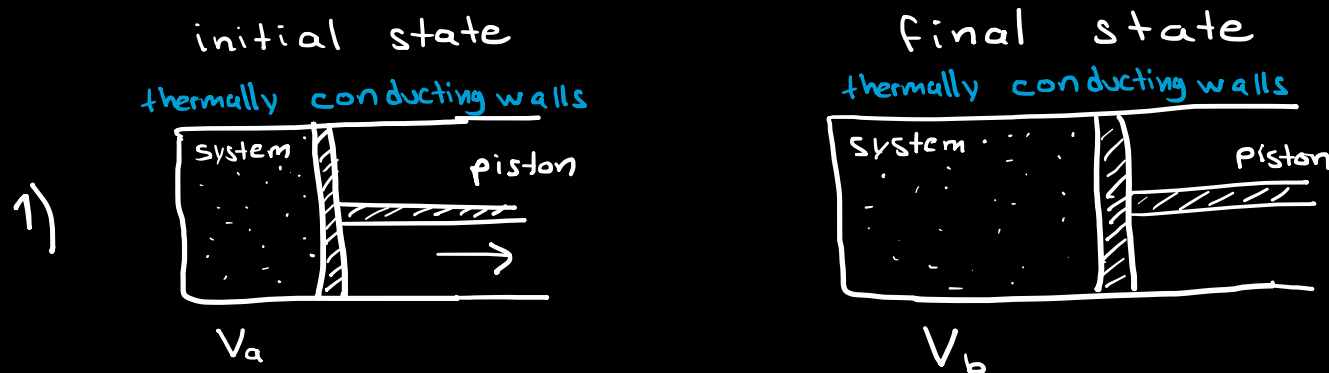
$$\Delta S(\text{system}) = \int_a^b \left( \frac{dQ}{T} \right)_{\text{rev}} \equiv \text{definition of entropy change for reversible processes}$$

but:  $dE_{\text{int}} = dQ - dW = 0 \Rightarrow dQ = dW$

$\downarrow$  1<sup>st</sup> law       $\downarrow$  Since T is constant

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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$$\text{but: } dE_{\text{int}} = dQ - dW = 0 \quad \Rightarrow \quad dQ = dW$$

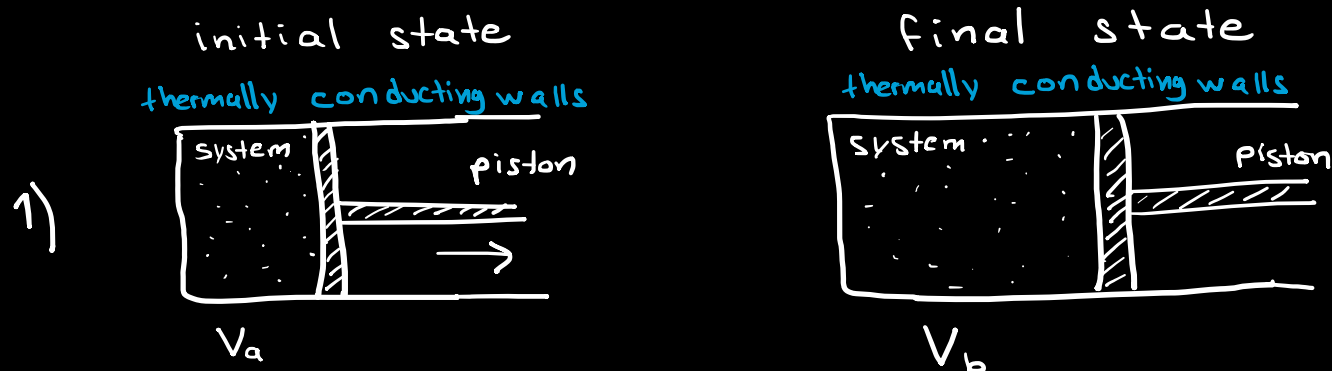
$$\Rightarrow \Delta S(\text{system}) = \frac{1}{T} \int_a^b dW = \frac{1}{T} \int_{V_a}^{V_b} P dV = N k_B \ln \left( \frac{V_b}{V_a} \right)$$

↓  
ideal gas law  $PV = N k_B T$



# Entropy and the 2<sup>nd</sup> law of thermodynamics

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Isothermal expansion  
 $T_a = T_b$   
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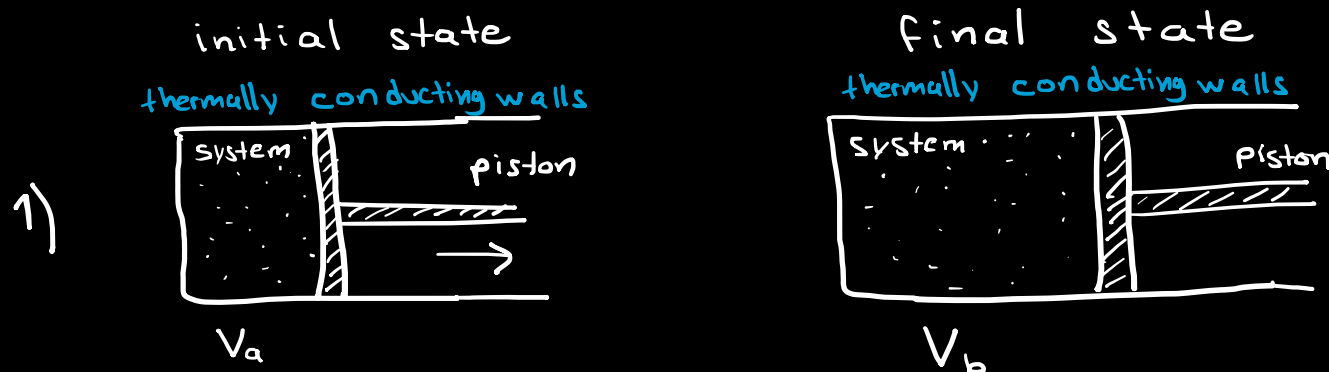
$$\Delta S(\text{system}) = \int_a^b \left( \frac{dQ}{T} \right)_{\text{rev}}$$

$$\Rightarrow \Delta S(\text{system}) = N k_B \ln \left( \frac{V_b}{V_a} \right)$$

ideal gas  
isothermal process

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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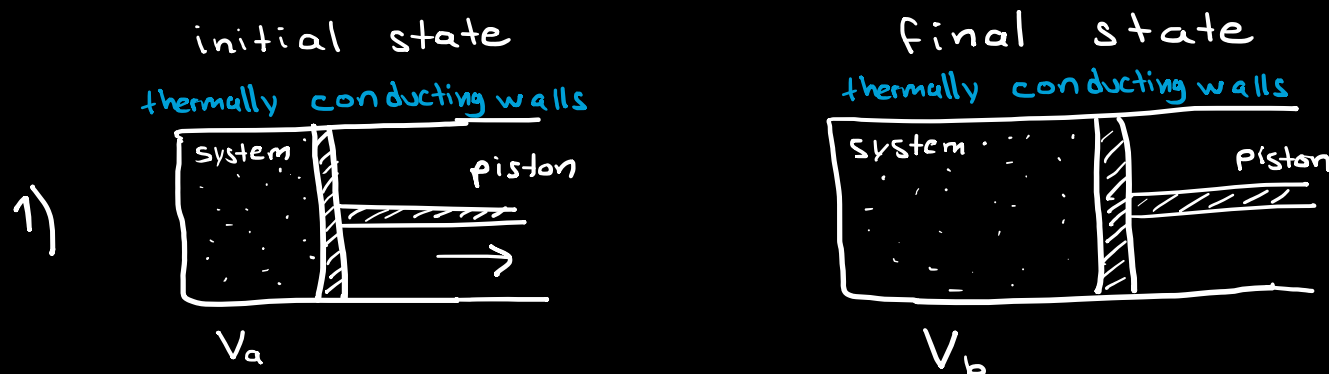
ideal gas  
isothermal process

On the other hand:  $\Delta S(\text{surroundings}) = \int_a^b \left( \frac{dQ}{T} \right)_{\text{rev}}^{\text{surroundings}}$

but we know for this case:  $dQ^{\text{surroundings}} = -dQ^{\text{system}}$  and  $T^{\text{surroundings}} = T^{\text{system}}$   
↓  
thermal equilibrium  
(thermally conducting walls)

# Entropy and the 2<sup>nd</sup> law of thermodynamics

→ Isothermal expansion (Boyle's law) is reversible



Isothermal expansion  
 $T_a = T_b$   
 $V_b > V_a$

$$\Delta S(\text{system}) = \int_a^b \left( \frac{dQ}{T} \right)_{\text{rev}}$$

$$\Rightarrow \Delta S(\text{system}) = N k_B \ln \left( \frac{V_b}{V_a} \right)$$

ideal gas  
isothermal process

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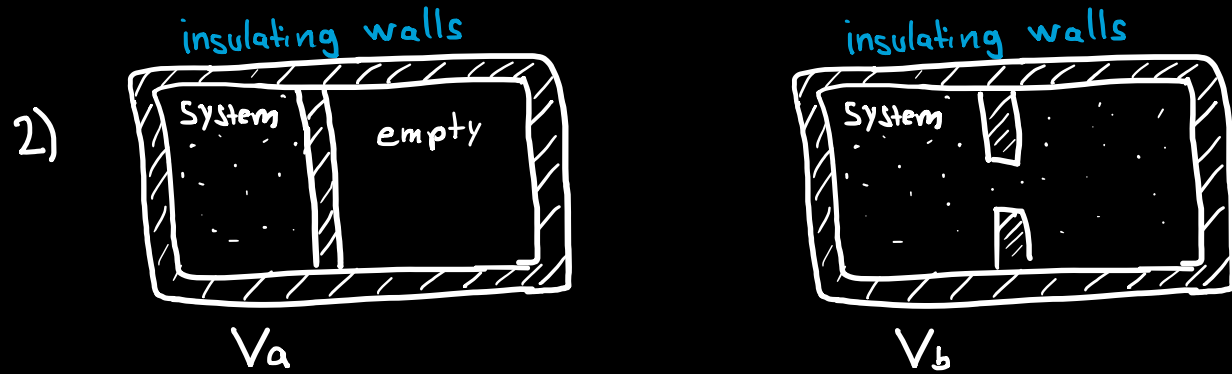
but we know for this case:  $dQ_{\text{surroundings}} = -dQ_{\text{system}}$  and  $T_{\text{surroundings}} = T_{\text{system}}$

$$\Rightarrow \Delta S(\text{surroundings}) = -\Delta S(\text{system}) \Rightarrow \Delta S(\text{system} + \text{surroundings}) = 0$$

2<sup>nd</sup> law of  
Thermodynamics  
(reversible)

# Entropy and the 2<sup>nd</sup> law of thermodynamics

→ "Free expansion" is irreversible



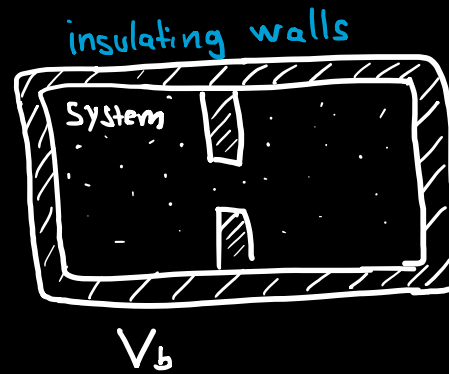
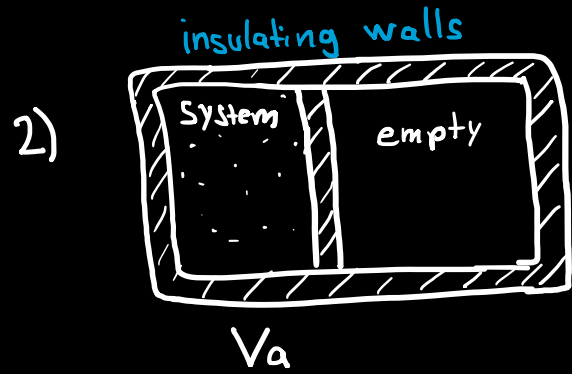
Isothermal  
"Free expansion"  
 $T_a = T_b$   
 $V_b > V_a$

\* Since this is an irreversible process, we cannot use the formula  $\Delta S = \left(\frac{\Delta Q}{T}\right)_{rev}$

→ In fact  $\Delta Q = 0$  for free expansion (insulating walls)

# Entropy and the 2<sup>nd</sup> law of thermodynamics

→ "Free expansion" is irreversible



Isothermal  
"Free expansion"  
 $T_a = T_b$   
 $V_b > V_a$

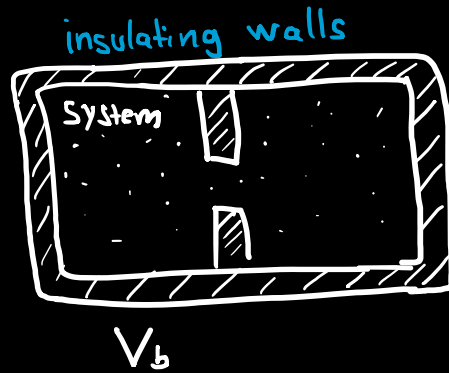
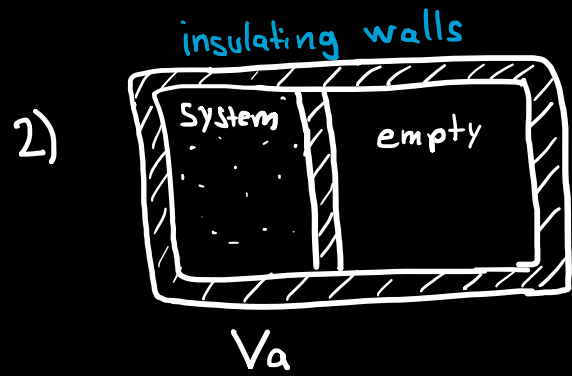
\* Since this is an irreversible process, we cannot use the formula  $\Delta S = \left(\frac{\Delta Q}{T}\right)_{\text{rev}}$

→ But, entropy is a state variable, which means that it is path-independent, the change of entropy between an initial and a final state is the same regardless of the process that took the state from one to the other

$$\Rightarrow \Delta S(\text{system})^{\text{free expansion}} = \Delta S(\text{system})^{\text{isothermal expansion}} = Nk_B \ln\left(\frac{V_b}{V_a}\right)$$

# Entropy and the 2<sup>nd</sup> law of thermodynamics

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 $T_a = T_b$   
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$$\Rightarrow \Delta S(\text{system})^{\text{free expansion}} = \Delta S(\text{system})^{\text{isothermal expansion}} = Nk_B \ln\left(\frac{V_b}{V_a}\right)$$

→ Also, since the system is isolated from the surroundings:  $\Delta S(\text{surroundings})^{\text{free expansion}} = 0$

$$\rightarrow \Delta S(\text{system} + \text{surroundings})^{\text{free expansion}} = Nk_B \ln\left(\frac{V_b}{V_a}\right) > 0$$

2<sup>nd</sup> law of  
Thermodynamics  
(irreversible)

# Entropy: the microscopical interpretation

- Entropy is a difficult concept. From the macroscopic point of view, it was proposed as a consequence of looking for state variables of the system that would be directly connected to the heat exchange (which is not a state variable).
- Since heat exchange and temperature are connected to atomic/molecular motions, entropy has a microscopical origin that is fully understood today in the area of Physics known as statistical mechanics.

# Entropy: the microscopical interpretation

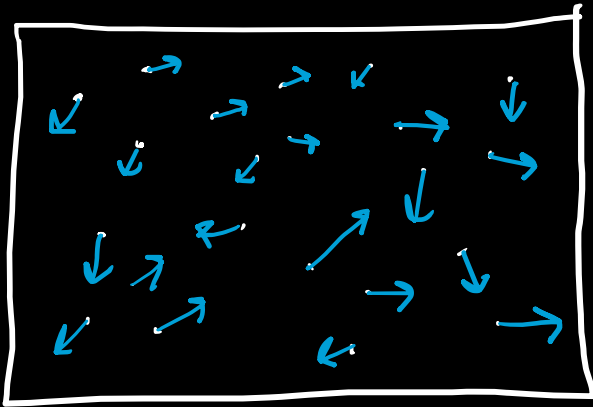
- Entropy is a difficult concept. From the macroscopic point of view, it was proposed as a consequence of looking for state variables of the system that would be directly connected to the heat exchange (which is not a state variable).
- Since heat exchange and temperature are connected to atomic/molecular motions, entropy has a microscopical origin that is fully understood today in the area of Physics known as statistical mechanics.
- Microscopically, entropy is related to the number of all possible microscopical configurations that the system can have in the same macroscopical state (i.e. the same pressure, volume, temperature,...). This is a connection that was formally established by Boltzmann in the 1870's.



# Entropy: the microscopical interpretation

- Microscopically, entropy is related to the number of all possible microscopical configurations that the system can have in the same macroscopical state (i.e. the same pressure, volume, temperature,...).

What is a microscopical configuration of a Thermodynamic system?



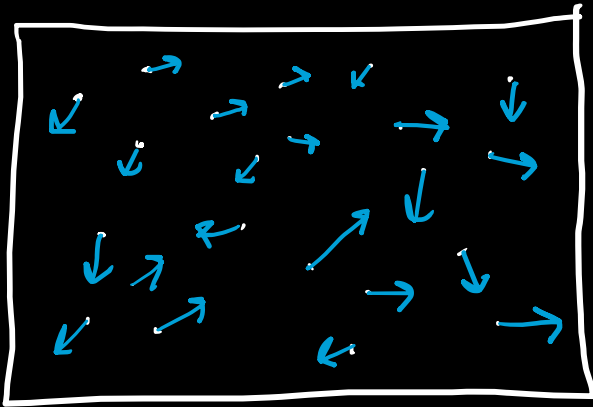
→ The blue arrows represent the individual velocity vectors of each particle in the system

Ideal gas in a container  
at a temperature ' $T$ '  
( $N$  particles)

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Ideal gas in a container  
at a temperature 'T'  
(N particles)

Since temperature  
is related to  $\langle v^2 \rangle$ :

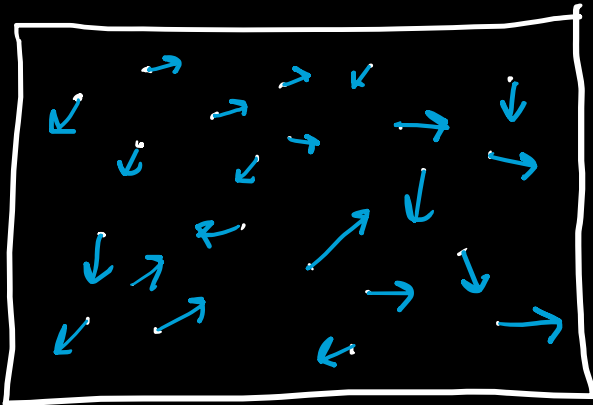
$$\langle v^2 \rangle = \frac{3k_B T}{m} \quad (\text{ideal gas})$$

⇒ simply having the  
same speeds for all  
particles but with different  
directions, will give the  
same  $\langle v^2 \rangle$  and thus  
the same temperature

# Entropy: the microscopical interpretation

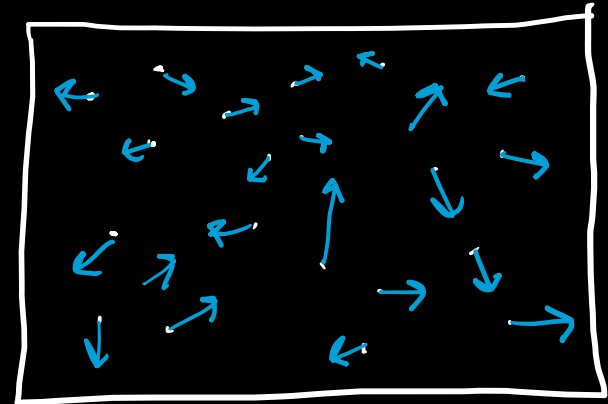
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What is a microscopical configuration of a Thermodynamic system?



Ideal gas in a container  
at a temperature 'T'  
(N particles)

⇒ Given a number of N particles, there is a very large number of possibilities (microscopical configurations) in which the system has the same macroscopical state



Same macroscopical state as on the left, but a different microscopical configuration

\* Boltzmann proved that the larger the number of possible configurations, the larger the entropy

# Entropy: the microscopical interpretation

- Microscopically, entropy is related to the number of all possible microscopical configurations that the system can have in the same macroscopical state (i.e. the same pressure, volume, temperature,...).

⇒ A system with high entropy has a higher degree of disorder than a low entropy system

\* Boltzmann proved that the larger the number of possible configurations, the larger the entropy

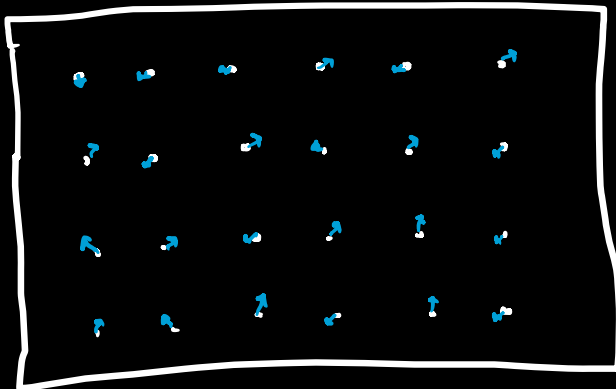
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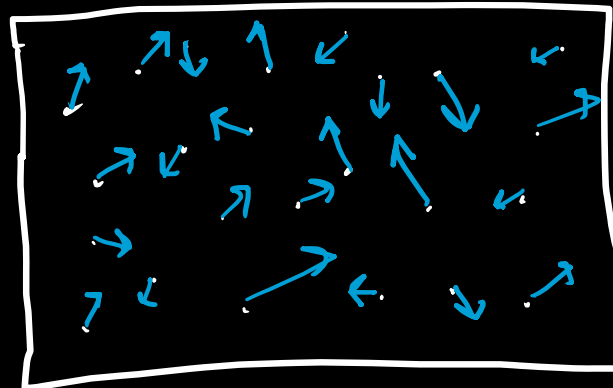
low entropy



Ice

(highly ordered system,  
"quiet" molecular activity)

high entropy



Steam

(highly chaotic/disordered system,  
"loud" molecular activity)

\* There are many more possible configurations if water is in the vapour than in the solid phase

# Entropy: the microscopical interpretation

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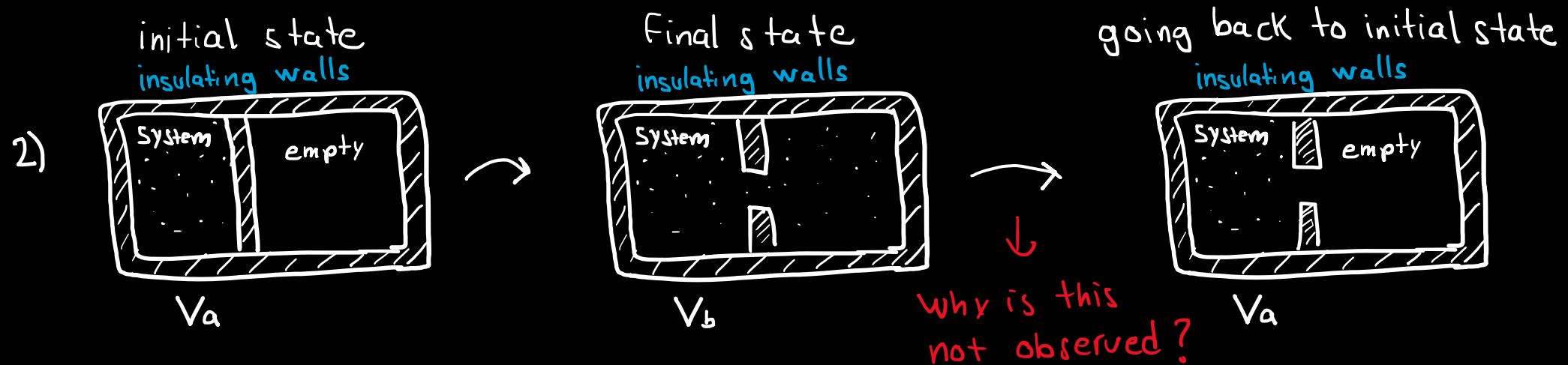
⇒ A system with high entropy has a higher degree of disorder than a low entropy system

\* Boltzmann proved that the larger the number of possible configurations, the larger the entropy

- The 2<sup>nd</sup> law states that system tend to evolve naturally (if not interfered with) from highly ordered configurations (less probable) to highly disordered configurations (more probable).

# Entropy: the microscopical interpretation

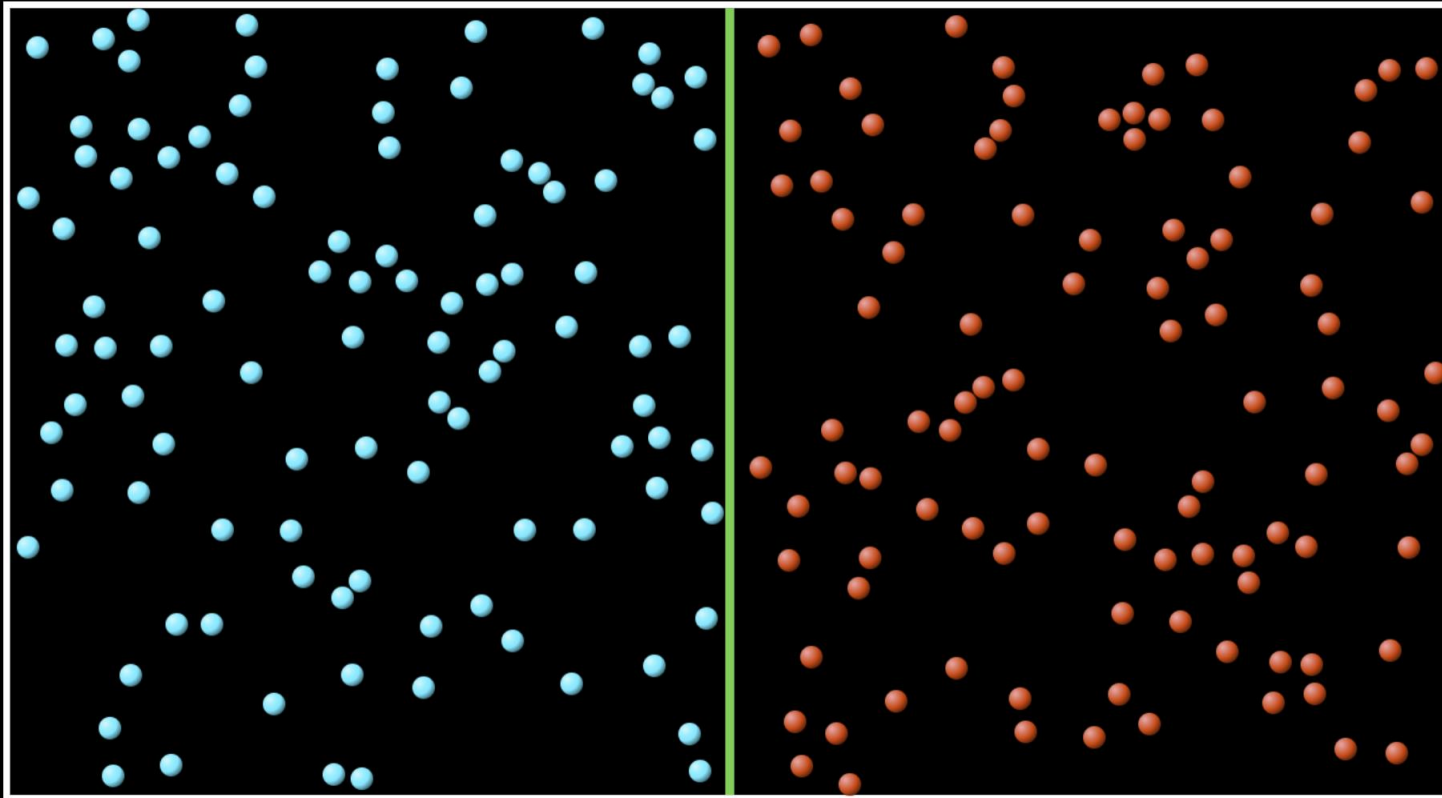
The concept of irreversibility is connected to something fundamental:  
Why is it not observed in nature that the gas in the free expansion case spontaneously moves back to the left of the container to occupy its initial state?



→ From the microscopic perspective this question is solved: because the initial state has a lower entropy (less probable) than the final state (more probable)

# Entropy: the microscopical interpretation

– Another way to visualize it

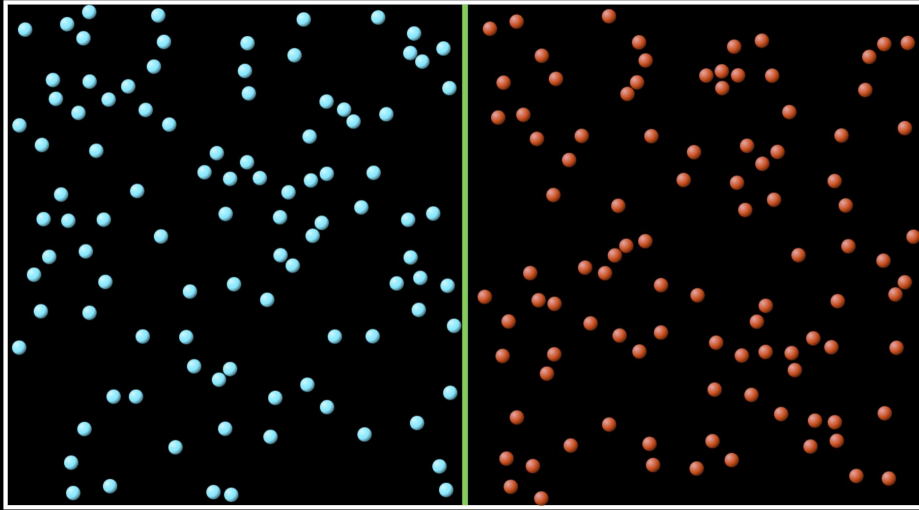


[link to PHET simulation](#)

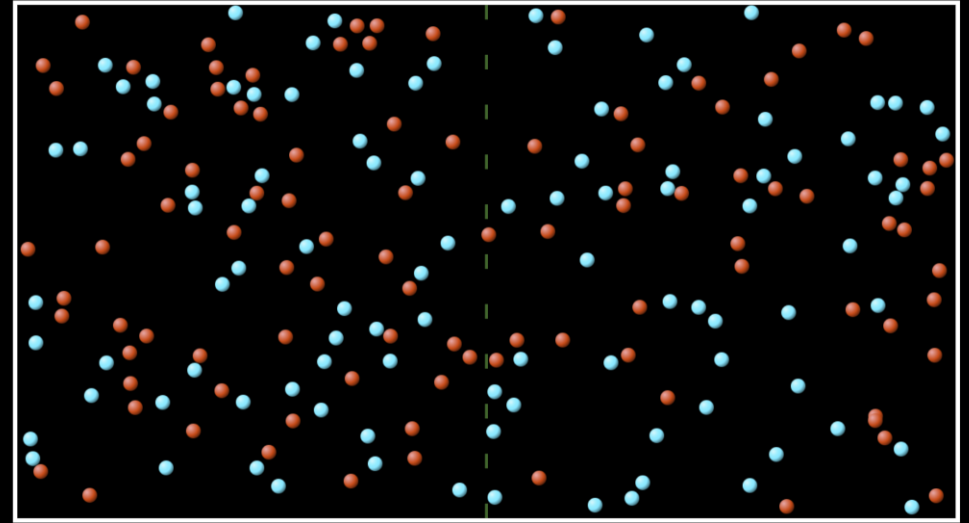


# Entropy: the microscopical interpretation

— Another way to visualize it



lower entropy



higher entropy

Notice that having all red (blue) particles on the left (right) is physically possible (in fact, there are many ways to arrange this configuration), but is vastly less likely that the system finds itself in such a subset of states, than in the much larger subset of states that have a mixed configuration. In real systems with very large number of atoms/molecules, we never observe such an extremely unlikely occurrence.