Fundamentals on energy

Igor Neri - September 3, 2019

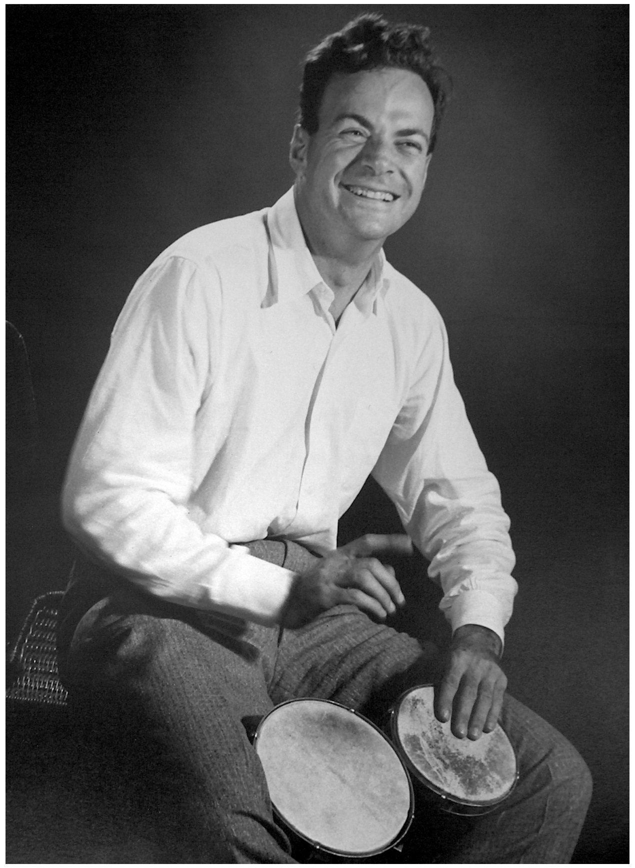
Outline

- Energy: a hint of history
- Energy: form and transformation
- Thermodynamic
- Heat: the kinetic theory
- Energy and entropy
- Irreversibility and Brownian motion

Energy: definition

In physics, energy (Ancient Greek: ἐνέργεια energeia "activity, operation”) is an indirectly observed quantity that is often understood as the ability of a physical system to do work on other physical systems

Capability of doing WORK… WORK = FORCE x Displacement



"It is important to realise that in physics today, we have no knowledge what energy is.”

Richard Feynman, in The Feynman Lectures on Physics (1964) Volume I, 4-1

Energy: a hint of history

- The *vis viva* (living force), which **Goffried Leibniz** defined as the product of the mass of an object and its velocity squared; he believed that total vis viva was conserved.

- To account for slowing due to friction, Leibniz theorised that thermal energy consisted of the random motion of the constituent parts of matter, a view shared by **Isaac Newton**, although it would be more than a century until this was generally accepted.

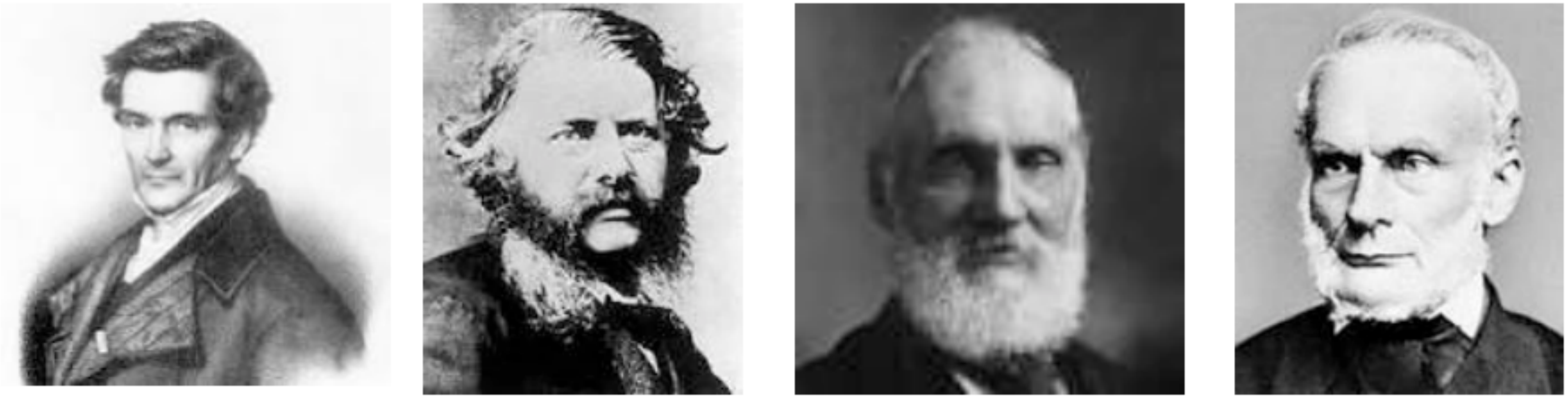
Energy: a hint of history

- The conservation of energy was proposed by Goffried Leibniz over the period 1676–1689, the theory was controversial as it seemed to oppose the theory of conservation of momentum advocated by Sir Isaac Newton and René Descartes. The two theories are now understood to be complementary.

- In 1807, **Thomas Young** was possibly the first to use the term "energy" instead of *vis viva*, in its modern sense.

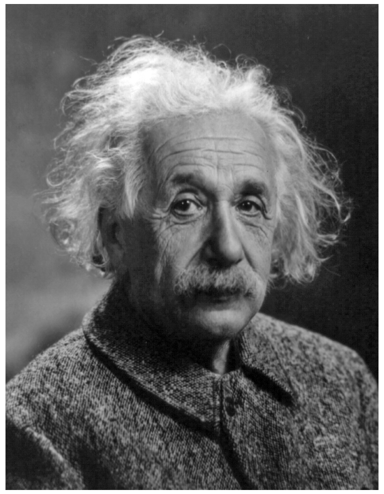
Energy: a hint of history

- **Gustave-Gaspard Coriolis** described "kinetic energy" in 1829 in its modern sense.
- In 1853, **William Rankine** coined the term "potential energy".
- **William Thomson** (Lord Kelvin) amalgamated all of these laws into the laws of thermodynamics, which aided in the rapid development of explanations of chemical processes by Rudolf Clausius, Josiah Willard Gibbs, and Walther Nernst.



Energy: a hint of history

- It also led to a mathematical formulation of the concept of entropy by Clausius and to the introduction of laws of radiant energy by **Jožef Stefan**.

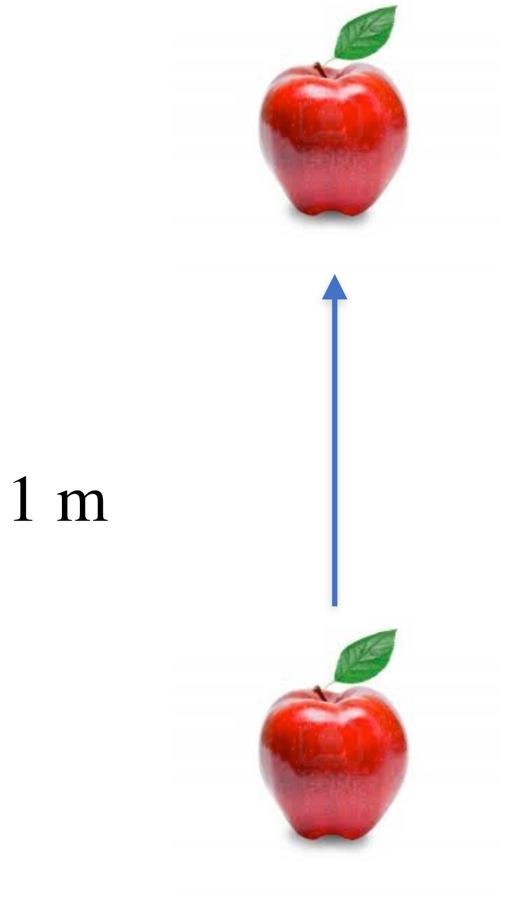


- **Albert Einstein** proposed mass–energy equivalence in 1905 in a paper entitled "Does the inertia of a body depend upon its energy-content?”

- Since 1918 it has been known that the law of conservation of energy is the direct mathematical consequence of the translational symmetry of the quantity conjugate to energy, namely time (**Emmy Noether**).

Energy: how to measure

- Unit of measure: Joule = 1 J = 1 N x 1 m
- Power = Energy /time



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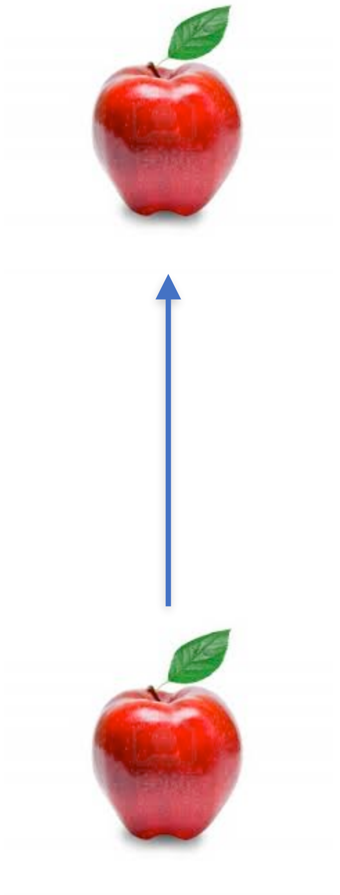

Task	Power W
Operate a microwave oven	
Full power car engine	
Full power aircraft fighter	
Average power of a Boing 747 airplane	
Low power radio module	
Brain functioning for an average human	
Sleep mode of a microcontroller	
Emission of a standard WI-FI router	
Functioning of a miniature FM receiver	
Mobile phone calling	
Functioning of a LED light	
1 bit information erasure at room T (min)	
Being alive for an average adult human	
Operation of a quartz oscillator	
Functioning o a wireless sensor node	
Functioning of a quartz wristwatch	

Energy: how to measure

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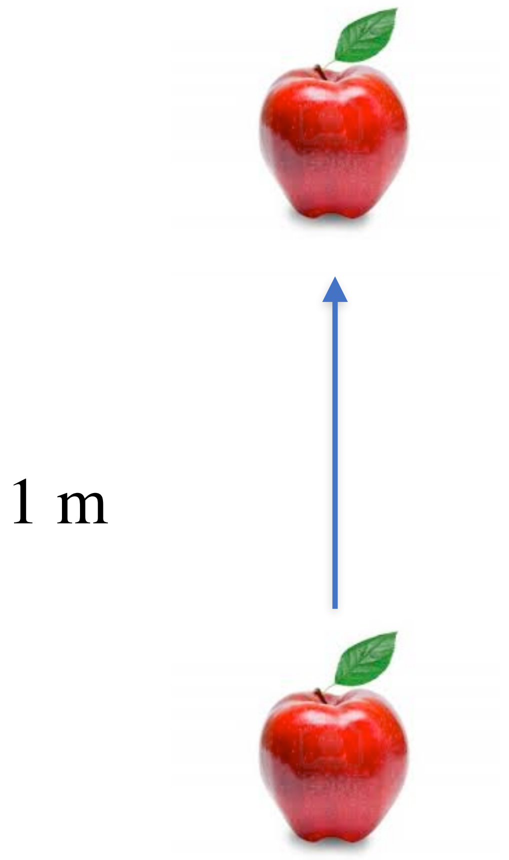

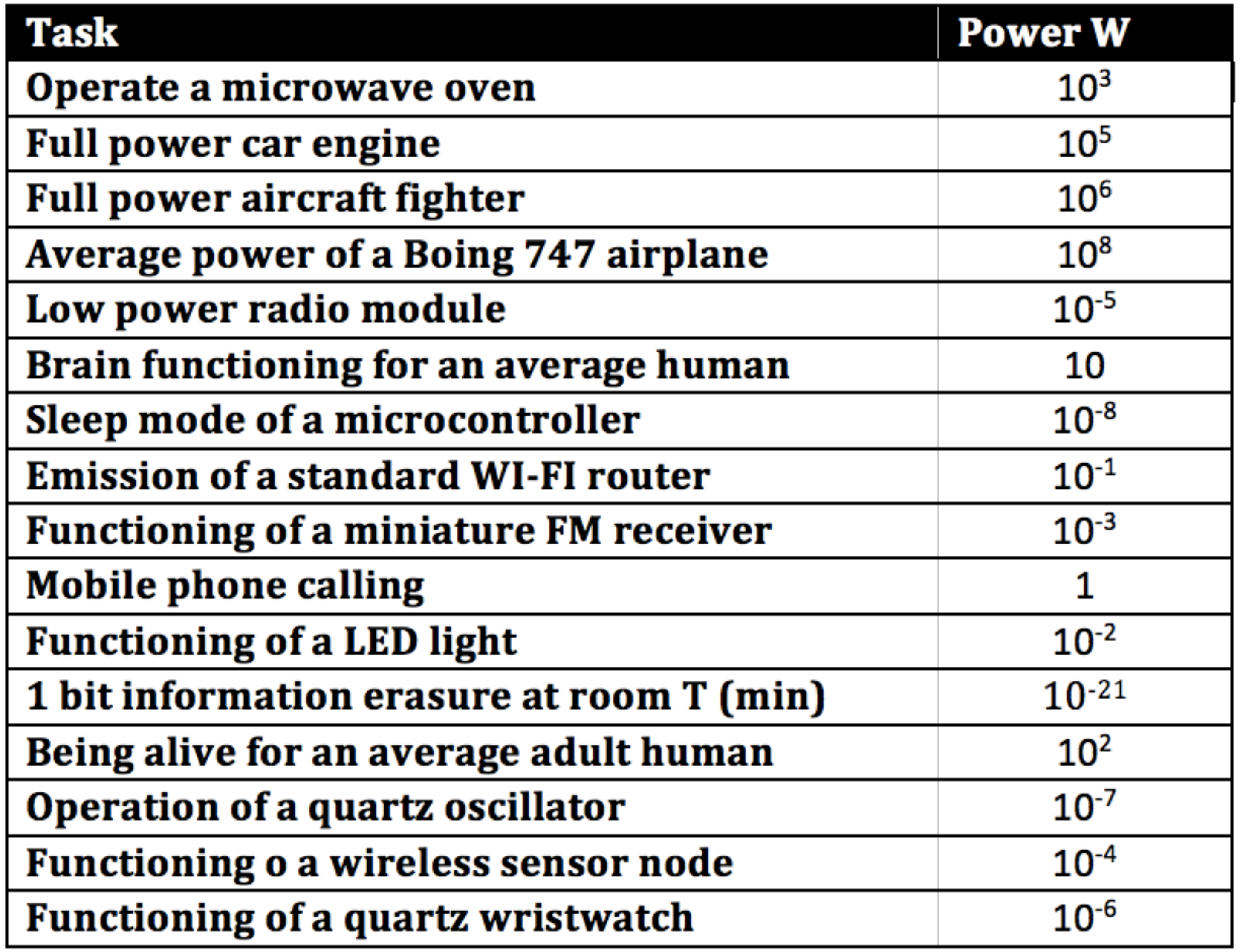

Task	Power W
Operate a microwave oven	10^{3}
Full power car engine	10^{5}
Full power aircraft fighter	10^{6}
Average power of a Boing 747 airplane	10^{8}
Low power radio module	10^{-5}
Brain functioning for an average human	10
Sleep mode of a microcontroller	10^{-8}
Emission of a standard WI-FI router	10^{-1}
Functioning of a miniature FM receiver	10^{-3}
Mobile phone calling	1
Functioning of a LED light	10^{-2}
1 bit information erasure at room T (min)	10^{-21}
Being alive for an average adult human	10^{2}
Operation of a quartz oscillator	10^{-7}
Functioning o a wireless sensor node	10^{-4}
Functioning of a quartz wristwatch	10^{-6}

Energy: how to measure

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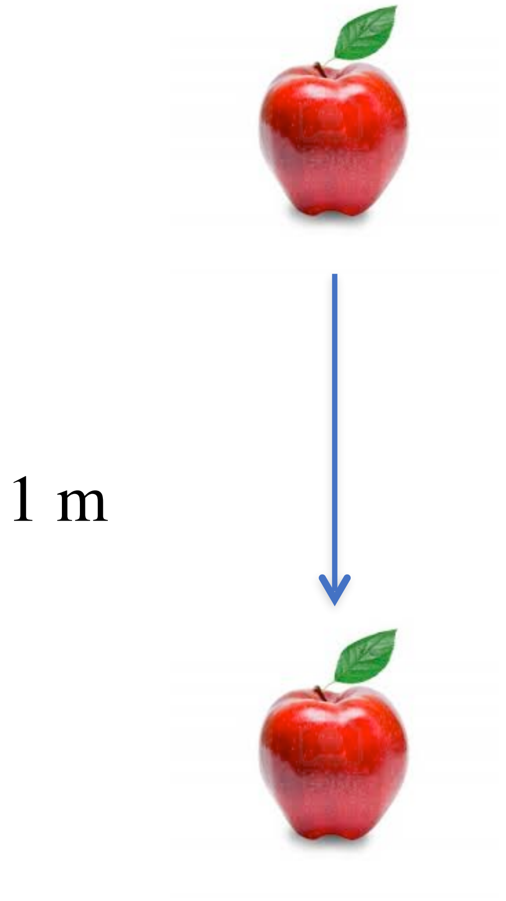

Energy: how to measure

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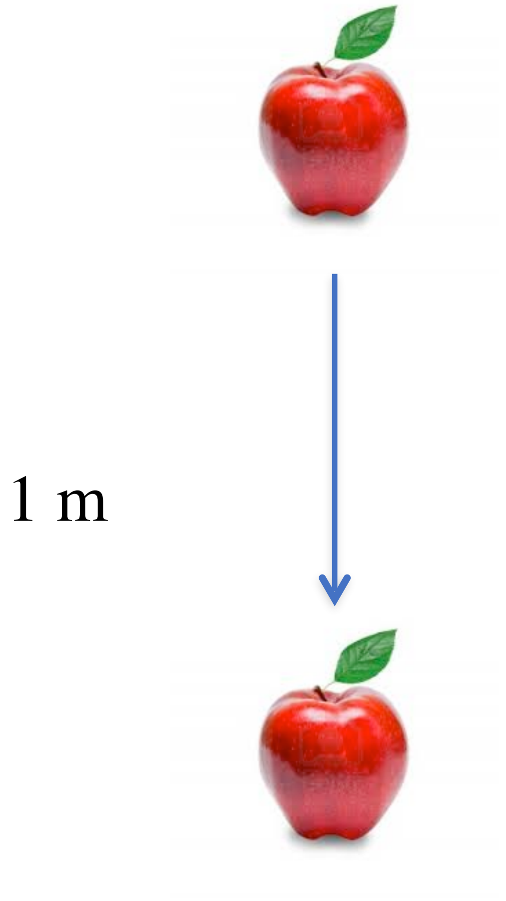


It goes also the other way around…

Energy: how to measure

Energy: how to measure

Yes!

We can warm it up!

Forms of Energy

Energy exists in many different forms. Examples of these are: light energy, heat energy, mechanical energy, gravitational energy, electrical energy, sound energy, chemical energy, nuclear or atomic energy and so on. Each form can be converted or changed into the other forms.

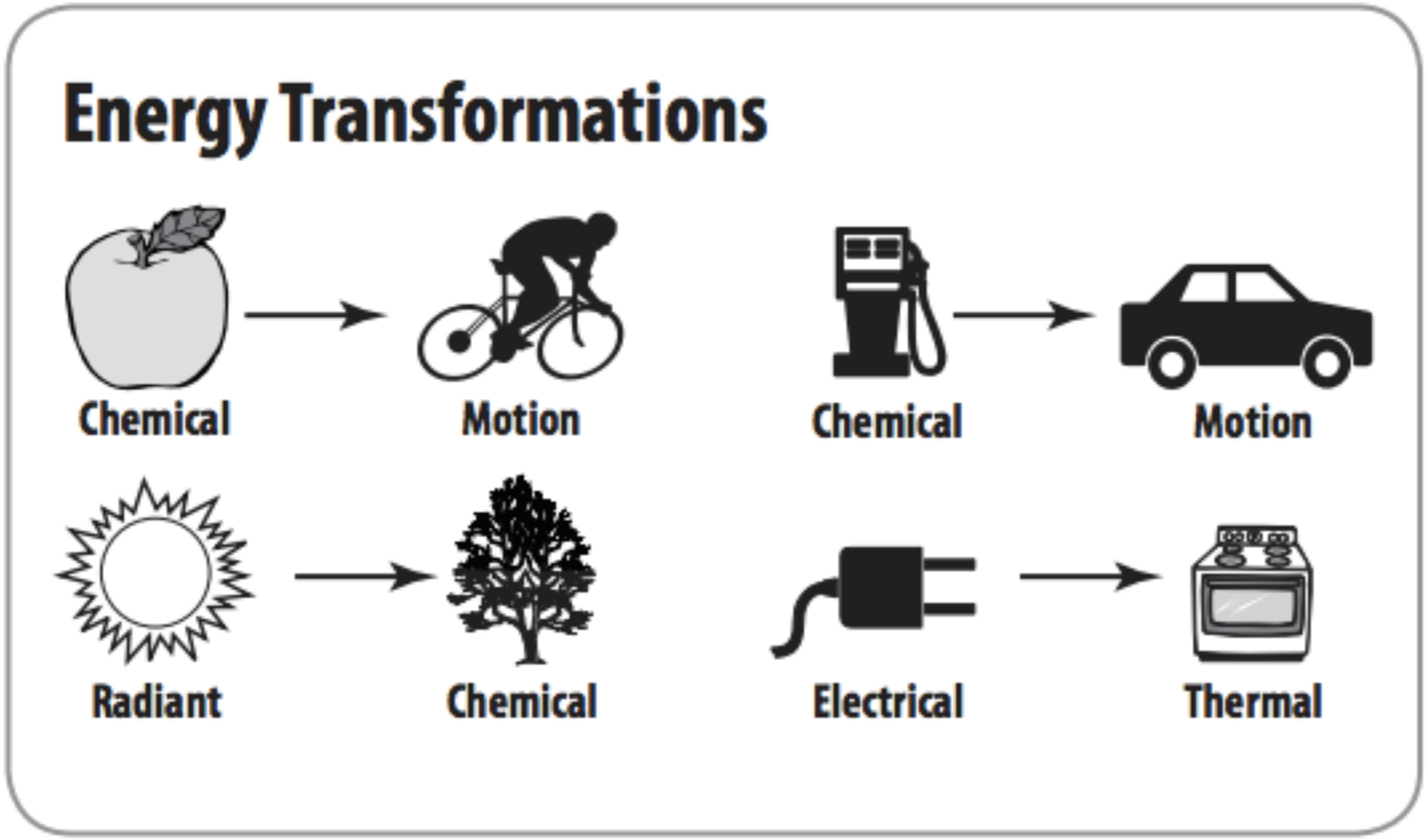
Although there are many specific types of energy, the two major forms are Kinetic Energy and Potential Energy.

- **Kinetic energy** is the energy in moving objects or mass. Examples include mechanical energy, electrical energy etc.

- **Potential energy** is any form of energy that has stored potential that can be put to future use. Examples include nuclear energy, chemical energy, etc.

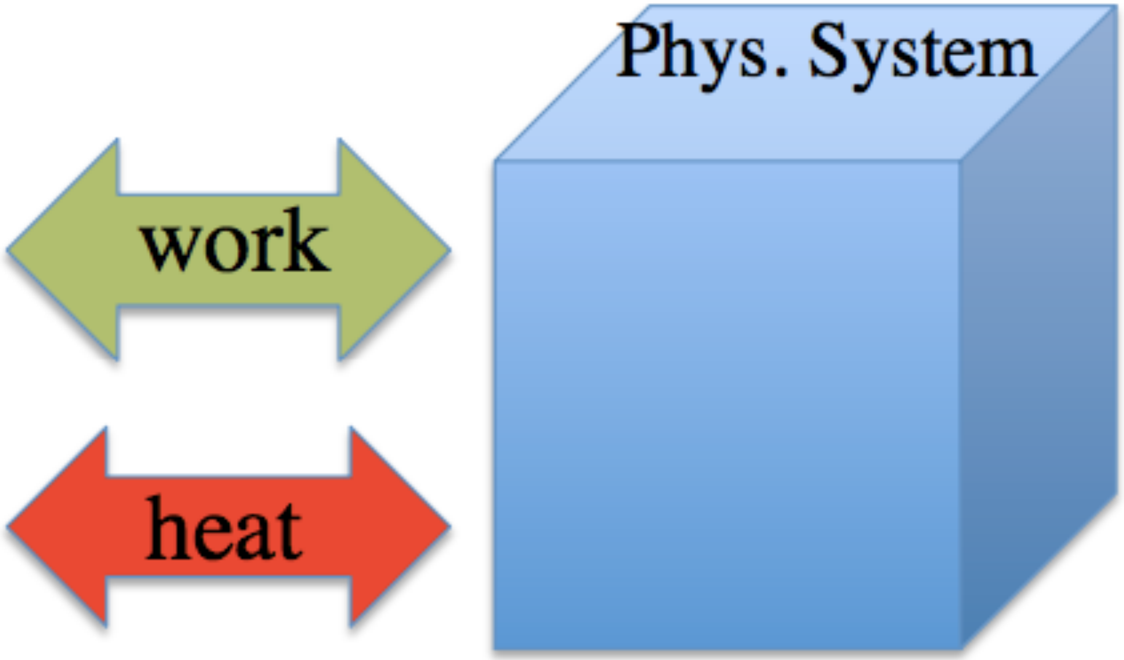
Forms of Energy

- Any energy in any single form can be transformed into another form
- The total energy of a system can only change if energy is transferred into or out of the system



Energy

- The energy content of a system can be changed via exchanges of work and heat but there are some limitations…

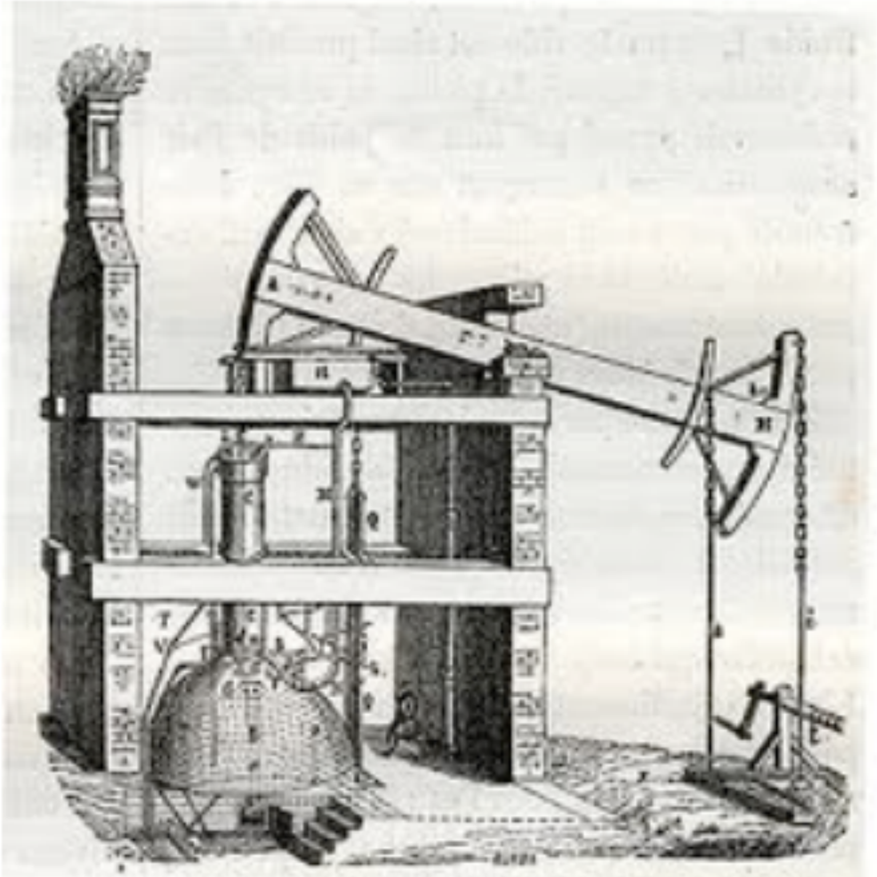


Energy

Energy is a property of physical systems that can be used to perform work and usually comes inside physical objects like a hot gas or a gasoline tank.

Thinking about it we can ask questions like:

- how can we make the energy contained in a litre of gasoline to push forward a car?
- how can we use the heat produced by burning coal to make the train run?

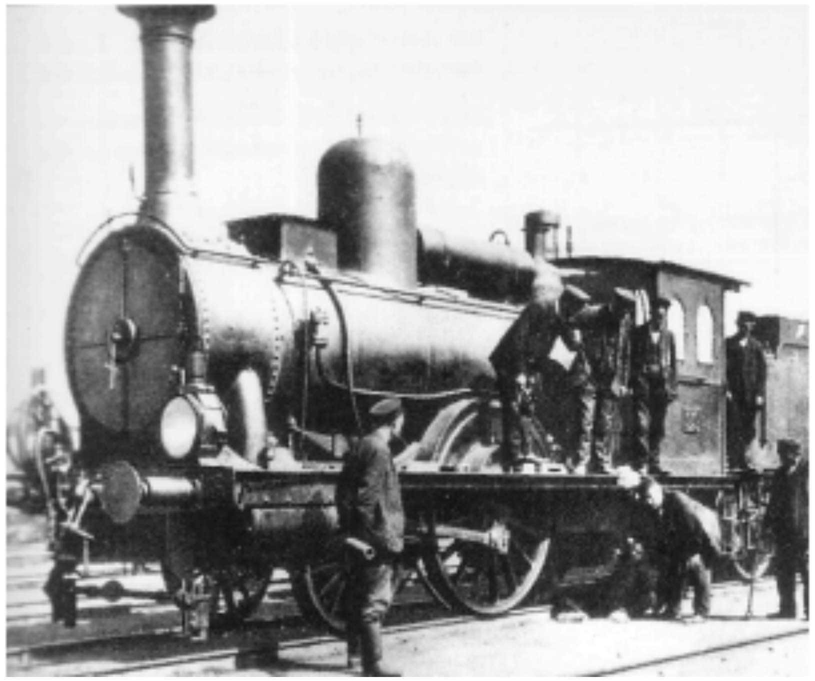


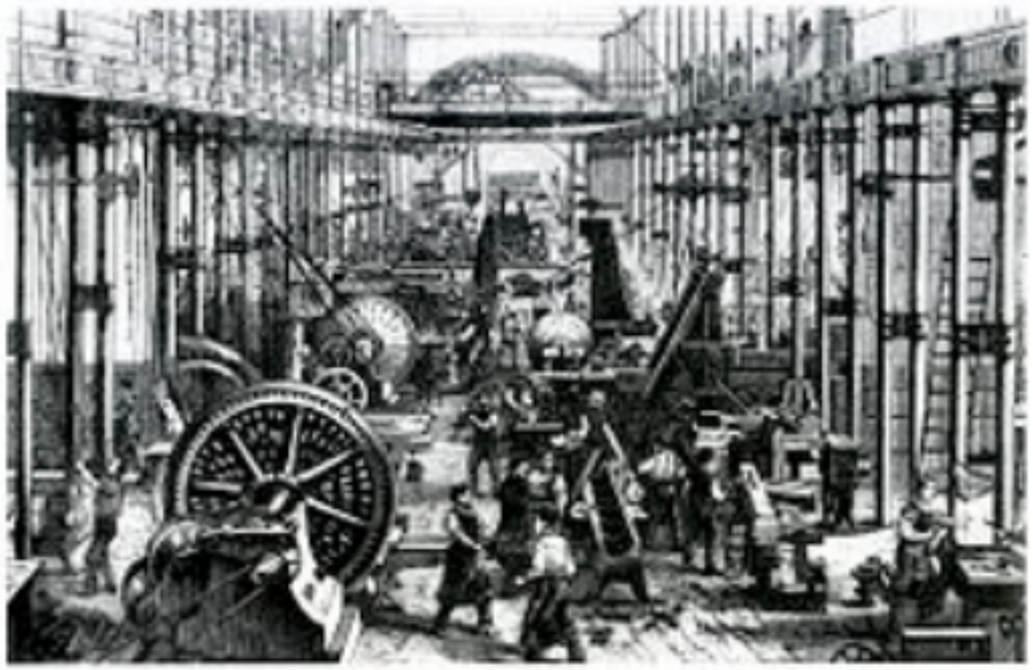
Questions like these were at the very base of the activities performed in the early seventeen hundreds by the first inventors of the so-called thermal machines.

People like **Thomas Newcomen** (1664-1729) who built the first practical steam engine for pumping water and **James Watt** (1736-1819) who few decades after proposed an improved version of the same machine.

Thermal machine

It is thanks to the work of scientists like **Sadi Carnot** (1796-1832) and subsequently of **Émile Clapeyron** (1799 - 1864), **Rudolf Clausius** (1822 - 1888) and **William Thomson** (Lord Kelvin) (1824 – 1907) that studies on the efficiency of these machines aimed at transforming heat (just a form of energy) into work brought us the notion of entropy and the laws of thermodynamics.





These laws do not tell us much about what energy is but they are very good in ruling what can we do and what we cannot do with energy.

The first law

- **The first law** of thermodynamics states that **the total energy of an isolated physical system is conserved during any transformation the system can go through**.

- It was initially formulated in this form by **Julius Robert von Mayer** (1814 - 1878) and subsequently reviewed by **James Prescot Joule** (1818-1889) and **Hermann Ludwig Ferdinand von Helmholtz** (1821-1894).

The first law

The first law is often formulated by stating that the change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings.

- **dU=dQ-dW (Clausius convention)**
- dU=dQ+dW (IUPAC convention)
- dU=dW-dQ (stochastic energetic convention)

Equivalently, perpetual motion machines of the first kind are impossible.

The second law

"Now, in the *second* law of thermodynamics . . . "

The second law states that there are limitations to how much work we can get from a given amount of energy present in the form of heat.

The second law

The second law states that there are limitations to how much work we can get from a given amount of energy present in the form of heat. There exist different formulations that are all equivalent.

The two most popular are ascribed to Clausius and Kelvin:

- Clausius formulation: “**No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature**”.
- Kelvin formulation: “**No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work**”.

The second law: consequences

- An important consequence of the second law is that there is a **limit to the efficiency of a thermal machine**. This limit was discovered by **Sadi Carnot** in 1824 when he was only 28. He introduced the concept of thermal machine, generalising the concept popular at that time of “steam engine”, and showing that the efficiency of any thermal machine operating between two temperatures is bounded by a quantity that is a function of the two temperatures only.

- Few years after the work of Carnot, **Clausius** used this result to introduce a quantity that is useful in describing how much heat can be changed into work during a transformation. He proposed the name “**entropy**” for his quantity.

The second law: consequences

Clausius proved a theorem that states that during a **cyclic transformation**, if you do the transformation carefully enough not to loose any energy in other ways (like friction), then the sum of the heat exchanged with the external divided by the temperature at which the exchange occurs is zero:

$$\oint \frac{dQ}{T} = 0$$

This is equivalent to say that it exists a state function S defined as:

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

If you are not careful enough and you loose energy during the transformation than the inequality holds instead:

$$\oint \frac{dQ}{T} \leq 0$$

A transformation like this is also called an irreversible transformation

$$S_B - S_A \geq \int_{A\,irr}^B \frac{dQ}{T}$$

Spontaneous transformation

We call a transformation spontaneous if it can happen without any external work.

If we consider an infinitesimal transformation we have:

$$dS \geq \frac{dQ}{T} \quad \text{or} \quad TdS \geq dQ$$

where the equal sign hold during a reversible transformation only.

Let’s suppose that we have a transformation where no heat nor work is exchanged. It is called an adiabatic spontaneous transformation. In this case we have:

$$dS > 0$$

Thus we conclude that during a spontaneous adiabatic transformation (i.e. without external work nor heat) the entropy always increases.

The second law: consequences

The quantity of heat Q that appears in the Clausius equation is the amount of energy that goes into the increase of entropy.

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

It is useful to interpret the quantity **TdS as the amount of heat** (meaning thermal energy) **that cannot be used to produce work**.

In other words during a transformation, even if we are carefully enough not to waste energy in other ways, we cannot use all the energy we have to do useful work. Part of this energy will go into producing an increase of the system entropy. **If we are not carefully enough the situation is even worst and we get even less work**.

This is sometimes accounted by the introduction of the so-called **Free energy**. The concept of Free energy was proposed by **Helmholtz** in the form: **F = U - TS**. The free energy **F** measures the maximum amount of energy that we can use when we have available the internal energy **U** of a system.

Equilibrium

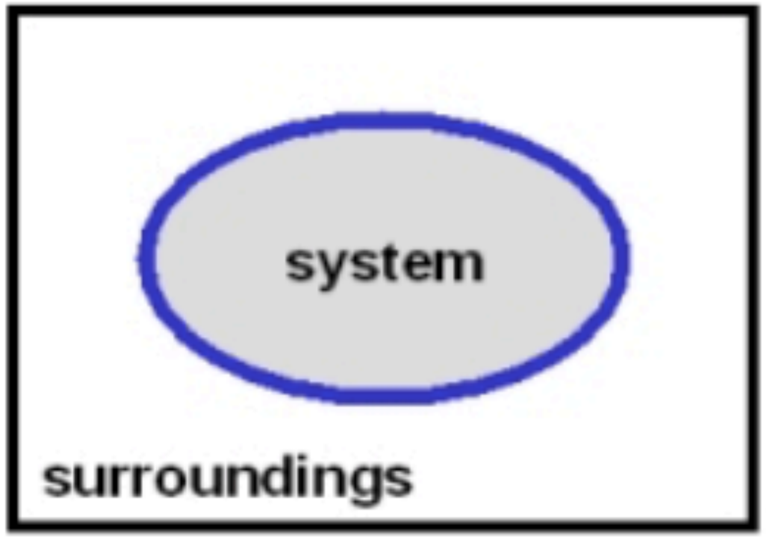
A system can undergo a **spontaneous transformation** until it reaches a state of equilibrium.

What is it?

Preliminary notions:

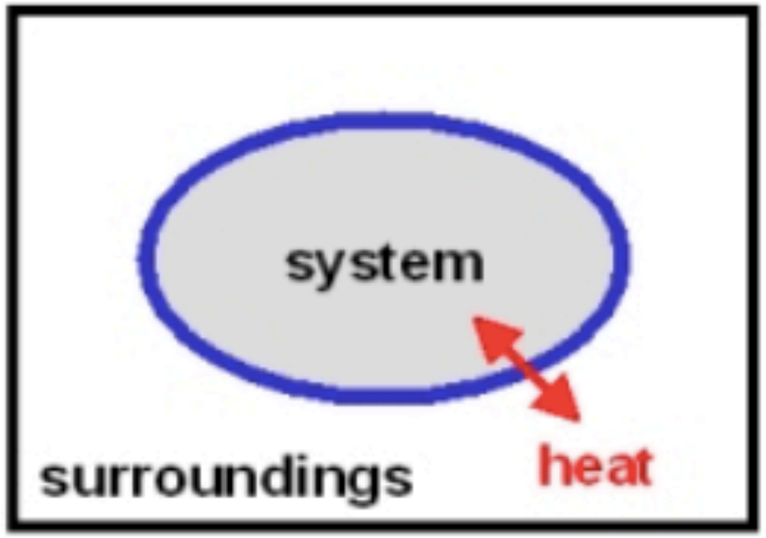
- The notion of system (boundaries, open, closed, isolated)
- The notion of state of a system (state variables)
- Intensive and extensive variables
- Transformations

System



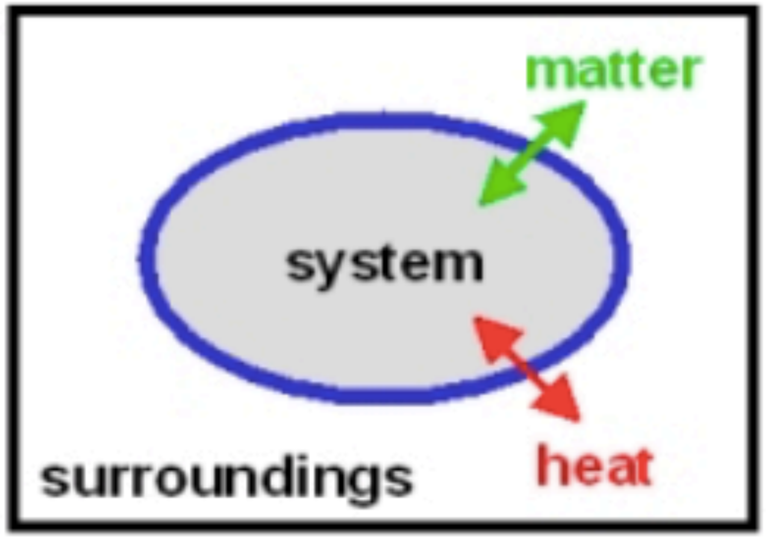
“Isolated” system:

- no exchange of matter
- no exchange of heat



“Closed” system:

- no exchange of matter
- can exchange heat energy



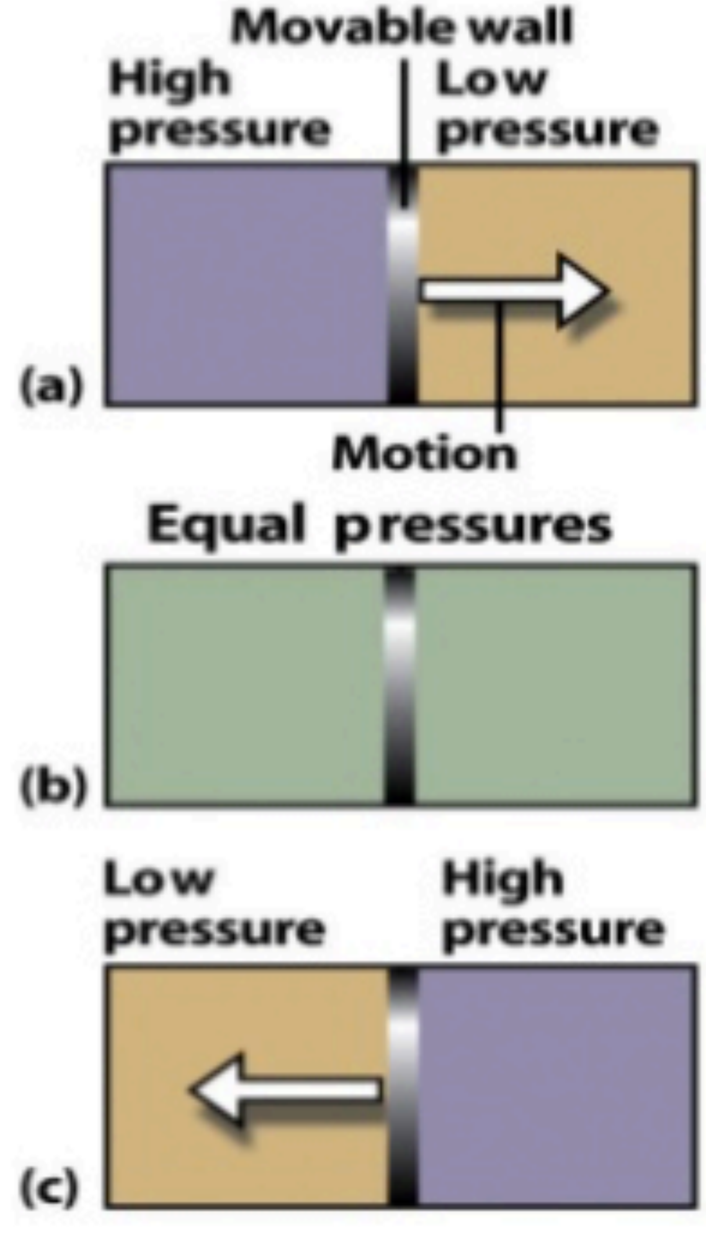
“Open” system:

- can exchange matter
- can exchange heat energy

Mechanical equilibrium

- Condition of equality pressure on either side of a movable wall

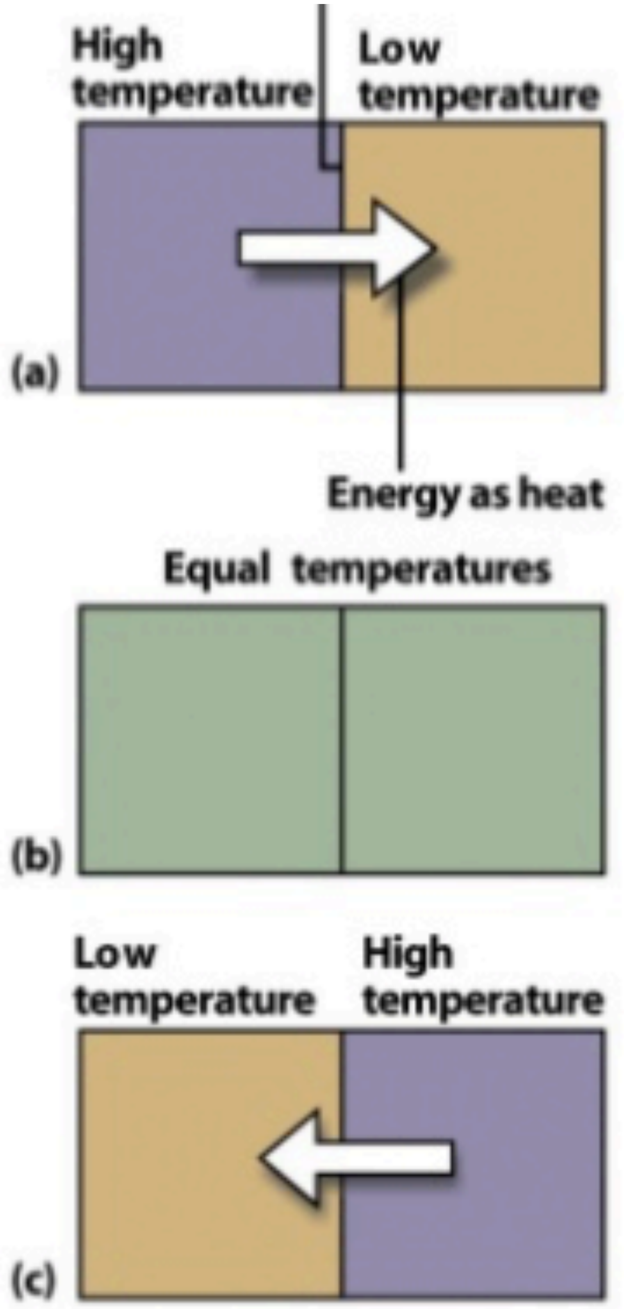
- No unbalanced forces act on or within the system - does not undergo acceleration or no turbulence insides the system



Thermal equilibrium

- Thermal equilibrium between system and the surrounding, is a condition in which there is no change in the properties od the system or surroundings when they are separated by a thermally conduction wall

- In other words, Thermal Equilibrium is a condition in which no change od state occurs when two objects A to B are in contact though a diathermic boundary



Material equilibrium

- Concentration of chemical species in the various parts of the system are constant with time
- No net chemical reactions are occurring in the system
- There is no net transfer of matter from one part of the system to another or between the system and its surroundings

Thermodynamic equilibrium

- For thermodynamic equilibrium, al three kinds of equilibrium must be present:
  - mechanical
  - thermal
  - material
- No matter what is the initial state of an isolated system, eventually it will reach the state of thermodynamic equilibrium

Equilibrium

The importance of the notion of relaxation time

Equilibrium (within a given relaxation time) is the competition of the tendency of:

Energy to reach a minimum   Entropy to reach a maximum

$$F = U - T S$$

Minimum free energy

Equilibrium

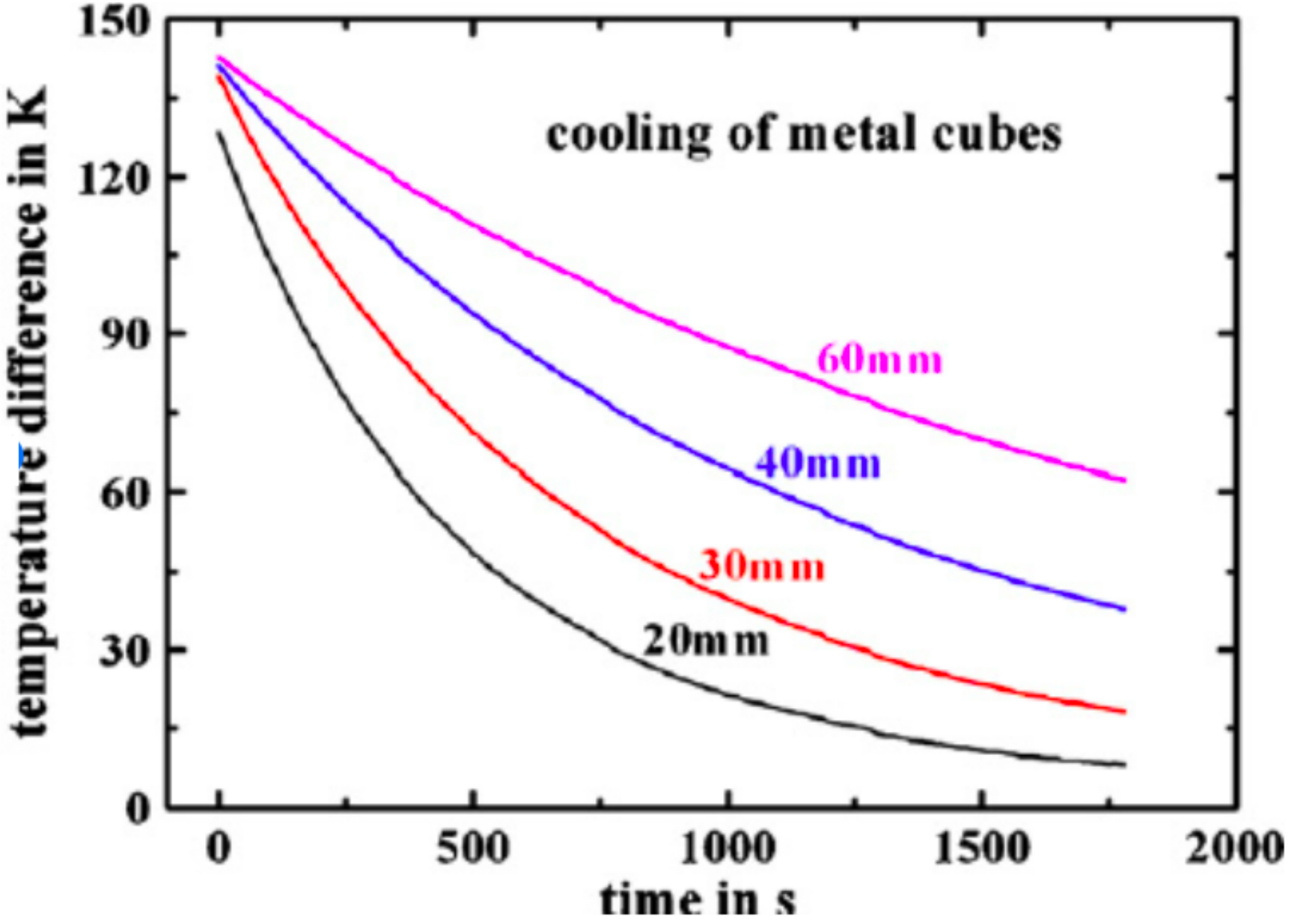
The importance of the notion of relaxation time

1) What is the time evolution of the temperature T?

2) What is the law regulating the temperature vs time?

Equilibrium

The importance of the notion of relaxation time



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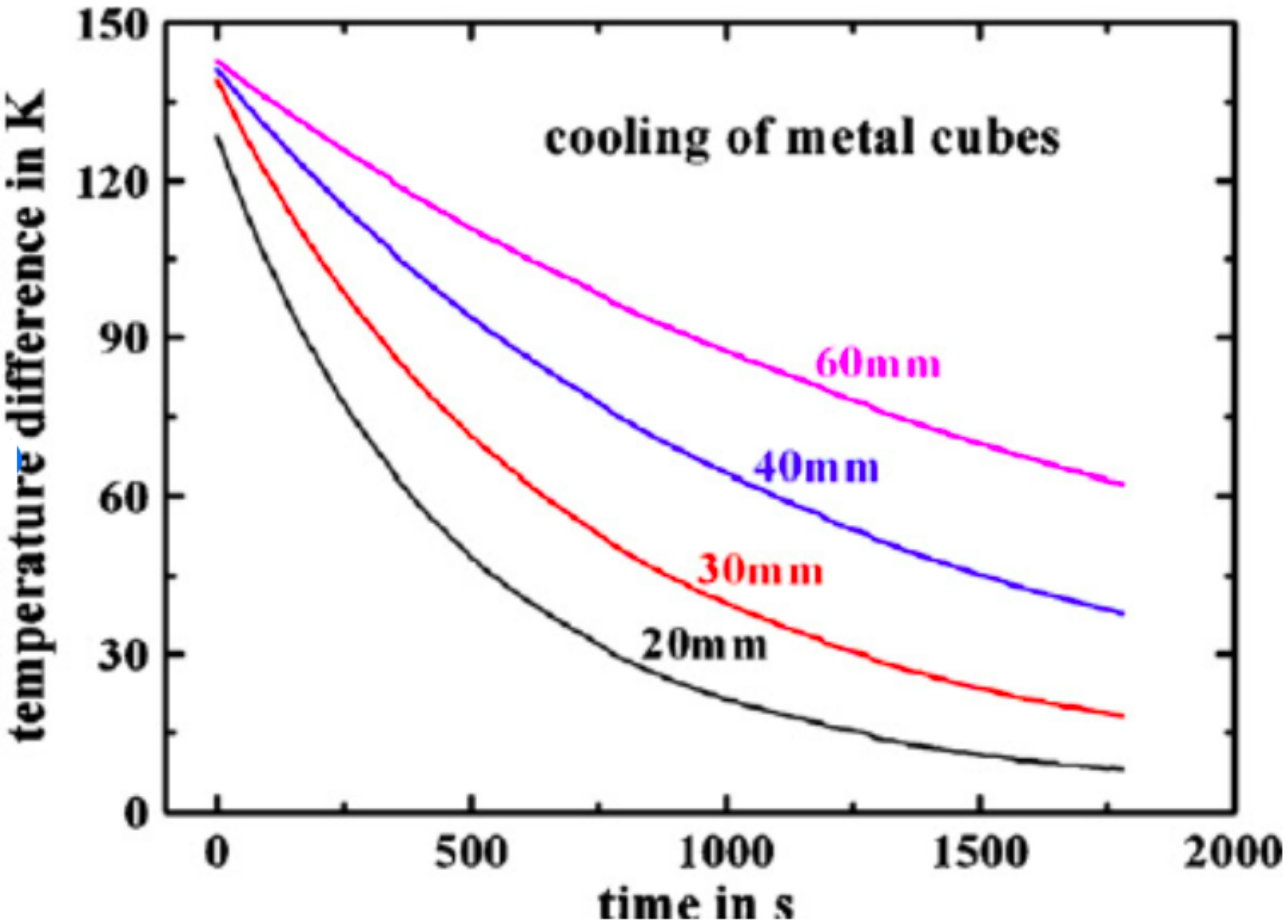
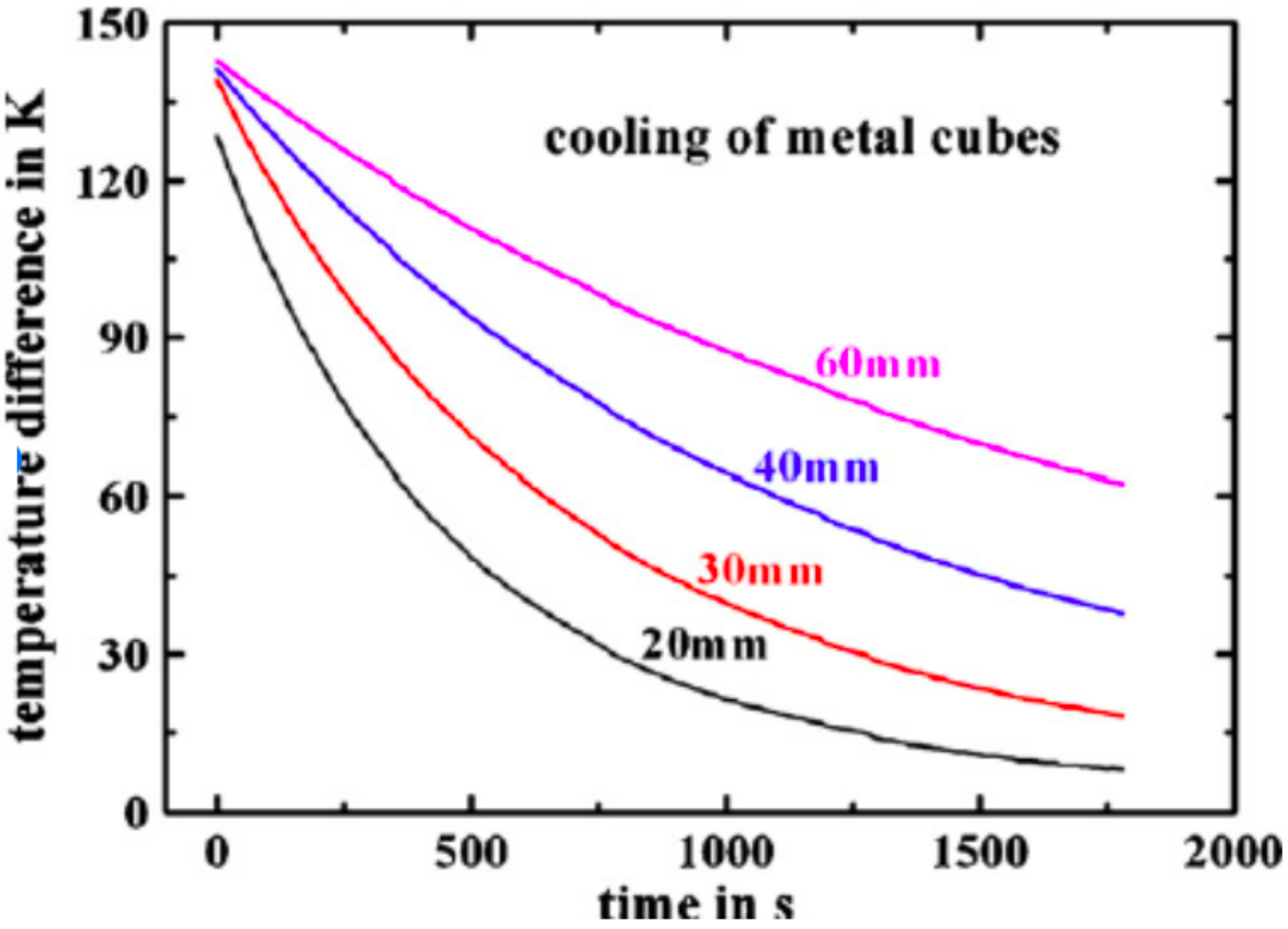


1) What is the time evolution of the temperature T?

Exponential dependence on time



1) What is the time evolution of the temperature T?

Exponential dependence on time

2) What is the law regulating the temperature vs time?

$$\frac{dT}{dt} = -r(T(t) - T_{amb})$$

$$r = \frac{1}{\tau}$$

Relaxation time τ

$$T(t) = T_{amb} + (T(0) - T_{amb})e^{-rt}$$

$$\tau = \frac{C}{hA}$$

C heat capacity
h heat transfer coeff.
A contact surface

What is heat?

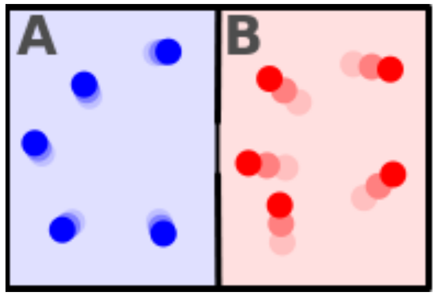
- In approximately 50 BCE, the Roman philosopher Lucretius proposed that apparently static macroscopic bodies were composed on a small scale of rapidly moving atoms all bouncing off each other.

The microscopic interpretation of heat: the kinetic theory

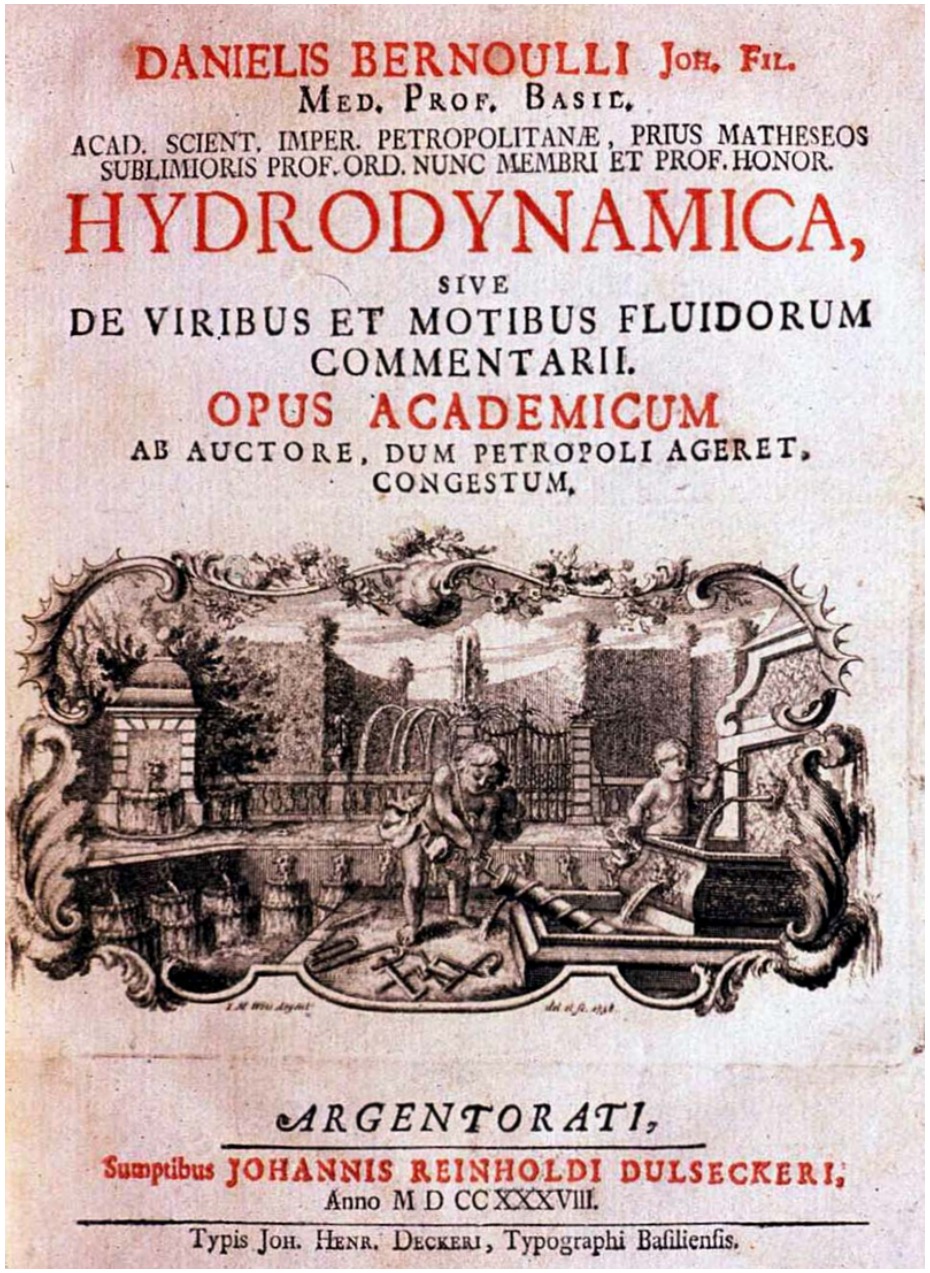
In 1738 Daniel Bernoulli published Hydrodynamica, which laid the basis for the kinetic theory of gases.

Physicist James Clerk Maxwell, in his 1871 classic Theory of Heat, was one of many who began to build on the already established idea that heat has something to do with matter in motion.

This was the same idea put forth by Benjamin Thompson in 1798, who said he was only following up on the work of many others.



$T_1 < T_2$



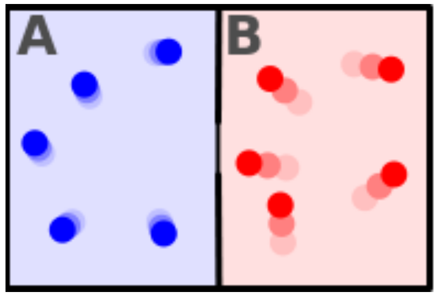
DANIELIS BERNOULLI JOH. FIL.
MED. PROF. BASIL.
ACAD. SCIENT. IMPER. PETROPOLITANÆ, PRIUS MATHESEOS
SUBLIMIORIS PROF. ORD. NUNC MEMBRI ET PROF. HONOR.
HYDRODYNAMICA,
SIVE
DE VIRIBUS ET MOTIBUS FLUIDORUM
COMMENTARII.
OPUS ACADEMICUM
AB AUCTORE, DUM PETROPOLI AGERET,
CONGESTUM.

ARGENTORATI,
Sumptibus JOHANNIS REINHOLDI DULSECKERI,
Anno M D CCXXXVIII.
Typis JOH. HENR. DECKERI, Typographi Baſilienſis.

The microscopic interpretation of heat: the kinetic theory

The theory for ideal gases makes the following assumptions:

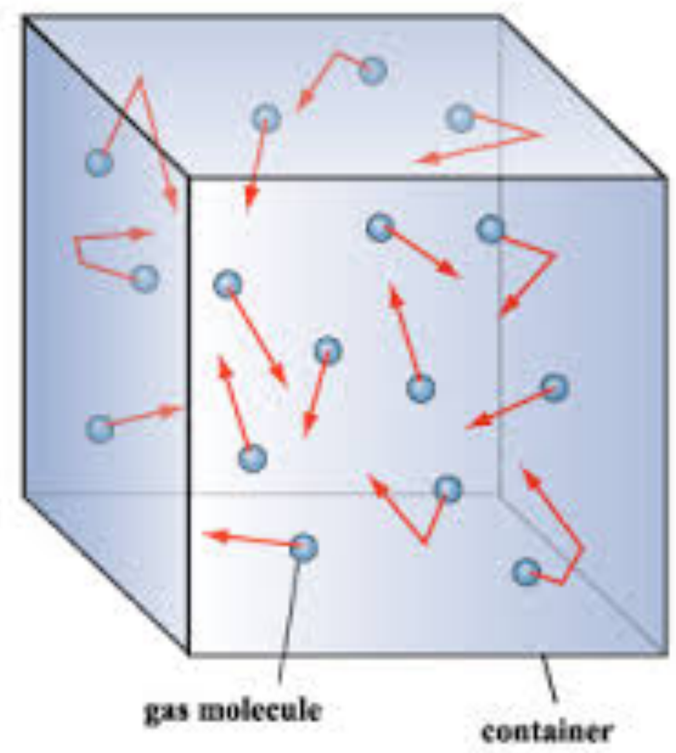
- The gas consists of very small particles known as molecules. The average distance separating the gas particles is large compared to their size.
- These particles have the same mass.
- The number of molecules is so large that statistical treatment can be applied.
- These molecules are in constant, random, and rapid motion.
- The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic.
- Except during collisions, the interactions among molecules are negligible. (That is, they exert no forces on one another.)



$$T_1 < T_2$$

How do we link Temperature and Energy?

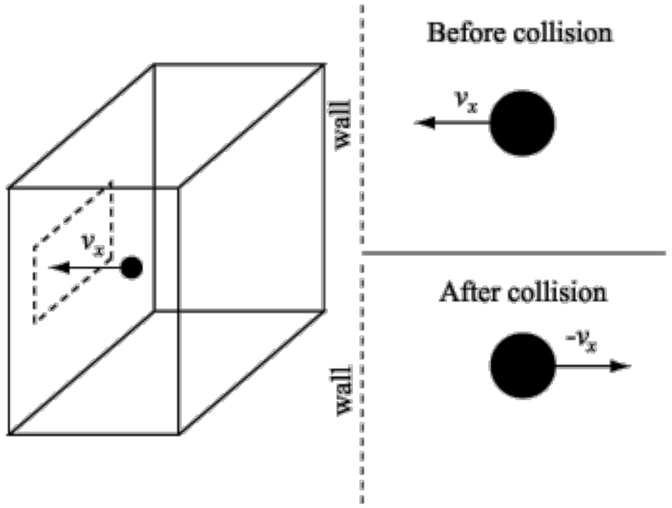
Pressure



Pressure is explained by kinetic theory as arising from the force exerted by molecules or atoms impacting on the walls of a container.

Consider a gas of N molecules, each of mass m, enclosed in a cuboidal container of volume $V=L^3$.

Pressure



When a gas molecule collides with the wall of the container perpendicular to the x coordinate axis and bounces off in the opposite direction with the same speed (an elastic collision), then the momentum lost by the particle and gained by the wall is:

$$\mathbf{\Delta p = 2\ m\ v}$$

The particle impacts one specific side wall once every $\Delta t = 2L/v$ (where L is the distance between opposite walls).

The force due to this particle is: $F = \Delta p/\Delta t = m\, v^2/L$

The total force on the wall is $F = Nm\, v^2/3L$ (avg. on the 3 dirs.)

And thus the pressure is

$$P = \frac{F}{L^2} = \frac{Nm\overline{v^2}}{3V}$$

Temperature

Thus

$$PV = \frac{Nm\overline{v^2}}{3}$$

By comparing with the ideal gas law: $PV = Nk_BT$

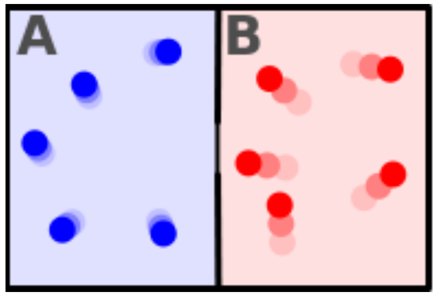
we have

$$k_BT = \frac{m\overline{v^2}}{3},$$

and thus:

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT.$$

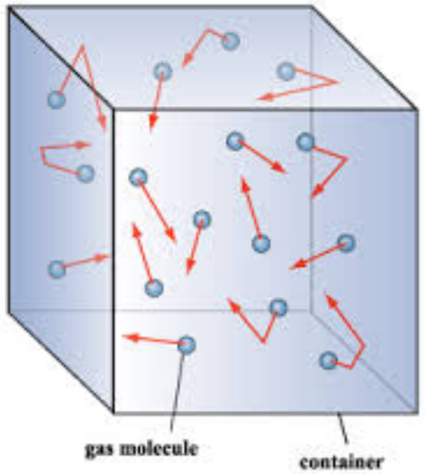
Then links average **kinetic energy** of a molecule with temperature.



$T_1 < T_2$

The microscopic interpretation of heat: the kinetic theory

OK fine.



But what about Entropy?

Energy and entropy: microscopic interpretation

In general the entropy remained an **obscure quantity** whose physical sense was (and somehow still is) difficult to grasp.

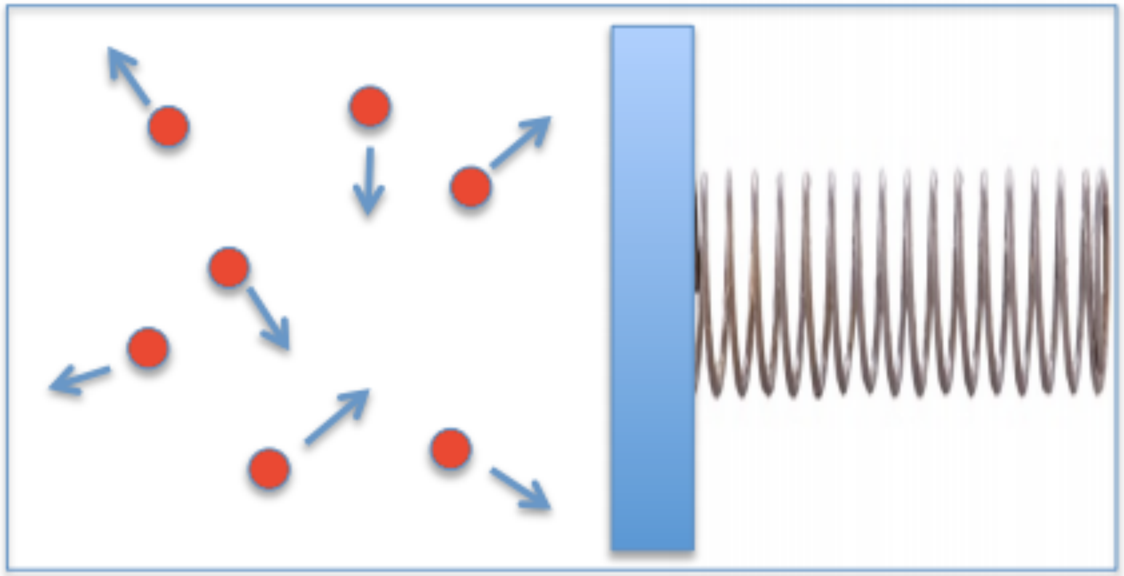
It was the work of **Ludwing Boltzmann** (1844 – 1906) that shed some light on the microscopic interpretation of the second law (and thus the entropy).

Energy and entropy: microscopic interpretation

If a system can be in a number of different states, all compatible with the conservation laws, then it will evolve in order to attain the equilibrium condition identified with the **most probable state** among all the possible states it can be in.

The ideal world of Boltzman

- The ideal world of Boltzmann is made by physical systems constituted by many small parts represented by colliding small spheres



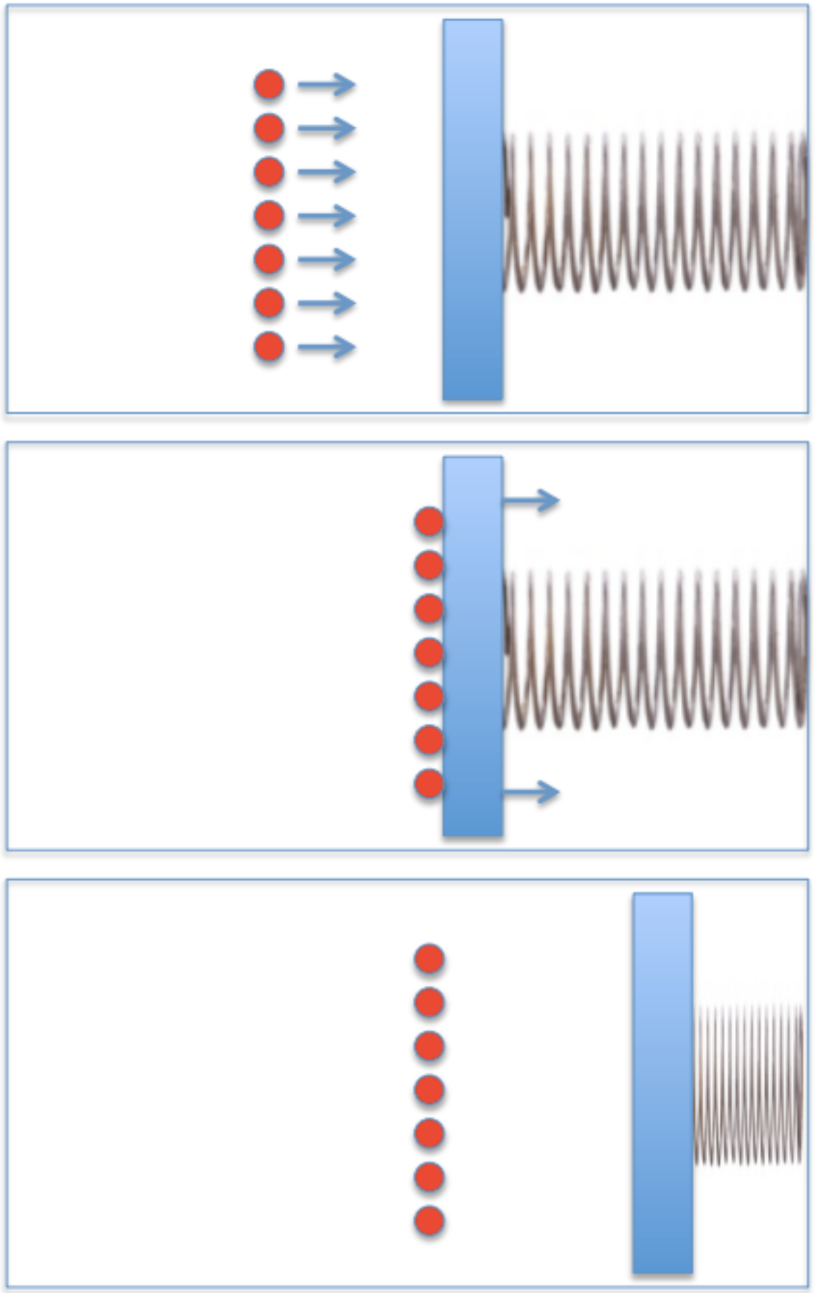
- Each sphere has the same mass *m* and velocity *v*

First case

Let’s suppose that these particles are contained in a box that has a moving set of mass $M = Nm$. The set is connected to a spring of elastic constant k, as in the figure, and is at rest.
If all the particles have the same velocity v and collide perpendicularly with the moving set at the same time, they will exchange velocity with the set. This will compress the spring up to an extent x_1 such that

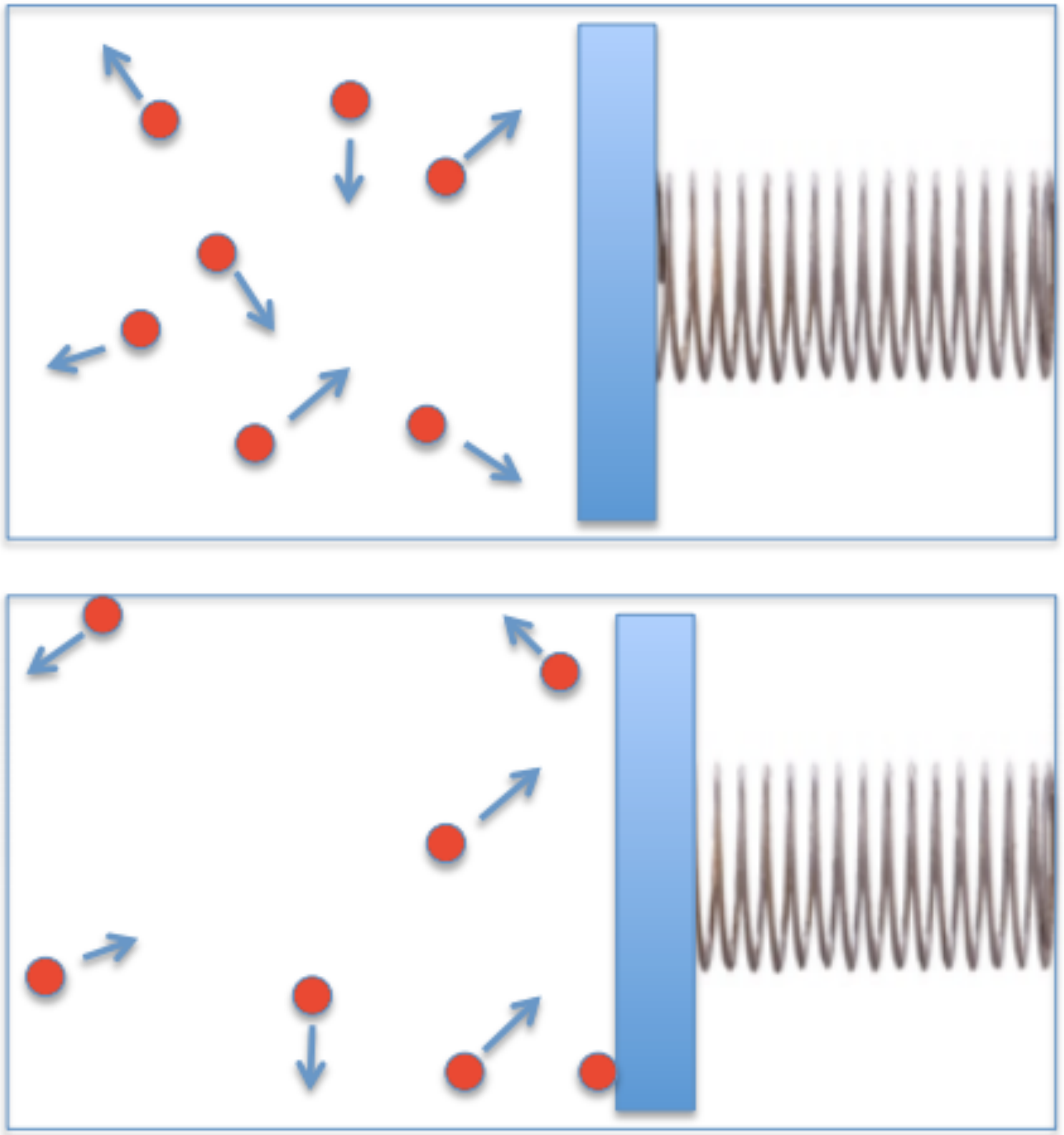
$$\frac{1}{2}Mv^2 = \frac{1}{2}kx_1^2 = U$$

We can always recover the potential energy U when we desire and use it to perform work. In this case we can completely transform the energy of the gas particle into work.



Second case

What is on the contrary the most probable configuration for the particle in the gas? Based on our experience (and on some common sense as well) it is the configuration in which all the particles, although each with the same velocity *v*, are moving with random direction in the box.



The **energy of the gas is still the same (so is its temperature *T*)** but in this case the set will be subjected at random motion with an average compression of the spring such that its average energy is *U/N*.

This is also the maximum work that we can recover from the potential energy of the movable set.

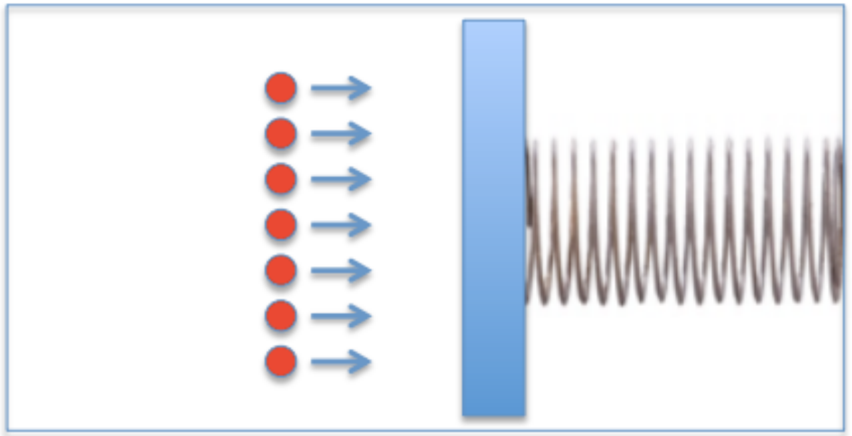
Entropy

According to the definition of Free energy, the quantity that limits our capability of performing work is the entropy.

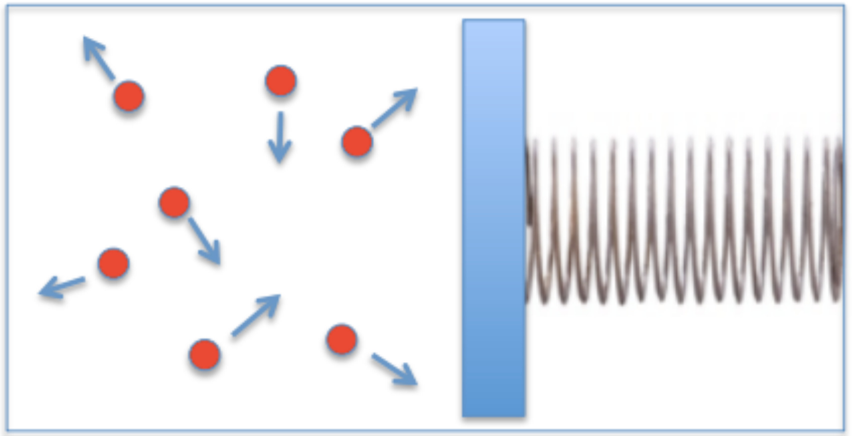
Thus the systems that have the smallest entropy have the largest capability of performing work.

Accordingly we can use the entropy to **put a label on the energetic content** of a system.

Two systems may have the same energy but the system that has the **lower entropy** will have the “**most useful**” energy.



low entropy



high entropy

The microscopic perspective

This example helped us to understand how energy and entropy are connected to the microscopic properties of the physical systems.

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This concept of “way of moving” was made clear by Boltzmann at the end of 1800, who proposed for the entropy the following definition:

$$S = k_B \log W$$

where k_B is the famous Boltzmann constant and W is also called the “number of configurations” and represents the number of ways we can arrange all the particles in the system without changing its macroscopic properties.

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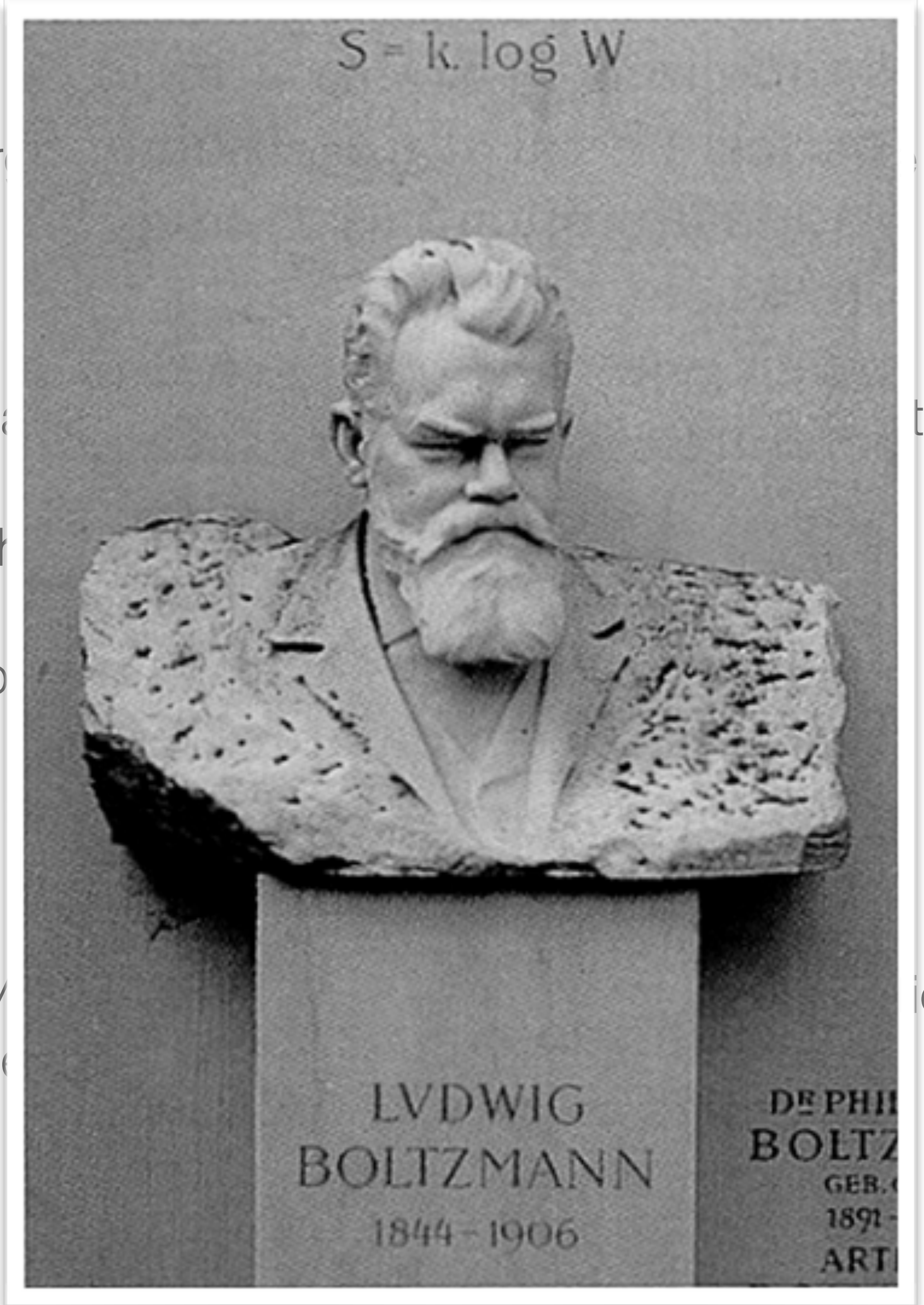


Where does the irreversibility come from?

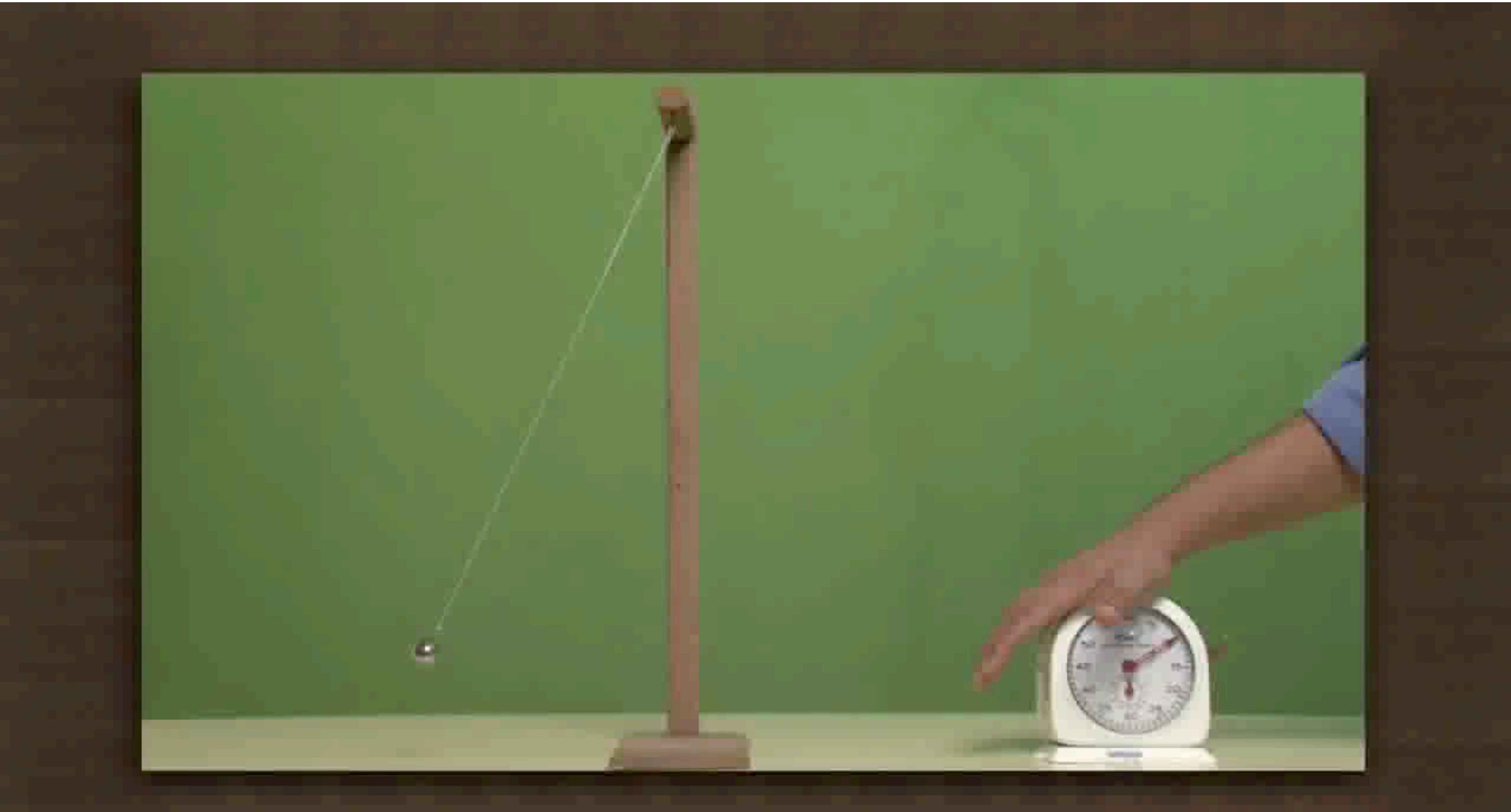
Thermodynamic:

- Equilibrium states exist
- After a given time no exchange of energy
- The variables that describe the systems do not present time dependance
- Processes without an inverse temporal evolution exist

Mechanics:

- Thermodynamic assumptions seam to be unjustified

Where does the irreversibility come from?



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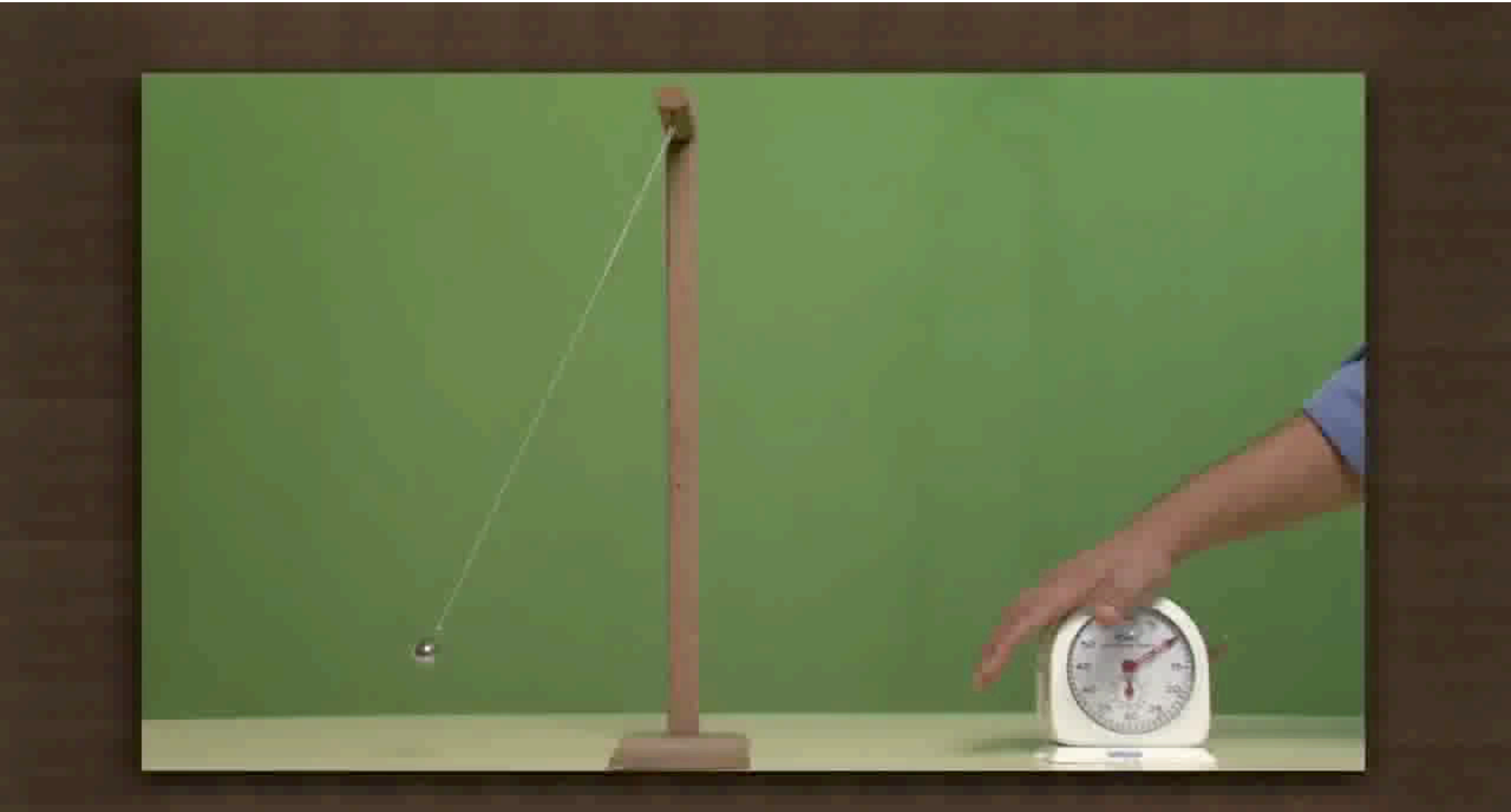

Where does the irreversibility come from?

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- Let’s assume an isolated system composed by *N* particles with interacting forces F_i and which depend only by the position of the particle x_i

$$m_i \frac{\mathrm{d}^2\mathbf{x}_i}{\mathrm{d}t^2} = \mathbf{F}_i(\mathbf{x}_1, \ldots, \mathbf{x}_N) \qquad (i = 1, 2, \ldots, N)$$

- If $(\mathbf{x}_1(t), \ldots, \mathbf{x}_N(t)) \equiv \{\mathbf{x}_i(t)\}$ is an allowed solution, describing an evolution of the particles then $\{\mathbf{x}_i(-t)\}$ describing an inverse evolution is allowed

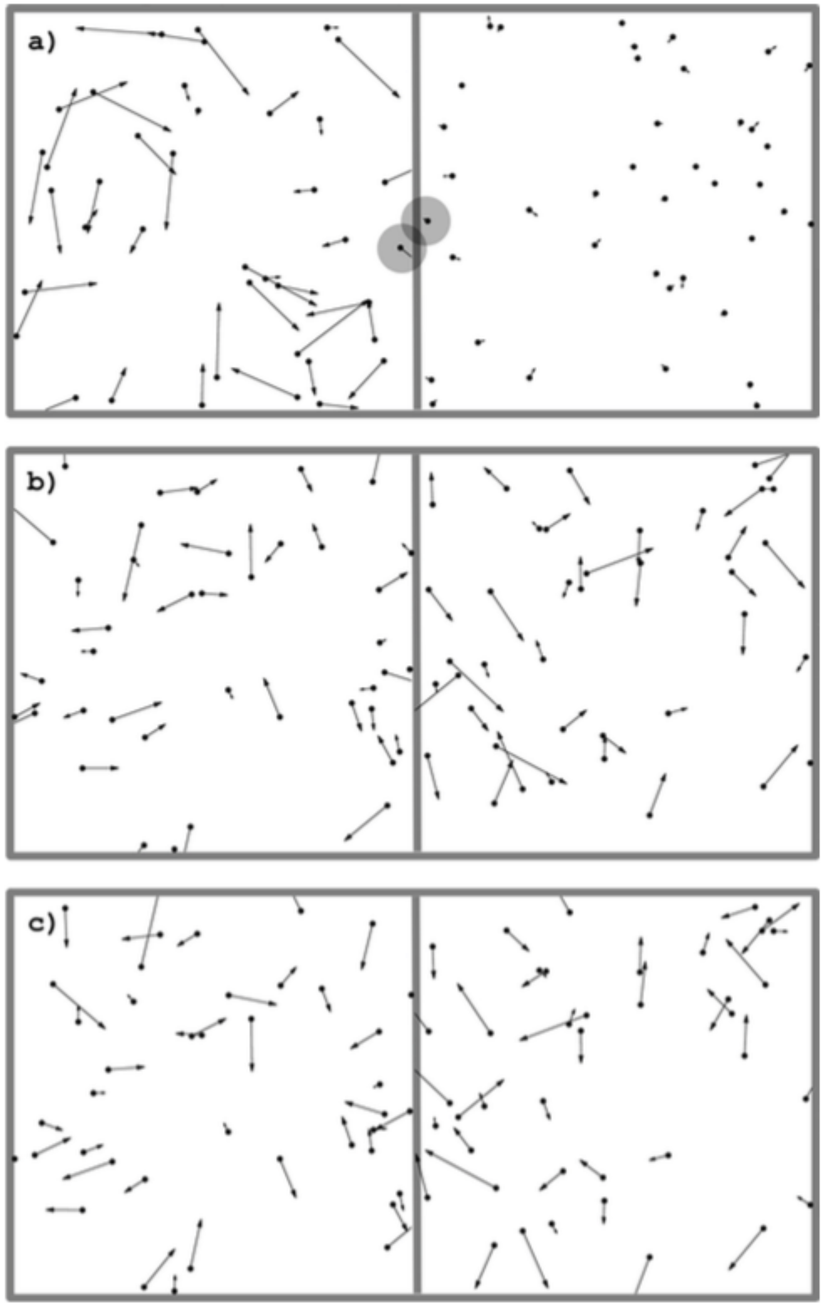
Where does the irreversibility come from?

$$E_{tot} = \sum_{i=1}^{N} \frac{1}{2} m \mathbf{v}_i^2 + V(\{\mathbf{x}_i\})$$

$$E_{tot} = \sum_{i=1}^{N_A} \frac{1}{2} m \mathbf{v}_i^2 + V_A + \sum_{i=1}^{N_B} \frac{1}{2} m \mathbf{v}_i^2 + V_B + V_{AB} \equiv E_A + E_B + V_{AB}$$

- Starting from non equilibrium
- After a time t the system is at the thermodynamic equilibrium

$$E_A^{eq} + E_B^{eq} + V_{AB}^{eq} = E_A(t) + E_B(t) + V_{AB}(t) = E_{tot}$$



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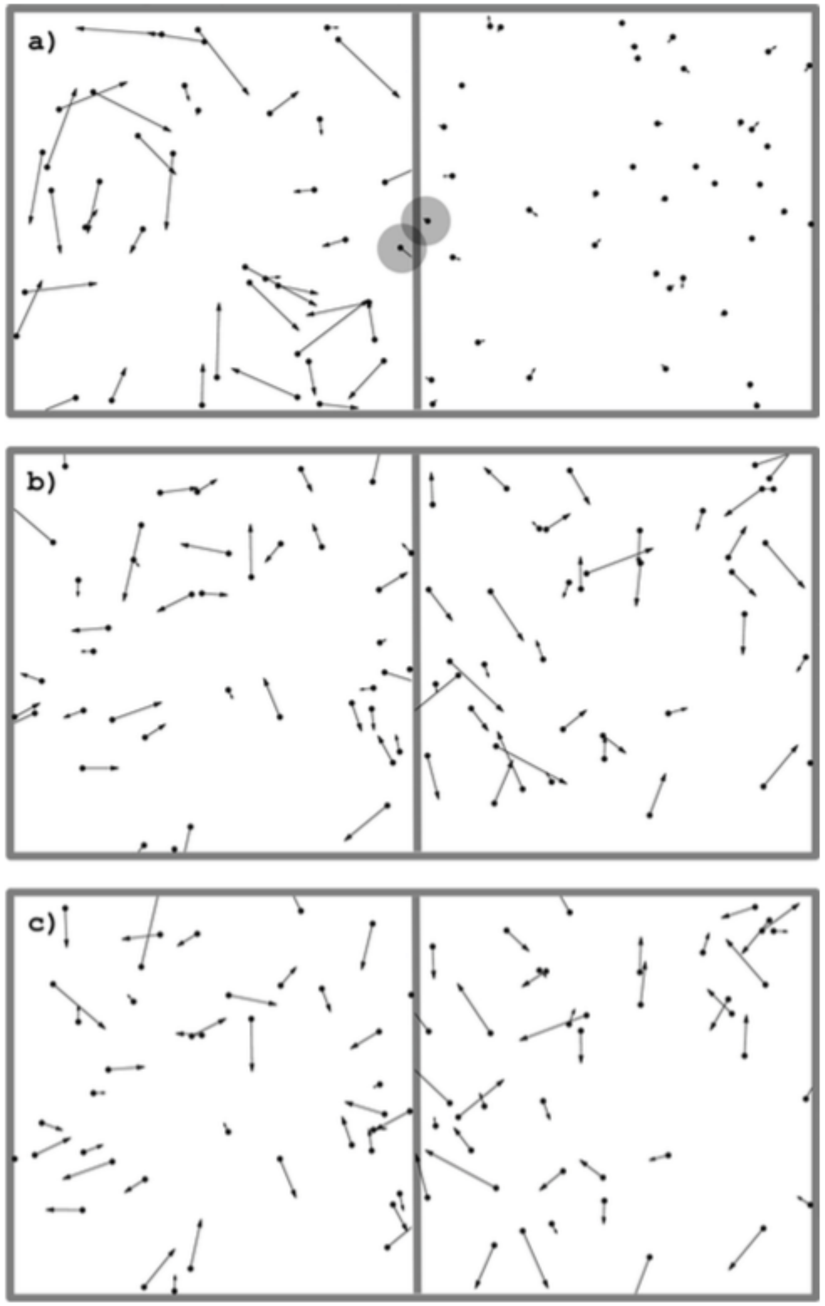


- According to the Poincaré's theorem after a given time t the system goes (infinite times) in the same status

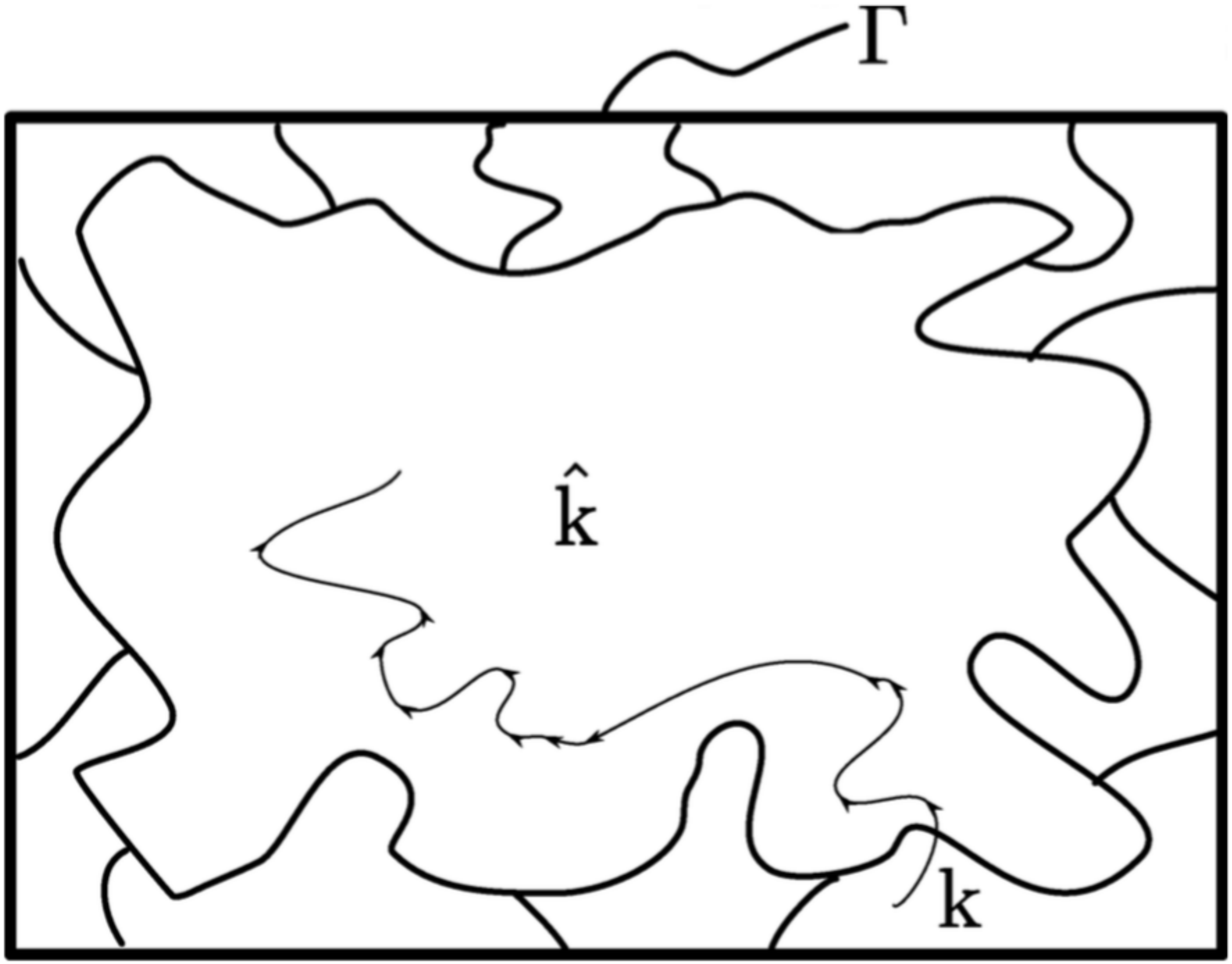
- After a finite time the system goes near the initial state of non equilibrium

Where does the irreversibility come from?

Two paradoxes:

- Loschmidt's paradox (reversibility paradox)
- Zermelo's paradox (Poincaré’s recurrence theorem)

Where does the irreversibility come from?



Ergodic hypothesis

- In physics and thermodynamics, the **ergodic hypothesis** says that, over long periods of time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the volume of this region.

- All accessible microstates are equiprobable over a long period of time.

Boltzmann entropy

Two fundamental ingredients needed for irreversibility:

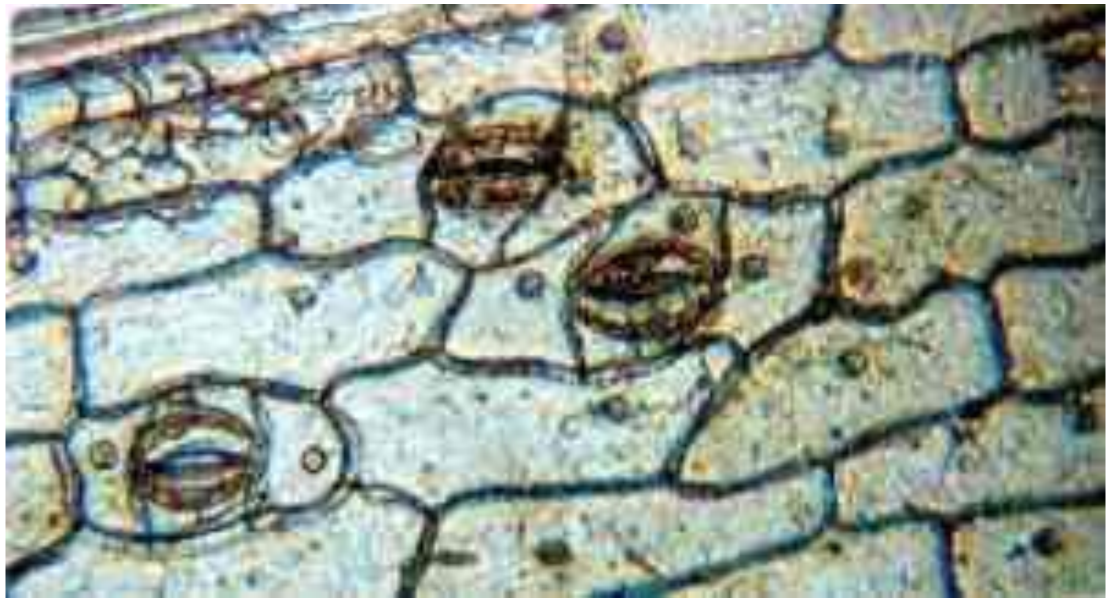
- Large number of particles (atoms or molecules), thus big inequality between microscopic and macroscopic scale
- Suitable initial conditions (molecular chaos)
  - Not all the microscopic systems evolve in an irreversible way, most of that do!

Brownian motion

- Discovered by Scottish botanist **Robert Brown** in 1827 while studying pollens of Clarkia (primrose family) under his microscope

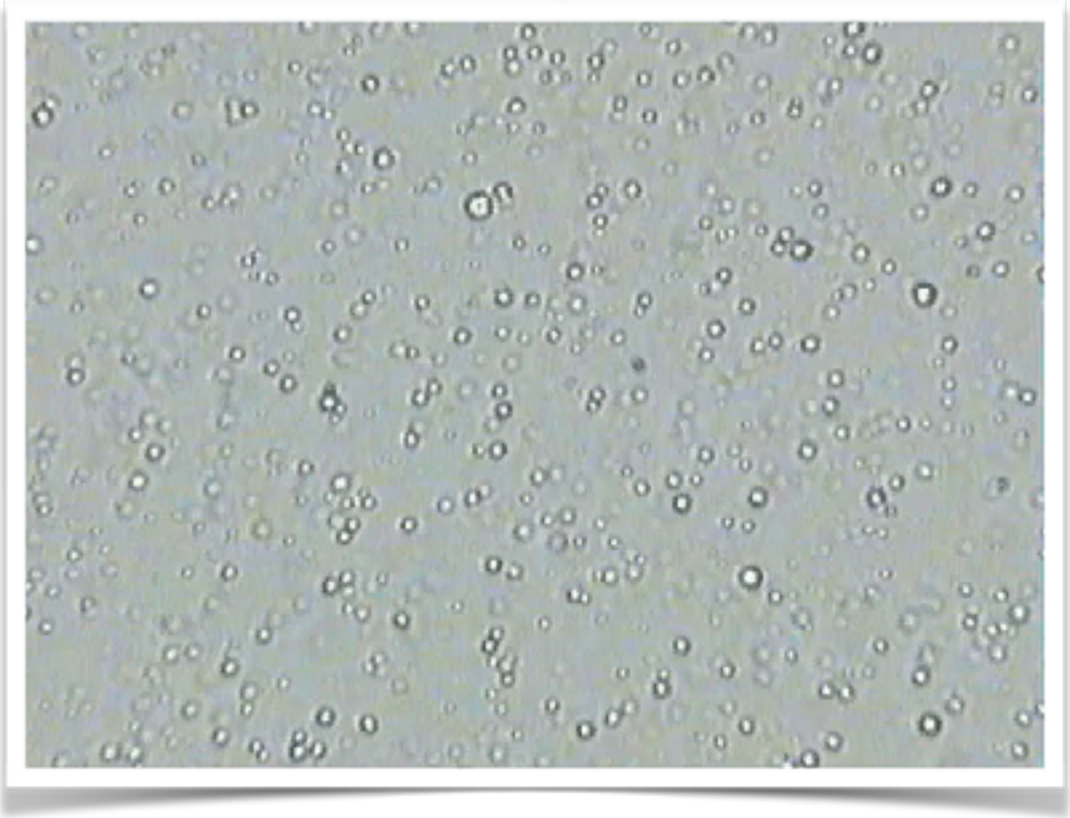
Robert Brown

- Robert Brown's main claim to fame is his discovery of the cell nucleus when looking at cells from orchids under his microscope
- 20 orchid epidermal cells showing nuclei (and 3 stomata) seen under Brown's original microscope preserved by the Linnean Society London



Brown’s Microscope

- And Brownian motion of milk globules in water seen under Robert Brown’s microscope



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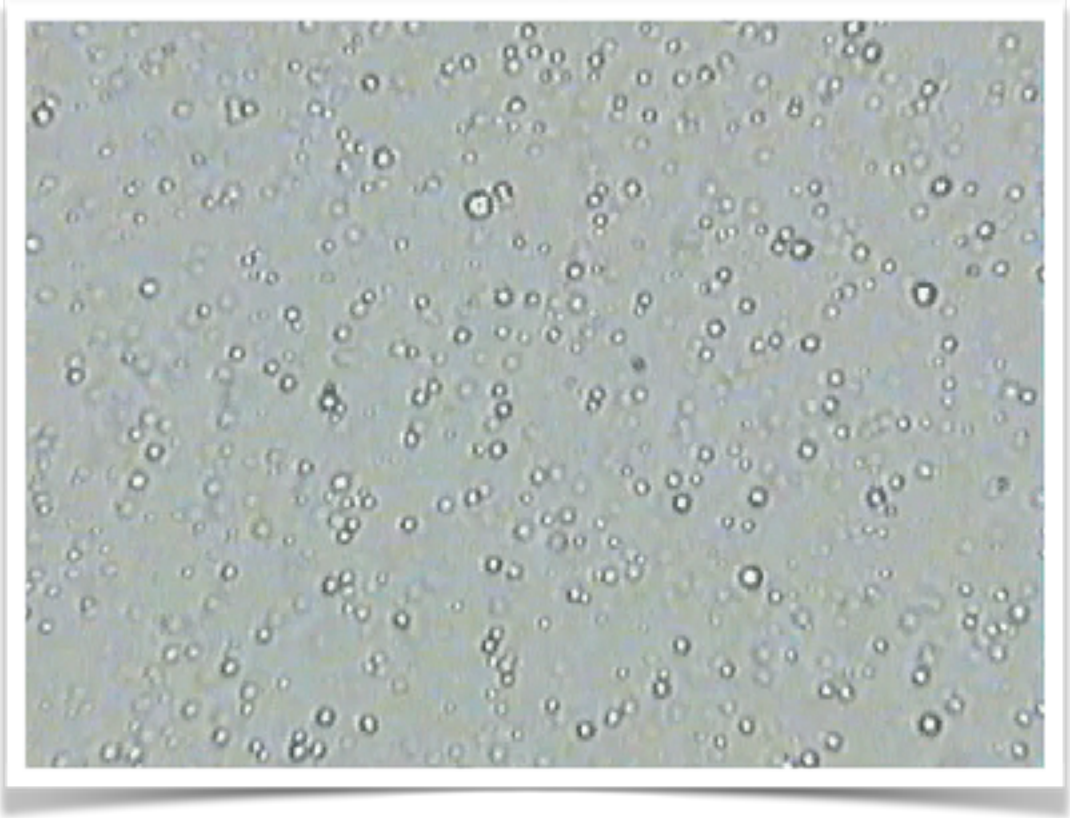

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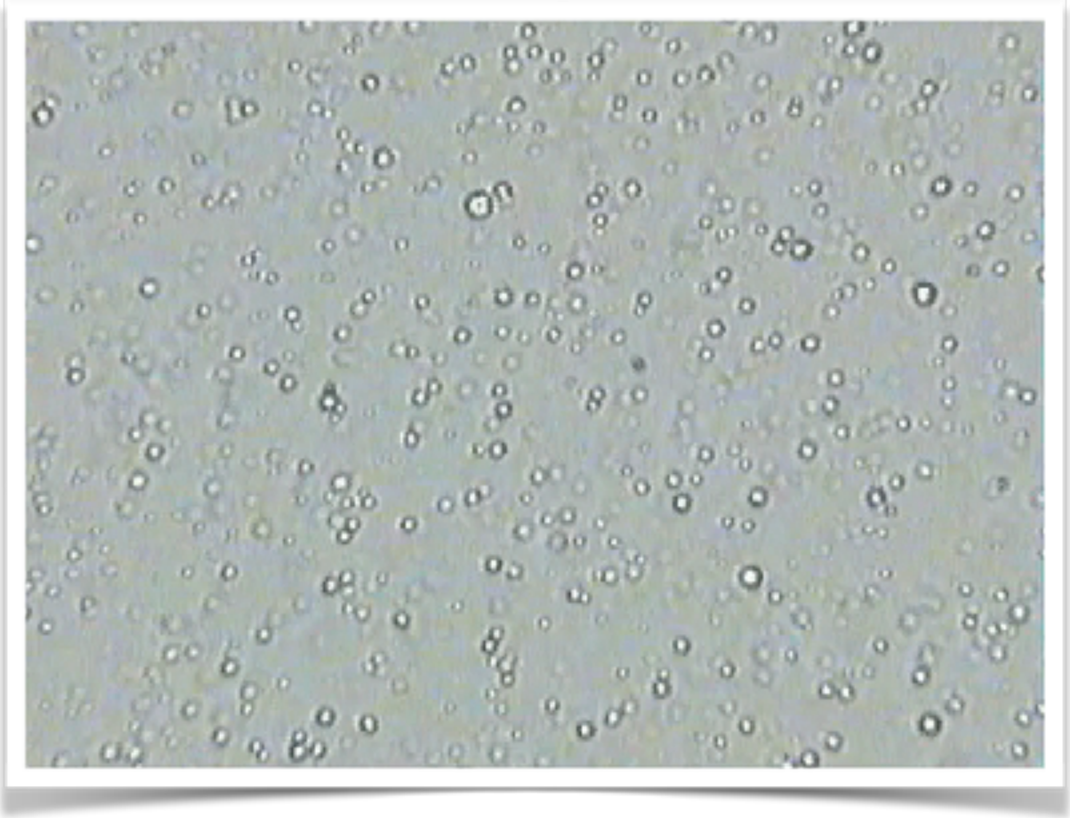


Deutsch D. H. “Did Robert Brown observe Brownian Motion: probably not”. *Bulletin of the American Physical Society* **36** (4): 1374 April 1991. Reported in *Scientific American* **265**: 20 1991.

Brown observations

- At first Brown suspected that he might have been seeing locomotion of pollen grains (i.e. they move because they are alive)

- Brown then observed the same random motion for inorganic particles…thereby showing that the motion is physical in origin and not biological.

1827-1900

Desaulx (1877):

- “In my way of thinking the phenomenon is a result of thermal molecular motion (of the particles) in the liquid environment”

G.L. Gouy (1889):

- observed that the "Brownian" movement appeared more rapid for smaller particles

F. M. Exner (1900)

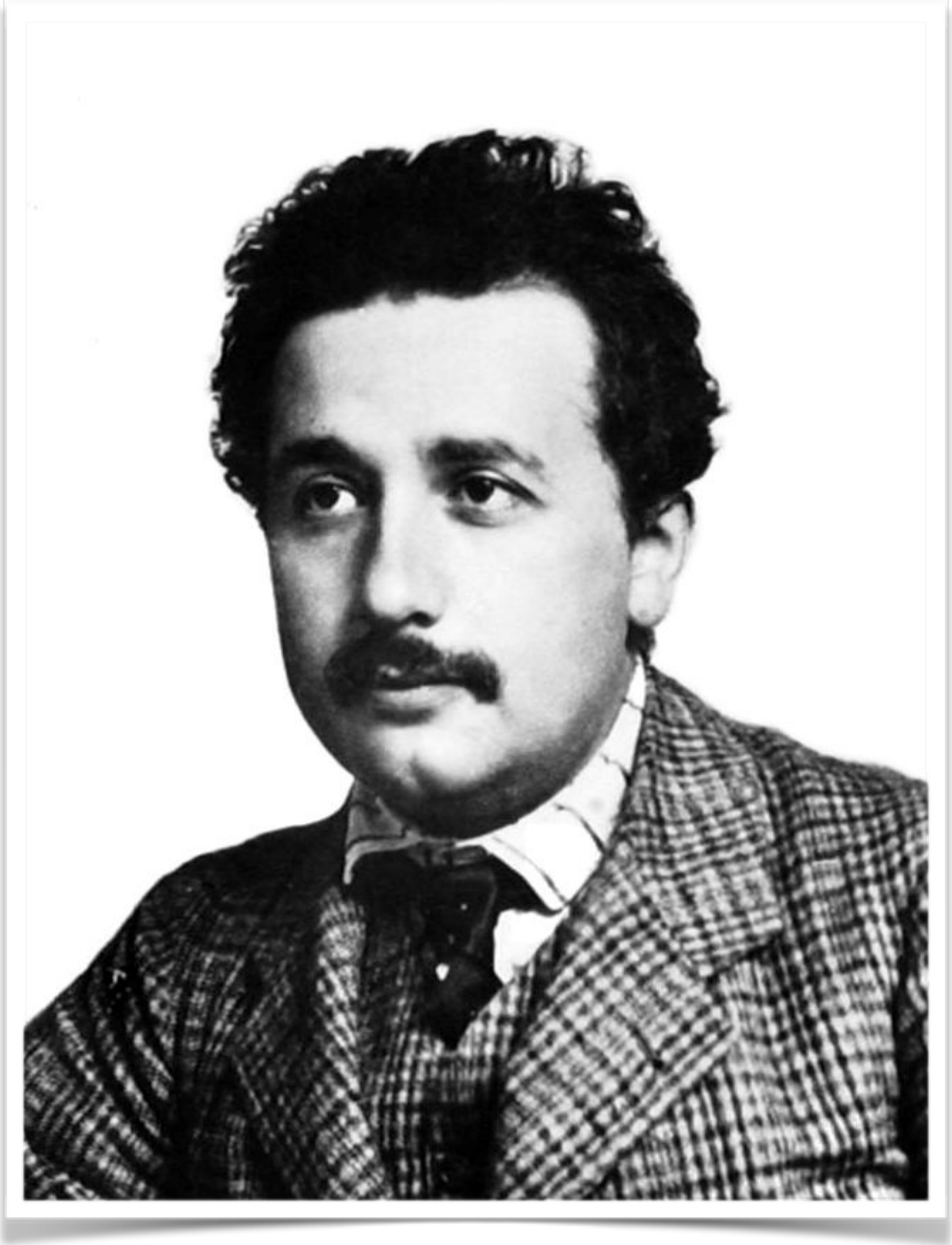
- First to make quantitative studies of the dependence of Brownian motion on particle size and temperature
- Confirmed Gouy’s observation of increased motion for smaller particles
- Also observed increased motion at elevated temperatures

Louis Bachelier (1870-1946)

- Ph.D Thesis (1900): "Théorie de la Spéculation" Annales de l'Ecole normale superiure
- Inspired by Brownian motion he introduced the idea of "**random-walk**" to model the price of what is now called a barrier option (an option which depends on whether the share price crosses a barrier).

Albert Einstein

- Worked out a **quantitative description** of Brownian motion based on the **Molecular-Kinetic Theory of Heat**
- Published as the third of the famous three 1905 papers
- Awarded the Nobel Prize in 1921 in part for this.



Einstein’s 1905 papers

- On a Heuristic Point of View on the Creation and Conversion of Light (Photo-Electric Effect)
- On the Electrodynamics of Moving Bodies (Theory of Special Relativity)
- Investigation on the Theory of the Brownian Movement

Historical context

- Einstein’s analysis of Brownian Motion and the subsequent experimental verification by Jean Perrin provided the first “smoking gun” **evidence for the Molecular-Kinetic Theory of Heat**

- Kinetic Theory is **highly controversial** around 1900… scene of epic battles between its proponents (e.g. Boltzmann) and its detractors

Molecular-Kinetic Theory

- All matter are made of molecules (or atoms)
- Gases are made of freely moving molecules
- U (internal energy) = mechanical energy of the individual molecules
- Average internal energy of any system: $\langle U \rangle = n k_B T/2$, n are the number of degrees of freedom
- Boltzmann: Entropy $S = k_B \log W$ where W are the number of microscopic states corresponding to a given macroscopic state

Einstein approach

- In hindsight Einstein’s paper of 1905 on Brownian Motion takes a more circuitous route than necessary.
- He opted for physical arguments instead of mathematical solutions
- Alternative derivation by Paul Langevin (1908)

Einstein approach

- Einstein reviews the Law of Osmotic Pressure discovered by J. van’t Hoff who won the Nobel Prize in Chemistry for this in 1901

- Einstein also argues that from the point of view of the Kinetic Theory the Law of Osmotic Pressure should apply equally to suspension of small particles

Einstein approach: diffusion

- Minimising Helmholtz free energy Einstein shows that a particle (in suspension) in a concentration gradient (in x) will experience a force K given (in magnitude) by

$$K\nu = \frac{\partial \pi_o}{\partial x} = \frac{RT}{N}\frac{\partial \nu}{\partial x}$$

- The particles will reach terminal velocity of

$$V_T = \frac{K}{6\pi\eta a}$$

- And a resistive force of

$$\overrightarrow{F_R} = -6\pi\eta a\overrightarrow{V}$$

$$\pi_o = \frac{RT}{N}\nu$$

π_o = osmotic pressure
ν = solute concentration
N = Avogadro’s number
R = gas constant
T = absolute temperature

Einstein approach: diffusion

- The resulting flux of particles is then given by

$$\Phi \equiv D\frac{\partial \nu}{\partial x} = \frac{K\nu}{6\pi\eta a}$$

- Resulting in a definite prediction for the diffusion constant D given by

$$D = \frac{RT}{N}\frac{1}{6\pi\eta a}$$

$$\pi_o = \frac{RT}{N}\nu$$

π_o = osmotic pressure
ν = solute concentration
N = Avogadro's number
R = gas constant
T = absolute temperature

Einstein approach: random walk

- Einstein then analyses the Brownian Motion of particles suspended in water as a 1-d random walk process.
- Unaware of the work of Bachelier his version of random walk was very elementary
- He was able to show with his own analysis that this random walk problem is identical to the 1-d diffusion problem

Einstein approach: random walk

- The 1-d diffusion equation is

$$\frac{\partial f(x,t)}{\partial t} = D\frac{\partial^2 f(x,t)}{\partial x^2}$$

- This equation has the Green’s Function (integral kernel) given by

$$f(x,t) = \frac{f_0}{\sqrt{4\pi D}}\frac{\exp(-x^2/4Dt)}{\sqrt{t}}$$

Einstein approach: random walk

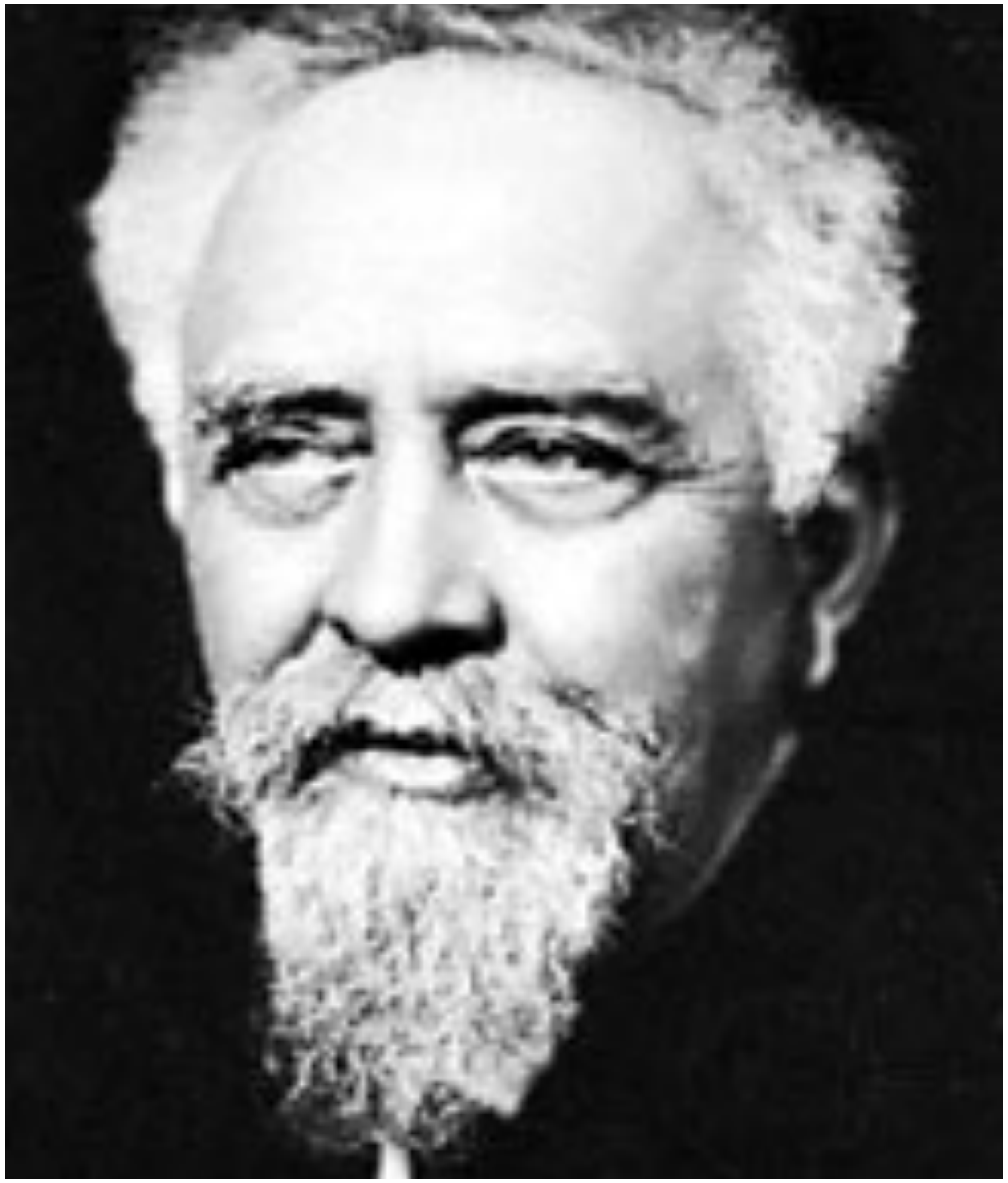
- Taking the initial position of each particle to be its origin then the average x^2 is then given by

$$\langle x^2 \rangle = 2Dt = \left(\frac{RT}{N} \frac{1}{3\pi\nu a} \right) t$$

- Einstein finishes the paper by suggesting that this diffusion constant D can be measured by following the motion of small spheres under a microscope

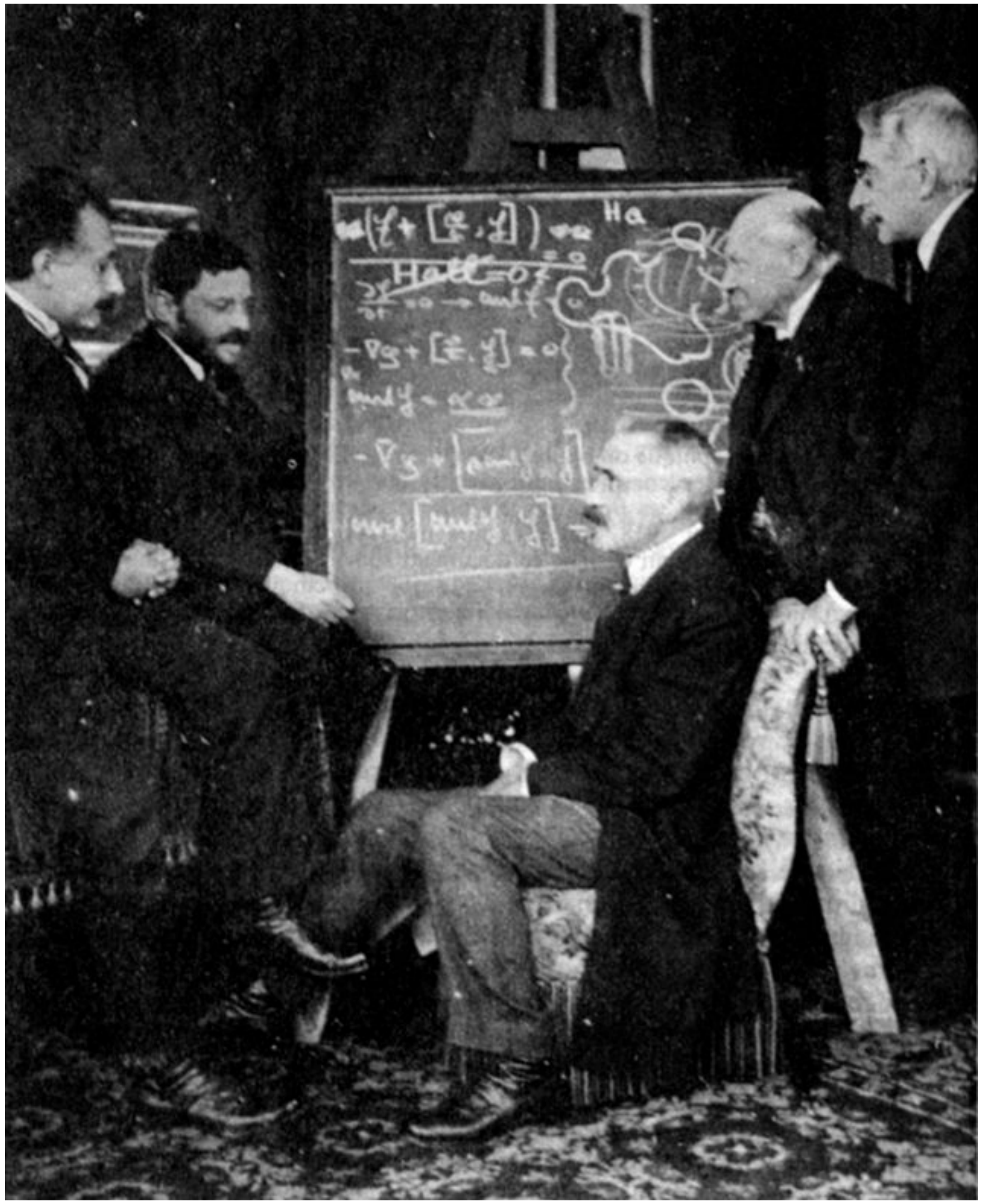
Jean Perrin (1870-1942)

- Using ultra-microscope Jean Perrin began quantitative studies of Brownian motion in 1908
- Experimentally verified Einstein's equation for Brownian Motion
- Measured Avogadro's number to be $N = 6.5\text{-}6.9 \times 10^{23}$
- From related work he was the first to estimated the size of water molecules
- Awarded Nobel Prize in 1926



Paul Langevin (1872-1946)

- Most known for:
  - Developed the statistical mechanics treatment of paramagnetism
  - Work on neutron moderation contributing to the success to the first nuclear reactor
- The Langevin Equation and the techniques for solving such problems is widely used in econometrics



Langevin equation

- In 1908 Paul Langevin developed a more direct derivation based on a stochastic (differential) equation of motion. We start with Newton's 2nd Law (Langevin Equation):

$$m\ddot{r} = -6\pi\eta a\dot{r} + F_{ext}$$

Langevin equation

- After variable change and opportune manipulation we obtain

$$\frac{1}{2}m\ddot{u} + 3\pi\eta a\dot{u} = 2\left\langle \frac{1}{2}mV^2 \right\rangle + \left\langle \overrightarrow{r}\overrightarrow{F_{ext}} \right\rangle$$

- By **Equipartition Theorem** we have

$$\left\langle \frac{1}{2}mV^2 \right\rangle = nk_BT$$

where *n* is the number of spatial dimensions involved and k_B is again the Boltzmann Constant.

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Solving the Differential Equation

$$\frac{d^2u}{dt^2} + \frac{1}{\tau}\frac{du}{dt} = \kappa$$

where

$$\tau = M / 6\pi\eta a \qquad \kappa = 2nkT / M = 2\left\langle V^2 \right\rangle$$

$$\boxed{u \equiv \left\langle r^2 \right\rangle = (\kappa\tau)t - C_1\tau \exp(-t/\tau) + C_2}$$

Langevin: t >> τ case

$$\langle r^2 \rangle \xrightarrow[t>>\tau]{} \kappa\tau(t-\tau) \approx (\kappa\tau)t$$

$$= \left(\frac{2nkT}{M} \times \frac{M}{6\pi\eta a}\right)t = \left(\frac{nkT}{3\pi\eta a}\right)t$$

- Which is the same as Einstein’s result but with an extra factor of *n* (Note Einstein’s derivations were for a 1-d problem)

Summary

- Energy: a hint of history
- Energy: form and transformation
- Thermodynamic
- Heat: the kinetic theory
- Energy and entropy
- Irreversibility and Brownian motion

Thank you for your attention!

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