2
Energy transformations at micro scales

Luca Gammaitoni

ICT-Energy Summer school 2016, Aalborg

Content

The microscopic interpretation of **energy**.
The microscopic interpretation of **entropy**
The **energy** transformation at small scale

The microscopic interpretation of heat: the kinetic theory

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.

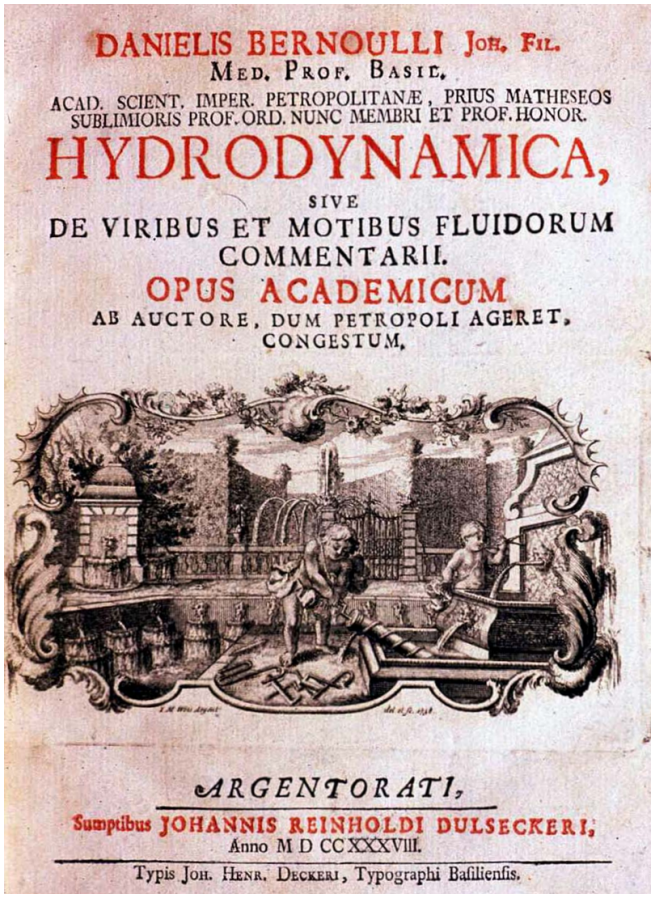
This Epicurean atomistic point of view was rarely considered in the subsequent centuries, when Aristotlean ideas were dominant.

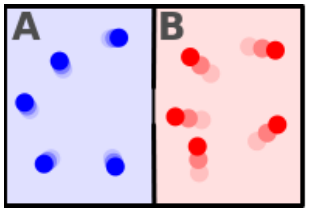
The microscopic interpretation of heat: the kinetic theory

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.


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 CC XXXVIII.
Typis Joh. Henr. Deckeri, Typographi Basilienſis.

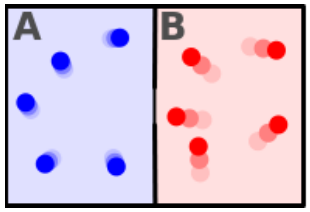


$T_1 < T_2$

The microscopic interpretation of heat: the kinetic theory

The theory for ideal gases makes the following assumptions:

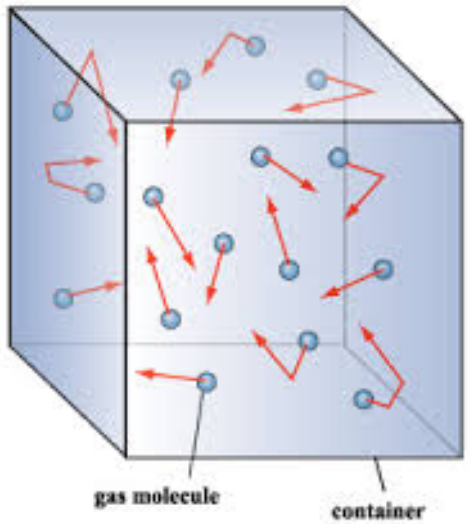
- The gas consists of very small particles known as molecules. The average distance separating the gas particles is large compared to their size.
- These particles have the same mass.
- The number of molecules is so large that statistical treatment can be applied.
- These molecules are in constant, random, 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.)



$T_1 < T_2$

The microscopic interpretation of heat: the kinetic theory

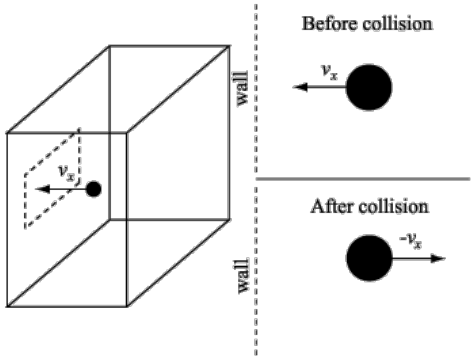
Pressure



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:

$$\Delta p = 2\ m\ v$$

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

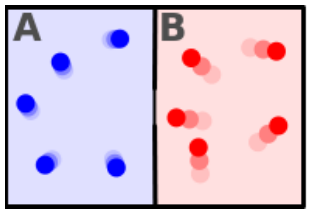
The force due to this particle is: $F = \Delta p/\Delta t = m\ v^2/L$

The total force on the wall is $F = Nm\ v^2/3L$ (averaging on the 3 directions)

And thus the pressure is

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

Temperature



$T_1 < T_2$

From before we have

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

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

we have

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

and thus:

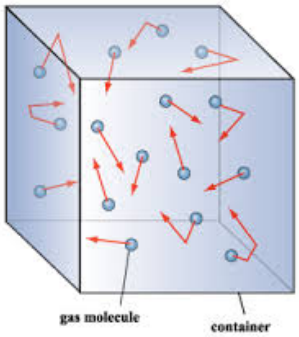
$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT.$$

Than links average kinetic energy of a molecule with temperature.

The microscopic interpretation of heat: the kinetic theory

OK fine.

But what about Entropy?



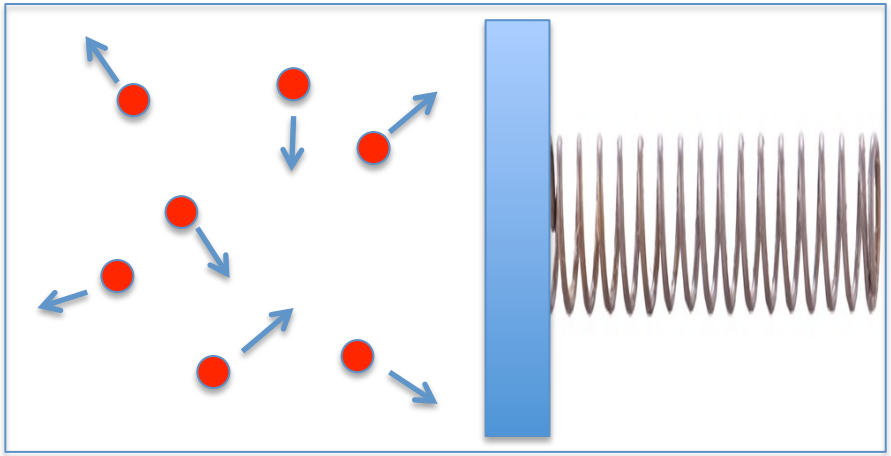
Energy and Entropy: the microscopic interpretation

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).

To grasp the meaning of entropy at small scales…

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*

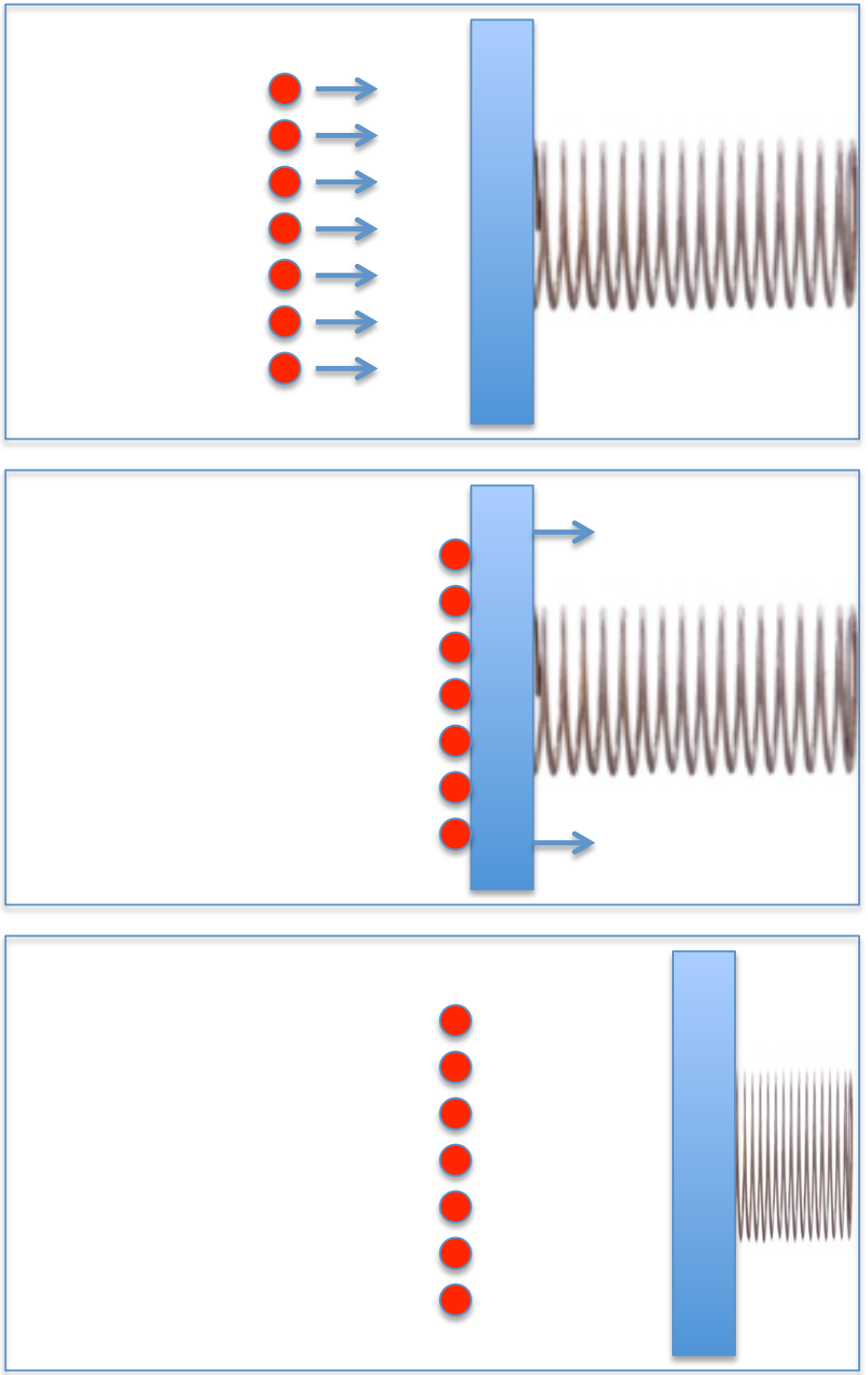
Consider the two cases…

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

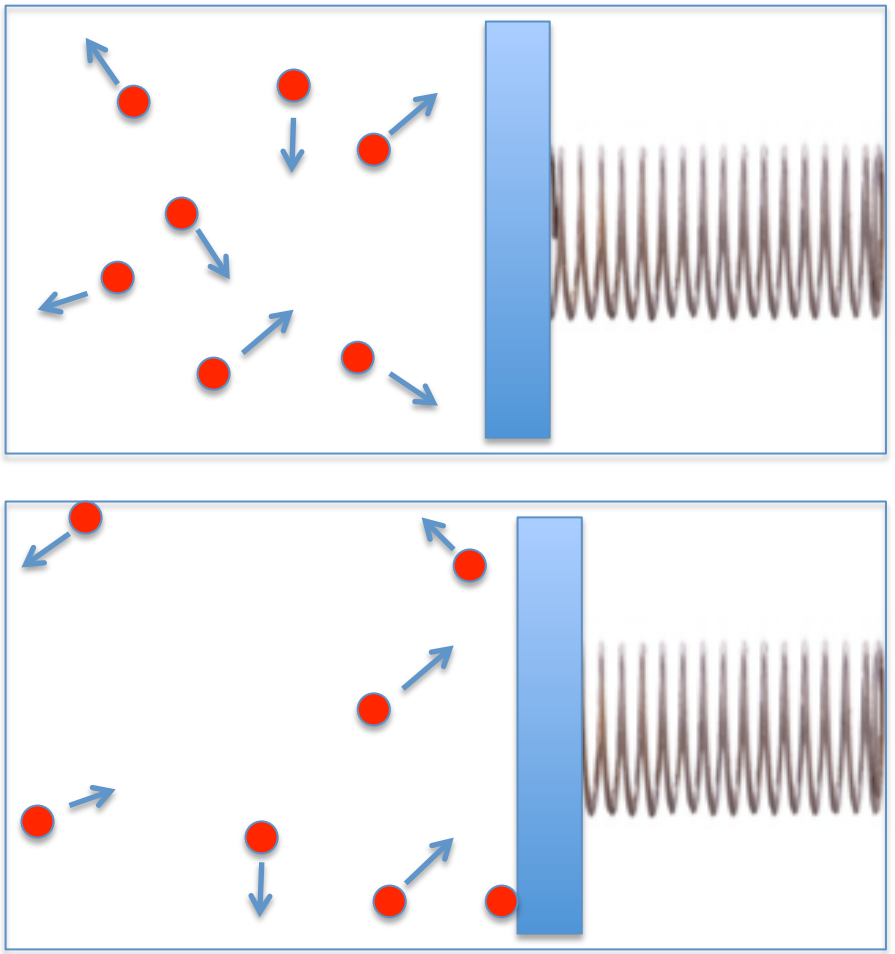
$$\frac{1}{2} M v^2 = \frac{1}{2} k x_1^2 = U$$

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.

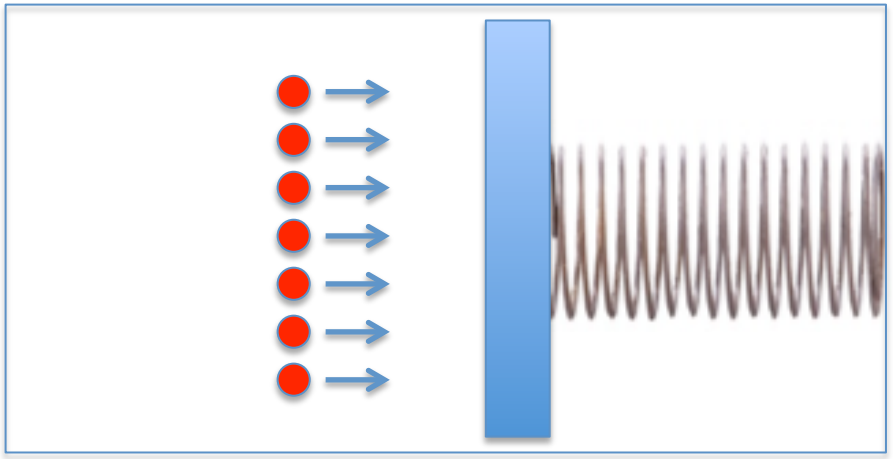
This is also the maximum work that we can recover from the potential energy of the movable set.

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

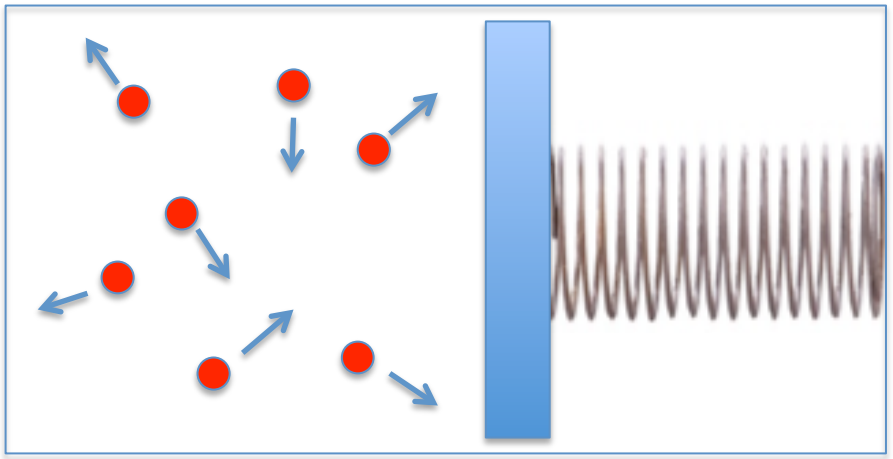
Thus the systems that have the smaller entropy have the larger capability of performing work.

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.

In the simple case of an ideal gas, the system energy is nothing else than the sum of all the kinetic energies of the single particles.
We can say that the energy is associated with "how much" the particles move.

On the other hand we have seen that there is also a "quality" of the motion of the particles that is relevant for the entropy.
We can say that the entropy is associated with "the way" the particles moves.

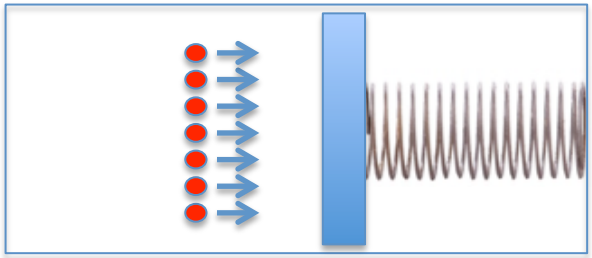
The microscopic perspective

The entropy is associated with "the way" the particles moves.

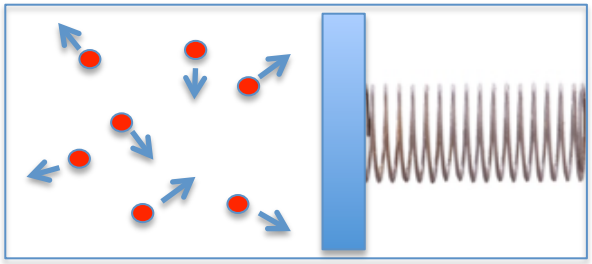
This concept of "way of moving" was made clear by Boltzmann at the end of 1800, who proposed for the entropy the following definition:

$$S = K_B \log W$$

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.



Few ways = low entropy



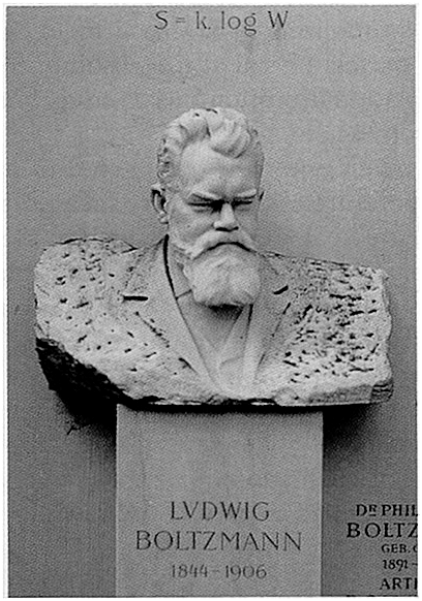
many ways = high entropy

The microscopic perspective

The second principle

In a spontaneous transformation the entropy always increases

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.



What about the Friction?

During an irreversible transformation the entropy always increase more that what was expected, due to the Clausius equality that becomes ***inequality***:.

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

Why is that? The answer is that in addition to the *physiological* increase there is an extra contribution due to the *dissipative effect* of the non-equilibrium processes. With *dissipative effect* we intend a way in which some low-entropy energy is changed into high-entropy energy. A typical example of dissipative process is friction.

How can we describe friction?

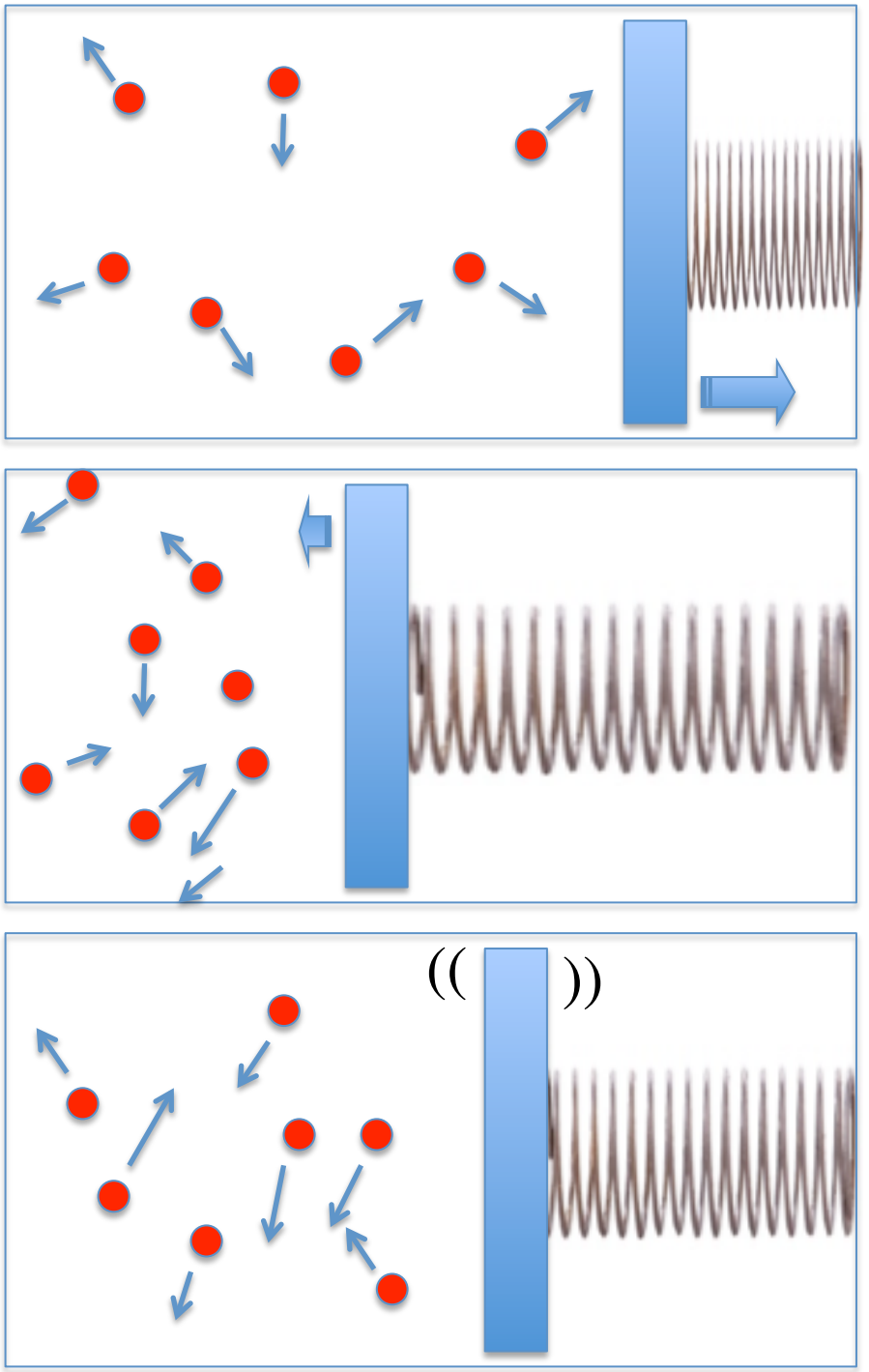
Consider the two cases…

First case

We compress the spring to some extent and then we release the compression leaving it free to oscillate.

After few oscillations we observe that the oscillation amplitude decreases as a consequence of what we call the friction (viscous damping force) action due to the presence of the gas.
The decrease ceases when the oscillation amplitude reaches a certain equilibrium value and after that it remains constant (on average).

Some energy has been dissipated into heat.

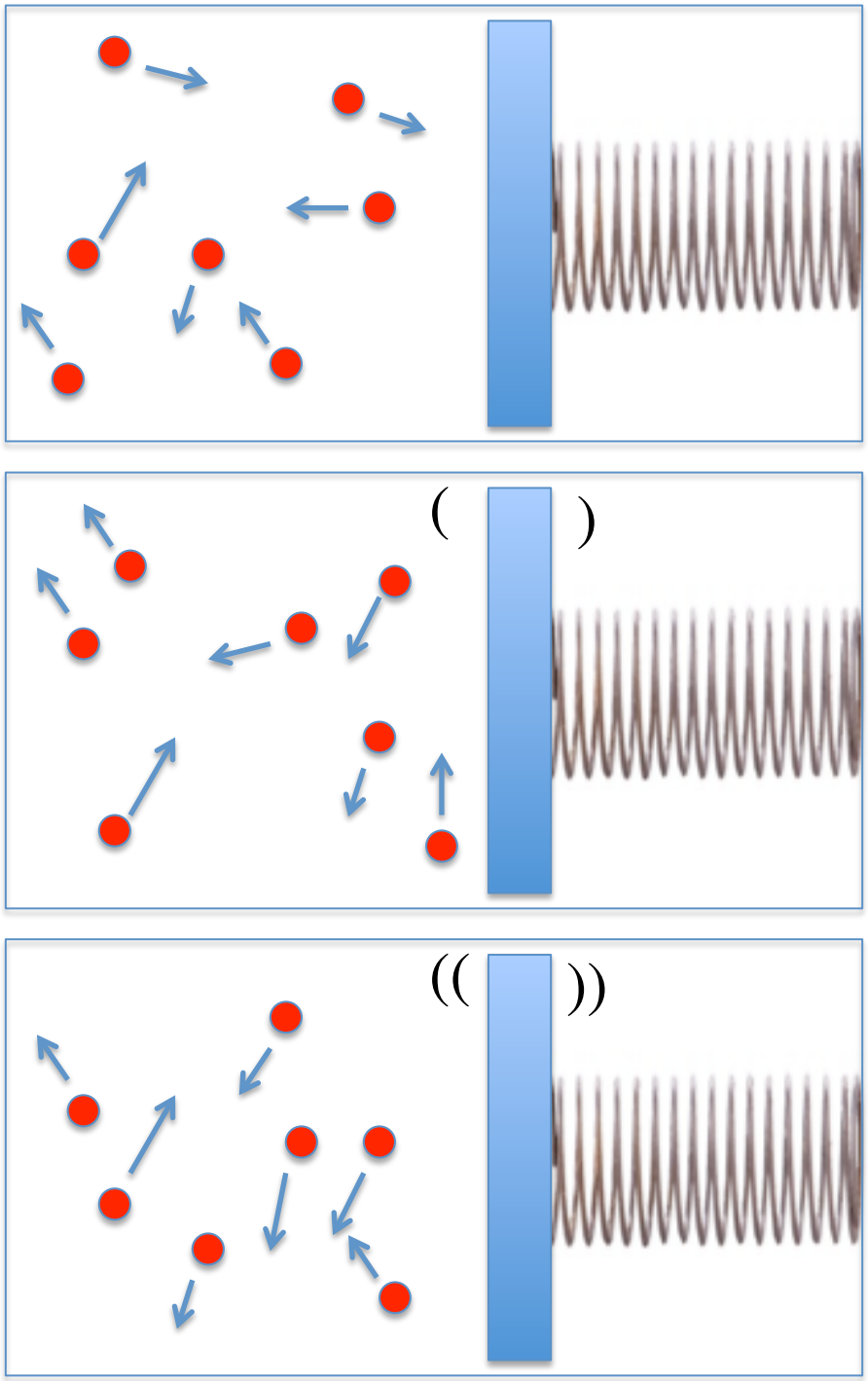


Second case

We now start with the movable set at rest and leave it free.

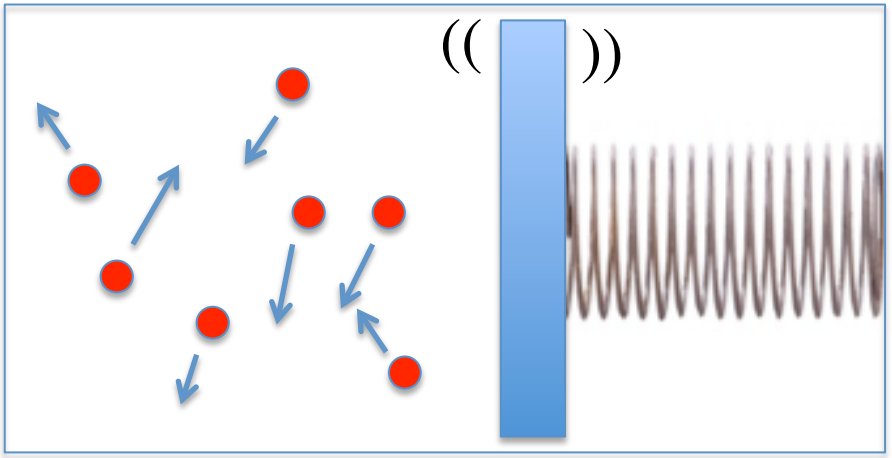
After few seconds we will see that the set starts to move with increasing oscillation amplitude that soon reaches **an equilibrium condition** at the very same value (on average) of the first case.

In both cases the two different roles of damping-force and pushing-force has been played by the gas.
This fact led to think that there must be a **connection between the process of dissipating energy** (a typical irreversible, i.e. non-equilibrium process) and the process of **fluctuating at equilibrium** with the gas.



Fluctuation-Dissipation connection

This fact led to think that there must be a **connection between the process of dissipating energy** (a typical irreversible, i.e. non-equilibrium process) and the process of **fluctuating at equilibrium** with the gas.



In order to unveil such a link we need to introduce a more formal description of the dynamics of the movable set.

This problem has been addressed and solved by Albert Einstein (1879 - 1955) in his 1905 discussion of the Brownian motion and subsequently by **Paul Langevin** (1872 - 1946) who proposed the following equation:

$$m\ddot{x} = -m\gamma\dot{x} - \frac{dU}{dx} + \xi(t)$$

Fluctuation-Dissipation connection

$$m\ddot{x} = -m\gamma\dot{x} - \frac{dU}{dx} + \xi(t)$$

x(t) is the random force that accounts for the incessant impact of the gas particles on the set, assumed with zero mean, Gaussian distributed and with a flat spectrum or, delta-correlated in time (white noise assumption):

$$\langle \xi(t_1)\xi(t_2) \rangle = 2\pi\, G_R \delta(t_1 - t_2)$$

G_R accounts for the fluctuation intensity. There must be a connection with the dissipation γ.

This relation has been established within the linear response theory (that satisfies the equipartition of the energy among all the degrees of freedom) initially by **Harry Theodor Nyquist** (1889 - 1976) in 1928, and demonstrated by **Callen and Welton** in 1951.

$$G_R = \frac{mK_BT}{\pi}\gamma$$

Fluctuation-Dissipation Theorem FDT

Why is FDT important?

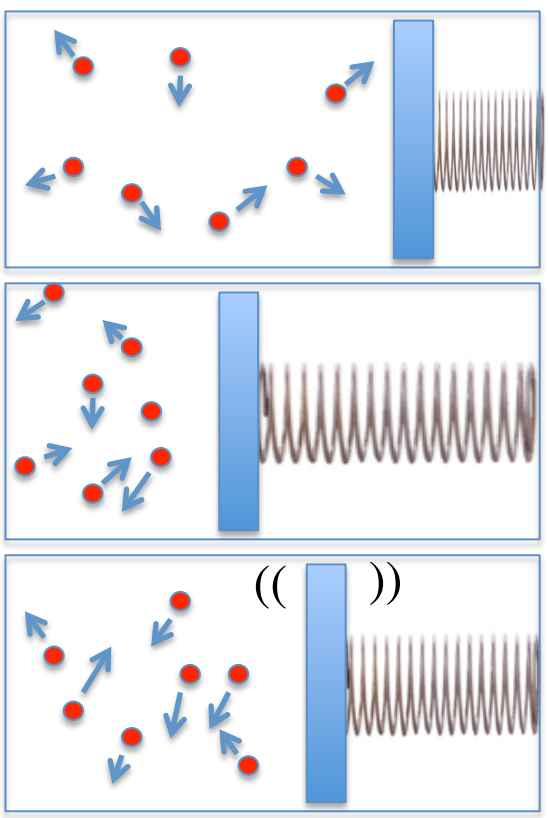
It is important because it represent an ideal bridge that connects:

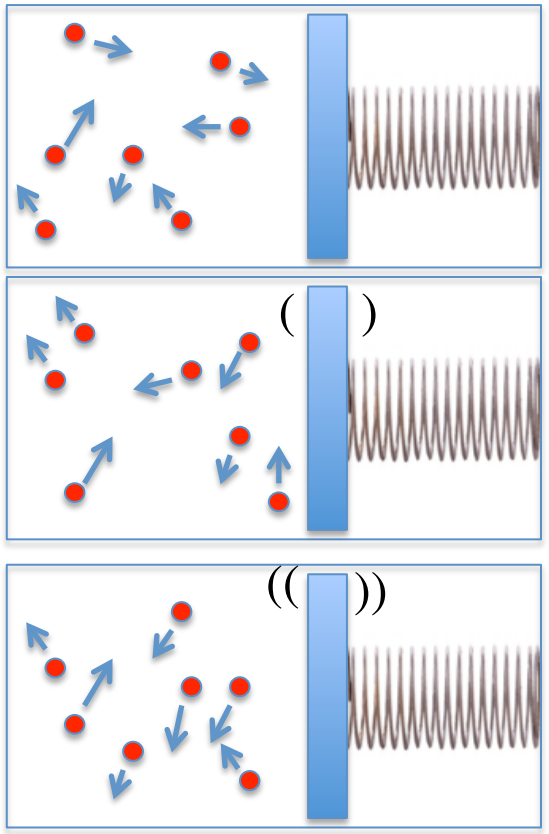
the equilibrium properties of our thermodynamic system
(represented by the amplitude and character of the fluctuations)

with

the non-equilibrium properties
(represented here by the dissipative phenomena due to the presence of the friction).

ENTROPY production – FLUCTUATION CONNECTION





dissipative properties = the capacity to produce entropy, are intrinsically connected to the equilibrium fluctuations.

Summary

- All matter is made by particles
- We can say that the energy is associated with “how much” the particles move.
- We can say that the entropy is associated with “the way” the particles moves.
- Entropy according to Boltzmann: $S = K_B \log W$
- W is the number of configurations

Second Principle: “In a spontaneous transformation the entropy always increases“ Is equivalent to say that “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. ”

Friction: there is a connection between the process of dissipating energy (a typical irreversible, i.e. non-equilibrium process) and the process of fluctuating at equilibrium with the gas: the Fluctuation-Dissipation Theorem.

To learn more:

Energy Management at the Nanoscale
L. Gammaitoni

in the book "ICT - Energy - Concepts Towards Zero - Power Information and Communication Technology" InTech, February 2, 2014