The Physics of Energy

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Entropy

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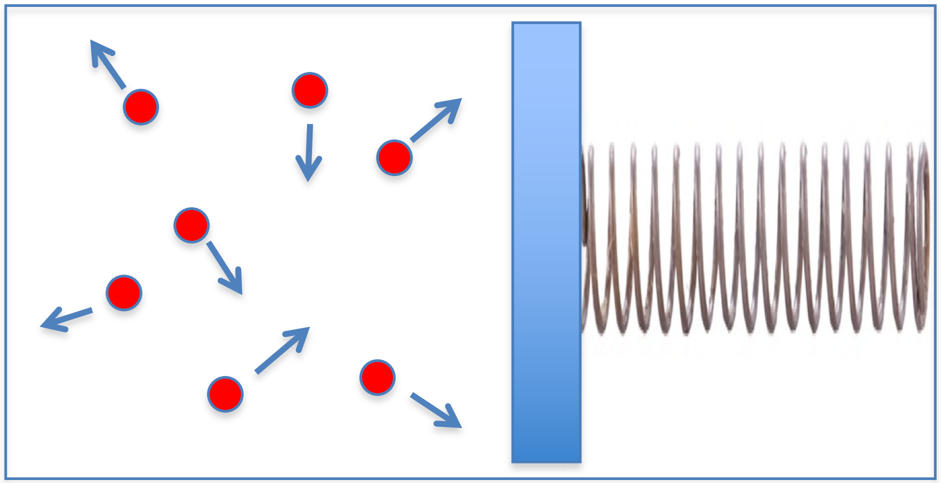
Energy and Entropy: the microscopic interpretation

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…

Let's consider the usual ideal gas in the kinetic theory



Each sphere has the same mass m and velocity v

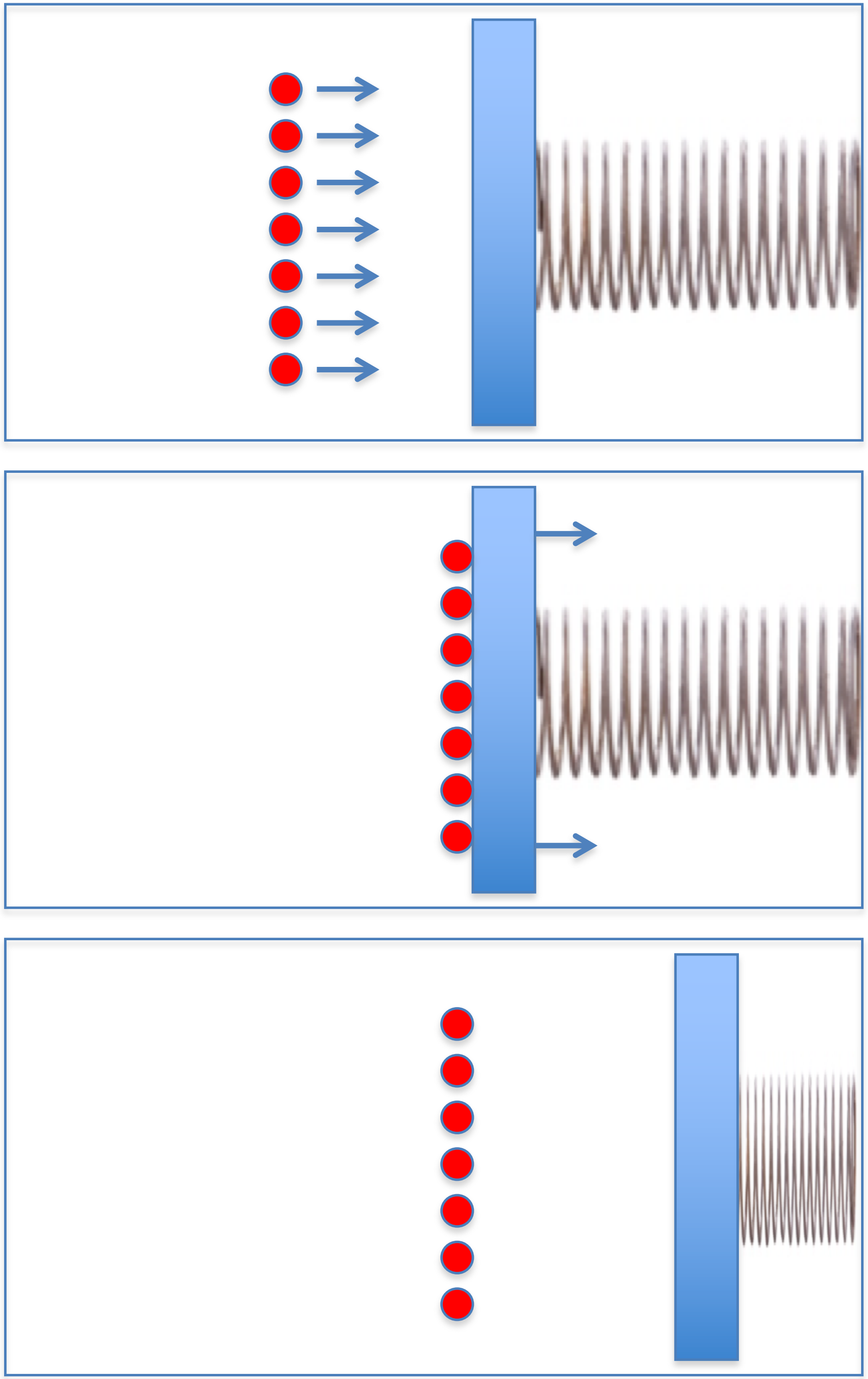
Consider the two cases…

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

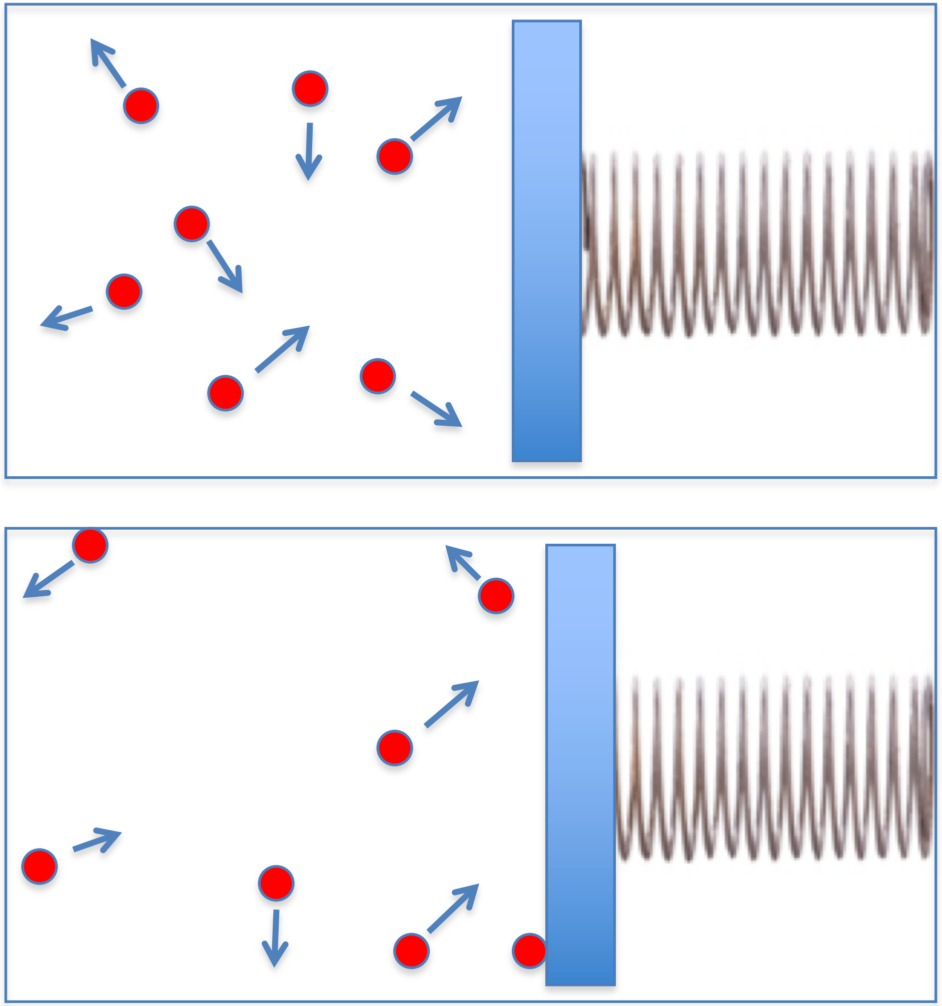
$$\frac{1}{2} M\, v^2 = \frac{1}{2} k\, x_1^2 \ = U$$



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.



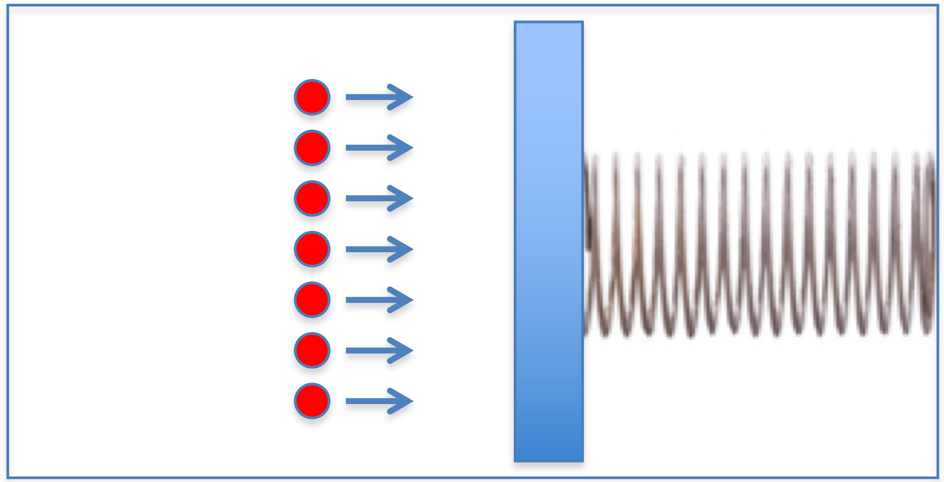
The **energy of the gas is still the same (so is its temperature T)** but in this case the set will be subjected at random motion with an average compression of the spring such that its average energy is U/N.
This is also the maximum work that we can recover from the potential energy of the movable set.

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

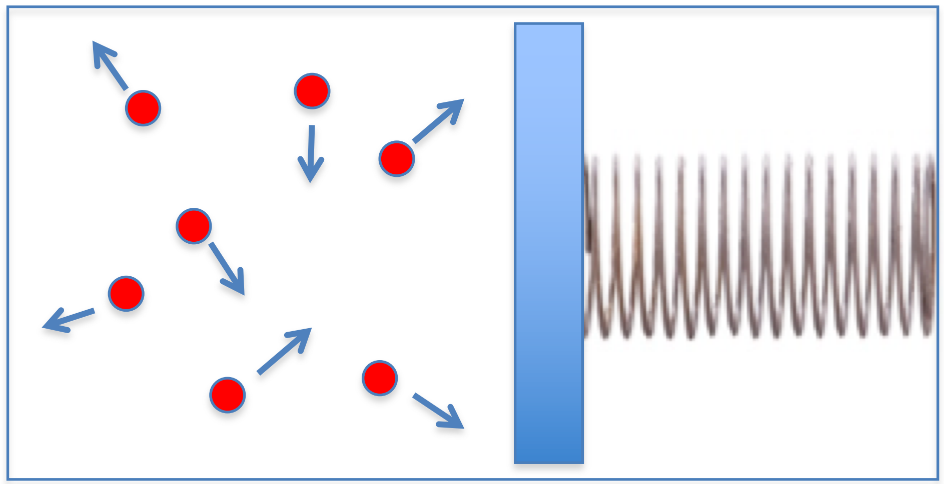
Thus the systems that have the smaller entropy have the larger capability of performing work.

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.

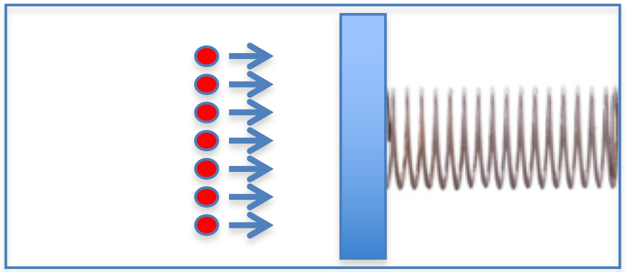
The microscopic perspective

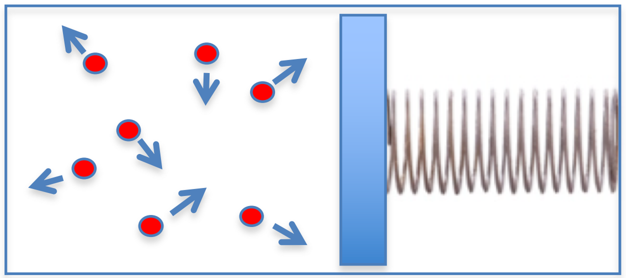
The entropy is associated with “the way” the particles moves.

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

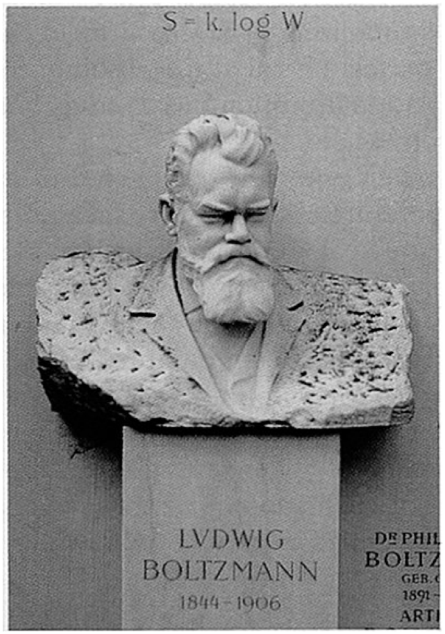
many ways = high entropy

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.

FRICTION

How can we describe friction on a microscopic scale?

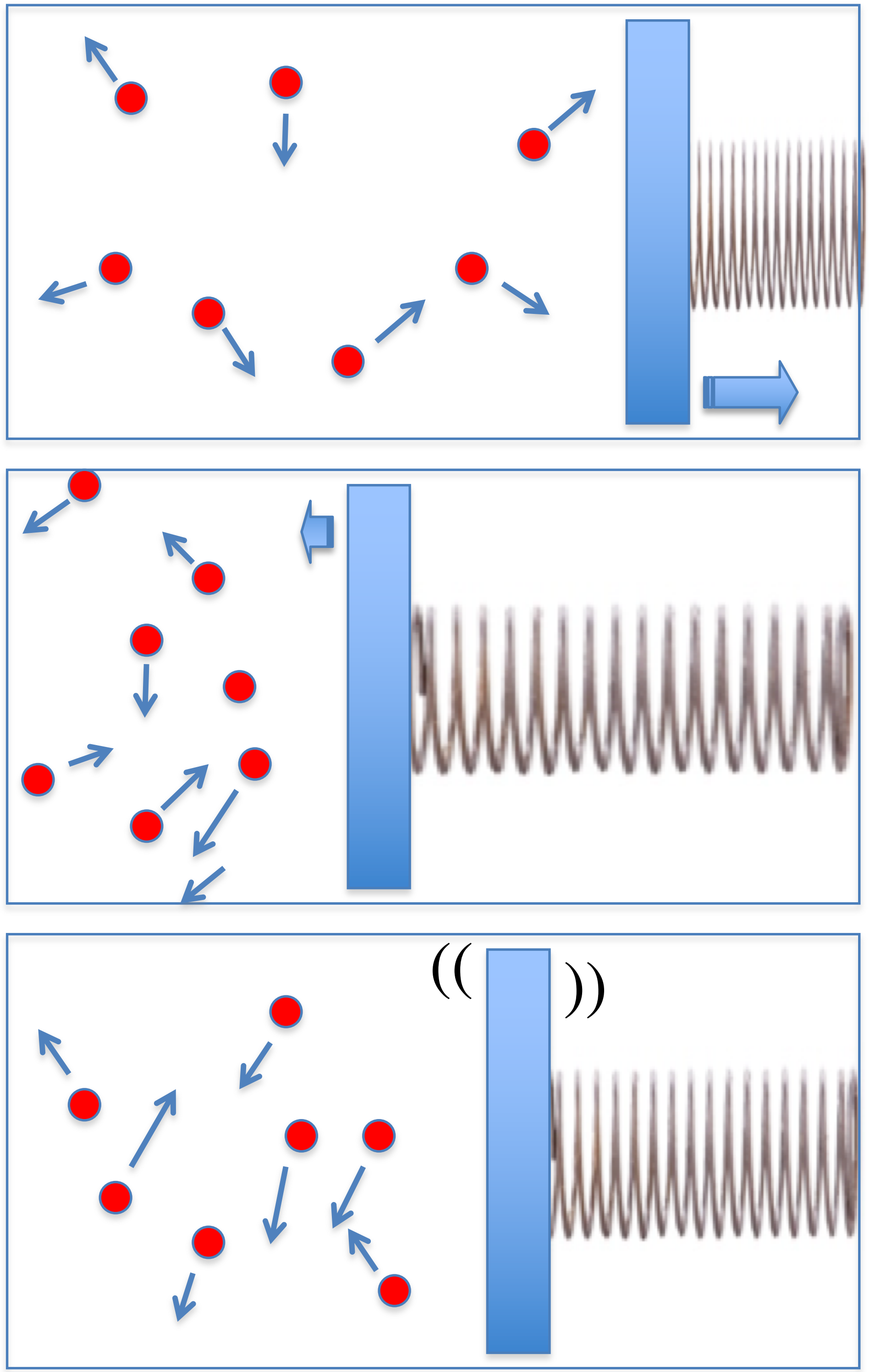
Consider the two cases…

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.

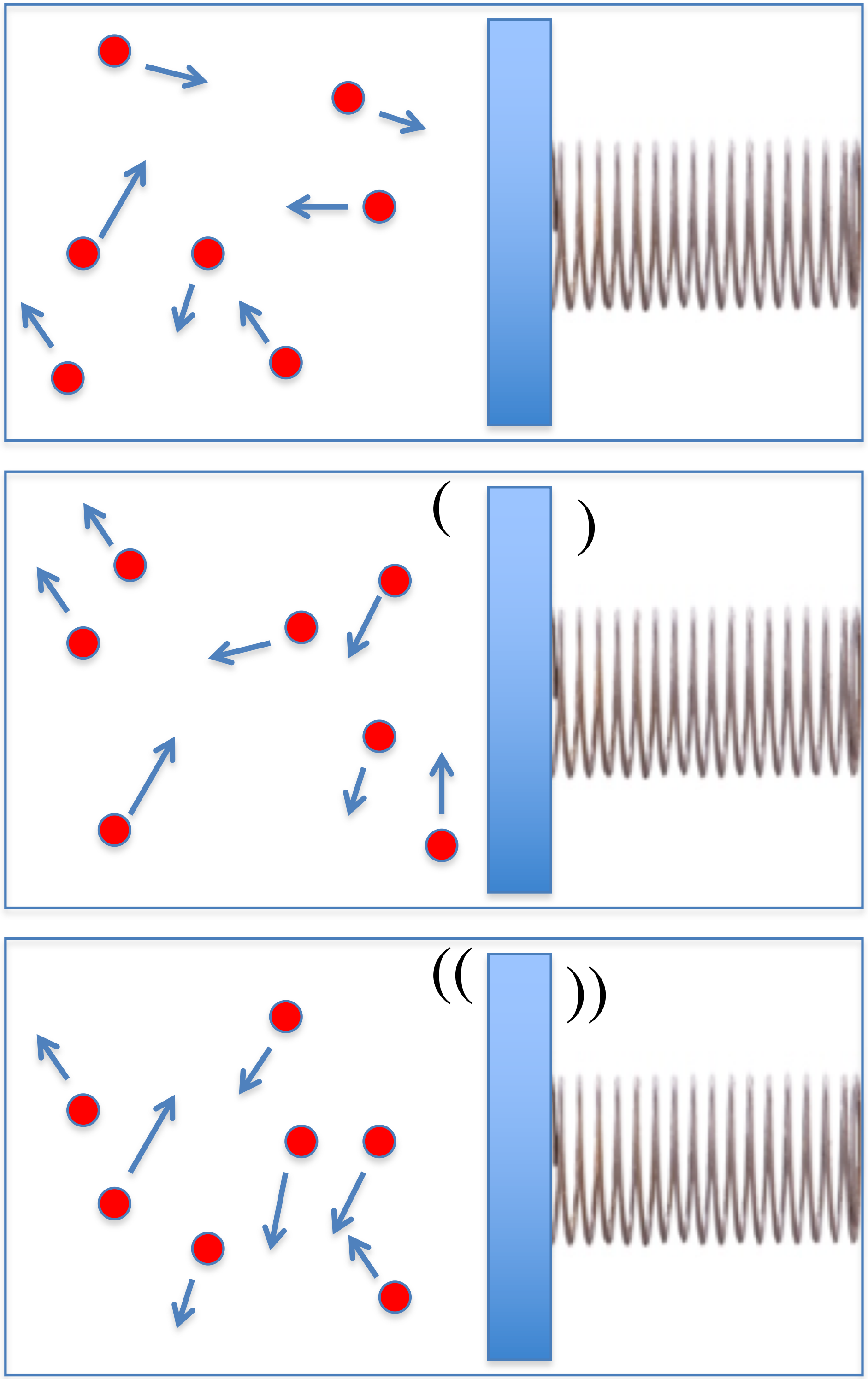


Second case

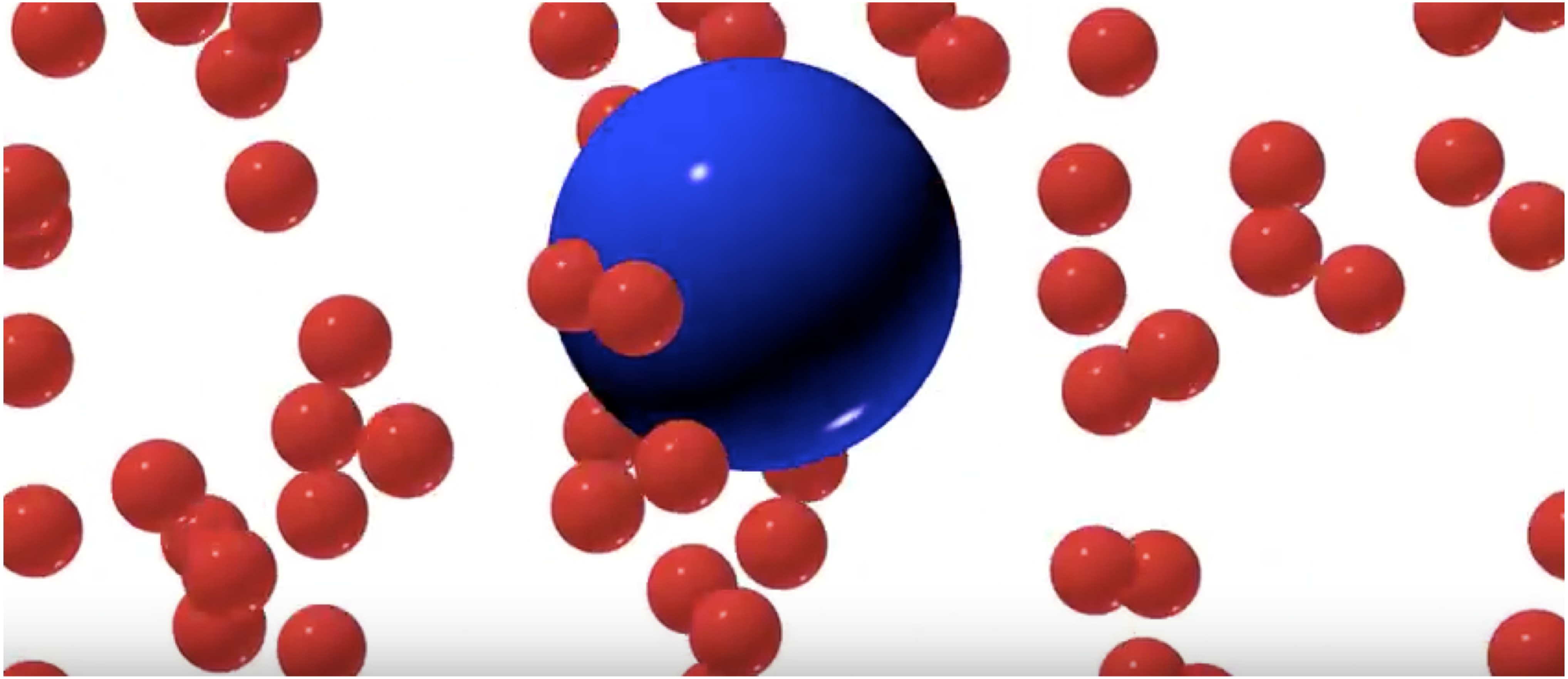
We now start with the movable set at rest and leave it free.

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.



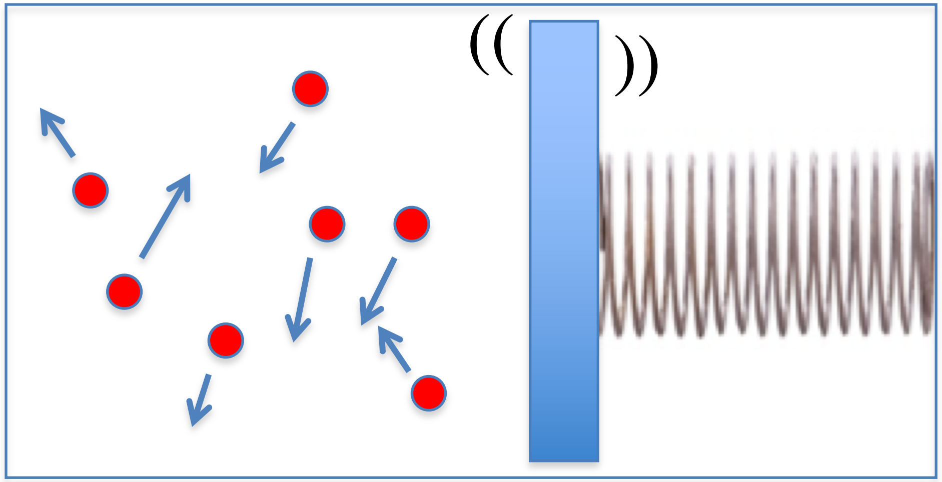
Brownian motion



https://www.youtube.com/watch?v=6VdMp46ZIL8

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) .

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