The Physics of Energy

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Relaxation processes

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The Physics of Energy

Equilibrium

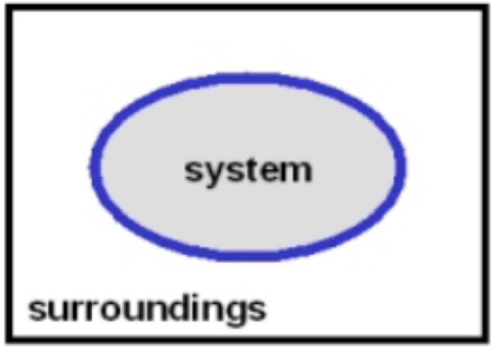
A system can undergo a spontaneous transformation until it reaches a state of equilibrium.

What is it?

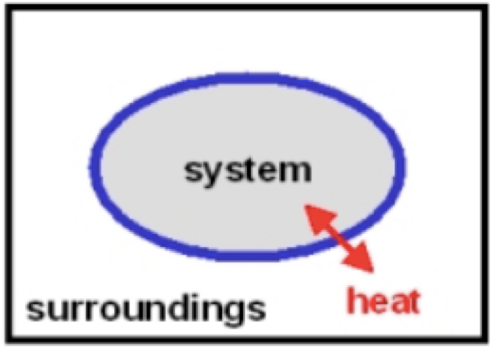
Preliminary notions

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

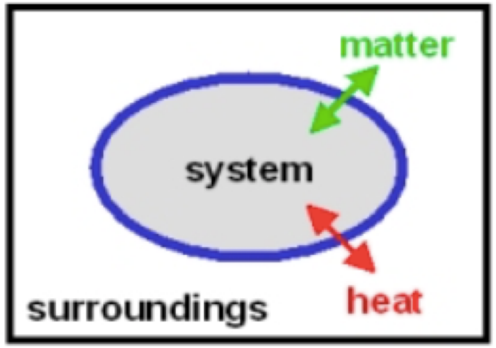
System



"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

Equilibrium

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

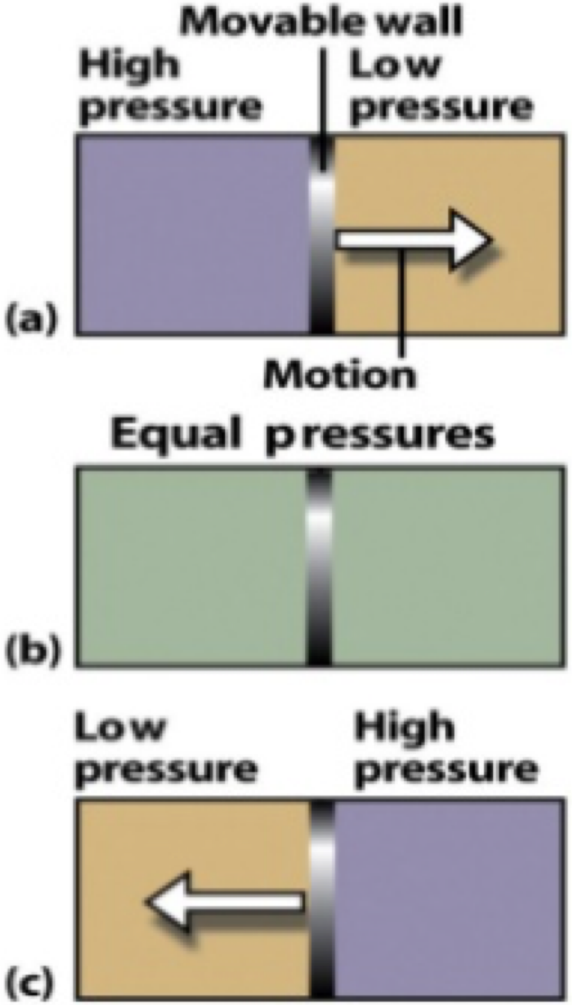
What is it?

The importance of the notion of relaxation time

Mechanical equilibrium

The condition of equality of pressure on either side of a movable wall / boundary.

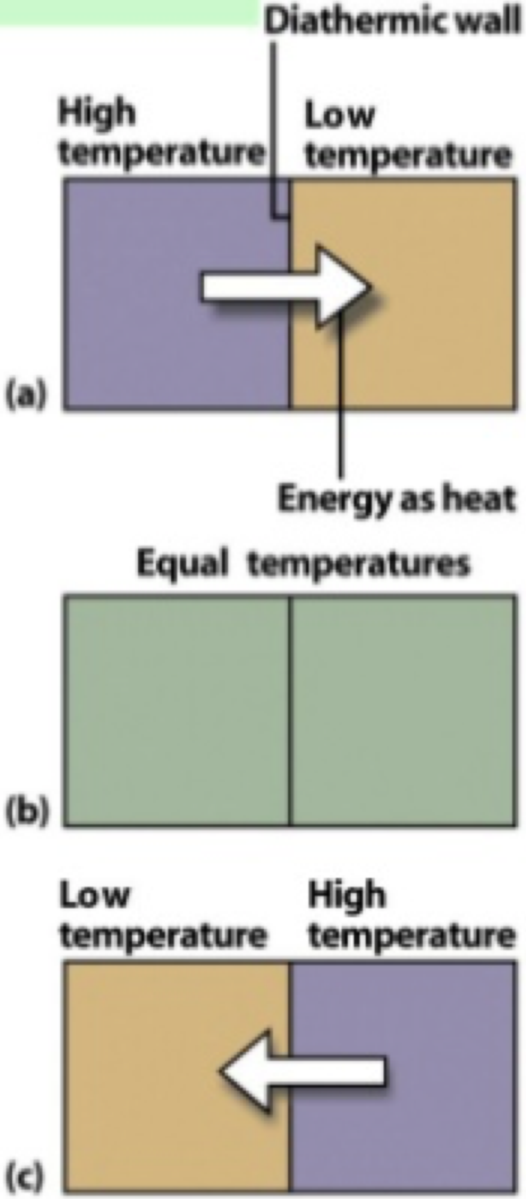
No unbalanced forces act on or within the system – does not undergo acceleration or no turbulence inside the system



Thermal equilibrium

Thermal equilibrium between system and the surroundings, is a condition in which there is no change in the properties of the system or surroundings when they are separated by a thermally conducting wall.

In other words, **Thermal Equilibrium** is a condition in which no change of state occurs when two objects A to B are in **contact through a diathermic boundary.**



Material Equilibrium

Concentrations of the chemical species in the various parts of the system are constant with time

a) No net chemical reactions are occurring in the system

b) There is no net transfer of matter from one part (phase) of the system to another or between the system and its surroundings

Phase: a homogeneous part of a system is called a phase

For thermodynamic equilibrium, all three kinds of equilibrium must be present

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

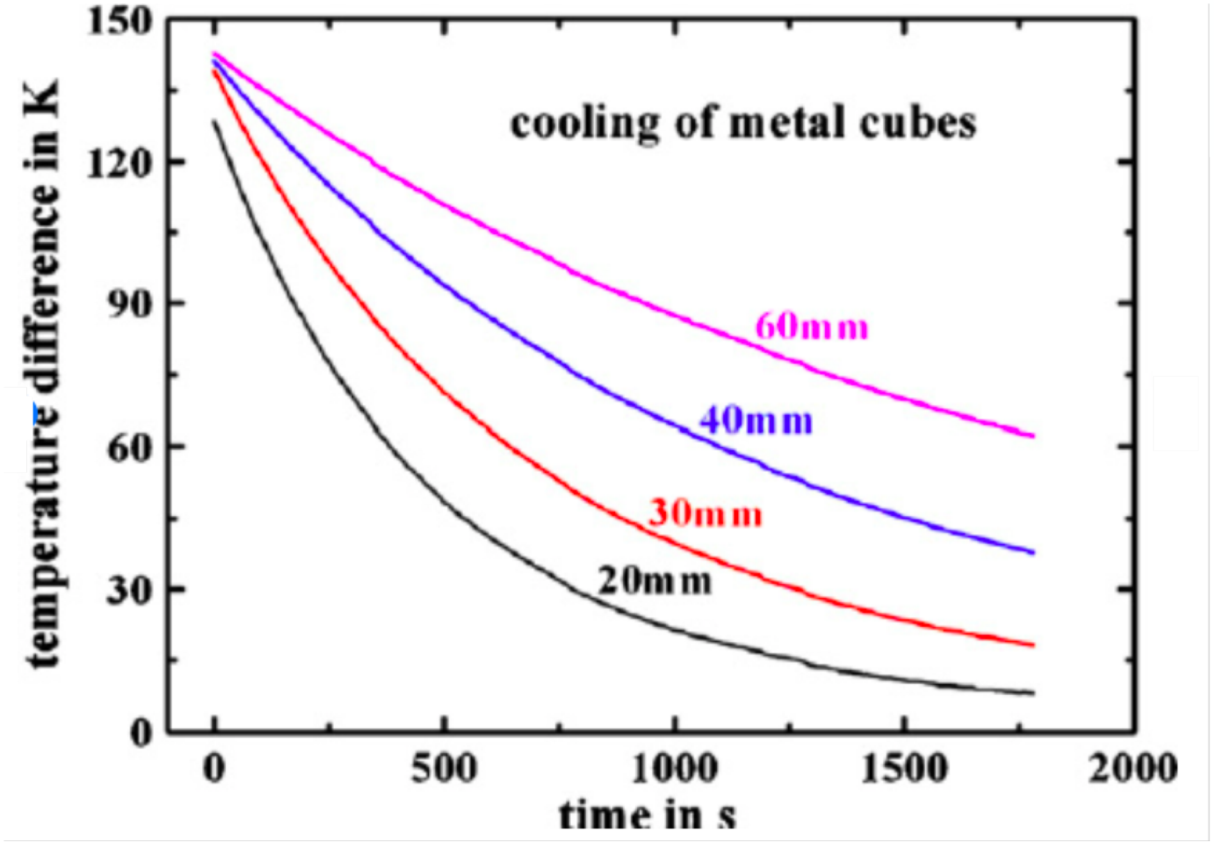
Entropy to reach a maximum

$$F = U - T S$$

Minimum free energy

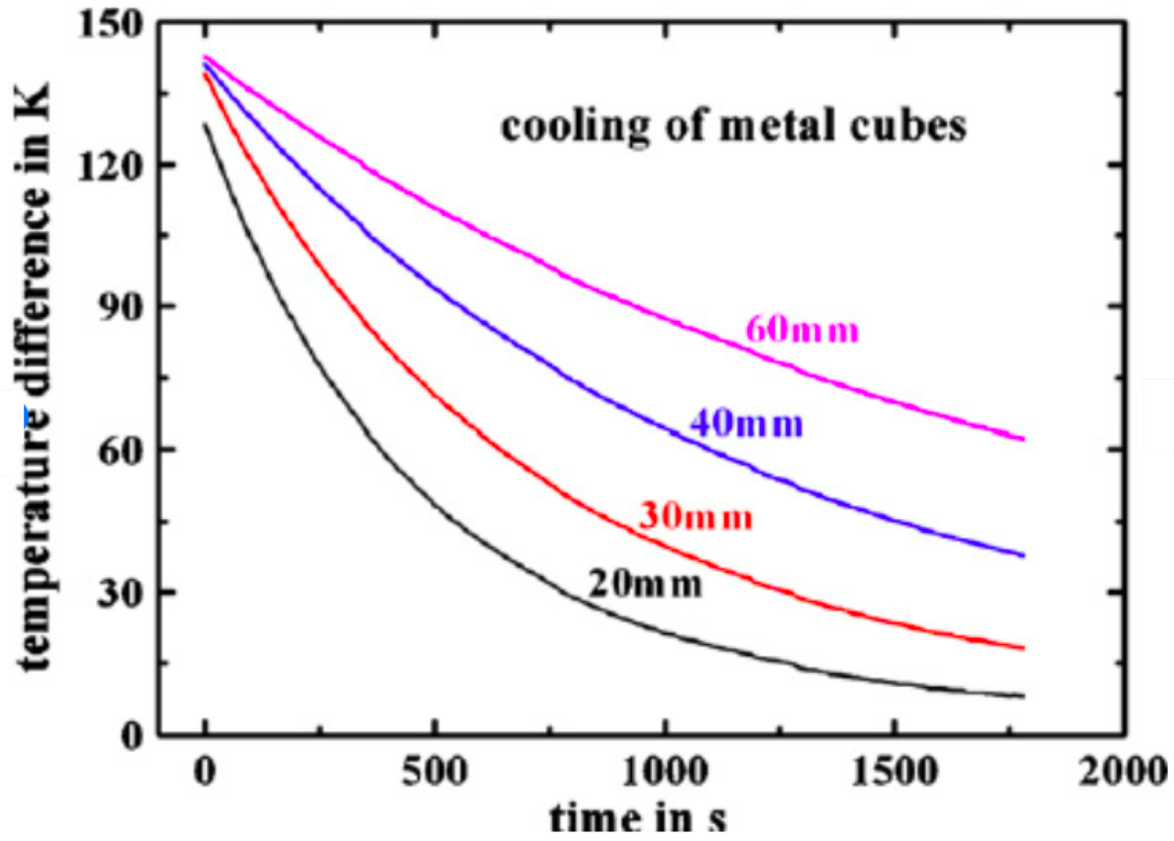
Equilibrium

Example: cooling of a metal cube in a fluid.



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

2) What is the law regulating the temperature vs 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.

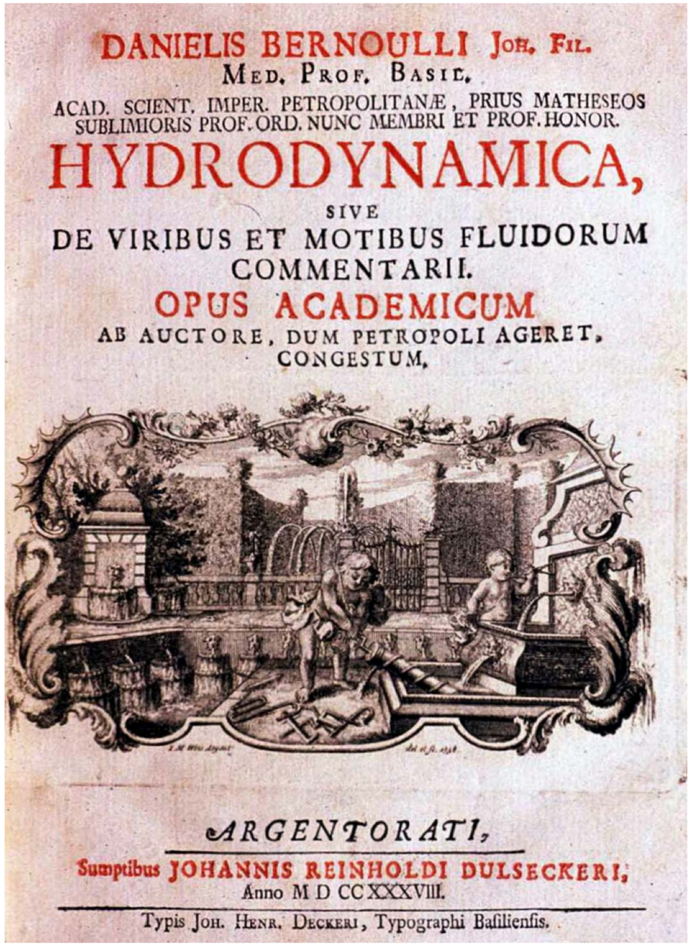
This Epicurean atomistic point of view was rarely considered in the subsequent centuries, when Aristotlean ideas were dominant.

The microscopic interpretation of heat: the kinetic theory

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

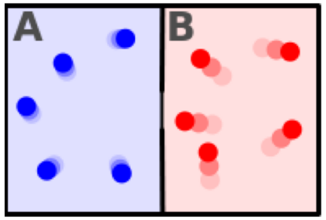
Physicist James Clerk Maxwell, in his 1871 classic Theory of Heat, was one of many who began to build on the already established idea that **heat has something to do with matter in motion.**

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 CCXXXVIII.
Typis Joh. Henr. Deckeri, Typographi Baſilienſis.

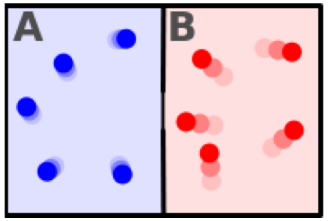


$T_1 < T_2$

The microscopic interpretation of heat: the kinetic theory

The theory for ideal gases makes the following assumptions:

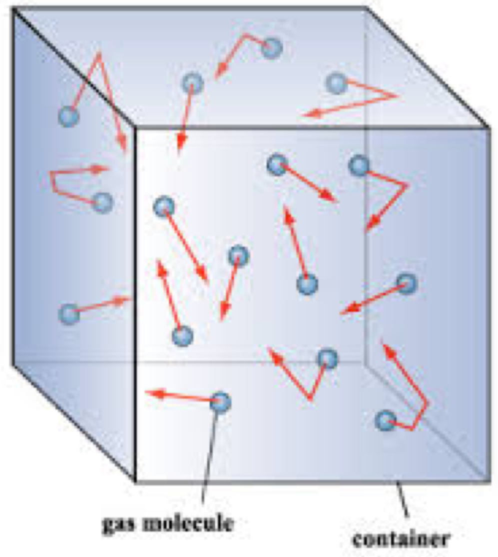
- The gas consists of very small particles known as molecules. The average distance separating the gas particles is large compared to their size.
- These particles have the same mass.
- The number of molecules is so large that statistical treatment can be applied.
- These molecules are in constant, random,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



$T_1 < T_2$

How do we link Temperature and Energy?

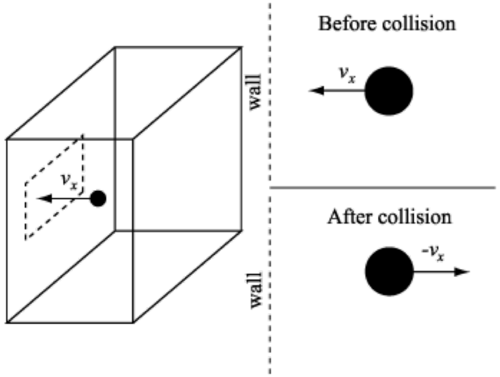
Pressure



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:

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

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

Thus

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

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

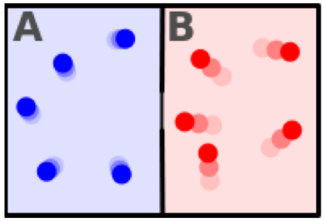
we have

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

and thus:

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

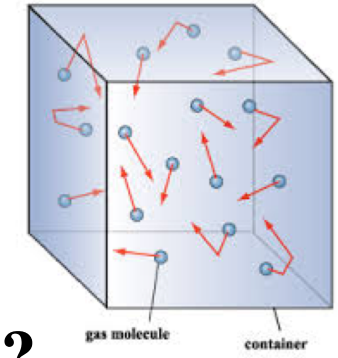
Than links average **kinetic energy** of a molecule with temperature.



$T_1 < T_2$

The microscopic interpretation of heat: the kinetic theory

OK fine.



But what about Entropy?

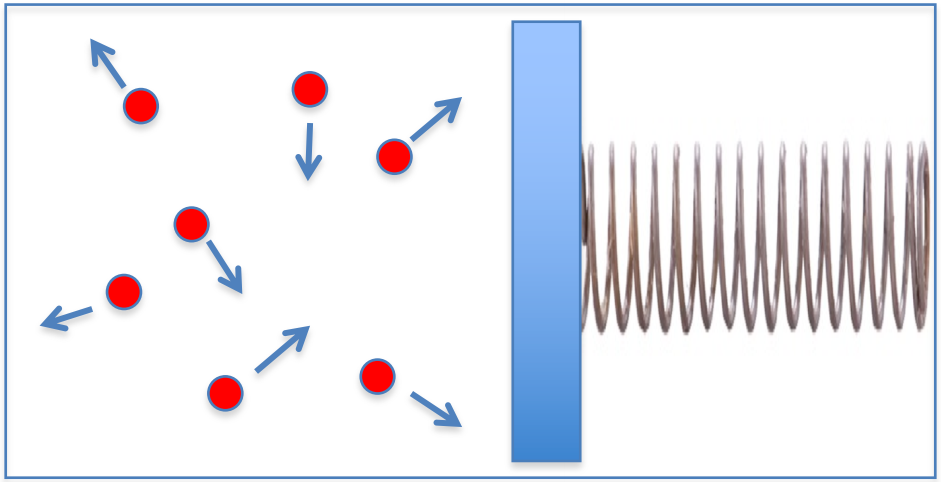
Energy and Entropy: the microscopic interpretation

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…

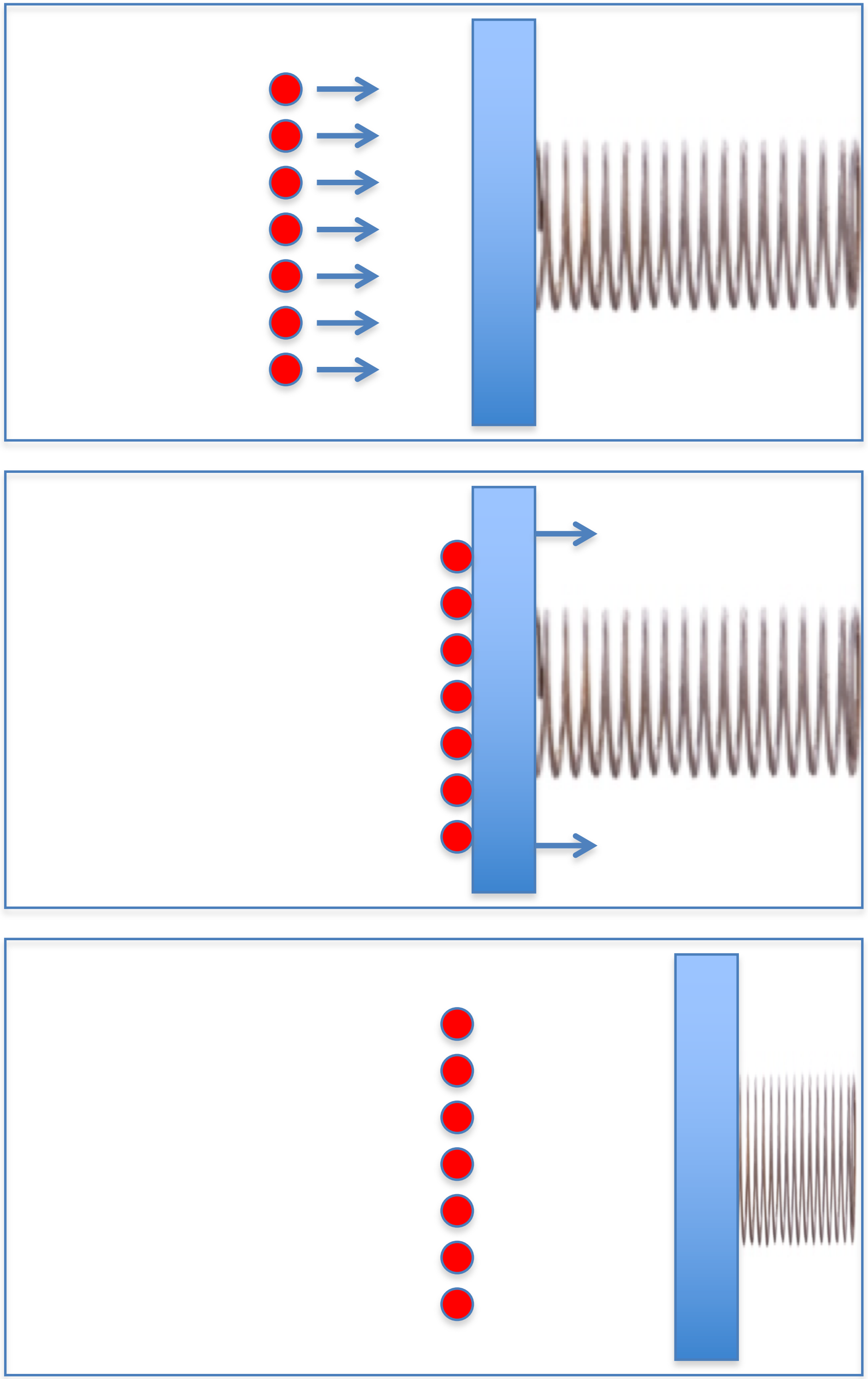
First case

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

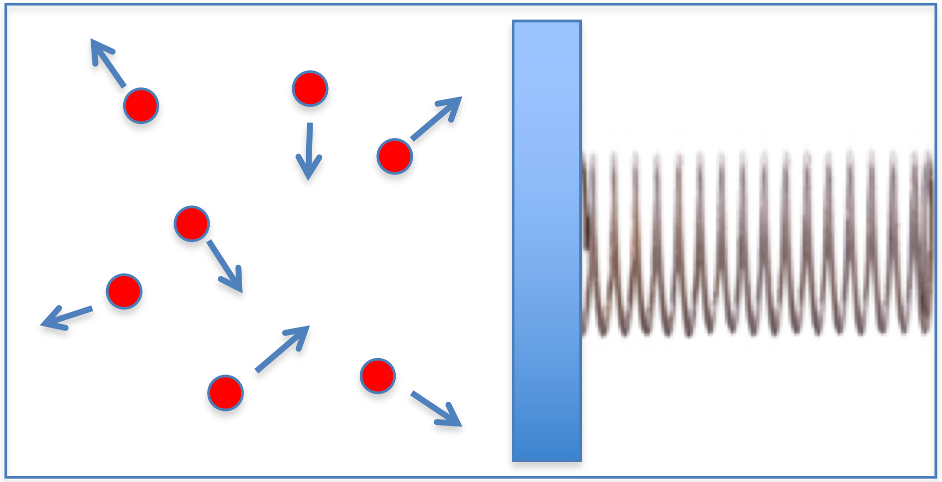
$$\frac{1}{2}M\,v^2 = \frac{1}{2}k\,x_1^2 = U$$

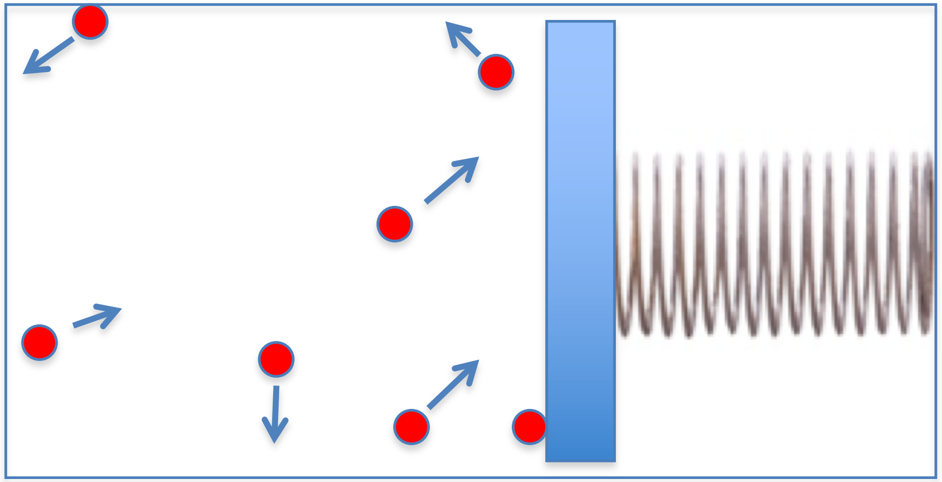
We can always recover the potential energy U when we desire and use it to perform work. In this case we can completely transform the energy of the gas particle into work.



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.

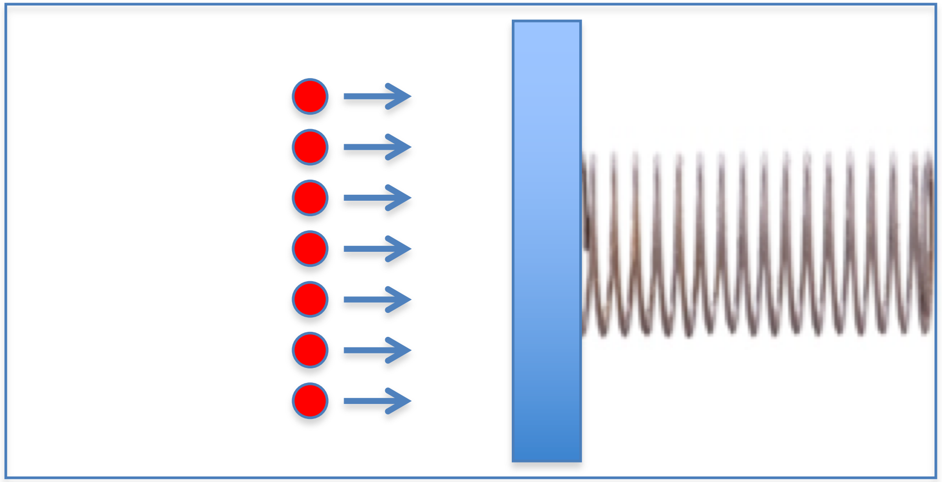
This is also the maximum work that we can recover from the potential energy of the movable set.

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

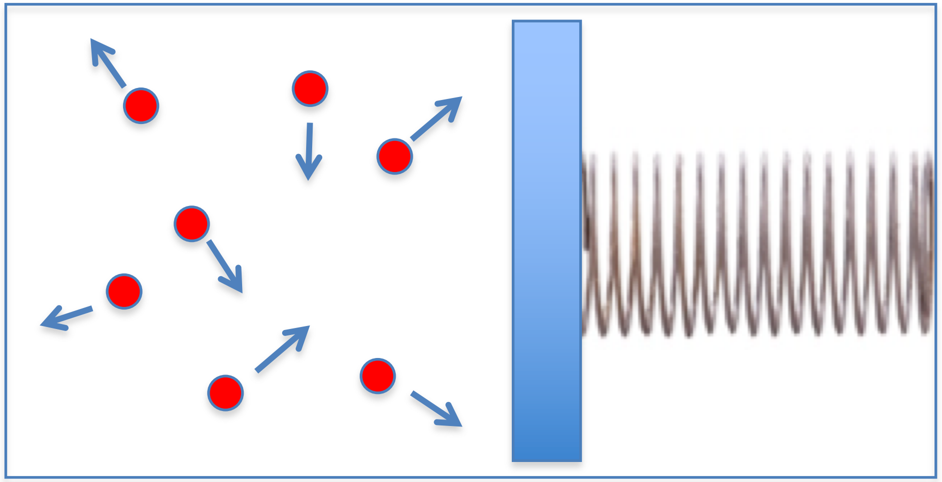
Thus the systems that have the smaller entropy have the larger capability of performing work.

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

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