From microscopic to macroscopic
Some consideration and examples on statistical mechanics in and out of equilibrium.

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Plan of the talk.

- Introduction to the physics of gases.
- Classical heuristic results.
- The Kac model and gas kinetic.
- Classical results on the Kac model.

A gas is an example of a system composed by a large number of microscopic element (the atoms or molecules) interacting on a microscopic scale. Or at least this is what we have been told in high school.

Atoms and molecules move very fast and collide like little billiard balls. At the macroscopic level this room looks extremely chaotic.

At the macroscopic level, we do not see atoms or molecules, collisions or interactions, everything look pretty stable or "in equilibrium".

We know how to characterize this equilibrium with few physical quantities: temperature T, pressure P and density δ.

These quantities satisfy precise and simple relations, the most famous of those being the Law of Perfect Gases:

$$P = \delta k_B T.$$

Question: how can this two pictures be consistent? Even better: can we derive the macroscopic behaviour form the microscopic laws?

Here are some physical quantities for oxygen at ambient condition

- temperature $T = 273$ K
- pressure $P = 1.01 \times 10^5$ N/m^2
- number density $\delta = M/V = 2.7 \times 10^{25}$ molecules/m^3
- kinetic radius $r = 1.73 \times 10^{-10}$ m
- occupied volume fraction $4\pi r^3 \delta/3 = 5.85 \times 10^{-4}$
- average speed $v = 1.58 \times 10^2$ m/s
- mean free path $\rho = 1.0 \times 10^{-7}$ m
- mean free time $\lambda = 0.6 \times 10^{-5}$ s

How does the Law of Perfect Gases, and many other macroscopic laws, emerge from this microscopic chaos?

Gas Kinetic.

A very simplified model of a gas at temperature $T = \beta^{-1}$ has the following ingredients:

1. a very large number M of particles in a container of volume V;

2. the particles are hard spheres of small radius r;

3. the collisions are elastic;

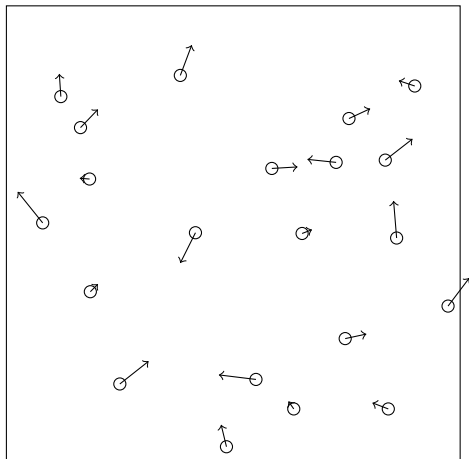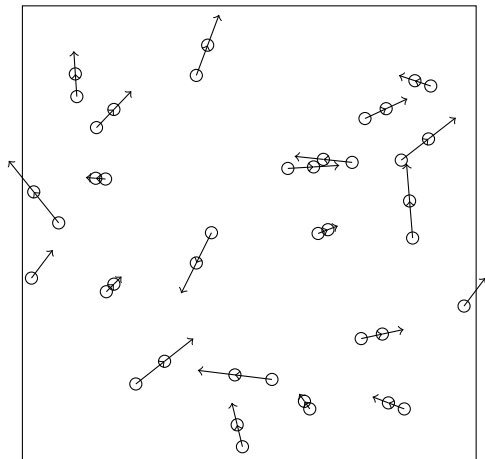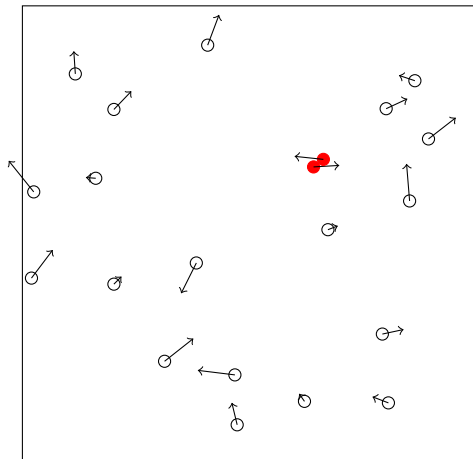4. the average kinetic energy of the particles is proportional to T.

1000 particles initially confined in a quarter of the container and with independent velocity uniformly distributed in $[-1, 1]$.
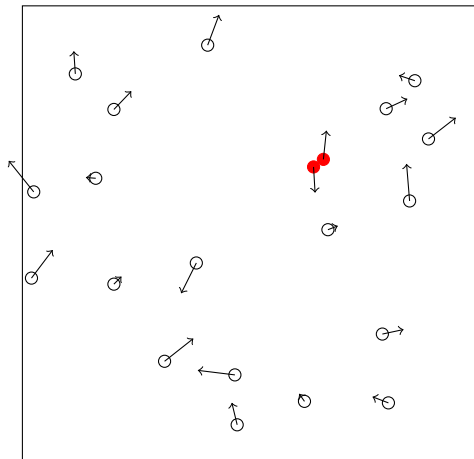
Left panel: positions. Right panel: histogram of the x-velocity (time smoothed).
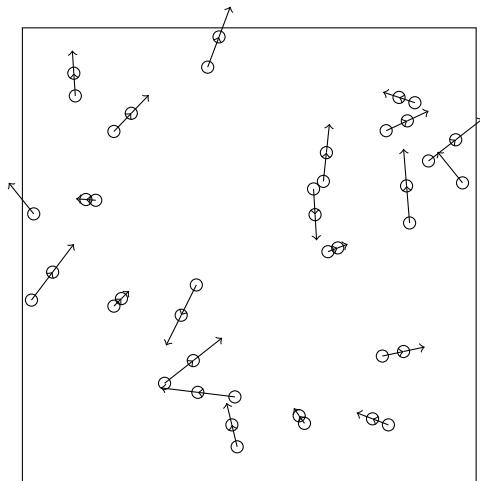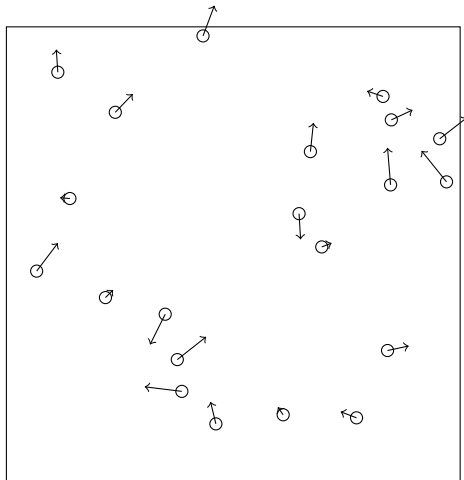
Heat, like gravity, penetrates every substance of the universe, its ray occupy all parts of space. The object of our work is to set forth the mathematical laws which this element obeys. The theory of heat will hereafter form one of the most important branches of general physics.

— *Théorie analytique de la chaleur, 1822*
— Jean Baptiste Joseph Fourier

But whatever may be the range of mechanical theories, they do not apply to the effects of heat. These make up a special order of phenomena, which cannot be explained by the principles of motion and equilibria.

— *Ibidem*

Consider a gas in a thermally isolating container and let

- V be the container with volume $|V|$;

- $N \simeq 10^{25}$ be the number of particles.

- If the temperature is high enough we can neglect quantum effect: particle are classical. They can be thought as hard spheres of radius r and mass m.

- The i-th particle has a momentum $\mathbf{p}_i \in \mathbb{R}^3$ and a position $\mathbf{q}_i \in V$

The system is thus described by a point in

$$\mathscr{T} = \mathbb{R}^{3N} \times V^N.$$

A particle moves on straight line with velocity $\mathbf{p}_i/m$ till it collides with another particle or with the walls of the container.

The gas is in equilibrium.

We can assume that the probability $f(\mathbf{p}_i, \mathbf{q}_i)$ of finding particle i at position $\mathbf{q}_i$ with momentum $\mathbf{p}_i$ is independent of $\mathbf{q}_i$ (system is uniform) and depends only on $|\mathbf{p}_i|$ (rotational invariance).

Let ΔS be a small part of the wall with area $|\Delta S|$ and inward normal vector $\mathbf{n}$.
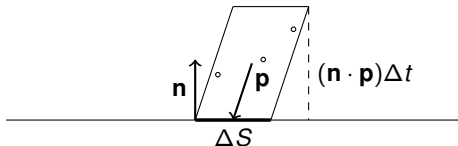
The number of particle with momentum $\mathbf{p}$ that will collide with ΔS in the next Δt is

$$(\mathbf{p} \cdot \mathbf{n})\Delta S \Delta t \ \ f(\mathbf{p}) \, d\mathbf{p} \ \ \frac{\delta}{m}$$

where $\delta = N/|V|$ is the number density.

Since during a collision a particle momentum changes by 2($\mathbf{p} \cdot \mathbf{n}$), the total momentum exchanged by the gas with ΔS in the time Δt is

$$\Delta \mathbf{P} = 2 \int_{(\mathbf{p} \cdot \mathbf{n} < 0)} \frac{1}{m} (\mathbf{p} \cdot \mathbf{n})^2 f(\mathbf{p}) \, d\mathbf{p} \, \Delta S \Delta t = \frac{2}{3} \int \frac{|\mathbf{p}|^2}{2m} f(\mathbf{p}) \, d\mathbf{p} \, \Delta S \Delta t$$

But we know that the average kinetic energy is proportional to the temperature. More precisely

$$\int \frac{|\mathbf{p}|^2}{2m} f(\mathbf{p}) \, d\mathbf{p} = \frac{3}{2} k_B T$$

where k_B is the Boltzmann constant and T the temperature.

Clearly the pressure is given by

$$P = \frac{\Delta \mathbf{P}}{|\Delta S| \Delta t}$$

Since during a collision a particle momentum changes by $2(\mathbf{p} \cdot \mathbf{n})$, the total momentum exchanged by the gas with ΔS in the time Δt is

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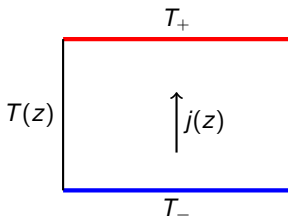where k_B is the Boltzmann constant and T the temperature.

Clearly the pressure is given by

$$P = \frac{\Delta \mathbf{P}}{|\Delta S| \Delta t} = \delta k_B T$$

What about heat conduction.

Suppose now that the top of V is in contact with a "heat reservoir" at temperature T_+ and the bottom with a heat reservoir at temperature T_-.

This is called a Non Equilibrium Steady State. It is non equilibrium because we have a flux of energy through the system. But it is a steady state because the local density, pressure and temperature do not vary in time.

The temperature $T(z)$ of the gas and the heat current $j(z)$ will depend on the position in V only through the vertical coordinate z.

Fourier's Law states that

$$j(z) = -c(T)\frac{dT(z)}{dz}$$

where $j(z)$ is the heat current in the z direction and $c(T)$ is the thermal conductivity.

Local Equilibrium

What is $T(z)$? I know what is the temperature of a gas in equilibrium. We saw it is linked to the mean kinetic energy of the atoms (or molecules) that form the gas.

We draw a grid on our system and imagine that it is made up of a large number of small "virtual" boxes. In one cubic meter of oxygen there are roughly 10^{25} molecules. If we divide each side in 10^5 small intervals we get 10^{15} small boxes of side 10^{-5} meters. Each of them still contains 10^{10} molecules!
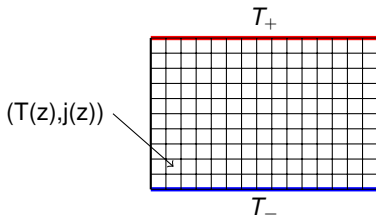
Each of this small box can be considered as a thermodynamical system in equilibrium. It interacts with its neighbor boxes via exchange of particles or collisions between particles near their boundary.

This is called the *local equilibrium* description of a macroscopic gas (or any other object).

Local equilibrium with 25 volume elements.

It will now be assumed that, although the total system is not in equilibrium, there exists within small mass elements a state of "local" equilibrium for which the local entropy s is the same function of u, v and c_k as in real equilibrium.

— *Non-Equilibrium Thermodynamics, 1962*
— Sybren Ruurds de Groot and Peter Mazur

The hypothesis of "local" equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it.

— *Ibidem*

The number of collision ν a particle suffers in a time t is:

$$\nu = \pi d^2 \, \bar{v} t \, M/V$$

and $n_V = $ molecules per unit volume
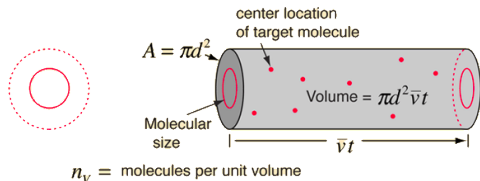
Thus the time between two collisions of the same particle (*mean free time*) is:

$$\lambda \simeq \frac{1}{\bar{v} \delta r^2}$$

and the space travelled by the particle between two collisions (*mean free flight*) is:

$$\rho = \lambda \bar{v} \simeq \frac{1}{\delta r^2}.$$

A particle initially at height z with $p_z > 0$ will travel for a distance ρ and will reach, in average, a height $z + \rho/\sqrt{3}$.

It will thus carry a kinetic energy proportional to $T(z)$ from z to $z + \rho/\sqrt{3}$.

In the same way a particle initially at $z + \rho/\sqrt{3}$ with $p_z < 0$ will carry a kinetic energy proportional to $T(z + \rho/\sqrt{3})$ from $z + \rho/\sqrt{3}$ to z.

As before, the flux of particle with momentum **p** through a surface perpendicular to the z axis is proportional to p_z and the number density δ.

Finally the momentum of the particles at z is, in average, proportional to $\sqrt{T(z)}$.

Putting all together we get

$$j(z) \simeq \delta \sqrt{T(z)} \left(T(z) - T(z + \rho/\sqrt{3}) \right) \simeq -r^{-2} \sqrt{T(z)} \frac{dT(z)}{dz}$$

Thus we find that

$$c(T) = Kr^{-2} \sqrt{T(z)}$$

where K is a universal constant. Observe that:

- c is independent from the density δ;

- it behave as $\sqrt{T}$.

- ρ is a good size for our "volume elements". In our oxygen sample we have $\rho \simeq 10^{-7}$ meters. A little small but ...

The above properties are well verified experimentally at least if T is not too low (quantum effect) or too high (particles are not hard spheres).

We have *M* particles in 1, 2 or 3 dimensions that are initially uniformly distributed in space.

In every time interval dt there is a probability $\lambda_M dt$ that a collision take place.

When a collision take place two particles are randomly and uniformly selected, independently of their position.

The incoming velocities of the two particles are randomly updated in such a way to preserve energy and, in dimension 2 or 3, momentum.

λ_M is fixed in such a way that the average time between two collision of a given particle is independent of *M*. That is $\lambda_M = 1/(M-1)$. This is called Boltzmann-Grad limit.

The main simplifications we have introduced are:

1. Collisions times are stochastic and independent from the position and velocity of the particles.
2. Energy and momentum are redistributed randomly.
3. the collision rate between two particles does not depend on their velocities. This are often called "Maxwellian Molecules".

State of the system

$$f(\underline{v}) : \mathbb{R}^M \to \mathbb{R} \qquad \underline{v} = (v_1, v_2, \ldots, v_M) \in \mathbb{R}^M,$$

probability of finding the system with velocities V. We take f invariant under permutation of its arguments.

If f is the state of the system before particle i and j collide, just after the collision the state is

$$R_{i,j}f(\underline{v}) = \int f(r_{i,j}(\theta)\underline{v})d\theta$$

where

$$r_{1,2}(\theta)\underline{v} = (v_1 \cos(\theta) - v_2 \sin(\theta), v_1 \sin(\theta) + v_2 \cos(\theta), v_3, \ldots)$$

that is, $r_{i,j}(\theta)$ is a rotation of angle θ in the i, j plane.

The evolution.

The effect of a collision of a randomly picked pair of particles is

$$Qf = \frac{1}{\binom{M}{2}} \sum_{i<j} R_{i,j} f$$

while the probability of having k collision in a time t is

$$\frac{t^k}{k!} e^{-Mt}$$

so that the evolution is given by

$$F_t = e^{-Mt} \sum_{k=0}^{\infty} \frac{t^k}{k!} Q^k f_0 = e^{\mathscr{L}_S t} F_0$$

where

$$\mathscr{L}_S = \frac{2}{M-1} \sum_{i<j} (R_{i,j} - I) = \frac{2}{M-1} \mathscr{K}$$

Thus F_t satisfies the equation:

$$\dot{F}(t) = \mathscr{L}_S f(t) \, .$$

The evolution generated by this equation preserves the total kinetic energy. Thus every rotationally invariant distribution is a steady state.

Given an initial distribution $f(\underline{v})$, the evolution brings it toward its projection on the rotationally invariant distributions, that is toward

$$F_R(\underline{v}) = \int_{S^{M-1}} F(|\underline{v}|\omega) d\sigma(\omega)$$

where $d\sigma(\omega)$ the normalized volume measure on the unit sphere S^{M-1}.

This observation "explain" the movie shown at the beginning.

Carlen-Carvalho-Loss (2000) showed that

$$\left\| e^{t\mathscr{L}_S} f - f_R \right\|_2 \leq C e^{-L^{(1)}t}$$

where $\| \cdot \|_2$ is the $L^2(\mathbb{R}^M)$ norm and

$$L^{(1)} = \frac{1}{2}\frac{M+1}{M-2}.$$

The L^2 norm has one major problem. Assume that

$$f(\underline{v}) = \prod_{i=1}^{M} F(v_i) \qquad \text{and} \qquad g(\underline{v}) = \prod_{i=1}^{M} G(v_i)$$

then

$$\|f - g\|_2 \simeq C^M \|F - G\|_2 \qquad \text{with} \qquad C > 1.$$

The entropy with respect to the steady state is defined as

$$\mathscr{S}(f \mid f_R) = \int f(\underline{v}) \log\left(\frac{f(\underline{v})}{f_R(\underline{v})}\right) d\underline{v}$$

In general

$$\mathscr{S}(f \mid f_R) \geq 0 \qquad \mathscr{S}(f \mid f_R) = 0 \quad \Leftrightarrow \quad f = f_R$$

and

$$\frac{d}{dt}\mathscr{S}(f(t) \mid f_R) \leq 0$$

and

$$f(\underline{v}) = \prod_{i=1}^{M} F(v_i) \qquad \Rightarrow \qquad S(f \mid f_R) = O(M).$$

Cercignani Conjecture

For the realistic kinetic evolution Cercignani conjectured

$$\mathscr{S}(f(t)\,|\,f_R) \leq e^{-c\,t}\mathscr{S}(f(0)\,|\,f_R).$$

For the Kac model

$$-\sup_F \frac{\dot{\mathscr{S}}(f\,|\,f_R)}{\mathscr{S}(f\,|\,f_R)} \geq \frac{1}{M}$$

but for every δ there exists C_δ and f_δ such that

$$-\frac{\dot{\mathscr{S}}(f_\delta\,|\,f_R)}{\mathscr{S}(f_\delta\,|\,f_R)} \leq \frac{C_\delta}{M^{1-\delta}}.$$

Villani (2003), Einav (2011)
Mischler and Muhot obtained polynomial decay unifrom in M.

Boltzmann-Kac Equation

Suppose that, at least in some approximate form, for every t we have

$$f(\underline{v}, t) = \prod_{i=1}^{M} F(v_i, t).$$

This is a strong form of the *Stosszahlansatz* or molecular Chaos hypothesis (actually introduced by Maxwell).

From the evolution equation, integrating over all variables but one, we get the *Boltzmann-Kac equation*

$$\frac{d}{dt} F(v, t) = 2 \int dw \int d\theta \big(F(v \cos \theta - w \sin \theta, t) F(v \sin \theta + w \cos \theta, t) - F(v, t) F(w, t) \big)$$

Clearly even if $f(\underline{v}, 0)$ is a product, in general $f(\underline{v}, t)$ is not.

Boltzmann Property

Given a symmetric distribution $f_M(\underline{v}_M)$ we define the k particle marginal as

$$F_M^k(\underline{v}_k) = \int f_M(\underline{v}_M)\, dv_{k+1} \cdots dv_M$$

A sequence of distributions $f_M(\underline{v}_M)$ forms a *chaotic sequence* if

$$F^k(\underline{v}_k) := \lim_{M \to \infty} F_M^k(\underline{v}_k) = \prod_{i=1}^{k} F^1(v_i).$$

Classical example: the uniform distribution on the sphere of radius $\sqrt{M}$ in $\mathbb{R}^M$ in which case $F^1(v)$ is the Maxwellian distribution.

Theorem (Mc Kean)

If $f_M(\underline{v}, 0)$ forms a chaotic sequence then also $f_M(\underline{v}, t)$ forms a chaotic sequence. It follows that $F^1(v, t)$ satisfies the Boltzmann-Kac equation.

Idea of the proof.

Let $\phi : \mathbb{R}^k \to \mathbb{R}$ be a k variables test function. Then

$$\int_{\mathbb{R}^M} f_M(\underline{v}_M, t)\phi(\underline{v}_k) d\underline{v}_M = \sum_n \frac{t^n}{n!} \int_{\mathbb{R}^M} f_M(\underline{v}_M, 0)(\mathscr{L}_S)^n \phi(\underline{v}_k) d\underline{v}_M$$

But

$$\mathscr{L}_S \phi = \frac{2}{M-1} \sum_{1 \leq i < j \leq k} (R_{i,j} - I)\phi + \frac{2(M-k)}{M-1} \sum_{i=1}^k (R_{i,k+1} - I)\phi \to_{M \to \infty}$$

$$2 \sum_{i=1}^k (R_{i,k+1} - I)\phi := \Lambda\phi$$

Observe that if $\phi : \mathbb{R}^{k_1} \to \mathbb{R}$ and $\psi : \mathbb{R}^{k_2} \to \mathbb{R}$

$$\Lambda\phi \otimes \psi = (\Lambda\phi) \otimes \psi + \phi \otimes (\Lambda\psi)$$

where $\phi \otimes \psi(v_1 \ldots, v_{k_1+k_2}) = \phi(v_1 \ldots, v_{k_1})\psi(v_{k_1+1} \ldots, v_{k_1+k_2})$.

If now we take $\phi : \mathbb{R} \to \mathbb{R}$, with some straightforward algebra we get

$$\sum_n \frac{t^n}{n!} \Lambda^n \phi^{\otimes k} = \sum_{n_1, n_2, \ldots n_k} \prod_{i=1}^k \frac{t^{n_k}}{n_k!} \Lambda^{n_k} \phi$$

so that

$$\lim_{M \to \infty} \int_{\mathbb{R}^M} f_M(\underline{v}_M, t) \phi^{\otimes k}(\underline{v}_k) d\underline{v}_M = \sum_{n_1, n_2, \ldots n_k} \prod_{i=1}^k \frac{t^{n_k}}{n_k!} \int_{\mathbb{R}^{n_k+1}} (F^1)^{\otimes n_k+1} \Lambda^{n_k} \phi d\underline{v}_{n_k+1} =$$
$$\left(\sum_n \int_{\mathbb{R}^{n+1}} (F^1)^{\otimes n+1} \Lambda^n \phi d\underline{v}_{n+1} \right)^k$$

while in the same way we get

$$\lim_{M \to \infty} \int_{\mathbb{R}^M} f_M(\underline{v}_N, t) \phi(v_1) d\underline{v}_M = \sum_n \int_{\mathbb{R}^{n+1}} (F^1)^{\otimes n+1} \Lambda^n \phi d\underline{v}_{n+1}$$

Thank you.