

Lecture notes

Phénomènes de transport

2003-2004

Résumé

Introduction

Describe the course.

Insist on the similarity between the heat equation (Fourier law) and the diffusion equation (Fick law).

Recent work on related subjects :

Heat transfer and Fourier law :

- “Anomalous heat conduction and anomalous diffusion in one dimensional systems”, B. Li and J Wang, Phys. Rev. Lett. 91, 044301 (2003); cond-mat/0306554.
- “Thermal conduction in classical low dimensional lattices” S. Lepri, R. Livi and A. Politi, Phys. Rep 377, 1 (2003).
- “Fourier law : a challenge for theorists” F. Bonetto, J. Lebowitz, L. Rey-Bellet, math-phys/0002052.

Applications of kinetic theory beyond simple gases

- “Kinetic theory and hydrodynamics for rapid granular flow : a perspective” J. W. Duffy cond-mat/0108444.

Anomalous diffusion

- “” J-P Bouchaud and A. Georges, Phys. Rep.

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Plan of the course

1. Heat transfer and black body radiation (2h)

TD1

- (a) Study of the hollow cylinder.
- (b) Some limit cases of Planck's distribution, classical limit and Rayleigh-Jeans, Wien's displacement law, problems in the ultraviolet limit.
- (c) Radiation of a nickel.

2. Kinetic theory (4h)

- (a) Introduction and assumptions
- (b) Pressure and kinetic energy
- (c) Kinetic energy and temperature
- (d) Maxwell distribution. Average and root-mean-square velocity.
- (e) Equipartition
- (f) Mean-free path

TD2 : Study of Maxwell and Boltzmann distribution.

- (a) Study of Maxwell's distribution.
- (b) Study of Boltzmann's distribution.
- (c) Equipartition for a quadratic degree of freedom.

TD3 : Applications of the kinetic theory.

- (a) Review of collisions.
- (b) Example of cylinder.
- (c) Something else.
- (a)

3. Brownian motion (3h)

- (a) (2h) The random walk in 1 dimension. Binomial distribution. Averages. Displacement, explain diffusion coefficient. Continuum limit, time-dependent distribution $p(x, t)$. Extension to higher dimensions.
- (b) (1h) Einstein's approach to the same problem.
- (c) (1h) The Langevin equation. Example of a stochastic differential equation. Generalities. What is the origin of the noise and the friction coefficient. What can one compute with this equation, averages, displacement and recall diffusion coefficient (mention Einstein's result, comment on Smoluchowski's mistake and Langevin's correction).

Brownian motion TD (2h)

- (a) (1h) The random walk in 1 dimension. Some extra calculation with the discrete 1d Brownian motion, eg. averaged position when the motion is biased or continuous limit of the binomial to reach a Gaussian (we did not do this calculation in the Statistics course; we can either ask them to do it here, or ask them to quote the result, based on central limit theorem, that they know).
- (b) (1h) The Langevin equation. The relation between friction and noise-noise correlation as shown by Langevin (using equipartition of the kinetic energy). Ask them to compute some other averaged quantity with the Langevin formalism.

4. Molecular movement (1h)

- (a) Review : Random motion of a gas molecule, root mean square, velocity, mean free path, collision frequency, in the context of this problem.

5. Diffusion equation : Space-time evolution of the density (2h)

- (a) (1h) Diffusion equation.
- (b) (1h) Particle conservation, current and Fick's law.

Space-time evolution of the density TD (2h)

- (a) (1h) Diffusion across a porous membrane, hemodialysis.
- (b) (1h) Perrin's experiment to determine Avogadro's number.

1 Heat transfer

Heat is a form of energy, as stated by the first law of thermodynamics.

Heat transfer occurs from a body at higher temperature to one at lower temperature that is in good thermal contact with the first one. This is the statement of the second law of thermodynamics. Sources of energy and, hence, transmission of heat are ubiquitous in nature. One can distinguish three forms that, even if in general they appear entangled, in most cases of practical interest one of them prevails :

- i. Heat conduction.* It is the exchange of energy between different bodies in contact, or different parts of a single body. It may be due to the elastic collisions between molecules in gases, oscillations in non-conducting solids, the motion of electrons in metals, etc.

The fundamental law of heat conduction is in one-to-one correspondance with the law of electrical conduction. It is due to Fourier (based on previous work by Biot) and reads :

$$dQ = -kA \frac{dT}{dx} dt . \quad (1)$$

dQ denotes the heat energy conducted in the direction x during the time interval dt , through a surface (perpendicular to dx) of constant area A . k is the *thermal conductivity* and $[k]=J/(s \text{ m K})$ with J denoting the unit of energy Joule and K the unit of temperature Kelvin.

- ii Heat convection.* It is the exchange and transport of energy that occurs in a fluid due to mixing. It is controlled by the laws of fluid dynamics, mixed with the ones of heat conduction. The basic law of heat convection is due to Newton.

- iii. Heat radiation.* It is identical with light radiation. It quantifies the effect of temperature on radiation through a transparent medium or empty space.

For a perfect black body of area A (one that that absorbs all the radiation that reaches it) at absolute temperature T heat radiation is determined by the Stefan-Boltzmann law

$$Q = \sigma AT^4 , \quad (2)$$

with σ a fundamental constant, $\sigma = 5.67 \times 10^{-8} \text{ watts}/(m^2 K^4)$, A the area of the object and T the absolute temperature. The proof of this equation needs the extension of classical to quantum mechanics. For grey bodies a similar equation holds in which σ must be replaced by a different factor.

Heat can be stored in the form of energy. The basic equation for the heat dQ stored during an infinitesimal time dt in a volume V of a medium of density ρ and specific heat at constant pressure c_p when the temperature increases by dT is

$$dQ = c_p \rho V \frac{\partial T}{\partial t} dt . \quad (3)$$

In this course we shall focus on heat conduction and heat radiation, taken as independent phenomena. We shall not touch the problem of heat convection.

1.1 Heat conduction

1.1.1 Analogy between heat and electrical conduction

Electric current is the flow of electrons in, e.g., a wire. In a metal the outer electrons are not bound to an atom and they move freely, usually randomly, through the lattice of positive ions. When the wire is connected to a cell, they are pushed away from the negative terminal and drawn to the positive one. The drift velocity of the cloud is about 3mm/s. Within the cloud the electrons are still moving randomly at much higher speeds.

Ohm's law for electrical conduction reads

$$I \equiv \frac{dQ}{dt} = k_e A \frac{dE}{dx} = \frac{dE}{dR_e} \quad (4)$$

where I is the electric current, k_e the electric conductivity, E the electric potential and $R_e \equiv dx/(k_e A)$ the electric resistance. This law has, clearly, the same form as Fourier's law of heat conduction, after identifying E with T . (1).

The similarity with the electric conductivity can be exploited to define thermal resistance and treat problems of heat transfer as done with electric circuits. Defining a thermal resistance

$$dR \equiv \frac{dx}{kA} \quad (5)$$

(to be compared with dR_e) one has the resulting thermal resistances of two bodies labelled 1 and 2 connected in series and parallel :

$$R_3 = R_1 + R_2 \quad \text{Series ,} \quad (6)$$

$$R_3 = \frac{R_1 R_2}{R_1 + R_2} \quad \text{Parallel .} \quad (7)$$

We shall discuss some applications of this analogy in the TDs.

1.1.2 Three dimensions

Fourier law in three dimensions reads

$$\partial Q(\vec{x}, t) = -A \vec{k} \cdot \vec{\nabla} Q(\vec{x}, t) . \quad (8)$$

1.1.3 Heat conduction in a substance at rest

We shall derive an equation that expresses the conservation of energy. The sum of the energy entering an infinitesimal volume, dQ_1 , and developing within it, dQ_2 , must be equal to the sum of the energy stored in it, dQ_3 , and leaving it, dQ_4 , in the infinitesimal time interval dt . According to Eq. (1) if the direction of heat flow is x and the infinitesimal volume is a cube $dV = dx dy dz$ with faces placed at x_0 and $x_0 + dx$, y_0 and $y_0 + dy$ and z_0 and $z_0 + dz$, one has

$$dQ_{1x} = -k(dydz) \frac{dT}{dx}(x_0, y, z) dt \quad (9)$$

$$dQ_{4x} = -k_x(dydz) \frac{\partial}{\partial x} T(x_0 + dx, y, z) dt \quad (10)$$

Using

$$T(x_0 + dx, y, z) \approx T(x_0, y, z) + \frac{\partial}{\partial x} T(x, y, z) \Big|_{x_0} dx = T(x_0, y, z) + \frac{\partial}{\partial x_0} T(x_0, y, z) dx, \quad (11)$$

we find

$$\begin{aligned} dQ_{4x} &= -k_x(dydz) \frac{\partial}{\partial x_0} \left(T(x_0, y, z) + \frac{\partial T(x_0, y, z)}{\partial x_0} dx \right) dt \\ &= -k_x(dydz) \left(\frac{\partial T(x_0, y, z)}{\partial x_0} + \frac{\partial^2 T(x_0, y, z)}{\partial x_0^2} dx \right) dt. \end{aligned} \quad (12)$$

Note that we assumed that the thermal conductivity k_x is constant along dx . Similar equations hold for the other two directions, y and z . The total energies entering and leaving the volume dV are

$$dQ_1 = dQ_{1x} + dQ_{1y} + dQ_{1z}, \quad (13)$$

$$dQ_4 = dQ_{4x} + dQ_{4y} + dQ_{4z}. \quad (14)$$

The energy stored in dV is given by Eq. (3) with $V \rightarrow dV = dx dy dz$. Finally, heat can be developed in dV during dt :

$$dQ_2 = q dx dy dz dt \quad (15)$$

where q is just the heat developed per unit volume and unit time. Thus, we have that $dQ_1 + dQ_2 = dQ_3 + dQ_4$ implies

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_p} \left(k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} \right) + \frac{q}{\rho c_p} \quad (16)$$

where we dropped the subindex 0 in the positions to simplify the notation. The constant $k_x/(\rho c_p)$ is usually called the *thermal diffusivity* along the direction x . Similarly for y and z .

1.1.4 Steady state with no generation of heat

An infinite plane plate

Let us study the variation of temperature and heat conduction across an infinite plane plate with one surface at x_1 kept at constant temperature T_1 and the other at $x_2 = x_1 + L$ kept at constant temperature T_2 . We also assume that temperature does not depend on time, $\partial T/\partial t = 0$, there is no generation of heat, $q = 0$, and heat can only be transferred in the x direction. Thus, Eq. (16) becomes

$$\frac{d^2 T}{dx^2} = 0. \quad (17)$$

This equation is solved by $T(x) = ax + b$, with the origin of the x axis fixed at any arbitrary position, and a and b two constants that are fixed by the boundary conditions

$$T(x_1) = T_1 \quad T(x_1 + L) = T_2 \quad (18)$$

and yield

$$a = \frac{T_2 - T_1}{L} \quad b = \frac{T_1(L + x_1) - T_2x_1}{L} . \quad (19)$$

The heat transfer across the area A on the plate is

$$dQ = -k_x A \frac{dT}{dx} dt \quad \Rightarrow \quad \frac{dQ}{dt} = -k_x A \frac{T_2 - T_1}{L} \quad (20)$$

Heat conduction in an infinitely long cylinder at constant conductivity

The next simplest example is the case of heat conduction across the radial direction of a hollow cylinder of inner radius r_1 , outer radius $r_2 = r_1 + \Delta r$ and length L that we take to be very long. In this case, one can derive an equation similar to Eq. (16) in cylindrical coordinates, (r, θ, z) . Using Eq. (1) the heat flow into the cylinder occurs only along the radial direction and it is

$$dQ_1 = -kL2\pi r \frac{dT(r_1, \theta, z)}{dr} dt \quad (21)$$

while the heat flow out of the cylinder is

$$dQ_2 = -kL2\pi(r + dr) \frac{dT(r_1 + dr, \theta, z)}{dr} dt \quad (22)$$

that using

$$T(r_1 + dr, \theta, z) \approx T(r_1, \theta, z) + \frac{\partial T(r_1, \theta, z)}{\partial r_1} dr \quad (23)$$

becomes

$$dQ_2 = -kL2\pi(r + dr) \frac{\partial}{\partial r} \left(T(r, \theta, z) + \frac{\partial T(r, \theta, z)}{\partial r} dr \right) dt . \quad (24)$$

If there are no heat sources or sinks and the system is in steady state conditions, these two flows must be equal, thus one finds

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = 0 \quad (25)$$

where we have dropped the term $O((dr)^2)$ with respect to the terms $O(dr)$. The general solution to this differential equation is

$$T(r) = a \ln r + b \quad (26)$$

and using the boundary conditions are $T = T_1$ at $r = r_1$ and $T = T_2$ at $r = r_1 + \Delta r$ one fixes the two constants of integration a and b :

$$a = \frac{T_1 - T_2}{\ln r_1 - \ln(r_1 + \Delta r)} \quad b = \frac{T_2 \ln r_1 - T_1 \ln r_1}{\ln r_1 - \ln(r_1 + \Delta r)} . \quad (27)$$

From this equation one readily finds the heat transferred across the cylinder :

$$\frac{dQ}{dt} = -kL2\pi \frac{T_1 - T_2}{\ln r - \ln(r + \Delta r)}. \quad (28)$$

1.2 Black body radiation

By the end of the XIXth century it was understood that heated bodies should radiate. Indeed, it was known that heat causes atoms to vibrate, since these were complicated patterns of charges, and Maxwell's prediction that an oscillating charge will radiate electromagnetic waves was confirmed experimentally by Hertz and others at a macroscopic scale. The question remained as if it could also be applied at the microscopic atomic scale.

Boltzmann presented a proof of the Stefan-Boltzmann black body radiation law based on thermodynamic arguments. However, this same law could not be obtained by applying the classical laws of nature (Newton mechanics) to the microscopic world. Indeed, the first evidence against classical physics was given by the analysis of the black body radiation.

A black body is one that absorbs all the radiation that reaches it and heats up in the process. In order to understand this effect, think of two cases that are extreme counter-examples of black bodies. A piece of normal glass lets all the light that reaches go through it (the reason being that the electrons that can vibrate due to the incoming light have resonant frequencies that are very different from those of visible light). A piece of shiny metal reflects all the light that reaches it (in a metal, electrons are free to move and once heated by the incoming light, they re-radiate reflecting the light). On the contrary, a black body like a black tee-shirt, gets heated when light reaches it.

Now, any body at any temperature above absolute zero will radiate to some extent, but the intensity and the frequency distribution of the radiation depend on the details of the body (and not on the details of the radiation absorbed). To start with, let us then focus on a body which is a perfect absorber, a "black body". The simplest model of a black body is a box with a tiny hole in one side, that is to say a perforated cavity. Radiation entering the box is scattered around inside the box. Many "collisions with the walls" are needed before the radiation can come out of the box, by hitting the hole again. At each "collision" part of the radiation is absorbed, and part is reflected. After many scatterings the intensity of the remaining radiation is very weak and one can imagine that for a very small hole only a tiny fraction of radiation is re-emitted by escaping the box. In the limit of a vanishing size of the hole, no radiation escapes the cavity.

Thus, we take the inverse process in which we take an "oven", a box with a tiny hole. The radiation generated by the oven can be thought as being produced by standing (stationary) waves or resonant modes of the cavity. Experimentally, a beam of radiation from the hole is passed through a diffraction grating and it is projected on to a screen where it is separated by frequency and how much radiation, $p(f)df$, is emitted in the interval $[f, f + df]$ is collected with a detector.

It is found experimentally that the curve $p(f)$ has a bell-shape with a maximum at f_{max} . Its form depends on temperature, with

$$f_{max}(2T) = 2f_{max}(T) , \quad (29)$$

that is called Wien's displacement law. This is a well-known heuristic fact : when one heats a piece of iron, it first looks red (the lowest frequency visible light), when T increases it becomes orange, then yellow, and finally, after further increasing T , it looks white meaning that all frequencies are roughly equally emitted.

From the study of the T dependence of $p(f)$ one finds the Stefan law

$$P = \sigma AT^4 \quad \sigma = 5.67 \times 10^{-8} \text{ watts}/(m^2K^4) , \quad (30)$$

for the power emitted from the area A at temperature T .

What can be predicted analytically for the amount of radiation in a given frequency range? It should be proportional to the number of modes in that range. By solving the stationary wave equation (Maxwell's electromagnetic theory) with boundary conditions that require that the electric field cancels at the walls of the box, one finds

$$\rho(f) = \frac{8\pi f^2}{c^3} \quad (31)$$

modes per unit frequency per unit volume with c the speed of light. Classically all modes contribute the same energy, $k_B T$ (see the discussion on equipartition to be presented later in the course), and one finds Rayleigh-Jeans radiation law :

$$S(f) = \frac{8\pi f^2 k_B T}{c^3} . \quad (32)$$

This is a quadratic increase with frequency of the radiated energy that describes correctly the experimental data for low values of f but departs importantly from the bell-shaped curve at f 's that are close and larger than f_{max} (see Fig. ??).

The explanation of the black body experiment required a modification of the classical laws of physics. Planck followed an interesting path to find a way to describe the data. First, we empirically found that the formula in Eq. (34) described the data accurately (with h an adjustable constant that he fixed by requiring that the law fit the data). Next, we looked for a way to derive this equation analytically.

In a few words, Planck's analytic reasoning goes as follows. He realised that he could derive Eq. (34) by simply modifying the calculation of the average energy per mode. He represented the radiation at frequency f in the cavity by the absorption and emission of radiation by the walls of the cavity. He then assumed that the latter can be represented by an ensemble of harmonic oscillators with all possible frequencies (equivalently, harmonic constants), including f and that the average energy radiated at f was identical with the averaged energy of the wall's harmonic oscillator of frequency f . A classical calculation of the average energy of a harmonic oscillator yields the equipartition result $k_B T$ (to be discussed later in the course). So, Planck proposed to modify this calculation by proposing that not all values of the energy were allowed. Indeed, he proposed that only $E = nhf$ with h

Planck's constant and n a natural number, were allowed. Thus, the averaged energy per mode is given by its quantum energy hf times the probability that this mode be occupied, that is

$$\frac{hf}{e^{\beta hf} - 1}. \quad (33)$$

This expression times the density of modes at a frequency f , Eq. (31), yields Planck radiation formula

$$S(f) = \frac{8\pi h}{c^3} \frac{f^3}{e^{\beta hf} - 1}, \quad (34)$$

for the energy per unit frequency and unit volume.

The radiated power per unit frequency and unit area is just

$$P(f) = \frac{c}{4} S(f) = \frac{2\pi h}{c^2} \frac{f^3}{e^{\beta hf} - 1} \quad (35)$$

the factor $1/4$ is of geometric origin, the factor c sets the units of a power, since $[P] = [E]/[t]$ (note that the energy we computed was per unit volume while the power is per unit area).

Planck's result has the correct bell-shape form and it describes correctly the dependence on T of the experimental data. The Stefan law follows from integrating over all frequencies to get the total power radiated. Wien's displacement law is obtained by searching the maximum of the formula (35).

Interestingly enough, Planck's quantization proposal was not taken seriously by the community until Einstein used it to explain the photoelectric effect some years later.

2 Kinetic theory

The aim of the kinetic theory is to give a microscopic justification to macroscopic properties of matter like pressure, temperature, etc. Stricly speaking, it applies to the gaseous state of matter only and it simply assumes that the gas is made of particles that obey Newton laws of mechanics and undergo elastic collisions. Clausius revived the atomisti view by 1850 to explain some thermodynamic laws. Maxwell realized in 1859 that to solve Newton equations for all particles was on the one hand impossible and on the other useless. Indeed, since the number of particles is huge ($N \gg 1$) statitital methods can be used.

In the table below, we remind the main difference between the three (main) states of matter, solid, liquid and gas.

2.1 Assumptions

The main assumptions of the kinetic theory are

- (a) The volume of the particles is negligible with respect to the total volume of the gas, in other words, the density is very low.
- (b) The gas is made of particles in constant motion.

	Solid	Liquid	Gas
Kinetic energy	Very low	Low	High
Motion	Vibration	Free	Random motion
Rate of diffusion	Very Slow	Slow	Fast
Interaction	Strong	Weak	Negligible
Ordering	Regular	Random	Random
Shape	Fixed	Variable	Variable
Volume	Fixed	Fixed	Variable
Compressibility	Incomp	Slightly comp	Very comp
Density	High	High	Low

- (c) There are no interactions between the particles.
- (d) The particles undergo two-body elastic collisions. This means that there are no dissipative forces acting during the collision and both the total momentum and the total kinetic energy are conserved.

Note that this model is very much like a model of billiard balls moving around a billiard table.

Clausius himself modified the kinetic theory to describe some aspects of liquids (interactions are not completely negligible) and their evaporation. More recently, this theory has also been adapted to describe granular matter (collisions are not elastic), etc. We shall not discuss these cases here but focus on gases.

2.2 Relation between pressure and kinetic energy

The first to understand the reason why a gas in a container exerts pressure on the container walls, and to relate this pressure to the motion of the molecules in the gas, was Daniel Bernoulli in 1738.

The mechanism for the generation of pressure is very easy to understand with a one-dimensional one particle toy model. Take a particle confined to move in one direction in a tube of length L . It bounces back and forth between a piston and a wall that close the two ends of the tube. After each elastic collision between the particle and the piston, the former undergoes a variation in its momentum, $\Delta p = 2mv$. After the collision with the piston the particle moves at constant velocity towards the wall closing the other extreme of the tube. It collides elastically with it and returns in the direction of the piston. The time between two consecutive collisions, and the frequency of collisions, are

$$t = \frac{2L}{v} \quad \Rightarrow \quad f = t^{-1} = \frac{v}{2L} . \quad (36)$$

Newton's law relates the rate of change of the momentum between two collisions taking place at t_1 and $t_1 + t$ and the force applied by the particle on the wall :

$$\int_{t_1}^{t_1+t} dt F = \int_{t_1}^{t_1+t} dt \frac{dp}{dt} \quad \Rightarrow \quad Ft = p(t_1 + t) - p(t_1) , \quad (37)$$

thus

$$F = 2mv \frac{v}{2L} = \frac{mv^2}{L}. \quad (38)$$

The calculation above can be easily generalized to the case of a three dimensional cubic box of linear size L confining a gas made of N atoms. Let us compute the force exerted by the gas on one wall, say perpendicular to the x direction. The relevant velocities are then the x components of the $3d$ velocities. The total force is just the sum over the forces applied by each particle during collision :

$$F_x = \sum_{i=1}^N F_{ix} = \sum_{i=1}^N \frac{mv_{ix}^2}{L} = \frac{m}{L} \sum_{i=1}^N v_{ix}^2 \quad (39)$$

When N is large the sum can be replaced by N times the average squared velocity along the x direction. Thus, the pressure is

$$P = \frac{F_x}{A} = \frac{mN}{LA} \langle v_x^2 \rangle = \frac{mN}{V} \langle v_x^2 \rangle, \quad (40)$$

where V is the volume of the box. Since the particles are equally likely to move in any of the three directions, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. Moreover, $v^2 = v_x^2 + v_y^2 + v_z^2$ implies $\langle v_x^2 \rangle = \langle v^2 \rangle / 3$, and

$$P = \frac{mN}{3V} \langle v^2 \rangle = \frac{2}{3V} \langle E_c \rangle, \quad (41)$$

where

$$\langle E_c \rangle \equiv N \frac{m \langle v^2 \rangle}{2} \quad (42)$$

is the averaged kinetic energy of the gas.

2.3 Kinetic energy and absolute temperature

Newton was the first to observe that perfect gases satisfied the relation

$$PV = f(T) \quad (43)$$

where $f(T)$ is a universal function of temperature. Later, it was checked that one can write

$$PV = nRT \quad (44)$$

where n is the number of mols in the gas, i.e. $n = N/N_A$ with N_A Avogadro's number ¹, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ is the fundamental molar gas constant and T is the temperature measured in Kelvin units ²

Putting together Eqs. (41) and (44) one has

$$\langle E_c \rangle = \frac{3R}{2N_A} T = \frac{3}{2} k_B T, \quad (45)$$

with $k_B = R/N_A$ defining the Boltzmann constant, $k_B = 1.38 \cdot 10^{-23} \text{ J/K}$. Thus, we see that the temperature of the gas is in direct linear relation with the averaged kinetic energy.

¹Avogadro realized in 1811 that equal volumes of gases at equal pressure and temperature contain the same number of molecules. By definition, a mol is made of N_A molecules.

²The relation between the Celsius and Kelvin scales of temperature is linear, $T_K = T_c + 273$.

2.4 Maxwell distribution

Maxwell realized that the relevant information one needs to characterize the macroscopic properties of a gas is not the position and momenta of each particle but their distribution functions. Moreover, he no longer assumed, like Clausius, that all particles have the same speed. Instead he fully introduced statistical concepts in the kinetic theory by proposing that the positions and velocities in a gas are distributed according to a particular PDF.

The more general PDF of positions and velocities is

$$P(\vec{x}_1, \dots, \vec{x}_N, \vec{v}_1, \dots, \vec{v}_N, t) \prod_{i=1}^N d^d x_i d^d v_i, \quad (46)$$

where i is a labelled that distinguishes each particle in the gas. \vec{x}_i and \vec{v}_i are d -dimensional vectors. For a gas in thermal equilibrium this distribution must be stationary or independent of time :

$$P(\vec{x}_1, \dots, \vec{x}_N, \vec{v}_1, \dots, \vec{v}_N) \prod_{i=1}^N d^d x_i d^d v_i. \quad (47)$$

One can also assume, without much loss of generality, that the positions and velocities are independent variables (note that certainly for gases and in many cases the energy is a sum of terms in which the velocities and positions are not coupled) and hence factorize the joint PDF :

$$P_x(\vec{x}_1, \dots, \vec{x}_N) \prod_{i=1}^N d^d x_i P_v(\vec{v}_1, \dots, \vec{v}_N) \prod_{i=1}^N d^d v_i. \quad (48)$$

Moreover, ignoring tiny corrections due to gravity, the distribution of particles in the container is homogeneous. Thus,

$$P_x(\vec{x}_1, \dots, \vec{x}_N) \prod_{i=1}^N d^d x_i = \frac{1}{V} \prod_{i=1}^N d^d x_i. \quad (49)$$

The only remaining unknown is now the velocity distribution function. Maxwell found this PDF using the following argument. First, the probability of finding a particle with velocity in the x direction comprised between v_x and $v_x + dv_x$ is

$$f(v_x) dv_x \quad (50)$$

Since there is nothing special to the x direction, the other two directions, y and z should behave, statistically, in an identical manner, thus the probability of finding a particle with x component velocity within v_x and $v_x + dv_x$, y component velocity within v_y and $v_y + dv_y$, and z component velocity within v_z and $v_z + dv_z$, is

$$f(v_x) dv_x f(v_y) dv_y f(v_z) dv_z \quad (51)$$

(at least far away from the walls). Next, Maxwell argued that the probability density in this expression should depend only on the modulus of the velocity :

$$f(v_x) f(v_y) f(v_z) = F(v_x^2 + v_y^2 + v_z^2) \quad (52)$$

with $F(u)$ another unknown function. Now, the only function $f(u)$ that can transform a product into the function of a sum is the exponential. Hence

$$f(v_x) = Ae^{-Bv_x^2}. \quad (53)$$

The minus sign in the exponential is justified by the fact that we want to have a normalizable distribution. The constants A and B are fixed by the normalization condition and by the requirement that the averaged kinetic energy be given by Eq. (45). One finds

$$P(v_x, v_y, v_z)dv_xdv_ydv_z = Z^{-1}e^{-\beta\frac{m(v_x^2+v_y^2+v_z^2)}{2}}dv_xdv_ydv_z, \quad (54)$$

with $Z = A^{-3}$ the normalization constant.

2.4.1 Distribution of the modulus of the velocity

One might be interested in working with the PDF of the modulus of the velocity, $P(v)dv$ with $v^2 = v_x^2 + v_y^2 + v_z^2$. A simple change of variables from the Cartesian system of coordinates (v_x, v_y, v_z) to the spherical one (θ, ϕ, v) yields

$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\beta\frac{mv^2}{2}}. \quad (55)$$

2.4.2 The average and root-mean-squared velocity

The average velocity is

$$\langle v \rangle \equiv \int_0^\infty dv v P(v) = \sqrt{\frac{8RT}{\pi M}}, \quad (56)$$

with M the molar mass, $M = N_0 m$. The root-mean-squared velocity is

$$v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \left(\int_0^\infty dv v^2 P(v)\right)^{1/2} = \sqrt{\frac{3RT}{M}}. \quad (57)$$

Note that $\langle v \rangle \neq v_{rms}$.

Both values are increasing functions of the temperature. Most of the molecules in a gas at high temperature have a high velocity; however, some molecules with low velocity also exist. Vice-versa, a gas at low T is made mostly of molecules with low speeds, however, this does not imply that no quickly moving molecules exist.

2.5 Boltzmann distribution

Boltzmann generalized Maxwell's distribution to the case in which the energy is not only kinetic but also potential, $E = mv^2/2 + E_p(x)$. He then proposed that the probability for a system to be in a state of energy E is

$$P(E) = Z^{-1}e^{-\beta E}. \quad (58)$$

The Boltzmann distribution states that the probability of finding a molecule with energy E decreases exponentially with E . This implies that the probability that a molecule has an energy that is much higher than the expected value is very low : $P(E \gg \langle E \rangle) \ll 1$.

2.6 Equipartition of energy

The analysis of the averaged kinetic energy showed that this quantity is given by

$$\langle E_c \rangle = \frac{1}{2} k_B T \times \text{Number of degrees of freedom} . \quad (59)$$

Indeed, in the case we treated the particles can move in three directions and there are three independent velocity components that act as three degrees of freedom yielding the result $3/2 k_B T$.

More generally, it has been observed that the so-called *equipartition* theorem that states that the averaged energy of a system is $k_B T/2$ per degree of freedom applies in a variety of cases. It does however fail in several known cases that posed problems at the beginning of the XXth century. What can be rigorously proven is that any degree of freedom that contributes quadratically to the energy yields a contribution $k_B T/2$ to the averaged energy. Other degrees of freedom with different dependencies deviate from this rule. Moreover, at very low temperatures, where quantum effects become important, this classical equipartition rule does no longer hold.

2.7 Mean-free path

The mean-free path concept was developed by Clausius to refute the criticism of Buys-Ballot (a Dutch meteorologist) to his early kinetic energy approach. Buys-Ballot noticed that the mean-square-velocity of typical gases at room temperature calculated by Clausius considering that molecules have totally negligible size was much too high to be compatible with the *diffusion* of one gas within another. Indeed, in more modern terms and using the expression of the mean-square-velocity, that arises from the Maxwell distribution, of, say, oxygen molecules (molecular mass ~ 32 g/mol) at room temperature ($T = 25^\circ\text{C}$) yields $v_{rms} \sim 481$ m/s = 1726 km/h. This means that, on average the molecules move much faster than an airplane jet! This would indicate that a gas molecule moves across a room almost instantaneously. However, this is not so. Gas molecules *diffuse* very slowly (it takes about a minute for an odorous gas spread on one end of a room to reach the other). Clausius argued that the reason for this is that the particles are not punctual but have a finite radius and hence they travel a very short distance in a straight line before being deflected in another direction by a collision with another particle.

The *mean-free-path*, ℓ , is the average distance that a particle travels between two interaction of a given type. In the case under study, these are just collisions with other particles in the gas. ℓ is inversely proportional to the probability that a particle will collide with another one as it moves through the gas. For spheres of diameter d this probability is proportional to the collision cross section, $\sigma \propto d^2$, and to the number of molecules per unit volume, N/V , thus

$$\ell = c \frac{V}{N d^2} , \quad (60)$$

where c is a numerical constant of order one and of geometric origin. As temperature raises the mean-free-path increases, it also increases as the pressure decreases, and as the size of the molecules decreases.

The *Knudsen number* is an adimensional number that compares the mean-free-path to a typical size of the system :

$$K_n = \frac{\ell}{L}, \quad (61)$$

where L is, for example, the linear size of the container. According to the value of the Knudsen number one has three flow regimes :

- Viscous flow. $\ell \ll L$. Gas-gas collisions dominate. Molecules drag one another in the flow. Air at standard conditions falls in this category since the mean free path is very short, of the order of 0.05 microns.
- Intermediate. $\ell \sim L$. Complicated flow.
- Molecular flow. $\ell \gg L$. Gas-wall collisions dominate and molecules move independently of one another.

Heuristically one finds that when $K_n \leq 0.01$ the medium is viscous while when $K_n > 1$ one has a molecular flow.

The *collision frequency* is the number of collisions that a molecule undergoes per second and it can be calculated as the ratio between the root-mean-square velocity and the mean-free-path :

$$f = \frac{v_{rms}}{\ell}. \quad (62)$$

The mean-free-path notion goes well beyond the study of gases. It appears in the study of electrons in solid state physics as the averaged length that an electron travels before its trajectory changes direction due to, e.g. the interaction with a nucleus, the distance that a radical travels before interacting chemically with another molecule, etc.

2.8 Viscosity of gases

Maxwell incorporated the mean-free-path notion into his own kinetic theory and he related it to the concept of viscosity. He proposed that the viscosity of a gas is due to the momentum transfer that occurs when a molecule from a faster moving region collides with a particle in a layer moving with a lower speed. Since the rate of transfer of momentum increases with the average molecular speed, the viscosity of a gas *increases* with temperature! (This result is the opposite of what observed in liquids where interactions are important.)

Note that viscosity is not defined in the molecular flow regime since collisions between the molecules are very infrequent.

2.9 Random motion

The approach developed in this section is based then on the constant motion and collision between the molecules in the gas. If one follows the motion of one tagged molecule one expects then to see it undergo a zigzag motion with very sudden changes in the direction and modulus of its velocity occurring very frequently. This kind of motion is called a *random walk*. In the next section we shall study several aspects of random walks and the mathematical theory that describes them.

3 Random walks

One of the clearest evidences for the atomic nature of matter is the Brownian motion experiment.

3.1 Brownian motion

Brownian motion is the erratic motion of a massive, colloidal, particle immersed in an equilibrated fluid made up of much lighter molecules. The motion of the colloidal particle is due to the collisions with the molecules in the liquid that seem to take place in a sequence of apparently discrete steps. It was first observed by the biologist J. Ingenhousz in 1785, later forgotten, and then rediscovered by the Scottish botanist Brown in 1828 who initially thought that he was observing the motion of a living particles.

There exist several theoretical approaches to this problem. the first mathematical theory is based on the kinetic theory and it was developed by Einstein in 1905. Later, Langevin proposed a different and very appealing approach that establishes the basis of a formalism used to study more generic and complicated stochastic processes.

3.2 Random walk

Random walks have very interesting mathematical properties that depend on the dimensionality of space, whether the walk is confined to a regular lattice, etc.

3.2.1 One dimensional random walk on a regular lattice

The simplest random walk is a stochastic process consisting of a series of discrete steps of the same length on a one-dimensional regular lattice. The position of the walker coincides with the vertices of this one-dimensional lattice and they are labelled by $\vec{r} = ai$ with a the lattice constant and i an integer taking values in $(-\infty, \infty)$ if the space is unlimited. At each time-step the walker occupies a position ak and it moves to the right with probability p and to the left with probability $q = 1 - p$. If $p \neq 1/2$ the walker is *biased* since it prefers to move to the right (left) if $p > 1/2$ ($p < 1/2$). The probability for the walker to chose j steps towards the right out of n time steps (n tries) is a binomial

$$P(n, j) = \binom{n}{j} p^j (1-p)^{n-j} . \quad (63)$$

Its position after n steps in which it moved j times towards the right and $n - j$ times towards the left is

$$ai = a[j - (n - j)] = a(2j - n) . \quad (64)$$

From this equation we obtain

$$j = \frac{n + i}{2} \quad (65)$$

and, replacing in Eq. (63),

$$P(n, i) = \binom{n}{\frac{n+i}{2}} p^{\frac{n+i}{2}} (1-p)^{\frac{n-i}{2}}, \quad (66)$$

for the probability that the walker occupies the position ai after n steps.

The mean and variance of Eq. (63) are

$$\mu = \langle j \rangle np \quad \sigma^2 = \langle (j - \langle j \rangle)^2 \rangle = np(1-p), \quad (67)$$

and these imply

$$\langle i \rangle = \langle 2j - n \rangle = 2\langle j \rangle - n = 2np - n = n(2p - 1) \quad (68)$$

$$\langle (i - \langle i \rangle)^2 \rangle = 4\langle (j - \langle j \rangle)^2 \rangle = 4np(1-p) \quad (69)$$

The average position of a biased random walk is positive or negative depending on $p > 1/2$ or $p < 1/2$. Instead, when $p = 1/2$ one finds $\langle i \rangle = 0$. The standard deviation, $\langle (i - \langle i \rangle)^2 \rangle^{1/2}$, that measures the half-width of the distribution $P(n, i)$ is proportional to \sqrt{n} . Comparing the standard deviation to the average one finds

$$\frac{2\sqrt{np(1-p)}}{pn} = \frac{2\sqrt{1-p}}{\sqrt{np}} \rightarrow 0 \quad \text{when } n \rightarrow \infty. \quad (70)$$

This means that when $n \gg 1$ the PDF is very narrowly peaked about the mean and large excursions away from the mean are rare.

The variance (69) is proportional to n . From the continuum limit of this equation, that we shall discuss below, one defines the *diffusion constant*, as one-half of the proportionality constant between σ^2 and n .

3.2.2 The Gaussian limit

When the number of time-steps n tends to infinity, and the average and variance of the binomial PDF also diverge, a longish but easy calculation shows that this PDF approaches a Gaussian form :

$$P(n, i) \sim \sqrt{\frac{2}{\pi n}} e^{-i^2/(2n)}, \quad (71)$$

where i is the integer labelling the position on the one-dimensional lattice.

3.2.3 The continuum limit

In the limit $n \rightarrow \infty$ we want to establish the probability density for finding the particle in an interval of length dx starting at a distance x away from the origin. The position x is simply given by

$$x = ai \quad \Rightarrow \quad i = \frac{x}{a}. \quad (72)$$

Replacing in (71) one has

$$P(n, i = x/a) \sim \sqrt{\frac{2}{\pi n}} e^{-x^2/(2a^2n)}. \quad (73)$$

Now, the probability that the particle lies in the interval $[x, x + dx]$ is given by the sum of $P(n, i)$ over all the values i leading to values of x in this interval :

$$p(n, x)dx \sim \sum_{i \in [x, x+dx]} P(n, i). \quad (74)$$

One can estimate the value of this sum by assuming that, since the interval is very narrow, one can approximate $P(n, i) \approx P(n, i = x/a)$ and simply multiply this value by the number of i 's that fall in the interval. The distance between two consecutive displacements

$$\dots \quad x = (i - 2)/a \quad x = i/a \quad x = (i + 2)/a \quad \dots \quad (75)$$

equals $2a$, *i.e.* two lattice units. Therefore, an interval of length dx includes $dx/(2a)$ values of i within it. Thus

$$p(n, x)dx = \sqrt{\frac{1}{2\pi na^2}} e^{-x^2/(2a^2n)} dx. \quad (76)$$

In a second step we can eliminate the reference to the number of time-steps n by trading it by the total time t divided by the time-interval between two displacements t_c :

$$n = \frac{t}{t_c} \quad (77)$$

Thus,

$$p(x, t)dx = \sqrt{\frac{t_c}{2\pi ta^2}} e^{-x^2 t_c/(2a^2 t)} dx. \quad (78)$$

Defining the *diffusion constant*

$$D \equiv \frac{a^2}{2t_c}, \quad (79)$$

that depends on two “unknown and microscopic” parameters, one has

$$p(x, t)dx = \sqrt{\frac{1}{4\pi Dt}} e^{-x^2/(4Dt)} dx. \quad (80)$$

With a simple calculation one shows that the mean square displacement is given by

$$\langle (x - \langle x \rangle)^2 \rangle = 2Dt \quad (81)$$

This quantity is measurable experimentally and it determines the value of the diffusion constant D for a given random walk process.

As we shall see later, the diffusion constant characterises the migration of particles of a given kind, in a given medium and at a given temperature. In general, it depends on the size of the particle, the structure of the medium, and T . For a small molecule in water one finds $D = 10^{-5} \text{ cm}^2/\text{s}$.

3.2.4 d -dimensional random walk on a regular cubic lattice

This is a simple generalization of the one-dimensional case that we discussed in detail above.

The walker occupies the vertices of a regular cubic lattice. Its position is then described by a d dimensional vector \vec{r} with discrete components, $\vec{r} = (ai, aj, ak)$ where a is the lattice spacing and i, j, k are integers taking values between $-\infty$ and ∞ if the space is unbounded. At each time step the walker chooses to move to one of the nearest-neighbours with equal probability $1/(2d)$.

After a large number of steps, one can assume that the walker did n/d steps in each spatial direction. Since the movement in each direction is independent of the others, one can propose that the probability of being at a vertex situated at $\vec{r} = (ai, aj, ak)$ after n time-steps is

$$P(\vec{r}, n) = P(ai, n/d)P(aj, n/d)P(ak, n/d) = \left(\frac{6}{\pi n}\right)^{3/2} e^{-3/(2n)(i^2+j^2+k^2)} \quad (82)$$

that implies

$$p(x, y, z, t)dx dy dz = \left(\frac{3t_c}{2\pi ta^2}\right)^{3/2} e^{-3t_c/(2ta^2)(x^2+y^2+z^2)} dx dy dz . \quad (83)$$

Defining

$$D \equiv \frac{a^2}{6t_c} \quad (84)$$

we have

$$p(\vec{r}, t)d^d r = \left(\frac{1}{4\pi Dt}\right)^{3/2} e^{-r^2/(4Dt)} dx dy dz . \quad (85)$$

The random walk yields the simplest description of a variety of physical and biological problems. For instance, a polymer can be described by a walk on a three dimensional regular lattice. Several quantities of interest in the polymer science context can then be calculated. Some of them are : the end-to-end vector,

$$\vec{r}_{ete} \equiv \vec{r}_n - \vec{r}_0 , \quad (86)$$

and the radius of gyration,

$$\vec{r}_{rg} \equiv \frac{1}{n} \sum_{i=0}^n \left(\vec{r}_i - \frac{1}{n} \sum_{k=1}^n \vec{r}_k \right) . \quad (87)$$

3.3 Einstein's approach

In a series of papers published between 1902 and 1908 Einstein developed the molecular kinetic theory of gases to describe several physical effects and, notably, Brownian motion [4].

Einstein's argument goes as follows. Take N particles suspended on a liquid. Discretize time in intervals of length τ such that the motion of each particle can be taken to be independent of one another and of what happened to it in the previous

interval. For simplicity we focus on a one-dimensional case, the extension to higher dimensions being straightforward.

$$p(x, y, z, t) dx dy dz = \left(\frac{3t_c}{2\pi a^2} \right)^{3/2} e^{-3t_c/(2ta^2)(x^2+y^2+z^2)} dx dy dz . \quad (88)$$

When time increases by one τ unit each particle a will move a quantity Δ_a , different for each particle and that can be positive or negative. Among the total number N , dN particles will move by a quantity comprised in the interval $[\Delta, \Delta + d\Delta]$ during this time step. This number can be expressed as

$$dN = N\phi(\Delta)d\Delta \quad (89)$$

with

$$\int_{-\infty}^{\infty} d\Delta\phi(\Delta) = 1 . \quad (90)$$

If there are no external forces, one expects a symmetric motion in which $\phi(\Delta) = \phi(-\Delta)$ and, moreover,

$$\int_{-\infty}^{\infty} d\Delta\Delta^{2k+1}\phi(\Delta) , \quad (91)$$

where k is any integer. Moreover, $\phi(\Delta)$ is expected to be very peaked around $\Delta = 0$ since large displacements should be rare.

We now define $f(x, t)dx$ as the fraction of particles that lie in the interval $[x, x + dx]$ at time t (that is to say, the number of particles satisfying this condition, dN' , over the total number of particles, N). The conservation of the total number of particles implies $\int_{-\infty}^{\infty} dx f(x, t) = 1$ for all times t .

We can now combine these definitions to derive an equation for the evolution in time of $f(x, t)$. Indeed, during the time-step of duration τ , some of the particles lying in the desired interval $[x, x + dx]$ will leave it, others will enter it and other will remain within it. The evolution equation we are looking for should establish a balance between these contributions.

Thus, the fraction of particles that lie in the interval $[x, x + dx]$ at time $t + \tau$ is

$$f(x, t + \tau) = \int_{-\infty}^{\infty} d\Delta f(x + \Delta, t)\phi(-\Delta) . \quad (92)$$

Indeed, each particle contributes to the right-hand-side. A particle present at $x + \Delta$ at time t and that moves by $-\Delta$ during the time-interval τ , falls into the desired interval at time $t + \tau$. The integral then represents the sum over the contribution of all particles, where one multiplies the probability of presence at $x + \Delta$ at time t times the probability of jumping by the needed length $-\Delta$, that is $\phi(-\Delta)$. Since we can safely assume that the latter is a symmetric function of its argument we then write :

$$f(x, t + \tau) = \int_{-\infty}^{\infty} d\Delta f(x + \Delta, t)\phi(\Delta) . \quad (93)$$

The next step is to use some Taylor expansions to render this equation useful. First, since we assume that $\tau \ll t$ we can express the left-hand-side as

$$f(x, t + \tau) \approx f(x, t) + \frac{\partial f(x, t)}{\partial t} \tau \quad (94)$$

where we dropped all higher order terms in the series. Second, since we expect $\phi(\Delta)$ to be peaked around $\Delta = 0$, only small values of Δ will contribute to the integral. This allows us to expand the function $f(x + \Delta, t)$ as

$$f(x + \Delta, t) \approx f(x, t) + \frac{\partial f(x, t)}{\partial x} \Delta + \frac{\partial^2 f(x, t)}{\partial x^2} \frac{\Delta^2}{2} \quad (95)$$

where, again, we dropped all higher order terms in the Taylor expansion. Note, however, that we now kept the quadratic term too. It will become clear below why this is indeed needed.

Inserting these two approximate expressions in Eq. (93) we have

$$\begin{aligned} f(x, t) + \frac{\partial f(x, t)}{\partial t} \tau &= \int_{-\infty}^{\infty} d\Delta f(x, t) \phi(\Delta) + \\ &\int_{-\infty}^{\infty} d\Delta \frac{\partial f(x, t)}{\partial x} \Delta \phi(\Delta) + \int_{-\infty}^{\infty} d\Delta \frac{\partial^2 f(x, t)}{\partial x^2} \frac{\Delta^2}{2} \phi(\Delta) . \end{aligned} \quad (96)$$

Using the symmetry and normalization of $\phi(\Delta)$, see Eqs. (91) and (90), the first and second term in the right-hand-side simply yield $f(x, t)$ and 0, respectively. Thus,

$$\frac{\partial f(x, t)}{\partial t} \tau = \frac{\partial^2 f(x, t)}{\partial x^2} \int_{-\infty}^{\infty} d\Delta \frac{\Delta^2}{2} \phi(\Delta) . \quad (97)$$

Defining now the *diffusion constant*

$$D \equiv \frac{1}{\tau} \int_{-\infty}^{\infty} d\Delta \frac{\Delta^2}{2} \phi(\Delta) , \quad (98)$$

we finally obtain

$$\frac{\partial f(x, t)}{\partial t} = D \frac{\partial^2 f(x, t)}{\partial x^2} . \quad (99)$$

This is the *diffusion equation* from which one obtains the Gaussian distribution (80) and the diffusion law (81).

3.4 Langevin's approach

The Langevin equation [3] first appeared as a phenomenological approach to Brownian motion. Knowing that each individual collision deflects the trajectory of the particle by a tiny amount, Langevin proposed to collect the effect of all molecules in the fluid in a time-dependent random force. If the particle moves in d dimensions, has mass m , its center of mass position at time t is represented by $\mathbf{x} = (x_1, \dots, x_d)$ and its velocity is $\mathbf{v} = \dot{\mathbf{x}}$, Newton's equation reads

$$m\dot{\mathbf{v}}(t) = \mathbf{F}(t) + \mathbf{f}(t) . \quad (100)$$

The force \mathbf{F} designates all external deterministic forces while \mathbf{f} represents the force exerted by all the individual molecules in the fluid on the massive particle. The former is usually absent in the Brownian motion problem. The latter depends on the time-dependent positions of all the molecules and is a rapidly fluctuating function

of time with no preferred direction. The characteristic time for the variation of this force is related to the time interval between successive collisions, that we call τ_c , and can be estimated to be of the order of the pico-second or even shorter for a typical liquid.

Due to its rapid fluctuations, the time-dependence of the force \mathbf{f} cannot be specified. One can, instead, make reasonable assumptions about its average over a large number of identical macroscopic situations and characterize it in statistical terms. More precisely, one considers an ensemble of many copies of the system, say n , that are prepared in identical conditions, and defines ensemble-average quantities

$$\langle \mathcal{O}(t) \rangle = \frac{1}{n} \sum_{k=1}^n \mathcal{O}_{\mathbf{f}}^{(k)}(t), \quad (101)$$

with the label k identifying the copy in the ensemble and \mathcal{O} being any functional of the force \mathbf{f} . Equation (100) implies that the position and velocity of the particle are both fluctuating quantities that depend on \mathbf{f} . The aim is then to predict the average result of a large number of experiments performed in identical conditions.

In the absence of external forces, the problem is fully isotropic and the ensemble-averaged velocity vanishes. If the particle acquires a non-vanishing velocity \mathbf{v}_0 at a given instant, leading to $\langle \mathbf{v} \rangle \neq 0$, the fluctuating force must be such that after a short transient it restores the vanishing value $\langle \mathbf{v} \rangle = 0$. Thus, one can propose the decomposition

$$\mathbf{f} = \mathbf{f}_1(\mathbf{v}) + \xi, \quad (102)$$

where \mathbf{f}_1 is some function of \mathbf{v} that ensures $\langle \mathbf{v} \rangle \rightarrow 0$, and ξ is a purely random force, a *thermal noise*, that keeps the agitation of the particle.

The simplest choice for $\mathbf{f}_1(\mathbf{v})$ is the usual *friction force* :

$$\mathbf{f}_1(\mathbf{v}) = -\gamma \mathbf{v}, \quad (103)$$

that opposes the motion of the particle. The *friction coefficient*, γ , is in linear relation with the *shear viscosity* of the medium³, $\gamma = c\eta > 0$, with c a constant of geometric origin that depends on the size and shape of the colloidal particle. When the medium is a normal fluid, and the particle is a sphere of radius a that is much larger than the mean free-path of the particle one has $c = 6\pi a$ and one recovers the *Stokes law* for a spherical particle in a viscous fluid. γ is of the order of $n_p \tau_c k_B T$ with n_p the density of particles in the fluid, τ_c the average time between collisions, k_B Boltzmann's constant and T the temperature. For a typical liquid, like water in normal conditions, the viscosity is of the order of 0.01 Poise.⁴ With the choice (103) Eq. (100) becomes

$$m\dot{\mathbf{v}}(t) = -\gamma \mathbf{v}(t) + \mathbf{F}(t) + \xi(t). \quad (104)$$

³The shear viscosity of a system measures its resistance to flow. A flow field can be established by placing the system between two plates and pulling them apart in opposite directions creating a *shear force*. The rate at which the plates are pulled apart is called the *shear rate*. Other geometries are also possible.

⁴The friction coefficient and the viscosity are measured in units of [mass]/[time] and Poise \equiv [energy \times time]/[volume] in the CGS system, respectively.

The simplest choice for the time-dependent thermal noise $\xi(t)$ is a Gaussian random force with zero mean and delta-correlated :

$$\langle \xi_i(t) \rangle = 0 \quad \forall i \text{ and } t, \quad (105)$$

$$\langle \xi_i(t) \xi_j(t') \rangle = 2A \delta_{ij} \delta(t - t') \quad \forall i, j \text{ and } t, t', \quad (106)$$

while all higher correlation functions, involving more than two factors of $\xi_i(t)$ can be deduced from these two due to the Gaussian character. The choice of the constant $2A$ in the correlation between the noise evaluated at two different times is very important to ensure that this *stochastic process* lead to the good asymptotic limit. We shall see below and in TD 4 that one is forced to use

$$2A = 2k_B T. \quad (107)$$

The average over different realizations of the history of the system introduced in Eq. (101) corresponds now to an average over histories of the time-dependent random force, ξ . Indeed, each realization of the thermal-noise time-series leads to a particular trajectory $(\mathbf{v}_\xi, \mathbf{x}_\xi)$ of the particle. meaning information corresponds to an average over all possible thermal noise realizations. Thus, the procedure to obtain useful information from the Langevin equation is then the following. One first obtains an expression for (\mathbf{v}, \mathbf{x}) as functions of the thermal noise ξ . One then inserts these expressions in the observable \mathcal{O} one is interested in. For example, if \mathcal{O} is the kinetic energy of the particle, $\mathcal{O} = m\mathbf{v}_\xi^2/2$ where the subindex ξ indicates that \mathbf{v} depends on the particular realization of ξ .

3.4.1 Irreversibility and dissipation

The friction force $-\gamma\mathbf{v}$ in the Langevin equation (104) explicitly breaks the time-reversal ($t \rightarrow -t$) invariance, a property that has to be respected by any set of microscopic dynamic equations. However, the Langevin equation is an effective equation that takes into account the dynamics of the particle *and* the one of the molecules in the liquid that interact with it via collisions. Time-reversal can be broken in such a *reduced* equation in which one passes from a closed system (the dynamics of the particle and the fluid in interaction) to an open one (the dynamics of the particle under the influence of the fluid). In Sect. ?? we shall see this calculation at work. The energy of the particle is not conserved during the evolution and, in general, it flows to the bath leading to *dissipation*. At very long times, the particle may attain a stationary regime in which the transmission of energy becomes symmetric on average, with the particle giving and receiving energy from the bath at equal rate.

3.4.2 Generation of memory

The Langevin equation (104) is a first order differential equation. The full dynamics of the particle is determined by this equation together with $\mathbf{v}(t) = \dot{\mathbf{x}}(t)$ which is also a first-order differential equation.

The discretization of stochastic equations is a difficult subject that we shall not discuss in detail here. In general one evaluates the deterministic forces in the right-hand-side of (104) in a linear combination of the extremes of the time-interval considered. Different choices for the coefficients lead to different stochastic calculi, the best-known ones being due to Itô and Stratonovich. The noise is always evaluated at the lower end point of each partition subinterval. If the noise is white this value is totally uncorrelated from the values taken by the noise in previous time-steps.

These features imply that the velocity of the particle at time $t + \delta$ depends on the velocity of the particle at time t with δ an infinitesimal time-step. Thus, the full set of equations defines a *Markov process*, in other words, a stochastic process that does not depend on its history. Note, however, that the same problem could be described by the single second-order differential equation

$$m\ddot{\mathbf{x}}(t) + \gamma\dot{\mathbf{x}}(t) = \mathbf{F}(t) + \xi(t) . \quad (108)$$

Having replaced the velocity by its definition in terms of the position the Markov character of the process is lost. This is a very general feature : integrating away some degrees of freedom one generates memory in the evolution. Generalisations of the Langevin equation, such as the one that we present in Sect. ??, and the ones that will be generated in the slow evolution of super-cooled liquids and glasses, do have memory.

3.4.3 Fluctuation – dissipation relation of the second kind

In the heuristic derivation of the Langevin equation that we presented the constant A is not fixed. The simplest way of setting this parameter is by studying the velocity fluctuations of a Brownian particle in a constant external force. The time-dependent velocity of the particle follows from the integration over time of Eq. (104)

$$\mathbf{v}(t) = \mathbf{v}_0 e^{-\frac{\gamma}{m}t} + \frac{1}{m} \int_0^t dt' e^{-\frac{\gamma}{m}(t-t')} [\mathbf{F} + \xi(t')] , \quad (109)$$

with \mathbf{v}_0 the initial velocity at $t = 0$. Using the fact that the noise has zero average one finds

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}_0 e^{-\frac{\gamma}{m}t} + \frac{\mathbf{F}}{\gamma} (1 - e^{-\frac{\gamma}{m}t}) \rightarrow \frac{\mathbf{F}}{\gamma} \quad \text{when } t \gg t_c \equiv \frac{m}{\gamma} . \quad (110)$$

Using the noise-noise auto-correlation in Eq. (??), and setting $\mathbf{v}_0 = \mathbf{0}$ for simplicity, one readily calculates the mean-square displacement of the velocity in each direction of space, $\sigma_{v_i}^2(t) \equiv \langle (v_i(t) - \langle v_i(t) \rangle)^2 \rangle$,

$$\sigma_{v_i}^2(t) = \frac{1}{m^2} \int_0^t dt' \int_0^t dt'' e^{-\frac{\gamma}{m}(2t-t'-t'')} \langle \xi_i(t') \xi_i(t'') \rangle = \frac{A}{\gamma m} (1 - e^{-\frac{2\gamma}{m}t}) . \quad (111)$$

Since we expect the Langevin equation to drive the velocity to equilibrium at temperature T , this quantity must saturate to the static expected value calculated with the canonical distribution. Thus,

$$\lim_{t \gg t_c} \sigma_{v_i}^2(t) = \frac{A}{\gamma m} = \langle (v_i - \langle v_i \rangle)^2 \rangle_{eq} = \frac{k_B T}{m} , \quad (112)$$

where $\langle \cdot \rangle_{eq}$ denotes an average taken with Maxwell's velocity distribution. In order to match this equality one enforces

$$A = \gamma k_B T . \quad (113)$$

This relation is known under the name of fluctuation–dissipation theorem (FDT) of the second kind [?]. It is important to note that it applies to the fluid since it relates the noise-noise correlation to the friction coefficient. In the case of the Brownian particle this relation ensures that after a transient of the order of t_c , the bath maintains the mean kinetic energy of the particle constant and equal to its equilibrium value. The Gaussian distribution of the noise and the linear relation linking it to the velocity imply that the velocity of the particle is indeed distributed with Maxwell's distribution. We shall see later that even when the environment satisfies a fluctuation – dissipation relation (FDR) the system which is set in contact with it does not necessarily follow and satisfy an FDR itself. This is one of the main characteristics of non-equilibrium systems in contact with equilibrated environments.

3.5 Diffusion

Diffusion is the random migration of molecules or small particles arising from motion due to thermal energy. A simple experience demonstrating this phenomenon consists in layering aqueous solutions of a dye into water. After matching the specific gravity of the dye to that of the water (e.g. by adding sucrose to the water), one sees that the dye diffuses in all directions (towards the top and the bottom of the test tube) until it becomes uniformly dispersed.

A simple derivation of Fick's law is based on the random walk problem. Take a one dimensional random walk. J_x is defined as the number of particles that move across unit area in unit time :

$$J_x(x, t) \equiv \frac{\# \text{ part. that move from } x \text{ at } t \text{ to } x + \delta \text{ at } t + \tau}{A\tau} \quad (114)$$

The number of particles at position x ($x + \delta$) at time t is $N(x)$ ($N(x + \delta)$). Half of the particles at x at time t move to the right (i.e. to $x + \delta$) while the other half move to the left (i.e. to $x - \delta$) during the time-step τ . Similarly, half of the particles at $x + \delta$ at time t move to the right (i.e. to $x + 2\delta$) while the other half move to the left (i.e. to x). Thus, the net number of particles that move from x to $x + \delta$ when $t \rightarrow t + \tau$ is

$$\# \text{ part. that move from } x \text{ at } t \text{ to } x + \delta \text{ at } t + \tau = -\frac{1}{2} [N(x + \delta, t) - N(x, t)] . \quad (115)$$

Thus,

$$\begin{aligned} J_x(x, t) &= -\frac{\delta^2}{2\tau} \frac{1}{\delta} \left[\frac{N(x + \delta, t)}{A\delta} - \frac{N(x, t)}{A\delta} \right] \\ &= -D \frac{[C(x + \delta, t) - C(x, t)]}{\delta} \end{aligned} \quad (116)$$

with $C(x, t)$ the concentration of particles at position x at time t . In the limit $\delta \rightarrow 0$ one finds

$$J_x(x, t) = -D \frac{\partial C(x, t)}{\partial x}. \quad (117)$$

Fick's second law follows from (117) provided the number of particles is conserved (there are no sources or sinks). If one takes a box of volume $A\delta$, in the time-interval τ , $J_x(x, t)A\tau$ particles enter the box from the left while $J_x(x + \delta, t)A\tau$ particles leave it from the right. Therefore, the number of particles in the volume increases at the rate

$$\begin{aligned} \frac{[C(x, t + \tau) - C(x, t)]}{\tau} &= -\frac{1}{\tau} [J_x(x + \delta, t) - J_x(x, t)] \frac{A\tau}{A\delta} \\ &= \frac{[J_x(x + \delta, t) - J_x(x, t)]}{\delta} \end{aligned} \quad (118)$$

that in the limit $\delta \rightarrow 0$ becomes

$$\frac{\partial C(x, t)}{\partial t} = -\frac{\partial J_x(x, t)}{\partial x} = D \frac{\partial^2 C(x, t)}{\partial x^2}. \quad (119)$$

This equation tells us how an initial distribution $C(x, 0)$ will redistribute in time. The border conditions play a very important role in determining the form of the time-dependent concentration $C(x, t)$.

3.6 Three dimensions

Fick's laws (117) and (119) are very easy to generalize to the three dimensional case. It suffices to notice that similar equations hold in the y and z direction and to reconstruct then

$$\vec{J}(\vec{x}, t) = -D \vec{\nabla} C(\vec{x}, t), \quad (120)$$

$$\frac{\partial C(\vec{x}, t)}{\partial t} = D \nabla^2 C(\vec{x}, t). \quad (121)$$

3.7 Diffusion with drift

When a constant external force, say in the x direction is applied on the system, the flux at point x increases by $v_d C(x, t)$ where v_d is the drift velocity, $v_d \equiv d\langle x(t) \rangle / dt$. Thus, Fick's equations become

$$\vec{J}(\vec{x}, t) = -D \nabla C(x, t) + v_d \hat{x} C(x, t), \quad (122)$$

$$\frac{\partial C(x, t)}{\partial t} = D \nabla^2 C(\vec{x}, t) - v_d \hat{x} \frac{\partial C(\vec{x}, t)}{\partial x}. \quad (123)$$

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Phénomènes de transport

1 TD 1 : Transfer et radiation de la chaleur

On étudiera plusieurs aspects du transfert de la chaleur sous la forme de la lois de Fourier et la lois du corps noir.

Transfer de la chaleur

- (a) Prenons un cylindre troué de rayon interne r_1 et rayon externe $r_1 + \Delta r$ et longueur $L \gg r_1 + \Delta r$. On s'intéresse à étudier la conduction de la chaleur à travers une direction radiale du cylindre si la parois interne est maintenue à la température fixe T_1 et celle externe est maintenue à la température fixe T_2 .
- Écrire la lois de Fourier en coordonnées cylindriques.
 - Trouver le différentiel de chaleur entrant dans le cylindre par unité de temps. On l'appellera dQ_1 .
 - Trouver le différentiel de chaleur sortant du cylindre par unité de temps. On l'appellera dQ_4 .
 - Quelles peuvent-être les autres deux sources de chaleur ?
 - S'il n'y a pas de sources de chaleur supplémentaires, trouver une équation différentielle aux dérivés partielles que détermine la variation de la température le long de la direction radiale.
 - Trouver la solution de cette équation. Fixer les constantes d'intégration à l'aide des conditions aux bords.
 - Calculer le transfert de la chaleur, dQ/dt , le long de la direction radiale du cylindre.
- (b) L'analogie avec la conductivité électrique peut être exploitée pour obtenir les propriétés conductrices de chaleur d'objets composés. Prenons une parois composée de deux "layers" d'épaisseurs L_1 et L_2 , conductivités thermiques k_1 et k_2 , et avec la même surface A . La surface externe à gauche est maintenue à une température fixe T_1 tandis que la surface à droite est maintenue à une autre température fixe T_3 . L'interface entre les deux layers sera à une température T_2 qu'on déterminera.
- Est-il un système en série ou en parallèle ?
 - Calculer la resistance thermique de la parois composée.
 - Comparer la variation de la température dans la direction perpendiculaire à la surface dans les deux layers.
 - Calculer le taux de flux de chaleur dQ/dt qui traverse la parois d'une surface externe à l'autre.
 - Calculer la température à l'interface (T_2).

Radiation de corps noir

- (a) L'énergie d'un oscillateur harmonique de masse m et fréquence f dépend de sa position et de sa vitesse et elle est donnée par

$$E = E_c + E_p \quad E_c = \frac{1}{2}mv^2 \quad E_p = \frac{1}{2}mf^2x^2. \quad (124)$$

- i. Si on suppose que la position x et la vitesse v sont des variables aléatoires indépendantes distribuées selon la distribution de Gibbs-Boltzmann :

$$p(v, x) = Z^{-1} e^{-\beta(\frac{m}{2}v^2 + \frac{m}{2}f^2x^2)}, \quad (125)$$

calculer la valeur moyenne de l'énergie cinétique E_c et de l'énergie potentielle E_p .

Sont ces deux valeurs identiques ?

Ce résultat correspond à la lois classique d'équipartition de l'énergie : un degré de liberté, x , donnant une contribution quadratique à l'énergie, $E = ax^2 + E'$, où E' est indépendant de x , donne une contribution $k_B T/2$ à la valeur d'expectation de l'énergie.

- ii. Si les valeurs possibles de l'énergie sont quantifiés, *i.e.* si $E = nhf$ avec $n = 0, 1, 2, \dots$, h la constante de Planck et f la fréquence de l'oscillateur, et elle est distribuée selon

$$p(E) = e^{-\beta E}, \quad (126)$$

calculer la valeur moyenne de l'énergie.

- iii. Comparer le résultat classique trouvé en 5(a)i au résultat quantique calculé en 5(a)ii.

- (b) On étudiera divers aspects de la lois de Planck pour la radiation $S(f)$.

- i. Montrer que la lois de Planck devient celle de Rayleigh-Jeans pour les petites fréquences.
- ii. Trouver la lois du déplacement de Wien, *i.e.* comment se comporte-t-il la fréquence f_{max} avec la température ?
- iii. Trouver le comportement asymptotique de la lois de Planck pour les grandes fréquences. Comment se compare-t-il à la lois de Rayleigh-Jeans ?

- (c) On étudiera la radiation d'une pièce de monnaie de diamètre $d = 2.14$ cm, épaisseur $h = 0.2$ cm et masse $m = 5.1$ gr à température ambiante $T = 22$ C.

- i. Si l'on suppose que la lois de Planck gouverne l'énergie radiée par la pièce de monnaie ; quelle est la radiation de cette pièce à température ambiante par seconde ?
- ii. Cette radiation est associée à l'émission de photons. On estimera l'énergie moyennes des photons émis par $E = hf_{max}$ avec f_{max} la fréquence du maximum de la courbe de radiation du corps noir. Calculer f_{max} à température ambiante et l'énergie moyenne des photons qu'on appellera E_{photon} .
- iii. Combien de photons partent de la pièce de monnaie par seconde ?

Phénomènes de transport

2 TD 2 : Etude des distributions de probabilité

La distribution de Maxwell

On étudiera la distribution de Maxwell pour le module de la vitesse d'une molécule :

$$P(v) = Z^{-1} e^{-\beta \frac{1}{2} m v^2} \quad (127)$$

avec $\beta = (k_B T)^{-1}$ et Z la constante de normalisation.

- Calculer la normalisation de la distribution de Maxwell.
- Calculer la valeur d'expectation du module de la vitesse v qu'on appellera $\langle v \rangle$.
- Calculer la valeur la plus probable du module de la vitesse. Comparer le résultat à $\langle v \rangle$.
- Calculer la probabilité d'avoir $v > \alpha \langle v \rangle$ avec α une constante. Discuter ce résultat en fonction de la température.

La distribution de Boltzmann

On étudiera la distribution de Boltzmann

$$P(E) = Z^{-1} e^{-\beta E} \quad (128)$$

avec $\beta = (k_B T)^{-1}$ et Z la constante de normalisation.

- Calculer la normalisation de la distribution de Boltzmann.
- Calculer la valeur d'expectation de l'énergie E .
- Calculer la variance de la distribution $P(E)$ qu'on appellera σ_E .
- Identifier la valeur la plus probable de l'énergie. Est-elle égale à $\langle E \rangle$?
- Calculer la probabilité d'avoir $E > \alpha \langle E \rangle$ avec α une constante. Discuter ce résultat en fonction de la température.
- Tracer, à l'aide de SciLab, la distribution de Boltzmann pour plusieurs valeurs de la température. Identifier les valeurs calculés précédement ($\langle E \rangle$, σ_E , la valeur la plus probable).

Phénomènes de transport

3 TD 3 : Applications de la théorie cinétique

- (a) Dans un premier temps nous rappellerons les propriétés plus importantes des collisions (**exercice à faire à la maison**).
- Deux billes se déplacent dans l'espace à trois dimensions. La première a une masse m_1 et une vitesse \vec{v}_1 tandis que la deuxième a une masse m_2 et une vitesse \vec{v}_2 .
- Etablir les lois de conservation si les deux billes entrent en collision élastique.
 - Dans ce cas Trouver l'expression de la vitesse finale de chaque bille.
 - Calculer la vitesse finale de chaque bille dans le cas plus simple où la deuxième bille est au repos ($\vec{v}_2 = 0$). Combien de solutions a-t-on ? Discuter les propriétés de ces solutions.
 - Etablir les lois de conservation si la collision est inélastique.
 - Calculer la vitesse finale des deux billes si après collision elles partent ensemble, i.e. avec la même vitesse.
- (b) On prend une particule dans un cylindre de longueur L à une dimension. Le cylindre est fermé par une paroi et un piston. La particule se déplace avec une vitesse \vec{v}_p suivant la direction du cylindre et elle effectue des collisions parfaitement élastiques avec la paroi et le piston.
- Décrire le mouvement de la particule.
 - Décrire le mouvement de la particule si l'on déplace le piston à vitesse constante \vec{v}_{piston} de façon telle qu'on réduit la longueur du cylindre. Que se passe-t-il avec la vitesse de la particule après chaque collision avec la paroi et le piston ?
 - Si, au contraire, l'on déplace le piston à vitesse constante $-\vec{v}_{piston}$ de façon à accroître la longueur du cylindre, que se passe-t-il avec la vitesse de la particule après collisions ?
 - Peut-on utiliser cet exemple pour expliquer pourquoi un gaz se refroidit/rechauffe quand il entre en compression/expansion ?
- (c) On étudiera la vitesse moyenne d'une particule de masse m qui se déplace dans un espace trois dimensionnel.
- Déterminer la vitesse carré moyenne, $\langle v_x^2 \rangle$, où v_x est la vitesse selon l'axe x supposée en équilibre thermodynamique.
 - La particule en question est une molécule de la protéine lysozyme en solution aqueuse à température ambiante. Un mol de cette protéine a une masse 1.4×10^4 gr. Estimer la vitesse instantanée de la protéine en m/s. Que peut-on dire sur ce valeur ?

- (d) Un vent très fort a une vitesse $v = 30$ m/s. Si la densité de l'air est $\rho = 1.2$ kg/m³, calculer la pression exercée par ce vent sur une parois perpendiculaire à sa direction.
- (e) Quelle est la température à la quelle un atome d'hélium ($m = 6.63 \times 10^{-27}$ kg) dans un gaz à l'équilibre thermique a une vitesse carrée moyenne $v_{rms} = 3000$ m/s.
- (f) L'énergie cinétique moyenne d'un gaz idéal à $T = 10$ °C est $\langle E_c \rangle(T_1)$. A quelle température T_2 on aura $\langle E_c \rangle(T_2) = 2\langle E_c \rangle(T_1)$?
- (g) Un gaz monoatomique idéal est fait de molécules de masse m . Initialement la vitesse carrée moyenne des molécules est $\langle v_i^2 \rangle$, la pression est P_i et le volume est V_i . Le gaz est laissé s'expand a quatre fois le volume initial, $V_f = 4V_i$. Pendant l'expansion la pression est maintenue constante $P_i = P_f$.
- Que doit-on faire avec la température pour permettre ce processus ? Donner la valeur de la température finale du gaz.
 - Quelle est la vitesse carrée moyenne finale des molécules ?
 - Calculer le travail effectué par le gaz pendant l'expansion.
 - Calculer la chaleur fournie pendant l'expansion isobarique.

Phénomènes de transport

4 TD 4 : Marches au hasard et équation de Langevin

Marche au hasard de biais

On considère un marcheur sur un réseau unidimensionnel qui, à chaque pas de temps, passe sur le site de droite avec la probabilité p ou sur celui de gauche avec la probabilité q ($p + q = 1$). Le marcheur ne peut pas rester sur place. La maille du réseau est δ .

1. Calculer (directement) la probabilité $P_n(i)$ qu'il se trouve sur le site numéro i après n pas de temps, étant parti du site $i = 0$.
2. Calculer la moyenne et la variance (ou le déplacement) de la position $x = i\delta$ du marcheur.

Comparer les résultats obtenus pour $p \neq q$ and $p = q = 1/2$.

Identifier le coefficient de diffusion quand $p = q = 1/2$.

Comparer la dépendance temporelle de $\langle x \rangle$ et $\langle (x - \langle x \rangle)^2 \rangle^{1/2}$ avec celle du déplacement d'un point matériel avec vitesse constante. Discuter séparément les cas $p \neq q$ et $p = q = 1/2$.

Calculer $d\langle x \rangle / dt$ où le temps est $t = \tau n$ avec τ l'intervalle infinitesimal de saut pour $p = 1/2 + \frac{F\delta}{4k_B T}$ et $q = 1 - p$. Exprimer le résultat en fonction de la constante de diffusion, la force F et $k_B T$.

3. Tracer 5 trajectoires schématisées en tenant compte des résultats trouvés précédemment. Comparer au cas déterministe.
4. Si la constante de diffusion d'une petite molécule (e.g. lysozyme) en solution aqueuse à température ambiante est $D = 10^{-5} \text{ cm}^2/\text{s}$, et sa vitesse instantanée est estimée par $v_i = \langle v_x \rangle^{1/2}$, trouver le longeur spatiale et temporelle de chaque pas de la marche au hasard qu'elle a effectuée. Combien de pas effectuée-t-elle par seconde?
5. À l'aide de la formule de Stirling : $N! \sim N^N \exp(-N) \sqrt{2\pi N}$, donner la limite $\rho(x, t)$ de la loi $P_n(i)$ pour une description continue. Quelle loi de probabilité a-t-on trouvé?

Le modèle de Langevin du mouvement brownien

Le mouvement brownien est le mouvement complexe, de type erratique, effectué par une particule lourde immergée dans un fluide, subissant des collisions avec les molécules de ce fluide. Toute quantité physique observée expérimentalement est accompagnée de fluctuations dues à l'agitation thermique microscopique dans le fluide. Nous allons travailler, par souci de simplicité, en dimension $d = 1$. La généralisation au cas d dimensionnel est immédiate.

1. On considère une particule sphérique de rayon a , de masse m , se déplaçant à la vitesse v dans un fluide à température T . Si la viscosité du fluide est η , quelles sont les forces exercées par le fluide sur la particule ? Écrire l'équation d'évolution de la particule (équation de Langevin).
2. Discuter le bruit thermique $\xi(t)$. Quelle est l'hypothèse la plus simple pour ses propriétés statistiques ? Characteriser sa moyenne et sa corrélation.
3. Sachant que la vitesse de la particule parvient à l'équilibre pour des temps longs, donner la distribution de probabilité de la vitesse et l'énergie cinétique moyenne de la particule.
4. On va déduire, d'une façon simple, la relation d'Einstein qui relie la constante de diffusion et les paramètres $k_B T, \eta, a$. Pour ce faire, on va résoudre l'équation de Langevin puis calculer le déplacement quadratique moyen de la particule par rapport à la position initiale $\langle (x(t) - x(0))^2 \rangle$ en s'aidant des indications suivantes :
 - (a) Multiplier l'équation de Langevin par $x(t)$ et moyenner sur la force aléatoire. Quels sont les termes non nuls ? Pourquoi ?
 - (b) Donner une expression pour $d\langle x^2 \rangle / dt$. La constante temporelle $\tau = \gamma^{-1}$ valant typiquement $\tau \sim 10^{-8} s$, quelle est la valeur asymptotique de $d\langle x^2 \rangle / dt$?
 - (c) Finalement, trouver la constante de diffusion D définie par

$$\langle (x(t) - x(0))^2 \rangle = 2Dt \tag{129}$$

La relation entre D et les paramètres $k_B T, \eta, a$ s'appelle la relation d'Einstein.

- (d) Quelle a été l'hypothèse qui a permis de déduire la relation d'Einstein ?

On note que cette dérivation est celle présentée par Langevin dans son papier celebre.

5. On ajoute une force externe dérivant d'un potentiel, qui ne dépend que de la position de la particule : $F(x(t))$. On se place dans la limite où le terme d'inertie est négligeable. L'équation de Langevin devient :

$$\begin{aligned} m\gamma\dot{x}(t) &= F(x(t)) + \xi(t) \\ \langle \xi(t)\xi(t') \rangle &= 2k_B T m \gamma \delta(t - t') \end{aligned} \tag{130}$$

où nous avons supposé que le bruit $\xi(t)$ est blanc.

- (a) Par soucis de simplicité on considère seulement le cas d'une force constante, $F(x(t)) = F$. Résoudre l'équation de Langevin et exprimer $x(t)$ en fonction de la force et du bruit thermique.
- (b) Calculer la moyenne de la position, $\langle x(t) \rangle$.
- (c) Calculer le déplacement quadratique moyen, $\langle (x(t) - \langle x(t) \rangle)^2 \rangle$. Comparer aux résultats trouvés pour la marche au hasard de biais.

Phénomènes de transport

5 TD 5 : Equation de diffusion

On étudiera l'équation de diffusion.

1. Soit un espace à trois dimensions avec une densité initiale de particules constante dans le demi-espace $z < 0$ et nulle dans le demi-espace $z > 0$.

Resoudre l'équation de diffusion et trouver $C(\vec{x}, t)$.

5.0.1 Three dimensions

Fourier law in three dimensions reads

$$\partial Q(\vec{x}, t) = -A\vec{k} \cdot \vec{\nabla} Q(\vec{x}, t) \quad (131)$$

ON PEUT FAIRE CE PROBLEME DANS LE CONTEXTE DE LA CONDUCTION DE CHALEUR...

(a) xxx

1 TP 1 : Mesure du nombre d'Avogadro

1. Mesures préliminaires

Le premier propos de ce TP est de visualiser le mouvement de particules de latex en suspension dans une solution aqueuse très diluée et de faire des mesures de leur déplacement à différentes échelles de temps afin de pouvoir les analyser quantitativement et les comparer au modèle théorique du mouvement brownien.

Afin de pouvoir effectuer des mesures quantitatives, il est nécessaire de déterminer préalablement le grossissement du système de visualisation utilisé : microscope, caméra et écran. On utilise à ce but une échelle micrométrique gravée sur une lame de verre qui, visualisée à l'écran, permet de noter la longueur **correspondante** à $1 \mu\text{metre}$.

Déposer dans la cuve de la lame porte-objet quelque goutte de suspension, couvrir la cuve pleine avec une lamelle en faisant attention à éviter la formation de bulles. Placer l'échantillon sur le microscope. Faire la mise au point en regardant l'image à écran.

Enregistrer les images pour une durée de 10 minutes environs.

2. Détermination du nombre d'Avogadro

En utilisant les images enregistrées, un chronomètre et un transparent fixé à l'écran, suivre une particule des yeux et pointer sa position toutes les $\Delta t = 30$ secondes, en prenant soin de joindre chaque point au précédent. Effectuer **une dizaine** de pointés pour chaque particule, répéter la mesure pour **une dizaine** de particules.

Avec une règle graduée, mesurer sur les transparents les déplacements $L(t_i)$ correspondants à chaque pas temporel et dresser un tableau de ces valeurs **dans excel**. Évaluer la précision des pointés, donc l'incertitude sur les $L(t_i)$.

En supposant que le modèle du mouvement brownien (2-dimensionnel) soit vérifié, quelle est la relation attendue entre les déplacements $L(t_i)$ effectués pendant un pas de temps et ce temps Δt ? Donner cette relation en fonction du coefficient de diffusion D des particules.

Il est donc possible de déterminer le nombre d'Avogadro à partir des mesures effectuées, en utilisant la loi de Stokes

$$D = \frac{k_B T}{6\pi\eta a} \quad (132)$$

qui relie le coefficient de diffusion d'une particule de rayon a au paramètres caractérisant le milieu dans lequel elle diffuse, notamment la viscosité η et la température T .

Déterminer d'abord l'estimation expérimentale du coefficient de diffusion D des particules de latex, et son incertitude. En déduire la valeur expérimentale du nombre d'Avogadro N_A et son incertitude, la comparer à la valeur théorique, $\mathcal{N}_A = 6.022126 \times 10^{23} \text{ mol}$.

Pour le calcul, on pourra utiliser les valeurs suivantes :

$$R = 8,32 \text{ J mol}^{-1} \text{ K}^{-1} \quad \eta = 0,8513 \text{ mPa s} \quad T = 300 \text{ K} \quad a = 0,501 \text{ mm}.$$

3. Autosimilarité des trajectoires

Utiliser à nouveau les images enregistrées et un transparent pour tracer la “trajectoire” d’une particule en pointant sa position toutes les 20 secondes., en prenant soin de joindre chaque point au précédent. Effectuer une dizaine de pointés. Reprendre en suite l’enregistrement des déplacements de la même particule et tracer sur le même transparent sa trajectoire toutes les 10 secondes, puis toutes les 5 secondes. Qu’est-ce qu’on s’attend pour le déplacement moyen $\langle L(t_i) \rangle$ dans les trois cas ? Commenter les “trajectoires” tracées en proposant une méthode statistique pour mettre en évidence leur autosimilarité. Jusqu’à quel niveau cette propriété reste valable ?

4. Verification de la loi d’évolution

Déterminer une méthode pour vérifier, en utilisant les trajectoires tracées en 2, si le mouvement des particules de latex peut être effectivement décrit par le modèle du mouvement brownien. Essayer de faire cette vérification en effectuant un choix approprié des mesures à faire. Conclusions ?

2 TP 2 : Étude optique de la diffusion d'un corps dissout

Diffusion à une dimension dans une solution

Le propos de ce TP est l'étude de la diffusion des molécules de glycérine, contenues dans une solution aqueuse, dans l'eau. Dans une solution, il est difficile d'imposer des conditions stationnaire; nous allons étudier le régime dynamique obtenu en imposant des conditions initiales appropriées.

L'équation que nous allons utiliser est l'équation de conservation de la matière (loi de Fick) :

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (133)$$

où c indique la concentration volumique des particules diffusantes et D leur coefficient de diffusion. Pour réaliser une diffusion unidimensionnelle nous allons réaliser une géométrie telle que à temps $t = 0$ la concentration des particules est constante dans un semi-espace ($z \leq 0$) et nulle dans l'autre :

$$c(z, t = 0) = c_0 \theta(-z). \quad (134)$$

La géométrie du dispositif expérimental est montré schématiquement en figure.

Calculer (Rappeler) la solution de l'équation de diffusion pour ce choix des conditions initiales. Estimer la largeur de la zone de diffusion (où le gradients de concentration prend une valeur notable).

Aspect optique

Compte tenu de la diffusion, l'indice de réfraction varie dans la zone de diffusion; en première approximation, l'ordre de grandeur du gradient d'indice au centre de la zone de diffusion peut s'écrire

$$\frac{\partial n(z, t)}{\partial z} = \frac{\Delta n}{\Delta z} = \frac{n_0 - n_{eau}}{\Delta z}. \quad (135)$$

D'autre part dans un milieu d'indice variable le rayon de courbure R d'un faisceau lumineux est donné par

$$\frac{1}{R} = \frac{1}{n} \vec{N} \cdot \vec{grad} n, \quad (136)$$

où \vec{N} est la normale au faisceau. Dans notre cas, le rayon incident est presque perpendiculaire au gradient de concentration; cependant, il ne l'est pas totalement et ceci suffit à induire une déviation dans la direction parallèle à $\vec{grad} n$.

Estimer approximativement l'angle $\alpha \ll 1$ de déviation verticale subi par un faisceau lumineux traversant la solution avec une direction initiale perpendiculaire à Oz, si l'épaisseur de la cuve utilisée, noté d (voir figure a), est faible. Dans ce cas, on peut raisonnablement assumer que la déviation verticale de chaque rayon est petite, et donc que la concentration et le gradient de concentration dans la région

traversée sont presque constants.

Le rayon ainsi dévié subi une deuxième réfraction en correspondance de la face de sortie de la cuve. **Évaluer, à l'aide de la loi de Snell, l'angle β de sortie corriger figure a, qui détermine la déflexion vertical obtenue sur l'écran.** L'approximation de petits angles sera encore considérée comme valable.

Étude optique de la diffusion

Les considérations précédentes permettent de relier la variation au cours du temps de la déflexion verticale h des rayons de lumière au coefficient de diffusion des molécules de glycérine dans l'eau **corriger figure c.**

Écrire la relation qui relie h à β , puis à D .

On utilise pour cette expérience une solution diluée de glycérine. Verser tout d'abord l'eau dans la cuve à faces parallèles sur une demie-hauteur de 2 à 3. Placer la cuve près du bord du support du côté de l'écran, puis introduire la burette le long d'un bord jusqu'au fond de la cuve et verser très délicatement la solution de glycérine en évitant les remous qui entraîneraient le mélange des solution. Pour la même raison on laissera la burette en cette position sans essayer de la sortir de la cuve.

En dirigeant le faisceau laser normalement à la cuve, observer qu'il n'y a aucune déviation lorsque la lumière traverse l'eau ou la solution pure, alors que dans la zone de diffusion on observe une déviation vers le bas en accord avec la théorie.

Placer maintenant la lentille cylindrique inclinée à 45° sur la trajectoire du laser de façon à élargir le faisceau pour former une nappe laser qui traverse la cuve en diagonal sur toute son hauteur. **Observer la trace du faisceau sur l'écran placé à une distance L d'environ 50 cm de la cuve. Relever la distance L exacte.**

Relever la déflexion maximum h en fonction du temps (pendant une heure environs). Relever aussi approximativement la largeur à mi-hauteur de la courbe. Comment ces deux grandeurs sont reliées l'une à l'autre? Comparer les résultats obtenus expérimentalement pour la largeur de la courbe aux prédictions théoriques.

Utiliser les valeurs de h recueillies pour déterminer, sur la base d'un graphe approprié et des considérations théoriques précédentes, la valeur du coefficient de diffusion D de la glycérine dans l'eau.

Conclusions

Estimer l'incertitude sur la valeur de D obtenue. Quels sont les facteurs qui influencent le plus la précision de la mesure?

Comparer les résultats obtenus avec ceux qui sont obtenus par les autres groupes qui ont travaillé avec des solutions de concentration différente. Qu'est-ce qu'on peut prévoir pour cette comparaison sur la base de la relation de Stokes-Einstein,

$$D = \frac{k_B T}{6 \pi \eta a} ? \quad (137)$$

3 TP 4 : Analogie électrique de transferts thermiques

Dans la première partie de cette manipulation, nous allons étudier expérimentalement l'élévation de la température d'un bloc de cuivre mis en contact thermique avec un thermostat. Nous disposons d'un modèle simple pour ce phénomène, vu en TD, et basé sur l'analogie entre le transfert de chaleur à travers une paroi et le passage d'une charge électrique à travers une résistance. Cependant, nous verrons que le phénomène observé dans le système réel ne correspond pas au modèle idéal.

Le comportement observé dans le système thermique peut être difficile à expliquer. L'analogie avec le système électrique peut alors aider : dans la deuxième partie de l'expérience nous allons donc utiliser l'analogie électrique pour essayer de reproduire le même comportement et de l'interpréter.

Rappel de l'analogie électrique du transfert de chaleur

Expliquer brièvement l'analogie entre la charge d'un condensateur dans un circuit RC et le passage de chaleur à travers un isolant mince séparant un thermostat à température fixé T_0 et un corps de capacité calorifique C .

Rappeler en particulier les lois physiques qui gèrent les deux phénomènes, leur application dans les cas spécifiques considérés, les grandeurs physiques correspondantes et les lois d'évolution temporelle obtenues.

Étude du transfert thermique

3.0.2 Mesures

Le dispositif utilisé est montré sur la figure 1. Il comprend un grand bloc de cuivre dont la température est réglée autour de 80°C , et qui nous sert de thermostat ; un petit bloc de cuivre dont la température peut être mesurée grâce à un thermomètre ; un isolement thermique extérieure en araldite.

Vérifier que le thermostat ait atteint sa température d'équilibre T_{th} , et la noter.

Mesurer la température initiale du petit bloc de cuivre, puis le mettre en contact avec le thermostat et mesurer l'évolution de sa température $T(t)$. Attention, l'évolution temporelle de $T(t)$ est très rapide : se préparer à la mesure avant de mettre le bloc sur le thermostat. Mesurer la température initialement tous les 10 ou 15 secondes, puis réduire éventuellement la fréquence des mesures. Bien vérifier que une température d'équilibre stable T_e est bien atteinte à la fin de la mesure.

3.0.3 Analyse des résultats

Tracer le graphe de $T(t)$. Quel type de loi d'évolution on doit prévoir sur la base du modèle simple ? Comment peut-on vérifier cette loi ?

Tracer le graphe de la fonction $T_e - T(t)$, dans l'échelle la plus appropriée pour étudier la réponse temporelle obtenue. Est-ce que la prévision est vérifiée ? Pouvez vous proposer une fonction qui pourrait décrire l'allure de la courbe obtenue ?

En effet, la courbe obtenue peut être modélisée par une bi-exponentielle du type $Ae^{-t/\tau} + A'e^{-t/\tau'}$. Déterminer les deux constantes de temps, τ et τ' , en utilisant la méthode décrite en annexe.

Interprétation des résultats à travers l'analogie électrique

À différence de ce que le modèle simple prévoit, donc, on peut observer dans le cas réel la présence de deux échelles de temps. Pouvez-vous donner une explication pour ce résultat ?

Nous allons essayer de comprendre cet effet du point de vue de l'analogie électrique. Notre système de base est donc le circuit RC, qui nous allons modifier pour essayer de reproduire les résultats désirés.

Monter un circuit RC (figure 2) avec $R = 50k\Omega$, $C = 0.14\mu F$, et alimenté avec une tension carrée $e(t)$ d'amplitude maximale $E \approx 1V$. Choisir la fréquence de $e(t)$ de façon à visualiser l'exponentielle qui caractérise le retour à l'équilibre de la tension $u_C(t)$ mesurée aux bornes du condensateur. Mesurer la constante de temps τ (méthode de la tangente) et la comparer à la valeur théorique.

$$1/50k * 0.14\mu = 143 \text{ s}$$

Comment pourrait-on transformer le circuit RC pour obtenir deux constantes de temps ?

Réaliser le circuit schématisé sur la figure 3, avec C et R comme dans le circuit précédent, $C' = 0.084\mu F$ et $R' = 65k\Omega$. Observer l'évolution vers l'équilibre des tensions $v_B(t)$ et $v_A(t)$. Mesurer ces tensions pour des valeurs différentes du temps t et tracer les courbes correspondants (une vingtaine de points par graphe). Tracer aussi les graphes des différences par rapport aux valeurs d'équilibre, $v_A(t) - V_A$ et $v_B(t) - V_B$, dans l'échelle appropriée.

Quelle est l'allure des deux tensions ? Laquelle des deux tensions peut modéliser la température du bloc de cuivre mesurée dans la manipulation thermique ? Que représente alors l'autre tension ? Comment interprétez-vous, sur la base des observations précédentes, l'allure en double exponentielle observée pour l'évolution de $T(t)$?

Essayez de vérifier vos conclusions en faisant varier la capacité C' et ou la résistance R' .

Conduction de la chaleur le long d'une barre

L'étude théorique de la transmission de la chaleur le long d'une barre conductrice fait intervenir un "découpage" idéal de la barre en tranches d'épaisseur infinitésimale, de telle sorte à pouvoir considérer la chaleur échangée entre tranches voisines.

Pouvez vous expliquer, sur la base des conclusions de la partie précédente, pourquoi ce phénomène peut être modélisé par une ligne de cellules RC identiques en cascade ?

On dispose d'une ligne de 5 ou 10 cellules RC en cascade. Alimenter la ligne avec un créneau basse fréquence, et visualiser la réponse à un signal en créneau des tensions successives $v_i(t)$ (figure 3). Observer les valeurs d'équilibre atteintes par chacune des tensions, la déformation progressive du créneau, et le retard de la tension du dernier point.

Relever un tableau des valeurs prises par les tensions $v_i(t)$ à des instants successifs identiques pour toutes les tensions, de façon à pouvoir tracer les profils instantanés des tensions dans la ligne en fonction de i .

Expliquer comment les observations faites se traduisent dans le cas de la transmission de la chaleur le long d'une barre conductrice.

Annexe : Mise en évidence de deux constantes de temps

Si, sur le graphique en coordonnées semi-logarithmique $A(t)$, les points représentatifs des mesures ne s'alignent pas sur une droite, la question se pose de savoir si l'évolution de A vers son asymptote A_∞ ne pourrait pas être décrite par la superposition de deux exponentielles décroissantes du temps.

Dans l'exemple proposé sur la figure, il y a un premier indice en ce sens...
etc etc