Key Concepts of Statistical Physics

ESPCI Paris 3rd year

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This document is the result of a compilation of notes taken by the students. It was first compiled in french by Romain De Oliveira, Promotion 133 ; let us thank him here for this wonderful work. Later it was adapted and translated in english by the teachers.

July 2017

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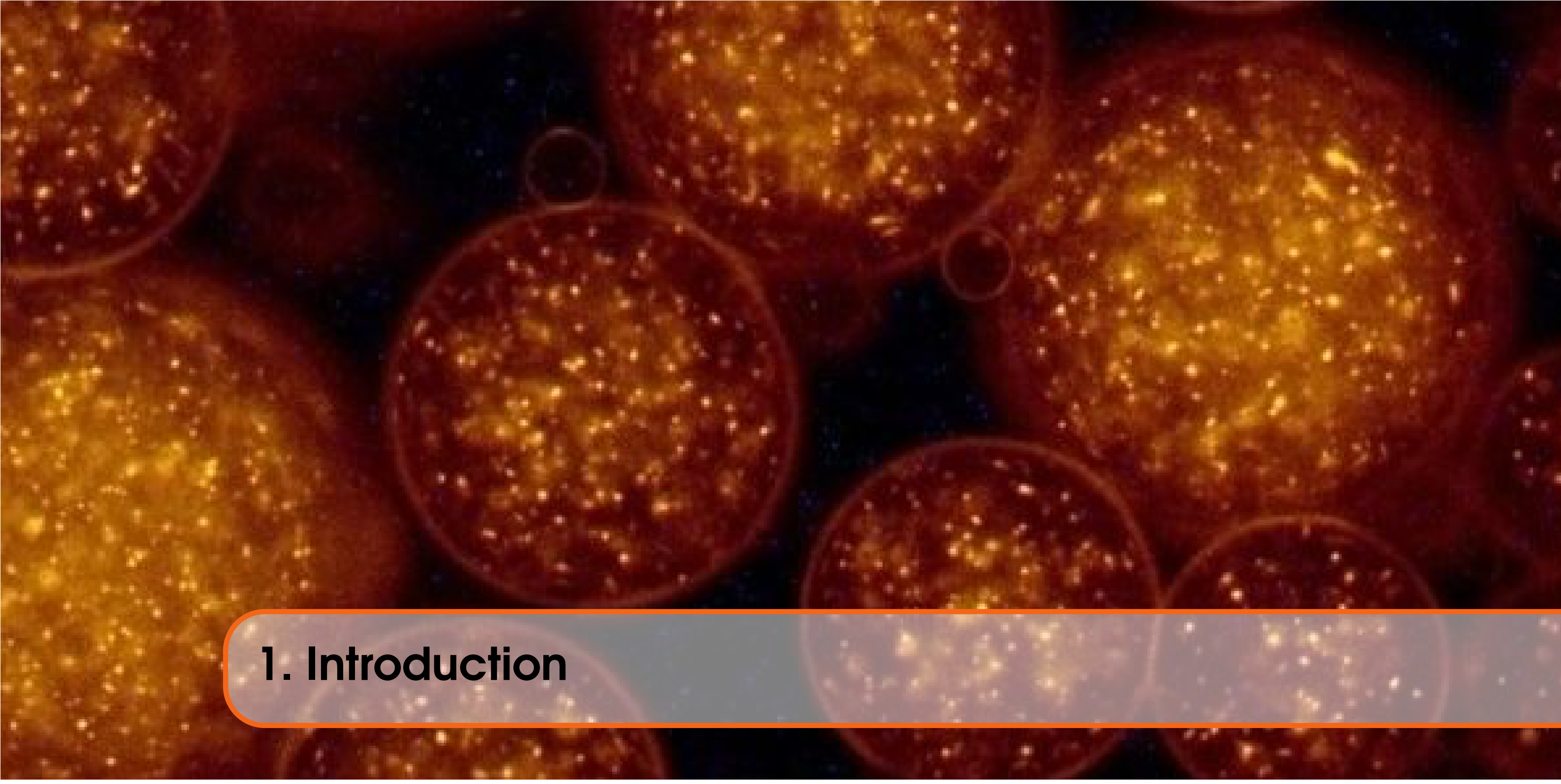


1. Introduction

The main goal of statistical physics is to describe systems composed of a very large number of entities such as atoms and molecules, without computing the detailed dynamics of all these constituent. It has been extremely successful in the past century in computing equilibrium phase diagrams and transitions between phases, such as the condensation of a gas into a liquid, the crystallization of liquids into a solids, or the spontaneous magnetization of ferro-magnetic materials.

Statistical physics also allows to study the dynamics of these systems when they are relaxing towards equilibrium or when they are driven steadily out of equilibrium.

The system of interest can be ordered, like crystals ; they may contain impurities, which introduce some disorder or be fully disordered like liquids. They can be classical or quantum systems. The complexity emerging from the presence of disorder and the connection between classical and quantum systems are fascinating topics, which are still a matter of active research.

Also, in the past decades, statistical physics has started to be used outside the realm of material sciences and now covers a wide range of topics such as the description of protein folding, evolution and population dynamics, stock-market analysis, big-data, algorithmic, neural networks and machine learning...

In the present course, we shall certainly not cover all these topics. Our main goal is to provide the reader with (i) an overview of the concepts underlying statistical physics, (ii) a panorama, or rather a typology of the topics that can be studied using statistical physics and (iii) the very basic tools anyone should know when being interested in studying further such topics.

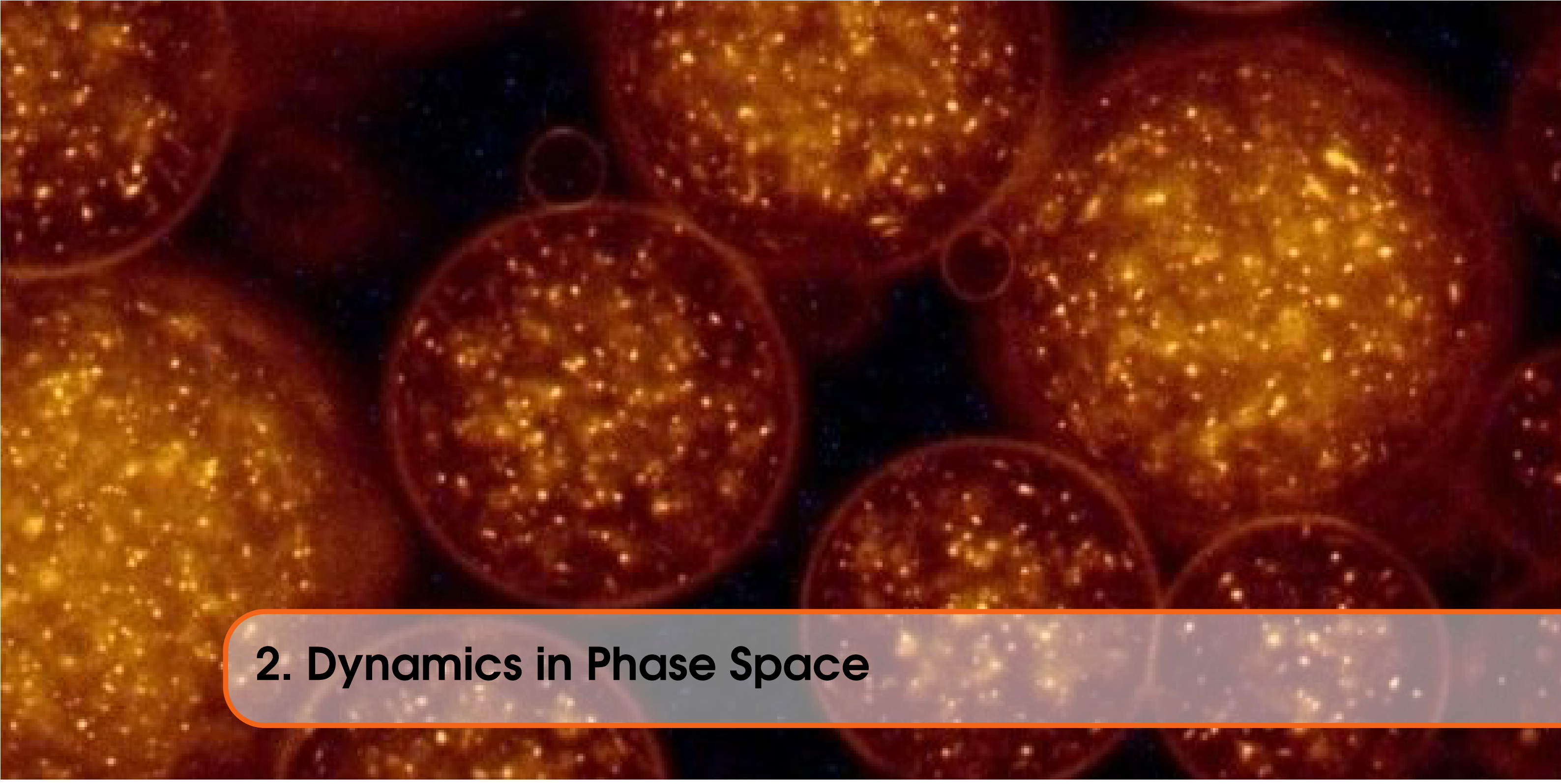
The course is organized in four parts. Part I introduces the reader to the foundation of statistical physics and concludes with a panorama of the topics it covers. This is also the occasion to list the topics that will be discussed later in the course, a minor part of them... Part II deals with the description of classical Hamiltonian systems, namely the classical description of matter. This will lead us to Part III, with the fascinating world of critical phenomena, where statistical physics acquired nobility. Finally Part IV deals with the stochastic approach to statistical physics : replacing the deterministic Hamiltonian dynamics by an effective stochastic dynamics first brings considerable simplifications to the computation of out of equilibrium properties, second allows to generalize the methods to non-hamiltonian dynamics and thereby expand the field of statistical physics to virtually all many-body problems.

The course is of a first year master level, and should be seen as a good introduction to more specific topic courses as provided in 2nd year of master. References to standard textbook chapters will be provided to complement this introductory material.

Let us thank again Romain De Oliveira, who made the first attempt of putting these notes together. We also thank all students for their participation and the numerous questions they raised. The latter have helped a lot in clarifying concepts and we hope the future students will keep asking questions, and providing critics to these notes, which are doomed to evolve, hopefully increasing in clarity.

I

Statistical Physics : Basic Concepts



2. Dynamics in Phase Space

2.1 Phase space

Let's consider a system entirely specified by N degrees of freedom $\vec{X} = (x_1, x_2, ..., x_N)$. The N-dimensional space, in which one specific microscopic state, or microscopic configuration of the system, is represented by the point of coordinates $(x_1, x_2, ..., x_N)$ is the so-called phase space. For a gas of mono-atomic molecules, the degrees of freedom would typically be the positions and velocities of the molecules. For a magnet, it could be the magnetic polarization of each atom. For a polymer, one would need to take into account the constraints imposed to the positions and velocities of the monomers by the links joining them. For a port-folio of market shares, it could be the price of those shares. Note that the coordinates x_i do not need be real numbers ; they can be integers ; they can be bounded or not. Identifying the relevant and useful degrees of freedom is a matter of educated choice. Fundamental laws of physics stemming from invariance properties and symmetries are very useful in this matter. When dealing with less conventional systems, such as biological or social ones, deciding of the relevance of such or such degrees of freedom is a crucial step of the analysis.

The evolution of one system, starting from an initial condition $\vec{X}(0)$, is given by a dynamical operator $\mathscr{D}$, which prescribes a *unique* $\vec{X}(t)$, given $\vec{X}(0)$ and time t :

$$\vec{X}(0) \rightarrow \vec{X}(t) = \mathscr{D}(\vec{X}(0), t). \tag{2.1}$$

This evolution is represented by one trajectory in phase space and each initial condition will lead to a different trajectory (see fig. 2.1-left).

Performing a measurement at time t provides a number, $O(t)$, also called an observable, which depends on the state of the system at time t : $O(t) = \mathscr{O}(\vec{X}(t))$.

Now, consider a glass of water. Its volume, its temperature, its pressure are everyday concepts, which can be measured easily. But how are they related to the instantaneous state of the system (position and velocities of all the water molecules) at the time of the measure ? This is by far not obvious ! Can one compute them and establish relations between them ? It seems clear that

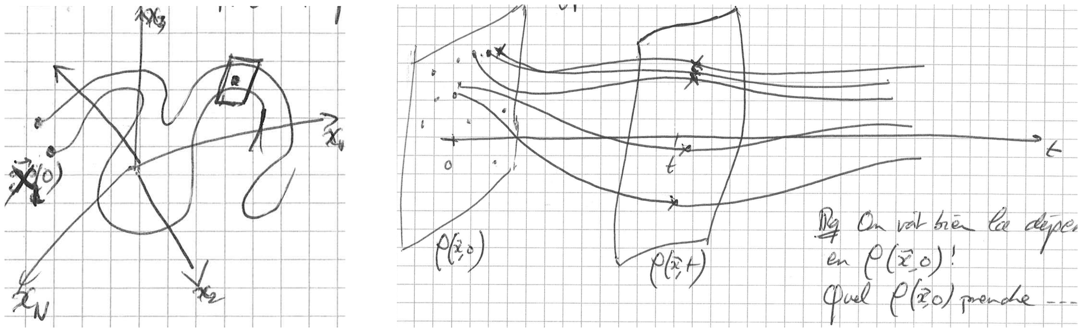


FIGURE 2.1 – Artistic view of the N-dimensional phase space dynamics with (left :) two trajectories, (right :) many trajectories, starting from different initial conditions

following the trajectory of the system in phase space, that is the trajectories of *all* the molecules in the real space from some ancestral initial condition is hopeless. This is also not what one wants. It would be perfectly satisfactory to know what is the typical value of the volume for a certain amount of water molecules, at a given temperature and under given pressure conditions.

The goal of statistical physics is precisely to give a precise meaning to the above concepts, such as temperature, pressure, ... and provide a way to compute the typical or average values of observables without computing the details of the microscopic dynamics. More generally one is interested in the statistical properties of the observables, including their fluctuations, their temporal and spatial correlations.

To do so, one must replace the dynamical description by a statistical one in order to give a precise meaning to the concept of average.

2.2 Micro-state density

Let's consider a very large number $\mathcal{N}$ of systems with different initial conditions $\vec{X}_\alpha(0)$, taken randomly, according to some distribution $\rho_0(\vec{X})$. Each initial condition leads to a different trajectory, and at time t the $\mathcal{N}$ systems are in states $\vec{X}_\alpha(t)$, which define a new distribution of states $\rho(\vec{X},t)$ (see fig. 2.1-right). Namely, the probability $\mathbb{P}$ that one system, α, is in the vicinity of a state $\vec{X}$ is given by :

$$\mathbb{P}\left(\vec{X}_\alpha(t) \in \left[\vec{X};\vec{X}+d\vec{X}\right]\right) = \rho(\vec{X},t)d\vec{X}. \tag{2.2}$$

The probability density $\rho(\vec{X},t)$ in general depends on the choice of the density $\rho_0(\vec{X})$. As a probability density, it should be normalized such that $\int \rho(\vec{X};t)d\vec{X} = 1$, where the integral is computed over the whole phase space.

Proposition 2.2.1 — Conservation of the probability density. The probability density obeys the conservation equation :

$$\frac{\partial \rho}{\partial t} + \mathrm{div}_N(\rho\vec{V}) = 0, \text{ where } \vec{V} = \frac{d\vec{X}}{dt}, \text{ and } \mathrm{div}_N(\rho\vec{V}) = \sum_{i=1}^{N} \frac{\partial \rho V_i}{\partial X_i}, \tag{2.3}$$

which simply tells that, at a fix position in phase space, the density in a given volume only evolves through the fluxes $\rho\vec{V}$ across its surface. As a result the evolution of $\rho(\vec{X},t)$ along a trajectory is given by :

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + (\vec{V}.\vec{\nabla})\rho = -\mathrm{div}_N(\vec{V})\,\rho, \tag{2.4}$$

which says that the volume containing a fraction n of trajectories dilates and compresses according to $\mathrm{div}_N(\vec{V})$.

One simple way to derive the above result is exactly analogous to the way the conservation of mass is derived in hydrodynamics. The fraction of trajectories n contained at a time t in an arbitrary volume of phase space υ is simply given by :

$$n = \int_{\upsilon} \rho(\vec{X};t)d\vec{X} \tag{2.5}$$

Because no trajectories suddenly appear or disappear, the variation of n is entirely given by the flux of trajectories through the boundaries of the volume υ. Hence :

$$\frac{dn}{dt} = \int_{\upsilon} \frac{\partial \rho}{\partial t} d\vec{X} = \int_{\sigma} -\rho \left(\vec{V} \cdot \vec{s}\right) d\vec{X} = \int_{\upsilon} -\mathrm{div}_N(\rho \vec{V})\, d\vec{X} \tag{2.6}$$

with $\vec{s}$, the unit vector normal to and pointing outward the surface σ of the volume υ and where the last equality comes from the Green-Ostrogradsky theorem.

2.3 Ensemble average

One can now define a proper averaging procedure. The ensemble average value of the observable $O(t) = \mathscr{O}(\vec{X}(t))$ at time t is given by

$$\langle O \rangle (t) = \frac{1}{\mathscr{N}} \sum_{k=1}^{\mathscr{N}} \mathscr{O}(\vec{X}_k(t)) \simeq \int d\vec{X} \rho(\vec{X},t) \mathscr{O}(\vec{X}) \tag{2.7}$$

Note that in this last formula, the observable is computed at all points in phase space, independently of the dynamics, while the dynamics is encoded in the evolution of the probability density. This is the essence of any statistical physics methods. Let's recall that $\rho(X,t)$ in general will depend on the statistical ensemble of systems selected at $t = 0$.

2.4 Steady state

Under certain circumstances, the probability density may evolve towards a stationary or steady state distribution $\rho_{ss}(\vec{X})$, which does not evolve anymore (see fig. 2.2). The $\mathscr{N}$ systems still evolve according to the dynamics, but in a way that their distribution in phase space remains identical to itself. One also talks about the invariant measure of the dynamics.

Finding a steady state distribution consists in solving

$$\frac{\partial \rho_{ss}(\vec{X},t))}{\partial t} = 0. \tag{2.8}$$

When the steady state distribution exists, one sees from equation 2.7 that the average value of any observable become time-independant.

R

A steady state measure may not exist
When it exists, it is not clear that it is unique (it a priori depends on the initial distribution)
In general, it can be a very complicated function over the N-dimensional phase space.

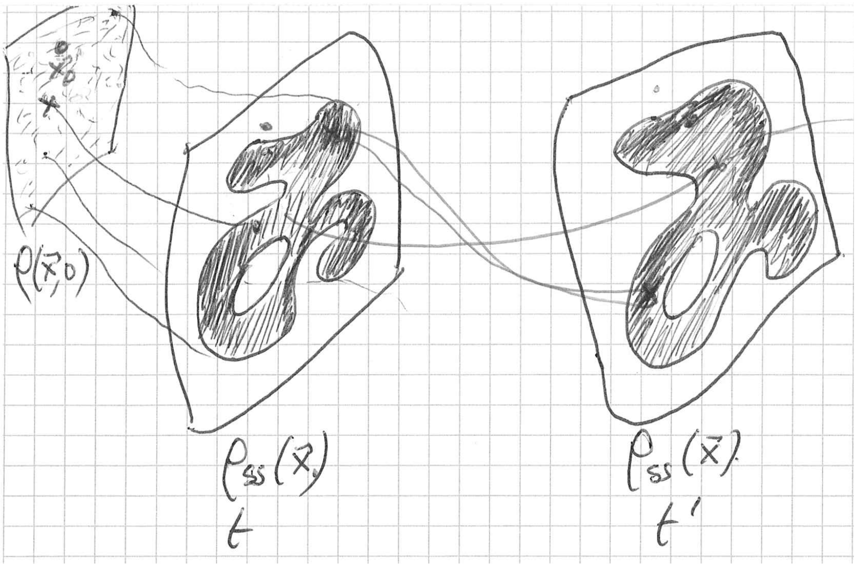


FIGURE 2.2 – Sketch of the probability density in phase space converging towards the steady state distribution

2.5 Ergodicity

The ergodic hypothesis consists in *assuming* that in a steady state, averaging the instantaneous values taken by an observable as a function of time on a given system converges, in the limit of a very long lasting measurements, towards the averaged value computed from the steady state distribution. In other words, the value obtained from a typical experimental measurement can be theoretically computed, without integrating the dynamics, provided that the system has reached a steady state and that the corresponding steady state distribution is known. This is statistical physics !

$$O_{exp} = \frac{1}{T}\int O(t)dt \rightarrow \langle O\rangle = \int d\vec{X}\rho_{ss}(\vec{X})\mathscr{O}(\vec{X}) \tag{2.9}$$

In general it is extremely difficult to prove the ergodicity hypothesis for a specific dynamics. Obviously the dynamics must have a steady state measure. Second, the steady state measure should be unique or, if not, it should attract the vast majority of initial conditions. It is mandatory that if the initial density is within the support of the steady state measure, than the dynamics converges towards it. With such properties of the dynamics, it becomes reasonable to consider that any system, starting from a reasonable initial condition, will essentially explore the phase space according to the steady state measure. In other words, considering a compact set of initial conditions, it should be well stir all across the phase space to finally map the steady state measure. In that case, the temporal average is dominated by the average over the steady state distribution.

R Statistical physics may also be interested in non-steady phenomena, typically the way a system relaxes to the steady state. In that case, it is quite clear that the steady state distribution cannot be used. The way to proceed then is to average over the distribution of initial conditions. But how to decide what is the distribution of initial conditions ? One way of doing is to fix some control parameter of the dynamics, wait for the steady state to be established and then suddenly change (one also says "quench") the system to some other value of the control parameter. The system will relax to a new steady state, starting from a known initial distribution, namely that of the steady state before changing the control parameter of the dynamics.

2.6 Hamiltonian Dynamics

We now specify a particular dynamics, namely that of a classical system of N particules. For a physical space of dimensionality d, Each particle k is described by its position $q_{(k-1)d,..kd}$ and its impulsion $p_{(k-1)d,..kd}$. The phase space has thus $2Nd$ dimensions. The system is described by its Hamiltonian $H(\{q_i, p_i\})$, that is its energy, and obeys the dynamics prescribed by the Hamilton equations. For $i \in [1, dN]$:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{2.10}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{2.11}$$

In most situations, the Hamiltonian takes the form $H = \sum_{i=1}^{dN} \frac{p_i^2}{2m} + V(\{q_i\})$, where V is the interaction potential. The equations then take the form of the simple Newton equations :

$$\dot{q}_i = \frac{p_i}{m} \tag{2.12}$$

$$\dot{p}_i = m\ddot{q}_i = -\frac{\partial V}{\partial q_i} = F_i. \tag{2.13}$$

Any observable $A(t) = A(\{q_i(t), p_i(t)\})$ then evolves according to :

$$\dot{A} = \sum_i \dot{q}_i \frac{\partial A}{\partial q_i} + \dot{p}_i \frac{\partial A}{\partial p_i} = \sum_i \frac{\partial H_i}{\partial p_i}\frac{\partial A}{\partial q_i} - \frac{\partial H_i}{\partial q_i}\frac{\partial A}{\partial p_i} \equiv -\{H, A\}. \tag{2.14}$$

where the last notation is called the Poisson bracket. It is a linear differential operator and has all the standard properties of such an object.

In particular, one sees, taking $A = H$, that $\frac{dH}{dt} = 0$; the total energy is conserved. One can show that this is a direct consequences of the invariance under translation in time of the dynamics. As a matter of fact, a very general theorem called the Noether's theorem (see Wikipedia) states that a conserved quantity is associated to each continuous symmetry under which the dynamics is invariant. Classical examples are the total impulsion and the total kinetic momentum, which are respectively associated to the translational and the rotational invariance in physical space.

As a consequence, the dynamics in phase space is constrained to a manifold where such conserved quantities are fixed by the initial conditions (see fig 2.3)

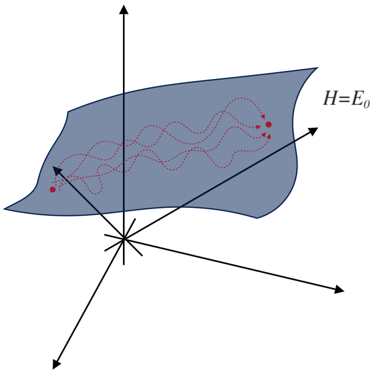


FIGURE 2.3 – Hamiltonian dynamics in the 2Nd dimensional phase space.

In the case of an Hamiltonian dynamics, one can simplify the law of conservation for the probability density, discussed in the proposition 2.2.1. First one has

$$(\vec{V}\cdot\vec{\nabla})\rho = \sum_i \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} = -\{H,\rho\}. \tag{2.15}$$

Second, and most importantly, $\mathrm{div}_{2Nd}(\vec{V}) = 0$:

$$\mathrm{div}_{2Nd}(\vec{V}) = \mathrm{div}_{2Nd}\begin{pmatrix}\dot{q}_i\\ \dot{p}_i\end{pmatrix} = \sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \sum_i \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} = 0 \tag{2.16}$$

As a result the conservation of the probability density takes now a very simple form

$$\frac{\partial \rho}{\partial t} = \{H,\rho\}. \tag{2.17}$$

and is called the Liouville equation. It expresses the fact that the volume in phase space is conserved along a trajectory : there is no condensation of the density ρ.

We conclude this chapter by discussing the nature of the steady state distribution in the case of Hamiltonian dynamics.

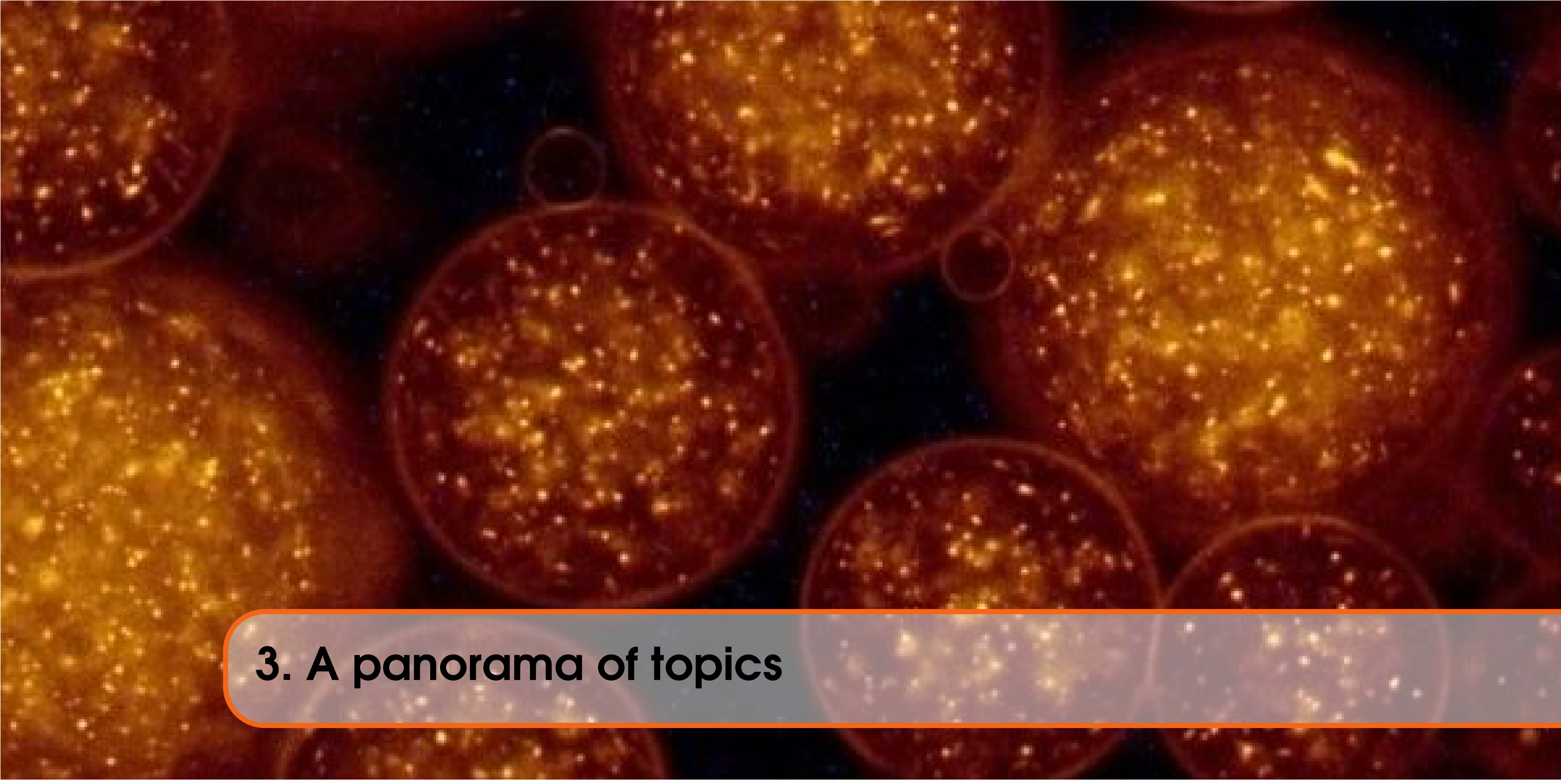
Proposition 2.6.1 — The steady state distribution of Hamiltonian systems is uniform. On one hand the Liouville equation states that the volume of phase space is conserved. This implies that the weights accorded to the different parts of the energy manifold by the dynamics are identical. As a result the uniform measure remains uniform; it is a steady state solution. Is it the only solution? Suppose the measure is non uniform, while the dynamics is stirring the phase space (ergodic hypothesis). Because the volume of phase space is conserved, any region of phase space will evolves simultaneously towards denser and less dense regions. This phenomena will amplify until the phase space is essentially separated in an infinitely dense and an infinitely loose region, which in turn break the ergodicity hypothesis. So the uniform measure is the only one that satisfies simultaneously the ergodicity hypothesis and the conservation of volume in phase space.

However, first the time reversibility of the Hamilton equations prevent the steady state distribution from being attractive. At best $\rho(t)$ is close to the steady state density ρ_{ss}, most of the time, so that temporal averages are dominated by the steady state distribution. Second the ergodic hypothesis is only a working hypothesis... As a matter of fact there even is a theorem, dating back to 1913, called the Plancherel-Rosenthal theorem or the No-go theorem (sic !), which states that an Hamiltonian dynamics cannot be ergodic.

R Another theorem, by Sinaï, establishes that a gas of hard sphere in a box is ergodic in a weak sense...

R In practice, the non ergodicity of the Hamiltonian dynamics, namely the existence of many tiny regions of phase space that are never explored, is wiped out by the limited resolution of any realistic observation, as well as by the presence of any source of external noise, which adds to the dynamics.

Leaving aside these highly technical and conceptual issues, we shall resume this chapter in saying that for an Hamiltonian system, the steady state distribution is uniform over the manifold on which the system is ascribed to evolve by the conservation laws.



3. A panorama of topics

In the light of what we have said in the previous chapter one can classify sub-fields of statistical physics along the following lines. The system of interest obeys an Hamiltonian dynamics – or a dynamics which share the same essential properties – or not. One is interested in the steady states of the system, or not. The goal of the following paragraphs is to provide the reader with a very fast overview of topics and keywords.

3.1 Equilibrium Statistical Physics

Equilibrium statistical physics deals with the steady states of Hamiltonian – or equivalent – dynamics. One is interested in the equations of state of the system, namely explicit relation relating averages of macroscopic quantities. Computing the fluctuations of the macroscopic quantities, one accesses the linear response functions of the system : the susceptibilities, compressibility, heat capacity and so forth. Many system of interest exist in several phases, depending on the external conditions. This is the case of particles systems with their gas-liquids-solids phases, but also that magnetic systems with their paramegentic-ferromagnetic phases. Studying the phase-transitions is one central topic of equilibrium statistical physics. We shall see that in some cases, when the transition are critical, many very precise prediction can be done, which are robust for large classes of different microscopic systems. One say that they belong to the same universality class. Such transitions can be studied at the level of mean-field approximations, which is a first instructive approach, often the only easy one. One can also investigate the role of the so-called critical fluctuations, which take place at the transition. This ultimately leads to the study of the renormalization group theory.

The system of interest can either be ordered or disordered. The archetype of ordered systems are crystals, without impurities. The particles are stuck on a regular lattice and the positional degrees of freedom are limited to vibrations around the lattice nodes. One then study the statistical properties of these vibrations, the phonons. One can also forget about the positional degrees of freedom and focus on the remaining degrees of freedom of interest, such as the magnetic momenta, which may interact in various ways. The introduction of disorder can take two forms. It may consist in impurities inside de crystal, which alter the interaction amongst the components of the lattice ; this is the so called physics of quenched disorder, the epitome of which are the so called spin-glasses. Alternatively one can have structural disorder : the particles are no more sitting on a lattice ; they move in the continuous space. This is the field of the liquid state theory and glasses. Amongst the theories and methods associated with the description of equilibrium disordered systems are the so-called replica theory, and the cavity method.

3.2 Out-of-Equilibrium Statistical Physics

It is clear that this field is ill-defined since there are at least two very different ways of being out of equilibrium. The dynamics is Hamiltonian but the phenomenon of interest is unsteady or the dynamics is neither Hamiltonian, nor similar to it.

Let's focus on the first situation, where the microscopic dynamics has all the properties of a Hamiltonian dynamics, but the system is not in the steady state. This is what is often meant by Out-of-Equilibrium Statistical Physics.

First, one can be interested in the relaxation towards equilibrium. Namely, one starts with an initial condition, out of the steady state, and considers how the system relaxes to the equilibrium steady state. This is the field of fluctuation-dissipation theorems.

Second the system can be permanently driven out of equilibrium. Typical examples are the transfer of heat between a hot and a cold reservoir, or the conduction of electrons, under a difference of electric potential. In such situations, one is interested in the currents induced by the external forcing and their fluctuations. Note that these currents can be stationary themselves ; one then talk about non equilibrium steady states (NESS). This should not be confuse with the equilibrium steady state.

The tools used to study out of equilibrium dynamics are numerous. Starting from the microscopic Hamiltonian dynamics, one can derive evolution equations for the macroscopic quantities, assuming that they vary slowly, both in time and space.This is the so-called kinetic theory, and its long-range hydrodynamics developments. The first and most famous equation of kinetic theory is the Boltzmann equation.

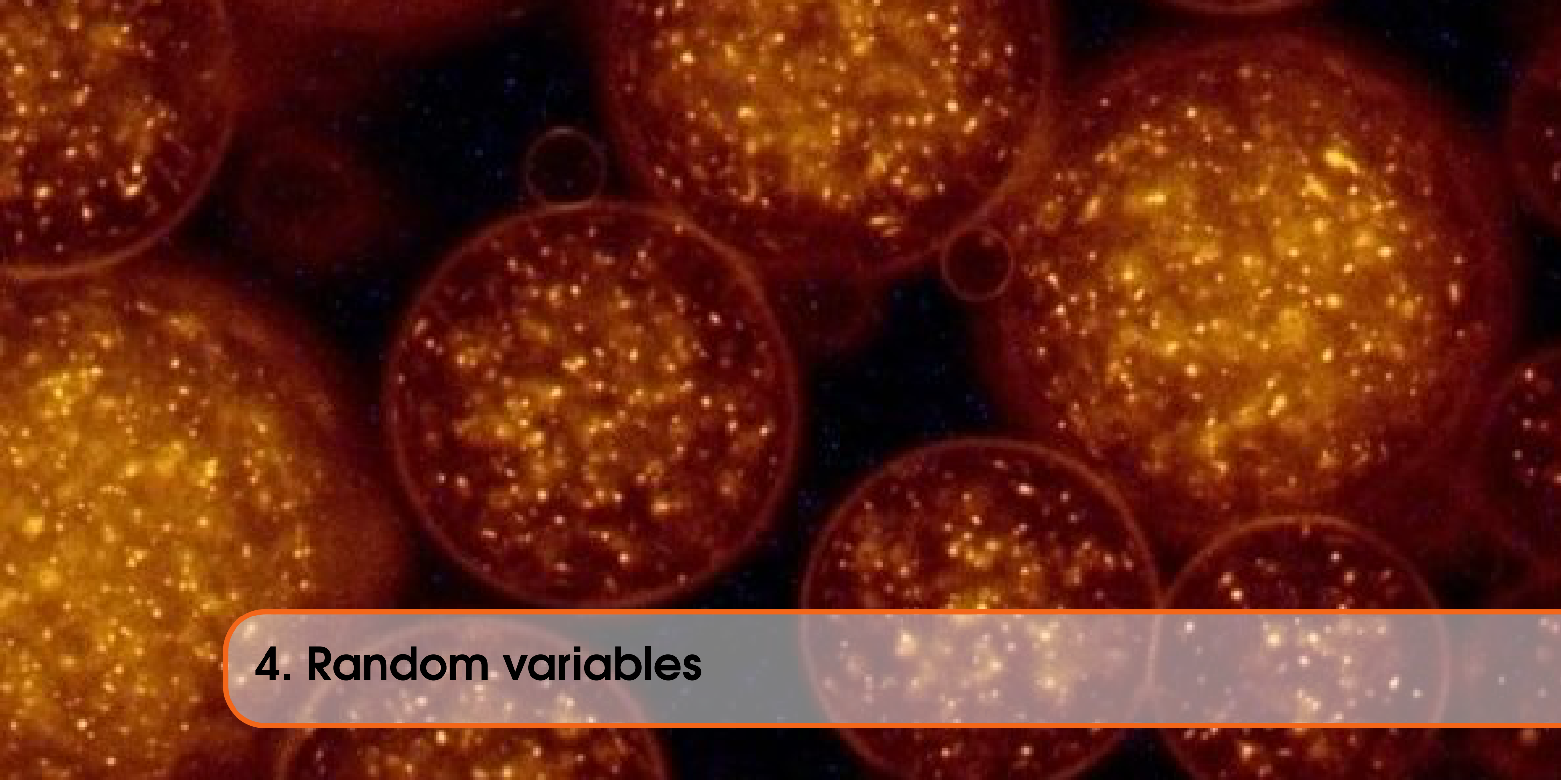
It is often convenient not to start from the microscopic dynamics. For instance, consider a micron-sized particle in suspension in a fluid, which exhibits Brownian motion. It is known that this motion comes from the collisions of the molecules composing the solvent. On one hand they kick the particles randomly, on the other side they induce a drag force, via the viscosity of the fluid. This kind of description where the fluid is simultaneously considered as a continuum medium responsible for the drag and as a source of noise leads to an effective stochastic description called the Langevin dynamics. The fact that, at the molecular level, the dynamics are Hamiltonian, imposes specific constraints on the form of these dynamics, which must satisfy a fluctuation-dissipation relation.

Finally, one can consider even more abstract, or effective, dynamics, which are then described by random processes, in which the system jumps from one configuration to another with certain transition rates. These processes obey a master equation. Here also, this type of equations must satisfy some constraint, the so called detailed balance, to ensure its connection with Hamiltonian dynamics.

Both the fluctuation-dissipation relation and detailed balance encode the temporal reversibility of the Hamiltonian dynamics.

3.3 Complex systems

Ultimately, one can relax the constraint of an underlying Hamiltonian dynamics. This is actually mandatory, if the degrees of freedom of interest are say stock-markets or neurons or birds... For such systems, which we could called complex system, none of the results established for equilibrium systems or standard non equilibrium situations hold. Concepts such as temperature or pressure are even not clearly defined. Still one may be interested in computing averages and fluctuations of macroscopic quantities... and one must therefore invent their statistical physics...



4. Random variables

In the previous chapter, we have seen that the essence of statistical physics consist in replacing the integration of the dynamics to compute averages over time – which is what the experiments report – by a statistical average of the values taken by the observable in phase space, weighted with an appropriate distribution. The present chapter aims at recalling some basic tools and concepts that are useful when dealing with random variables. We shall also take this opportunity to present the Legendre transform, which has nothing to do with random processes, but which happens to be a major tool of statistical physics and thermodynamics.

4.1 Random variables and Generating Functions

Let's consider a random variable X with real value and its probability density $\rho(X)$. One defines the n-th order moment of X as

$$\mu_n := \langle X^n \rangle = \int_{-\infty}^{\infty} x^n \rho(x)\, dx. \tag{4.1}$$

Définition 4.1.1 — Moment-generating function. The moment-generating function of X is defined as

$$M_X(k) := \left\langle e^{kX} \right\rangle, \quad k \in \mathbb{R}, \tag{4.2}$$

wherever this expected value exists.

The reason for defining this function, also called the characteristic function, is that it can be used to find all the moments of the distribution. Indeed, writing the series expansion of e^{kX}, one gets

$$M_X(k) = \left\langle e^{kX} \right\rangle = 1 + k\langle X \rangle + \frac{k^2 \langle X^2 \rangle}{2!} + \frac{k^3 \langle X^3 \rangle}{3!} + \cdots + \frac{k^n \langle X^n \rangle}{n!} + \cdots \tag{4.3}$$

$$= 1 + k\mu_1 + \frac{k^2 \mu_2}{2!} + \frac{k^3 \mu_3}{3!} + \cdots + \frac{k^n \mu_n}{n!} + \cdots, \tag{4.4}$$

Hence

$$M_X(k) = \sum_{n=1}^{\infty} \mu_n \frac{k^n}{n!}, \quad \text{with} \quad \mu_n = \left.\frac{d^n M_X(k)}{dk^n}\right|_{k=0} \tag{4.5}$$

One also defines the centered momenta, as $\hat{\mu}_n := \langle (X-\mu_1)^n \rangle$, which characterize the distribution, after centering it on the average of X.

Définition 4.1.2 — Cumulant-generating function. The cumulants of a random variable X are defined using the cumulant-generating function, which is the logarithm of the moment-generating function : $K_X(k) = \log(M_X(k)) = \log\left\langle e^{kX}\right\rangle$.

The cumulants κ_n are again obtained from a power series expansion of the cumulant generating function :

$$K_X(k) = \sum_{n=1}^{\infty} \kappa_n \frac{k^n}{n!}, \quad \text{with} \quad \kappa_n = \left.\frac{d^n K_X(k)}{dk^n}\right|_{k=0} \tag{4.6}$$

The first cumulant is the expected value ; the second and third cumulants are respectively the second and third centered momenta (the second centered moment is the variance) ; but the higher cumulants are neither momenta nor centered momenta, but rather more complicated polynomial functions of the momenta. For instance $\hat{\mu}_4 = \kappa_4 + 3\kappa_2^2$.

Proposition 4.1.1

- If two distributions have the same moment or cumulant generating function, then they are identical at almost all points.
- The cumulant generating function, if it exists, is infinitely differentiable and convex, and passes through the origin.
- The cumulant-generating function exists if and only if the tails of the distribution are majored by an exponential decay.

For statistically independent random variables X and Y,

$$K_{X+Y}(k) = \log\left\langle e^{k(X+Y)}\right\rangle = \log\left(\left\langle e^{kX}\right\rangle\left\langle e^{kY}\right\rangle\right) = \log\left\langle e^{kX}\right\rangle + \log\left\langle e^{kY}\right\rangle = K_X(k) + K_Y(k), \tag{4.7}$$

so that each cumulant of a sum of independent random variables is the sum of the corresponding cumulants

4.2 Entropy of a distribution, joint and marginal distributions

Let X be a random variable with probability density $\rho(X)$

Définition 4.2.1 — The Kullback-Leibler divergence. The Kullback-Leibler divergence of the probability density $\rho(X)$ with respect to the probability density $h(x)$ is a functional defined as

$$D[\rho||h] = \int dx\, \rho(x) \log\left(\frac{\rho(x)}{h(x)}\right) \tag{4.8}$$

It measures how different is the probability density $\rho(x)$ from $h(x)$. In particular it is always positive and it is zero if and only if $\rho(x) = h(x)$.

Définition 4.2.2 — Entropy. The entropy of the probability density $\rho(X)$ is defined as

$$S[\rho] = -\int dx\, \rho(x) \log(\rho(x)) \tag{4.9}$$

It provides a characterization of the shape of the probability density. The larger the entropy the larger is the width of the distribution.

> R Please mathematician friends forgive the fact that the above definition includes taking the log of a dimensional quantity. One way of "solving" this problem, would be to see $S(\rho) = -D(\rho||\mu)$, with μ, the uniform measure. This is however not correct because the uniform measure cannot be normalized on unbounded domains... Assuming our friends keep their eyes closed, one could write $\mu = \frac{1}{\infty}$ and obtain
>
> $$S[\rho] = \int dx \rho(x) log(\infty) - D(\rho||\mu).$$
>
> From this we see that S is indeed maximal when ρ is uniform, actually infinite if the domain is unbounded, and that S decreases when going away from the uniform measure, namely when the width of ρ decreases. Also S[ρ] can be both positive and negative. If one feels uncomfortable with such little arrangements, he should come back to the case of discrete sets of configurations, where everything is well defined (see the discussion about the limiting density of discrete points on wikipedia.)

Up to now, we have only introduced random variables with values in $\mathbb{R}$. In order to compute averages like the ones introduced in the previous part (equations 2.9), we'll need to extend the above formalism to random variables in $\mathbb{R}^N$, where N is the number of degrees of freedom of the system of interest.

The joint probability density $\rho(\vec{X}) = \rho(X_1, X_2, \cdots X_N)$ is a prodigiously rich information about the system, since it describes the probability of all possible micro-states. In many cases, we'll see that one is often interested in a reduced information, namely the probability density of certain degrees of freedom, letting the others be anything.

Définition 4.2.3 — Marginal distributions. For simplicity and for visualization ease (see figure 4.1), let's consider a random variable $\vec{X} = (X_1, X_2)$.

The probability that $X_1 \in [X_1; X_1 + dX_1]$ and $X_2 \in [X_2; X_2 + dX_2]$ is :

$$\mathbb{P}\left(X_1 \in [X_1; X_1 + dX_1], X_2 \in [X_2; X_2 + dX_2]\right) = \rho_2(X_1; X_2) dX_1 dX_2, \tag{4.10}$$

where $\rho_2(X_1; X_2)$ is the joint-distribution of (X_1, X_2).

The probability that $X_1 \in [X_1; X_1 + dX_1]$, $\forall X_2$ is :

$$\mathbb{P}\left(X_1 \in [X_1; X_1 + dX_1], \forall X_2\right) = \left(\int \rho_2(X_1; X_2) dX_2\right) dX_1 = \rho_1(X_1) dX_1, \tag{4.11}$$

where $\rho_1(X_1)$ is called the marginal distribution of X_1. By symmetry one defines $\rho_1(X_2)$, the marginal distribution of X_2. Note that marginal distributions are naturally normalized.

The marginal distribution should not be confused with the conditional one. The probability that $X_2 \in [X_2; X_2 + dX_2]$, knowing X_1 is :

$$\mathbb{P}\left(X_2 \in [X_2; X_2 + dX_2], \text{knowing} X_1]\right) = \rho(X_2|X_1) dX_2. \tag{4.12}$$

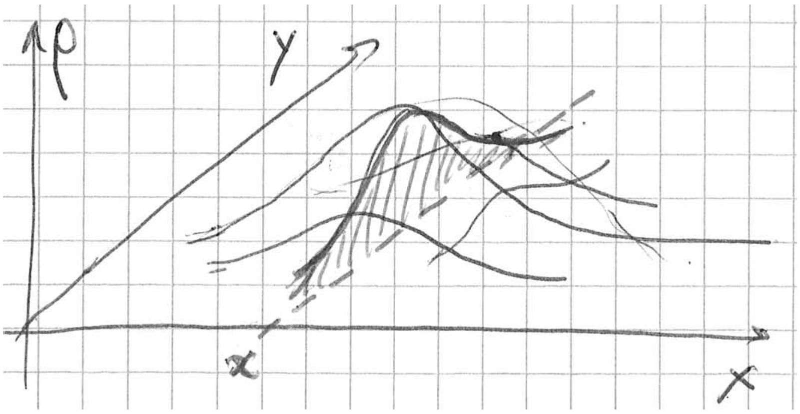


FIGURE 4.1 – Joint (the surface $\rho_2(x,y)$), marginal (integrated area $\rho_1(x)$) and conditional distribution (the weighted top curve $\rho(y|x)$)

where $\rho(X_2|X_1)$ is called the conditional probability of X_2, knowing X_1. By symmetry one defines $\rho(X_1|X_2)$ the conditional probability of X_1, knowing X_2. One clearly has :

$$\rho_2(X_1,X_2) = \rho(X_2|X_1)\rho_1(X_1) = \rho(X_1|X_2)\rho_1(X_2), \tag{4.13}$$

from which one easily checks that the conditional probabilities are also normalized.

If the variables X_1 and X_2 are independent, then knowing anything about X_1 will not condition the distribution of X_2. Hence for two independent variable $\rho(X_2|X_1) = \rho_1(X_2)$, and $\rho_2(X_1,X_2) = \rho_1(X_1)\rho_1(X_2)$.

If $\rho_2(X_1,X_2) = \rho_1(X_1)\rho_1(X_2)$ and $h_2(X_1,X_2) = h_1(X_1)h_1(X_2)$, then the Kullback-Leibler divergence is additive :

$$D(\rho_2(X_1,X_2)||h_2(X_1,X_2)) = D(\rho_1(X_2)||h_1(X_2)) + D(\rho_1(X_1)||h_1(X_1))$$

.

4.3 Gaussian variables

Let X be a random variable with a Gaussian distribution $G(\mu,\sigma)$:

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp -\frac{(x-\mu)^2}{2\sigma^2}. \tag{4.14}$$

The prefactor $\frac{1}{\sqrt{2\pi\sigma^2}}$ ensures that the distribution is normalized : $\int_{-\infty}^{\infty} \rho(x)dx = 1$.

Two very useful relations are the so-called Hubbard-Stratonovich transformations :

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} \exp\left[-\frac{x^2}{2\sigma^2} \pm kx\right] dx = \exp\left(\frac{\sigma^2 k^2}{2}\right) \tag{4.15}$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x \exp\left[-\frac{x^2}{2\sigma^2} \pm kx\right] dx = \pm\sigma^2 k \exp\left(\frac{\sigma^2 k^2}{2}\right) \tag{4.16}$$

Note that the argument in the exponential on the right-hand side is always coming with a positive sign if x is real. The only way to obtain a negative sign is to apply the same transformation with x being a pure imaginary number. It is actually in this context that the transformation was introduced; and you may be surprised to learn that it was introduced to transform the simple-looking right-hand side into the less simple looking left-hand side. But this is another story....

The moment generating function exists and is equal to (direct consequence of the Hubbard Stratonovitch transformation)

$M_X(k) = \left\langle e^{kX} \right\rangle = e^{\mu k} e^{\frac{1}{2}\sigma^2 k^2}$

The cumulant generating function is thus simply the quadratic polynomial

$K_X(k) = \log M(k) = \mu k + \frac{1}{2}\sigma^2 k^2$

Thus only the first two cumulants, namely the mean $\langle X \rangle = \mu$, and the variance $\kappa_2 = \hat{\mu}_2 = \mathrm{var}(X) = \left\langle (X - \langle X \rangle)^2 \right\rangle = \sigma^2$ are nonzero. This is actually an elegant way of computing the mean and the variance.

The entropy of the distribution $S(\sigma) = \frac{1}{2} + \log(\sqrt{2\pi\sigma^2})$ indeed increases with the distribution width as characterized by its variance.

What is remarkable is that the normal distribution is the only absolutely continuous distribution whose cumulants beyond the first two (i.e., other than the mean and variance) are zero. It is also the continuous distribution with the maximum entropy for a specified mean and variance.

4.4 Central Limit Theorem

The Gaussian distribution discussed above is key to statistical physics because it enters into the simplest version of the Central Limit Theorem (CLT). This theorem establishes that, in most situations, when independent random variables are added, their properly normalized sum tends toward a Gaussian distribution even if the original variables themselves are not normally distributed.

Let $(X_1, \ldots, X_N)$ be a set of independent and identically distributed random variables drawn from distributions of expected values given by μ and *finite* variances σ^2. Consider the normalized sum $S_N := \frac{1}{N}\sum X_i$ of these random variables, also called the empirical mean of X. Because the X_i are random variable, S_N also is.

For all N, the linearity of the average and the variance ensures that $\langle S_N \rangle = \mu$ and $Var(S_N) = \sigma^2/N$. In practice, one does not have access to $\langle S_N \rangle$ but only to a finite number of realizations and one would like to know how they are distributed. Intuitively, the larger N, the closer to μ should S_N be.

Proposition 4.4.1 — Law of Large Numbers. The law of large numbers indeed states that

$$\lim_{N\to\infty} S_N = \mu, \text{with probability one.} \tag{4.17}$$

Proposition 4.4.2 — Central Limit Theorem. The CLT precises the scaling in N in the following way : $Y_N = \frac{S_N - \mu}{\sigma/\sqrt{N}}$ converges in law to the Gaussian distribution G(0,1).

The usefulness of the theorem is that the distribution of S_N approaches Gaussianity regardless of the shape of the distribution of the individual X_i, provided that its variance is finite.

The central limit theorem has a number of variants. In its common form, the random variables must be independent and identically distributed. In variants, convergence of the mean to the normal distribution also occurs for non-identical distributions or for non-independent observations, given that they comply with certain reasonable conditions, which guarantee that the contribution of any individual random variable to the variance is arbitrarily small, for sufficiently large N, and that the correlations are not long ranged.

4.5 Legendre-Fenchel transfrom

Définition 4.5.1 — Legendre-Fenchel transform. We define the Legendre-Fenchel transfrom of a function $\lambda(k)$ as

$$I(s) = \sup_k \left[sk - \lambda(k)\right]. \tag{4.18}$$

One particular and easy case to consider, although not the general case as we shall see below, is when $\lambda(k)$ is a strictly convex function, $\frac{d^2\lambda}{dk^2} > 0$. It is therefore differentiable and, deriving the element to be maximized, one finds $s = \frac{d\lambda}{dk}\big|_k$. Since $\frac{d\lambda}{dk}\big|_k$ is a monotonic and growing function of k, it is invertible and k(s) is the locus of the unique maximum. The Legendre-Fenchel transform of $\lambda(k)$ is then the less general Legendre transform :

$$I(s) = s\,k(s) - \lambda(k(s))) \quad \text{with} \quad s(k) = \frac{d\lambda}{dk}, \quad \text{and } k(s) \text{ its inverse.} \tag{4.19}$$

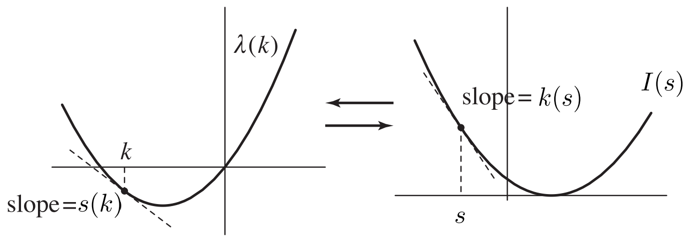


FIGURE 4.2 – Illustration of the Legendre transform.

R If $\lambda(k)$ is strictly concave, the same construction holds, provided that one defines $I(s) = \inf_x [s\,k - \lambda(k)]$.

Proposition 4.5.1 — Properties of the Legendre transform.
In the specific case, when $\lambda(k)$ is strictly convex, $\lambda(k)$ is the Legendre transform of $I(s)$.

Indeed :

$$\frac{dI}{ds} = k(s) + s\frac{dk}{ds} - \frac{d\lambda}{dk}\frac{dk}{ds} = k(s), \tag{4.20}$$

hence

$$\lambda(k) = ks(k) - I(s(k)), \quad \text{with} \quad k(s) = \frac{dI}{ds}, \quad \text{and } s(k) \text{ its inverse} \tag{4.21}$$

There is thus a systematic correspondance : $I'(s) = k <=> \lambda'(k) = s$, as illustrated on figure 4.2

It is also easy to check that :

$$\frac{d^2\lambda}{dk^2}\frac{d^2I}{ds^2} = 1, \qquad I(0) = -\lambda_{\min}, \qquad \lambda(0) = -I_{\min}. \tag{4.22}$$

R These propositions do not hold in the general case of the Legendre-Fenchel transform. Consider the case where $\lambda(k)$ is not differentiable in one point (see figure 4.3). There is no more a one to one correspondance between $I(s)$ and $\lambda(k)$: all function with the same convex envelope $I^{**}(s)$ share the same $\lambda(k)$ with a singularity for k corresponding to the slope of the straight part in the convexe envelope.

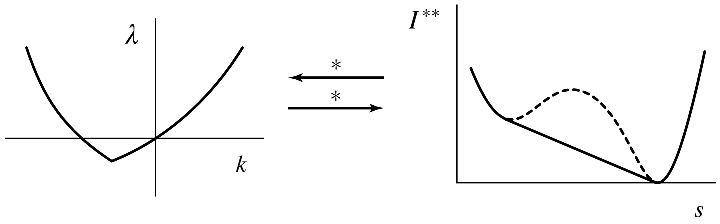


FIGURE 4.3 – Illustration of the Legendre-Fenchel transform in the case of a non differentiable $\lambda(k)$

We shall see now why the Legendre-Fenchel transform, and its specialized version, the Legendre transform are so present in statistical physics and thermodynamics.

4.6 Large deviations, Gärtner-Ellis and Cramér's theorems

In the context of statistical physics, we shall be interested in the statistics of some physical quantities, averaged over the N components of the system. Let S_N be such a random variable indexed by the integer N. One is interested in the statistical properties of this variable, namely its probability distribution $P(S_N = s)$ when N is very large.

Définition 4.6.1 — Large deviation principle. One says that $P(S_N = s)$ satisfies a large deviation principle with rate $I(s)$ if the following limit exists :

$$I(s) = -\lim_{N\to\infty}\frac{1}{N}\ln P(S_N = s), \quad \text{in other words} \quad P(S_N = s) \approx \exp[-NI(s)]. \tag{4.23}$$

The function $I(s)$ is called the rate function or the large deviation function. Be aware that the same wording sometime refers to $I(s)$, sometime to $-I(s)$.

Figure 4.4 provides an illustration of such a rate function, and the associated $P(S_N = s)$ for different N. One sees how the distributions becomes sharper and sharper around its most probable value, which corresponds to the minimum and zero of the rate function. Essentially, if the variable S_N satisfies a large deviation principle, the fluctuations outside the most probable value decreases exponentially fast to zero with N and the rate function tells us how exponentially fast. This is of course of primary importance to guarantee that most probable value are good estimates of the macroscopic variable of interest.

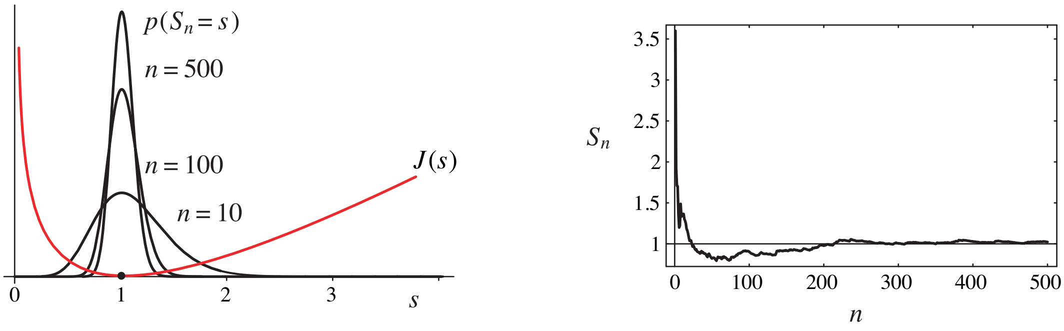


FIGURE 4.4 – Illustration of a Large deviation function and the associated variation of $P(S_N = s)$, with N and typical realization of S_N converging to its most probable value.

The theory of large deviations aims at establishing when a large deviation principle exists for a given random variable S_N, and at deriving the expression of the associated rate function.

In some rare case, one can compute explicitly $P(S_N = s)$ and derive the rate function from its asymptotic development at large N. In general, however, $P(S_N = s)$ cannot be computed. This is where the large deviation theory becomes useful. A key theorem of the theory is the Gärtner-Ellis theorem :

Proposition 4.6.1 — Gärtner-Ellis Theorem. One defines the *scaled* cumulant generating function of S_N by the limit

$$\lambda(k) = \lim_{N\to\infty} \frac{1}{N} K_{NS_N}(k) = \lim_{N\to\infty} \frac{1}{N} \log \left\langle e^{kNS_N} \right\rangle . \tag{4.24}$$

If $\lambda(k)$ exists and is differentiable for all k, then S_N satisfies a large deviation principle, with a rate function I(s) given by the Legendre–Fenchel transformation :

$$I(s) = \sup_k [ks - \lambda(k)] \tag{4.25}$$

It is instructive to consider the following heuristic argument for the expression of the rate function. Assuming the existence of the large deviation principle, one has in the limit of large N

$$P(S_N = s) \approx \exp[-NI(s)], \tag{4.26}$$

and

$$\left\langle e^{kNS_N} \right\rangle \approx \int e^{N[ks-I(s)]} ds \approx e^{N \sup_s [ks-I(s)]}, \tag{4.27}$$

where the last equality results from the celebrated *saddle-point, or Laplace's approximation* (see below). One thus finds that $\lambda(k)$ is the Legendre transform of $I(s)$ and therefore, if $I(s)$ is strictly convex, that $I(s)$ is the Legendre transform of $\lambda(k)$

$$\lambda(k) = \sup_s [ks - I(s)], \quad \text{and} \quad I(s) = \sup_k [ks - \lambda(k)]. \tag{4.28}$$

We thus see that the Gärtner-Ellis Theorem is essentially a consequence of the large deviation principle combined with the Laplace's approximation and that the Legendre-Fenchel transform appears into this theory as a natural consequence of Laplace's approximation.

Here we have used the Laplace’s approximation in its crudest form. At the next order one has, in the limit of large N, for a function g with its maximum in s^* :

$$\int e^{Ng(s)}ds \approx e^{Ng(s^*)}\int e^{-\frac{N}{2}g''(s^*)(s-s^*)^2}ds = e^{Ng(s^*)}\left(\frac{2\pi}{N\,|g''(s^*)|}\right)^{1/2} \tag{4.29}$$

Nota Bene : The rate functions obtained from the Gärtner-Ellis Theorem are necessarily strictly convex. Unfortunately rate functions are not all strictly convex ; some may even have local minima in addition to global ones... Those rate function can thus not be found using the Gärtner-Ellis theorem...

The Gärtner-Ellis theorem best applies to an extension of the Central Limit Theorem, called the Cramér’s theorem.

Proposition 4.6.2 — Cramérs Theorem. Like for the central limit theorem, let $(X_1,\ldots,X_N)$ be a set of (i.i.d) random variables drawn from distributions of expected values given by μ and *finite* variances σ^2 and consider the normalized sum $S_N := \frac{1}{N}\sum X_i$ of these random variables. The theorem states that S_N satisfies a large deviation principle and that the rate function

$$I(s) = \sup_k [ks - K_X(k)], \tag{4.30}$$

where $K_X(k)$ is simply the cumulant generating function of the X_i’s.

The proof is the simple result of the fact that for (i.i.d), $K_{NS_N}(k) = NK_X(k)$, and therefore that $\lambda(k) = K_X(k)$.

The rate function $I(s)$ inherits some interesting properties from those of the cumulant generating function $\lambda(k) = K_X(k)$. Remember that the cumulant generating function of a random variable is always convex (although not strictly convex).

- $\lambda(0) = 0 \;=>\; I(s) \geq 0$; proof : $\lambda(0) = \sup_s[0k - I(s)] = -\inf[I(s)]$.
- $\lambda'(0) = \mu \;=>\; I'(\mu) = 0$: μ is the minimum of the rate function
- $\lambda''(0) = \sigma^2 \;=>\; I''(\mu) = 1/\sigma^2$.

The Central Limit Theorem states that, for any well behaved distribution for the X_i’s, $I(x)$ has a parabolic shape of width $\frac{\sigma}{\sqrt{N}}$ around the maximum $x = \mu$. It is clear that further away from the maximum, the parabolic shape is not guaranteed unless strictly speaking when $N \to \infty$. The above theorem provides a way to compute the deviations, far away from the maximum, hence the name "Large deviations" of the theory

■ **Exemple 4.1 — The case of Gaussian variables.** Let the X_i’s obey a Gaussian distribution of mean μ and variance σ^2. We have seen that $K_X(k) = \log\left\langle e^{kX}\right\rangle = \mu k + \frac{1}{2}\sigma^2 k^2$. Hence

$$I(s) = sup_k[ks - K_X(k)] = k^*s - K_X(k^*), \quad \text{with} \quad \frac{dK_X}{dk}\Big|_{k^*} = s, \quad \text{or} \quad k^* = \frac{s-\mu}{\sigma^2} \tag{4.31}$$

$$I(s) = \frac{1}{2}\frac{(s-\mu)^2}{\sigma^2}. \tag{4.32}$$

In the case of Gaussian variables, the large deviation function is a parabola itself. ■

■ **Exemple 4.2 — The case of Poisson variables.** Let the X_i’s be integer variables obeying a Poisson distribution $\rho(x) = \frac{\lambda^x e^{-\lambda}}{x!}$. One can show that $\langle X\rangle = \lambda$ and the variance $var(X) = \lambda$. The cumulant generating function $K_X(k) = \log\left\langle e^{kX}\right\rangle = \lambda\left(e^k - 1\right)$. Hence

$$I(s) = sup_k[ks - K_X(k)] = k^*s - K_X(k^*), \quad \text{with} \quad \frac{dK_X}{dk}\Big|_{k^*} = s, \quad \text{or} \quad k^* = \log\left(\frac{s}{\lambda}\right) \tag{4.33}$$

$$I(s) = s\log\left(\frac{s}{\lambda}\right) - s + \lambda. \tag{4.34}$$

We here see that the large deviation function is certainly not a parabola. It is however easy to check that its maximum takes place at $s = \lambda$ and that the parabolic shape around that maximum has width $\sqrt{\lambda}$, as prescribed by the CLT (see figure 4.5). ∎

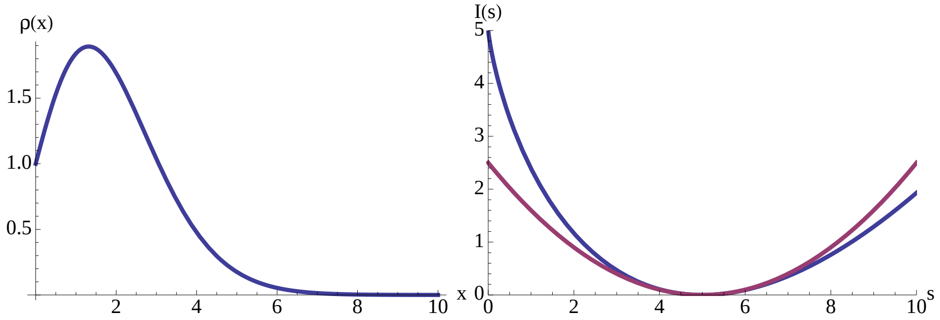
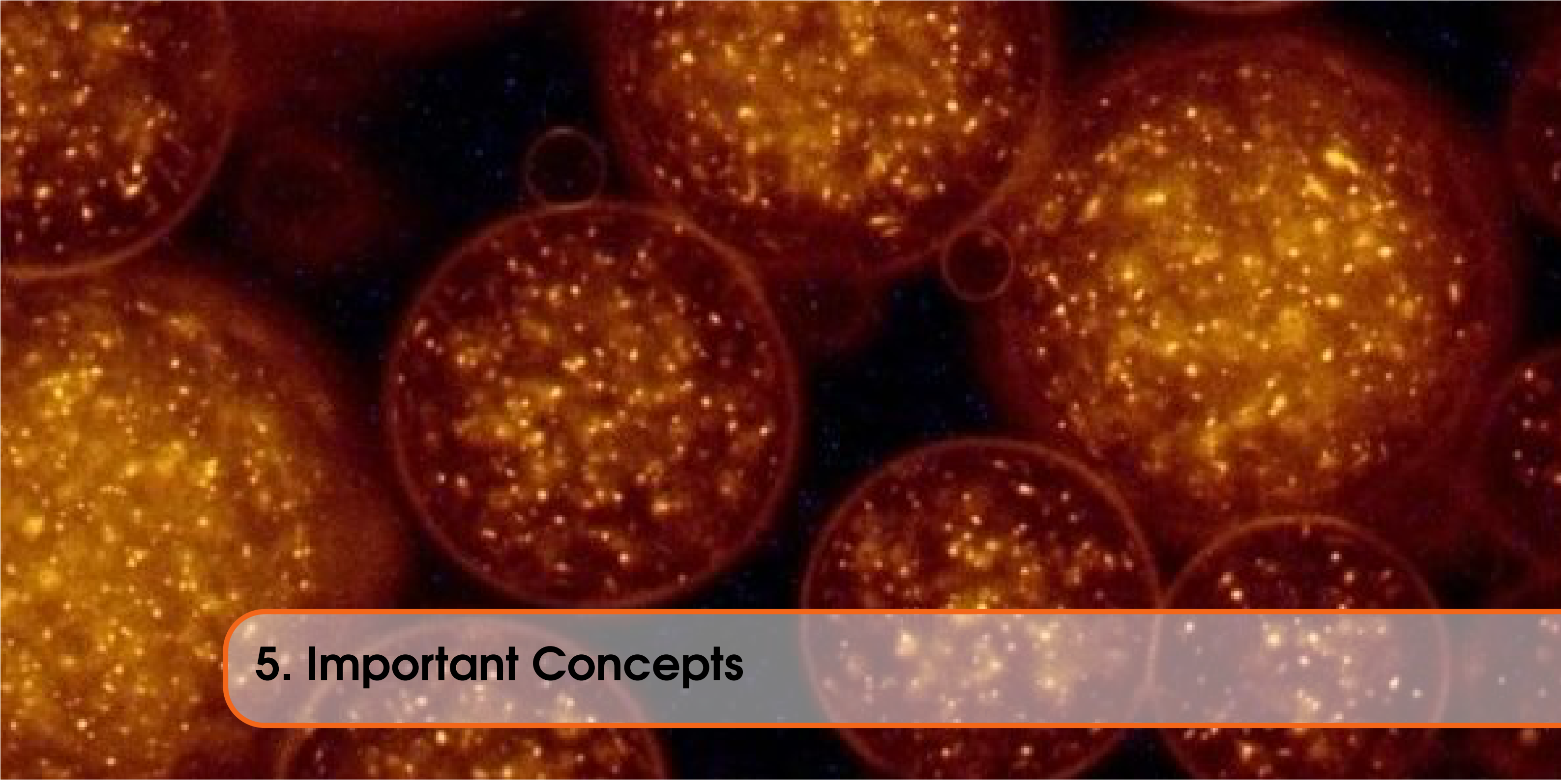


FIGURE 4.5 – Poisson distribution on the left and large deviation function for a sum of Poisson variables together with the parabola provided by the CLT (dashed) on the right ; (here $\lambda = 5$).



5. Important Concepts

In this chapter, we shall discover the very basic concepts of statistical physics in a very general context.

For now, we forget completely the underlying dynamics and consider a system of N individual units x_i, defining the configurations $X = \{x_{i,i=1\ldots N}\}$, which are sampled from a probability distribution $h(X)$. One can think of a chain, or a polymer, made of N links with orientations θ_i, or the trajectory of a drunk man made of N steps x_i, or a set of spins $s_i = \pm 1$, or N beads distributed in q small boxes etc etc...

Now imagine, one takes many configurations of such a system and for each configuration, measures a macroscopic quantity $A_N(X)$. Typical examples are the energy, the kinetic energy, or the magnetization of a system; but one can think of many others such as the velocity of a birds flock, or the valorization of a stock market etc... Such macroscopic quantities often take the form of a sum over the N elementary units of the corresponding microscopic quantity. In the following A_N is supposed to be additive and extensive.

Définition 5.0.1 — Additivity quantity. A macroscopic quantity A is said to be additive with respect to two subsystems with configurations $\{x_{i,i=1\ldots n}\}$ and $\{x_{i,i=n+1\ldots N}\}$ if $A(X) = A(\{x_{i,i=1\ldots n}\}) + A(\{x_{i,i=n+1\ldots N}\})$.

Définition 5.0.2 — Extensivity quantity. A macroscopic quantity A is extensive if the ratio $\langle A \rangle / N$, reaches a constant in the limit $N \to \infty$. In the following, we shall use capital letters for extensive variables and small letter for their intensive counterpart, that is when they are divided by N.

Mathematically speaking additivity does not ensure extensivity, and extensivity does not require additivity. However, in most cases encountered in physics, additivity does imply extensivity. Furthermore, in many models of physical systems, it is usually the non-additive part of the macroscopic quantity of interest which diverges in the limit of large N and is thus responsible for the non extensivity.

The same value of A_N will be obtained from many different configurations. Think of playing dices, say with two non biased dices : the probability of getting $(6,6)$ is the same as that of getting any other pair, say $(3,4)$, but the probability that the sum $S=12$ is much lower than that $S=7$, which can be obtained from any of the combinations $(1,6),(6,1),(2,5),(5,2),(3,4),(4,3)$.

The typical object of interest in statistical physics is the probability of observing a certain value A of A_N. It is given by the statistical weight of the configurations X, such that $A_N(X)=A$

$$\mathbb{P}(A_N=A)=\int dXh(X)\delta(A_N(X)-A), \tag{5.1}$$

that is the normalized histogram of the values taken by A_N, in the limit of a very large sampling.

5.1 Two illustrative examples

Let's illustrate how the tools introduced in the previous chapter can be used, *or not*, to determine the probability of a macroscopic quantity, in the present case the total magnetization of a system of spins.

■ Exemple 5.1 — Independent spins. Consider $s=(s_1,s_2,...,s_N)$, a set of N independent random spins, taking the value -1 or 1 with equal probability. The total magnetization M_N, for a configuration with a fraction q of spins pointing upward $(s_i=+1)$, is given by :

$$M_N=\sum_{i=1}^{N}s_i=(qN\times(+1)+(1-q)N\times(-1))=N(2q-1). \tag{5.2}$$

Since the spins are independent, and each spin takes its value ±1 with equal probability, all configurations of spins $\{s_i\}$ are equiprobable and their probability is simply

$$\mathbb{P}_0(\{s_i\})=\frac{1}{K_0(N)} \tag{5.3}$$

where $K_0(N)=2^N$ is the total number of configurations. The statistical weight of the configurations, which leads to the observation of a total magnetization $M_N=Nm$ is thus simply given by the relative number of configurations with a fraction q of spins up :

$$\mathbb{P}_0(m,N)=\frac{\Omega(m,N)}{K_0(N)}=\frac{1}{2^N}\frac{N!}{[qN]![((1-q)N)]!}, \quad \text{with} \quad q=\frac{1}{2}(1-m). \tag{5.4}$$

Using the Stirling approximation $\ln N!\simeq N\ln N-N$, one finds for large N the form

$$\mathbb{P}_0(m,N)\simeq e^{-NI_0(m)} \quad \text{with} \quad I_0(m)=\ln 2+\frac{1+m}{2}\ln\frac{1+m}{2}+\frac{1-m}{2}\ln\frac{1-m}{2} \tag{5.5}$$

One sees that $\mathbb{P}_0(m,N)$ satisfies a large deviation principle, with $I_0(m)$ the rate function.

This suggest, that we could have found it using the Gärtner-Ellis theorem :

$$I_0(m)=\sup_k(km-\lambda_0(k)), \text{with} \quad \lambda_0(k)=\lim_{N\to\infty}\frac{1}{N}\log\left[\langle e^{Nk\frac{M_N}{N}}\rangle\right] \tag{5.6}$$

The spins are independent, so that the Cramérs version of the theorem holds and :

$$\lambda_0(k)=\log[\cosh(k)] \tag{5.7}$$

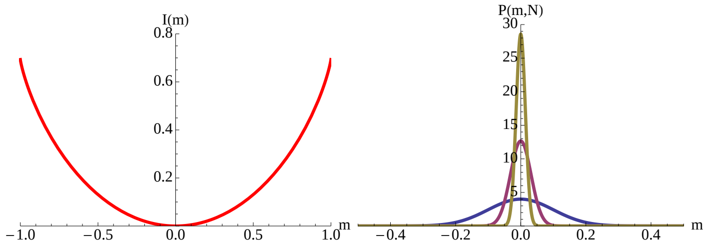
$\lambda_0(k)$ is differentiable, which confirms the existence of the rate function $I_0(m)$. $\lambda_0'(k) = \tanh(k)$. Solving for $\lambda_0'(k^*) = m$ leads to :

$$k^* = \operatorname{atanh}(m) = \frac{1}{2}\log\frac{1+m}{1-m}, \tag{5.8}$$

$$I_0(m) = k^* m - \lambda(k^*) = \frac{m}{2}\log\frac{1+m}{1-m} + \frac{1}{2}\log(1-m^2), \tag{5.9}$$

which is indeed (one line of calculus) the rate function found using the direct combinatorial calculation. It is remarkable that there is no need of any combinatorial talent in this case.

Figure 5.1 provides an illustration of $I_0(m)$, and $\mathbb{P}_0(m,N)$. Note the dependance on N of $\mathbb{P}_0(m,N)$. Also note that here $N = [100, 1000, 5000]$, which are ridiculously small values as compared for instance to the Avogadro number... ■



(a)

(b)

FIGURE 5.1 – Illustration of (a) the rate function $I_0(m)$, and the probabilities (b) $\mathbb{P}_0(m,N)$ for the magnetization per spin of $N = [100, 1000, 5000]$ (color [blue, red, green]-ish), independent spins (example 5.1)

■ **Exemple 5.2 — Fully connected spins.** We now consider the case of N spins interacting with each other. Each spins interacts with all others, but only through pairwise interactions : for instance the probability of a configuration of 3 spins $\mathbb{P}(s_1,s_2,s_3) = f(s_1,s_2)f(s_2,s_3)f(s_3,s_1)$ and we set $f(s_i,s_j) = \exp(\frac{\alpha}{N}s_i s_j)$. More generally, a configuration of N spins $\{s_i\}$ has a probability :

$$\mathbb{P}_\alpha(\{s_i\}) \propto e^{\frac{\alpha}{N}\sum\limits_{i,j>i} s_i s_j} = e^{\frac{\alpha}{2N}\sum\limits_{i,j\neq i} s_i s_j} \tag{5.10}$$

Since $M_N = \sum\limits_i s_i$, $M_N^2 = N + \sum\limits_{i,j\neq i} s_i s_j$ and $\mathbb{P}_\alpha(\{s_i\}) \propto e^{\frac{\alpha}{2}(\frac{M_N^2}{N}-1)}$.
Normalizing the distribution, we finally get

$$\mathbb{P}_\alpha(\{s_i\}) = \frac{e^{\alpha\frac{M_N^2}{2N}}}{K_\alpha(N)}, \quad \text{with} \quad K_\alpha(N) = \sum_{\{s_i\}} e^{\alpha\frac{M_N^2}{2N}} = \int dm\,\Omega(m,N)\,e^{N\alpha\frac{m^2}{2}}. \tag{5.11}$$

In this case the configurations are not all equiprobable. A highly specific feature of their probability is that it depends only on the total magnetization per spin. This happens because all the spins are connected and it is a signature of what we shall later call mean-field like models.

Let's now proceed to a direct calculation of $\mathbb{P}_\alpha(m,N) \equiv \mathbb{P}_\alpha(M_N = Nm, N)$.

$$\mathbb{P}_\alpha(m,N) = \frac{1}{K_\alpha(N)}\sum_{\{s_i\}} e^{\alpha\frac{M_N^2}{2N}}\,\delta\left(M_N(\{s_i\}) - Nm\right) = \frac{\Omega(m,N)}{K_\alpha(N)}e^{N\alpha\frac{m^2}{2}}. \tag{5.12}$$

Using the same Stirling approximation as above for $\Omega(m,N)$, one obtains

$$\mathbb{P}_\alpha(m,N) \simeq e^{-NI_\alpha(m)}, \quad \text{with} \quad I_\alpha(m) = I_0(m) - \frac{\alpha}{2}m^2 + \frac{1}{N}\log\frac{K_\alpha(N)}{K_0(N)}. \tag{5.13}$$

Equations (5.11), (5.12) and (5.13) for the model of fully connected spins correspond to equations (5.3), (5.4) and (5.5) for the model of independent spins. Again one finds that the total magnetization per spin obeys a large deviation principle. Before trying to compute it using the Gärtner-Ellis theorem, as we did in the case of independent spins, it is interesting to look at the shape of the rate function $I_\alpha(m)$. Its derivative

$$I'_\alpha(m) = I'_0(m) - \alpha m = \frac{1}{2}\log\frac{1+m}{1-m} - \alpha m = \operatorname{atanh}(m) - \alpha m \tag{5.14}$$

Hence for $\alpha \leq 1$, $I_\alpha(m)$ has a single minimum in zero, while for $\alpha > 1$, $I_\alpha(m)$ has two minima $\pm m^*$ and one maxima in zero (see figure 5.2). Note the interesting case of $\alpha = 1$: the rate function has only one minimum, but it is extremely flat, as one can check that $I''_1(0) = 0$. As a consequence the distributions $P_1(m,N)$ are much broader.

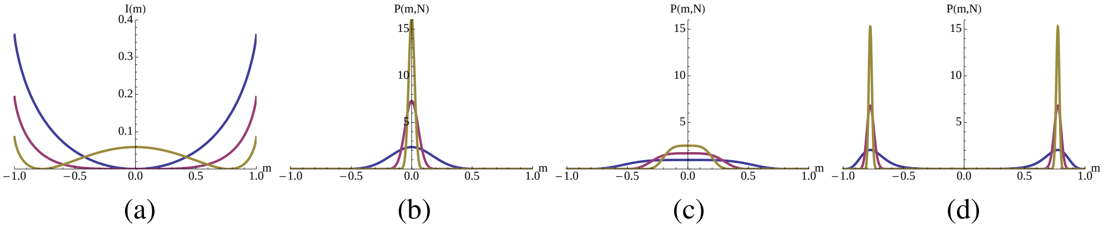


FIGURE 5.2 – Illustration of (a) the rate function $I_\alpha(m)$ for $\alpha = 2/3, 1, 4/3$, and (b),(c),(d) the probabilities $\mathbb{P}_\alpha(m,N)$ for $\alpha = 2/3, 1, 4/3$ for the magnetization per spin of $N = [100, 1000, 5000]$ (color [blue, red, green]-ish), independent spins (example 5.2)

Let us come back to the computation of $I_\alpha(m)$ using the Gärtner-Ellis theorem. The point is that, this time, we can not use the Cramérs version of the theorem anymore. We thus write explicitly

$$\langle e^{Nk\frac{M_N}{N}} \rangle = \sum_{\{s_i\}} \frac{e^{N(\frac{\alpha}{2}m^2+km)}}{K_\alpha(N)} = \frac{1}{K_\alpha(N)} \int dm\, \Omega(m,N)\, e^{N(\alpha\frac{m^2}{2}+km)} = \int dm\, e^{-N(I_\alpha(m)-km)}. \tag{5.15}$$

One immediately realizes that the calculation of $\lambda_\alpha(k)$ requires the knowledge of $I_\alpha(m)$. In this case the Gärtner-Ellis theorem is of no use. Furthermore, should one insist to continue the calculation using the Laplace approximation, he would find that

- for $\alpha < 1$, $\lambda_\alpha(k)$ is differentiable and $I_\alpha(k) = I_\alpha(k)$ ...
- for $\alpha > 1$, $\lambda_\alpha(k)$ is not differentiable in $k = 0$ and $\sup_k(km - \lambda_\alpha(k))$ only provides the convex envelope of the correct $I_\alpha(k)$.

One should however not conclude too fast that the Gärtner-Ellis theorem is useless. You may have noted that also for the fully connected spin model, it is necessary to know $\Omega(m,N)$, the number of configurations with magnetization m for the independent spins model. Its large N behavior was obtained in a straightforward manner, using the Cramèrs theorem... ■

5.2 Partition and Thermodynamic parameter

We again consider a system of N individual units x_i, defining the configurations $X = \{x_{i,i=1\ldots N}\}$, which are sampled from a probability distribution $h(X)$. We assume that the probability density of observing a certain value A of the macroscopic, additive and extensive quantity A_N obeys a large deviation principle with a rate function $I_0(a)$:

$$\mathbb{P}_0(A_N = A) = \int dX h(X) \delta(A_N(X) - A) \propto e^{-NI_0(A/N)} \tag{5.16}$$

We are interested in the statistics of the configurations of a *part* of the system, composed of $n < N$ degrees of freedom $x = \{x_{i,i=1,...n}\}$, and that of the same macroscopic quantity measured on this part, $A_n(x)$.

To do so, we will need to add two key hypothesis :

- $h(X)$ factorizes : $h(x_1,...,x_N) = h(x_1,...,x_n)h(x_n+1,...,x_N)$.
- $A_n(x)$ is independent of the $\{x_{i,i=n+1,...N}\}$ degrees of freedom : $A_n(X) = A_n(x)$.

We will consider essentially four situations :

1. The free setting : the whole system is free of any constraint.
2. The micro-canonical setting : a constraint is imposed on the total value of A in the form $A_n(\{x_{i,i=1,...n}\} + A_{N-n}(\{x_{i,i=n+1,..N}\}) = A_0$.
3. Two systems in contact : this is a direct extension of the previous case, in which the two parts are considered as different systems (1) and (2), with degrees of freedom $x = \{x_{i,i=1,...n}\}$ and $y = \{y_{i,i=n+1,...N}\}$; the two systems share a fixed amount of A : $A_1(x) + A_2(y) = A_0$
4. The canonical setting : the system of interest is much smaller than the one it is in contact with $1 \ll n \ll N$

The first case is straightforward to handle with :

- The probability density of a configuration X of the whole is by definition $\rho_0(X) = h(X)$.
- The probability density of a configuration x of the part is obtained by *averaging out* the external degrees of freedom, using the fact that $h(X)$ factorizes :

$$\rho_0(x) = \int \prod_{i,i=n+1..N} dx_i\, h(X) = h(x). \tag{5.17}$$

- The probability of observing A in the part of interest is

$$\mathbb{P}_0(A_n = A) = \int dx\, \rho_0(x)\delta(A_n(x) - A) = \int dx\, h(x)\delta(A_n(x) - A). \tag{5.18}$$

  In particular, $\mathbb{P}_0(A_n = A)$ obeys a large deviation principle with the *same* rate function $I_0(a)$.

In this first setting, the whole system is free of constraints. We have however seen in the first Chapter that systems obeying Hamiltonian dynamics conserve energy. This type of conservation law imposes a constraint on the system : for any partition of the system into subsystems, the sum of the energies of the subsystems must remain constant. This is the motivation for considering the second setting.

5.3 The micro-canonical setting

The micro-canonical setting consists in imposing a constraint of the form $A_N = A_n + A_{N-n} = A_0$. Among all the configurations $X = \{x_{i,i=1...N}\}$, which are sampled from the probability distribution $h(X)$, those which do not satisfy the constraint have a probability zero to occur.

The probability of a configuration X of the whole, under the constraint $A_N = A_0$ is thus simply

$$\rho_\mu(X; A_0) = \frac{1}{Z_\mu(A_0, N)} h(X)\delta(A_N(X) - A_0), \quad \text{with} \quad Z_\mu(A_0, N) = \int dX\, h(X)\delta(A_N(X) - A_0). \tag{5.19}$$

Note that the normalization constant is nothing but the probability of A_0 in the absence of constraint, $Z_\mu(A_0, N) = \mathbb{P}(A_N = A_0)$.

The difference from the unconstrained setting can be quantified using the Kullback-Leibler divergence or its opposite, also called the relative entropy of $\rho_\mu(X)$ with respect to $h(X)$ or simply the micro-canonical entropy :

$$S_\mu(A_0,N) \equiv -D\left[\rho_\mu || h\right] = -\int dX \rho_\mu(X;A_0) \ln \frac{\rho_\mu(X)}{h(X)} = \infty - \ln Z_\mu(A_0,N) = \infty - N I_0(a_0) \quad (5.20)$$

The presence of this ∞ is a bit annoying; it is again related to the fact that we use continuous variables in a physicist way... At the same time it guarantees the entropy to be positive. We will omit it in practice. One sees that the large deviation principle satisfied by A_N guarantees that $S_\mu(A_0,N)$ is extensive.

***

The probability density of a configuration x of the part is again obtained by *averaging out* the external degrees of freedom :

$$\rho_\mu(x) = \int \prod_{i=n+1}^{N} dx_i\, \rho_\mu(X;A_0) = \frac{1}{Z_\mu(A_0,N)} \int \prod_{i=n+1}^{N} dx_i\, h(X)\delta(A_N(X) - A_0) \quad (5.21)$$

Under the same two hypothesis as before

$$\rho_\mu(x) = \frac{h(x)}{Z_\mu(A_0,N)} \int \prod_{i=n+1}^{N} dx_i\, h(x_{n+1,\dots N})\delta(A_n + A_{N-n} - A_0) = \frac{h(x)Z_\mu(A_0 - A_n, N-n)}{Z_\mu(A_0,N)} \quad (5.22)$$

***

While A_N is fixed, A_n can still take all values compatible with the constraint $A_n + A_{N-n} = A_0$. Hence the probability of observing A in the part of interest $\mathbb{P}_\mu(A_n = A)$ is given by :

$$\begin{aligned}
\mathbb{P}_\mu(A_n = A) &= \int \prod_{i=1}^{n} dx_i\, \rho_\mu(x)\, \delta(A_n(X) - A) && (5.23)\\
&= \frac{Z_\mu(A_0 - A, N-n)}{Z_\mu(A_0,N)} \int \prod_{i=1}^{n} dx_i\, h(x)\delta(A_n(X) - A) && (5.24)\\
&= \frac{Z_\mu(A,n) Z_\mu(A_0 - A, N-n)}{Z_\mu(A_0,N)}. && (5.25)
\end{aligned}$$

in other words, taking the logarithm

$$\ln \mathbb{P}_\mu(A_n = A) = S_\mu(A,n) + S_\mu(A_0 - A, N-n) - S_\mu(A_0,N). \quad (5.26)$$

These two forms of the same formula are remarkable in the sense that the statistical properties of A_n, under the constraint that $A_N = A_0$ are given by the product, or the sum, of the same function Z_μ, or S_μ, taken with different arguments, where $Z_\mu(A,N)$ is simply the probability of A in the unconstrained system. Z_μ is called the micro-canonical partition function.

Remember that obtaining this remarkable result required three essential properties, the *additivity* of the macroscopic observable of interest, the *independence* of A_n from the degrees of freedom outside the partition where it is measured and the *factorizability* of $h(X)$.

***

By definition $\mathbb{P}_\mu(A_n = A)$ and $\ln\mathbb{P}_\mu(A_n = A)$ are maximal for $A_n = A^*$, the most probable value. Accordingly $\frac{\partial \ln \mathbb{P}_\mu(A_n=A)}{\partial A} = 0$ and

$$\frac{\partial S_\mu(A,n)}{\partial A}\Big|_{A^*} = \frac{\partial S_\mu(A_0 - A, N-n)}{\partial(A_0 - A)}\Big|_{A^*} \equiv -\zeta(a^* = \frac{A^*}{N}). \tag{5.27}$$

ζ, note the minus sign, is called the thermodynamic parameter associated to the constrained quantity A. S and A being extensive quantities, ζ is an intensive parameter. The function $\zeta(a)$ is an essential characteristic of the system. What is remarkable here is that $\zeta(a^*)$ is equal in both parts of the system.

5.4 Two systems in contact

One can easily generalize the above approach to the more interesting case of two different systems, which share and exchange a common additive macroscopic quantity, the total amount of which is fixed. The paradigmatic example of such a situation is the case of two different physical systems in contact exchanging energy between each other, while being isolated from the rest of the world.

The two systems (1) and (2) respectively take configurations $x = \{x_{i,i=1,\ldots n}\}$, and $y = \{y_{i,i=n+1,\ldots N}\}$, with probability densities $h_1(x)$ and $h_2(y)$.

The probability of a configuration (x,y) of the whole, under the constraint $A_N(x,y) = A_n(x) + A_{N-n}(y) = A_0$ is thus

$$\rho_\mu(x,y;A_0) = \frac{1}{Z_\mu(A_0,N)} h_1(x)h_2(y)\delta\left(A_n(x) + A_{N-n}(y) - A_0\right), \quad \text{with} \tag{5.28}$$

$$Z_\mu(A_0,N) = \int dxdy h_1(x)h_2(y)\delta(A_n(x) + A_{N-n}(y) - A_0). \tag{5.29}$$

The probability density of a configuration x of system (1) is again obtained by *averaging out* the external degrees of freedom, here those of system (2) :

$$\rho_\mu^{(1)}(x) = \int dy\, \rho_\mu(x,y;A_0) = \frac{1}{Z_\mu(A_0,N)}\int dy\, h_1(x)h_2(y)\delta\left(A_n(x) + A_{N-n}(y) - A_0\right) \tag{5.30}$$

$$\rho_\mu^{(1)}(x) = \frac{h^{(1)}(x) Z_\mu^{(2)}(A_0 - A_n, N-n)}{Z_\mu(A_0,N)} \tag{5.31}$$

The probability of observing A in system (1), $\mathbb{P}_\mu(A_n = A)$ is given by :

$$\mathbb{P}_\mu(A_n = A) = \int \prod_{i=1}^{n} dx_i\, \rho_\mu^{(1)}(x)\, \delta(A_n(X) - A) \tag{5.32}$$

Reproducing the same argument as above, one obtains

$$\mathbb{P}_\mu(A_n = A) = \frac{Z_\mu^{(1)}(A,n) Z_\mu^{(2)}(A_0 - A, N-n)}{Z_\mu(A_0,N)} \quad \text{with} \tag{5.33}$$

- $Z_\mu^{(1)}(A,n) = \int dx h_1(X)\delta(A_n(X) - A),$ (5.34)
- $Z_\mu^{(2)}(A_0 - A, N-n) = \int dy h_2(Y)\delta(A_{N-n}(Y) - (A_0 - A)).$ (5.35)

and, equivalently,

$$\ln \mathbb{P}_\mu(A_n = A) = S_\mu^{(1)}(A,n) + S_\mu^{(2)}(A_0 - A, N-n) - S_\mu(A_0, N). \tag{5.36}$$

Note that in this case, there are three different micro-canonical partition functions, the one of each system and that for the union of the two systems.

Again $\ln \mathbb{P}_\mu(A_n = A)$ is maximal in the more probable macroscopic state ($A = A^*$), and

$$\left.\frac{\partial S_\mu^{(1)}(A,n)}{\partial A}\right|_{A^*} = \left.\frac{\partial S_\mu^{(2)}(A_0 - A, N-n)}{\partial (A_0 - A)}\right|_{A^*} \quad \text{or} \quad \zeta_1(A^*) = \zeta_2(A_0 - A^*) \equiv \zeta^*. \tag{5.37}$$

Each system has its own function $\zeta(A)$. When put into contact, they share the macroscopic quantity A under the condition that the total amount A_0 is fixed. In the most probable macroscopic state, the two functions ζ_1 and ζ_2, evaluated respectively at the equilibrium values A^* and $A_0 - A^*$ take the same value ζ^*.

Proposition 5.4.1 — Equilibrium Stability and Fluxes back to Equilibrium. Suppose, two systems in contact (1) and (2) that are not in the most probable macroscopic state. By this we mean that the values of the macroscopic variables A's in each system are different from their most probable values A^*'s and that their associated intensive thermodynamic parameters ζ_A's are not equal in the two subsystems.

This situation can obviously not last for long and $\mathbb{P}_\mu(A_n = A)$ will rapidly grow back to its maximum ; hence

$$\frac{d \ln \mathbb{P}_\mu(A_n = A)}{dt} = \left(\frac{\partial S_\mu^{(1)}(A,n)}{\partial A} - \frac{\partial S_\mu^{(2)}(A_0 - A, n)}{\partial (A_0 - A)} \right) \frac{dA}{dt} = -(\zeta_1 - \zeta_2)\frac{dA}{dt} > 0 \tag{5.38}$$

As soon as the intensive thermodynamic parameter ζ is not equal in the two systems in contact, there is a restoring flux of the corresponding constrained quantity A from the system with the largest ζ to the one with the lowest one.

The equilibrium should also be stable. This can be expressed by the fact that $\frac{d^2 \ln \mathbb{P}_\mu(A_n=A)}{dt^2} < 0$. More intuitively, since the path towards equilibrium consists in flowing the macroscopic quantity A from the largest ζ_A to the lowest one ; it is necessary for this equilibrium to be stable that this same flow reduces the difference between the values of the ζ_A's. This implies

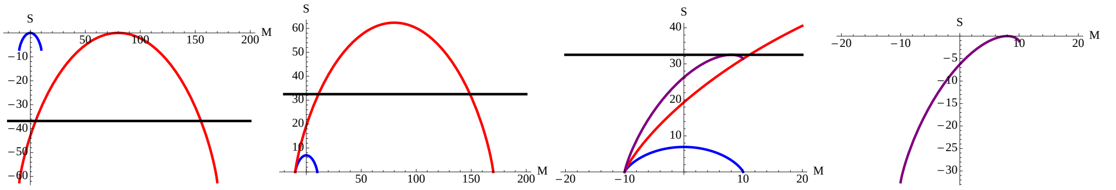
$$\frac{\partial \zeta_A}{\partial A} \geq 0 \tag{5.39}$$

5.5 The canonical setting

The canonical setting consist in considering the case where the system of interest (1) is small as compared to system (2), the so-called reservoir of A ; $(1 \ll n \ll N)$.

Figure (5.3) illustrates the use of equation (5.36), in the case $1 \ll n \ll N$, using the example (5.1) of N independent spins and their total magnetization, for which we had an explicit expression for S_μ.

The general features presented in this figure rely on the scaling in N of S_μ and are therefore quite general. In particular, when computing $\ln \mathbb{P}_\mu(A,n)$, only the part of $S_\mu^{(2)}(A_0 - A, N-n)$, close to the place where $S_\mu^{(1)}(A,n)$ is maximum, matters. Because $n \ll N$, $S_\mu^{(2)}(A_0 - A, N-n)$, on this interval, can legitimately be approximated by a straight line. Since we are interested in the statistical



(a) (b) (c) (d)

FIGURE 5.3 – Illustration of the computation of $\mathbb{P}(M_n = M)$ in the case of the N independent spins. (a) : $S^{(1)}_\mu(M,n)$ in blue, $S^{(2)}_\mu(M_0 - M, N-n)$ in red and $S_\mu(M_0,N)$ in black ; (b) $S^{(1)}_\mu(M,n) + n\ln(2)$ in blue, $S^{(2)}_\mu(M_0 - M, N-n) + (N-n)\ln(2)$ in red and $S_\mu(M_0,N) + N\ln(2)$ in black ; (c) same zooming on the domain of validity of $S^{(1)}_\mu(M,n)$, together with, in purple, the sum of the blue and red curves ; (d) finally $\ln\mathbb{P}_\mu(M_n = M)$, obtained from subtracting the black curve, from the purple one. (The $\ln(2)$ terms have been added for the clarity of the figures, but cancel altogether and are thus inessentials).

properties of A_n, it is natural to approximate $S^{(2)}_\mu(A_0 - A, N-n)$, close to the most probable value A^* of A_n, where

$$\left.\frac{\partial S^{(2)}_\mu(A_0 - A, N-n)}{\partial A}\right|_{A^*} = -\left.\frac{\partial S^{(1)}_\mu(A,n)}{\partial A}\right|_{A^*} = \zeta(A^*) = \zeta^* \tag{5.40}$$

so that the linearization of $S^{(2)}_\mu(A_0 - A, N-n)$ reads

$$S^{(2)}_\mu(A_0 - A, N-n) = S^{(2)}_\mu(A_0 - A^*, N-n) + \zeta^*(A - A^*). \tag{5.41}$$

After exponentiating to obtain $Z^{(2)}(A_0 - A, N-n)$, and substituting in equations (5.31) and (5.36), one obtains the expressions for $\rho^{(1)}_c(x)$ and $\mathbb{P}_c(A,n)$:

$$\rho^{(1)}_c(x;\zeta^*) = \frac{h_1(x)}{Z_c(\zeta^*,n)} e^{\zeta^* A(x)}, \tag{5.42}$$

$$\mathbb{P}_c(A,n) = \frac{Z^{(1)}_\mu(A,n)}{Z_c(\zeta^*,n)} e^{\zeta^* A} = \frac{1}{Z_c(\zeta^*,n)} e^{\zeta^* A + S^{(1)}_\mu(A,n)} = \frac{1}{Z_c(\zeta^*,n)} e^{n\left(\zeta^* \frac{A}{n} - I^{(1)}_0(a)\right)}, \tag{5.43}$$

with

$$\zeta^* = -\left.\frac{\partial S^{(1)}_\mu(A,n)}{\partial A}\right|_{A^*} = \left.\frac{\partial I^{(1)}_0(a)}{\partial a}\right|_{a^*} \tag{5.44}$$

and

$$Z_c(\zeta^*,n) = \int dx\, h_1(x) e^{\zeta^* A} = \int dA\, Z^{(1)}_\mu(A,n) e^{\zeta^* A} = \int dA\, e^{\zeta^* A - n I^{(1)}_0(a)}, \tag{5.45}$$

The normalization constant $Z_c(\zeta^*,n)$ absorbs all the terms independent from A. The index c replaces the index μ, when performing the linear approximation, to denote the canonical situation and underline the fact that the system of interest is small with respect to the reservoir. $Z_c(\zeta,n)$ is called the canonical partition function.

What is remarkable here is that the statistical properties of the system of interest in contact with the reservoir depend only on $S^1_\mu(A,n)$ and ζ^*. As a result A_n obeys a large deviation principle :

$$\mathbb{P}_c(A,n) = e^{-n I_c\left(\frac{A_n}{n}\right)}, \quad \text{with} \quad I_c(a) = I^{(1)}_0(a) - \zeta^* a. \tag{5.46}$$

Furthermore, in the canonical situation, $A^* \ll A_0$ and the equality of the thermodynamic parameters between two systems in contact $\zeta_1(A^*) = \zeta_2(A_0 - A^*)$ can be approximated by $\zeta_1(A^*) = \zeta_2(A_0)$. As a result, imposing the global constraint $A_n + A_{N-n} = A_0$ becomes equivalent to imposing $\zeta^* = \zeta_2(A_0)$. From this point of view, equation (5.44) can be seen as an implicit expression to be solved in order to obtain A^*.

Physical interpretation : When the system is free of constraint, the macroscopic quantity A fluctuates according to the distribution $\mathbb{P}(A,n) = e^{-nI_0(a)}$. In contact with a reservoir, with parameter ζ, it now fluctuates with probability $\mathbb{P}(A,n) = e^{-n(I_0(a)-\zeta a)}$. The reservoir biases the statistics. In particular the most probable value does not take place at the maximum of I_0, anymore, but at the maximum of $I_0(a) - \zeta a$, namely where the slope of $I_0(a)$ is ζ.

R Repeating many "experiments", in which different values of ζ^* are imposed and the A^*'s are measured, one would obtain a curve $A^*(\zeta^*)$ or equivalently $\zeta^*(A^*)$. Integrating equation (5.44), one would then determine $S_\mu^{(1)}(A,n)$ up to an additive constant, and thereby statistically characterize the system of interest.

Finally, in a way similar to the way we introduced the micro-canonical entropy as the relative entropy of the micro-canonical distribution with respect to $h(x)$, we can introduce the canonical entropy as the relative entropy of the canonical distribution with respect to $h(x)$:

$$S_c(\zeta^*,n) \equiv -D[\rho_c||h] = -\int dx \rho_c(x;\zeta^*) \ln \frac{\rho_c(x;\zeta^*)}{h(x)} = \ln Z_c(\zeta^*,N) + \zeta^* \langle A \rangle_{(\zeta^*)}. \tag{5.47}$$

Proposition 5.5.1 — $w(\zeta,n) = \frac{1}{n}\ln Z_c(\zeta,n)$ is the Legendre-Fenchel transform of $I_0(a) = -\frac{S_\mu(A)}{n}$.
This is a straightforward application of the Laplace approximation :

$$Z_c(\zeta,n) = \int dA\, Z_\mu(A,n) e^{\zeta A} = \int dA\, e^{n(\zeta a - I_0(a))} \approx e^{nw(\zeta)}, \tag{5.48}$$

$$\text{with :} \quad w(\zeta) = \sup_a (\zeta a - I_0(a)) = \zeta a^* - I_0(a^*), \tag{5.49}$$

5.6 Summary and Discussion

The following table summarizes the results obtained in the previous sections, concerning the statistics of a partition. Pay attention to the fact that X denotes the configuration of the whole system and x that of the part of interest.

	Prior	Micro-canonical setting	Canonical setting
$\rho(X)$	$h(X)$	$\rho_\mu(X) = \frac{h(X)\delta(A(X)-A_0)}{Z_\mu(A_0,N)}$	irrelevant
$\rho(x)$	$h(x)$	$\rho_\mu(x) = \frac{h(x)Z_\mu(A_0-A(x),N-n)}{Z_\mu(A_0,N)}$	$\rho_c(x) = \frac{h(x)}{Z_c(\zeta,n)} e^{\zeta A(x)}; \zeta = -\frac{\partial \ln Z_\mu(A,n)}{\partial A}$
$\mathbb{P}(A,n)$	$\simeq e^{-nI_0(a)}$	$\frac{Z_\mu(A,n)Z_\mu(A_0-A,N-n)}{Z_\mu(A_0,N)}$	$\frac{Z_\mu(A,n)}{Z_c(\zeta,n)} e^{\zeta A} \simeq \frac{1}{Z_c(\zeta,n)} e^{n(\zeta a - I_0(a))} \equiv \frac{1}{Z_c(\zeta,n)} e^{-nI_c(a,\zeta)}$
Z	$Z_0 = 1$	$Z_\mu(A,n) = \mathbb{P}_0(A,n) \simeq e^{-nI_0(A/n)}$	$Z_c(\zeta,n) \simeq e^{nw(\zeta)}$

TABLE 5.1 – Summary : together with $S_\mu = \ln Z_\mu$; $\zeta = -\frac{\partial S_\mu}{\partial A}$ and $w(\zeta) = \sup_a (\zeta a - I_0(a))$

Proposition 5.6.1 — Proposition.
$w(\zeta)$ is the scaled cumulant generating function of $\frac{A}{n}$ for the unconstrained statistics. Indeed $w(\zeta,n)=\frac{1}{n}\ln Z_c(\zeta,n)$ and

$$Z_c(\zeta,n)=\int dx\,h(x)e^{\zeta A(x)}=\int dA\,Z_\mu(A,n)e^{\zeta A}=\int dA\,\mathbb{P}_0(A,n)e^{\zeta A}=\langle e^{n\zeta\frac{A}{n}}\rangle_0; \tag{5.50}$$

Proposition 5.6.2 — Consequence I. As such it can be used to compute the cumulants of A :

$$\langle A\rangle_0=\frac{\partial\ln Z_c(\zeta,n)}{\partial\zeta}\Big|_{\zeta=0} \tag{5.51}$$

$$\langle A^2\rangle_0-\langle A\rangle_0^2=\frac{\partial^2\ln Z_c(\zeta,n)}{\partial\zeta^2}\Big|_{\zeta=0}=\frac{\partial\langle A\rangle_0}{\partial\zeta}\Big|_{\zeta=0}, \tag{5.52}$$

$$\kappa_{A,k}=\frac{\partial^k\ln Z_c(\zeta,n)}{\partial\zeta^k}\Big|_{\zeta=0}. \tag{5.53}$$

Proposition 5.6.3 — Consequence II. By application of the Gärtner-Ellis theorem, If $w(\zeta)=\frac{1}{n}\ln Z_c(\zeta,n)$ is differentiable, then $I_0(a)$ is the Legendre transform of $w(\zeta)$.

Warning : One can also use $w(\zeta)$ to compute the cumulants of A, in the canonical statistics. Indeed, it is straightforward to see that

$$\langle A\rangle_c=\frac{\partial\ln Z_c(\zeta,n)}{\partial\zeta}\Big|_{\zeta} \tag{5.54}$$

$$\langle A^2\rangle_c-\langle A\rangle_c^2=\frac{\partial^2\ln Z_c(\zeta,n)}{\partial\zeta^2}\Big|_{\zeta}=\frac{\partial\langle A\rangle_c}{\partial\zeta}\Big|_{\zeta}, \tag{5.55}$$

$$\kappa_{A,k}=\frac{\partial^k\ln Z_c(\zeta,n)}{\partial\zeta^k}\Big|_{\zeta}. \tag{5.56}$$

However $w(\zeta)$ is *not* the cumulant generating function of A in the canonical statistics ! Other wise by application of the Gärtner Ellis theorem, it would be the Legendre transform of $I_c(a)=I_0(a)-\zeta a$, and not that of $I_0(a)$...

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The two following propositions aim at discussing what is the statistical difference, between an isolated system of N degrees of freedom $X=\{x_{i,i=1,..N}\}$ under the constrained $A_N(X)=A$ and the *same* system in contact with a reservoir of A, at a given parameter ζ. As you can see, we now ignore the degrees of freedom of the reservoir, the effect of which is fully encoded in the value of ζ.

Proposition 5.6.4 — Interpretation of the canonical distribution.
For the isolated system, one has

$$\rho_\mu(X;A)=\frac{h(X)}{Z_\mu(A,N)}\delta(A(X)-A). \tag{5.57}$$

For the system in contact with the reservoir, one has

$$\rho_c(X;\zeta)=\frac{h(X)}{Z_c(\zeta,n)}e^{\zeta A(X)}=\int dA\frac{h(X)}{Z_c(\zeta,n)}e^{\zeta A}\delta(A(X)-A). \tag{5.58}$$

Hence

$$\rho_c(X;\zeta) = \int dA \frac{Z_\mu(A,n)}{Z_c(\zeta)} e^{\zeta A} \rho_\mu(X;A) = \int dA \mathbb{P}_c(A,n)\rho_\mu(X;A). \tag{5.59}$$

In other words, the canonical distribution, for a given value of ζ, is the superposition of the micro-canonical distributions for all possible values of A, weighted by the canonical weight of A prescribed by the value of ζ.

Proposition 5.6.5 — Ensemble equivalence. Since $\mathbb{P}_c(A,n)$ obeys a large deviation principle, it becomes more and more peaked around its most probable value A^*, when n increases. In the thermodynamic limit, $n \to \infty$, $\mathbb{P}_c(A,n) \to \delta(A-A^*)$. In this limit :

$$\rho_c(X;\zeta) \approx \rho_\mu(X;A = A^*(\zeta)). \tag{5.60}$$

The two statistics are equivalent.

Proposition 5.6.6 — Distribution of an observable O.
For the isolated system, one has

$$\mathbb{P}_\mu(O;A) = \frac{1}{Z_\mu(A)} \int dX h(X) \delta\left(O(X) - O\right) \delta(A(X) - A). \tag{5.61}$$

For the system in contact with the reservoir, one has, using now familiar algebra

$$\begin{aligned}
\mathbb{P}_c(O;\zeta) &= \frac{1}{Z_c(\zeta)} \int dX h(X) \delta\left(O(X) - O\right) e^{\zeta A(X)} && (5.62)\\
&= \frac{1}{Z_c(\zeta)} \int dA \int dX h(X) \delta\left(O(X) - O\right) e^{\zeta A(X)} \delta(A(X) - A) && (5.63)\\
&= \frac{1}{Z_c(\zeta)} \int dA\, e^{\zeta A} \int dX h(X) \delta\left(O(X) - O\right) \delta(A(X) - A) && (5.64)\\
&= \frac{1}{Z_c(\zeta)} \int dA\, \mathbb{P}_\mu(O;A) Z_\mu(A) e^{\zeta A} && (5.65)\\
&= \frac{1}{Z_c(\zeta)} \int da\, \mathbb{P}_\mu(O;A) e^{N(\zeta a - I_0(a))}. && (5.66)
\end{aligned}$$

In the large N limit, using the Laplace approximation, one obtains (see equation 5.49)

$$\mathbb{P}_c(O;\zeta) \simeq \frac{1}{Z_c(\zeta)} \mathbb{P}_\mu(O;A^*(\zeta)) e^{Nw(\zeta)} = \mathbb{P}_\mu(O;A^*(\zeta)), \tag{5.67}$$

where ζ satisfies $\zeta = \frac{\partial S_\mu(A,N)}{\partial A}$.

In other words, given an isolated system under the constrained $A_N(X) = A$, in the large N limit, if one puts it in contact with a reservoir with the value of ζ, which ensures that the most probable value $A^* = A$, then all observables have the same distribution in both configurations.

Proposition 5.6.7 — Generalization to two – or more – constraints. The above description can easily be generalized to an arbitrary number of constraints, as we shall now see in the case of two. The system of N degrees of freedom with configurations $X = \{x_{i,i=1..N}\}$ satisfies two independent constraints $A(X) = A_0$ and $B(X) = B_0$. One thus have

$$\rho_\mu(X) = \frac{h(X)}{Z_\mu(A_0,B_0,N)} \delta(A(X) - A_0) \delta(B(X) - B_0), \quad \text{with} \quad Z_\mu(A_0,B_0,N) \simeq e^{-NI_0(a_0,b_0)} \tag{5.68}$$

Following the above prescription, one defines $\zeta_A = \frac{\partial I_0}{\partial a}$ and obtains

$$\rho_c(x) = \frac{h(x)e^{\zeta_A A(x)}}{Z_c^A(\zeta_A, B, N)}\delta(B(x) - B_0) \tag{5.69}$$

$$\mathbb{P}_c(A,B) = \frac{Z_\mu(A,B,N)}{Z_c^A(\zeta_A,B,N)}e^{\zeta_A A} \simeq \frac{1}{Z_c^A(\zeta_A,B,N)}e^{N(\zeta_A a - I_0(a,b))} \tag{5.70}$$

$$w(\zeta_A, b) \equiv \frac{1}{N}\log Z_c^A(\zeta_A,B,N) = \zeta_A a^*(\zeta_A,b) - I_0(a^*,b) \tag{5.71}$$

Of course the same can be done, replacing A with B.

The next step is to reproduce the same scheme for B, replacing $h(x)$ by $h(x)e^{\zeta_A A(x)}$ and $Z_\mu(A_0,B_0,N)$ by $Z_c(\zeta_A,B,N)$. To do so we introduce

$$I_0^B(\zeta_A,b) = -\frac{1}{N}\log Z_c^A(\zeta_A,B,N), \quad \text{and} \quad \zeta_A^B = \frac{\partial I_0^B(\zeta_A,b)}{\partial b} \tag{5.72}$$

The apparent asymmetry between A and B is only apparent, as it should be, since the order in which the two constraints are considered should not matter :

$$\zeta_A^B = \frac{\partial I_0^B(\zeta_A,b)}{\partial b} = \frac{\partial\left[I_0(a^*,b) - \zeta_A a^*(\zeta_A,b)\right]}{\partial b} \tag{5.73}$$

$$= \frac{\partial a^*}{\partial b}\frac{\partial I_0}{\partial a} + \frac{I_0}{\partial b} - \zeta_A\frac{a^*}{\partial b} \tag{5.74}$$

$$= \frac{\partial I_0}{\partial b} \tag{5.75}$$

$$= \zeta_B \tag{5.76}$$

where it has been taken care to derive with respect to all the relevant arguments in the composite functions. One then obtains nice symmetric forms, for this new setting

$$\rho_{cc}(x) = \frac{h(x)}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{\zeta_A A(x) + \zeta_B B(x)} \tag{5.77}$$

$$\mathbb{P}_{cc}(A,B) = \frac{Z_\mu(A,B,N)}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{\zeta_A A + \zeta_B B} \simeq \frac{1}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{N(\zeta_A a + \zeta_B b - I_0(a,b))} \tag{5.78}$$

$$w(\zeta_A,\zeta_B) \equiv \frac{1}{N}\log Z_{cc}(\zeta_A,\zeta_B,N) = \zeta_A a^*(\zeta_A,\zeta_B) + \zeta_B b^*(\zeta_A,\zeta_B) - I_0(a^*,b^*) \tag{5.79}$$

Nota Bene : $\mathbb{P}_{cc}$ is a joint distribution for the variables A and B. One often is interested in the marginal, say for the variable B only :

$$\mathbb{P}_{cc}(B) = \int dx\, \rho_{cc}(x)\delta(B(x) = B) = \int dx \frac{h(x)}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{\zeta_A A(x) + \zeta_B B(x)}\delta(B(x) = B) \tag{5.80}$$

$$= \frac{1}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{\zeta_B B}\int dx\, h(x)e^{\zeta_A A(x)}\delta(B(x) = B) \tag{5.81}$$

$$= \frac{Z_c(\zeta_A,B,N)}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{\zeta_B B} \tag{5.82}$$

$$= \frac{1}{Z_{cc}(\zeta_A,\zeta_B,N)}e^{N(\zeta_B b + w(\zeta_A,b))} \tag{5.83}$$

II

Equilibrium : Steady state of Hamiltonian Dynamics

6. Equilibrium ensembles, Ideal Systems

6.1 Equilibrium Ensembles

Equilibrium holds when a system obeying Hamiltonian dynamics has reached a steady state, and is not submitted to any external driving. This is of course a rather restrictive view, and you shall see in the last part of this course that there exist other dynamics, in particular stochastic dynamics, which can be considered as equilibrium dynamics. One can see these stochastic dynamics as effective dynamics, the law of which have been chosen, to ensure equilibrium properties.

Those equilibrium properties are :

- the uniformity of the measure on the manifolds of the conserved quantities
- some form of temporal reversibility

For the moment let's focus on the case of Hamiltonian dynamics. We have seen in section (2.6) that the steady state measure for Hamiltonian dynamics is uniform over the manifolds where the system is ascribed to evolve by the conservation laws. The translational invariance in time and space, together with the rotational invariance, imposes three conservation laws, that of the energy E_0, the momentum $\mathbf{P}_0$ and the kinetic momentum $\mathbf{K}_0$, the last two being d-dimensional vectors. Furthermore, there will be situations where the volume and the number of particles shall also be fixed or let to fluctuate in contact with a reservoir.

From what we have learnt in the previous chapters, (see table 7.1), we immediately infer the so-called micro-canonical measure, which describes the situation of an isolated system of N_0 units or particles with configurations $X = \{q_i, p_i\}$ in a container of volume V_0. The measure being uniform, $h(x) = 1$, one simply has

$$\rho_\mu(\{q_i,p_i\}) = \frac{1}{\Omega(E_0,V_0,N_0,\mathbf{P}_0,\mathbf{K}_0)}\delta(H(q_i,p_i)-E_0)\delta(V(q_i,p_i)-V_0)\delta(N(q_i,p_i)-N_0)\ldots$$
$$\ldots\delta(\mathbf{P}(q_i,p_i)-\mathbf{P}_0)\delta(\mathbf{K}(q_i,p_i)-\mathbf{K}_0).$$

where

$$\Omega(E_0, V_0, N_0 \mathbf{P}_0, \mathbf{K}_0) = \int \prod_i dq_i dp_i \delta(H(q_i, p_i) - E_0) \delta(V(q_i, p_i) - V_0) \delta(N(q_i, p_i) - N_0) \ldots$$
$$\ldots \delta(\mathbf{P}(q_i, p_i) - \mathbf{P}_0) \delta(\mathbf{K}(q_i, p_i) - \mathbf{K}_0)$$

is the volume in phase space of all the configurations of N_0 particles with energy E_0, volume V_0, momentum $\mathbf{P}_0$ and kinetic momentum $\mathbf{K}_0$. Ω is nothing but the micro-canonical partition function Z_μ in the case of a uniform measure.

We have here three scalar and two vectorial constraints ; without thinking further we thus define as many thermodynamics parameters :

Définition 6.1.1 — Thermodynamic parameters.

$$\zeta_E \equiv -\frac{\partial \log \Omega(E, V, N, \mathbf{P}, \mathbf{K})}{\partial E} = -\frac{\partial S}{\partial E} \equiv -\beta = -\frac{1}{T} \tag{6.1}$$

$$\zeta_V \equiv -\frac{\partial \log \Omega(E, V, N, \mathbf{P}, \mathbf{K})}{\partial V} = -\frac{\partial S}{\partial V} \equiv -\beta P \tag{6.2}$$

$$\zeta_N \equiv -\frac{\partial \log \Omega(E, V, N, \mathbf{P}, \mathbf{K})}{\partial N} = -\frac{\partial S}{\partial N} \equiv \beta \mu \tag{6.3}$$

$$\zeta_{\mathbf{P}} \equiv -\frac{\partial \log \Omega(E, V, N, \mathbf{P}, \mathbf{K})}{\partial \mathbf{P}} = -\frac{\partial S}{\partial \mathbf{P}} \tag{6.4}$$

$$\zeta_{\mathbf{K}} \equiv -\frac{\partial \log \Omega(E, V, N, \mathbf{P}, \mathbf{K})}{\partial \mathbf{K}} = -\frac{\partial S}{\partial \mathbf{K}} \tag{6.5}$$

where we have used that $S = \log \Omega$, a direct consequence of the uniformity of the measure, and where the last part of the equalities actually provide a statistical definition of the commonly used thermodynamic parameters.

It is important to remark, that, at this stage of the theory, the physical meaning of the intensive thermodynamic parameter ζ's,remains unclear. You may have recognized β, because of your scientific culture, but nothing actually tells you that it is the inverse of our everyday life temperature. In the following, we shall see that T and P are indeed the familiar temperature and pressure defined at the thermodynamic and mechanical level. Regarding the last two equalities, which define less familiar vectorial thermodynamic parameter, the reader is invited to read the complement (II.E) of [**Diu**]. Let us just say that $\zeta_{\mathbf{P}}$ is the velocity of the center of mass and $\zeta_{\mathbf{K}}$ is the solid body rotational velocity. For the purpose of simplicity, let's assume that our system of interest is attached in our lab, which can be seen as a reservoir of momenta, both translational and rotational, with $\zeta_{\mathbf{P}} = \zeta_{\mathbf{K}} = 0$.

In this simplified framework we can forget about the constraints other than the conserved energy, the volume and the total number of particles. Note however that there can be several species of particles, hence as many constraints, and as many corresponding chemical potentials μ_k's. Disposing of several constraints, one can define many different settings, deciding which quantities are fixed, and which are free to fluctuate around an average value fixed by the contact with a reservoir with a given thermodynamic parameter.

The most commonly used settings are

— the micro-canonical setting : E, V, N fixed
— the canonical setting : β, V, N fixed

— the grand-canonical setting : β, V, μ fixed
— the PT or Gibbs setting : β, P, N fixed

From proposition (5.6.7) and definitions (6.1.1), one obtains all distributions of interest.

Canonical setting : $A \to E$, $\zeta_E = -\frac{1}{\beta}$, $I_0 = -\frac{1}{N}\ln Z_\mu = -\frac{1}{N}S(E,V,N)$

$$\rho_c(X;\beta,V,N) = \frac{1}{Z_c(\beta,V,N)}e^{-\beta H(X)}, \tag{6.6}$$

$$\mathbb{P}_c(E;\beta,V,N) = \frac{1}{Z_c(\beta,V,N)}e^{S(E,V,N)-\beta E}, \tag{6.7}$$

$$W_c = \log Z_c = S(E^*,V,N) - \beta E^*(\beta,V,N) \equiv -\beta F(\beta,V,N), \tag{6.8}$$

$$\langle E \rangle = -\frac{\partial \ln Z_c(\beta,V,N)}{\partial \beta}; \quad \langle \delta E^2 \rangle = \frac{\partial^2 \ln Z_c}{\partial \beta^2} = -\frac{\partial \langle E \rangle}{\partial \beta}; \tag{6.9}$$

where $F(\beta,V,N) = E^*(\beta,V,N) - TS(E^*,V,N)$ is the familiar free energy in the thermodynamic limit.

PT, or Gibbs setting : $A \to E$, $B \to V$, $\zeta_E = -\frac{1}{\beta}$, $\zeta_V = -\beta P$, $I_0 = -\frac{1}{N}\ln Z_\mu = -\frac{1}{N}S(E,V,N)$

$$\rho_{pt}(X;\beta,P,N) = \frac{1}{Z_{pt}(\beta,P,N)}e^{-\beta H(X)-\beta PV(X)}, \tag{6.10}$$

$$\mathbb{P}_{pt}(E,V;\beta,P,N) = \frac{1}{Z_{pt}(\beta,P,N)}e^{S(E,V,N)-\beta E-\beta PV}, \tag{6.11}$$

$$W_{pt} = \log Z_{pt} = S(E^*,V^*,N) - \beta E^*(\beta,P,N) + \beta PV^*(\beta,P,N) \equiv -\beta G(\beta,P,N), \tag{6.12}$$

$$\langle E \rangle = -\frac{\partial \ln Z_{pt}(\beta,V,N)}{\partial \beta}; \quad \langle \delta E^2 \rangle = \frac{\partial^2 \ln Z_{pt}}{\partial \beta^2} = -\frac{\partial \langle E \rangle}{\partial \beta}, \tag{6.13}$$

$$\langle V \rangle = -\frac{\partial \ln Z_{pt}(\beta,P,N)}{\partial \beta P}; \quad \langle \delta V^2 \rangle = \frac{\partial^2 \ln Z_{pt}}{\partial \beta P^2} = -\frac{\partial \langle V \rangle}{\partial \beta P}; \tag{6.14}$$

where $G(\beta,P,N) = E^*(\beta,P,N) - TS(E^*,V^*,N) + PV^*(\beta,P,N)$ is the Gibbs free energy.

Grand Canonical setting : $A \to E$, $B \to N$, $\zeta_E = -\frac{1}{\beta}$, $\zeta_N = \beta\mu$, $I_0 = -\frac{1}{N}\ln Z_\mu = -\frac{1}{N}S(E,V,N)$

$$\rho_{gc}(X;\beta,V,\mu) = \frac{1}{Z_{gc}(\beta,V,\mu)}e^{-\beta H(X)+\beta\mu N(X)}, \tag{6.15}$$

$$\mathbb{P}_{gc}(E,N;\beta,V,\mu) = \frac{1}{Z_{gc}(\beta,V,\mu)}e^{S(E,V,N)-\beta E+\beta\mu N}, \tag{6.16}$$

$$W_{gc} = \log Z_{gc} = S(E^*,N^*) - \beta E^*(\beta,V,\mu) + \beta\mu N^*(\beta,V,\mu) \equiv -\beta J(\beta,V,\mu), \tag{6.17}$$

$$\langle E \rangle = -\frac{\partial \ln Z_{gc}(\beta,V,\mu)}{\partial \beta}; \quad \langle \delta E^2 \rangle = \frac{\partial^2 \ln Z_{gc}}{\partial \beta^2} = -\frac{\partial \langle E \rangle}{\partial \beta}, \tag{6.18}$$

$$\langle N \rangle = \frac{\partial \ln Z_{gc}(\beta,V,\mu)}{\partial \beta\mu}; \quad \langle \delta N^2 \rangle = \frac{\partial^2 \ln Z_{gc}}{\partial \beta\mu^2} = \frac{\partial \langle N \rangle}{\partial \beta\mu}; \tag{6.19}$$

where $J(\beta,V,\mu) = E^*(\beta,V,\mu) - TS(E^*,V,N^*) - \mu N^*(\beta,V,\mu)$ is the so called "Grand-potential"

Nota Bene : In the Grand-Canonical setting, since the number of particles is not fixed, the sum over all configurations must include a sum over all the possible number of particles inside the configuration. Hence

$$Z_{gc}(\beta,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_c(\beta,V,N). \tag{6.20}$$

Warning!!! The expression $\mathbb{P}_c(E) \simeq e^{-\beta(E-TS(E))}$ suggests some easy identification between the argument of the exponential and $F(\beta) = E^* - TS(E^*)$. The two should however not be confused. $F(\beta)$, the free energy, is a number set by the reservoir, which also sets $E^*(\beta)$, the most probable value taken by the energy of the system in contact with this reservoir. $\mathbb{P}_c(E;\beta)$ is a *function of* E, which describes the probability for the energy to take the value E. Its maximum is realized for $E = E^*$.

Proposition 6.1.1 — Relating free energy and the large deviations of the energy. It is note rare to hear someone calling $E - TS(E)$, the free energy and saying that the free energy is the large deviation function of the energy... while the correct statement is the following translation of proposition (5.6.1) :

If $-\beta f(\beta)$ is differentiable, $-s(e)$ is the Legendre transform of $-\beta f(\beta)$ and the large deviation function of the energy is $-s(e) + \beta e$.

The proposition 5.4.1, we saw in the previous chapter, provides a first hint of the meaning of the intensive thermodynamic parameters. In the case of $A = E$ and ζ_E, one expects from the everyday experience that energy flows from high to low temperatures. The form $\zeta_E = -\beta = -1/T$ is compatible with such an observation; but this is certainly not a formal identification. In the case of $A = V$ and ζ_V, one expects the volume to flow from low to high mechanical pressure (so that high pressure regions expand). Here also, this is compatible with $\zeta_V = -\beta P$, with P the mechanical pressure, but this is again not a formal identification.

As a matter of fact the physical meaning of the intensive thermodynamic parameters will become apparent by computing macroscopic relations, the so called equation of states, which were empirically measured using quantities defined at the thermodynamic level, such as the pressure, the volume, and the temperature. This is what we shall do now for ideal systems.

6.2 The ideal gas

The ideal gas is defined as a gas of point particles, with mass m, which do not interact amongst each other.

Let's first compute the properties of the ideal gas in the micro-canonical setting.

The Hamiltonian of the ideal gas is $H(\{q_i, p_i\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} = \sum_{\alpha=1}^{3N} \frac{p_\alpha^2}{2m}$. Since the total energy E is fixed, this formula is nothing but the equation of a sphere of radius $\sqrt{2mE}$ in a space of dimension $D = 3N$. Using the formula $\mathscr{A}_D(R) = \frac{D\pi^{D/2}}{\Gamma(D/2+1)} R^{D-1}$ for the surface of a sphere of radius R in dimension D, where $\Gamma(x) = \int_0^\infty du u^{x-1} e^{-u}$, we find :

$$\Omega(E,V,N) = \frac{1}{N!h^{3N}} \int \prod_i dq_i dp_i \delta(H(q_i,p_i) - E) = \frac{3N\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)} \frac{V^N}{N!} \frac{\sqrt{2mE}^{3N-1}}{h^{3N}}, \tag{6.21}$$

where the $\frac{1}{N!h^{3N}}$ comes from the fact that $dq_i dp_i$ must satisfy the uncertainty principle and the fact that any permutation of the particles lead to the same configuration. In the limit of large N, one finds

$$S(E,V,N) = \log\Omega(E,V,N) = \frac{3N}{2}\ln E + N\ln V - \frac{5}{2}N\ln N \tag{6.22}$$

$$s(e,v) = \frac{1}{N}S(E,V,N) = \frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N}. \tag{6.23}$$

From this we extract the intensive thermodynamic parameter

$$\beta = \frac{\partial S(E,V,N)}{\partial E} = \frac{3N}{2E}. \tag{6.24}$$

Note that in the micro-canonical setting used in this calculation, we have fixed E and computed T. First this is not the standard physical situation; second this required the knowledge of the surface of a sphere in D dimension...

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Let's reproduce the above calculation in the canonical setting. Again $H(\{q_i,p_i\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$ and :

$$\mathbb{P}_c(\{q_i,p_i\}) = \frac{1}{Z_c(\beta,N,V}e^{-\beta H(\{q_i,p_i\})} \tag{6.25}$$

$$Z_c(\beta,N,V) = \frac{1}{N!h^{3N}}\int\prod_{i=1}^{N} dq_i dp_i e^{-\beta\sum_i\frac{p_i^2}{2m}} = \frac{V^N}{N!h^{3N}}\left(\int_{-\infty}^{\infty} dp e^{-\beta\frac{p^2}{2m}}\right)^{3N} = \frac{V^N}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3N}{2}} \tag{6.26}$$

$$Z_c(\beta,N,V) = \frac{1}{N!}\left(\frac{V}{\Lambda_T^3}\right)^N \tag{6.27}$$

where the last equality of the second line results from a simple gaussian integration. $\Lambda_T = \sqrt{\frac{h^2\beta}{2\pi m}}$ is the de Broglie thermal wavelength. Never forget that it is a function of temperature. From this simple relation, we derive :

$$\langle E\rangle = -\frac{\partial \ln Z_c(\beta,N,V)}{\partial\beta} = \frac{3N}{2\beta} = \frac{3}{2}NT \tag{6.28}$$

$$\zeta_V = \frac{\partial \ln Z_c(\beta,N,V)}{\partial V} = \frac{N}{V} \tag{6.29}$$

$$\zeta_N = \frac{\partial \ln Z_c(\beta,N,V)}{\partial N} = \ln\Lambda^3\rho. \tag{6.30}$$

The first equation is equivalent to equation (6.24); in application of the ensemble equivalence. These equations , by identification with the equipartition theorem and the perfect gas law suggests that $\beta = \frac{1}{k_B T}$ and $\zeta_V = \beta P$.

Since $-\beta f(\beta, v = \frac{V}{N}) = \frac{1}{N}\ln Z_c(\beta,v) = \ln v - \frac{3}{2}\ln\frac{h^2\beta}{2\pi m}$ is differentiable, one can recover the expression of $s(e)$, via the Legendre transform $s(e) = -\sup_\beta(-\beta e + \beta f(\beta))$ (exercise).

The probability density of the energy is given by $\mathbb{P}_c(\frac{E}{N} = e) = \frac{1}{Z(\beta)}e^{-\beta e + s(e)}$ and is displayed on figure

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Now let's see how to compute the density fluctuations. Since the density $n = N/V$, one could study its fluctuations by studying a fixed number of particles and let the volume fluctuate, or a fixed volume within which the number of particles is free to fluctuate. Defining the volume of a fixed number of particles is actually not an easy task and the second strategy is the good one. We thus use the grand-canonical setting :

$$Z_{gc}(\beta,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_c(\beta,V,N) = \sum_{N=0}^{\infty} \frac{\left(V/\Lambda_T^3\, e^{\beta\mu}\right)^N}{N!} = exp\left(\frac{V}{\Lambda_T^3}e^{\beta\mu}\right) \tag{6.31}$$

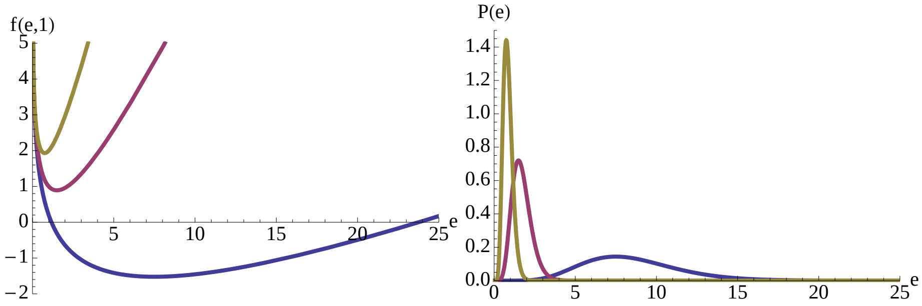

FIGURE 6.1 – Large deviation function and probability density of the energy of an ideal gaz (N=5) for $\beta = [0.2, 1, 2]$, (blue,purple,brown).

We then know that the joint-probability of $\tilde{e} = \frac{E}{V}$ and $n = N/V$ is given by

$$\mathbb{P}_{gc}(E,N;\beta,V,\mu) = \frac{1}{Z_{gc}(\beta,V,\mu)} e^{S(E,V,N)-\beta E+\beta\mu N}, \tag{6.32}$$

$$= \frac{1}{Z_{gc}(\beta,V,\mu)} e^{V(\tilde{s}(\tilde{e},V,n)-\beta\tilde{e}+\beta\mu n)}; \tag{6.33}$$

while the marginal probability of n is given by

$$\mathbb{P}_{gc}(N;\beta,V,\mu) = \frac{1}{Z_{gc}(\beta,V,\mu)} e^{W_c(\beta,V,N)+\beta\mu N}, \tag{6.34}$$

$$\mathbb{P}_{gc}(N;\beta,V,\mu) = \frac{1}{Z_{gc}(\beta,V,\mu)} e^{V(\tilde{w}_c(\beta,V,n)+\beta\mu n)}; \tag{6.35}$$

where $W_c(\beta,V,N) = \ln Z_c(\beta,V,N)$. We see here that the extensive quantity used to scale the large deviation function is now the volume and not the number of particles.

The final step consists in using the Gartner-Ellis theorem :

$$-\tilde{s}(\tilde{e},n) = \sup_{\beta}\left(-\beta\tilde{e} - \tilde{w}_c(\beta,n)\right), \tag{6.36}$$

$$-\tilde{w}_c(\beta,n) = \sup_{\beta\mu}\left(\beta\mu\tilde{n} - \tilde{w}_{gc}(\beta,\beta\mu)\right); \tag{6.37}$$

with $\tilde{w}_{gc} = \frac{1}{V}\ln Z_{gc}$. You will for instance obtain that $\tilde{s}(\tilde{e},n) = \frac{3}{2}n\ln\tilde{e} - \frac{5}{2}n\ln n$, which is indeed the result obtained trough the micro-canonical distribution $s(e,v) = \frac{3}{2}\ln e + \ln v$, if you remember that $v = 1/n$, $\tilde{e} = ne$ and $\tilde{s} = ns$...

6.3 Independent spins in a field

The second example of an ideal systems consists in N spins $s_i = \pm 1$ in a field h. The hamiltonian of the system reads $H(\{s_i\}) = -h\sum_{i=1}^{N} s_i$.

We start by considering the micro-canonical setting. Knowing the number of spins up, N^+, and down, N^-, is enough to compute the energy of the system :

$$E = -h(N^+ - N^-) = -h(2N^+ - N). \tag{6.38}$$

The number of configurations with energy E is thus simply the combinatorial result :

$$\Omega(E) = \Omega(N^+) = \frac{N!}{N^+!(N-N^+)!} = \frac{N!}{\left(\frac{1}{2}(N-\frac{E}{h})\right)!\left(\frac{1}{2}(N+\frac{E}{h})\right)!} \tag{6.39}$$

and

$$S(E) = \ln \Omega(E) \simeq N \ln N - \left(\frac{N - \frac{E}{h}}{2} \right) \ln \left(\frac{N - \frac{E}{h}}{2} \right) - \left(\frac{N + \frac{E}{h}}{2} \right) \ln \left(\frac{N + \frac{E}{h}}{2} \right) \tag{6.40}$$

This is of course the same kind of result has the one obtained for the magnetization of a system of independent spins, because the energy is nothing but $E = -hM$. We then obtain :

$$\beta = \frac{\partial S(E,N)}{\partial E} = \frac{1}{2h} \ln \frac{N - \frac{E}{h}}{N + \frac{E}{h}} \tag{6.41}$$

Again note that the energy is fixed and we have computed $\beta(E)$.

***

Moving to the canonical setting, we have :

$$\mathbb{P}_c(\{s_i\}) = \frac{1}{Z_c(\beta,N)} e^{-\beta H(\{s_i\})} \tag{6.42}$$

$$Z_c(\beta,N) = \sum_{\{s_i\}} e^{\beta h \sum_i s_i} = \sum_{\{s_i\}} \prod_i e^{\beta h s_i} = \prod_i \sum_{s_i = \pm 1} e^{\beta h s_i} = \prod_i \left(e^{\beta h} + e^{-\beta h} \right) = (2 \cosh \beta h)^N \tag{6.43}$$

from which we derive

$$\langle E \rangle = -\frac{\partial \ln Z_c(\beta,N)}{\partial \beta} = -Nh \tanh \beta h \tag{6.44}$$

$$\langle M \rangle = -\frac{\partial \ln Z_c(\beta,N)}{\partial \beta h} = -N \tanh \beta h = -\frac{\langle E \rangle}{h} \tag{6.45}$$

Note that, without knowing that $\text{atanh} x = \frac{1}{2} \ln \frac{1+x}{1-x}$, the equivalence of the two settings does not jump out immediately.

We also have the whole distribution of the energy and the magnetization :

$$\mathbb{P}_c(E) = \frac{1}{Z_c(\beta,N)} e^{-N(\beta e - s(e))} \tag{6.46}$$

$$\mathbb{P}_c(M) = \frac{1}{Z_c(\beta,N)} e^{-N(\beta h m - s(m))} \tag{6.47}$$

with $s(e) = \frac{1}{N} \ln \Omega(E,N)$, where $\Omega(E)$ results from the above combinatorial calculation. Alternatively, since $f(\beta)$ is differentiable $-s(e)$ is also given by the Legendre transform of $-\beta f(\beta) = \frac{1}{N} \ln Z_c(\beta,N)$, which is exactly the calculation conducted in equations (5.7),(5.8),(5.9).

One sees that the computation in the canonical ensemble is usually more direct, and generally allows to recover the expression of $s(e)$, hence of the large deviation function of E, via the Legendre transform of $-\beta f(\beta)$. Of course the ideal systems here characterize themselves by the absence of interactions amongst their components. We are thus in the situation where the Gärtner-Ellis theorem, turns into the simpler Cramers one, for which the cumulant generating function factorizes. This is actually why, it is so easy to compute the canonical partition function. Life will not remain as simple in the presence of interactions...

7. Systems with interactions

7.1 Elements of Liquid state Theory

Liquid state theory is a whole big chapter of statistical physics, and by no way we can cover it in this course. We shall however give some basic ideas and introduce the logic behind it to illustrate the importance of correlations, when the units composing the system of interest, here the particles, interact amongst each other.

We first consider any gas, namely a set of N particles $\{q_i, p_i\}$ confined in a container of volume V, which obey the Hamilton equations.. These particles interact amongst each other, hit the walls of the container and generate a pressure P defined as the averaged force per unit surface exerted by the particles on the container.

Proposition 7.1.1 — The Virial theorem. This theorem is of purely mechanical origin. Let's consider $G = \sum_{i=1}^{N} q_i \cdot p_i$. Using the Hamilton equations, one readily obtains :

$$\frac{dG}{dt} = \sum_{i=1}^{N} q_i \cdot f_i + \sum_{i=1}^{N} \frac{p_i^2}{m_i} = \mathscr{V} + 2E_c, \tag{7.1}$$

where E_c is the kinetic energy of the system and the rather "bizarre" quantity $\mathscr{V} = \sum_{i=1}^{N} q_i \cdot f_i$ is called the Virial, from the latin *vis* for force. Computing the *temporal* average of this equation, in the limit of an infinitely long time window, and assuming that G is bounded, one has that :

$$\langle \frac{dG}{dt} \rangle_t \equiv \lim_{t\to\infty} \frac{1}{t} \int dt' \frac{dG}{dt'} = 0 \tag{7.2}$$

and thus

$$\langle E_c \rangle_t = -\frac{1}{2}\langle \mathscr{V} \rangle_t = -\frac{1}{2}\langle \sum_{i=1}^{N} q_i \cdot f_i^{ext} \rangle_t - \frac{1}{2}\langle \mathscr{V}^{int} \rangle_t, \tag{7.3}$$

where we have dissociated the forces acting on the particle i, which come from the outside and those which come from the interactions among the particles.

In the case where the particles are confined in a container, the external forces, averaged over time, are precisely the integral over the surface of the container of minus the pressure $-P$ per surface unit. Hence the external part of the Virial can be evaluated as :

$$\langle \mathcal{V}^{ext} \rangle_t = -\int_\Sigma P q \cdot ds = -P \int_V \mathrm{div}\, q\, dq = -3PV. \tag{7.4}$$

Finally one obtains a very simple Virial relation

$$\langle E_c \rangle_t = \frac{3}{2} PV - \frac{1}{2} \langle \mathcal{V}^{int} \rangle_t . \tag{7.5}$$

As stated at the beginning, this relation is of purely mechanical origin and very general. It gains a statistical physics aspect when calling the ergodic hypothesis : then the temporal average is replaced by the statistical one.

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The hamiltonian of a liquid composed of N monoatomic particles (a simple liquid) with positions and impulsions $\{q_i, p_i\}$ is

$$H(\{q_i, p_i\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V_{int}(\{q_i\}) \tag{7.6}$$

and, as for the perfect gas, one supposes that the liquid is confined in a volume V. The partition function then simply reads

$$Z = \frac{1}{N! h^{3N}} \int \prod_i dp_i dq_i e^{-\beta H(\{q_i, p_i\})} \tag{7.7}$$

$$Z = \frac{1}{N! h^{3N}} \left(\int dp e^{-\beta \frac{p^2}{2m}} \right)^N \int \prod_i dq_i e^{-\beta V_{int}(\{q_i\})} \tag{7.8}$$

$$Z = \frac{1}{N!} \left(\frac{V}{\Lambda_T^3} \right)^N \frac{1}{V^N} \int \prod_i dq_i e^{-\beta V_{int}(\{q_i\})} \tag{7.9}$$

$$Z = Z_{IG} Z_{int} \tag{7.10}$$

Hence the partition function of a simple liquid factorizes into that of the ideal gas and a purely configurational one, which encodes the interactions. The following table derives the main thermodynamic quantities of interest from this partial knowledge of Z, where we have separated the kinetic contribution, the configurational part of the ideal gas and the configurational part coming from the interactions

R It is amazing to note that the Kinetic contribution to $\beta P(\beta, V)$ is null. If you think about the virial theorem, according to which the pressure is directly related to the average of the kinetic energy, this is a bit puzzling... The reason is that the kinetic part is already fully encoded in the factor β, because the distribution of the p_i's is entirely encoded in it. Indeed ...

R The canonical probability of a configuration also factorizes :

$$\mathbb{P}_c(\{q_i, p_i\}) = \frac{1}{Z} e^{-\beta H(\{q_i, p_i\})} = \left(\frac{1}{\Lambda_T^3} e^{-\beta \frac{p^2}{2m}} \right)^N \frac{N!}{V^N} \left(\frac{1}{Z_{int}} e^{-\beta V_{int}(\{q_i\})} \right) \tag{7.11}$$

	Kinetic	IG configurations	Interaction configurations
$\beta F(\beta) = -\ln Z(\beta,N,V)$	$\frac{3}{2}N\ln\Lambda_T{}^2$	$-N\ln\frac{V}{N} = N\ln\rho$	$-\ln Z_{int}(\beta,N,V)$
$\beta P = \frac{\partial \ln Z(\beta,N,V)}{\partial V}$	0	$\frac{N}{V} = \rho$	$\frac{\partial \ln Z_{int}(\beta,N,V)}{\partial V}$
$\langle E\rangle = -\frac{\partial \ln Z(\beta,N,V)}{\partial \beta}$	$\frac{3}{2}NT$	0	$-\frac{\partial \ln Z_{int}(\beta,N,V)}{\partial \beta}$

TABLE 7.1 – Thermodynamical properties of simple liquids ; the Boltzmann constant is set to one.

> As a result the distribution of the velocities, called the Maxwellian distribution, is a Gaussian distribution, the properties of which is entirely encoded in its second cumulant, proportional to the temperature. It does not depend on the configuration. In practice this means that the particles in a gas, a liquid – whatever its viscosity – or a cristal, coexisting at the same temperature, move with the same velocity distributions...

The main task of liquid state theory is thus to compute Z_{int}, or at minima, the equation of states $\langle E\rangle(N,V,T)$ and $P(N,V,T)$. Because of the interactions between the particles,Z_{int} does not factorize and it is in general not possible to obtain an exact solution. There is one famous case, where the partition function of a gas with hard core repulsion can be computed exactly, the Tonks Gas, which we shall solve below.

In all cases, a reasonable hypothesis is to consider that the interaction potential is pairwise and additive (this is almost the definition of a "simple" liquid).

$$V_{int}(\{q_i\}) = \sum_{i<j} V(q_i - q_j) \equiv \sum_{i<j} V_{ij} \tag{7.12}$$

In this case

$$Z_{int} = \frac{1}{V^N}\int \prod_i dq_i e^{-\beta\sum_{i<j}V_{ij}} = \frac{1}{V^N}\int \prod_i dq_i \prod_{i<j} e^{-\beta V_{ij}} \tag{7.13}$$

***

The Tonk gas is a one dimensional gas of infinitely hard particles of length $2a$ in a box of size L. The potential (the Boltzmann weight) is infinite (resp. zero) if the particles overlap and zero (resp. one) otherwise. In this situation, computing the configurational part of the partition function amounts to count the number of configurations with no overlap :

$$Z_{int} = \frac{1}{L^N}\int_a^{x_2-2a} dx_1 \int_{x_1+2a}^{x_3-2a} dx_2 ... \int_{x_{i-1}+2a}^{x_{i+1}-2a} dx_i ... \int_{x_{N-1}+2a}^{L-a} dx_N \tag{7.14}$$

The trick is to make the change of variable $X_i = x_i - 2ia$, which leads to the very simple form :

$$Z_{int} = \frac{1}{L^N}\int_{-a}^{X_2} dX_1 \int_{X_1}^{X_3} dX_2 ... \int_{X_{i-1}}^{X_{i+1}} dX_i ... \int_{X_{N-1}}^{L-a-2Na} dx_N, \tag{7.15}$$

which correspond to that of a gaz of point particles in a box of length $L - 2Na$, and therefore is

$$Z_{int} = \left(\frac{L-2Na}{L}\right)^N = (1-\phi)^N = (1-2a\rho)^N. \tag{7.16}$$

We thus find using the results of table 7.1 :

$$\beta F(\beta) = -\ln Z(\beta,N,V) = \frac{3}{2}N\ln\Lambda_T^2 + N\ln\frac{\rho}{1-2a\rho}, \tag{7.17}$$

$$\beta P = \frac{\partial \ln Z(\beta,N,V)}{\partial V} = \frac{\rho}{1-2a\rho}, \tag{7.18}$$

$$\langle E\rangle = -\frac{\partial \ln Z(\beta,N,V)}{\partial \beta} = \frac{3}{2}NT. \tag{7.19}$$

Note that the average energy of the system is that of the ideal gas ; the reason is that the particles being infinitely hard, there is no energy scale in the potential, hence Z_{int} remains independent of the temperature.

***

As stated above, there is usually no such nice change of variables and even the hard discs gas in two dimensions does not have an exact solution. More generally, a typical shape of the interaction potential between two particles separated by a distance r is provided on figure (7.1). There is a hard core repulsion at short distance, an attractive part at intermediate distance, and it goes to zero for large enough distances. As a result $e^{-\beta V_{ij}}$ is a function that goes to 1 for large r, which is not very nice for integration... It is thus a good idea to introduce the so-called Mayer function :

$$f_{ij} = e^{-\beta V_{ij}} - 1, \tag{7.20}$$

also represented on figure (7.1). It takes finite value everywhere and goes to zero for large r. Writing $e^{-\beta V_{ij}} = 1 + f_{ij}$, where the 1 corresponds to the ideal gas, one can see that the Mayer function is the natural formulation to characterize the corrections to the ideal gas brought by the interactions. Note that the Mayer function depends on the temperature. Introducing the Mayer functions in the computation of Z_{int}, one obtains an infinite sum of integrals to evaluate :

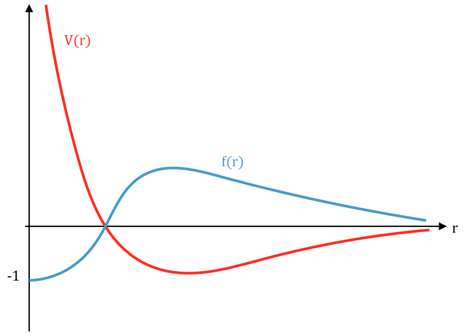

FIGURE 7.1 – Interaction potential (in red) and the Mayer function for a given β (in blue)

$$Z_{int} = \frac{1}{V^N}\int\prod_i dq_i \prod_{i<j}(1+f_{ij}) = \frac{1}{V^N}\int\prod_i dq_i\left(1+\sum_{i<j} f_{ij} + \sum_{i<j,l<m} f_{ij}f_{lm} + \dots\right) \tag{7.21}$$

This infinite sum is called the cluster expansion. After some tedious calculation, it is possible to show that this infinite sum recombines into an exponential

$$Z_{int} = e^{N\Phi} \quad \text{with} \quad \Phi = \sum_{k=1}^{\infty}\frac{\beta_k\rho^k}{k+1} \tag{7.22}$$

where the β_k's are the so called irreducible integrals :

$$\beta_0 = 1, \quad \beta_1 = \int d^3 r f_\beta(\vec{r}), \quad \beta_2 = \int d^3 r_1 d^3 r_2 f_\beta(\vec{r}_1) f_\beta(\vec{r}_2) f_\beta(\vec{r}_1 - \vec{r}_2). \tag{7.23}$$

From the knowledge of Z_{int}, we obtain that of the free energy $\beta F(\beta, N, V) = \beta F_{IG} - N\Phi(\beta, \rho)$ and that of the pressure, the the so called virial expansion – which is not to be confused with the virial theorem.

$$\beta P = \rho \left(1 - \frac{1}{2}\beta_1(\beta)\rho - \frac{2}{3}\beta_2(\beta)\rho^2 + \dots\right) \tag{7.24}$$

The above method offers a clear separation between the effects of temperature and that of density. However, it is unfortunately extremely painful to implement in practice. The functions β_k often have to be evaluated numerically at each temperature of interest. Furthermore the convergence of the expansion can be very slow.

One can still use it to find the Van der Waals equation, using the following trick. For a potential with a short distance repulsion for $r < a$ and long distance Van der Waals attraction $V_{int}(r) = -V_0 \left(\frac{a}{r}\right)^6$ for $r > a$, one can evaluate the first virial coefficient :

$$\beta_1 = v(-1 + \beta V_0), \quad \text{with} \quad v = \frac{4}{3}\pi a^3 \tag{7.25}$$

and the pressure at first order reads

$$\beta P = \rho \left(1 + \frac{v}{2}(1 - \beta V_0)\rho\right) \tag{7.26}$$

The trick consists in assuming that $1 + \frac{v\rho}{2}$ is the beginning of the development of $\left(1 - \frac{v\rho}{2}\right)^{-1}$ in the limit of low densities $v\rho \ll 1$. One then indeed recovers the Van der Waals equation

$$\left(P + V_0 \frac{v\rho^2}{2}\right)\left(V - N\frac{v\rho}{2}\right) = N k_B T \tag{7.27}$$

***

The difficulties encountered above happens because the interactions generate coupling amongst the positions of the particles, hence correlations in the structure of the liquid. These correlations are fully encoded into the configurational probability distribution

$$\mathbb{P}(\{q_{i=1,\dots N}\}) = \left(\frac{1}{Z_{int}} e^{-\beta V_{int}(\{q_i\})}\right), \tag{7.28}$$

which contains too much information. The ideal is to say, let us limit ourselves to the two-body correlations. Namely, one would like to consider the marginal distributions (see definition 4.2.3) :

$$\rho^{(1)}(q_1) = \frac{N!}{(N-1)!}\mathbb{P}(q_1) = N \int dq_{i=2,\dots N} \mathbb{P}(\{q_{i=1,\dots N}\}) \tag{7.29}$$

$$\rho^{(2)}(q_1, q_2) = \frac{N!}{(N-2)!}\mathbb{P}(q_1, q_2) = N(N-1) \int dq_{i=3,\dots N} \mathbb{P}(\{q_{i=1,\dots N}\}) \tag{7.30}$$

which are respectively the probability that any particle is at position q_1, and the probability that any two particles are at positions q_1 and q_2.

It is intuitively clear, and it is easily shown using the normalization $\int dq_{i=1,\dots N}\mathbb{P}(\{q_{i=1,\dots N}\}) = 1$, that for an homogeneous system $\rho^{(1)}(q_1) = \frac{N}{V} = \rho$. In the absence of correlations the distribution $\rho^{(2)}$ factorizes, $\rho^{(2)}(q_1,q_2) = \rho^{(1)}(q_1)\rho^{(1)}(q_2) = \rho^2$, and one introduces the so-called pair correlation function

$$g(r) = \frac{\rho^{(2)}(0,r)}{\rho^2}, \tag{7.31}$$

where the system has been assumed isotropic and translational invariant. It is the conditional probability that a particle sits at the distance r from the origin, given that one particle sits at the origin. It contains the first level, but already very rich description of the structure of a liquid and can be measured very accurately using X-ray scattering (see figure (7.2).

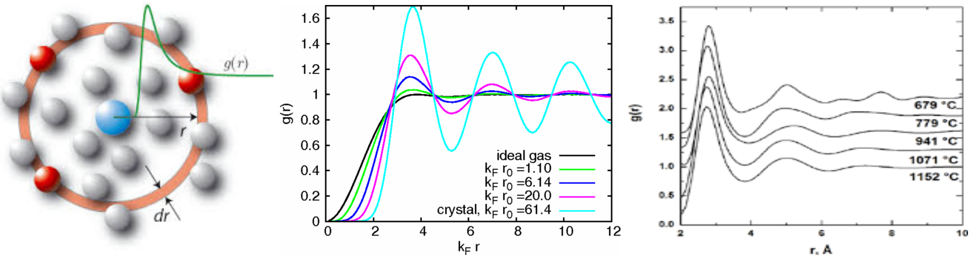

FIGURE 7.2 – Pair correlation function : from left to right a sketch of the meaning of it, $g(r)$ in a model liquid in the gas,liquid and crystalline phase, $g(r)$ measured in a liquid at different temperature.

Proposition 7.1.2 — The potential of mean force. . We shall show that

$$g(q_1,q_2) = \frac{\rho^{(2)}(q1,q2)}{\rho^2} = e^{-\beta w(q_1,q_2)}, \quad \text{with} \quad w(q_1,q_2) = \langle V(\{q_i\})\rangle_{(q_1,q_2)\ \text{fixed}} \tag{7.32}$$

Indeed

$$\frac{d}{dq_1}\ln g(q_1,q_2) = \frac{d}{dq_1}\ln\int dq_{i=3,\dots N}\mathbb{P}(\{q_{i=1,\dots N}\} \tag{7.33}$$

$$= -\beta\frac{\int dq_{i=3,\dots N}\frac{dV\{q_i\}}{dq_1}\mathbb{P}(\{q_{i=1,\dots N}\}}{\int dq_{i=3,\dots N}\mathbb{P}(\{q_{i=1,\dots N}\}} = -\beta\frac{d}{dq_1}\langle V(\{q_i\})\rangle_{(q_1,q_2)\ \text{fixed}} \tag{7.34}$$

$w(q_1,q_2)$ is called the potential of mean force, because $-\frac{d}{dq_1}\langle V(\{q_i\})\rangle_{(q_1,q_2)\ \text{fixed}}$ can be understood as the mean force acting on particle 1, maintaining fixed particles 1 and 2.

Finally we shall see how, the pair correlation function can be used to compute $\langle E_{int}\rangle$ and P_{int}, the contributions of the interactions to the energy and pressure.

$$\langle E_{int}\rangle = -\frac{\partial \ln Z_{int}(\beta,N,V)}{\partial \beta} \tag{7.35}$$

$$= \frac{1}{Z_{int}}\int dq_{i=1,..N}V(\{q_i\})e^{-\beta V(\{q_i\})} \tag{7.36}$$

$$= \int dq_{i=1,..N}\sum_{i<j}V(\{q_i,q_j\})\mathbb{P}(\{q_{i=1,...N}\}) \tag{7.37}$$

$$= \frac{N(N-1)}{2}\int dq_1dq_2V(\{q_1,q_2\})\int dq_{i=3,..N}\mathbb{P}(\{q_{i=1,...N}\}) \tag{7.38}$$

$$= \frac{1}{2}\int dq_1dq_2\rho^{(2)}(q_1,q_2)V(\{q_1,q_2\}) \tag{7.39}$$

$$= \frac{\rho^2V}{2}\int_0^\infty dr4\pi r^2g(r)V(r), \tag{7.40}$$

where the last line results from isotropy and translational invariance.

For the pressure, one can also start from the statistical physics definition $\beta P = \frac{\partial \ln Z(\beta,N,V)}{\partial V}$ and would rediscover, as a first step, the Virial theorem, see proposition (7.1.1) :

$$\frac{\beta P}{\rho} = 1+\frac{\beta}{3N}\langle\sum_i f_iq_i\rangle, \tag{7.41}$$

where the equipartition $\langle E_c\rangle = \frac{3}{2}NT$ has also been used.

Then, using $f_i = -\frac{\partial V(\{q_i\})}{\partial q_i} = -\sum_{i<j}\frac{\partial Vij}{\partial q_j}$, the symmetry of the action-reaction principle and the translational invariance of the potential, one finds, following the exact same procedure as for the energy :

$$\left\langle\sum_i f_iq_i\right\rangle = -\frac{1}{2}\left\langle\sum_{i\neq j}(q_i-q_j)\frac{\partial V(q_i-q_j)}{\partial(q_i-q_j)}\right\rangle \tag{7.42}$$

$$= -\frac{\rho^2V}{2}\int_0^\infty dr4\pi r^2g(r)rV'(r) \tag{7.43}$$

and

$$\frac{\beta P}{\rho} = 1-\frac{2\pi}{3}\beta\rho\int_0^\infty drr^3g(r)V'(r) \tag{7.44}$$

R For hard spheres $V'(r\to d)\to\infty$. It is useful to replace $g(r)$ by $y(r)e^{-V(r)}$ then integrate by part, using $\frac{de^{-V(r)}}{dr} = \delta(r-d)$, and one finds $\frac{\beta P}{\rho} = 1-\frac{2\pi}{3}\rho d^3g(d)$.

Altogether, we see that knowing the pair correlation of the liquid gives access to all the macroscopic quantities of interest.

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On the experimental side, we have seen that the pair correlation function can be measured using X-ray scattering. On the theoretical side, the idea is to find a self consistent equation for it.

The first step consists in the so called Ornstein-Zernike equation, introduced by Ornstein and Zernike in 1914.

$h(r_{12}) = g(r_{12}) - 1$, the total correlation function, measures the "influence" of particle 1 on particle 2 at a distance r_{12}. The idea, see figure (7.3), is to split this influence into two contributions, a direct and indirect part.

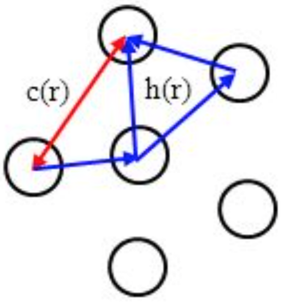

FIGURE 7.3 – Illustration of the Ornstein-Zernike decomposition of the influence of particle 1 on particle 2, into a direct part and an indirect one

This indirect effect must be weighted by the density and averaged over all the possible positions of particle 3 ; hence

$$h(r_{12}) = c(r_{12}) + \tilde{h}(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13}) h(r_{32}), \tag{7.45}$$

where $c(r_{12})$ is called the direct part of the correlation and $\tilde{h}(r_{12})$, the indirect part.

This equation alone is of no use ; it is almost a formal definition of $c(r_{12})$. Also what we are interested in is $h(r_{12})$. Still it may guide the intuition to propose a closure relation, which relates $c(r)$ to $h(r)$. This is precisely what was proposed by Percus and Yevick in 1958. The closure relation relies on the use of the potential of mean force to gain some intuition. Since $h(r) = g(r) - 1 = e^{-\beta w(r)} - 1$, suppose that the complement to the direct part is obtained by subtracting to the potential of mean force, the pair interaction potential $V(r)$: $\tilde{h}(r) = e^{-\beta(w(r) - V(r))} - 1$. This immediately provides a relation between $c(r)$ and $h(r)$, which closes the Ornstein-Zernike equation :

$$c(r) = (h(r) + 1)\left(1 - e^{\beta V(r)}\right) \tag{7.46}$$

The resolution of the resulting integral equation remains a complicated exercise. It happens that for hard spheres, there is an analytical solution proposed by Wertheim in 1963. Today the most used closure relation is the Hypernetted chain approximation, which is an extension of the Percus-Yevick approximation.

7.2 Spins in interactions

Models of spins are used to describe magnetic materials.. Essentially it consists in fixing the magnetic moments onto the underlying cristalline lattice of the material and let them interact at more or less short distance. The dimension and shape of the lattice may vary, the interaction amongst the magnetic moments favor alignment or anti-alignment, and the spins can take discrete or continuous values. The best know of these models, and the first one was introduced by Ernst Ising, during his PhD, in 1924. In this case the spins take values $s_i = \pm 1$ and the interactions favor alignment. The Hamiltonian of a system of N spins in a field reads :

$$H(\{s_i\}) = -J \sum_i \sum_{jv(i)} s_i s_j - h \sum_i s_i \tag{7.47}$$

where $\sum_{jv(i)}$ is the sum over the first neighbors spins of s_i.

By contrast with the case of independent spins, the knowledge of the number of spins up and down, does not allow to compute the energy. The details of the configurations matter. It is thus in general impossible to evaluate $\Omega(E,N)$ via combinatorial approaches. Regarding the canonical setting, the partition function does not factorize and is thus not easier to evaluate.

In some rare cases, there are exact solutions to the problem. This is the case for the 1d chain of ising spins, which we shall solve below. It is also the case for the 2d square lattice, but the solution is a real tour de force accomplished by Onsager in 1944, and we shall not expose its derivation here.

7.2.1 The 1D chain of Ising spins

The energy of the one-dimensional Ising model on a lattice of N sites is

$$H(\{s_i\}) = -J \sum_{i=1}^{N-1} s_i s_{i+1} - h \sum_i s_i \tag{7.48}$$

If $h = 0$, it is very easy to obtain the free energy in the case of free boundary condition, i.e. when $s_1 = \pm 1$ and $s_N = \pm 1$. Then the model factorizes under the change of variables $s'_j = s_j s_{j-1}$ for $j \geq 2$ and the partition function can easily be evaluated :

$$Z_c(\beta, h=0, N) = \sum_{s_{i,i=1\dots N}} \prod_{i=1}^{N} e^{\beta J s_i s_{i+1}} = \sum_{s'_{j,j=2\dots N}} 2 \prod_{j=2}^{N} e^{\beta J s'_j} = 2 \prod_{j=2}^{N} \sum_{s'_j} e^{\beta J s'_j} = 2 \left[e^{\beta J} + e^{-\beta J} \right]^{N-1} . \tag{7.49}$$

where the factor two comes from the fact that two configurations of $s_i s_{i+1}$ lead to the same configuration s'_j, and the dimensionless free energy per spin reads :

$$\beta f(\beta, h=0) = -\ln \left[e^{\beta J} + e^{-\beta J} \right] = -\ln \left(2 \cosh \beta J \right) . \tag{7.50}$$

If $h \neq 0$, we need the transfer matrix method. For the periodic boundary conditions case, i.e $s_1 = s_{N+1}$, the partition function is

$$Z_c(\beta, h, N) = \sum_{s_{i,i=1..N}} e^{\beta h s_1} e^{\beta J s_1 s_2} e^{\beta h s_2} e^{\beta J s_2 s_3} \dots e^{\beta h s_N} e^{\beta J s_N s_1} = \sum_{s_{i,i=1\dots N}} \prod_{i=1}^{N} V_{s_i, s_{i+1}} , \tag{7.51}$$

where the coefficients $V_{s,s'}$'s can be seen as the entries of a $(2x2)$ symmetric matrix :

$$V_{s,s'} = e^{\frac{\beta h}{2} s} e^{\beta J s s'} e^{\frac{\beta h}{2} s'} \quad \text{or} \quad V = \begin{bmatrix} e^{\beta(h+J)} & e^{-\beta J} \\ e^{-\beta J} & e^{-\beta(h-J)} \end{bmatrix} . \tag{7.52}$$

Noting that $\sum_{s_i} V_{s_{i-1},s_i} V_{s_i,s_i+1} = V^2_{s_{i-1},s_{i+1}}$, one finds :

$$Z_c(\beta,h,N) = \sum_{s_1=\pm 1} V^N_{s1,s1} = \mathrm{Tr}\left(V^N\right) = \lambda_1^N + \lambda_2^N = \lambda_1^N \left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right] \simeq \lambda_1^N, \tag{7.53}$$

where λ_1 is the highest eigenvalue of V :

$$\lambda_1 = e^{\beta J} \cosh \beta h + \sqrt{e^{2\beta J} (\sinh \beta h)^2 + e^{-2\beta J}} \tag{7.54}$$

and the dimensionless free energy per spin reads :

$$\beta f(\beta,h) = -\ln \lambda_1. \tag{7.55}$$

Most text book would conclude here saying that the knowledge of the free energy contains all the information to compute the relevant quantities of interest. Very well, but let's see how it works. The relevant quantities of interest are the energy and the magnetization. We will see that indeed it is quite straightforward to obtain their average, and their fluctuations, as a function of the temperature $1/\beta$ and the field h. However wouldn't it be more instructive to obtain their full distribution ?

Let's start with the energy. The average and the fluctuations of the energy are indeed very easy to obtain, especially in the absence of external field.

$$\langle E\rangle = -\frac{\partial \ln Z_c(\beta,N)}{\partial \beta}\bigg|_{h=0} = N \tanh(\beta J) \tag{7.56}$$

$$\langle E^2\rangle - \langle E\rangle^2 = \frac{\partial^2 \ln Z_c(\beta,N)}{\partial \beta^2}\bigg|_{h=0} = NJ\left(1 - \tanh^2(\beta J)\right). \tag{7.57}$$

In the presence of a field, the algebra is slightly more involved, but Mathematica will do it for you.

To obtain the distribution of e, we shall restrict the calculation to the zero field case. Again we apply the Gärtner Ellis theorem. $-\beta f(\beta) = \ln(2\cosh \beta J)$ is differentiable, hence

$$\mathbb{P}_c(e) = \frac{1}{Z(\beta,0,N)} e^{-N(\beta e - s(e))}, \quad \text{with} \quad -s(e) = \sup_{\beta} \left[\beta e - \ln(2\cosh \beta J)\right] \tag{7.58}$$

The maximizing $\beta = \beta^*$ is solution of $e = \tanh \beta^* J$, hence $\beta^* J = \mathrm{atanh}(e) = \frac{1}{2J} \ln \frac{1+e}{1-e}$, which we inject back into the function to maximize, to obtain

$$s(e) = -\frac{e}{2J} \ln \frac{1+e}{1-e} + \frac{1}{2} \ln(1-e^2) \tag{7.59}$$

Now let's consider the magnetization. There is no conservation law for the total magnetization and there is no reason why it should be fixed ! Hence one cannot derive a "grand-canonical" formalism associated to this quantity and one must deal with it in the thermal-canonical setting. Fortunately, there is a kind of miracle in the linear form of the coupling between the external field and the spins. Because of this, one has that $\frac{1}{N} \ln Z_c(-\beta,h,N)$ is also the scaled cumulant generating function of $m = \frac{M}{N}$:

$$\kappa_{M,k} = \frac{\partial^k \ln Z_c(\beta,h,N)}{\partial(\beta h)^k}. \tag{7.60}$$

which in turn implies, by virtue of the Gärtner-Ellis theorem that if $\lambda(\beta,\beta h) = \lim_{N\to\infty} \frac{1}{N} \ln Z(\beta,h,N)$ is differentiable *with respect to* βh, then M satisfies a large deviation principle and $\gamma(m,\beta) =$

$\sup_{\beta h}\left[\beta hm-\lambda(\beta,\beta h)\right]$ is the corresponding rate function. Altogether, everything takes place as if the thermal-canonical setting associated with the conservation of energy was also a field-canonical setting for the magnetization. In other words the canonical formalism holds because the field imposes a constraint on the magnetization in the same way as the temperature does on the energy. The field however does not have the status of an intensive thermodynamic parameter. In particular there is no equilibration of the field between two subsystems.

In the present case,

$$\langle M\rangle = \frac{\partial \ln Z_c(\beta,h,N)}{\partial \beta h}, \tag{7.61}$$

$$\langle M^2\rangle - \langle M\rangle^2 = \frac{\partial^2 \ln Z_c(\beta,h,N)}{\partial(\beta h)^2} = \frac{\partial\langle M\rangle}{\partial \beta h}. \tag{7.62}$$

can be computed, again using your favorite formal calculator, to obtain an explicit expression ; for instance

$$\langle M\rangle = \frac{\beta e^{\beta}\sinh[\beta h] + \frac{(\beta e^{2\beta}\cosh[\beta h]\sinh[\beta h])}{\sqrt{e^{-2\beta}+e^{2\beta}\sinh[\beta h]^2}}}{\beta\left(e^{\beta}\cosh[\beta h] + \sqrt{e^{-2\beta}+e^{2\beta}\sinh[\beta h]^2}\right)}. \tag{7.63}$$

Well, this is not such a nice expression, but it is exact, and the same can be done for the variance... The latter provides an explicit expression for the magnetic susceptibility defined as the response of the magnetization to a field variation : $\chi \equiv \frac{\partial M}{\partial h} = \beta Var(M)$; which is again a response-fluctuation relation.

Regarding $\mathbb{P}_c(m,h,N) \simeq e^{-N\gamma(m,\beta)}$ and the computation of $\gamma(m,\beta)$, figure (7.4) displays $\lambda(\beta,\beta h)$ and its derivative for different β, which are needed to compute the Legendre transform of $\lambda(\beta,\beta h)$

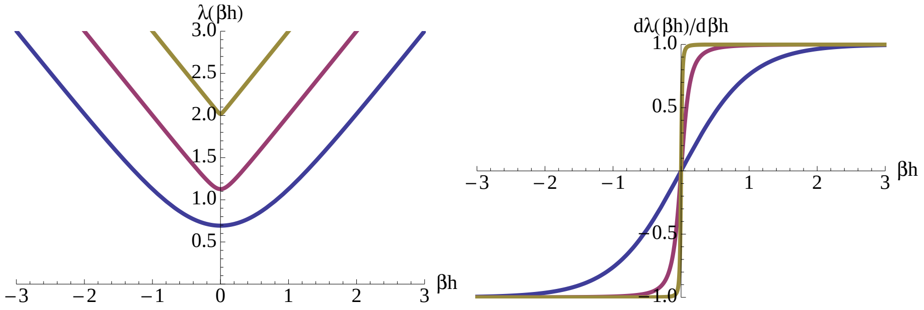

FIGURE 7.4 – Useful plot for evaluating $\gamma(m,\beta)$, for $\beta=[0,1,2]$

Note that for increasing β, or lower T, $\lambda(\beta,\beta h)$ develops a singular behavior in 0. Still, one can show that, as long as β is finite, $\lambda(\beta,\beta h)$ is differentiable with respect to βh and one can solve

$$m = \frac{d\lambda(\beta,\beta h)}{d\beta h} \tag{7.64}$$

to obtain $(\beta h)^*$, the position of the maximum of $\beta hm-\lambda(\beta,\beta h)$ and compute this maximum $\gamma(m,\beta)$.

Figure (7.5) displays the statistical properties of the energy and magnetization of the 1d-chain of Ising spins, we just obtained. It deserves some comments about the physics taking place in the system. At the end of the day, all these calculations are not an end in themselves... At high T, the

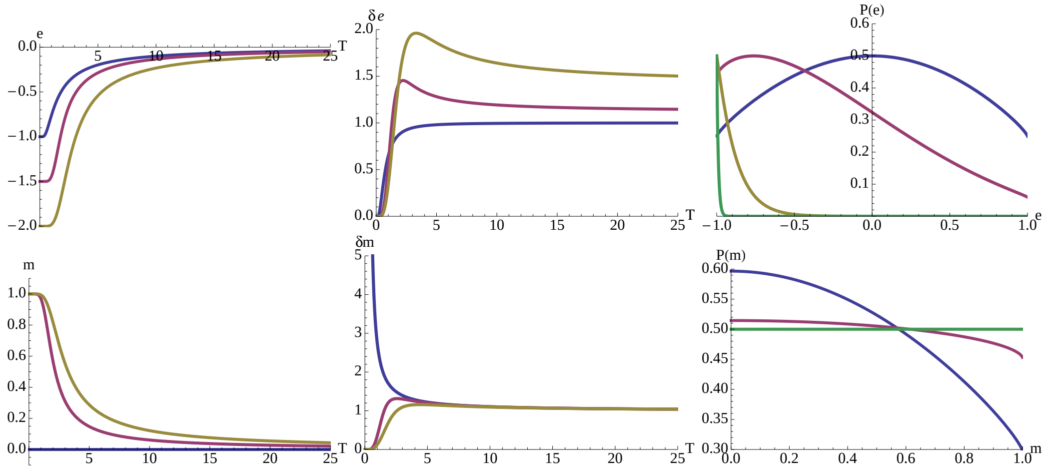

FIGURE 7.5 – Statistical properties of the energy (top) and magnetization (bottom) for a $1d$-chain of Ising spins. From left to right : mean, then standard deviation of the energy (resp. magnetization) as a function of $T = 1/\beta$, for $h = [0, 0.5, 1]$, in (blue,purple,brown) and $\mathbb{P}_c(e)$ (resp. $\mathbb{P}_c(m)$) for $h = 0$ at $T = [\infty, 1, 10^{-1}, 10^{-2}]$ in (blue,purple,brown,green). NB : Here $N = 1$, so that one can actually see the shape of the probability, which otherwise is very rapidly extremely peaked, especially for small T. Only the positive side of $\mathbb{P}_c(m)$ is shown ; it is of course symmetric.

energy is maximum, the magnetization is very weak, even in the presence of an external field and the standard deviation is of order one. When the temperature decreases, the energy also and the magnetization grow, *except* in the case of zero field. In this case, we note that approaching $T = 0$, the fluctuations of magnetization increase very sharply. This is further confirm by the distributions. While the distribution of energy essentially narrows with decreasing T, the one of magnetization broadens. At low T all the values of the magnetization are almost equiprobable ! So, although the average magnetization remains zero, the system actually behaves very differently. We shall see in the next chapter, that these features signal the approach of a phase transition, which here only exists at $T = 0$.

7.2.2 Fully connected spins in a field

An other important case of interest, which can be solved exactly, is the so called fully connected case, where the spins are assumed to interact with all the others. In that case, the hamiltonian reads

$$H_{fc}(\{s_i\}) = -J\sum_i \sum_{j>i} s_i s_j - h\sum_i s_i = -\frac{J}{2N}M_N^2 - hM_N + \text{cst}, \quad \text{with} \quad M_N = \sum_i s_i \tag{7.65}$$

and the canonical distribution of the configurations reads :

$$\mathbb{P}_c(\{s_i\}) = \frac{1}{Z(\beta,h,N)}e^{-\beta H} = \frac{1}{Z(\beta,h,N)}e^{\beta J \sum_{i,j>i} s_i s_j + \beta h \sum_i s_i} \tag{7.66}$$

For $h = 0$, the distribution is exactly the one we dealt with in example (5.2), with $\alpha = \beta J$. The calculation generalizes without difficulty to the case $h \neq 0$:

$$\mathbb{P}_c(m,\beta,h) = \frac{1}{Z(\beta,h,N)} \sum_{\{s_i\}} e^{\beta J \frac{M_N^2}{2N} + \beta h M_N} \delta\left(M_N(\{s_i\}) - Nm\right) \tag{7.67}$$

$$= \frac{\Omega(m,N)}{Z(\beta,h,N)} e^{N\left(\beta J \frac{m^2}{2} + \beta h m\right)} = \frac{1}{Z(\beta,h,N)} e^{-N\gamma(m,\beta,h)} \tag{7.68}$$

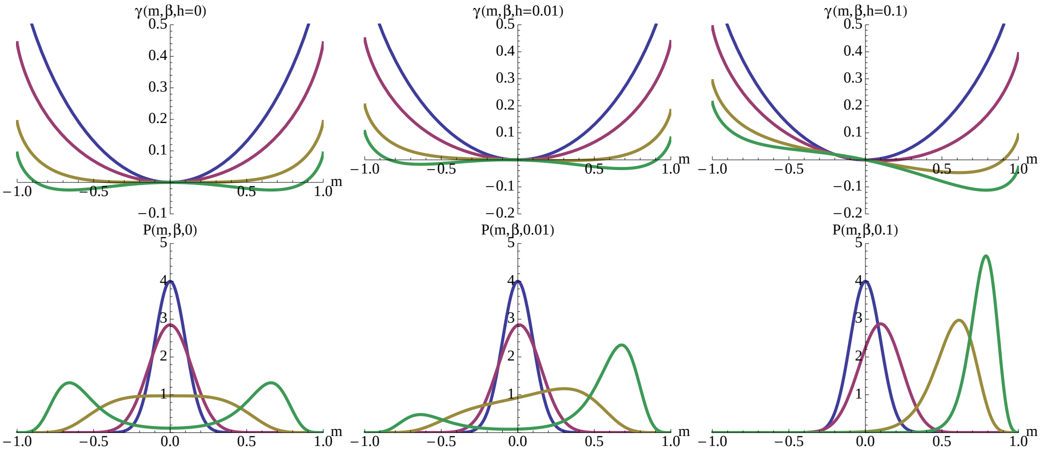

FIGURE 7.6 – Large deviation function (top row) and Probability distribution (bottom row) for the magnetization of $N = 100$ fully connected spins for $h = 0$ (left column), $h = 0.01$ (center) and $h = 0.1$ (right column), for three values of the temperature $T = 1/\beta$, with $\beta = [0, 0.5, 1, 1.2]$ in [blue,purple,brown,green] ; $J = 1$

with

$$\gamma(m,\beta,h) = -(s(m) + \beta J \frac{m^2}{2} + \beta h m), \tag{7.69}$$

$$s(m) = -\frac{1+m}{2} \ln \frac{1+m}{2} - \frac{1-m}{2} \ln \frac{1-m}{2} \tag{7.70}$$

In the present case, one could directly access the distribution of the magnetization because the energy of a configuration is entirely encoded into its magnetization $H(\{s_i\}) = H(M\{s_i\})$. Figure (7.6) displays the large deviation function $\gamma(m,\beta,h)$ and the associated probability $\mathbb{P}_c(m,\beta,h)$, for several values of β and h in the case $J = 1$.

At high temperature, $(T > T_c = 1/J)$ the large deviation function has only one minimum. In the absence of external field the Hamiltonian is symmetric with respect to the inversion of the spin signs, and the only minimum is $m_0 = 0$. The presence of a positive external field biases this minimum towards $m_0 > 0$.

At low temperature, for $T < T_c = 1/J$, the number of minima depends on the field intensity. In the absence of external field, there are two minima, which take opposite values $m_\pm = \pm m^*$, the equivalently most probable magnetization. Note that because of this symmetry the average magnetization is still zero and therefore differs from the most probable value, whichever it is. For low enough external fields, the two minima subsist, but they are no more symmetric in value, nor in probability : there is only one absolute minimum, which corresponds to the most probable magnetization, the equilibrium stable state. The other minimum is called a meta-stable state. When the external field is large enough, the highest minimum disappears.

The distribution of the energy per particle $\mathbb{P}_c(e = \frac{E}{N}$ can also be computed, from the knowledge of $\mathbb{P}_c(m)$ using the change of variable $e = -J\frac{m^2}{2} - hm$. However one should pay attention to the fact that for fields $h < J$, there are two possible magnetizations $m_{1,2}(e)$ leading to the same energy value. As a result the law for changing variables $\mathbb{P}(e)de = \mathbb{P}(m(e)) \left|\frac{dm}{de}\right| de$ must be adapted to $\mathbb{P}(e)de = \mathbb{P}(m_1(e)) \left|\frac{dm_1}{de}\right| de + \mathbb{P}(m_2(e)) \left|\frac{dm_2}{de}\right| de$.

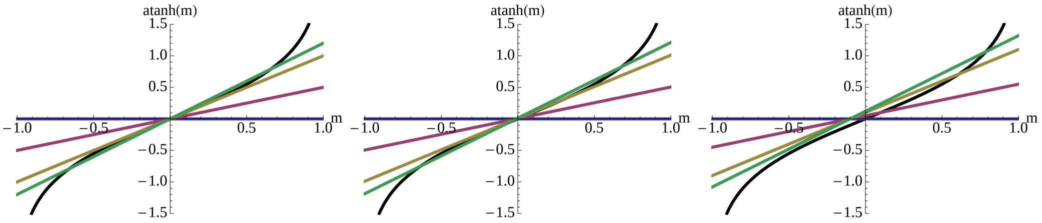

FIGURE 7.7 – Graphical solution for the sadde-node equation of the fully-connected Ising model. From left to right : $h = 0, 0.01, 0.1$; $T = 1/\beta$, with $\beta = [0, 0.5, 1, 1.2]$ in [blue,purple,brown,green] ; $J = 1$;

Finally let's compute the partition function $Z(\beta, h, N)$.

$$Z(\beta,h,N) = \int dm e^{N\left(s(m)+\beta J \frac{m^2}{2} + \beta h m\right)} \simeq e^{N\left(s(m^*)+\beta J \frac{m^{*2}}{2} + \beta h m^*\right)} \tag{7.71}$$

where m^*, the most probable value of the magnetization, obeys the saddle node equation :

$$\left.\frac{ds(m)}{dm}\right|_{m^*} + \beta J m^* + \beta h = 0, \tag{7.72}$$

$$\text{atanh}(m^*) = \beta J m^* + \beta h \tag{7.73}$$

This equation has no analytical solution, but can be studied graphically, see figure (7.7). One recovers of course the same observations as on the plot of the magnetization probability. Depending on the temperature and on the amplitude of the field the equation has one or three solutions. In the latter case, one is always a minimum. In the presence of a field, one of the two maxima is the global maxima. In the absence of the field the two maxima are equivalent.

We have seen that, in the absence of external field, $\langle m \rangle = 0$ for symmetry reasons. Although there is no analytical expression for $Z(\beta, \beta h, N)$, one can still compute

$$\langle m \rangle = \frac{1}{N} \frac{\partial \ln Z(\beta, \beta h, N)}{\partial \beta h} \tag{7.74}$$

$$= \frac{\partial}{\partial \beta h} \left(s(m^*) + \beta J \frac{m^{*2}}{2} + \beta h m^* \right) \tag{7.75}$$

$$= m^*(\beta, h) \tag{7.76}$$

This result was earlier presented as a general result. It is interesting here to consider the limit $h \to 0$, which for $T < T_c$ will pick up the positive maximum for $m^*(\beta, h \to 0)$ and not the true average. The interpretation is as follow. In the presence of the field, however small, the symmetry is broken and the unique global maximum is the positive magnetization. Once the system is in this macroscopic state, it remains there, when the field goes to zero. Although the above statistical computation knows nothing about the dynamics, it actually captures what is really going on in a real material : at low temperature, although the two orientations of the magnetization are equally probable, once the system has selected one orientation, it will stick to it because thermal fluctuations will never provide the energy required to flip it, within a reasonable amount of time.

The splitting of the magnetization distribution into two separated peaks at low temperature is the hallmark of what is called a phase transition, the central topic of the next chapter.

8. Phase Transitions

At the end of the previous chapter, we just saw a situation in which the probability distribution of a macroscopic variable has two maxima. In some situations, the two maxima may even have the same probability. Each of the maxima correspond to a different set of microscopic configurations of the system. In the case of the fully connected spins in an external field h, the two sets of configurations corresponds to those where the majority of the spins are aligned, respectively anti-aligned, with the field. These two sets of microscopic configurations define two different macroscopic phases.

In the presence of the field, one of this phase is more probable than the other and the relative weight of the probability grows exponentially with N. How does the system behave when the field is progressively inverted ? This is one of the question we would like to discuss in the present chapter.

Another appealing behavior of the probability distribution of the magnetization, is the extreme flatening of the distribution in the absence of external field, when approaching the critical temperature T_c. The fluctuations of the magnetization around its most probable value must become very large ! And if the fluctuation are large, the response to an infinitesimal field will be as large. The goal of this chapter is to be much more quantitative about these statements.

8.1 Thermodynamics of Phase Transition

Phase transitions has been first studied at the macroscopic level and it is useful to bridge the gap between the statistical physics description we have discovered in the previous chapters and the traditional thermodynamic one. We have already seen in section (6.1), how to connect the thermodynamic potentials to the *most probable values* of the energy, the volume and the number of particles depending on the ensemble of interest :

$$F(\beta,V,N) = E^*(\beta,V,N) - TS(E^*,V,N), \tag{8.1}$$

$$J(\beta,V,\mu) = E^*(\beta,V,\mu) - TS(E^*,V,N^*) - \mu N^*(\beta,V,\mu), \tag{8.2}$$

$$G(\beta,P,N) = E^*(\beta,P,N) - TS(E^*,V^*,N) + PV^*(\beta,P,N), \tag{8.3}$$

Although, we are going to remove the * in the following notation, it is crucial to remember that thermodynamics is the world of $N \to \infty$: all the macroscopic variable are at their most probable value. And let's recall that

$$\frac{\partial S}{\partial E} = \beta = \frac{1}{T}, \tag{8.4}$$

$$\frac{\partial S}{\partial V} = \beta P = \frac{P}{T}, \tag{8.5}$$

$$\frac{\partial S}{\partial V} = -\beta\mu = \frac{-\mu}{T} \tag{8.6}$$

or equivalently that

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN. \tag{8.7}$$

From this last equation, one obtains all the following totale derivatives,

$$dE = TdS - PdV + \mu dN, \tag{8.8}$$

$$dF = -SdT - PdV + \mu dN, \tag{8.9}$$

$$dJ = -SdT - PdV - Nd\mu, \tag{8.10}$$

$$dG = -SdT + VdP + \mu dN \tag{8.11}$$

and by consequences the expression of all possible partial derivatives. On top of this, using the celebrated Schwartz's theorem $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$, one also obtains the so called Maxwell relations between the partial derivatives.

Proposition 8.1.1 — Euler's theorem. The extensivity of E, S, V, N ensures that $E(S,V,N)$ is a first-order homogeneous function : $E(\eta S, \eta V, \eta N) = \eta E(S,V,N)$. The Euler theorem states that, as a result, $E = S\frac{\partial E}{\partial S} + V\frac{\partial E}{\partial V} + N\frac{\partial E}{\partial N}$. Proof : simply derive by η and set $\eta = 1$.

As a result one obtains

$$E = TS - PV + \mu N, \tag{8.12}$$

$$F = -PV + \mu N, \tag{8.13}$$

$$J = -PV, \tag{8.14}$$

$$G = \mu N; \tag{8.15}$$

and the Gibbs-Duhem relation $SdT - VdP + Nd\mu = 0$.

***

The classical setting used to describe phase transition is the Gibbs one, where the system is in contact with a reservoir, which fixes the pressure and the temperature. The appropriate thermodynamic potential is thus $G(P,T,N) = N\mu(P,T)$, where we consider only one specie system for the purpose of simplicity. Although we consider here the most probable values, both the energy and the volume are free to fluctuate according to the probability distribution

$$\mathbb{P}_{pt}(E,V,N;\beta,P) = \frac{1}{Z_{pt}(\beta,P,N)} e^{-N(\beta e - s(e,v) + \beta P v)} \tag{8.16}$$

with $G(P,T,N) = -T \log Z_{pt}(\beta,P,N) \simeq N(e^*(\beta,P) - Ts(e^*,v^*) + Pv^*) = N(f(\beta,v^*) + Pv^*)$.

As long as the probability distribution has only one maximum, the corresponding large deviation function has only one minimum, the system is in one phase and the value of this minimum is $\mu(P,T)$. However, we have seen that depending on the values of P,T, (or h,T for the case of fully connected spins), the system can be in one or another minimum, with different values of μ in those minima.

This is what is illustrated on figure (8.1), where the values of μ in each phase are represented as a function of P and T. Each is a surface, and the two surfaces intersect on a line in the P,T plane. In the thermodynamic limit, the system must be at its most probable value, that is, it must take the minimal value of μ. This is why the surfaces interrupt themselves at the intersection : the largest one, on each side, corresponds to the unstable phase, that is the lower minima in the distributions of the fluctuating quantities. The coexistence line is simply given by the solution of $\mu^{\alpha}(P,T) = \mu^{\beta}(P,T)$.

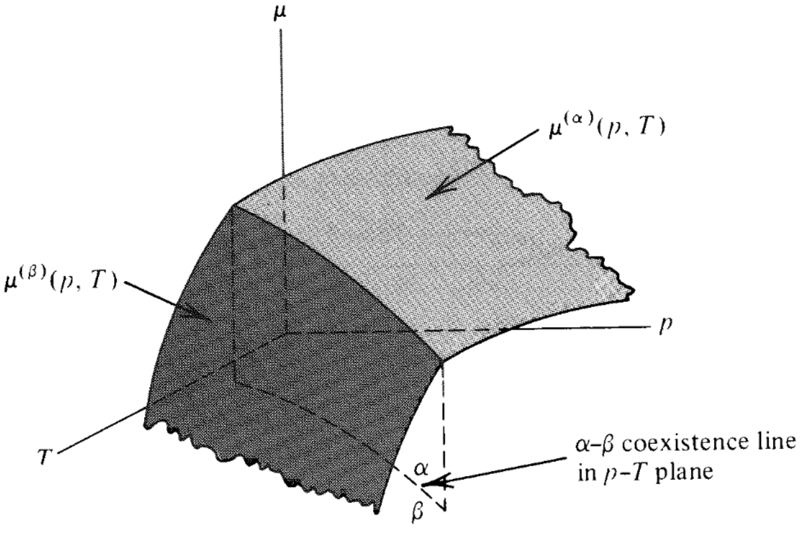

FIGURE 8.1 – Gibbs surfaces for a mono-component system of particles.

The equations of state of such a system describes how the most probable values of the energy and the volume depends on the pressure and temperature set by the reservoir.

$$E(P,T,N) = Ne(P,T) \tag{8.17}$$
$$V(P,T,N) = Nv(P,T) \tag{8.18}$$

Note that $v = 1/\rho$, where ρ is the usual density.

The reader will have noticed that the partial derivatives of $\mu(T,P)$ are discontinuous at the coexistence line. Those derivatives are

$$v = \frac{\partial \mu}{\partial P}, \tag{8.19}$$
$$-s = \frac{\partial \mu}{\partial T} \tag{8.20}$$

Hence there is a jump in the volume per particle and in the entropy per particle, when crossing the coexistence line. This discontinuity can be observed in figure (8.2), where we illustrate the first equation of state $v(P,T)$

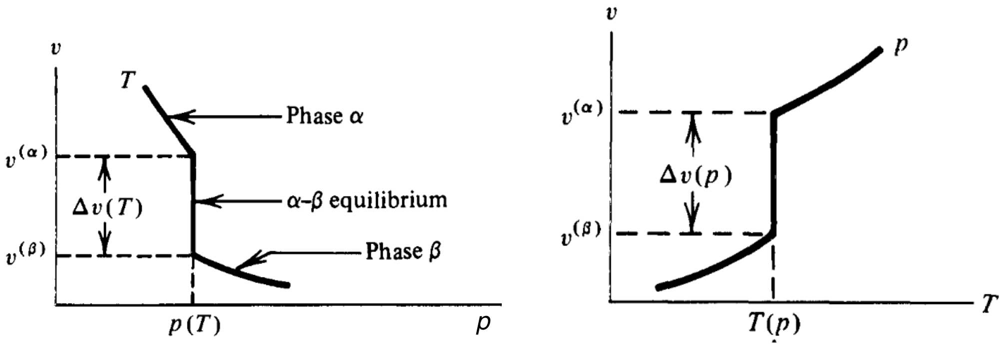

FIGURE 8.2 – Equation of state of a mono-component fluid at the gas-liquid transition for a mono-component system of particles.

Proposition 8.1.2 — Gibbs rule. The Gibbs rule prescribes how many phases can coexist and when they do, how many variables are fixed by the coexistence rule. Consider a system with r different species of particles distributed amongst ν coexisting phases. Each phase of this system is described by two variables P and T, which are equal in all coexisting phases, and the $(r-1)$ fraction of each specie, present in that phase. The chemical potentials associated with each specie, $\mu_{k,k=1..r}$, must be equal in all the phases. This translates into $r(\nu-1)$ equations. Hence the number of independent variables is

$$f = 2+\nu(r-1)-r(\nu-1) = 2+r-\nu \tag{8.21}$$

For a one specie system, one phase will be described by two variables P,T. Two phases will coexist on the line $P(T)$, three phases will coexist only at one point in the parameter space P^*,T^*. It is impossible to see more than three phases coexisting.

R The Gibbs rule is very general. One should however remember that the number 2 comes from the fact that the description of the monophasic system we are considering are described by the two variables T,P plus the fractions of the species. For a system of spins on a lattice, there are again two variables T,h, because the volume is irrelevant. Should one study a liquid of spins, there would be three variables T,P,h, where h is the external field, to describe each phase and the Gibbs rule should be adapted.

Proposition 8.1.3 — Fluctuations of v. We know from the fundamental proposition 5.6.1 and its consequences that if $w(\beta,P)=\frac{1}{N}\log Z(\beta,P,N)=-\frac{\beta}{N}G(\beta,P,N)=-\beta\mu(\beta,P)$ were differentiable with respect to P, then the large deviation function of V, would be $-\beta Pv-\beta f(\beta,v)$, with $-\beta f(\beta,v)$ given by the Legendre transform of $w(\beta,P)$ with respect to $-\beta P$.

However, in the present case, the signature of the phase coexistence is precisely that $G(\beta,P,N)$ is not differentiable. We are thus in the same situation as that of figure (4.3). One can still perform the Legendre transform of $-\beta\mu(\beta,P)$ where it is differentiable or separately in each phase, but there is a domain of $v\in[v^\alpha,v^\beta]$, corresponding to the coexistence regime, where it is undefined, see figure (8.3).

To complement the curve, we should remember that in the coexistence regime $\mu^\alpha(\beta,P)=\mu^\beta(\beta,P)$, which translates into $f^\alpha(\beta,v^\alpha)+Pv^\alpha=f^\beta(\beta,v^\beta)+Pv^\beta$, or

$$f^\alpha(\beta,v^\alpha)-f^\beta(\beta,v^\beta)=-P(v^\alpha-v^\beta), \tag{8.22}$$

which is nothing but the equation for the bi-tangent. Hence the equality of the chemical potential complements the shape of f in the region where it can not be obtained by the Legendre transform of $-\beta\mu$.

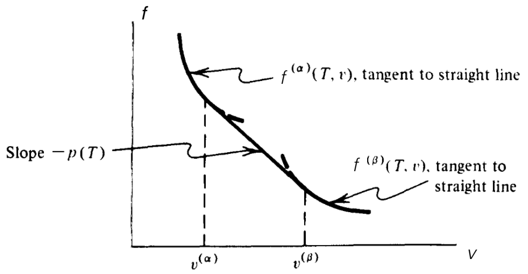

FIGURE 8.3 – Isotherm of the Legendre transform of $-\beta\mu(T,P)$ with respect to $-\beta P$. It is well defined only for $v < v^{\alpha}$ and $v > v^{\beta}$. In between, the bi-tangent construction reflects the equality of the chemical potential in the coexistence regime.

We stress that the large deviation function of V is $-\beta f(\beta, v) - \beta P v$. In other words it corrects for the slope of the bi-tangent and sets it horizontal : the two possible values $v^{\alpha} = \frac{1}{\rho^{\alpha}}$ and $v^{\beta} = \frac{1}{\rho^{\beta}}$ have the same probability, hence their coexistence.

Finally, when the temperature is varied, the values of v^{α} and v^{β} will vary. There are two possible scenarii. Both are observed in systems of attractive particles exhibiting the usual gas-liquid-solid transition scenario. In the case of the liquid-gas transition, the coexistence region shrinks when the temperature is increased and the two coexisting values of v collides in a so-called critical point, (T_c, P_c), above which there is no more distinction between the gas and the liquid ; one talks about a super-critical fluid (see figure 8.4). In the case of the liquid-solid transition, there is no critical point ; the two coexisting values of v never equalize, whatever the temperature. The underlying reason is that a liquid and a solid having different structural symmetry, there can be no path going continuously from one to the other.

Different phases at the macroscopic level correspond to different maxima in the probability distribution of the local specific volume, hence different minima of its large deviation function. The latter is thus not convex. This in turn translates into the fact that the Gibbs free energy $\mu(\beta, P) = -k_b T \log(Z(\beta, h))$ is not a strictly convex function. It has singularities. We just saw that indeed the first derivative are discontinuous on the coexistence line. One talk then about first order phase transition.

At the critical point there is no more discontinuity of the first derivative. But the free energy still has singular behavior at higher orders. One talk then of a second order phase transition, or more generally of critical phenomena. Discussing such critical behavior, is the purpose of the next section.

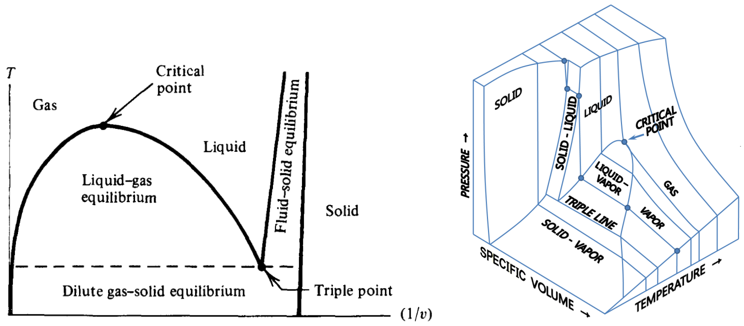

FIGURE 8.4 – Phase diagram : Constant pressure plane, $T, 1/v$ plane (left) and the full (P, T, v) view (right). Remember that these diagram should be seen as a surface $v(T,P)$ or $\rho(T,P)$, whith T, P set by a reservoir and v or ρ the most probable value of the observable V/N or N/V.

8.2 The ferro-paramagnetic phase transition

One of the fundamental properties of an electron (besides that it carries charge) is that it has a magnetic dipole moment, i.e., it behaves like a tiny magnet, producing a magnetic field. This dipole moment comes from the more fundamental property of the electron that it has quantum mechanical spin. Due to its quantum nature, the spin of the electron can be in one of only two states ; with the magnetic field either pointing "up" or "down" (for any choice of up and down). Atoms with filled electron shells have a total dipole moment of zero, because the electrons all exist in pairs with opposite spin, which cancel each other. So only atoms with partially filled shells can have a non-zero magnetic moment. These unpaired dipoles (often called simply "spins" even though they also generally include angular momentum) tend to align in parallel to an external magnetic field, an effect called paramagnetism. Ferromagnetism involves an additional phenomenon, however : in a few substances the dipoles tend to align spontaneously, giving rise to a spontaneous magnetization, even when there is no applied field. Only a few substances are ferromagnetic. The common ones are iron, nickel, cobalt and most of their alloys, and some compounds of rare earth metals.

Ferromagnetism only occurs at temperatures below a certain critical temperature, called the Curie temperature. This ferro-paramagnetic transition is the epitome of critical phenomena. Intuitively one understand that the thermal fluctuations destroy the ordering of the spins on large distances responsible for the macroscopic magnetization. The way the ordering take place when lowering the temperature and crossing the critical temperature is the topic of this chapter.

8.2.1 Similarities with the liquid-gas transition

The Hamiltonian of a system of N spins in a field reads :

$$H(\{s_i\}) = H^{int}(\{s_i\}) - hM(\{s_i\}) = -J\sum_{<i,j>} s_i s_j - h\sum_i s_i = -\frac{J}{2}\sum_i\sum_{jv(i)} s_i s_j - h\sum_i s_i \tag{8.23}$$

where $\sum_{jv(i)}$ is the sum over the first neighbors spins of s_i. H_{int} denotes the Hamiltonian in the absence of external field and J is the so called coupling constant.

The probability of a microscopic configuration of spins $\{s_i\}$ in the canonical setting is thus

$$\rho(\{s_i\};\beta,h,N) = \frac{1}{Z(\beta,h,N)} e^{-\beta H^{int}(\{s_i\})+\beta hM(\{s_i\})} \tag{8.24}$$

The probability for the magnetization per spin is

$$\mathbb{P}_c(m;\beta,h,N) = \sum_{\{s_i\}} \rho(\{s_i\})\delta(M(\{s_i\}) = Nm) = \frac{1}{Z_c(\beta,h,N)} e^{-N\beta(f(m,\beta)-hm)} \tag{8.25}$$

with

$$-N\beta f(m,\beta) = \log\sum_{\{s_i\}} e^{-\beta H^{int}(\{s_i\})}\delta(M(\{s_i\}) = Nm) \tag{8.26}$$

and

$$Z_c(\beta,h,N) = \sum_{\{s_i\}} e^{-\beta H^{int}(\{s_i\})+\beta hM(\{s_i\})} = \int dm\, e^{-N\beta(f(m,\beta)-hm)} \tag{8.27}$$

The large deviation function of m is thus $-\beta f(\beta,m) + \beta hm$, which is the formal analogue of the large deviation of the volume per particle $-\beta f(\beta,v) - \beta Pv$, in the case of the study of the

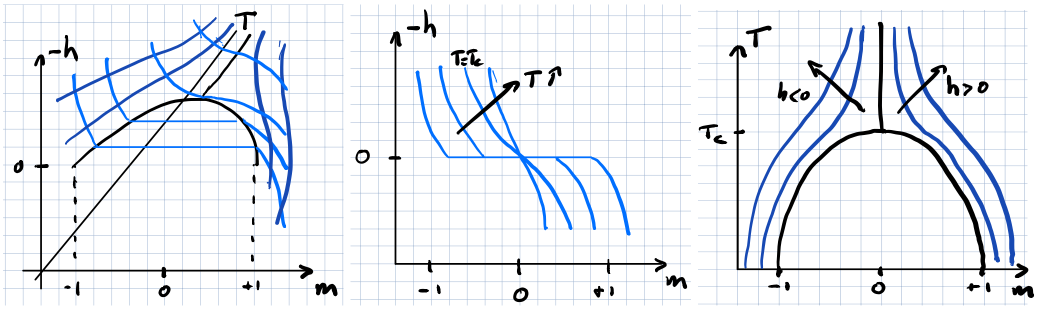

FIGURE 8.5 – Phase diagram for the Ising model in 2 dimensions

liquid-gas transition. As already discussed, everything happens as if h was playing the role of an intensive thermodynamic parameter, here $-P$.

One thus expects the same kind of thermodynamic phase diagram as those presented on figures (8.2) and (8.4). There is however a noticeable difference as can be seen on figure (8.5). Because of the $(s_i,h) \to (-s_i,-h)$ symmetry of the Hamiltonian, the isothermal coexistence lines all take place at $h=0$. As a result there is a first order transition for $T<T_c$, when the field change signs. But it has no equivalent when varying T at constant h. Either $h \neq 0$ and there is a field induced magnetization at all temperature, or $h=0$ and magnetization takes place spontaneously *through* the critical point.

8.2.2 Critical behavior

Leaving aside the discussion of the first order transition, we now concentrate on the critical transition taking place at $(T_c,h_c)=(T_c,0)$. Such critical transition are also signed by the presence of singularities in the "Gibbs" free energy $g(\beta,h) = -\frac{1}{N}\log Z_c(\beta,h,N)$. These singularities are described by critical exponents.

R Warning : the wording Gibbs free energy in the case of magnetic system is commonly replaced by free energy, even denoting it f. The confusion is total : the same letter and same wording are used for two different functions $f(m;\beta)$ and $g(\beta,h)$... Here we will stick to the notation $g(\beta,h)$, but we shall also call it free energy, and ... we shall later give a new name, the Landau free energy, to $f(m;\beta)$. Sorry, history has long time tails...

It is important to note that for any finite N, the partition function is a finite sum of regular functions, and as such cannot be singular at any finite temperature. Singularities in the free energies only arise in the thermodynamic limit $N\to\infty$.

The first derivatives of the free energy are continuous but remain singular. One introduces two critical exponents to describe the average magnetization close to the critical point $(t_c = \frac{T-T_c}{T_c}, h_c) = (0,0)$:

$$\langle m\rangle \sim -t^{\beta}, \tag{8.28}$$

$$\langle m\rangle \sim |h|^{1/\delta} \tag{8.29}$$

Further exponents are introduced to describe the response functions :

$$C_v \equiv \frac{\partial\langle e\rangle}{\partial T} = -\frac{1}{k_b T^2}\frac{\partial\langle e\rangle}{\partial\beta} = \frac{N}{k_b T^2}\delta e^2 \sim t^{-\alpha,-\alpha'}, \tag{8.30}$$

$$\chi \equiv \frac{\partial\langle m\rangle}{\partial h} = \frac{1}{k_b T}\frac{\partial\langle m\rangle}{\partial\beta h} = \frac{N}{k_b T}\delta m^2 \sim t^{-\gamma,-\gamma'}, \tag{8.31}$$

(8.32)

where the primes indicate the possibility that the exponent can be different on both sides of the transition and δx^2 is a generic notation for $\langle x^2\rangle - \langle x\rangle^2$.

An essential elements of critical phenomena are the correlations amongst the individual units, composing the system. As a matter of fact the only way for a system of locally interacting units to build up spontaneously a macroscopic quantity such as the magnetization, is to develop long range spatial correlations. The spatial correlation between two spins s_i and s_j separated by a distance r_{ij} reads :

$$C(r_{ij}) \equiv \langle s_i s_j\rangle - \langle s_i\rangle\langle s_j\rangle \sim \frac{1}{r_{ij}^{d-2+\eta}} e^{-r_{ij}/\xi(t)}, \quad \text{with} \quad \xi \sim t^{-\nu,\nu'}. \tag{8.33}$$

This last formula expresses that the correlations develop a power-law dependence, with an exponential cut-off for distances larger than ξ, with ξ diverging at the transition.

It is now easy to understand why the response function diverges. Because the spins are correlated on long distances, when they respond, they do so collectively. It thus induces macroscopic change of the magnetization. Formally, one can indeed relate the amplitude of the fluctuations of m to the integral over space of the correlation function.

One thus expect relations between the exponents ; and indeed, the exponents describing the response functions (α, α') and (γ, γ') are related to those of the correlation function (ν, ν') and η, as we shall see in more details in the following sections.

Finally, the above exponents exclusively refer to the static properties of a critical system. However dynamic properties of the system may become critical, too. Especially, the characteristic time τ, on which *temporal correlations* decreases, also diverges and is related to the correlation length by a dynamical exponent z : $\tau \sim \xi^z$.

Why are these exponents so important ? Experimentally, the exponent β has been measured in different magnetic systems and was found to be very similar $\beta = 0.31 \pm 0.01$ in all systems. Even more surprising the shape of the liquid-gas coexistence curve close to the critical point was shown to also follow $\rho_l - \rho_g \sim t^\beta$ with $\beta = 0.32 \pm 0.005$ in sulfurhexafluoride and in ^{3}He. This so called universal behavior suggests that the value of β must be rooted in some fundamental property, irrespective of the details of the system of interest. Furthermore, we shall see that the so-called mean field approximations actually fail in predicting the correct value for β as well as that of the other critical exponents. One of the central achievement of statistical physics is to have understood the deep physical origin of these discrepancies. On the way, it has provided physicists with a set of new concepts, which are now used in many fields of physics, and beyond : the renormalisation group ideas.

8.2.3 The role of dimensionality

We have seen in section (7.2) that for the 1d-chain, there are anomalous behaviors for the magnetization and its fluctuations when $T \to 0$, but nothing significant occurs at any finite temperature. Onsager has solved the 2d-Ising model on a square lattice and has thereby proven the existence of a phase transition at finite temperature. It is actually possible, following Landau and Peierls to show that there should be a phase transition at finite temperature for the Ising model in 2 dimension, at odd with the 1d case.

Proposition 8.2.1 — Peierls argument. Starting from a fully magnetized state at $T = 0$, the argument consist in evaluating the change in free energy of the system if one creates a domain with a finite fraction of spins, with opposite magnetization, as illustrated on figure (8.6) below.

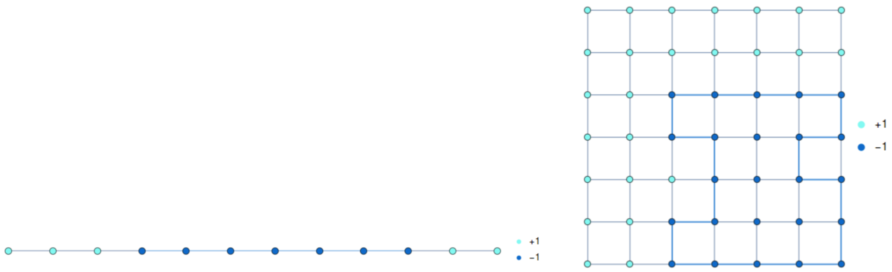

FIGURE 8.6 – Droplets of -1 spins in a surrounding system of + 1 spins in 1d (right) and 2d (left).

In 1d, the energy cost for creating a domain $\Delta E = 4J$ and the entropy gain $\Delta S = \log 2N$ (each boundary of the domain has N possible positions). Hence $\Delta F = 4J - T\log 2N$. In the thermodynamic limit, $\Delta F \to -\infty$, so that domains will form at any finite temperature. Domain walls spontaneously appear everywhere for entropic reasons and there is no possible long range ordering of the spins at finite T.

In 2d, for a droplet with a perimeter composed of $n = qN$ spins, with $0 < q < 1$, the energy cost depends on the exact shape of the boundary but scales like $\Delta E \sim 2nJ$. The number of configurations for such a domain scales like $(z-1)^n$, where z is the lattice coordination, because starting from any point of the boundary, there are typically $z-1$ possible directions to proceed in drawing the boundary. This is however an over estimation. Hence $\Delta S \sim n\log(z-1)$ and $\Delta F = qN(2J - T\log(z-1))$. The free energy changes sign for $T_c = 2J/\log(z-1)$. In the thermodynamic limit, for $T > T_c$ $\Delta F \to -\infty$ and again droplets form and destroy long range order, while for $T < T_c$, $\Delta F \to +\infty$, forming droplet is infinitely unfavored and the ordered phase is stable.

In 3d, there is also a transition at finite temperature, but there is no exact result.

In 4d and above, the critical exponents take the values prescribed by mean field approximations

The dimension above which a given transition occurs for T > 0 is referred to as the lower critical dimension and the one above which the critical behavior is captured by mean field approximations is called the upper critical dimension.

8.2.4 Mean field approximations

The most famous mean field approximation for the Ising model is the Curie Weiss approximation. The idea is to consider a specific spin say s_i and consider that the coupling to its neighbors acts as an external field of amplitude $z\langle m\rangle$, where z is the number of neighbors and $\langle m\rangle$ is the average magnetization per spin. In this case the Hamiltonian reads :

$$H_{CW}(\{s_i\}) = -J\sum_{<i,j>} s_i s_j - h\sum_i s_i = -(Jz\langle m\rangle + h)\sum_i s_i. \tag{8.34}$$

One recognizes the Hamiltonian of a system of independent spins in an external effective field $h_{eff} = Jz\langle m\rangle + h$. Using the results of section (6.3), one obtains, recalling that for independent spins $m = -e/h$:

$$\mathbb{P}(m;\beta,h) = \frac{1}{Z(\beta,h)} e^{N(\beta h_{eff} m + s(m))} \quad \text{with} \tag{8.35}$$

$$s(m) = -\frac{1+m}{2}\ln\frac{1+m}{2} - \frac{1-m}{2}\ln\frac{1-m}{2} \quad \text{and} \tag{8.36}$$

$$Z(\beta,h) = (2cosh(\beta h_{eff})^N \tag{8.37}$$

The key point is that h_{eff} is a function of the average magnetization : the above equations are not closed. Indeed computing the average magnetization, one finds

$$\langle m\rangle = \frac{\partial \log Z(\beta,h)}{\partial \beta h} = \tanh(\beta Jz\langle m\rangle + \beta h), \tag{8.38}$$

which must be solved to find $\langle m\rangle(\beta,h)$ and inject it into the above two equations. This last equation is a self-consistent equation for the mean field approximation : when the magnetization takes its average value, the effective field should lead to an average magnetization consistent with it.

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In the above formulation, the shape of the distribution $\mathbb{P}(m;\beta,h)$ is not very apparent. An alternative approach, although very similar, is not to average the magnetization, but consider it as a random variable, which fluctuates from one configuration to another, but is homogeneous over the configuration $s_i = m(\{s_i\})$. In this case one has that

$$\sum_{jv(i)} s_j = zm \tag{8.39}$$

and the mean field Hamiltonian reads

$$H_{MF}(\{s_i\}) = -\frac{J}{2}\sum_i s_i \sum_{jv(i)} s_j - h\sum_i s_i = -\left(\frac{Jz}{2}m(\{s_i\}) + h\right)\sum_i s_i = -\frac{Jz}{2}m^2(\{s_i\}) - hm(\{s_i\}). \tag{8.40}$$

One recognizes the Hamiltonian of a system of fully connected spins in a field h. Using the results of section (7.2.2), one finds :

$$\mathbb{P}(m;\beta,h) = \frac{1}{Z(\beta,h)}e^{N(s(m)+\beta hm})= \frac{1}{Z(\beta,h)}e^{N(s(m)+\beta\frac{Jz}{2}m^2+\beta hm)}, \quad \text{with} \tag{8.41}$$

$$s(m) = -\frac{1+m}{2}\ln\frac{1+m}{2} - \frac{1-m}{2}\ln\frac{1-m}{2} \quad \text{and} \tag{8.42}$$

$$Z(\beta,h) = \int dm e^{N(s(m)+\beta\frac{Jz}{2}m^2+\beta hm)} \tag{8.43}$$

This time there is no effective field. To obtain the mean magnetization, one computes $Z(\beta,h)$ using the Laplace approximation :

$$Z(\beta,h) = e^{N(s(m^*)+\beta\frac{Jz}{2}m^{*2}+\beta hm^*)} \tag{8.44}$$

with m^*, the most probable value of m, which satisfies

$$\beta Jzm^* + \beta h = -s'(m^*) = \text{atanh}(m^*), \tag{8.45}$$

which is exactly the same self consistent equation as in the case of the Curie-Weiss approach...

Altogether we have started with a model of spins with short range interactions. The Curie-Weiss approximation turns it into a model of independent spins in an effective field ; and the final solution is that of a model of fully connected spins ! In particular, we had solved equation (8.45) graphically (see figure 7.7) ; in the zero field case $(h = 0)$:

- for $\beta Jz < 1, (i.eT > T_c = Jz)$, there is only one solution $\langle m\rangle = m^* = 0$
- for $\beta Jz > 1, (i.eT < T_c = Jz)$, there are two symmetric solutions $\langle m\rangle = \pm m^*$

The two above approaches corresponds to the two ways to see why mean field approximations simplify so much the calculation. In the first one, it transforms a Hamiltonian of interacting entities in a Hamiltonian of independent units, for which the partition function easily factorizes. In the second one it allows to express the interaction part of the hamiltonian as a function of the macroscopic variable of interest only : $H_{MF}^{int}(\{s_i\}) = H_{MF}^{int}(m(\{s_i\}))$; so that one can directly compute the large deviation function :

$$\beta f_{MF}(m,\beta) = \frac{-1}{N} \log \sum_{\{s_i\}} e^{-\beta H_{MF}^{int}(\{s_i\})} \delta(M(\{s_i\}) = Nm) \tag{8.46}$$

$$= \frac{-1}{N} \log \left[\Omega(m,N) e^{-\beta H_{MF}^{int}(m)} \right] = \beta e_{MF}^{int}(m) - s(m). \tag{8.47}$$

***

Let's come back to the critical exponents, which describe the way the magnetization depends on $t = \frac{T-T_c}{T_c}$ and h, close to the critical point $(t_c, h_c) = (0,0)$. These exponents are entirely encoded in the shape of the large deviation function $\beta f_{MF}(m,\beta)$ close to the critical point :

$$\beta f_{MF}(m;\beta,h) = -\frac{\beta J z}{2} m^2 - \beta h m + \left[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right] \tag{8.48}$$

Since the magnetization begins very small at the transition, one can expand the above expression in m close to zero and find

$$\beta f_{MF}(m;\beta,h) \simeq t\frac{m^2}{2} + \frac{m^4}{12} - \beta h m, \tag{8.49}$$

from which it is straightforward to obtain the equation satisfied by the minima m^* of f_{MF} :

$$m^{*3} = -3tm^* + 3\beta h \tag{8.50}$$

It is now clear that

— for $h = 0$, and $t < 0$, $m^* \sim t^{\beta}$, with $\beta = 1/2$
— for $t = 0$, $m^* \sim h^{\frac{1}{\delta}}$, with $\delta = 3$

Deriving the equation satisfied by m^*, with respect to the field, one obtains a relation for the magnetic susceptibility

$$\chi = \frac{\beta}{m^{*2} + t} \tag{8.51}$$

and the associated scaling, valid both for $t > 0$, where $m^* = 0$, and $t < 0$, where $m^{*2} \sim t$: $\chi \sim t^{-\gamma,\gamma'}$ with $\gamma = \gamma' = 1$.

Finally, recalling that, in the mean field approximation, $e^* = -Jz\frac{m^*}{2} - hm^*$, one finds that the specific heat

$$c_v \equiv \left.\frac{\partial e^*}{\partial T}\right|_{h=0} = T_c \frac{\partial e^*}{\partial t} = -m^* \frac{\partial m^*}{\partial t} \tag{8.52}$$

from which one finds that

— for $h = 0$, and $t > 0$, $c_v = 0$
— for $h = 0$, and $t < 0$, $c_v = 3/2$

and concludes that the specific heat is discontinuous at the transition and that $\alpha = \alpha' = 0$.

R Apart from the connectivity z of the network, which in all finite dimension is just a number, the result of the calculation is independent from the dimension. Hence the mean field approximation predicts a transition at finite temperature in 1d. This is completely wrong ; we have seen that there is no phase transition at finite T in 1d.

R Table (8.1) compares the values of the exponents obtained from the mean field approximation, with those obtained exactly from the Onsager solution in 2d, and from the best numerical estimates in 3d. The least to say, is that the mean field prediction are pretty off in dimension 2. They are slightly better in dimension 3 and exact in dimension 4 !

	$d=2$	$d=3$	$d=4$	MF
α	0	0.11008(1)	0	0
β	1/8	0.326419(3)	1/2	1/2
γ	7/4	1.237075(10)	1	1
δ	15	4.78984(1)	3	3
η	1/4	0.036298(2)	0	0
ν	1	0.629971(4)	1/2	1/2

TABLE 8.1 – Critical exponents for the Ising model in dimensions 2,3,4 and in mean field (MF).

What did we assume in the mean field calculation, that went so wrong ? First less stress that sufficiently away from the critical point the mean field calculation essentially does the job. It predicts a zero magnetization at high temperature and the fact that the symmetry is spontaneously broken at T_c. So the issue must be related to the physics at the proximity of the critical point.

Computing the difference between the true Hamiltonian and the Curie-Weiss one

$$H(\{s_i\}) - H_{CW}(\{s_i\}) = -J \sum_{<i,j>} s_i(s_j - \langle m \rangle) \tag{8.53}$$

one clearly sees that we have neglected the fluctuations. Essentially we have supposed that the average over the neighboring spins is equal to the magnetization per spin, that is the average over all the spins. At high temperature, the spins are fluctuating almost independently from each other, and the system must look like an old black and white TV white noise. In that case, taking a very local average, will indeed already lead to a zero magnetization, which is equal to the large scale average. At low temperature, most of the spins are, say $+1$, and there are few small regions where the spins are -1. Since the energy cost is in the interfaces, these small regions must take the shape of droplets, with sharp interfaces. In this case computing a local average, will most of the time produce $m = 1$, sometime $m = -1$, which is also correct. We understand from this analysis that the organisation of the configurations, close to T_c must be highly specific. The magnetization is close to zero ; so there must be as many spins $+1$ and -1. However the spins cannot be organized independently from each other, like the high T white noise, otherwise the response function would not be large. In the critical region there must be large domains, which collectively respond to a tiny external field. But they can also not be organized into two well separated phases, otherwise that would be phase coexistence, the signature of a discontinuous transition. Try to imagine the organisation of the spins ... before looking at figure 8.7.

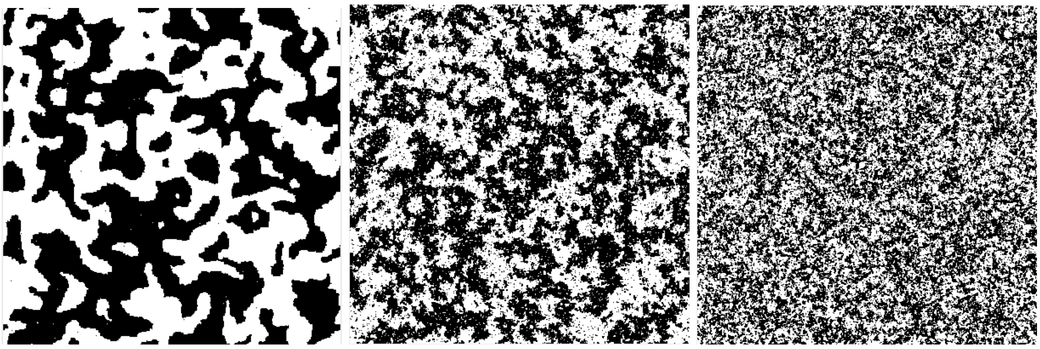


FIGURE 8.7 – 2D Ising model, with $J = 1$, $T_c = \frac{2}{\log(1+\sqrt{2})}$, $h_c = 0$. From left to right $T = 1$, $T = 2.269 \simeq T_c$, $T = 3$.

At the critical point the spins organize in a scale free, fractal structure. In other words there is no characteristic size, such that the local average would equal the global one, hence the failure of the above mean field approach. Also it is this structure which is responsible of the divergence of the correlation length, hence of the response function.

8.3 Landau and Ginzburg-Landau theories

Landau has proposed in 1937 a phenomenological approach to describe most phase transitions, on the basis of very general concepts.

We have seen above (eq. 8.49) that the critical exponents were obtained from the expansion of the free energy close to zero, in the vicinity of the critical temperature. Landau's idea was that the shape of this expansion is entirely governed by the symmetries of the system and the type of the so-called order parameter. In the case of the Ising spins para-ferro transition the Hamiltonian is invariant under a change of all spins s_i into $-s_i$, and the free energy of the system should obey this same symmetry. Also the magnetization m is a scalar quantity. Hence the expansion in m of the free energy should only contain even terms in m. Whatever the detailed shape of the exact free energy, the expansion will always be of the same form, therefore the critical exponents will also take the same value for all systems sharing the same symmetries.

R This is a wonderful abstraction that justifies the observation of universal behaviors. It is also of practical interest to classify systems in universality classes. Here the symmetries are quite obvious; but think about richer systems such as liquid crystals or magnetic systems with a spin taking all possible orientations in space....

Unfortunately at that level of description, the Landau theory is doomed to recover only the meanfield values of the critical exponents.

The Ginzburg-Landau theory, first introduced to describe superconductivity, is a rather natural extension of the Landau theory to take into account the spatial fluctuations, which are missing in Mean Field theories. It simply states that the order parameter can fluctuate in space and replace the homogeneous magnetization m, by a spatial field $m(\vec{r})$, where $\vec{r}$ denotes the position in space. Now the free energy must be a functional of $m(\vec{r})$. The simplest assumption, following the same spirit as that of Landau, is then to write this functional as an expansion in m, and in its successive spatial derivatives ∇m, while preserving the symmetries of the system, and the fact that the free energy is a scalar. For instance in the case of the para-ferro transition of a system of Ising spins :

$$F(m(\vec{r})) = \int d\vec{r}\,(f(m) + K\nabla m^2 + \ldots) \quad \text{with} \quad f(m) = \frac{t}{2}m^2 + um^4 + \ldots \tag{8.54}$$

Then the usual integral on m, used to compute the partition function, must be replaced by a functional integral over all possible functions $f(\vec{r})$ and the derivatives with respect to h or m, used to compute the average magnetization, or the susceptibilities, must be replaced by functional derivatives with respect to functions $h(\vec{r})$ and $m(\vec{r})$. One sees that the algebra may become more complicated, but the general ideas exposed above remain valid and, because we are now playing with spatially varying quantities, it is also possible to directly compute the spatial correlations from the functional derivatives of the free energy.

Beyond technical difficulties, there are a number of issues one can think of when implementing the Ginzburg Landau theory. How should one determine the minimal degree of the expansion in m and in ∇m, and how to be sure that they are consistent ? Is it clear that the integrals we have to compute are convergent ? Finally, and not the least, how good an expansion in gradients can be to describe the kind of self-similar pattern, one can observe at T_c on fig 8.7 ?

Dealing with these questions goes beyond the scope of the present course, and constitutes the realm of statistical field theories.

8.4 Scaling laws and Renormalisation Group

8.4.1 Scaling laws

Expanding the free energy as done in the Landau theory requires the assumption that the free energy is regular in the order parameter. As a consequence the singularities are all encompassed in the dependance of the order parameter on the control parameters, such as the temperature and the external field.

An alternative way of thinking is to consider that the free energy dependance on the order parameter and the temperature is singular itself close to the critical temperature, and that the singular part f_s must obey some specific property at the root of the values of the critical exponents. Domb, Kadanoff and Widom, made the hypothesis that f_s obeys a scaling invariance property :

$$f_s(\lambda^p t, \lambda^q h) = \lambda^d f_s(t,h) \tag{8.55}$$

From this relation we shall now demonstrate that all exponents are in fact not independent.

Taking the partial derivative with respect to h gives a scaling relation for $m(t,h)$:

$$\lambda^q m(\lambda^p t, \lambda^q h) = \lambda^d m(t,h) \tag{8.56}$$

Setting $h = 0$ and $\lambda = (-t)^{-1/p}$ in this equation yields $m(t,0) \propto (-t)^{\frac{d-q}{p}}$, from which we obtain $\beta = \frac{d-q}{p}$. Similarly, setting $t = 0$ and $\lambda = h^{-1/q}$ into the scaling relation for m yields $\delta = \frac{q}{d-q}$.

Taking one more partial derivative with respect to h gives a scaling relation for the susceptibility $\chi(t,h)$:

$$\lambda^{2q} \chi_T(\lambda^p t, \lambda^q h) = \lambda^d \chi_T(t,h) \tag{8.57}$$

Setting $h = 0$ and $\lambda = (t)^{-1/p}$ for $t \downarrow 0$ (resp. $\lambda = (-t)^{-1/p}$ for $t \uparrow 0$) yields $\gamma = \gamma' = \frac{2q-d}{p}$.

Deriving twice with respect to t, one finds that the specific heat c_h obeys the scaling relation

$$\lambda^{2p} c_h(\lambda^p t, \lambda^q h) = \lambda^d c_h(t,h) \tag{8.58}$$

Setting $h = 0$ and $\lambda = (t)^{-1/p}$ for $t \downarrow 0$ (resp. $\lambda = (-t)^{-1/p}$ for $t \uparrow 0$) yields $\alpha = \alpha' = 2 - \frac{d}{p}$. Hence, as a consequence of Widom scaling, not all critical exponents are independent but they can be parameterized by two numbers p, q with inter-relations such as

$$\alpha = \alpha' = 2 - \beta(\delta + 1) \tag{8.59}$$

$$\gamma = \gamma' = \beta(\delta - 1) \tag{8.60}$$

Note that p and q can be real numbers, hence allowing for non fractional critical exponents.

These relations are experimentally well verified for magnetic systems and fluids and therefore suggest that the Widom scaling hypothesis is indeed verified. But why ?

8.4.2 The renormalization group

General idea

The ideas behind the renormalization group methods allow to give a precise meaning to the concept of universality classes and the resulting scaling laws which appear in the neighborhood of a critical point.

We have seen that assuming a uniform order parameter, or assuming that a local average is a good estimator of the order parameter are very poor hypothesis because they neglect the fluctuations and their correlations, which not only exist, but also must be very specific to account for a pattern such as the one of fig (8.7) at T_c. Now let's imagine you consider a magnetic system with $T \gtrsim T_c$ and *instead at staring at all the details of the fluctuations* you un-zoom and look at less details, while the system itself remains unchanged. Once un-zoomed, the system is described by less degrees of freedom (like a picture with a lower resolution would contain less pixels). Then you iterate this operations many times up to the point where the system is only described by a few numbers, if not simply one, say the magnetization. This magnetization is zero, because the system is in the paramagnetic phase. Repeat the operation, starting with $T \lesssim T_c$. You would find after many iteration that the system is magnetized, because the system is in the ferromagnetic phase. Finally, start with a system precisely at T_c. You would not be able to conclude wether the system is in the ferromagnetic phase, or in the paramagnetic phase because you are precisely at the transition. So we see that the two well-defined phases (para and ferro) behave as attractors for this iterative process, while the transition point acts as an unstable fixed point (whenever you start a little bit above or below T_c, the process leads you to a clear conclusion about the phase in which the system is). The renormalization methods consist in formalizing the procedure we just described.

To be more precise, let's consider a system with $N \simeq L^d$ degrees of freedom, where L is the physical extension of the system and d is the space dimension. This system is at some temperature T, and the degrees of freedom are coupled by some coupling constant J. Un-zooming consists in a procedure by which the system size is reduced to $L' = L/b$, $b > 1$ and the number of degrees of freedom is reduced to $N' = (L/b)^d$. To do so, we will need to propose a specific way to aggregate the degrees of freedom, which will depend on the specific system of interest (see below). We also want the system to remain unchanged by this procedure. What do we mean by this ? Well, we want its macroscopic properties to remain unchanged. In other words we want its partition function $Z(T,J)$ or $F(T,J) = k_b T log(Z(J,T))$ to retain its most essential properties. Since we have modified the degrees of freedom, it is likely that the couplings will need to be adapted, and maybe the temperature too. That is we will have to find the renormalization group transformation $(T',J') = R_b(T,J)$ such that $F'(J',T') \simeq F(J,T)$, where the $\simeq$ sign denotes the equality of the essential properties (to be made precise below).

Illustration on the case of the site percolation

In the site percolation problem, each node of a lattice of size L^d is occupied with a probability p and the probability of a configuration $\mathscr{C}$ is given by

$$\mathbb{P}(\mathscr{C}) = p^{n_{occ}} p^{n_{free}} \tag{8.61}$$

In this purely geometrical problem, we shall replace the partition function by the percolation probability $\mathbb{P}_{perc}(L,p)$ that there exists a continuous path of occupied sites from one side to the other of the lattice of size L :

$$\mathbb{P}_{perc}(L,p) = \sum_{\mathscr{C}\text{with path}} \mathbb{P}(\mathscr{C}) \tag{8.62}$$

which is a growing polynomial of p, the shape of which is sketched on fig. (8.4.2). We therefore want to find $p' = R_b(p)$ such that $\mathbb{P}_{perc}(L',p') = \mathbb{P}_{perc}(L,p)$, with $L' = L/b$, $b > 1$. The general problem is not so easy to solve. However, in the limit of small p, the only existing paths are the straight lines from one side to the other, hence $\mathbb{P}_{perc}(L, p \to 0) \sim Lp^L(1-p)^{(L^2-L)} \sim Lp^L$. In the limit of p close to one, the only way not to have a path is to have an empty row across the system, hence $\mathbb{P}_{perc}(L, p \to 1) \sim 1 - L(1-p)^L p^{(L^2-L)} \sim 1 - L(1-p)^L$. Imposing the equality of $\mathbb{P}_{perc}$ for the original and the un-zoomed system, one finds that for $p \to 0$, $p' = (bp)^b$ and for $p \to 1$, $1 - p' = (b(1-p))^b$, from which one infers the right drawing of fig. (8.4.2). Here the renormalization group transformation is a simple one dimension iteration. It is straightforward to see that there are three fixed points, two stable ones $p = (0,1)$ and one unstable one $p = p_c$. This example clearly illustrates the ideas expressed in the previous section. Iterating the renormalization group transformation, the iteration proceeds towards one or the other stable fixed points, which correspond to the caricatures of the non-percolated (empty lattice) and percolated (fully occupied lattice) phases, except if it is initiated exactly at the unstable fixed points p_c, which denotes the critical transition.

Finally, close to the transition, one expects that the pattern of occupied sites is highly non trivial and characterized by a diverging correlation length $\xi \sim A\,|p - p_c|^{-\nu}$. If the original system and the un-zoomed system are identical, then all lengths must be zoomed out, in particular, $\xi(p) = b\xi(p')$,

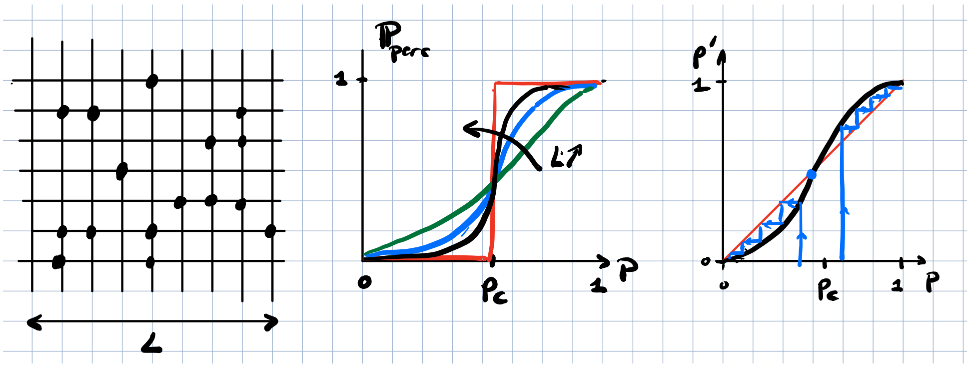


FIGURE 8.8 – Site percolation (from left to right) : a lattice of size L with n_{occ} occupied sites, $\mathbb{P}_{perc}(p)$ for increasing L and the renormalization transformation $p'(p)$ with two iteration paths.

namely $A\,|p-p_c|^{-\nu} = bA\,|p'-p_c|^{-\nu}$. One sees that we cannot gain any information on A, the prefactor of the singularity. However, by *linearizing* $p' = R_b(p)$ close to $p_c : p' = p_c + \frac{dR_b}{dp}(p-p_c)$, we find that

$$\left(\frac{dR_b}{dp}\Big|_{p_c}\right)^{\nu} = b; \tag{8.63}$$

in other words that the critical exponent ν is a direct expression of the linearized dynamics of the RG transformation in the neighborhood of the critical point.

Computing ν thus requires the knowledge of the transformation for large L, close to p_c, while we only know it close to $p=0$ and $p=1$. Still, let us perform a so-called uncontrolled approximation : let's compute Rb for a system with $L=2$, when we divide it by a factor $b=2$ and assume it is a good approximation for L large !... By a simple examination of all configurations, one finds that $\mathbb{P}_{perc}(L=2,p) = 2p^2 - p^4$ and $\mathbb{P}_{perc}(L=1,p') = p'$, hence $p' = R_b(p) = 2p^2 - p^4$ from which one deduces $p_c = 0.618$ and $\nu = 1.635$. Not so bad given that the correct values are $p_c = 0.5931$ and $\nu = 1.33$, certainly much better than the mean field results $p_c = 0.5$ and $\nu = 0.5$!

Back to the concept of universality

We shall illustrate this concept following Kadanoff and a real space renormalization scheme that he proposed for a system of spins on a lattice. The idea is to group the spins $\sigma_i = \pm 1$ by blocks and replace the block by a meta-spin $s_I = sign(\sum_{i\in I}\sigma_i)$. The probabilities of the configurations in the original system and in the un-zoomed one are respectively :

$$\mathbb{P}(\{\sigma_i\}) = \frac{1}{Z}\exp -\beta H(\{\sigma_i\}) \tag{8.64}$$

$$\mathbb{P}(\{s_I\}) = \frac{1}{Z'}\exp -\beta' H'(\{s_I\}) = \frac{1}{Z}\sum_{\{\sigma_i/s_I\}} \exp -\beta H(\{\sigma_i\}) \tag{8.65}$$

In general H' is far more complex than H : even if H contains interaction amongst nearest neighbors only, H' would contain interactions amongst next nearest neighbors. And further iterating would lead to a nightmare of interactions. But let's imagine for the purpose of clarity that we consider systems with interactions between first (coupling constant J_1) and second (coupling constant J_2) nearest neighbors, such that the RG transformation does not create more complex interactions. Then the RG transformation is described by a flow in the 2 dimension parameter space $(K_1 = \beta J_1, K_2 = \beta J_2)$ as illustrated on fig. (8.9).

Consider first the left panel. A specific physical system is defined by the values of the coupling constants (J_1, J_2). Decreasing the temperatures amounts to vary (K_1, K_2) along the green straight

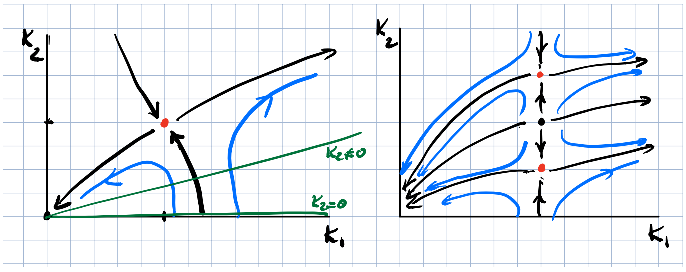


FIGURE 8.9 – Two RG flows : left, with a single universality class and right, with two universality classes each one associated to a different critical points (in red), separated by a so-called tri-critical point (in black).

lines starting from the origin ($\beta = 0, T \to \infty$). For a given T, corresponding to a given point in this K-parameter space, following the RG-flows tells us wether the system is in the disordered high temperature phase (the origin fixed point), or in the ordered cold temperature one (here the fixed point at infinity). When the green straight line crosses the black arrow pointing towards the unstable (red) fixed point, corresponds to the critical temperature. One sees that for different systems (different green straight lines) the critical temperature does change. However the linearization of the RG flow around the critical point, and more precisely the positive eigenvalue of the linearized operator will set the same critical exponents for all these different systems. One says they belong to the same universality class. The right panel describes a more complex situation where there are two universality classes.

> **R** Stating that the RG-flow remains confined to the initial two or one parameter space of the model is in general wrong. Note however that at the conceptual level, this is not an issue. If one starts with a model whose Hamiltonian that takes into account all possible couplings, then the RG-flow will remain by definition in the parameter space of the initial model, and the conceptual drawing presented here remains valid.

Two examples for systems of Ising spins

The 1D Ising chain
Given that we know that there is no phase transition in 1D, we shall not expect great news here. But we will learn an aggregation procedure called decimation.

Consider N spins in a chain, the partition function of which is

$$Z = \sum_{s_1=\pm1}\sum_{s_2=\pm1}\dots\sum_{s_N=\pm1} e^{-\beta H} = \sum_{s_1=\pm1}\sum_{s_2=\pm1}\dots\sum_{s_N=\pm1} e^{\beta J \sum_i s_i s_{i+1}} \tag{8.66}$$

Let's group the odd and even spins (assume N is even) :

$$\begin{aligned} Z &= \sum_{s_1=\pm1}\sum_{s_3=\pm1}\dots\sum_{s_{N-1}=\pm1}\left[\sum_{s_2=\pm1}\sum_{s_4=\pm1}\dots e^{-\beta H}\right] && (8.67)\\ &= \sum_{s_1=\pm1}\sum_{s_3=\pm1}\dots\sum_{s_{N-1}=\pm1}\left[\sum_{s_2=\pm1} e^{Ks_2(s_1+s_3)} \sum_{s_4=\pm1} e^{Ks_4(s_3+s_5)}\dots\right] && (8.68)\end{aligned}$$

where $K = \beta J$.

It is easy to check case by case, because spins only takes values ±1, that

$$\sum_{s_2=\pm1} e^{Ks_2(s_1+s_3)} = 2\cosh K(s_1+s_3) = e^{g+K's_1s_3} \tag{8.69}$$

with $g = \ln\left[2\,(\cosh 2K)^{1/2}\right]$ et $K' = \ln\left[(\cosh 2K)^{1/2}\right]$.

The same holds for all $N/2$ even spins, so that :

$$Z(N,K) = e^{Ng(K)} \sum_{\text{odd spins}} e^{K'\sum_{\text{odd spins}} s_i s_{i+1}} = e^{Ng(K)} Z(N' = N/2, K'). \tag{8.70}$$

We therefore have an explicit relation between the partition function of the decimated system and that of the initial system, which are identical, up to a regular pre-factor, provided that the coupling constant are renormalized according to the relation $K' = R_b(K)$ we just derived.

Solving for the fixed point of the RG-transformation R_b, one finds that there is no other fixed point that $K = 0$, corresponding to the inifinite temperature, disordered phase : no phase transition in 1D.

Hierarchical Networks
Given that the whole idea of universality classes, is that the microscopic details of the system does not matter, why not implementing the Ising model on a lattice which is 2D, but at the same time allows for an exact treatment of the RG flows ?

Convenient lattices are hierarchical ones such as the Berker lattice (Fig. 8.10). Note that the lattice is built, starting from the completely aggregated lattice towards the original system with N spins. The RG iteration, of course goes the other way round as usual.

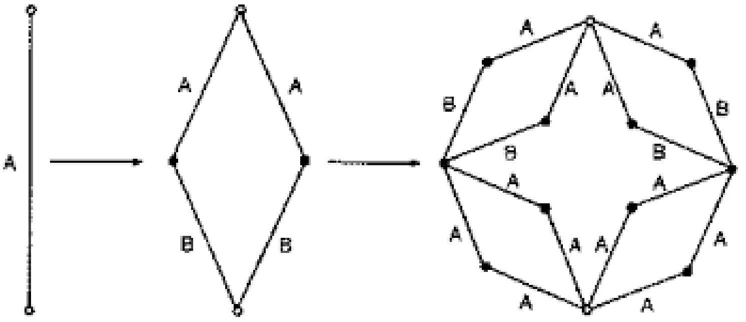


FIGURE 8.10 – Berker lattice

The calculation consists, in way directly analogous to the previous one, in performing the sum of the partition functions grouping the spins that have only two neighbors, and are therefore not connected to the spins outside the diamond they belong to. Inside each diamond, one must compute :

$$\sum_{s_2,s_3=\pm1} e^{K(s_1s_2+s_1s_3+s_4s_2+s_4s_3)} = \sum_{s_2,s_3=\pm1} e^{K(s_2+s_3)(s_1+s_4)} \tag{8.71}$$

$$= 2+2\cosh(2K(s1+s4)) \tag{8.72}$$

$$= 2+e^{g+K's_1s_4}. \tag{8.73}$$

with $g = \ln\left[2\left(\cosh 4K\right)^{1/2}\right]$ et $K' = \ln\left[\left(\cosh 4K\right)^{1/2}\right]$. The tiny difference with the previous case, is that here the RG transformation has a non trivial fixed point.

This fixed point $K_c \simeq 1/4$, is small enough that, we can approximate $K' = R_b(K)$ by $K' \simeq 4K^2$, close to K_c. Then, linearizing in the neighbor of K_c, we find

$$\left(\left.\frac{dR_b}{dK}\right|_{K_c}\right)^{\nu} = 2^{\nu} = b; \tag{8.74}$$

where b is the scaling factor of the decimation process. Here the number of bonds at each iteration is divided by 4. So is the number of spins in the large N limit. Accordingly $b^d = 4$, with $d = 2$, hence $b = 2$ and $\nu = 1$, which is the correct value for this critical exponent for the para-ferro transition of the Ising model in two dimension !

It should however not be concluded that all the critical exponents of the Ising model in 2d can be found this way. Hierarchical lattice still miss parts of the correlations close to the critical point.

Hyperscaling

The ideas of the renormalization group also allow to establish relations between the exponents. Wen performing the aggregation of spins to un-zoom from the original system, we have found that the partition function typically takes the form :

$$Z(N,K) = e^{Ng(K)} Z(N' = N/b^d, K') \tag{8.75}$$

hence the dimensionless free energy density follows

$$f(N,K) = g(K) + \frac{1}{b^d} f(N/b^d, K') \text{ and, in the limit of large } N,\; f(K) = g(K) + \frac{1}{b^d} f(K') \tag{8.76}$$

From this, we shall now see how the singularity of the free energy at a critical point are related to the linearized RG-flow in the vicinity of this critical point. At the fixed point,

$$\begin{aligned} f(K_c) &= g(K_c) + \frac{1}{b^d} f(K_c) && (8.77)\\ &= g(K_c) + \frac{1}{b^d}\left(g(K_c) + \frac{1}{b^d}\left(g(K_c) + \frac{1}{b^d}(\ldots)\right)\right) && (8.78)\\ &= \sum_{n=0}^{\infty}\left(\frac{1}{b^d}\right)^n g(K_c). && (8.79) \end{aligned}$$

The series is convergent because $1/b^d < 1$. However let's proceed the same way with the successive derivatives of $f(K)$:

$$f'(K) = g'(K) + \frac{1}{b^d}\frac{dK'}{dK} f'(K'). \tag{8.80}$$

At the fixed point,

$$f'(K_c) = g'(K_c) + \frac{1}{b^d}\frac{dK'}{dK}\bigg|_{K_c} f'(K_c); \tag{8.81}$$

from which we extract again a series, with $\frac{1}{b^d}$, replaced by $\frac{1}{b^d}\frac{dK'}{dK}\Big|_{K_c} > \frac{1}{b^d}$, because $\frac{dK'}{dK}\Big|_{K_c} > 1$ since the critical point is an unstable fixed point of the RG flow. This series might still be convergent, but already less than the previous one. Proceeding further in the order of derivatives, the more dangerous term in the series for the nth derivative is $\frac{1}{b^d}\left(\frac{dK'}{dK}\Big|_{K_c}\right)^n$, which for some finite n will lead to a diverging series, hence a singularity of $f(K)$.

Altogether we see that when asking for the system to remain unchanged during the renormalization process, what really matters is the singular part of the free energy, namely :

$$f_{sing}(K) = \frac{1}{b^d} f_{sing}(K') \tag{8.82}$$

This last expression shows how the Widom scaling hypothesis actually takes its root in the ideas of the renormalization group.

Finally, recalling that the second derivative of f, with respect to β, has the singularity of the heat capacity characterized by the critical exponent α, one has $f_{sing}(K) \sim (K - K_c)^{2-\alpha}$. Injecting this expression in eq. 8.82 and linearizing $K'(K)$ close to K_c, one finally obtains

$$\left(\frac{dR_b}{dK}\bigg|_{K_c}\right)^{2-\alpha} = b^d; \tag{8.83}$$

from which we derive, using eq.8.74 the so called hyper-scaling relation

$$2 - \alpha = d\nu \tag{8.84}$$

which comes as a complement to the previous relations, we had already found

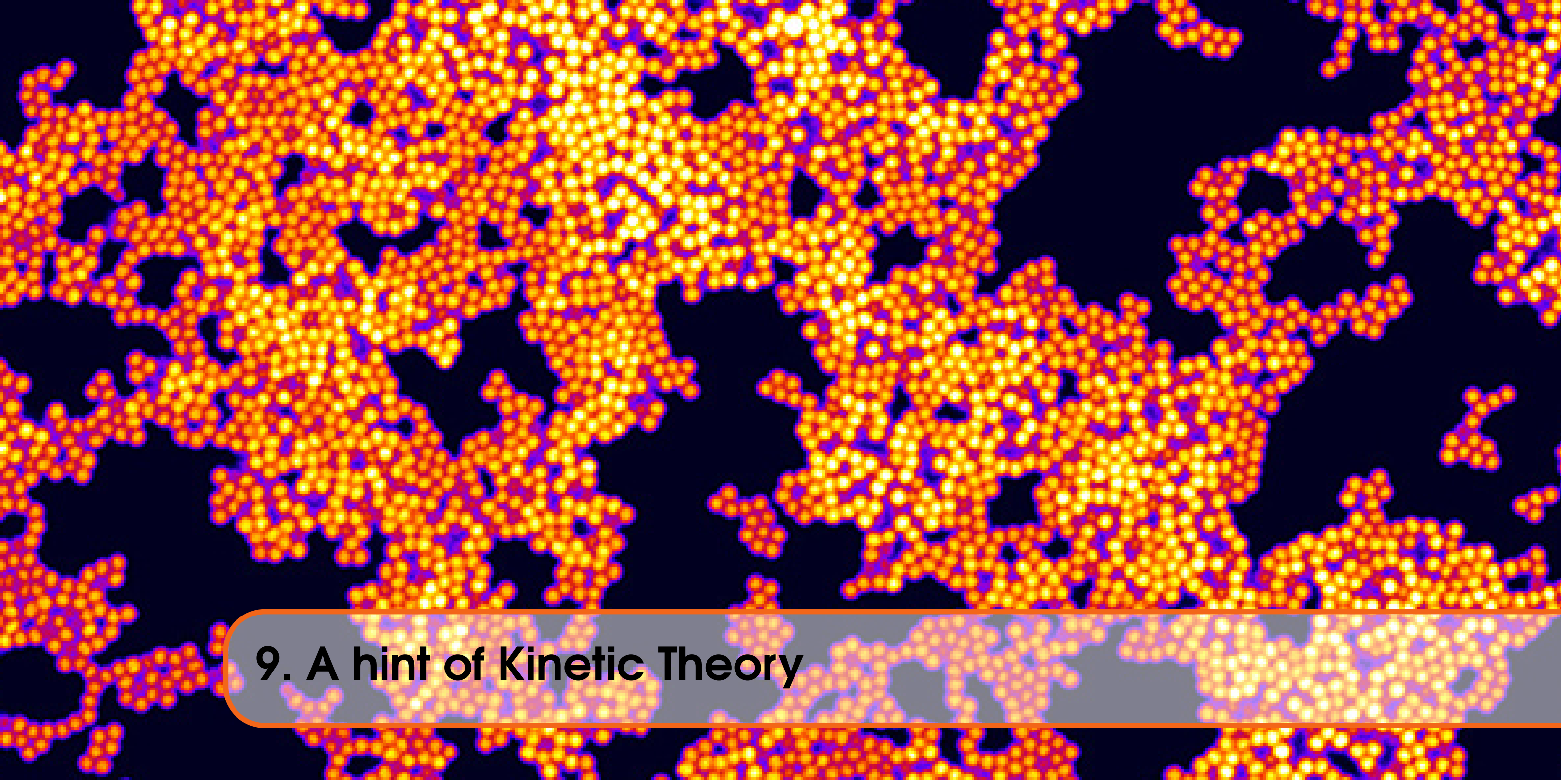
$$2-\alpha=\beta(\delta+1) \tag{8.85}$$

$$\gamma=\beta(\delta-1) \tag{8.86}$$

Altogether, we have seen how the renormalization group ideas offer a paradigm for the scaling properties of the singular part of the free energy, which in turn allow to reduce the number of independent critical exponents. More importantly, we have seen how these ideas provide a framework for the concept of universality and universality classes. We have also illustrated some practical implementation of these ideas on very specific models. Identifying the RG-flow for a given class of systems is in general very difficult. There are a number of techniques, taking place either in real space or in the momentum space, for lattice models or field theories, including several kind of controlled or un-controlled approximation. Exploring these techniques goes beyond the scope of this course, but the general ideas expressed here are underlying all of them.

III

Out of Equilibrium Statistical Physics



9. A hint of Kinetic Theory

It might be a good idea before reading this chapter to refresh your mind with reading again Chapter 2. At the end of that chapter, we had introduced the Hamiltonian dynamics for a classical system of N particules $(k = 1..N)$ in a physical space of dimension d, described by their positions $q_{(k-1)d,..kd}$ and impulsions $p_{(k-1)d,..kd}$ in the phase space of dimension $2Nd$.

The system is described by its Hamiltonian $H(\{q_i, p_i\})$, that is its energy, and obeys the dynamics prescribed by the Hamilton equations. For $i \in [1, dN]$:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{9.1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{9.2}$$

Any observable $A(t) = A(\{q_i(t), p_i(t)\})$ then evolves according to :

$$\dot{A} = \sum_i \dot{q}_i \frac{\partial A}{\partial q_i} + \dot{p}_i \frac{\partial A}{\partial p_i} = \sum_i \frac{\partial H_i}{\partial p_i}\frac{\partial A}{\partial q_i} - \frac{\partial H_i}{\partial q_i}\frac{\partial A}{\partial p_i} \equiv -\{H, A\}. \tag{9.3}$$

where the last notation is called the Poisson bracket. It is a linear differential operator and has all the standard properties of such an object. In particular, one sees, taking $A = H$, that $\frac{dH}{dt} = 0$; the total energy is conserved. The dynamics in phase space is constrained to a manifold where conserved quantities are fixed by the initial conditions. In the case of an Hamiltonian dynamics, the law of conservation for the probability density, discussed in the proposition 2.2.1 simplifies and reads :

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}. \tag{9.4}$$

which is called the Liouville equation. It expresses the fact that the volume in phase space is conserved along a trajectory : there is no condensation of the density ρ.

In the first part of this book, we concentrated on the steady state of this equation, which happens to be the uniform distribution, reduced to the manifold of constant conserved quantities, namely the equilibrium distribution in the micro-canonical ensemble. In the following we want to consider out-of-equilibrium situations, where $\rho(\{q_i, p_i\}, t)$ depends on time.

Proposition 9.0.1 — The entropy of the universe is conserved!. This seemingly unusual statement is very easy to proof. Consider the entropy of the probability distribution $\rho(\{q_i, p_i\}, t)$:

$$S(t) = -\int \Pi_i dq_i dp_i \rho(\{q_i, p_i\}, t) \ln(\rho(\{q_i, p_i\}, t)) \tag{9.5}$$

and compute its derivative with respect to time, remembering that the Poison bracket behaves as a first order derivative operator :

$$\begin{aligned}
\frac{dS}{dt} &= -\int \Pi_i dq_i dp_i \left(\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial t} \ln \rho\right) && (9.6)\\
&= -\int \Pi_i dq_i dp_i \{H, \rho\} - \int \Pi_i dq_i dp_i \{H, \rho\} \ln \rho && (9.7)\\
&= -\int \Pi_i dq_i dp_i \{H, \rho\} + \int \Pi_i dq_i dp_i \rho \{H, \ln \rho\} && (9.8)\\
&= -\int \Pi_i dq_i dp_i \{H, \rho\} + \int \Pi_i dq_i dp_i \{H, \rho\} && (9.9)\\
&= 0 && (9.10)
\end{aligned}$$

We see here that there is no issue with time reversibility of macroscopic system at the level of the universe, namely the N isolated particles. The microscopic dynamics is reversible and there is no macroscopic arrow of time !

Okay, but what is this story of entropy growing unless equilibrium is reached then ? The answer resides in the fact that we never consider the whole universe, or a perfectly isolated system. To proceed further we need to consider a subset of particles in interaction with the rest of the universe and obtain an equation for the dynamics for the marginal distribution describing only this subset of $S < N$ particles. This is the goal of the so called BBGKY hierarchy from the names of the gentlemen who worked on its derivation and applications : Bogolioubov, Born, Green, Kirkwood et Yvon.

9.1 BBGKY hierarchy

The so-called S-particles probability density is given by integrating out the degrees of freedom corresponding to the other $N - S$ particles, and assuming the symmetry by permutation of the particles,

$$\rho_s(\{q_1, p_1; q_2, p_2; ...;; q_S, p_S\}, t) = \frac{N!}{(N-S)!} \int \prod_{i=S+1}^{N} dq_i dp_i \rho(\{q_i, p_i\}, t) \tag{9.11}$$

Note that the S particles of interest do interact with the other $N - S$ particles. The energy of the system of S particles is therefore not conserved.

The first step is to separate the Hamiltonian describing the systems into three parts, one describing the S particles, excluding their interaction with the $N - S$ other particles, one describing the $N - S$ particles, excluding their interactions with the S particles of interest and one describing the interactions amongst the two populations :

$$H = H_S(q_i, p_{i;i=1,..S}) + H_{N-S}(q_i, p_{i;i=S+1,..N}) + H'(q_i, q_{j;i=1,..S;j=S+1,..N}) \tag{9.12}$$

with (9.13)

$$H' = \sum_{i=1}^{S} \sum_{j=S+1}^{N} V_{int}(\|\vec{q}_i - \vec{q}_j\|) \tag{9.14}$$

Therefore, one has

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=S+1}^{N} dq_i dp_i \frac{\partial \rho}{\partial t} = \int \prod_{i=S+1}^{N} dq_i dp_i \left[\underbrace{\{H_S, \rho\}}_{\boxed{1}} + \underbrace{\{H_{N-S}, \rho\}}_{\boxed{2}} + \underbrace{\{H', \rho\}}_{\boxed{3}} \right] \tag{9.15}$$

For the term $\boxed{1}$, the variables involved in the integration and that involved in the differential operator, symbolized by the Poisson brackets, are different; one can than exchange the order of the integration and the derivation operators

$$\boxed{1} = \left\{ H_S, \int \prod_{i=S+1}^{N} dq_i dp_i \rho \right\} = \{H_S, \rho_S\} \tag{9.16}$$

For the term $\boxed{2}$ the variables of both operators are precisely the same. We thus deal with an integral of the form

$$\boxed{2} = \int \prod_{i=S+1}^{N} dq_i dp_i \{H_{N-S}, \rho\} \cong \int_a^b du \frac{d}{du} f = f(b) - f(a) \tag{9.17}$$

Considering that f cancels at infinity, we find that

$$\boxed{2} = 0 \tag{9.18}$$

The term $\boxed{3}$ requires a longer calculation, which can be found for instance in *Statistics Physics of Particles*, Cambridge University Press, written by Mehran Kardar, and one obtains :

Proposition 9.1.1 — Hierarchie BBGKY(Bogolioubov, Born, Green, Kirkwood et Yvon).

$$\frac{\partial \rho_S}{\partial t} = \{H_S, \rho_S\} + \sum_{i=1}^{S} \int dq_{S+1} dp_{S+1} \frac{\partial V(q_i - q_{S+1})}{\partial q_i} \frac{\partial \rho_{S+1}}{\partial p_i} \tag{9.19}$$

This equation shows that the knowledge of the evolution of ρ_S depends on the dynamics of ρ_{S+1}, hence the name hierarchy for this set of equations. In the present form such a hierarchy is not very helpful, but is will set the base for successive approximations.

9.2 Dynamics of the one and two particles densities

Let's start with the first equation ($S = 1$) of the above hierarchy :

$$\underbrace{\frac{\partial \rho_1}{\partial t} - \{H_1, \rho_1\}}_{A_1} = \underbrace{\int dq_2 dp_2 \frac{\partial V(q_1 - q_2)}{\partial q_1} \frac{\partial \rho_2}{\partial p_1}}_{B_1} \tag{9.20}$$

$$\text{with} \quad A_1 = \left[\frac{\partial}{\partial t} - \frac{\partial U_{ext}}{\partial q_1} \frac{\partial}{\partial p_1} + \frac{p_1}{m} \frac{\partial}{\partial q_1} \right] \rho_1 \tag{9.21}$$

All terms present in A_1 are homogeneous to an inverse time. In particular the second term describes the spatial gradients of the external potential, which take place on a macroscopic length L :

$$\frac{\partial U_{ext}}{\partial q_1}\frac{\partial}{\partial p_1} \approx \frac{1}{\tau_U} \approx \frac{v}{L} \tag{9.22}$$

where τ_U is an extrinsic timescale, describing the time it takes for a particle with velocity v to probe the gradient of the external potential.

Let's move to the second equation $(S = 2)$ of the hierarchy :

$$\underbrace{\frac{\partial \rho_2}{\partial t} - \{H_2, \rho_2\}}_{A_2} = \underbrace{\int dq_3 dp_3 \left[\frac{\partial V(q_1 - q_2)}{\partial q_1}\frac{\partial}{\partial p_1} + \frac{\partial V(q_2 - q_3)}{\partial q_2}\frac{\partial}{\partial p_2}\right]\rho_3}_{B_2} \tag{9.23}$$

$$A_2 = \left[\frac{\partial}{\partial t} - \underbrace{\frac{\partial U_{ext}}{\partial q_1}\frac{\partial}{\partial p_1}}_{1/\tau_U} - \underbrace{\frac{\partial U_{ext}}{\partial q_2}\frac{\partial}{\partial p_2}}_{1/\tau_U} + \frac{p_1}{m}\frac{\partial}{\partial q_1} + \frac{p_2}{m}\frac{\partial}{\partial q_2} - \underbrace{\frac{\partial V(q_1 - q_2)}{\partial q_1}\left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2}\right)}_{1/\tau_{coll}}\right]\rho_2 \tag{9.24}$$

In the term A_2, we recover two terms corresponding to the same timescale τ_U. We also notice the presence of a new characteristic time, which involves the interaction potential. This time, $\tau_{coll} = l_{int}/v$, is the collision time, namely the typical time during which two particles are within their interaction range l_{int}. For weak interactions such as Van der Waals or Lenard-Jones interactions, the range of which $l_{int} \simeq 10^{-10}m$, this collision time is often the shortest timescale to consider.

We finally notice the presence of a similar collision term in the terms B_1 and B_2, from which we identify a third characteristic time. The integrals B_1 and B_2 are non zero, only within the typical interaction volume l_{int}^3. The ratio ρ_3/ρ_2 and ρ_2/ρ_1 are of order N times to the probability of finding a particle per unit volume; it is thus the particle density. Hence, here for B_2 :

$$\frac{1}{\tau_x} \simeq \frac{B_2}{\rho_2} \simeq \frac{1}{\rho_2}\int dq_3 dp_3 \rho_3 \frac{1}{\tau_{coll}} \simeq n\frac{l_{int}^3}{\tau_{coll}} \tag{9.25}$$

These three characteristic times $\tau_U = \frac{L}{v}$, $\tau_{coll} = \frac{l_{int}}{v}$ and $\tau_x \equiv \frac{l_x}{v} = \frac{1}{n\sigma v}$, where $\sigma = l_{int}^2$ is called the cross section and l_x is called the mean free path, and their relative magnitudes are at the root of the approximations done in the kinetic theory. Two standard approximation schemes are as follows :

- For low density fluids, gases, of particles with short range interactions $\frac{\tau_{coll}}{\tau_x} = nl_{int}^3 \ll 1$, applying the separation of time scales to the above equations leads to the Boltzmann equation.
- For systems with long range interaction, $\frac{\tau_{coll}}{\tau_x} \gg 1$ and one obtains the Vlasov equation.

In both cases τ_U is considered to be larger than the two other intrinsic times.

9.3 Boltzmann Equation

For the equation governing the dynamics of ρ_2, the condition $\frac{\tau_{coll}}{\tau_x} \ll 1$ allows us to neglect the right hand side of the equation. In other words ρ_2 evolves as if any two pairs of particles is isolated from the rest of the system. The left hand side A_2 of this equation contains the two time scales τ_U and τ_{coll}. The shortest one characterizes the relaxation of ρ_2 on the duration of a collision : after the collision, and outside the interaction range L_{int}, the particles involved in a collision become independent and $\rho_2(q_1, p_1, q_2, p_2)$ relaxes towards $\rho_1(q_1, p_1)\rho_1(q_2, p_2)$. Then on the longer timescale τ_U, which is also the time scale of the relaxation of ρ_1 the system relaxes to the true steady state, compatible with the external potential (see fig. (9.1)

To deal with the right hand side B_1 of the first equation of the hierarchy, we need to know ρ_2 during this intermediate pseudo steady state, we just described. I this regime, one can neglect $\frac{\partial \rho_2}{\partial t}$ and the terms of order $1/\tau_U$ in the left hand side A_2 of the second equation of the hierarchy. Also, one can change the variables from (q_1, q_2) to that of the center of mass $Q = (q_1 + q_2)/2$ and the relative position $q = (q_1 - q_2)$ and realize, as one would expect, that the slow dynamics corresponds to that of the center of mass, and the fast dynamics to that of the relative position of the particles. Therefore $\frac{\partial \rho_2}{\partial q} \ll \frac{\partial \rho_2}{\partial Q}$ and $\frac{\partial \rho_2}{\partial q_2} \simeq -\frac{\partial \rho_2}{\partial q_1} \simeq \frac{\partial \rho_2}{\partial q}$. As a result :

$$\frac{\partial V(q_1 - q_2)}{\partial q_1} \left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right) \rho_2 \quad = - \left(\frac{p_1 - p_2}{m} \right) \frac{\partial \rho_2}{\partial q} \tag{9.26}$$

This equation describes how ρ_2 is constrained along the trajectories that describe the collision between two particles.

Substituting into the right hand side B_1 of the first equation of the hierarchy, one obtains

$$\frac{\partial \rho_1}{\partial t} - \{H_1, \rho_1\} = \int dq_2 dp_2 \frac{\partial V(q_1 - q_2)}{\partial q_1} \left(\frac{\partial \rho_2}{\partial p_1} - \frac{\partial \rho_2}{\partial p_2} \right) \tag{9.27}$$

$$= \int dq dp_2 \left(\frac{p_2 - p_1}{m} \right) \frac{\partial \rho_2}{\partial q} (q_1, p_1, q, p_2, t) \tag{9.28}$$

Remember that all q_i and p_i are vectors. The integrand in this last equation is a derivative of ρ_2, with respect to q along the direction of relative motion $p = p_2 - p_1$. The convenient system of coordinate for q is illustrated on fig : (9.2) : a is the component of q parallel to $p_2 - p_1$ ($a < 0$ before the collision and $a > 0$ after the collision) and b, the so-called impact vector lies in the plane perpendicular to the collision axis, so that $dq = da\, d^2b$.

Therefore integrating along a, one finds

$$\frac{\partial \rho_1}{\partial t} - \{H_1, \rho_1\} = \int d^2b dp \left| \frac{p_2 - p_1}{m} \right| \left[\rho_2(q_1, p_1, p, q^+, t) - \rho_2(q_1, p_1, p, q^-, t) \right] \tag{9.29}$$

where $q^- = (a^-, b^-)$ and $q^+ = (a^+, b^+)$ denote the relative position before and after the collision. Since ρ_2 varies significantly only over the interaction range, we shall consider that the collision is

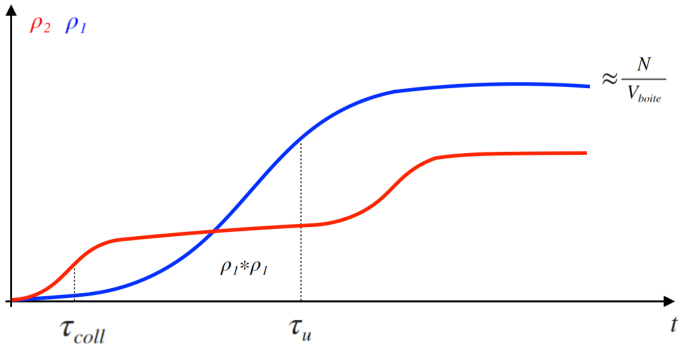


FIGURE 9.1 – Relaxation of the densities ρ_1 and ρ_2 : ρ_1 relaxes on τ_U the timescale set by the external potential, while ρ_2 relaxes in two steps, a fast one, on the collision time τ_{coll}, towards the factorized distribution $\rho_1 * \rho_1$ and a slow one, slaved to the dynamics of ρ_1.

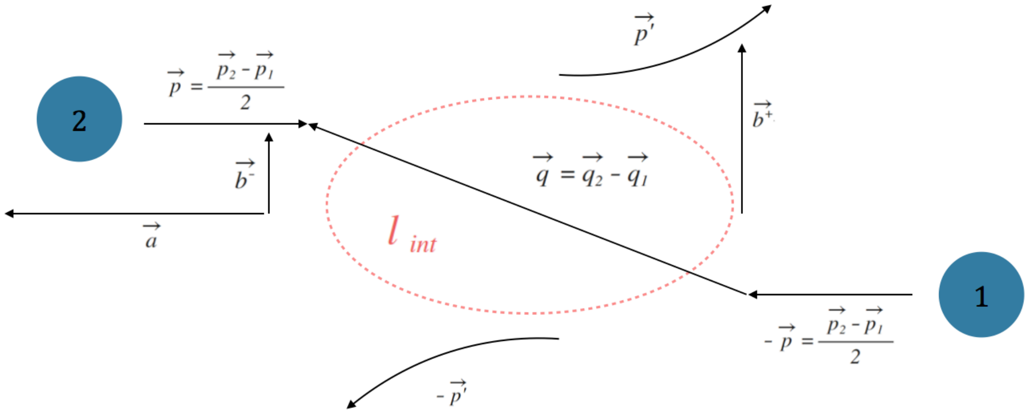


FIGURE 9.2 – Collision kinematics

ponctual and assimilate a^- and a^+, which amounts to perform some coarse graining in space that ignore variations on scale smaller than l_{int}. While it is legitimate to assume that the particles are uncorrellated before the collision, because of their very different chaotic histories, (the molecular chaos hypothesis) this cannot be true after the collision : the collision itself does create some correlations.

The trick is to relate the density ρ_2 after the collision to the one before the collision, via the equations governing the collision : indeed any configuration (q_1, p_1, q_2, p_2) of the two particles following the collision must come from a precise configuration (q_1', p_1', q_2', p_2') before the collision. Hence $\rho_2(q_1, p_1, p, q^+) = \rho_2(q_1', p_1', p', q^-)$, where the configuration (q_1', p_1', p', q^-) is such that it produces (q_1, p_1, p, q^+) via the collision. Of course the prime quantities are complicated functions of the non prime quantities resulting from the integration of the equation of motion backward in time during the collision. But the counterpart of it is that, now, all densities are evaluated before the collision, where the two body probability density can be assumed to factorize, following the Molecular Chaos Hypothesis.

Accordingly we finally obtain the closed form Bolzmann equation for $\rho_1(q_1, p_1)$:

Proposition 9.3.1 — Boltzmann Equation.

$$\frac{\partial \rho_1}{\partial t} - \{H_1, \rho_1\} = \int dp_2\, d^2b \left|\frac{p_2 - p_1}{m}\right| \left[\rho_1(q_1, p_1', t)\rho_1(q_1, p_2', t) - \rho_1(q_1, p_1, t)\rho_1(q_1, p_2, t)\right] \tag{9.30}$$

The Boltzmann equation has a rather simple interpretation. The left hand side of the equation describes the evolution of the density for a single particle in an external potential. The right hand side describes how the probability of finding a particle of momentum p_1 at q_1 changes because of a collision with a particle of momentum p_2 at this same q_1. The second term preceded with a minus sign, integrates all collisions, starting with a momentum p_1, that will be turned into some other momentum ; and the first term integrates all collisions, starting with any momentum, which produce a momentum p_1.

Proposition 9.3.2 — The case of elastic collisions : a useful property inherited from symmetry considerations. Consider the right hand side of the Boltzmann equation, multiply it by a function $\Phi(p_1)$ and integrate it over p_1 :

$$Q[\Phi] \equiv \int dp_1 \int dp_2 d^2b \left|\frac{p_2 - p_1}{m}\right| \left[\rho_1'\rho_2' - \rho_1\rho_2\right] \Phi(p_1) \tag{9.31}$$

$$= \frac{1}{4}\int dp_1 \int dp_2 d^2b \left|\frac{p_2 - p_1}{m}\right| \left[\rho_1'\rho_2' - \rho_1\rho_2\right] \left[(\Phi(p_1) + \Phi(p_2)) - (\Phi(p_1') + \Phi(p_2'))\right] \tag{9.32}$$

where one should not confuse the notations : from now on $\rho_1 = \rho_1(q_1, p_1, t)$ and $\rho_2 = \rho_1(q_1, p_2, t)$

The proof consist in using the two following symmetries of Q : first exchanging the indices 1 and 2, Q remains unchanged; second *if the collision is elastic*, the Jacobian of the transformation $(p1', p2') \leftrightarrow (p1, p2)$ is one, and Q is antisymmetric under this change of variable.

9.4 H Theorem

Let's come back to our initial motivation and consider now the entropy of the one-particle distribution

$$S \equiv -\int dq_1 dp_1\, \rho_1(q_1, p_1, t) \ln(\rho_1(q_1, p_1, t)) \tag{9.33}$$

Boltzmann actually introduced H = -S as the function of interest, hence the name of the H-theorem, which states that *If* ρ_1*'s dynamics obey the Boltzmann equation then* $\frac{dS}{dt} \geq 0$. The proof goes has follows :

$$\frac{dS}{dt} = -\int dq_1 dp_1 \frac{\partial \rho_1}{\partial t}(1 + \ln \rho_1) \tag{9.34}$$

$$= -\int dq_1 dp_1 \frac{\partial \rho_1}{\partial t} \ln \rho_1 \tag{9.35}$$

$$= -\int dq_1 dp_1 \{H_1, \rho_1\} - \int dq_1 dp_1 \int dp_2 d^2b \left|\frac{p_2 - p_1}{m}\right| \left[\rho_1'\rho_2' - \rho_1\rho_2\right] \ln \rho_1 \tag{9.36}$$

$$= -\frac{1}{4}\int dq_1 dp_1 dp_2 d^2b \left|\frac{p_2 - p_1}{m}\right| \left[\rho_1'\rho_2' - \rho_1\rho_2\right] \ln\left(\frac{\rho_1\rho_2}{\rho_1'\rho_2'}\right) \tag{9.37}$$

The second line derives from the fact that $\int dqdp \frac{\partial \rho_1}{\partial t} = \frac{\partial \int dqdp\, \rho_1}{\partial t} = \frac{\partial 1}{\partial t} = 0$. The third line is obtained by applying the Boltzmann equation. $\int dqdp\, \{H_1, \rho_1\} = 0$ as can be shown by successive integration by parts. And the last line is obtained by applying eq. (9.32) to the case $\Phi(p_1) = \ln(\rho_1(q_1, p_1, t))$.

Finally, given that $\forall (X,Y) \in \mathbb{R}^{+2}, (X - Y)\ln(\frac{Y}{X}) \leq 0$, we find that $\frac{dS}{dt} \geq 0$.

How is it that starting with a reversible dynamics, we end up with an irreversible one, marked by a clear arrow of time ? Reconciling the reversibility of the microscopic laws of physics with the observed irreversibility of the macroscopic physics has been a matter of long debates. At the level of first principles, there is no reason to be so surprised : describing the world, retaining only macroscopic degrees of freedom is clearly an approximation. As such, there is no reason why it should retain all fundamental properties from the microscopic dynamics. As a matter of fact, the key to the irreversibility of the Boltzmann equation resides in the physically motivated approximation, we made to derive it. The troncature of the BBGKY hierarchy does not break the time reversibility itself. A first crucial step comes later when we have made the molecular chaos hypothesis before and not after the collision. This assumption, while being very reasonable, does break the time reversibility. A second step not less important, is the spatial and temporal coarse graining made when assuming the collision to be local and instantaneous. Doing so, we have introduces a resolution level below which we loose information, hence loosing time reversibility.

9.5 Conserved quantities and Hydrodynamics

The main success of kinetic theory is that it allows for a systematic derivation of the hydrodynamics equations, namely the equation describing the large scales motion of fluids. There are several way of proceeding, and we shall concentrate on the one which follow from the Boltzmann equation.

The central idea is to consider the dynamics of *conserved quantities* χ, which are left unchanged by the two-body collisions :

$$\chi(q,p_1,t)+\chi(q,p_2,t)=\chi(q,p_1',t)+\chi(q,p_2',t) \tag{9.38}$$

For such quantities, we have (eq. 9.32) that $Q[\chi]=0$.

Multiplying by $\chi(q,p,t)$, and applying the integral operator $\int dp$ on both sides of the Boltzmann equation then simply leads to

$$\int dp\chi\left[\frac{\partial}{\partial t}+\frac{p}{m}\frac{\partial}{\partial q}-\frac{\partial U}{\partial q}\frac{\partial}{\partial p}\right]\rho_1=0 \tag{9.39}$$

$$\int dp\left\{\left[\frac{\partial}{\partial t}+\frac{p}{m}\frac{\partial}{\partial q}-\frac{\partial U}{\partial q}\frac{\partial}{\partial p}\right](\rho_1\chi)-\rho_1\left[\frac{\partial}{\partial t}+\frac{p}{m}\frac{\partial}{\partial q}-\frac{\partial U}{\partial q}\frac{\partial}{\partial p}\chi\right]\right\}=0 \tag{9.40}$$

There are six terms ; the third one being zero because it is a complete derivative. Then introducing the spatial fields

$$n(q,t)=\int dp\,\rho_1(q,p,t) \tag{9.41}$$

$$\langle\chi(q,t)\rangle=\frac{1}{n(q,t)}\int dp\,\rho_1(q,p,t)\chi(q,p,t) \tag{9.42}$$

we find

$$\frac{\partial n\langle\chi\rangle}{\partial t}+\frac{\partial}{\partial q}\left(n\left\langle\frac{p}{m}\chi\right\rangle\right)-n\left\langle\frac{\partial\chi}{\partial t}\right\rangle-n\left\langle\frac{p}{m}\frac{\partial\chi}{\partial q}\right\rangle+n\frac{\partial U}{\partial q}\left\langle\frac{\partial\chi}{\partial p}\right\rangle=0 \tag{9.43}$$

The conservation of particles is obtained from setting $\chi=1$. The three last terms are null, hence

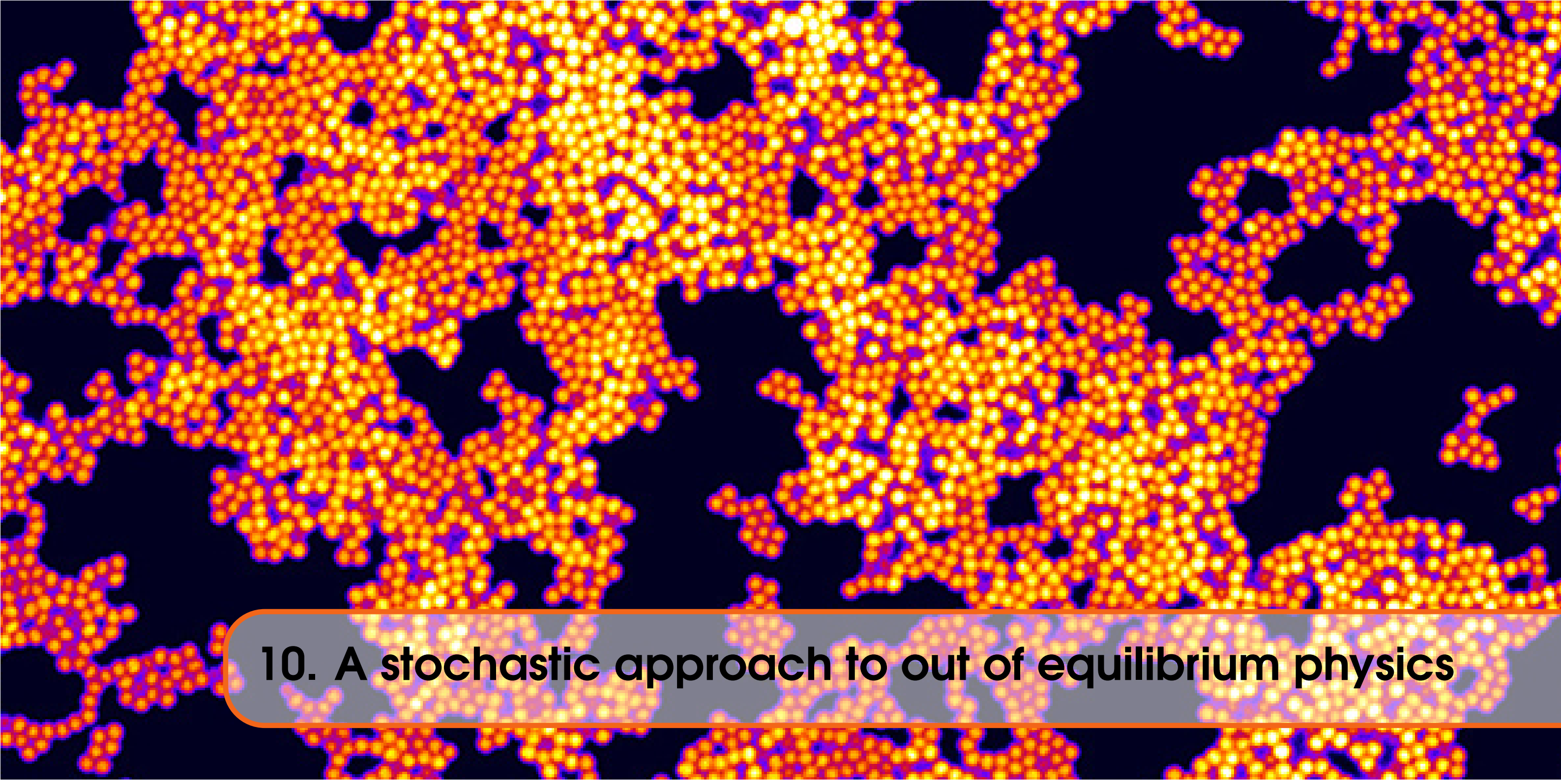
$$\frac{\partial n}{\partial t}+\frac{\partial nu}{\partial q}=0 \quad \text{with} \quad u\equiv\left\langle\frac{p}{m}\right\rangle \tag{9.44}$$

The conservation of momentum is obtained from setting $\chi=\frac{p}{m}-u$. After some lines of algebra, one obtains

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial q}=-\frac{1}{m}\frac{\partial U}{\partial q}-\frac{1}{mn}\frac{\partial\sigma}{\partial q} \quad \text{with} \quad \sigma\equiv mn\langle c\otimes c\rangle \tag{9.45}$$

Identifying σ with the stress tensor, one recognizes the two Navier-Stokes equations.

One sees that solving the hydrodynamics equations for n and u requires a closed form expression for σ. This one can also been obtain from the knowledge of ρ_1, solution of the Boltzmann equation. There are however further assumptions to consider, including the so-called local equilibrium, which we will not address in this course. The interested reader can go and look for these developments in the book *Statistical Physics of Particles*, already quoted above.



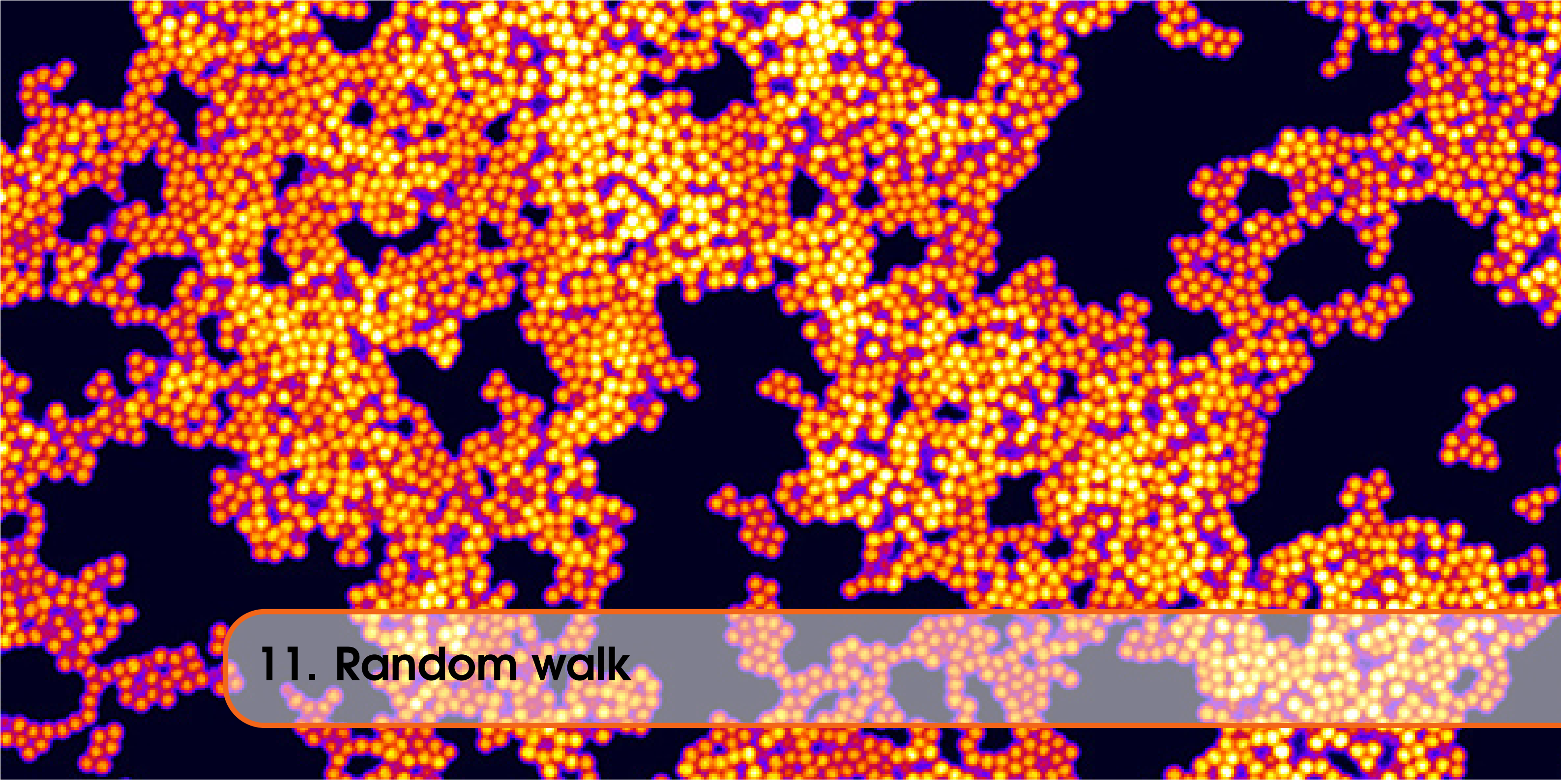
10. A stochastic approach to out of equilibrium physics

Equilibrium statistical physics gives the probability to observe a system in a given microscopic state. Here, we ask: how does a system evolve from a particular state towards the equilibrium probability distribution? Or, alternatively, what is the correlation between the microscopic state at time t and the microscopic state at a later time t'?

To answer these questions, we need to introduce a *dynamics* for the system, which is a law that rules its evolution. The dynamics should of course be compatible with the equilibrium probability distribution. In particular, it cannot be deterministic, in which case the probability distribution would be concentrated on a single state. The dynamics should thus contain a random term: it should be *stochastic*. Then, to a stochastic dynamics for the state of a system $x(t)$ can be associated a deterministic dynamics for the probability density $p(x,t)$.

How can a stochastic dynamics emerge for systems with a deterministic dynamics, such as Newtonian dynamics or the Liouville equation? In principle, we can write down a deterministic dynamics for *all the degrees of freedom* of the system, which is often impossible. A stochatic dynamics naturally appears if we are interested in only a part of the system, such as the hydrodynamic variables of a fluid, or the position of a colloid in a fluid. In these cases, the “hidden” part of the system generates noise (but not only noise, as we shall see), on the observed part.

Here, we do not derive stochastic equations from deterministic dynamics, but we write directly simple stochastic dynamics, and we analyse their behaviour. We then put constraints on these equations by enforcing the compatibility with equilibrium statistical physics. The dynamic approach allows us to discuss concepts such as microscopic reversibility, ergodicity, or free energy.



11. Random walk

11.1 Stochastic process

We introduce the simplest possible model to describe, for instance, the motion of a speck of dust (the particle) in the air. At time $t = 0$, the particle is at the origin: $x_0 = 0$. The particle moves on a lattice at discrete times: its position at time $t \in \mathbb{N}$ is given by $x_t \in \mathbb{Z}$ (Fig. 11.1). At each time, the particle moves by one unit to the left or to the right:

$$x_{t+1} = x_t + s_t, \tag{11.1}$$

where the jump s_t is -1 with probability $1/2$ and 1 with probability $1/2$. The jumps are independent. This is the first stochastic equation that we write.

We can write

$$x_t = \sum_{t'=0}^{t-1} s_{t'}, \tag{11.2}$$

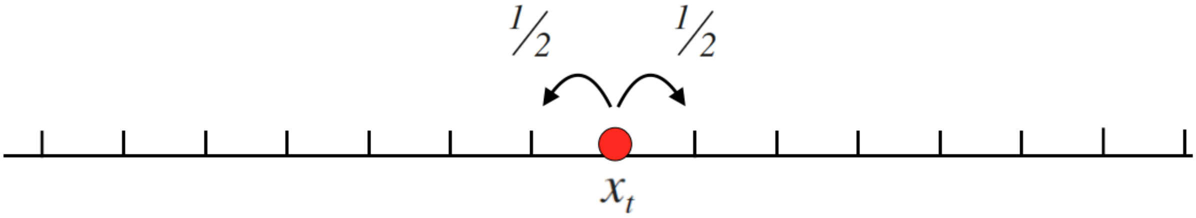


Figure 11.1 – Marche à aléatoire à temps discret sur $\mathbb{Z}$

which allows us to compute the mean and the variance of x_t:

$$\langle x_t \rangle = \sum_{t'=0}^{t-1} \langle s_{t'} \rangle = 0 \tag{11.3}$$

and

$$\begin{aligned}
\langle x_t^2 \rangle &= \left\langle \left(\sum_{t'=0}^{t-1} s_{t'} \right)^2 \right\rangle && (11.4)\\
&= \left\langle \sum_{t',t''=0}^{t-1} s_{t'} s_{t''} \right\rangle && (11.5)\\
&= \sum_{t',t''=0}^{t-1} \langle s_{t'} s_{t''} \rangle && (11.6)\\
&= \sum_{t',t''=0}^{t-1} \delta_{t',t''} && (11.7)\\
&= t. && (11.8)
\end{aligned}$$

We have used that $\langle s_t^2 \rangle = 1$ and $\langle s_t s_{t'} \rangle = 0$ if $t \neq t'$.

11.2 Probability distribution

11.2.1 Exact solution, long-time limit

The position x_t of the particle describes the microscopic state of the system. As the state of the system is random, we may be interested at the probability $p_{x,t}$ to find the particle at a position x at time t, i.e., to find the system in a given state. We call $p_{x,t}$ the *probabilistic state* of the system.

For the random walk on $\mathbb{Z}$, the probability distribution is given by the binomial law:

$$p_{x,t} = \begin{cases} 2^{-t} \binom{t}{\frac{x+t}{2}} & \text{if } x+t \text{ is even,} \\ 0 & \text{if } x+t \text{ is odd.} \end{cases} \tag{11.9}$$

The condition on the parity of $x+t$ comes from the fact that the particle cannot be at an odd position after an even number of steps.

From the *central limit theorem*, the normalised position $y_t = x_t/\sqrt{t}$ converges in distribution to the standard normal distribution: its density satisfies

$$f_{y_t}(u) \underset{t\to\infty}{\longrightarrow} \frac{1}{\sqrt{2\pi}} e^{-u^2/2}, \tag{11.10}$$

which can be written in a non rigorous way

$$p_{x,t} \underset{t\to\infty}{\approx} \frac{1}{\sqrt{2\pi t}} e^{-x^2/(2t)}. \tag{11.11}$$

11.2.2 Evolution

In the following, we will be more interested in the *evolution* of the probability distribution, as it is easier to generalise to other systems. To be in x at time $t+1$, the particle should have been in $x-1$

or $x+1$ at time t, and the jump towards x has a probability $1/2$, hence

$$p_{x,t+1} = \frac{p_{x-1,t}+p_{x+1,t}}{2}. \tag{11.12}$$

This is the first of the evolution equations for a probability distribution that we will see. We make a few remarks that remain true for other evolution equations. First, we write the difference between the distribution at time $t+1$ and the distribution at time t:

$$p_{x,t+1} - p_{x,t} = \frac{1}{2}p_{x-1,t} - p_{x,t} + \frac{1}{2}p_{x+1,t}. \tag{11.13}$$

This is the "*master equation*" of the problem.

The master equation is linear and can be written

$$p_{x,t+1} - p_{x,t} = \sum_{y\in\mathbb{Z}} M_{xy} p_{y,t}, \tag{11.14}$$

where M is a matrix (of infinite size), here given by

$$M_{xy} = \frac{1}{2}\delta_{x-1,y} - \delta_{x,y} + \frac{1}{2}\delta_{x+1,y}. \tag{11.15}$$

The probability is conserved ($\sum_x p_{x,t} = 1\ \forall t$) for every initial probability distribution, which implies

$$\sum_{x\in\mathbb{Z}} M_{xy} = 0. \tag{11.16}$$

With this matrix formulation, we can write the probability distribution at time t as

$$p_{x,t} = \sum_{y\in\mathbb{Z}} (\mathbf{1}+M)^t_{xy} p_{x,0}, \tag{11.17}$$

where $\mathbf{1}$ is the identity matrix.

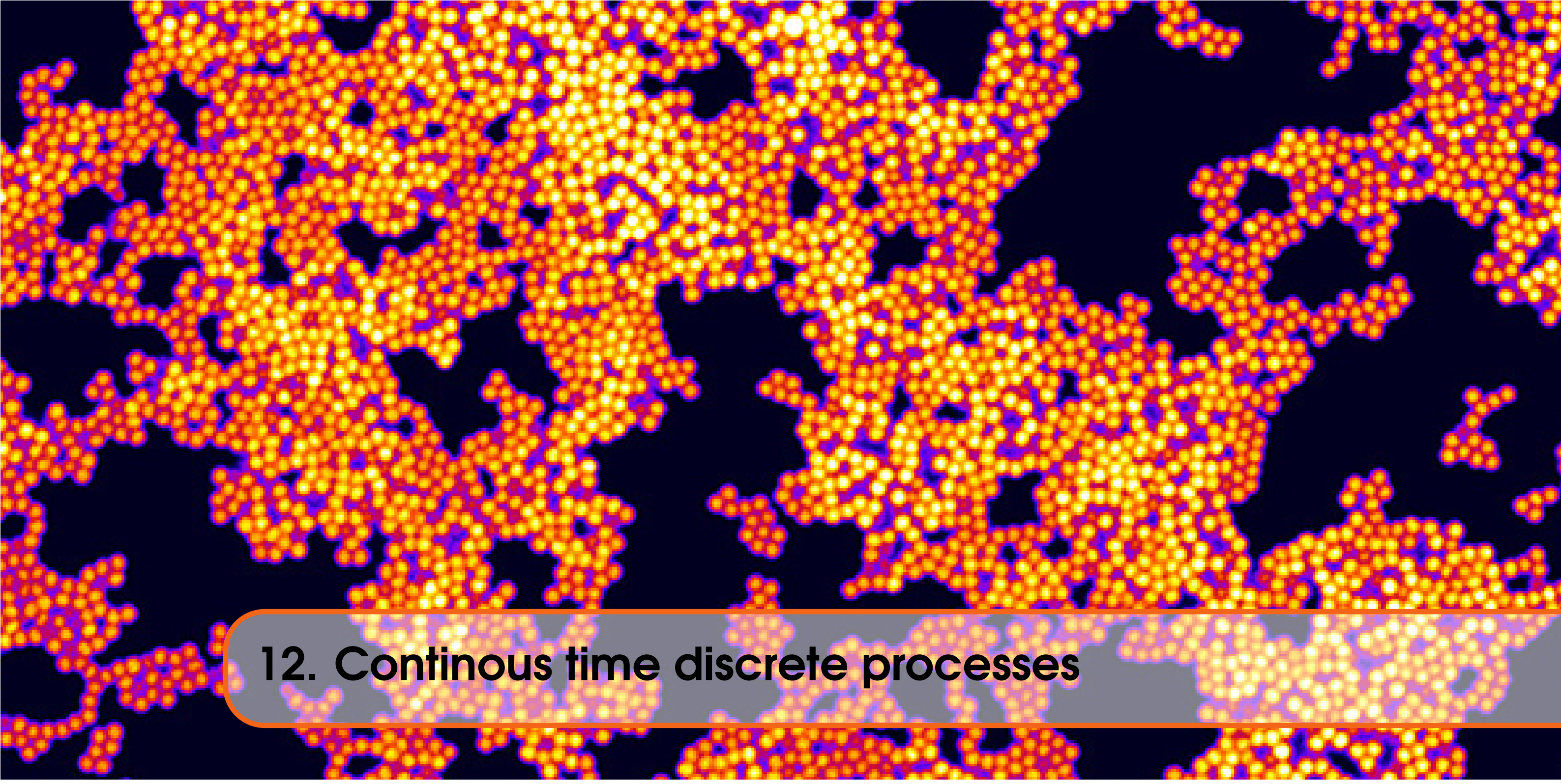
11.2.3 Stationnary solution

Last, we should check that the equilibrium distribution of our dynamics is given by the Gibbs-Boltzmann equilibrium distribution. Unfortunately, there is no equilibrium distribution for a random walk where all the positions are equiprobable. The condition for a distribution to be stationnary is

$$\forall x, \quad \sum_{y\in\mathbb{Z}} M_{xy} p^*_y = 0. \tag{11.18}$$

It is easy to check that there is no normalized stationnary distribution for the operator (11.15) associated to the random walk.

The probability conservation (11.16) means that the vector U, the components of which are all equal to one, is a left eigenvector for M with eigenvalue zero: $U^{\mathrm{t}}M = 0$, or $M^{\mathrm{t}}U = 0$. Since M and M^{t} have the same eigenvalues, there exists an eigenvector p^* of M with eigenvalue zero. If p^* can be normalized, it is the stationnary distribution.



12. Continous time discrete processes

12.1 Examples: continuous time lattice random walks

12.1.1 Random walk on $\mathbb{Z}$

We will see that it is easier to work with a continuous time, where the master equation (11.13) becomes a differential equation. We still consider a random walk on $\mathbb{Z}$, but now the particle can jump to the right or to the left with a probability $\delta t/2$ in a time interval δt (Fig. 12.1). The master equation reads now

$$p_x(t+\delta t) = (1-\delta t)p_x(t) + \frac{\delta t}{2}p_{x-1}(t) + \frac{\delta t}{2}p_{x+1}(t), \tag{12.1}$$

which becomes a differential equation in the limit $\delta t \to 0$:

$$\begin{aligned} \dot{p}_x(t) &= \frac{1}{2}p_{x-1}(t) - p_x(t) + \frac{1}{2}p_{x+1}(t), & (12.2)\\ &= \sum_y M_{xy}p_y(t), & (12.3) \end{aligned}$$

where the operator M is still given by (11.15). The probability distribution at time t can be written from the probability distribution at time 0:

$$p(t) = \mathrm{e}^{tM}p(0), \tag{12.4}$$

where $p(t)$ is seen as a vector with components $p_x(t)$.

12.1.2 Random walk on a circle

Let's now move to a process that admits a stationnary solution. We consider N sites disposed on a circle, which amounts to identify the sites N and 0 (this can be seen as a random walk on $\mathbb{Z}/N\mathbb{Z}$,

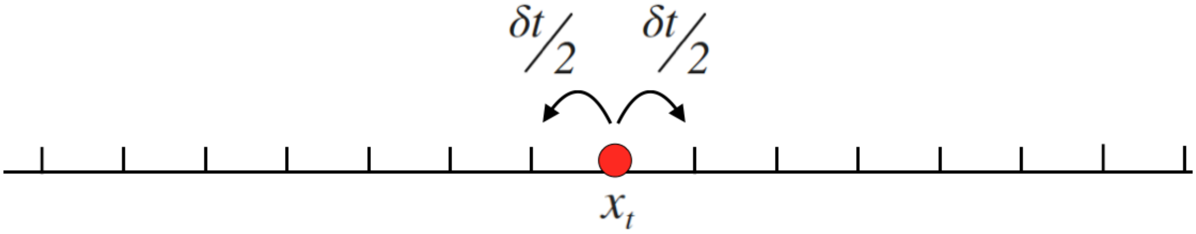


Figure 12.1 – Continuous time random walk on $\mathbb{Z}$.

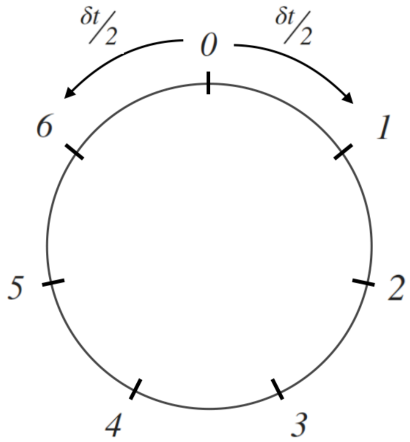


Figure 12.2 – Symmetric oriented continuous time random walk on a circle.

Fig. 12.2). The master equation is still given by (12.3), with the operator given by (11.15) where we have remplaced $-1 \to N-1$ and $N \to 0$. For instance, for $N = 6$, this matrix reads

$$M = \begin{pmatrix} -1 & 1/2 & 0 & 0 & 0 & 1/2 \\ 1/2 & -1 & 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & -1 & 1/2 & 0 & 0 \\ 0 & 0 & 1/2 & -1 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 & -1 & 1/2 \\ 1/2 & 0 & 0 & 0 & 1/2 & -1 \end{pmatrix}. \tag{12.5}$$

We can check that the sum of the coefficients over each column is zero.

It is easy to check that the uniform distribution, $p_x = 1/N \ \forall x$, is a stationnary distribution. This distribution corresponds to the Gibbs-Boltzmann equilibrium distribution for a uniform energy on the N sites of the circle.

12.1.3 Oriented random walk on a circle

We consider N sites disposed on a circle, but now the particle can only hop "to the right" (from site x to site $x+1$, or from site $N-1$ to site 0), with probability δt during the time interval δt

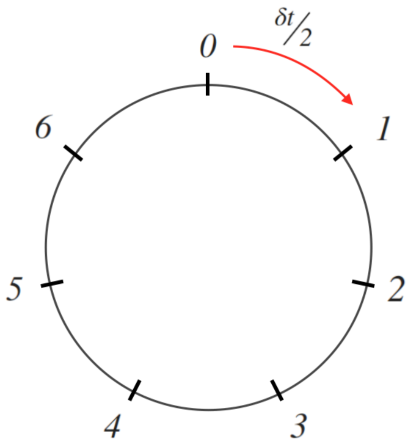


Figure 12.3 – Oriented continuous time random walk on a circle.

(Fig. 12.3). The associated matrix is now, for $N = 6$,

$$M = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{pmatrix}. \tag{12.6}$$

The uniform distribution is still stationnary for this dynamics, but, as we will see, the situation is different from the symmetric random walk.

12.2 Probability current, stationnary state and equilibrium state

Here we consider the general situation for a discrete system with a continous time. The possible states for a system are identified by $i \in \{1, \dots, N\}$ and the system can go from state i to state j with a *transition rate* $k_{j\leftarrow i}$: if the system is in state i at time t, it will be in state $j \neq i$ at time $t + \delta t$ with probability $k_{j\leftarrow i}\delta t$ (Fig. 12.4). The master equation still takes the form (12.3), and the coefficients of the matrix M are given by the transition rates:

$$M_{ij} = k_{i\leftarrow j}. \tag{12.7}$$

In order to satisfy the probability conservation (11.16), we define

$$k_{i\leftarrow i} = -\sum_{j\neq i} k_{j\leftarrow i}. \tag{12.8}$$

The right hand side represents the "leak" from i to other possible states.

When the system has the probability distribution p_i, we define the *probability current* from i to j by

$$j_{j\leftarrow i} = k_{j\leftarrow i}p_i - k_{i\leftarrow j}p_j. \tag{12.9}$$

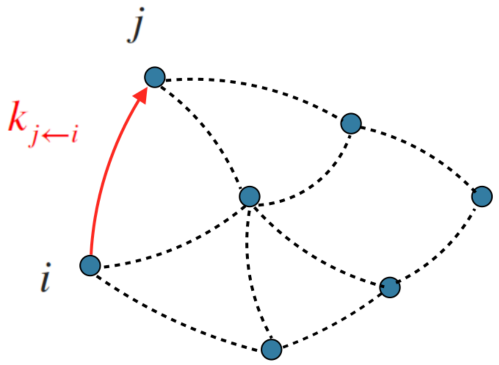


Figure 12.4 – General system with discrete states.

The first term corresponds to the transition from i to j, and the second term to the opposite transition, from j to i. We can write

$$\dot{p}_i = \sum_j k_{i\leftarrow j} p_j = \sum_{j\neq i} k_{i\leftarrow j} p_j + k_{i\leftarrow i} p_i \tag{12.10}$$

$$= \sum_{j\neq i} k_{i\leftarrow j} p_j - \sum_{j\neq i} k_{j\leftarrow i} p_i \tag{12.11}$$

$$= \sum_{j\neq i} j_{i\leftarrow j}. \tag{12.12}$$

In particular, in a stationnary state, for any state i, $\sum_{j\neq i} j_{i\leftarrow j} = 0$, the probability current towards the site i is zero.

Let's compute the probability current for the two random walks on a circle for the uniform distribution, which is stationnary. For the symmetric walk, the current from site 0 to state 1 is

$$j_{1\leftarrow 0} = k_{1\leftarrow 0} p_0 - k_{0\leftarrow 1} p_1 = 0. \tag{12.13}$$

For the oriented walk, we have instead

$$j_{1\leftarrow 0} = k_{1\leftarrow 0} p_0 - k_{0\leftarrow 1} p_1 = 1/N. \tag{12.14}$$

The nature of the stationnary state depends on the process: for the symmetric walk, the probability current vanishes, while there is a current "to the right" for the oriented walk. As the equations ruling the motion of atoms and molecules, such as the Newton equation, are reversible, the system is said to be *at equilibrium* only if the probability current vanishes. Otherwise we just say that the system is in a *stationnary state*.

12.3 Random walk in an energy landscape, detailed balance

Up to now, we have only considered dynamics with a uniform stationnary distribution. Now we look at the conditions under which the equilibrium distribution is the Boltzmann distribution for energies (E_i) for a system that can exchange energy with a reservoir:

$$p_i^{\mathrm{eq}} = \frac{1}{Z} \exp\left(-\frac{E_i}{T}\right), \tag{12.15}$$

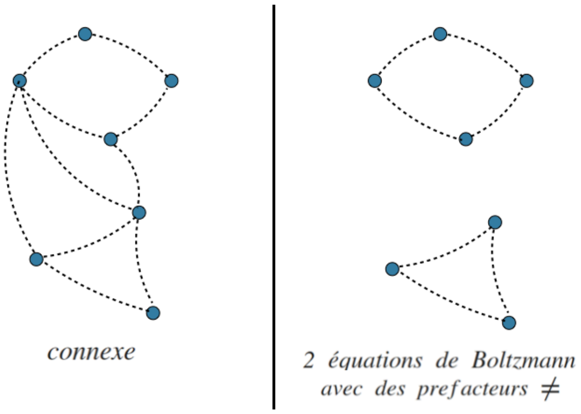


Figure 12.5 – Connected graph (left) and non connected graph (right).

where the Boltzmann constant has been set to one and Z is the canonical partition function, $Z = \sum_i \exp(-E_i/T)$. Using the equilibrium distribution in the definition (12.9) of the probability current, and assuming that the system is at equilibrium ($j_{i\leftarrow j}$ $\forall i, j$), we get the *detailed balance* condition:

$$k_{j\leftarrow i} e^{-E_i/T} = k_{i\leftarrow j} e^{-E_j/T}. \tag{12.16}$$

We note that the detailed balance condition is satisfied if the transition rates are zero: $k_{j\leftarrow i} = k_{i\leftarrow j} = 0$. This is not a problem, but in order to be able to reach equilibrium, the space of states should be *connected*, namely it should be possible to go from i to j for all i and j, possible through other states (Fig:connexe). This is the *ergodic hypothesis*, which states that the system is able to explore all the possible states (or, for a continuous phase space, that the trajectory of the system is dense in the phase space). For instance, the random walks on $\mathbb{Z}$ or on a circle are connected.

Infinitely many dynamics satisfy the detailed balance condition (12.16). In order to define a dynamics, we start by defining a graph of states, which represents the states that are directly connected together: $g_{ij} = 1$ if the states are connected (e.g., $k_{i\leftarrow j} \neq 0$ and $k_{j\leftarrow i} \neq 0$) and $g_{ij} = 0$ otherwise. Then, we define the rates for the connected states. Two common choices are

- Glauber dynamics:

  $$k_{i\leftarrow j} = g_{ij} \exp\left(-\frac{E_i}{T}\right). \tag{12.17}$$

  Here the transition rate depends only on the final state of the transition.
- Metropolis dynamics:

  $$k_{i\leftarrow j} = \begin{cases} g_{ij} & \text{si } E_i < E_j, \\ g_{ij} \exp(-[E_i - E_j]/T) & \text{si } E_i > E_j. \end{cases} \tag{12.18}$$

  Here the transition rate depends on the energy difference.

These dynamics can be used to

- Look for the minimum of a function without being trapped in local minima; this is the “simulated annealing” method.
- Explore a complex phase space in order to compute thermodynamic averages, e.g., for the Ising model.

12.4 Evolution of the free energy

The average energy in the probabilistic state p_i is

$$U = \sum_i p_i E_i, \tag{12.19}$$

and the entropy is given by

$$S = -\sum p_i \log(p_i). \tag{12.20}$$

The free energy is thus

$$F = U - TS = \sum_i p_i [E_i + T\log(p_i)]. \tag{12.21}$$

Let's compute the evolution of the free energy

$$\begin{aligned}
\dot{F} &= \sum_i [E_i + T\log(p_i) + T]\dot{p}_i, && (12.22)\\
&= \sum_i [E_i + T\log(p_i) + T] \sum_{j\neq i} j_{i\leftarrow j}, && (12.23)\\
&= \sum_{a\in\mathscr{A}} \left([E_{a_1} + T\log(p_{a_1}) + T] j_{a_1\leftarrow a_2} + [E_{a_2} + T\log(p_{a_2}) + T] j_{a_2\leftarrow a_1}\right), && (12.24)\\
&= \sum_{a\in\mathscr{A}} [E_{a_1} + T\log(p_{a_1}) - E_{a_2} - T\log(p_{a_2})]\, j_{a_1\leftarrow a_2}, && (12.25)
\end{aligned}$$

where $\mathscr{A}$ is the set of the edges of the graph of connected states, $a \in \mathscr{A}$ is an edge and a_1 and a_2 are the ends of the edge a. The probability current on the edge a, between the states (or nodes) a_1 and a_2, is

$$j_{a_1\leftarrow a_2} = k_{a_1\leftarrow a_2} p_{a_2} - k_{a_2\leftarrow a_1} p_{a_1} = k_a \left(e^{E_{a_2}/T} p_{a_2} - e^{E_{a_1}/T} p_{a_1}\right), \tag{12.26}$$

where

$$k_a = \mathrm{e}^{-E_{a_2}/T} k_{a_1\leftarrow a_2} = \mathrm{e}^{-E_{a_1}/T} k_{a_2\leftarrow a_1} \tag{12.27}$$

from the detailed balance condition (12.16). Using this expression in the free energy evolution (12.25), we get

$$\dot{F} = -\sum_{a\in\mathscr{A}} k_a [E_{a_1} + T\log(p_{a_1}) - E_{a_2} - T\log(p_{a_2})] \left[e^{E_{a_1}/T} p_{a_1} - e^{E_{a_2}/T} p_{a_2}\right]. \tag{12.28}$$

Introducing the "local free energy"

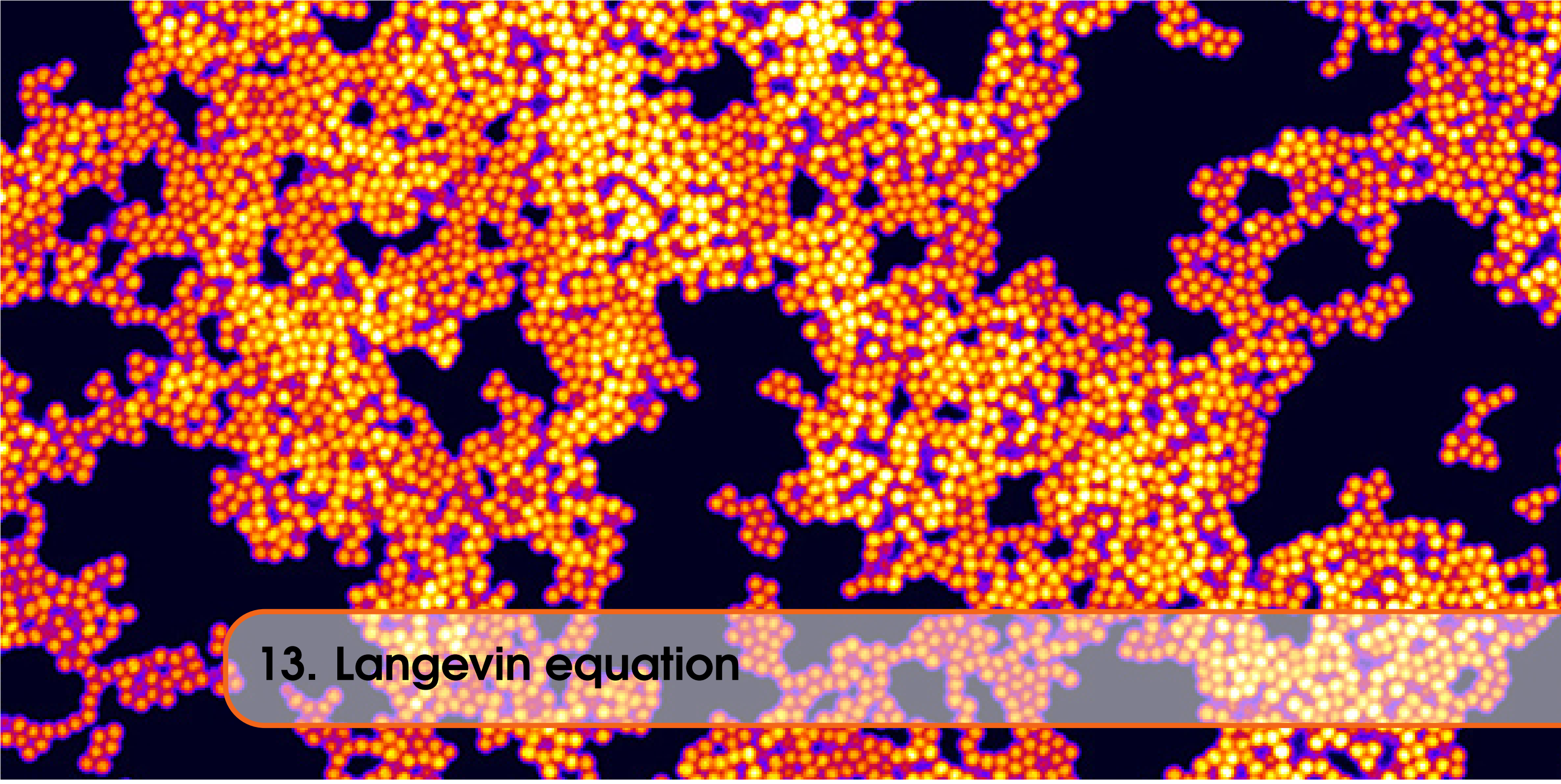
$$f_i = E_i + T\log(p_i), \tag{12.29}$$

we can write the evolution of free energy as

$$\dot{F} = -\sum_{a\in\mathscr{A}} k_a (f_{a_1} - f_{a_2}) \left(e^{f_{a_1}/T} - e^{f_{a_2}/T}\right) \leq 0. \tag{12.30}$$

The inequality comes from the fact that the exponential is an increasing function: for an increasing function f, $(x-y)\times[f(x)-f(y)] \geq 0$.

The free energy decreases with time: it is a *Lyapunov function* of the master equation (12.3). Its existence garanties that the thermodynamic equilibrium is stable.



13. Langevin equation

We introduce a stochastic equation of motion in continuous time and space.

13.1 White noise

We want to write a continous counterpart of the random walk introduced in Sec. 11.1. The properties of the jumps s_t are: $\langle s_t\rangle = 0$ and $\langle s_t s_{t'}\rangle = \delta_{t,t'}$, where δ is the Kronecker symbol. The *white noise* is a continuous version of these discrete jumps: it is a random function $\eta(t)$ satisfying

$$\langle \eta(t)\rangle = 0, \tag{13.1}$$

$$\langle \eta(t)\eta(t')\rangle = \delta(t-t'), \tag{13.2}$$

where now δ is the Dirac distribution. The probability distribution of $\eta(t)$ is usually assumed to be Gaussian, but we will not use it here. The white noise is termed "white" because its spectrum, i.e., the Fourier transform of its correlation (13.2), is uniform, as the white light spectrum. For a different correlation function, the noise would be called "colored".

The stochastic process defined as

$$\dot{x}(t) = \eta(t) \tag{13.3}$$

is the *Wiener process*, or *Brownian motion*. In order to illustrate the correlation function (13.2), let's compute the variance of $x(t)$ for a process starting at the origin, $x(0) = 0$:

$$\langle x(t)^2\rangle = \left\langle \left(\int_0^t \eta(t')\mathrm{d}t'\right)^2\right\rangle, \tag{13.4}$$

$$= \int_0^t \int_0^t \langle \eta(t')\eta(t'')\rangle \mathrm{d}t'\mathrm{d}t'', \tag{13.5}$$

$$= \int_0^t \int_0^t \delta(t'-t'')\mathrm{d}t'\mathrm{d}t'', \tag{13.6}$$

$$= t. \tag{13.7}$$

13.2 Langevin equation

13.2.1 Definition

Now that we have defined “mathematically” the white noise, we see how to incorporate it in an equation of motion accounting for the inertia of the considered particle and an external force. First, let’s discuss the physical meaning of the white noise. Consider a small particle (a colloid) in a liquid. Momentum is exchanged during the collisions of the liquid molecules with the colloid, and the colloid moves in a straight line between two collisions. Assuming that the momentum transfer is random, and that the time between two collisions is very short, we can model the collisions as a “noise” to add in the equation of motion of the colloid, which we write

$$m\ddot{x}(t) = -\lambda\dot{x}(t) + f(x(t),t) + a\eta(t). \tag{13.8}$$

λ is a friction coefficient, $f(x,t)$ is an external force depending on space and time and a is a coefficient setting the amplitude of the noise. The correlation function of the noise is still given by (13.2). This is the *Langevin equation*.

The Langevin equation seems very different from the Brownian motion (13.3) because it is of second order in time. We will see that this difference does not affect fundamentally the dynamics of the particle.

13.2.2 Mean squared displacement without external force

Without external force, the Langevin equation (13.8) is linear, and is solved by

$$x(t) = x(0) + \tau\left(1 - \mathrm{e}^{-t/\tau}\right)\dot{x}(0) + \frac{a}{\lambda}\int_0^t \left(1 - \mathrm{e}^{-\frac{t-t'}{\tau}}\right)\eta(t')\mathrm{d}t', \tag{13.9}$$

where we have defined the characteristic damping time

$$\tau = \frac{m}{\lambda}. \tag{13.10}$$

We compute, as before, the mean squared displacement. Setting $x(0) = 0$, since the initial velocity $v(0)$ is independent of the noise during the interval $[0,t]$, we find

$$\langle x(t)^2\rangle = \tau^2\left(1 - \mathrm{e}^{-t/\tau}\right)^2\langle\dot{x}(0)^2\rangle + \frac{a^2}{\lambda^2}\int_0^t\int_0^t \left(1 - \mathrm{e}^{-\frac{t-t'}{\tau}}\right)\left(1 - \mathrm{e}^{-\frac{t-t''}{\tau}}\right)\langle\eta(t')\eta(t'')\rangle\mathrm{d}t'\mathrm{d}t'' \tag{13.11}$$

$$= \tau^2\left(1 - \mathrm{e}^{-t/\tau}\right)^2\langle\dot{x}(0)^2\rangle + \frac{a^2}{\lambda^2}\left[t - 2\tau\left(1 - \mathrm{e}^{-t/\tau}\right) + \frac{\tau}{2}\left(1 - \mathrm{e}^{-2t/\tau}\right)\right]. \tag{13.12}$$

From this heavy expression we can identify two regimes:

$$\langle x(t)^2\rangle \underset{t\ll\tau}{\sim} \langle\dot{x}(0)^2\rangle t^2, \tag{13.13}$$

$$\langle x(t)^2\rangle \underset{t\gg\tau}{\sim} \frac{a^2}{\lambda^2}t = 2Dt. \tag{13.14}$$

At short time ($t \ll \tau$), the motion is ballistic: the particle moves in a straight line at constant speed $v(0)$. At long time ($t \gg \tau$), the motion is diffusive: the initial velocity is damped, the motion is due to the noise and takes the same form as for the Brownian motion (see (13.7)). We have defined the *diffusion coefficient* $D = a^2/(2\lambda^2)$; it is more convenient to use than a, and we will use it instead of a from now on. Note that the diffusion coefficient does not depend on the mass of the particle.

13.2.3 Small inertia limit

We have seen in the previous paragraph that the inertia of the particle has effects only for observation times smaller than the damping time $\tau = m/\lambda$. For small particles, this time is not accessible to observation and inertia can be neglected in the odel. The Langevin equation (13.8) becomes

$$\dot{x}(t) = \frac{1}{\lambda} f(x(t),t) + \sqrt{2D}\eta(t), \tag{13.15}$$

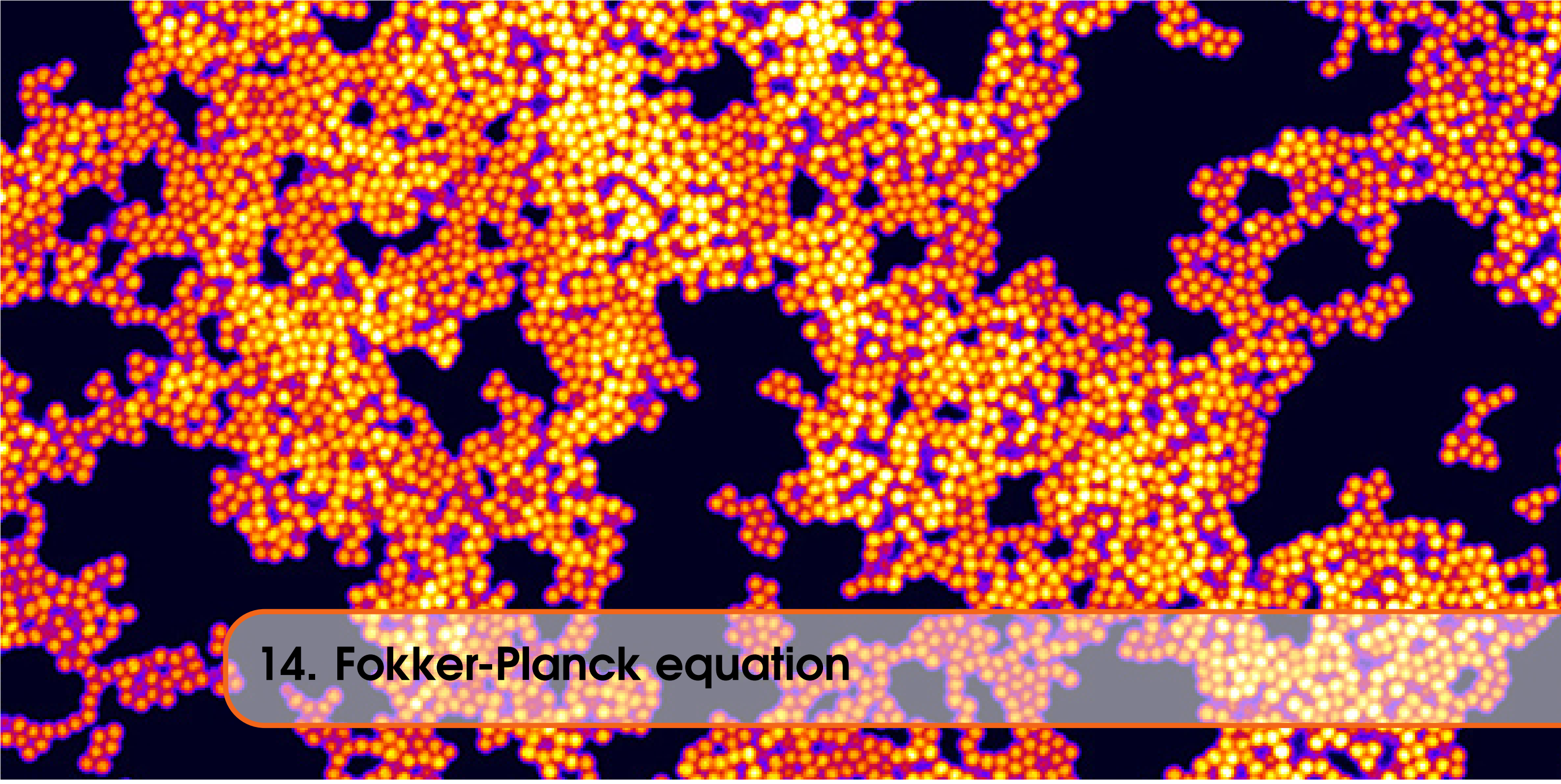
this is the *overdamped* Langevin equation.

Without external force, the solution (13.9) of the Langevin equation becomes in the overdamped regime

$$x(t) = x(0) + \sqrt{2D}\int_0^t \eta(t')\mathrm{d}t', \tag{13.16}$$

and the mean squared displacement (13.12) is now

$$\left\langle x(t)^2 \right\rangle = 2Dt. \tag{13.17}$$



14. Fokker-Planck equation

14.1 Derivation

We consider a motion described by the overdamped Langevin equation (13.15) and we look for an equation for the probability density $p(x,t)$. For a given function $g(x)$, we are interested in the average

$$\langle g(x(t))\rangle = \int g(x)p(x,t)\mathrm{d}x. \tag{14.1}$$

We compute the evolution of this average by two different routes. First, we write it with the evolution of the probability density:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle g(x(t))\rangle = \int g(x)\dot{p}(x,t)\mathrm{d}x. \tag{14.2}$$

Second, we use the Langevin equation:

$$\begin{aligned}
\langle g(x(t+\delta t))\rangle &= \left\langle g\left(x(t)+\frac{f(x(t),t)}{\lambda}\delta t+\sqrt{2D}\int_t^{t+\delta t}\eta(t')\mathrm{d}t'+o(\delta t)\right)\right\rangle, && (14.3)\\
&= \langle g(x(t))\rangle+\left\langle g'(x(t))\left[\frac{f(x(t),t)}{\lambda}\delta t+\sqrt{2D}\int_t^{t+\delta t}\eta(t')\mathrm{d}t'\right]\right\rangle && (14.4)\\
&\quad +\left\langle\frac{1}{2}g''(x(t))\left[\frac{f(x(t),t)}{\lambda}\delta t+\sqrt{2D}\int_t^{t+\delta t}\eta(t')\mathrm{d}t'\right]^2\right\rangle+o(\delta t) && (14.5)\\
&= \langle g(x(t))\rangle+\left\langle g'(x(t))\frac{f(x(t),t)}{\lambda}\right\rangle\delta t+\frac{1}{2}\left\langle g''(x(t))\right\rangle\times 2D\delta t+o(\delta t). && (14.6)
\end{aligned}$$

We have used the following properties:

- the noise on the interval $[t, t+\delta t]$ is independent of the position at time t (this is the *Itō convention*, opposed to the *Stratonovich convention*, where the noise and the position are correlated),
- the average of the noise is zero, and its correlation is given by (13.2).

We deduce

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle g(x(t))\rangle = \frac{1}{\lambda}\left\langle g'(x(t))f(x(t),t)\right\rangle + D\left\langle g''(x(t))\right\rangle \tag{14.7}$$

$$= \int \left[\frac{1}{\lambda}g'(x)f(x,t) + Dg''(x)\right]p(x,t)\mathrm{d}x, \tag{14.8}$$

$$= \int g(x)\left[-\frac{1}{\lambda}fp + Dp'\right]'(x,t)\mathrm{d}x. \tag{14.9}$$

We have integrated by parts to get the last line. The equations (14.2) and (14.9) hold for any function $g(x)$, hence we can identify the evolution of the probability distribution:

$$\dot{p}(x,t) = -\left[\frac{1}{\lambda}fp - Dp'\right]'(x,t). \tag{14.10}$$

The generalisation to any dimension of space is straightforward:

$$\dot{p}(x,t) = -\nabla\cdot\left[\frac{1}{\lambda}f(x,t)p(x,t) - D\nabla p(x,t)\right]. \tag{14.11}$$

This is the *Fokker-Planck equation*.

We note that the probability variation is written as the divergence of a probability current (or flux):

$$\dot{p}(x,t) = -\nabla\cdot j(x,t), \tag{14.12}$$

$$j(x,t) = \frac{1}{\lambda}f(x,t)p(x,t) - D\nabla p(x,t). \tag{14.13}$$

The probability current is the sum of a *convective* term and a *diffusive* term.

14.2 Equilibrium

We look for the equilibrium solution of the Fokker-Planck equation when the force derives from a potential:

$$f(x) = -\nabla V(x). \tag{14.14}$$

We have seen that the probability current must vanish at equilibrium: we thus look for a probability distribution $p^{\mathrm{eq}}(x)$ that satisfies

$$j(x,t) = -\frac{1}{\lambda}p^{\mathrm{eq}}(x)\nabla V(x) - D\nabla p^{\mathrm{eq}}(x) = 0. \tag{14.15}$$

Dividing by $p^{\mathrm{eq}}(x)$, we get

$$\nabla\log(p^{\mathrm{eq}}(x)) = -\frac{1}{\lambda D}\nabla V(x), \tag{14.16}$$

hence

$$p^{\mathrm{eq}}(x) = \frac{1}{Z}\exp\left(-\frac{V(x)}{\lambda D}\right). \tag{14.17}$$

Z is a normalisation constant.

This equilibrium distribution is the Boltzman distribution, $Z^{-1}\exp(-V(x)/(k_B T))$, if

$$D = \frac{k_B T}{\lambda}. \tag{14.18}$$

This is the *Einstein relation*. It is a fluctuation-dissipation relation: it relates the amplitude of the fluctuations (given by the diffusion coefficient D) and the dissipation (given by the friction coefficient λ).

14.3 Evolution of the free energy

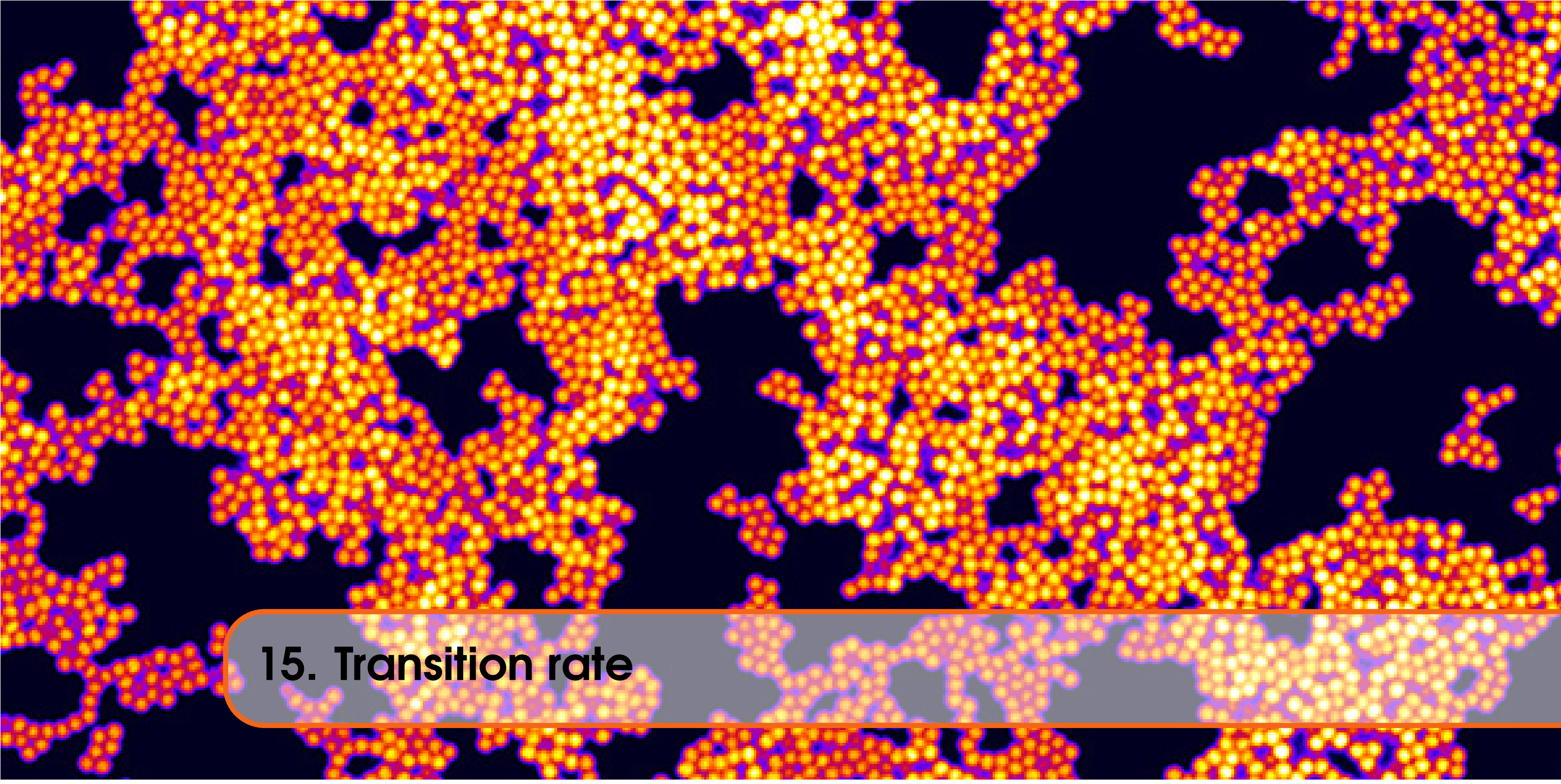
The free energy of a probability distribution $p(x)$ is given as in the discrete case (see (12.21)) by

$$F = U - TS = \int \left[V(x) + T\log(p(x))\right] p(x)\mathrm{d}x. \tag{14.19}$$

Let's compute the evolution of the free energy if the probability density follows the Fokker-Planck equation (we come back to a space of dimension 1):

$$\begin{aligned}
\dot{F}_t &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\int \left[V(x) + T\log(p(x,t))\right] p(x,t)\mathrm{d}x\right), && (14.20)\\
&= \int \dot{p}(x,t)\left[V(x) + T\log(p(x,t)) + T\right]\mathrm{d}x, && (14.21)\\
&= \int \left[\frac{1}{\lambda}V'p + Dp'\right]' \left[V + T\log(p) + T\right]\mathrm{d}x && (14.22)\\
&= -\int \left(\frac{1}{\lambda}V'p + Dp'\right)\left(V' + T\frac{p'}{p}\right)\mathrm{d}x && (14.23)\\
&= -\int \frac{p}{\lambda}\left(V' + T\frac{p'}{p}\right)^2 \mathrm{d}x && (14.24)\\
&\leq 0. && (14.25)
\end{aligned}$$

As in the discrete case, the free energy decreases with the time. The equality in the inequality above is reached when the current vanishes, i.e., at equilibrium.



15. Transition rate

15.1 Introduction

The escape from a meta-stable state due to a thermally activated event is ubiquitous. In chemistry, it can be associated to a chemical reaction. In this case, the rate of escape, or transition rate, is proportional to the reaction rate k. Arrhenius noted in 1889 that the rate of many chemical reactions depends on temperature as

$$k \sim \exp\left(-\frac{E_\mathrm{a}}{kT}\right), \tag{15.1}$$

where E_a is the activation energy. A consistent model to explain this dependence was introduced by Kramers in 1940: he describes the state of the system with a single continuous variable which undergoes a Brownian motion in a potential.

Here, we develop this approach: we consider a “particle” with an overdamped motion in a potential with two (meta)stable states (Fig. 15.1(a)). The density of probability of finding the particle at position x at time t, $p(x,t)$ follows the Fokker-Planck equation. We present different methods to derive the transition rate from one metastable state to the other.

The activated hopping across a potential barrier is analogous to tunnelling in quantum mechanics, which plays a role at smaller scales (e.g. in radioactive decay).

15.2 Kramers computation

The approach of Kramers is to compute the escape rate from a metastable state, “protected” by an energy barrier. The escape rate is computed using the “flux over population” method: we look for the stationnary density $p(x)$, with a uniform flux J, with an absorbing point a on the other side of the energy barrier. The rate k is then defined as the flux J divided by the population $\int_{-\infty}^{a} p(x)\mathrm{d}x$.

The flux is given by

$$J = -\frac{1}{\lambda}U'(x)p(x) - Dp'(x) = -D\left[u'(x)p(x) + p'(x)\right] = -De^{-u(x)}\partial_x\left[e^{u(x)}p(x)\right], \tag{15.2}$$

where we used Einstein's relation, $D = T/\lambda$ and introduced the reduced potential $u(x) = U(x)/T$. The absorbing barrier at a sets

$$p(a) = 0. \tag{15.3}$$

Integrating Eq. (15.2) between x and a, we get

$$p(x) = \frac{J}{D}e^{-u(x)}\int_x^a e^{u(x')}dx'. \tag{15.4}$$

$p(x)$ is not a probability density since it is not normalized; its integral is the *population*

$$n = \int_{-\infty}^a p(x)dx = \frac{J}{D}\int_{-\infty}^a\int_x^a e^{u(x')-u(x)}dx'dx. \tag{15.5}$$

The transition rate is then given by

$$k = \frac{J}{n} = D\left(\int_{-\infty}^a\int_x^a e^{u(x')-u(x)}dx'dx\right)^{-1}. \tag{15.6}$$

When the temperature is small enough compared the barrier height, the integral appearing in Eq. (15.6) can be computed with the saddle-point method. Its main contribution comes from $x = x_{\mathrm{min}}$ (local minimum of the potential—well) and $x' = x_{\mathrm{max}}$ (local maximum of the potential—barrier). Approximating the potential by parabolas close to these points, we get

$$\int_{-\infty}^a\int_x^a e^{u(x')-u(x)}dx'dx \simeq \frac{2\pi}{\sqrt{|u''(x_{\mathrm{min}})u''(x_{\mathrm{max}})|}}e^{u(x_{\mathrm{max}})-u(x_{\mathrm{min}})}. \tag{15.7}$$

Hence, the transition rate is

$$k \simeq \frac{\sqrt{|U''(x_{\mathrm{min}})U''(x_{\mathrm{max}})|}}{2\pi\lambda}e^{-\frac{U(x_{\mathrm{max}})-U(x_{\mathrm{min}})}{T}} \tag{15.8}$$

We recover the temperature dependence observed by Arrhenius, Eq. (15.1).

15.3 Smallest eigenvalue

Here, we look at the transition rates between the two wells of a double well potential. For this purpose, we compute the lowest non-vanishing eigenvalue of the Fokker-Planck operator and the corresponding eigenfunction. We show that there are intermediate time scales where the system can be mapped on a system with two states, and the dynamics described by transition rates between these two states.

This approach emphasizes the role of the spectrum of the matrix, or operator, entering in any master equation.

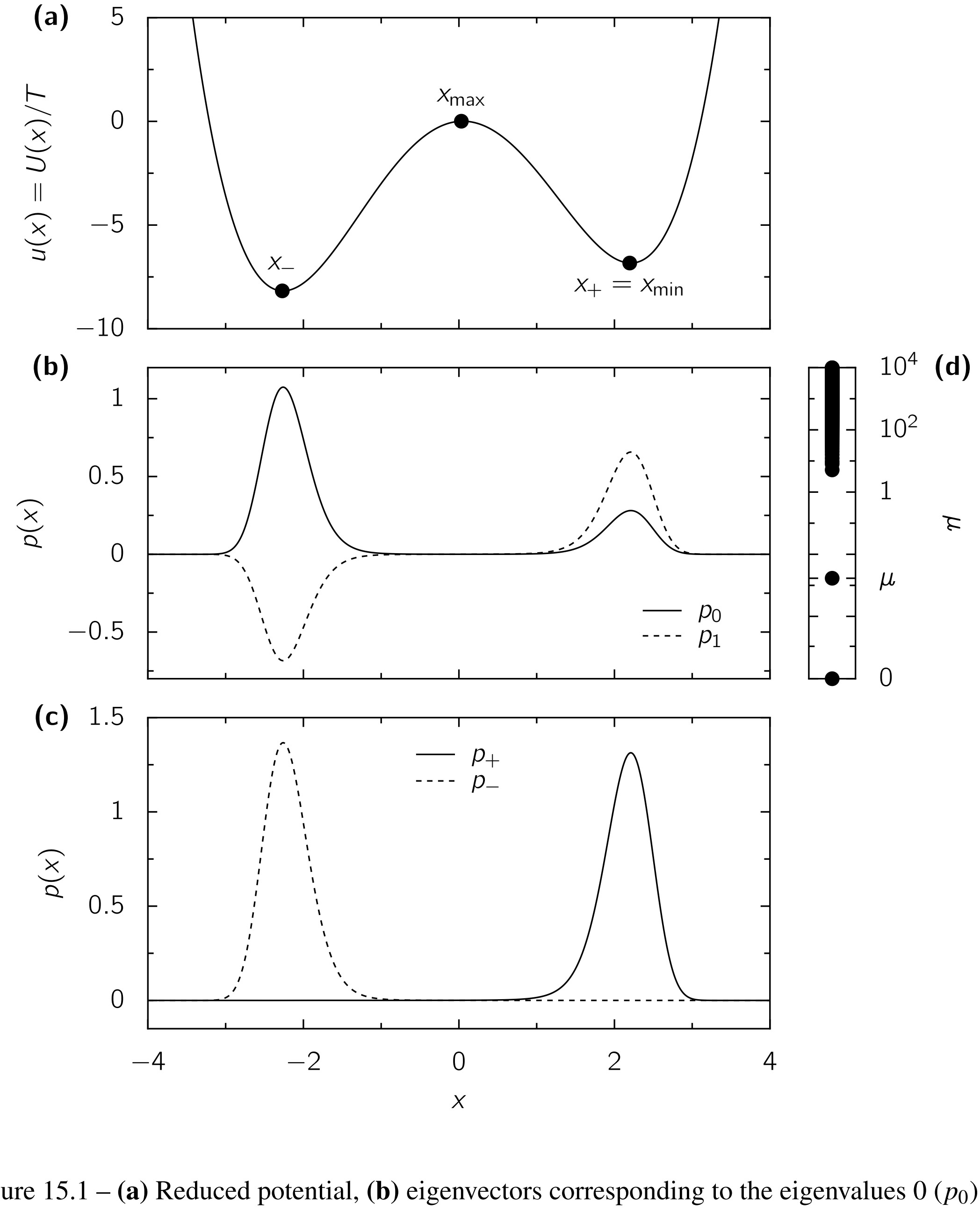


Figure 15.1 – **(a)** Reduced potential, **(b)** eigenvectors corresponding to the eigenvalues 0 (p_0) and μ (p_1), **(c)** Decomposition of the first two eigenvectors in densities localized in the left (p_-) and right (p_+) wells, **(d)** eigenvalues of the Fokker-Planck operator $\mathscr{L}$.

15.3.1 Fokker-Planck operator, definition and properties

First, we write the Fokker-Planck equation as

$$\partial_t p(x,t) = -D\mathscr{L}p(x,t), \tag{15.9}$$

where $\mathscr{L}$ is the Fokker-Planck operator,

$$\mathscr{L}p(x) = -\partial_x[u'(x)p(x) + p'(x)] = -\partial_x\left[\mathrm{e}^{-u(x)}\partial_x\left(\mathrm{e}^{u(x)}p(x)\right)\right]. \tag{15.10}$$

We are interested in the eigenvalues of the operator $\mathscr{L}$. We like self-adjoint operators since their eigenvalues are real. This is the case for $\mathscr{L}$: it is self-adjoint for the scalar product

$$\langle f,g\rangle = \int \mathrm{e}^{u(x)}f(x)g(x)\mathrm{d}x, \tag{15.11}$$

indeed,

$$\langle \mathscr{L}f,g\rangle = -\int \partial_x\left[\mathrm{e}^{-u(x)}\partial_x\left(\mathrm{e}^{u(x)}f\right)\right]\mathrm{e}^{u(x)}g(x)\mathrm{d}x \tag{15.12}$$

$$= \int \mathrm{e}^{-u(x)}\partial_x\left(\mathrm{e}^{u(x)}f(x)\right)\partial_x\left(\mathrm{e}^{u(x)}g(x)\right)\mathrm{d}x \tag{15.13}$$

$$= \langle f,\mathscr{L}g\rangle. \tag{15.14}$$

Moreover, the operator $\mathscr{L}$ is positive, $\langle \mathscr{L}f,f\rangle \geq 0$ (from Eq. (15.13)), hence its eigenvalues are positive. This was expected because the Fokker-Planck equation converges to the stationnary solution.

The equilibrium Boltzmann distribution, $p_0(x) = p_{\mathrm{eq}}(x) = Z^{-1}\mathrm{e}^{-u(x)}$, is the eigenvector of $\mathscr{L}$ associated to the eigenvalue 0. We are interested in the smallest non-vanishing eigenvalue μ and its associated eigenvector $p_1(x)$, $\mathscr{L}p_1 = \mu p_1$.

That the Fokker-Planck operator is self-adjoint implies that its eigenvectors associated to different eigenvalues are orthogonal for the scalar product (15.11). Applied to the equilibrium distribution p_0 and to the eigenvector p_n associated to the eigenvalue $\mu_n > 0$, it means that

$$0 = \langle p_0, p_n\rangle = \int p_n(x)\mathrm{d}x. \tag{15.15}$$

This property is also a consequence of probability conservation.

15.3.2 Mapping to the Schrödinger equation

The energy levels of a quantum particle in the one-dimensional potential $U_S(x)$ are obtained from the Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi''(x) + U_S(x)\psi(x) = E\psi(x). \tag{15.16}$$

Using the reduced potential $u_S(x) = 2mU_S/\hbar^2$, we arrive at the eigenvalue equation

$$-\psi''(x) + u_S(x)\psi(x) = \mu\psi(x). \tag{15.17}$$

The eigenvalue equation for the Fokker-Planck equation is

$$\mathscr{L}f = -\partial_x\left[\mathrm{e}^{-u}\partial_x\left(\mathrm{e}^{u}f\right)\right] = \mu f. \tag{15.18}$$

Using $f = \mathrm{e}^{-u/2}\psi$, this equation becomes

$$\mu\psi = -\mathrm{e}^{u/2}\partial_x\left[\mathrm{e}^{-u}\partial_x\left(\mathrm{e}^{u/2}\psi\right)\right] \tag{15.19}$$

$$= -\mathrm{e}^{u/2}\partial_x\left[\mathrm{e}^{-u/2}\left(\psi' + \frac{u'}{2}\psi\right)\right] \tag{15.20}$$

$$= -\psi'' + \left(\frac{u'^2}{4} - \frac{u''}{2}\right)\psi. \tag{15.21}$$

This is equivalent to the Schrödinger equation (15.17) in the potential

$$u_{\mathrm{S}} = \frac{u'^2}{4} - \frac{u''}{2}. \tag{15.22}$$

The transformation (15.19) makes the operator self-adjoint for the scalar product $\langle f, g\rangle = \int f(x)g(x)\mathrm{d}x$, which is the condition satisfied by the Hamiltonian in quantum mechanics.

This mapping between thermal (stochastic) and quantum systems makes a quantitative link between the transition rate across an energy barrier and quantum tunnelling.

15.3.3 Smallest eigenvalue and eigenvector

The eigenvector $p_1(x)$ associated to the eigenvalue μ satisfies

$$-\partial_x\left[\mathrm{e}^{-u(x)}\partial_x\left(\mathrm{e}^{u(x)}p_1(x)\right)\right] = \mu p_1(x). \tag{15.23}$$

We introduce $\psi(x) = \mathrm{e}^{u(x)}p_1(x) = p_1(x)/p_0(x)$, which obeys

$$-\partial_x\left[\mathrm{e}^{-u(x)}\psi'(x)\right] = \mu\mathrm{e}^{-u(x)}\psi(x). \tag{15.24}$$

Integrating this relation between a and x gives

$$\mathrm{e}^{-u(a)}\psi'(a) - \mathrm{e}^{-u(x)}\psi'(x) = \mu\int_a^x \mathrm{e}^{-u(x')}\psi(x')\mathrm{d}x', \tag{15.25}$$

which also reads

$$\psi'(x) = \mathrm{e}^{u(x)-u(a)}\psi'(a) - \mu\int_a^x \mathrm{e}^{u(x)-u(x')}\psi(x')\mathrm{d}x'. \tag{15.26}$$

Now, we integrate one more time this equation between a and x:

$$\psi(x) = \psi(a) + \mathrm{e}^{-u(a)}\psi'(a)\int_a^x \mathrm{e}^{u(x')}\mathrm{d}x' - \mu\int_a^x\int_a^{x'} \mathrm{e}^{u(x')-u(x'')}\psi(x'')\mathrm{d}x''\mathrm{d}x'. \tag{15.27}$$

Since p_1 has a vanishing integral, it should vanish at some point; we choose a to be the point where $p_1(a) = 0$, and thus $\psi(a) = 0$. The eigenvector p_1 is defined up to a constant, so that we can set $\mathrm{e}^{-u(a)}\psi'(a) = 1$. The previous equation now reads

$$\psi(x) = \int_a^x \mathrm{e}^{u(x')}\mathrm{d}x' - \mu\int_a^x\int_a^{x'} \mathrm{e}^{u(x')-u(x'')}\psi(x'')\mathrm{d}x''\mathrm{d}x'. \tag{15.28}$$

Since μ is the smallest non-vanishing eigenvalue, we assume that it is small and use it as an expansion parameter: we write $\psi = \psi^0 + \mu\psi^1 + \ldots$ with

$$\psi^0(x) = \int_a^x \mathrm{e}^{u(x')}\mathrm{d}x', \tag{15.29}$$

$$\psi^1(x) = -\int_a^x \int_a^{x'} \mathrm{e}^{u(x')-u(x'')}\psi^0(x'')\mathrm{d}x''\mathrm{d}x' \tag{15.30}$$

$$= -\int_a^x \int_a^{x'} \int_a^{x''} \mathrm{e}^{u(x')-u(x'')+u(x''')}\mathrm{d}x'''\mathrm{d}x''\mathrm{d}x'. \tag{15.31}$$

At order μ, this leads to

$$\psi(x) \simeq \int_a^x \mathrm{e}^{u(x')}\left[1 - \mu \int_a^{x'} \int_a^{x''} \mathrm{e}^{-u(x'')+u(x''')}\mathrm{d}x'''\mathrm{d}x''\right]\mathrm{d}x'. \tag{15.32}$$

Constraints on p_1 can be used to determine μ. The current associated to p_1 is proportional to

$$j(x) = \mathrm{e}^{-u(x)}\psi'(x) = 1 - \mu \int_a^x \int_a^{x''} \mathrm{e}^{-u(x'')+u(x''')}\mathrm{d}x'''\mathrm{d}x''. \tag{15.33}$$

This current should go to zero at infinity; this imposes that

$$\mu = \left(\int_a^\infty \int_a^x \mathrm{e}^{-u(x)+u(x')}\mathrm{d}x'\mathrm{d}x.\right)^{-1} \tag{15.34}$$

The expression should be the same when $x \to -\infty$, hence

$$\int_{-\infty}^a \int_x^a \mathrm{e}^{-u(x)+u(x')}\mathrm{d}x'\mathrm{d}x = \int_a^\infty \int_a^x \mathrm{e}^{-u(x)+u(x')}\mathrm{d}x'\mathrm{d}x. \tag{15.35}$$

This relation sets the value of a. The integrals appearing on both sides can be evaluated using the saddle point method when $u \gg 1$, as in the Kramers method. a should be located between the two local minima of the potential, around the local maximum. In the generic case where the two minima are different, for these integrals to be equal, the local maximum should be between a and the largest local minimum (i.e., not the global minimum). We use this local minimum x_{min} to evaluate the integral, leading to the same result as before:

$$\mu \simeq \frac{\sqrt{|u''(x_{\text{min}})u''(x_{\text{max}})|}}{2\pi}\mathrm{e}^{u(x_{\text{min}})-u(x_{\text{max}})}. \tag{15.36}$$

The eigenvectors p_0 and p_1 are shown on Fig. 15.1(b); the eigenvalue is shown in the spectrum of the operator $\mathscr{L}$ on Fig. 15.1(d).

15.3.4 Mapping on a two states system

We assume that the potential is large, so that the equilibrium distribution is peaked around the two local minima $x_\pm$: we decompose it into

$$p_0(x) = \alpha_- p_-(x) + \alpha_+ p_+(x), \tag{15.37}$$

where $p_\pm$ is peaked around $x_\pm$, and $p_\pm$ is normalized; this imposes $\alpha_+ + \alpha_- = 1$.

From the leading order in μ, Eq. (15.29), we see that the derivative of ψ is minimal close to the local minima; assuming that it is almost constant over the domains where $p_\pm$ takes “significant values”, we have

$$p_1(x) = \psi_- \alpha_- p_-(x) + \psi_+ \alpha_+ p_+(x), \tag{15.38}$$

where $\psi_\pm = \psi(x_\pm)$. Since the integral of p_1 is zero, we can write it as (up to a constant that does not matter)

$$p_1(x) = -p_-(x) + p_+(x). \tag{15.39}$$

The distributions $p_\pm$ are shown on Fig. 15.1(c).

If the probability density is a linear combination of p_- and p_+, $p(x,t) = a_-(t)p_-(x) + a_+(t)p_+(x)$, we can compute its evolution from

$$\mathscr{L} p_\pm = \mathscr{L}(p_0 \pm \alpha_\mp p_1) = \pm \alpha_\mp \mu p_1 = \pm \alpha_\mp \mu(-p_- + p_+). \tag{15.40}$$

Hence,

$$\mathscr{L} p = [-a_-(t)\alpha_+ + a_+(t)\alpha_-]\mu(-p_- + p_+). \tag{15.41}$$

Writing $\partial_t p = -D\mathscr{L} p$ and identifying the coefficients of $p_\pm$, we get

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} a_+ \\ a_- \end{pmatrix} = D\mu M \begin{pmatrix} a_+ \\ a_- \end{pmatrix}, \tag{15.42}$$

where

$$M = \begin{pmatrix} -\alpha_- & +\alpha_+ \\ \alpha_- & -\alpha_+ \end{pmatrix}. \tag{15.43}$$

One can check that the eigenvalues of M are 0 and -1.

On timescales larger than the relaxation time in one well and shorter than the transition rate between the two wells ($\sim 1/(D\mu)$), the dynamics of the system is described accurately by these two states system. We see that the spectrum of the Fokker-Planck operator $\mathscr{L}$ has a gap between the smallest non-vanishing eigenvalue μ and the second eigenvalue (Fig. 15.1(d)). In the two states system, there is only one timescale because the two transition rates are related through detailed balance.

15.4 First passage time

Here, we use the time of the first passage at a point a on the other side of the barrier as a measure of the time it takes to cross the barrier. First, we show that a precise definition can be given for the average first passage time, and that it obeys a simple equation. Second, we solve this equation to get the first passage time.

The first passage time is an intuitive observable to look at, since, e.g., a chemical reaction occur when the two reacting molecules meet for the first time. Another example comes from the optimization of search processes, where one wants to minimize the mean first passage time.

15.4.1 Definition of the first passage time

We consider an overdamped Langevin process starting at x_0, and we want to know the first time when it reaches the point a, $T_a(x_0)$, which is a random variable. We are interested in the mean first passage time (MFPT), $\bar{T}_a(x_0)$.

In order to determine the first passage time at a, we see a as an absorbing point: a distribution $p_a(x,x_0,t)$ of "particles" is localized at x_0 at $t=0$, and evolves following the Fokker-Planck equation, excepts that particles that hit a are removed from the sytem. This imposes the condition $p_a(a,x_0,t)=0$. Hence this distribution follows

$$p(x,x_0,0) = \delta(x-x_0), \tag{15.44}$$

$$\partial_t p(x,x_0,t) = -D\mathscr{L}p(x,x_0,t), \tag{15.45}$$

$$p(a,x_0,t) = 0. \tag{15.46}$$

The integral of the distribution at time t is the fraction of particles that have not reached a yet, i.e., $T_a > t$ for these particles:

$$\mathbb{P}[T_a(x_0) \geq t] = \int_{-\infty}^{a} p_a(x,x_0,t)\mathrm{d}x. \tag{15.47}$$

The MFPT can be obtained from this relation:

$$\bar{T}_a(x_0) = \int_0^\infty \mathbb{P}[T_a(x_0) \geq t]\mathrm{d}t \tag{15.48}$$

$$= \int_0^\infty \int_{-\infty}^{a} p_a(x,x_0,t)\mathrm{d}x\mathrm{d}t. \tag{15.49}$$

Now, we look for an equation satisfied by the MFPT.

15.4.2 Adjoint Fokker-Planck operator and equation for the mean first passage time

The Fokker-Planck equation relates the time derivative of the distribution $p(x,x',t)$ and the Fokker-Planck operator applied to the final position x. However, the MFPT is a function of the initial position, so that we have to relate the time derivative of $p(x,x',t)$ to an operator applied to the initial position x'. In order to derive this relation, we note that for all t',

$$p(x,x',t) = \int p(x,x'',t-t')p(x'',x',t')\mathrm{d}x''. \tag{15.50}$$

Differentiating with respect to t', we get

$$0 = \int [-\partial_t p(x,x'',t-t')p(x'',x',t') + p(x,x'',t-t')\partial_t p(x'',x',t')]\mathrm{d}x'' \tag{15.51}$$

$$= \int [-\partial_t p(x,x'',t-t')p(x'',x',t') - Dp(x,x'',t-t')\mathscr{L}_{x''}p(x'',x',t')]\mathrm{d}x'' \tag{15.52}$$

$$= -\int \left[\partial_t p(x,x'',t-t') + D\mathscr{L}^\dagger_{x''}p(x,x'',t-t')\right] p(x'',x',t')\mathrm{d}x'' \tag{15.53}$$

$$\tag{15.54}$$

Setting $t'=0$ so that $p(x'',x',t') = \delta(x''-x')$, we get

$$\partial_t p(x,x',t) = -D\mathscr{L}^\dagger_{x'}p(x,x',t). \tag{15.55}$$

We have used the definition of the adjoint operator $\mathscr{L}$ as

$$\langle f,\mathscr{L}g\rangle=\int f(x)\mathscr{L}g(x)\mathrm{d}x=\int(\mathscr{L}^\dagger f)(x)g(x)\mathrm{d}x=\langle\mathscr{L}^\dagger f,g\rangle, \tag{15.56}$$

and the index of $\mathscr{L}$ denotes the variable on which it applies. From this expression we can determine explicitly the adjoint operator:

$$\mathscr{L}^\dagger f(x)=-\mathrm{e}^{u(x)}\partial_x\left[\mathrm{e}^{-u(x)}\partial_x f(x)\right]. \tag{15.57}$$

We note that the definition of the adjoint of an operator depends on the scalar product that we use. The scalar product used here is not the same as the one defined in Eq. (15.11), for which $\mathscr{L}$ is self-adjoint. Here, obviously, $\mathscr{L}$ is not self-adjoint.

With Eq. (15.55) at hand, we can derive an equation for the MFPT. We consider the quantity

$$\int_0^\infty\int_{-\infty}^a\partial_t p_a(x,x_0,t)\mathrm{d}x\mathrm{d}t. \tag{15.58}$$

On one hand, the integral on the time can be computed:

$$\int_0^\infty\int_{-\infty}^a\partial_t p_a(x,x_0,t)\mathrm{d}x\mathrm{d}t=\int_{-\infty}^a p_a(x,x_0,\infty)\mathrm{d}x-\int_{-\infty}^a p_a(x,x_0,0)\mathrm{d}x=-1, \tag{15.59}$$

because when $t\to\infty$, all the particle have been absorbed. On the other hand, the time derivative can be expressed with Eq. (15.55):

$$\int_0^\infty\int_{-\infty}^a\partial_t p_a(x,x_0,t)\mathrm{d}x\mathrm{d}t=-D\int_0^\infty\int_{-\infty}^a\mathscr{L}_{x_0}^\dagger p_a(x,x_0,t)\mathrm{d}x\mathrm{d}t=-D\mathscr{L}^\dagger\bar{T}_a(x_0). \tag{15.60}$$

We thus get an equation for the MFPT:

$$\mathscr{L}^\dagger\bar{T}_a(x)=D^{-1}, \tag{15.61}$$

that should be completed with the boundary condition

$$\bar{T}_a(a)=0. \tag{15.62}$$

15.4.3 Computation of the first passage time

We solve the equations for the MFPT, Eqs. (15.61,15.62); explicitly,

$$\partial_x\left[\mathrm{e}^{-u(x)}\partial_x\bar{T}_a(x)\right]=-D^{-1}\mathrm{e}^{-u(x)}. \tag{15.63}$$

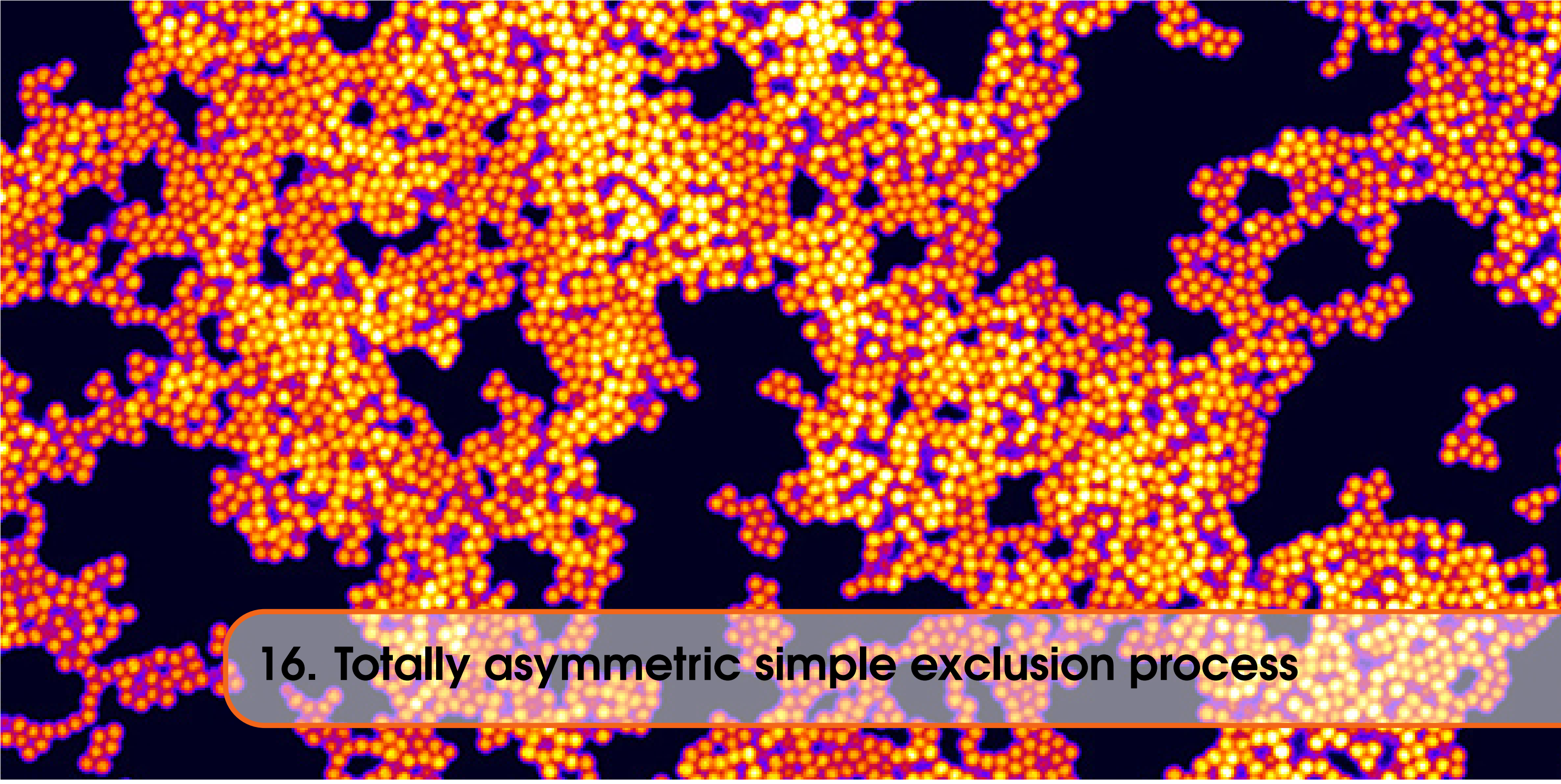
First, we integrate this equation between $-\infty$ and x, assuming that $\mathrm{e}^{-u(x)}\partial_x\bar{T}_a(x)\underset{x\to-\infty}{\to}0$:

$$\partial_x\bar{T}_a(x)=-D^{-1}\mathrm{e}^{u(x)}\int_{-\infty}^x\mathrm{e}^{-u(x')}\mathrm{d}x'. \tag{15.64}$$

Now, we integrate it between x and a, and use the boundary condition (15.62):

$$\bar{T}_a(x)=D^{-1}\int_x^a\int_{-\infty}^{x'}\mathrm{e}^{u(x')-u(x'')}\mathrm{d}x''\mathrm{d}x'. \tag{15.65}$$

This expression corresponds to the result obtained with the flow over population method, Eq. (15.6): $\bar{T}_a(-\infty)=1/k$.



16. Totally asymmetric simple exclusion process

In the totally asymmetric simple exclusion process (TASEP), "particles" move to the right along a line and cannot pass each other. Particles are injected at the left end of the line and remove at the right end. This model can represent vehicles in a traffic jam or molecular motors moving along actin filaments.

16.1 From abstract models to many-body systems

In the previous chapters, we have introduced the master equation that describes the evolution of the probability distribution of the system over discrete states, and the Fokker-Planck equation, which describes the evolution of the distribution of continuous degrees of freedom subject to deterministic forces and noise. We will see that these simple frameworks can be used to describe many-body systems, which may be counter-intuitive.

We start from the Fokker-Planck equation

$$\dot{p}(x,t) = -\nabla\cdot\left[\frac{1}{\lambda}f(x,t)p(x,t) - D\nabla p(x,t)\right], \tag{16.1}$$

where $x \in \mathbb{R}^d$, which describes the evolution of the probability distribution of a "particle" following the overdamped Langevin equation

$$\dot{x}(t) = \frac{1}{\lambda}f(x(t),t) + \sqrt{2D}\eta(t). \tag{16.2}$$

First, we consider a simple example: we want an equation analogous to the Fokker-Planck equation for an inertial particle, which follows the general Langevin equation

$$m\ddot{x}(t) = -\lambda\dot{x}(t) + f(x(t),t) + \sqrt{2D}\lambda\eta(t). \tag{16.3}$$

Incorporating inertia seems to change the level of difficulty of the problem, as it changes the order of the time derivative. However, if we introduce the velocity $v(t) = \dot{x}(t)$, the inertia just affects the dimension of the problem. The Langevin equation reads

$$\dot{x}(t) = v(t), \tag{16.4}$$

$$\dot{v}(t) = -\frac{1}{\tau}v(t) + f(x(t),t) + \frac{\sqrt{2D}\lambda}{m}\eta(t). \tag{16.5}$$

This is a first order equation for which it is straightforward to obtain a Fokker-Planck-like equation for the distribution $p(x,v,t)$. The currents in the x and v directions are given by

$$j_x(x,v,t) = vp(x,v,t), \tag{16.6}$$

$$j_v(x,v,t) = \left[-\frac{v}{\tau} + f(x,t)\right] p(x,v,t) - \frac{D\lambda^2}{m^2}\nabla_v p(x,v,t). \tag{16.7}$$

The evolution of the distribution is thus given by

$$\dot{p}(x,v,t) = -\nabla_x \cdot j_x - \nabla_v \cdot j_v, \tag{16.8}$$

$$= -v\cdot\nabla_x p + \nabla_v \cdot \left(\left[\frac{v}{\tau} - f(x,t)\right] p \right) + \frac{D\lambda^2}{m^2}\nabla_v^2 p(x,v,t). \tag{16.9}$$

This is the Kramers equation.

We now turn to a many body system, which is even simpler. We describe the collective motion of N particles interacting through a pair potential $U(x)$ and obeying the overdamped Langevin equation

$$\dot{x}_i(t) = -\lambda^{-1}\sum_{j\neq i}\nabla U(x_i(t) - x_j(t)) + \sqrt{2D}\eta(t). \tag{16.10}$$

The Fokker-Planck equation for the distribution $p(x_1,\ldots,x_N,t)$ reads

$$\dot{p}(x_1,\ldots,x_N,t) = \frac{1}{\lambda}\sum_{i=1}^{N}\nabla_i \cdot \left[p(x_1,\ldots,x_N,t)\sum_{j\neq i}\nabla U(x_i - x_j)\right] + D\sum_{i=1}^{N}\nabla_i^2 p(x_1,\ldots,x_N,t). \tag{16.11}$$

This equation is referred to as the Smoluchowski equation.

In this chapter, we use the discrete master equation to describe the motion of interacting particles along a line.

16.2 Definition of the TASEP

This model is defined on a one-dimensional lattice of N sites. Particles move on this lattice in a continuous time stochastic process that obeys the following rules: during a short time interval δt (see Fig. 16.1),

- a particle standing on the site i has a probability δt to move to the $i+1$, provided that this site is empty,
- if the site $i = 1$ is empty, it is filled with a particle with probability $\alpha\delta t$,
- if there is a particle on the site $i = N$, it is removed with a probability $\beta\delta t$.

This system is out of equilibrium, because the particles can only move to the right (i.e., it does not satisfy detailed balance). We are interested in the density profile and the current of particles in the stationnary state. The two parameters of the system are $\alpha > 0$ and $\beta > 0$.

Here, we solve it in the mean-field approximation. It has been solved exactly, but the solution is rather complicated [**Derrida1992**, **Derrida1993**].

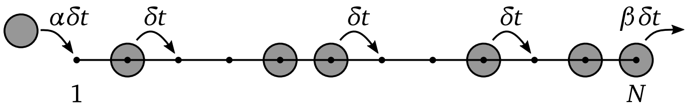


Figure 16.1 – Possible motions with their probabilities during a short time interval δt; the configuration is unchanged with probability $1-(3+\alpha+\beta)\delta t$.

16.3 Evolution of the average occupation numbers

At a given time, the state of the system is given by the occupation numbers $(\tau_i(t))_{1\leq i\leq N}$, $\tau_i(t)$ giving the number of particles on the site i at time t; $\tau_i(t)\in\{0,1\}$.

16.3.1 Direct derivation

The dynamic rules defining the model can be directly translated into equations of evolution of the occupation numbers $\tau_i(t)$. We consider a site i in the bulk (i.e., $i\notin\{1,N\}$):

— if $\tau_i(t)=0$ and $\tau_{i-1}(t)=1$, $\tau_i(t+\delta t)=1$ with probability δt,
— if $\tau_i(t)=1$ and $\tau_{i+1}(t)=0$, $\tau_i(t+\delta t)=0$ with probability δt,
— otherwise, $\tau_i(t+\delta t)=\tau_i(t)$.

This can be cast in the following form:

$$\tau_i(t+\delta t)=\begin{cases}\tau_i(t) & \text{with probability} \quad 1-2\delta t\\ \tau_i(t)+[1-\tau_i(t)]\tau_{i-1}(t) & \text{with probability} \quad \delta t\\ \tau_i(t)\tau_{i+1}(t) & \text{with probability} \quad \delta t\end{cases} \tag{16.12}$$

The same approach can be used at the boundaries, leading to

$$\tau_1(t+\delta t)=\begin{cases}\tau_1(t) & \text{with probability} \quad 1-(1+\alpha)\delta t\\ 1 & \text{with probability} \quad \alpha\delta t\\ \tau_1(t)\tau_2(t) & \text{with probability} \quad \delta t\end{cases} \tag{16.13}$$

and

$$\tau_N(t+\delta t)=\begin{cases}\tau_N(t) & \text{with probability} \quad 1-(1+\beta)\delta t\\ \tau_N(t)+[1-\tau_N(t)]\tau_{N-1}(t) & \text{with probability} \quad \delta t\\ 0 & \text{with probability} \quad \beta\delta t\end{cases} \tag{16.14}$$

Averaging and taking the limit $\delta t\to 0$, we get the time derivative of the average occupation numbers:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\tau_i\rangle=\langle\tau_{i-1}\rangle-\langle\tau_i\rangle+\langle\tau_i\tau_{i+1}\rangle-\langle\tau_{i-1}\tau_i\rangle, \tag{16.15}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\tau_1\rangle=\alpha-(1+\alpha)\langle\tau_1\rangle+\langle\tau_1\tau_2\rangle, \tag{16.16}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\tau_N\rangle=\langle\tau_{N-1}\rangle-\beta\langle\tau_N\rangle-\langle\tau_{N-1}\tau_N\rangle. \tag{16.17}$$

16.3.2 From the master equation

Master equation–

These equations can be obtained in a more rigorous manner by writing the master equation for this system. The master equation is an equation for the probability for the system to be in a given state. Here, a state is given by the set of the occupation numbers, $(\tau_i)_{1\leq i\leq N}$, hence we look for an equation for the probability $P((\tau_i);t)$. We write the equation and then explain the origin of the different contributions:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}P((\tau_i);t) = &-\left[\sum_{j=1}^{N-1}\tau_j(1-\tau_{j+1})\right]P((\tau_i);t)+\sum_{j=1}^{N-1}(1-\tau_j)\tau_{j+1}P(\ldots,1_j,0_{j+1},\ldots;t)\\ &-\alpha(1-\tau_1)P((\tau_i);t)+\alpha\tau_1P(0_1,\ldots;t)\\ &-\beta\tau_NP((\tau_i);t)+\beta(1-\tau_N)P(\ldots,1_N;t).\end{aligned} \tag{16.18}$$

The notation $(\ldots,1_j,0_{j+1},\ldots)$ is a shorthand for $(\tau_1,\ldots,\tau_{j-1},1,0,\tau_{j+2},\ldots,\tau_N)$. The first line corresponds to movements in the bulk, the second to particles entering the system and the third to particles leaving the system. In each line, the first term is a loss term and the last term is a gain term.

In the first line, the loss term corresponds to all the positions where the movement $j\to j+1$ is possible, i.e., where $\tau_j=1$ and $\tau_{j+1}=0$; in the case, $\tau_j(1-\tau_{j+1})=1$. The gain term corresponds to all the positions where the movement $j\to j+1$ may have happened recently, i.e., to all the positions where $\tau_j=0$ and $\tau_{j+1}=1$, or $(1-\tau_j)\tau_{j+1}=1$. If the movement $j\to j+1$ has happened, the previous configuration was $(\tau_1,\ldots,\tau_{j-1},1,0,\tau_{j+2},\ldots,\tau_N)$.

The second and last lines follow from the same analysis.

Evolution of the average occupation–

Now that we have the master equation, we can write the evolution of the average occupation number,

$$\langle\tau_k(t)\rangle=\sum_{(\tau_i)}\tau_kP((\tau_i);t). \tag{16.19}$$

We thus multiply Eq. (16.18) by τ_k and sum over (τ_i).

We first consider the first line, and take a particular j in the two sums. If $j\notin\{k-1,k\}$, we have

$$\sum_{(\tau_i)}\tau_k\left[-\tau_j(1-\tau_{j+1})P((\tau_i);t)+(1-\tau_j)\tau_{j+1}P(\ldots,1_j,0_{j+1},\ldots;t)\right] \tag{16.20}$$

$$=\sum_{(\tau_i)}\tau_k\left[-\tau_j(1-\tau_{j+1})P(\ldots,1_j,0_{j+1},\ldots;t)+\tau_j'(1-\tau_{j+1}')P(\ldots,1_j,0_{j+1},\ldots;t)\right] \tag{16.21}$$

$$=0. \tag{16.22}$$

We have used the fact that the first term is non zero only if $\tau_j=1$ and $\tau_{j+1}=0$ and in the second term we have changed variables $\tau_j'=1-\tau_j$, $\tau_{j+1}'=1-\tau_{j+1}$. This result is expected: a jump from j to $j+1$ does not affect the occupation of the site $k\notin\{j,j+1\}$. The same steps can be used to show that the second and last lines do not contribute if $j\notin\{1,N\}$.

Now assume that $j=k$ in the first line. Now we can use that $\tau_j^2=\tau_j$ and $\tau_j(1-\tau_j)=0$. We get

$$\sum_{(\tau_i)}\tau_k\left[-\tau_k(1-\tau_{k+1})P((\tau_i);t)+(1-\tau_k)\tau_{k+1}P(\ldots,1_k,0_{k+1},\ldots;t)\right] \tag{16.23}$$

$$=-\sum_{(\tau_i)}\tau_k(1-\tau_{k+1})P((\tau_i);t) \tag{16.24}$$

$$=-\langle\tau_k(t)[1-\tau_{k+1}(t)]\rangle. \tag{16.25}$$

The third possibility is $j = k-1$:

$$\sum_{(\tau_i)} \tau_k \left[-\tau_{k-1}(1-\tau_k)P((\tau_i);t) + (1-\tau_{k-1})\tau_k P(\ldots,1_{k-1},0_k,\ldots;t)\right] \tag{16.26}$$

$$= \sum_{(\tau_i)} (1-\tau_{k-1})\tau_k P(\ldots,1_{k-1},0_k,\ldots;t) \tag{16.27}$$

$$= \sum_{\tau_{k-1},\tau_k=0}^{1} (1-\tau_{k-1})\tau_k \sum_{(\tau_i)\setminus k-1,k} P(\ldots,1_{k-1},0_k,\ldots;t) \tag{16.28}$$

$$= 1 \times \sum_{(\tau_i)} \tau_{k-1}(1-\tau_k)P((\tau_i),\ldots;t) \tag{16.29}$$

$$= \langle \tau_{k-1}(t)[1-\tau_k(t)]\rangle. \tag{16.30}$$

Gathering Eqs. (16.25) and (16.30), we get

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \tau_k\rangle = \langle \tau_{k-1}\rangle - \langle \tau_k\rangle + \langle \tau_k \tau_{k+1}\rangle - \langle \tau_{k-1}\tau_k\rangle, \tag{16.31}$$

which is identical to Eq. (16.15).

The equations for the boundary terms can obtained in the same way.

16.3.3 Mean-field approximation

The equations for the evolution of the average occupation numbers, Eqs. (16.15-16.17), are not closed: they involve averages of products of occupation numbers. We could derive the evolution of the averages of these products, but it would involve, in turn, averages of products of three occupation numbers, and so on. This kind of hierarchy is called the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy and is common interacting particle systems.

In order to obtain a closed set of equations, we need to *close* the hierarchy at some level, making an approximation. The simplest approximation that we can make is the mean-field approximation, whereby the occupation numbers are assumed to be independent variables (this amounts to neglect the correlations between the occupation numbers):

$$\langle \tau_i(t)\tau_{i+1}(t)\rangle = \langle \tau_i(t)\rangle\langle \tau_{i+1}(t)\rangle. \tag{16.32}$$

Using the mean-field approximation in Eqs. (16.15-16.17) and introducing the density $\rho_i(t) = \langle \tau_i(t)\rangle$, we get

$$\frac{\mathrm{d}\rho_i}{\mathrm{d}t} = \rho_{i-1} - \rho_i + \rho_i(\rho_{i+1} - \rho_{i-1}), \tag{16.33}$$

$$\frac{\mathrm{d}\rho_1}{\mathrm{d}t} = \alpha - (1+\alpha)\rho_1 + \rho_1\rho_2, \tag{16.34}$$

$$\frac{\mathrm{d}\rho_N}{\mathrm{d}t} = \rho_{N-1} - \beta\rho_N - \rho_{N-1}\rho_N. \tag{16.35}$$

We note that evolution at the boundaries, Eqs. (16.34,16.35), are of the form of the evolution in the bulk, Eq. (16.33), with additionnal sites at 0 and $N+1$ with densities

$$\rho_0 = \alpha, \tag{16.36}$$

$$\rho_{N+1} = 1-\beta. \tag{16.37}$$

We note that the density at these “virtual” sites can be larger than 1 (for ρ_0) or negative (for ρ_{N+1}), because there is no upper bound on α and β.

16.3.4 Continuous limit

The equations for the density, Eqs. (16.33,16.36,16.37) can be solved exactly [**Derrida1992**]. However, we can get a better intuition on the behavior of these equations by taking a continuous limit in space. We should keep in mind that this approximation is not justified at all here, since the only length scale in there is no small scale in this system.

The continuous limit is obtained via a Taylor expansion:

$$\rho_i \to \rho(x), \tag{16.38}$$

$$\rho_{i\pm 1} \to \rho(x) \pm \rho'(x) + \frac{1}{2}\rho''(x). \tag{16.39}$$

Inserting this in Eq. (16.33), we get

$$\partial_t \rho = (2\rho - 1)\partial_x \rho + \frac{1}{2}\partial_x^2 \rho. \tag{16.40}$$

We notice that this equation can be written has a conservation equation with a current of particles j:

$$\partial_t \rho = -\partial_x j, \tag{16.41}$$

$$j = \rho(1-\rho) - \frac{1}{2}\partial_x \rho. \tag{16.42}$$

In an homogeneous system, $j = \rho(1-\rho)$. This expression has a simple interpretation: it is the product of the density, ρ, and the "velocity" $1-\rho$. Indeed, in the mean-field picture, the velocity is given by the rate of jumps (i.e., 1) times the probability for the next site to be empty, which is $1-\rho$.

16.4 Phase diagram

16.4.1 Stationnary regime and mapping to an overdamped particle in a potential

We look for stationnary density profiles. In the stationnary state, $\partial_x j = 0$, hence the current is uniform and we note $j(x) = J$. From Eq. (16.42), we have to solve:

$$\partial_x \rho = 2\rho(1-\rho) - 2J. \tag{16.43}$$

We are interested in the behavior in the thermodynamic limit, i.e., when the system is very large. The first term on the right hand side of Eq. (16.43) is bounded: $\rho(1-\rho) \in [0, 1/4]$. If J does not lie in this interval, there is a density gradient, and, since the system is very large, a large density difference between the two ends of the system. However, the density difference cannot exceed one, hence we deduce that $J \in [0, 1/4]$.

The equation satisfied by stationnary density profiles, Eq. (16.43), can be seen as the overdamped (i.e., without inertia) motion of a particle in a potential: we change notations as $x \to t$, $\rho \to X$, and introduce the potential

$$U(X) = 2JX - X^2 + \frac{2}{3}X^3, \tag{16.44}$$

then $X(t)$ follows

$$\dot{X}(t) = -U'(X(t)). \tag{16.45}$$

With this analogy, looking for the possible density profiles amounts to look for the possible trajectories for the overdamped particle.

The potential is shown in Fig. 16.2(a,b) for $J = 1/4$ and $J < 1/4$.

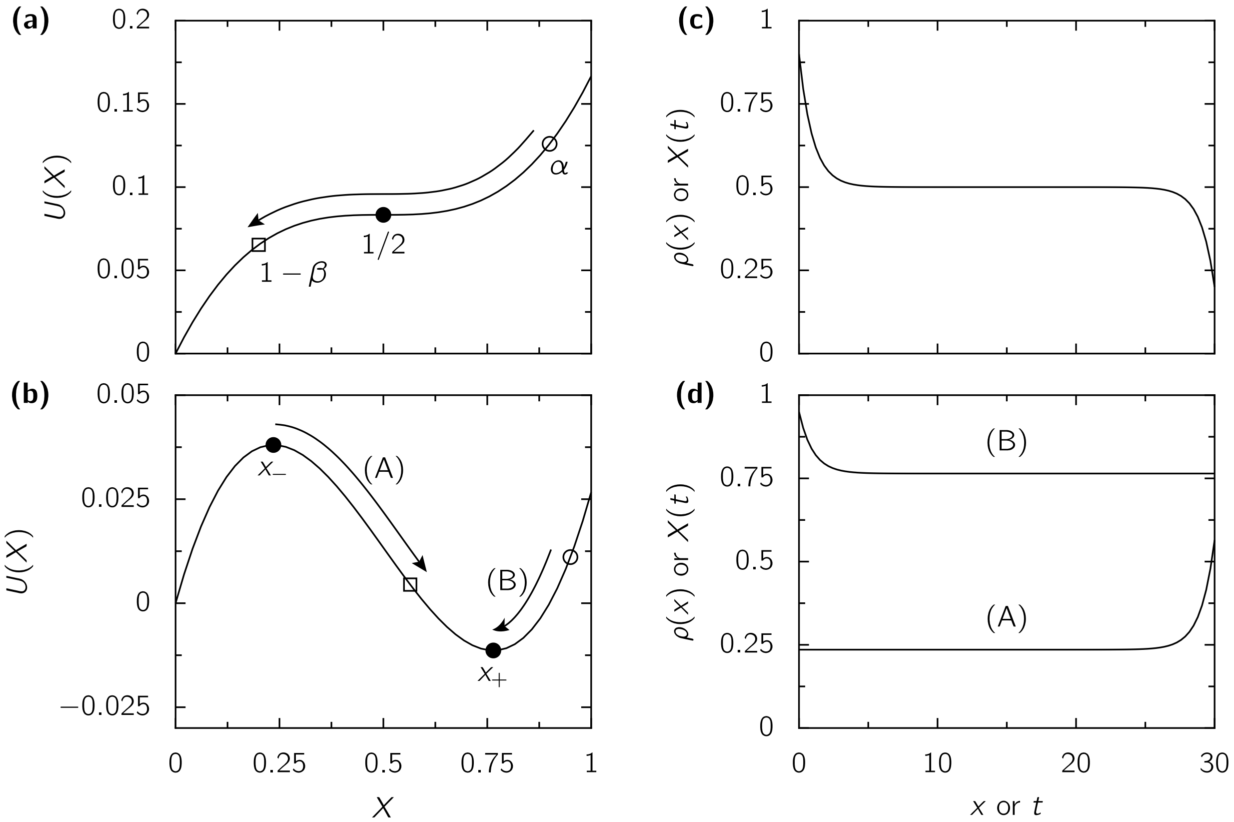


Figure 16.2 – Effective potential for the density profile for $J = 1/4$ (a) and $J = 0.18$ (b). Corresponding particle trajectories or density profiles (c,d).

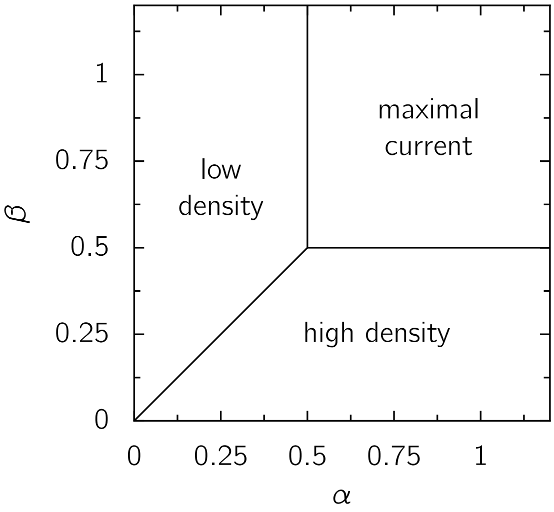


Figure 16.3 – Phase diagram of the TASEP model in the mean-field approximation.

16.4.2 $J = 1/4$

When $J = 1/4$, the potential has a single stationnary point at $X = 1/2$ (Fig. 16.2(a)). Since we work in the long time (i.e. large system) limit, the particle has to spend a long time at the stationnary point. Hence, the possible behavior for the particle is to start at $X(0) = \alpha > 1/2$, go to the stationnary point, spend a long time there, and finally slide down the potential to $X(N+1) = 1-\beta < 1/2$. The trajectory of the particle, or equivalently the density profile, is shown on Fig. 16.2(c). This situation corresponds to $\alpha > 1/2$ and $\beta > 1/2$. This phase is called the "maximal current" phase, since the current of particles takes its maximal value.

16.4.3 $J < 1/4$

When $0 < J < 1/4$, the potential has two extrema at x_- and x_+, where the particle can stay for a long time (Fig. 16.2(b)). They satisfy $x_- + x_+ = 1$. Two types of trajectories are possible:

(A) Start at $X(0) = \alpha = x_- < 1/2$, spend a long time here, and finally slide down to $X(N+1) = 1-\beta < x_+$. Hence, $\beta > 1 - x_+ = x_- = \alpha$. This phase is the "low density" phase, observed when $\alpha < 1/2$ and $\beta > \alpha$.

(B) Start at $X(0) > x_-$, slide down to x_+ and spend a long time there, so that $X(N+1) = 1-\beta = x_+ > 1/2$. This is the "high density" phase, observed when $\beta < 1/2$ and $\alpha > \beta$.

The corresponding density profiles are shown on Fig. 16.2(d).

If $\alpha = \beta$, the particle can start at $x_- = \alpha$, spend a long time here, slide to $x_+ = 1-\beta$, and spend a long time there. In the density profile, the slide corresponds to a domain wall.

The phase diagram is represented in Fig. 16.3. Obtained here in the mean-field approximation, it is unchanged with the exact solution.

16.5 Mapping to other systems: Burgers and KPZ

The TASEP model has connection with other systems coming from different domains. We quickly show that the equation for the time dependent density, Eq. (16.40) can be mapped to the Burgers equation or to the KPZ equation without noise.

In order to map it to the Burgers equation, we introduce $\psi(x,t) = \rho(x,t) - 1/2$; Eq. (16.40) becomes

$$\partial_t \psi = 2\psi \partial_x \psi + \frac{1}{2}\partial_x^2 \psi. \tag{16.46}$$

This is the Burgers equation, used to describe shocks (discontinuities that appear at a finite time from a regular initial profile).

Writing $\psi = \partial_x h$, the equation becomes

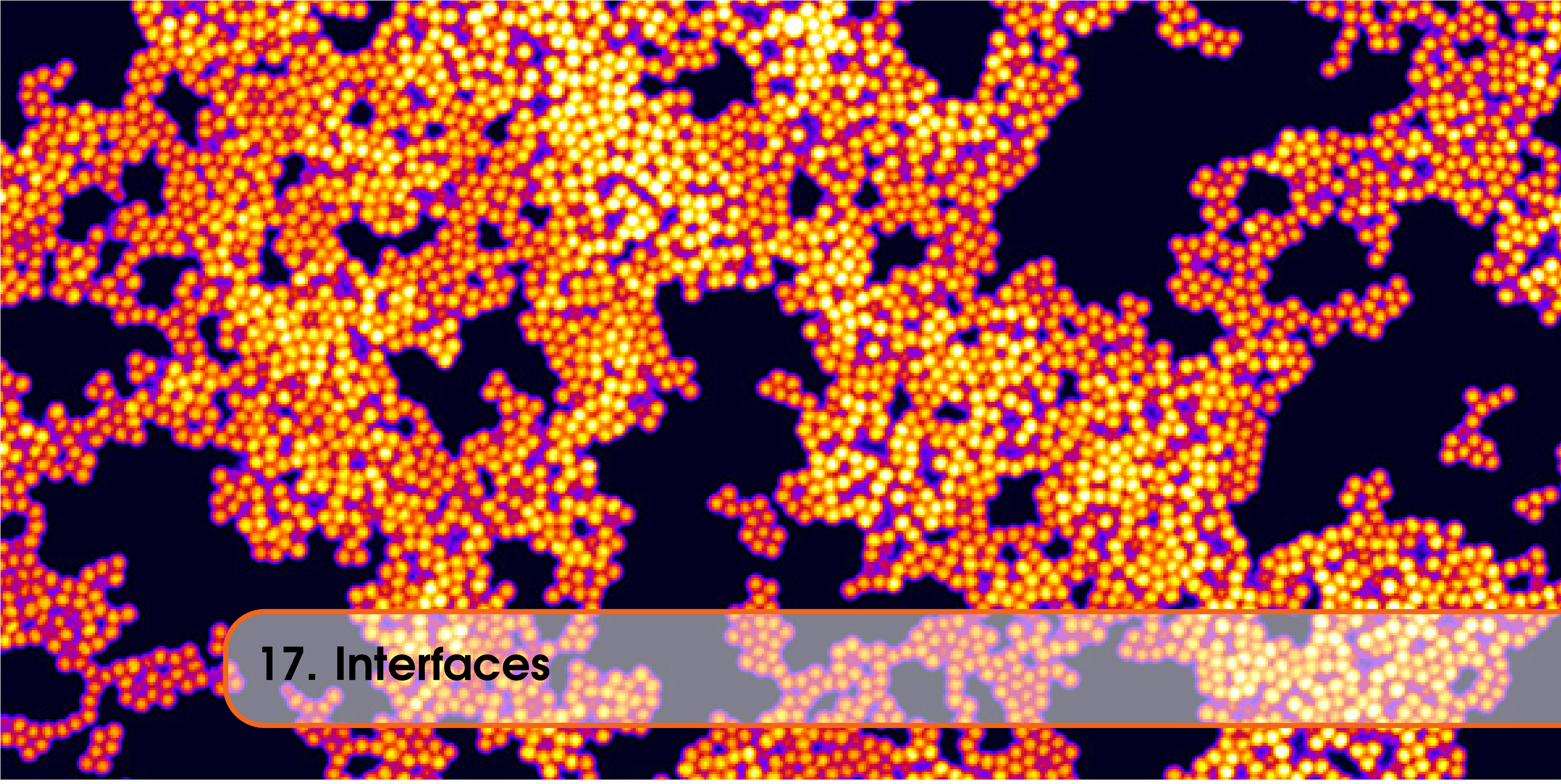
$$\partial_t \partial_x h = 2(\partial_x h)(\partial_x^2 h) + \frac{1}{2}\partial_x^3 h \tag{16.47}$$

$$= \partial_x \left[(\partial_x h)^2\right] + \frac{1}{2}\partial_x^3 h. \tag{16.48}$$

Integrating over x, without the integration constant, we get

$$\partial_t h = (\partial_x h)^2 + \frac{1}{2}\partial_x^2 h, \tag{16.49}$$

which is the Kardar-Parisi-Zhang (KPZ) equation without noise, an important model for interfaces.



17. Interfaces

Interfaces are ubiquitous in nature: they appear at the interface between a liquid and a gas, between magnetic domains with opposite orientations, at the imbibition front in a porous medium, or a the front of a fracture in a breaking sample. More generally, an interface refers to a narrow region separating two homogeneous phases. It is often more convenient to study the shape and dynamics of the interface itself rather than that of the neighbouring phases.

In this section, we discuss the models and observables used to describe interfaces.

17.1 Simple models

We give here two simple models for interfaces and use them to discuss the basic observable used to describe an interface, its roughness.

17.1.1 Interface of a liquid at equilibrium in dimension $d = 1$

We model the one dimensionnal interface between a liquid and a gas at the interface between up ($s = 1$) and down ($s = -1$) regions in a planar Ising model with coupling constant J. We assume that there are no overhangs nor bubbles, hence the shape of the interface is entirely given by its height h_i in the column i.

The energy difference between an interface with heights (h_i) and the flat interface (that we take as the energy reference) is

$$E((h_i)) = 2J\sum_i |h_{i+1} - h_i|. \tag{17.1}$$

We can introduce the height differences, or step sizes, as

$$y_i = h_i - h_{i-1}; \tag{17.2}$$

they allow to write the energy as

$$E((y_i)) = 2J\sum_i |y_i| = \sum_i e(y_i), \tag{17.3}$$

where $e(y) = 2J|y|$. This means that the step sizes are independent: we can study the properties of one step, and deduce the properties of the whole interface.

For one step, the partition function is

$$z = \sum_{y\in\mathbb{Z}} \mathrm{e}^{-e(y)/T} = \sum_{y\in\mathbb{Z}} \mathrm{e}^{-2j|y|} = \frac{2}{1-\mathrm{e}^{-2j}} - 1 = \frac{1+\mathrm{e}^{-2j}}{1-\mathrm{e}^{-2j}} = \coth(j), \tag{17.4}$$

where $j = J/T$. The average of y is zero by symmetry, $\langle y\rangle = 0$, and its variance is

$$\langle y^2\rangle = z^{-1}\sum_{y\in\mathbb{Z}} y^2\mathrm{e}^{-2j|y|} = \frac{1}{4z}\frac{\partial^2 z}{\partial j^2} = \frac{1}{2\sinh(j)^2}. \tag{17.5}$$

The difference between the heights at $i = L$ and $i = 0$ can be written as $h_L - h_0 = \sum_{i=1}^{L} y_i$, hence

$$\langle h_L - h_0\rangle = 0, \tag{17.6}$$

$$\left\langle [h_L - h_0]^2\right\rangle = L\langle y^2\rangle = \frac{L}{2\sinh(j)^2}. \tag{17.7}$$

The second equation defines the roughness, or width, of the interface, here

$$w(L) = \sqrt{\langle [h_L - h_0]^2\rangle} \sim \sqrt{L} = L^{\alpha}, \tag{17.8}$$

where $\alpha = 1/2$ is the *roughness exponent*.

In this model, we could define the roughness of an interface, but the interface is at equilibrium and its statistical properties do not evolve in time.

17.1.2 Random deposition model

Here, we want to describe an interface that “grows” with time. We take the example of molecular beam epitaxy, used to manufacture computer chips and other semiconductor devices. We start with a flat surface and start depositing atoms on it: atoms arrive at the interface after a ballistic motion and immediately stick to it.

We model this process with the random deposition model: the height of the interface is given by the heights $(h_i(t))$ of its columns. At each time interval δt, a column is chosen at random and its height is increased by 1: $h_i(t+\delta t) = h_i(t) + 1$.

If there are N columns, the probability that a given column has received k atoms during a time $n\delta t$ is

$$\mathbb{P}[h_i(n\delta t) = k] = \binom{n}{k}\left(1 - \frac{1}{N}\right)^{n-k}\frac{1}{N^k}. \tag{17.9}$$

We focus on large systems: we take the limit $N \to \infty$, keeping the injection rate per site λ constant, i.e. $N\delta t = 1/\lambda$. We distribution of the height of a column at a time t becomes

$$\mathbb{P}[h_i(t) = k] = \binom{t/\delta t}{k} \left(1 - \frac{1}{N}\right)^{(t/\delta t)-k} \frac{1}{N^k} \tag{17.10}$$

$$= \frac{(\lambda N t)!}{k!(\lambda N t - k)!} \left(1 - \frac{1}{N}\right)^{\lambda N t - k} \frac{1}{N^k} \tag{17.11}$$

$$\simeq \frac{(\lambda N t)^k}{k!} \mathrm{e}^{-\lambda t} \frac{1}{N^k} \tag{17.12}$$

$$= \mathrm{e}^{-\lambda t} \frac{(\lambda t)^k}{k!} : \tag{17.13}$$

The distribution of $h_i(t)$ is Poisson distribution with parameter λt. A Poisson variable with parameter α has mean and variance α.

The height difference between two sites i and j is thus given by

$$\left\langle [h_i(t) - h_j(t)]^2 \right\rangle = \left\langle h_i(t)^2 \right\rangle + \left\langle h_j(t)^2 \right\rangle - 2 \left\langle h_i(t) h_j(t) \right\rangle \tag{17.14}$$

$$= 2 \left[\left\langle h_i(t)^2 \right\rangle - \langle h_i(t) \rangle^2 \right] \tag{17.15}$$

$$= 2\lambda t. \tag{17.16}$$

We conclude that the width of the interface follows

$$w(L,t) \sim \sqrt{t} = t^\beta, \tag{17.17}$$

where $\beta = 1/2$ is the *growth exponent*. The width does not depend on L, but we can write $w(L) \sim L^\alpha$ with $\alpha = 0$, meaning that the interface is extremely rough.

Here, the interface grows in time but its spatial properties are trivial, because there is no “surface tension” that constraints the height fluctuations as in the previous model.

17.2 Generalities on stochastic growth models

17.2.1 Self-affine behavior and scaling laws

The width of a growing interface depends on its size L and the time t. We have seen simple models where $w(L,t)$ depends separately on this two variables; here, we want to combine these dependences in a single law for the width.

We can discuss the behavior of the width at short and long times in realistic models, with respect to a timescale $t^*(L)$ that is defined later:

— At short times, $t \ll t^*(L)$, points of the interface separated by a large distance do not have time to “communicate”, hence the width is not sensitive to the size L, but only to the time, and we have

$$w(L, t \ll t^*(L)) \sim t^\beta. \tag{17.18}$$

— At long times, $t \gg t^*(L)$, the interface has relaxed to the stationnary state, and its width does not depend on time:

$$w(L, t \gg t^*(L)) \sim L^\alpha. \tag{17.19}$$

As we will show, the characteristic time depends on the size of the system as a power law,

$$t^*(L) \sim L^\kappa, \tag{17.20}$$

with an exponent κ that is not independent of α and β.

Power law behaviors are characteristic of systems that are scale invariant, or *self-affine*, meaning that the height $h(r,t)$ has the same statistical properties as the rescaled height $h_b(s,u)$, defined by

$$h(r,t) = b^{-\alpha} h_b(br, b^\kappa t), \tag{17.21}$$

where b is a scaling factor. From this expression, we can determine the behavior of the width: the width of the interface h is related to the width of the interface h_b via

$$w(L,t) = b^{-\alpha} w_b(bL, b^\kappa t) = b^{-\alpha} w(bL, b^\kappa t) \tag{17.22}$$

because h and h_b have the same statistical properties. Since the scaling factor b is arbitrary, we can set it to $1/L$, leading to

$$w(L,t) = L^\alpha f\left(\frac{t}{L^\kappa}\right), \tag{17.23}$$

where $f(u) = w(1,u)$. This is the most general expression that we can get for a growing interface. We recognize the timescale $t^*(L) = L^\kappa$, and the asymptotic behavior of $f(u)$ can be deduced from Eqs. (17.18,17.19):

— Large times $t \gg t^*(L)$ correspond to $u \gg 1$, and $w(L,t) \sim L^\alpha$ implies that

$$f(u) \underset{u\to\infty}{\rightarrow} f(\infty). \tag{17.24}$$

— Short times $t \ll t^*(L)$ correspond to $u \ll 1$, and $w(L,t) \sim t^\beta$ implies that

$$f(u) \underset{u\to 0}{\sim} u^{\alpha/\kappa} = u^\beta, \tag{17.25}$$

hence

$$\kappa = \frac{\alpha}{\beta}. \tag{17.26}$$

17.2.2 Models

During its growth, the dynamics of an interface contains a deterministic part that depends on its shape and a noisy part:

$$\partial_t h(r,t) = F[h;r,t] + \eta(r,t). \tag{17.27}$$

The noise is usually taken to be a Gaussian white noise in space and time. Since it is Gaussian, its first two cumulants define it completely:

$$\langle \eta(r,t) \rangle = 0, \tag{17.28}$$

$$\langle \eta(r,t)\eta(r',t') \rangle = 2D\delta(r-r')\delta(t-t'), \tag{17.29}$$

where D is a “diffusion constant” (by analogy with the Langevin equation).

The deterministic part is constrained by symmetry considerations, such as invariance under translation and rotation of the space variable r, invariance in time, invariance under translation (but not necessarily inversion) in the direction of growth h. It can be non-local in space, but it is usually local in time, i.e., the system has no memory. Common examples are:

$$F[h;r,t] = \nu\nabla^2 h(r,t) + \lambda[\nabla h(r,t)]^2, \tag{17.30}$$

$$F[h;r,t] = \int \frac{h(r',t)-h(r,t)}{|r'-r|^2}\mathrm{d}r'. \tag{17.31}$$

Eq. (17.30) contains a surface tension term and a non-linear term that arises, e.g., in the KPZ equation (see discussion in Sec. **??**). Eq. (17.31) describes the elasticity of a fracture front or a contact line.

The deterministic part can sometimes be derived from an energy; here, we consider the case of surface tension. The surface energy is given by the area times the surface tension ν:

$$E[h] = \nu \int \sqrt{1+[\nabla h(r)]^2}\mathrm{d}r \simeq E_0 + \frac{\nu}{2}\int [\nabla h(r)]^2 \mathrm{d}r, \tag{17.32}$$

where we have used the small-slope approximation and E_0 is the energy of the flat interface. Now, we compute the change in energy due to a small change in height, $\delta h(r)$:

$$E[h+\delta h] - E[h] = \nu \int \nabla h(r)\cdot\nabla\delta h(r)\mathrm{d}r = -\nu\int \left[\nabla^2 h(r)\right]\delta h(r)\mathrm{d}r. \tag{17.33}$$

This expression allows to identify the functional derivative of the energy with respect to the change in height at r, that gives the force to the interface at this point:

$$F[h,r] = -\frac{\delta E}{\delta h(r)} = \nu\nabla^2 h(r); \tag{17.34}$$

we recover the surface tension term of Eq. (17.30).

Note that the first term of Eq. (17.30) and the expression in Eq. (17.31) tend to flatten the interface, while the noise makes the interface rough.

17.3 Edwards-Wilkinson model

17.3.1 Definition

The Edwards-Wilkinson model represents an interface growing with surface tension:

$$\partial_t h(r,t) = \nu\nabla^2 h(r,t) + \eta(r,t). \tag{17.35}$$

We denote as d the dimension parallel to the interface, i.e., the dimension of the vector r.

17.3.2 Scaling laws

We can determine the exponents by plugging the equation defining a self-affine interface, Eq. (17.21) in Eq. (17.35), leading to

$$b^{\kappa-\alpha}h_b(br,b^\kappa t) = \nu b^{2-\alpha}\nabla^2 h_b(br,b^\kappa t) + \eta(r,t). \tag{17.36}$$

We need to determine how the noise is rescaled; we use its variance:

$$\begin{aligned}
\langle \eta(r,t)\eta(r',t')\rangle &= 2D\delta(r-r')\delta(t-t') && (17.37)\\
&= 2D\delta(b^{-1}b[r-r'])\delta(b^{-\kappa}b^{\kappa}[t-t']) && (17.38)\\
&= 2Db^{d+\kappa}\delta(b[r-r'])\delta(b^{\kappa}[t-t']) && (17.39)\\
&= b^{d+\kappa}\langle \eta(br,b^\kappa t)\eta(br',b^\kappa t')\rangle, && (17.40)
\end{aligned}$$

so that the noise is self-affine with

$$\eta(r,t) = b^{\frac{d+\kappa}{2}}\eta(br, b^\kappa t) \tag{17.41}$$

Hence, the rescaled equation for the evolution of the height is

$$b^{\kappa-\alpha}h_b(br, b^\kappa t) = \nu b^{2-\alpha}\nabla^2 h_b(br, b^\kappa t) + b^{\frac{d+\kappa}{2}}\eta(br, b^\kappa t). \tag{17.42}$$

This equation is identical to the initial one if

$$\kappa - \alpha = 2 - \alpha = \frac{d+\kappa}{2}, \tag{17.43}$$

meaning that

$$\kappa = 2, \tag{17.44}$$

$$\alpha = 1 - \frac{d}{2}. \tag{17.45}$$

We find $\alpha = 1/2$ for a line ($d = 1$), as in the equilibrium interface discussed in Sec. **??**. For $d = 2$, $\alpha = 0$, meaning that the interface does not get wider as the interface gets larger (at least, not as a power law).

17.3.3 Exact solution

The Edwards-Wilkinson model can be solved exactly, and the width of the interface can be computed. In order to do so, we Fourier transform the height in space:

$$\tilde{h}(k,t) = \int \mathrm{e}^{-\mathrm{i}k\cdot r}h(r,t)\mathrm{d}r, \tag{17.46}$$

$$h(r,t) = \int \mathrm{e}^{\mathrm{i}k\cdot r}\tilde{h}(k,t)\frac{\mathrm{d}k}{(2\pi)^d}. \tag{17.47}$$

The evolution of the interface, Eq. (17.35), is now given by

$$\partial_t\tilde{h}(k,t) = -\nu k^2\tilde{h}(k,t) + \tilde{\eta}(k,t). \tag{17.48}$$

The correlation function of the noise is given by

$$\langle\tilde{\eta}(k,t)\tilde{\eta}(k',t')\rangle = \int \mathrm{e}^{-\mathrm{i}[k\cdot r + k'\cdot r']}\langle\eta(r,t)\eta(r',t')\rangle\mathrm{d}r\mathrm{d}r' \tag{17.49}$$

$$= 2D\delta(t-t')\int \mathrm{e}^{-\mathrm{i}[k\cdot r + k'\cdot r']}\delta(r-r')\mathrm{d}r\mathrm{d}r' \tag{17.50}$$

$$= 2D\delta(t-t')\int \mathrm{e}^{-\mathrm{i}(k+k')\cdot r}\mathrm{d}r \tag{17.51}$$

$$= 2(2\pi)^d D\delta(k+k')\delta(t-t'). \tag{17.52}$$

Now that the Fourier modes are decoupled, they can be determined independently:

$$\tilde{h}(k,t) = \int_0^t \mathrm{e}^{-\nu k^2(t-t')}\tilde{\eta}(k,t')\mathrm{d}t'. \tag{17.53}$$

We will need the correlation between two modes, at equal times (the correlation at different times is also interesting):

$$\left\langle \tilde{h}(k,t)\tilde{h}(k',t)\right\rangle = \int_0^t \int_0^t \mathrm{e}^{-\nu k^2(t-t')-\nu k'^2(t-t'')} \langle \tilde{\eta}(k,t')\tilde{\eta}(k',t'')\rangle \mathrm{d}t'\mathrm{d}t'' \tag{17.54}$$

$$= 2(2\pi)^d D\delta(k+k') \int_0^t \mathrm{e}^{-2\nu k^2(t-t')}\mathrm{d}t' \tag{17.55}$$

$$= \frac{(2\pi)^d D}{\nu k^2}\left[1-\mathrm{e}^{-2\nu k^2 t}\right]\delta(k+k'). \tag{17.56}$$

We want to determine the width of the interface, defined as

$$w(r,t)^2 = \left\langle [h(r,t)-h(0,t)]^2\right\rangle = 2\left[\left\langle h(0,t)^2\right\rangle - \langle h(r,t)h(0,t)\rangle\right] = 2[C(0,t)-C(r,t)]. \tag{17.57}$$

We have to compute

$$C(r,t) = \langle h(r,t)h(0,t)\rangle \tag{17.58}$$

$$= \int \mathrm{e}^{\mathrm{i}k\cdot r}\left\langle \tilde{h}(k,t)\tilde{h}(k',t)\right\rangle \frac{\mathrm{d}k\mathrm{d}k'}{(2\pi)^{2d}} \tag{17.59}$$

$$= \frac{D}{\nu}\int \mathrm{e}^{\mathrm{i}k\cdot r}\frac{1-\mathrm{e}^{-2\nu k^2 t}}{k^2}\frac{\mathrm{d}k}{(2\pi)^d}. \tag{17.60}$$

Finally,

$$w(r,t)^2 = \frac{2D}{\nu}\int k^{-2}\left(1-\mathrm{e}^{\mathrm{i}k\cdot r}\right)\left(1-\mathrm{e}^{-2\nu k^2 t}\right)\frac{\mathrm{d}k}{(2\pi)^d}. \tag{17.61}$$

We can extract the dependence on r and t without computing the integral. Changing the integration variable to $q = rk$ ($r = |r|$), we get

$$w(r,t)^2 = \frac{2D}{\nu}r^{2-d}\int q^{-2}\left(1-\mathrm{e}^{\mathrm{i}q_1}\right)\left(1-\mathrm{e}^{-2\nu q^2 t/r^2}\right)\frac{\mathrm{d}q}{(2\pi)^d} = \frac{2D}{\nu}r^{2\alpha}f\left(\frac{t}{t^*(r)}\right), \tag{17.62}$$

where q_1 is the component of the vector q parallel to r and $t^*(r) = r^2/\nu$. We recover $\alpha = 1-d/2$, $\kappa = 2$, and we have an explicit expression for the scaling function,

$$f(u) = \int q^{-2}\left(1-\mathrm{e}^{\mathrm{i}q_1}\right)\left(1-\mathrm{e}^{-2q^2 u}\right)\frac{\mathrm{d}q}{(2\pi)^d}. \tag{17.63}$$

We can easily get the derivative of f:

$$f'(u) = 2\int \left(1-\mathrm{e}^{\mathrm{i}q_1}\right)\mathrm{e}^{-2q^2 u}\frac{\mathrm{d}q}{(2\pi)^d} = \frac{2}{(8\pi u)^{d/2}}\left(1-\mathrm{e}^{-1/(8u)}\right). \tag{17.64}$$

In the long time limit, Eq. (17.60) becomes

$$C(r,\infty)\frac{D}{\nu}\int \frac{\mathrm{e}^{\mathrm{i}k\cdot r}}{k^2}\frac{\mathrm{d}k}{(2\pi)^d}. \tag{17.65}$$

Hence,

$$\nabla^2 C(r,\infty) = -\frac{D}{\nu}\int \mathrm{e}^{\mathrm{i}k\cdot r}\frac{\mathrm{d}k}{(2\pi)^d} = -\frac{D}{\nu}\delta(r). \tag{17.66}$$

This means that $C(r,\infty)$ has the form of the electrostatic potential created by a charge at the origin in dimension d.

17.3.4 Dependence on the dimension

$d = 1$–

In dimension $d = 1$, we can compute $f(u)$ for arbitrary u:

$$f(u) = \sqrt{\frac{2u}{\pi}}\left(1 - \mathrm{e}^{-1/(8u)}\right) + \frac{1}{2}\operatorname{erfc}\left(\frac{1}{\sqrt{8u}}\right). \tag{17.67}$$

Notably,

$$f(u) \underset{u\to 0}{\sim} \sqrt{\frac{2u}{\pi}}, \tag{17.68}$$

$$f(u) \underset{u\to\infty}{\to} \frac{1}{2}. \tag{17.69}$$

The solution to Eq. (17.66) is

$$C(x,\infty) = -\frac{D}{2\nu}|x|. \tag{17.70}$$

Hence the “width” at a scale x is

$$w(x,\infty)^2 = \frac{D|x|}{\nu}. \tag{17.71}$$

$d = 2$–

At short times, $f'(u) \simeq 1/(4\pi u)$, hence

$$f(u) \underset{u\to 0}{\sim} \frac{\log(u)}{4\pi}. \tag{17.72}$$

The solution to Eq. (17.66) is

$$C(r,\infty) = -\frac{D}{4\pi\nu}\log(r). \tag{17.73}$$

These logarithmic dependences are somehow problematic, they mean that the theory is ill defined and that additionnal regularizing terms are required.