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LINEAR RESPONSE THEORY FOR NONEQUILIBRIUM TIME-DEPENDENT SYSTEMS
EXTENSION OF FLUCTUATION-DISSIPATION RELATIONS

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Chapter 1

Introduction

1.1 The mesoscopic level

Any physical system can be described in two ways considering a macroscopic or a microscopic point of view. For example, a gas confined in a box can be thermodynamically described defining a temperature and a pressure. In this case we are considering a macroscopic point of view, since the involved observables are indeed macroscopic. On the other hand, the gas is made by a huge numbers (say N) of interacting particles. Each particle has a velocity and a position at each time. These observables, that are microscopic, are described (ignoring quantum aspect) by the Newton equations. If we could solve them we would obtain a gas interpretation equivalent to the macroscopic one. But, usually in physics most systems are too complicated to be solved by the Newton equations. In this case the dynamics is practically unpredictable.

Therefore, theoretically the two interpretations are equivalent, but practically their gap is unfillable. During the nineteenth century, due to Gibbs, a new theory began to rise in order to create a bridge between microscopic and macroscopic worlds, the Statistical Mechanics. The idea is to define two different kind of states: the microstate referred to the Newtonian/Hamiltonian dynamics and the macrostate referred to the macroscopic observables. As formulated within thermodynamics, the macrostate of an ideal gas in equilibrium is described by a small number of state functions such as energy E, temperature T, pressure P, and N. The space of macrostates is considerably smaller than the phase space spanned by microstates. Therefore, there must be a very large number of microstates corresponding to the same macrostate. The description of each microstate requires an enormous amount of information. Rather than following the evolution of an individual microstate, statistical mechanics examines an ensemble of microstates corresponding to a given macrostate. It aims to provide the probabilities for the ensemble. Therefore the starting point is the microscopic world (the phase space), from it we obtain a probability density in order to describe the macroscopic observables. These results are strictly related to the macroscopic world via the fluctuations. For example if we consider a canonical ensemble we suppose the energy of the system could fluctuate, but macroscopically the energy of a equilibrium gas is fixed. Given that the number of particles is huge there is no contradiction, since with increasing N the fluctuation intensity tends to zero.

In the end, the purpose of statistical mechanics is twofold: on the one hand to describe the macroscopic world, and derive its physical behavior, starting from the microscopic level. On the other hand, statistical mechanics makes more predictions than thermodynamics, because it also describes the deviations (fluctuations) from the average behavior. The statistical mechanics is a self contained probabilistic approach to equilibrium macroscopic properties of large numbers of degrees

of freedom. In this definition reported in [12], there is a fundamental and, meanwhile, constraining word: equilibrium. This theory is valid only if the system of particles is at equilibrium. What happens if the system is not at equilibrium? Thermodynamically (and macroscopically) there is a theory developed by Onsager for systems close to equilibrium [13]. Furthermore under some assumptions a nonequilibrium system can be described as sum of weakly interacting equilibrium subsystems. Microscopically, the Newtonian equations are still not solvable. Therefore again we are interested in finding a gap filling interpretation using stochastic processes.

As we have said the interaction between the particles makes the microscopic motion equations not solvable. This lack of knowledge can be probabilistically interpreted. In other words, the interaction can be seen as a random force acting on the probe and therefore its evolution can be described by a random variable. Evidently it is an approximation, but it becomes reasonable if we expect that not every detailed aspect of that dynamics is relevant for the macroscopic world. Most models in nonequilibrium statistical mechanics based on it are reduced descriptions, since they do not contain all the information of the macroscopic world. On the other hand, to be able to describe fluctuations from the typical macroscopic behavior, a more detailed description than the macroscopic one is needed. We then say that we are working on the mesoscopic level.

One should think of a mesoscopic model as describing a small system, for which the description is not detailed enough to be Newtonian, but is not big enough for the law of large numbers to apply. Fluctuations around the statistical averages are important. As a consequence a model describing a mesoscopic system can be a stochastic process. A stochastic process is therefore a very important tool in nonequilibrium statistical processes. An important part of the present day research is therefore committed to finding 'recipes' for defining stochastic processes that are physically relevant. One way to do this is via the local detailed balance assumption, which will be discussed in the next chapters, and is used throughout this text. In this part we will treat the jump processes. In the second one we will develop the diffusive processes. Though these processes present different characteristics, they both describe mesoscopic level dynamics.

1.2 Nonequilibrium examples

Before starting to present the stochastic calculus we want to introduce the nonequilibrium regime via examples:

- Consider a material (e.g. a metal rod) connected to a hot environment at one end and to a cold environment at the other end. Energy flows from the hot side to the cold side. The environments at different temperatures are "frustrating" the system and, on the appropriate time-scale where the conflicting reservoirs remain each at equilibrium keeping their temperatures fixed, a stationary heat current will be maintained in the system. Note however that heat will be flowing in/out of these reservoirs changing their energy. That gives rise to an entropy flux. Statistical mechanics wants to derive the transport equations (such as the Fourier law) and to understand also the more microscopic nature of thermal conductivity.

- In an electrical circuit, charges are displaced and these currents are usually created by an external source such as a battery. The battery works to displace electric charges maintaining a current which itself causes Joule heating in any resistor. That is a way of heat dissipation into the environment. There will also be fluctuations and noise on the potential and current over and through a resistor. Untill the difference of potential is maintained in the circuit,

the system (the charged particle) are kept out of equilibrium and entropy is produced, via the Joule effect.

- At the membrane of a biological cell, currents of ions are passing through pores due to gradients in electrical and/or chemical potential. These are influenced by the environment and are subject to fluctuations. Also within the cell there is transport and dissipation driven e.g. by the ATP-concentration. As we are dealing with active matter (e.g. molecular motors), there may be features in the relation between fluctuations and response of the currents that differ significantly from the case of passive elements as in the previous examples.

An important property of nonequilibrium systems, in contrast to equilibrium, is that time plays an important role. First of all because nonequilibrium processes are irreversible: an arrow of time is introduced. The question of how irreversibility emerges when going from the reversible microscopic world to the macroscopic world was already discussed by Boltzmann himself. Apart from that, it seems clear that nonequilibrium systems are by their very nature dynamical. This is because systems are either out of equilibrium because they are driven from equilibrium and are in some stationary regime in which there are particles or heat currents present, or because they are in the process of relaxing to equilibrium (or to a stationary state). This means that not only the microstates themselves are important, but also the way in which they change in time. Generally, we distinguish three ways for systems to be out of equilibrium:

- First, systems that are in the process of relaxing to equilibrium: when a parameter determined by the environment changes, like temperature or volume, the system always needs some time to relax to that new equilibrium state. For example, when a hot cup of coffee is placed in a room at room temperature, heat will start to flow from the coffee to the air of the room. After some time the coffee and the air will relax to a new equilibrium state: the coffee cools down to room temperature. Before that time, however, the coffee is not in equilibrium with the room, and the process is not reversible, this regime is called the transient regime. Here we observe the system undergoing important changes in time. Currents are growing or are disappearing. Phase segregation takes place or some order parameter relaxes to a stationary value. If it was reversible, then we would not be surprised to observe heat to flow spontaneously from the air to the coffee, heating it up again.

- Secondly there are systems that are driven from equilibrium by what we call time-independent forces. Usually after a relaxing time such systems converge to a stationary time-independent regime. For open and driven systems, we can have stationary profiles in density and currents. We speak then of the nonequilibrium steady state. The steady state regime for nonequilibrium systems has been drawing more attention only over the last 50 years or so. Note that all the examples we have presented converge to a stationary regime, if the temperature reservoirs (or the difference of potential or the chemical potential) are constant in time.

- Thirdly when time-dependent forces act on the system, it cannot converge to a stationary solution. We can for example imagine that the magnetic field on a ferromagnet is periodic. The behavior of such systems is also an important business of nonequilibrium physics. We apply time–dependent control or parametrization on the system. It could be in the form of a time–dependent external field or a time–dependent volume etc. All the time the system probably wants to relax to a condition corresponding to the instantaneous values of the parameters. In other words, the system gets frustrated by its always lagging behind the external situation.

1.3 Outline and preview of the results

The framework of this thesis is nonequilibrium. In the previous Section we have presented three examples of nonequilibrium regime. But in those cases after a relaxing time the system converges to a stationary state. What we are interested to study is the third way of being out of equilibrium, the time-dependent one. In particular we are interested in studying the periodic regime in which the system is kept out of equilibrium by a periodic force. We expect the system, after a relaxing time, will converge to a kind of stationary state. Evidently it could not be time-independent, but it should depend periodically in time.

1.3.1 Part I

In the first part we will study a particular case of Markovian time-dependent processes: the jump processes with continuous time. The evolution takes place through instantaneous transitions or "jumps" from a state to another, with exponentially distributed waiting times. This kind of process is characterized by two quantities that we will describe in the following:

- a distribution that gives at any time the probability of being in a certain state
- a matrix that gives the transition rates between the states. These rates determine the probability to stay in a certain state for a certain time and the probability to jump in another state.

In Chapter 2, using this kind of processes, we will study the entropy production, characteristic of nonequilibrium regime. It is very interesting since it is the link between the physics of nonequilibrium regime and mathematics of the stochastic processes. In order to do this we will present the local detailed balance principle, extension to nonequilibrium of detailed balance relation for time-independent Markov chains. While, in Chapter 3, we will study the linear response theory for jump processes for time-dependent potential perturbation. The linear response theory is an useful tool in order to study complex systems. In fact a complex system, even unsolvable, can be seen as a simpler system plus a perturbation. Expanding the perturbation to the first order, it is possible to study the perturbed dynamics in function of the unperturbed one. The aim of response theory is to predict and to characterize systematically the response of a system when it is perturbed in some way. The idea is explained in Chapter 3. The response formula for nonequilibrium systems depends on two terms, one is called entropic and it is related to the entropy flux from the system to the environment produced, the second is called frenetic and it depends on the dynamical activity (we will describe these two terms in the following). If the perturbation is time-dependent a new entropic term appears.

1.3.2 Part II

In the second part we will study another case of Markovian time-dependent processes: the diffusive process. For this kind of processes, the evolution takes place via a continuous stochastic trajectory given at any time by the Langevin equation. According to the Markovian logic it is possible to determine the value of the process at time $t+dt$ only knowing the value at time t. This is what the Langevin equation does. It is made by two contributions: one deterministic that depends on the forces acting on the system, one stochastic that depends on the environment action on the system that is probabilistically interpreted in agreement with what we have said about the mesoscopic level.

In Chapter 5 we will describe the meaning of the Langevin equation starting from the equilibrium regime, and we will extend it to nonequilibrium in Chapter 6. In this Chapter we will derive the Langevin equation for a probe particle embedded in a nonequilibrium fluid obtaining an expression for the friction perceived by the probe interacting with the fluid (nonequilibrium second fluctuation-dissipation relation). In order to do this, we will start in Chapter 5 from the equilibrium case: the motion of a probe particle embedded in an equilibrium fluid (equilibrium Brownian motion) introducing the equilibrium version of fluctuation-dissipation relation. At equilibrium it is equivalent to the Einstein-Smoluchowski relation that relates the friction and the noise perceived by the probe particles to the temperature of the fluid. This result is very important in order to explain why at equilibrium the properties of the probe particle can be derived from the surrounding fluid. The purpose is to extend it to the nonequilibrium case introducing the local detailed balance principle explained in 2.2.2. This principle allows to extend some equilibrium relation to the nonequilibrium framework with some considerations. Moreover, in Chapter 5, we will study the entropy production along the trajectories explaining the difference between stationarity and not-stationarity in the context of the diffusive processes.

Part I

Jump Processes

Chapter 2

Formalization of the problem

2.1 Markov dynamics

As said in the introduction in the following chapters we will develop some tools in order to describe complex systems with probabilistic approaches. Since we will work at the mesoscopic level we will have to start from the microscopic world, as done for the Statistical Mechanics. The difference is that now we will not consider statistical ensemble of microstates in the phase space, but we will study directly the evolution of the motion in the phase space, taking as fundamental ingredient the trajectory that, for example, a particle makes. This trajectory will be described using stochastic processes. In particular, in this part we will consider discrete stochastic processes that can assume a finite number of value. Consider a stochastic process x_t that can assume values from a discrete set S, suppose that x_t describes the position of a particle at time t. Its evolution is stochastic and it is determined by probability density $P_t(x)$. At any time, it gives the probability of assuming a certain value. The $P_t(x)$ must satisfy:

- $P_t(x) \geq 0 \qquad \forall x \in S$
- $\sum_{x \in S} P_t(x) = 1 \qquad \forall t$
- it must be differentiable and integrable with respect to t

Nevertheless, if we suppose that the values of x_t at different times are not independent, this procedure can be really complicated since we should take into account all the dynamics evolution in order to find the probability $P_t(x)$. This approach is very complicated, especially if at each time the position is affected by all the previous times. To go through this problem, an approximation is usually adopted.

A dynamics is called Markovian if, given where the probe is at time s, the future evolution ($t > s$) depends only on the system at time s and it does not depend on its previous history. In other words, once known the present, the future is independent of the past. A system that satisfies this condition is said memoryless. In fact, consider n values $x_1 \dots x_n$ assumed by x_t at time $t_1 \dots t_n$ chronologically arranged. The probability that x_t, using the Markov approximation, assumes all these values during its evolution is given by:

$$P(x_1, t_1; x_2, t_2; \dots; x_n, t_n \mid x_0, t_0) = P(x_1, t_1 \mid x_0, t_0)\, P(x_2, t_2 \mid x_1, t_1) \dots P(x_n, t_n \mid x_{n-1}, t_{n-1})$$

where the conditional probability is defined by:

$$P\left(x_2, t_2 \mid x_1, t_1\right) = Prob\left\{x_{t_2} = x_2,\ given\, x_{t_1} = x_1\right\} \tag{2.1.1}$$

In the following we will present with a mathematical approach the Markovian approximation and its properties.

2.1.1 Master equation

We consider a stochastic variable x_s that can assume m values from the set $S = \{1, \ldots, m\}$. We want to describe its evolution as an inhomogeneous continuous-time Markov chain on the set of states S. This approach can be used to describe several physical problems in the Markov approximation: for example the states can represent the position or velocity of a brownian particle moving in a fluid, or the direction of all the spins in a configuration for the Ising model. The starting point for any jump process is the master equation for the states:

$$\frac{dP_t\left(x\right)}{dt} = \sum_{y \neq x} \left[P_t\left(y\right) k_t\left(y, x\right) - P_t\left(x\right) k_t\left(x, y\right)\right] \tag{2.1.2}$$

where x is one of the m states. It gives the probability $P_t\left(x\right)$ at any time t. We have a system of m equations plus the condition of probability conservation. Generally, the probability evolution of being in a state depends on all the other states. The master equation can be written in a vectorial form introducing the matrix L_t:

$$\frac{dP_t}{dt} = P_t L_t \tag{2.1.3}$$

where L_t is called backward generator. This equation can be formally solved:

$$P_t = P_0 e^{\int_0^t ds\, L_s} \tag{2.1.4}$$

where P_0 is the initial distribution (we are going to call it μ). Since the transition rates depend on time, the matrix cannot be extracted from the integral. For example, the probability that the system will be in state y at time t if it was in x at time $t = 0$ is:

$$\mathbb{P}_t\left[x_t = y \mid x_0 = x\right] = \left(e^{\int_0^t ds\, L_s}\right)_{xy}$$

To calculate it, we have to integrate the matrix elements, get the exponential of the new matrix $\int_0^t ds\, L_s$ and finally take the desired matrix element.

2.1.2 Backward generator

Given that the set of states is discrete, the evolution is meant as a sequence of configurations in each of which the system assumes one of the m values with a certain probability. It is determined by the matrix associated to the Markov chain.

$$L_t = \begin{pmatrix} -\sum\limits_{x \neq 1} k_t\left(1, x\right) & k_t\left(1, 2\right) & k_t\left(1, 3\right) & \ldots & k_t\left(1, k\right) \\ k_t\left(2, 1\right) & -\sum\limits_{x \neq 2} k_t\left(2, x\right) & k_t\left(2, 3\right) & \ldots & k_t\left(2, k\right) \\ k_t\left(3, 1\right) & k_t\left(3, 2\right) & -\sum\limits_{x \neq 3} k_t\left(3, x\right) & \ldots & k_t\left(3, k\right) \\ \vdots & \vdots & & \ddots & \vdots \\ k_t\left(k, 1\right) & k_t\left(k, 2\right) & k_t\left(k, 3\right) & \ldots & -\sum\limits_{x \neq k} k_t\left(k, x\right) \end{pmatrix}$$

The off-diagonal elements are called transition rates:

$$k_t(x,y) = L_t(x,y) \qquad x \neq y$$

The diagonal elements are minus the so called escape rates:

$$\lambda_t(i) = \sum_{x \neq i} L_t(i,x) \tag{2.1.5}$$

It is important to note that all the rows sum to zero:

$$\sum_x L_t(i,x) = 0 \tag{2.1.6}$$

The transition rates describe how the system evolves. So, the choice of the matrix is based on the model with which we want to describe a physical phenomenon. Note that if the backward generator is time dependent a stationary distribution cannot exist. By definition a stationary distribution is found by putting the left-hand side of (2.1.2) equal to zero. But if the right-hand side is time-dependent this is not possible. We will consider a class of Markov process that cannot relax to stationarity in order to study nonequilibrium.

2.1.3 Transition rates

We assumed that the transition rates could depend on time (this is the origin of inhomogeneity). It assures that the system cannot be at equilibrium. Physically we can imagine that there is an external force that keeps it out of equilibrium and prevents it from converging to an invariant distribution. In addition such dependence on time makes impossible even the existence of a stationary state obtained from the master equation. It is useful to parametrize the transition rates $\forall\, x, y \in S$:

$$k_t(x,y) = a_t(x,y)\, e^{\frac{F_t(x,y)}{2}} \tag{2.1.7}$$

The opposite transition has rate:

$$k_t(y,x) = a_t(x,y)\, e^{-\frac{F_t(x,y)}{2}} \tag{2.1.8}$$

with $a_t(x \to y) = a_t(y \to x)$ time-symmetric and $F_t(x \to y) = -F_t(y \to x)$ time-antisymmetric:

- a_t is called reactivity of the transition and it gives its intensity, for this reason it is always not negative unless the transition is forbidden. Usually it is also called kinetic contribution since it has similarities with mechanical kinetic energy. In fact the kinetic energy for a probe moving with velocity v is $E_k = \frac{1}{2}mv^2$ regardless to the sign of the velocity, therefore it is invariant under time-reversal.

- F_t is called the drive of the transition because it gives probabilistically the direction. In fact, at any time, F_t can facilitate a transition to the detriment of the opposite one. This is due to its antisymmetry.

Generally we do not assume anything on the two functions. The ratio

$$\frac{k_t(x,y)}{k_t(y,x)} = e^{F_t(x,y)} \tag{2.1.9}$$

does not depend on the reactivity, it depends only on the direction of the transition. It is interesting to note that $F_t(x,y)$ cannot always be written in function of a potential if the number of states is bigger than 2. To demonstrate it we can consider a three states system. In fact, if for example we take $S = \{0,1,2\}$, possible values of $F_t(x,y)$ are:

$$F_t(0,1) = -F_t(1,0) \qquad F_t(0,2) = -F_t(2,0) \qquad F_t(1,2) = -F_t(2,1)$$

If $F_t(x,y)$ could be written as a potential we would have:

$$F_t(0,1) = U_t(0) - U_t(1) \qquad F_t(0,2) = U_t(0) - U_t(2) \qquad F_t(1,2) = U_t(1) - U_t(2)$$

Then, if we consider:

$$F_t(0,1) + F_t(1,2) = U_t(0) - U_t(1) + U_t(1) - U_t(2) = U_t(0) - U_t(2) = F_t(0,2)$$

In this case there is a condition between the values assumed by $F_t(x,y)$ and then the function cannot be general at all.

2.1.3.1 Example: periodic transition rates

Now we want to consider the case in which the time-dependence of the transition rates is periodic. For example:

$$k_t(x,y) = A\cos(\omega_{xy} t)$$

where ω_{xy} is the oscillation frequency for a particular transition. In general there is a different frequency for each transition. Since the rates are periodic we expect that also the backward generator will be periodic, but its period $\mathcal{T}$ depends on all the transition frequencies, since $\mathcal{T}$ is the greatest common divisor of all them. Using the (2.1.4) we can relate the periodicity of the backward generator to the probability. In fact the integration and the exponentiation are two operations that do not modify the periodicity of the matrix L_t. Then if we call:

$$M_t = e^{\int_0^t ds\, L_s}$$

We expect that:

$$L_{t+\mathcal{T}} = L_t \quad \Longrightarrow \quad M_{t+\mathcal{T}} = M_t$$

From this result it is easy to note that also the probability P_t is periodic. Therefore there is no an asymptotic behavior in the long-time limit, but the probability evolves in the same way for each time interval $[t, t+\mathcal{T}]$. For this reason the periodic time-dependence situation can be thought as the "stationary" state of the time-dependent Markov processes though, obviously, it is not stationary at all. It is interesting to demonstrate it with calculations. Nevertheless, to solve the master equation for a generic number of states is not analytically possible, therefore we have solved it for a two states system and simulated it for a generic number of states.

2.1.3.2 Example: two states system with periodic rates

For a two states system with $S = \{0,1\}$ the master equation is:

$$\begin{cases} \frac{dP_t(0)}{dt} = P_t(1)\,\beta_t - P_t(0)\,\alpha_t \\ \frac{dP_t(1)}{dt} = P_t(0)\,\alpha_t - P_t(1)\,\beta_t \end{cases}$$

Using the conservation of probability:

$$\frac{dP_t(0)}{dt} = (1 - P_t(0))\beta_t - P_t(0)\alpha_t = -(\alpha_t + \beta_t)P_t(0) + \beta_t$$

To do it we have to multiple both sides by a function r_t

$$r_t\frac{dP_t(0)}{dt} + r_t P_t(0)(\alpha_t + \beta_t) = r_t\beta_t$$

$$r_t\frac{dP_t(0)}{dt} + P_t(0)\frac{dr_t}{dt} = r_t\beta_t$$

If we call:

$$\begin{cases} \frac{dr_t}{dt} = r_t(\alpha_t + \beta_t) \\ \frac{dg_t}{dt} = \frac{d}{dt}(r_t P_t(0)) \end{cases}$$

We can now solve the equation for g_t:

$$g_t = r_t P_t(0) = r_0 P_0(0) + \int_0^t r_s\beta_s ds$$

The equation for r_t is easily solvable:

$$r_t = r_0 e^{\int_0^t(\alpha_s+\beta_s)ds}$$

If we insert the expression for r_t in equation for $P_t(0)$ we can find:

$$\begin{cases} P_t(0) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_0(0) + \int_0^t \beta_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\, ds\right) \\ P_t(1) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_0(1) + \int_0^t \alpha_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\, ds\right) \end{cases}$$

As we could expect there is no stationary solution in which the probabilities are time-independent. If we consider the periodic case:

$$\alpha_t = \alpha_0 + \varepsilon\cos\omega t \qquad\qquad \beta_t = \beta_0 - \varepsilon\cos\omega t$$

We assume that ε is small, so $\forall t$ the transition rates are positive. We will find:

$$\begin{cases} P_t(0) = e^{-(\alpha_0+\beta_0)t}\left(P_0(0) + \int_0^t (\beta_0 - \varepsilon\cos\omega s)\, e^{(\alpha_0+\beta_0)s}\, ds\right) \\ P_t(1) = e^{-(\alpha_0+\beta_0)t}\left(P_1(0) + \int_0^t (\alpha_0 + \varepsilon\cos\omega s)\, e^{(\alpha_0+\beta_0)s}\, ds\right) \end{cases}$$

Solving the integral:

$$\begin{cases} P_t(0) = e^{-(\alpha_0+\beta_0)t}\left(P_0(0) + \frac{\beta_0}{\alpha_0+\beta_0}\left(e^{(\alpha_0+\beta_0)t} - 1\right) - \varepsilon e^{(\alpha_0+\beta_0)t}\,\frac{(\alpha_0+\beta_0)\cos\omega t + \omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} + \varepsilon\,\frac{(\alpha_0+\beta_0)}{(\alpha_0+\beta_0)^2+\omega^2}\right) \\ P_t(1) = e^{-(\alpha_0+\beta_0)t}\left(P_0(1) + \frac{\alpha_0}{\alpha_0+\beta_0}\left(e^{(\alpha_0+\beta_0)t} - 1\right) + \varepsilon e^{(\alpha_0+\beta_0)t}\,\frac{(\alpha_0+\beta_0)\cos\omega t + \omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} - \varepsilon\,\frac{(\alpha_0+\beta_0)}{(\alpha_0+\beta_0)^2+\omega^2}\right) \end{cases} \tag{2.1.10}$$

Finally we obtain:

$$\begin{cases} P_t(0) = e^{-(\alpha_0+\beta_0)t}\left(P_0(0) - \frac{\beta_0}{\alpha_0+\beta_0} + \varepsilon\frac{(\alpha_0+\beta_0)}{(\alpha_0+\beta_0)^2+\omega^2}\right) + \frac{\beta_0}{\alpha_0+\beta_0} - \varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} \\ P_t(1) = e^{-(\alpha_0+\beta_0)t}\left(P_0(1) - \frac{\alpha_0}{\alpha_0+\beta_0} - \varepsilon\frac{(\alpha_0+\beta_0)}{(\alpha_0+\beta_0)^2+\omega^2}\right) + \frac{\alpha_0}{\alpha_0+\beta_0} + \varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} \end{cases}$$

If t increases the first term tends to zero exponentially. We have obtained a periodic expression for the probabilities:

$$\begin{cases} P_t(0) = \frac{\beta_0}{\alpha_0+\beta_0} - \varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} \\ P_t(1) = \frac{\alpha_0}{\alpha_0+\beta_0} + \varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2} \end{cases} \tag{2.1.11}$$

In this periodic solution the current between the two state is:

$$J_{0,1}(t) = \varepsilon\cos\omega t + 2\varepsilon(\alpha_0+\beta_0)\frac{\omega\sin\omega t + (\alpha_0+\beta_0)\cos\omega t}{(\alpha_0+\beta_0)^2+\omega^2}$$

As we could expect the current is not zero, otherwise the system will be in equilibrium, but it is periodic. We have described the system when the transition rates are periodic, but only the case in which α_t and β_t depend on cosine. It would be interesting to study the case in which α_t depends on cosine and β_t depends on sine. This situation is difficult as regards the calculations, so we will treat a simpler dependence.

$$\alpha_t = \alpha_0 + \varepsilon f(t) \qquad\qquad \beta_t = \beta_0 + \varepsilon g(t)$$

We suppose that the f and g can assume only two values (± 1) and that they change at fixed time τ, like a square wave. To simulate the phase displacement of the sine respect to cosine we suppose that when $f(t)$ assumes value $+1$, $g(t)$ assumes value -1 . We can give an analytic expression of the function with the Θ of Heaviside.

$$f(t) = \Theta(\tau - t) - \Theta(t-\tau) + 2\sum_{k=1}^{n}(-1)^{k+1}\Theta(t-(k+1)\tau)$$

$$g(t) = \Theta(t-\tau) + 2\sum_{k=1}^{n}(-1)^{k}\Theta(t-(k+1)\tau)$$

Where n is the number of times that f and g change value ($n\tau = t$). If we put this expression in the probabilities equation:

$$\begin{cases} P_0(t) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_0(0) + \int_0^t \beta_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\,ds\right) \\ P_1(t) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_1(0) + \int_0^t \alpha_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\,ds\right) \end{cases}$$

Firstly we note that:

$$e^{-\int_0^t(\alpha_s+\beta_s)ds} = e^{-\int_0^t\left(\alpha_0+\beta_0+\varepsilon\Theta(\tau-s)-\varepsilon\Theta(s-\tau)+2\varepsilon\sum\limits_{k=1}^{n}\left((-1)^{k+1}+(-1)^k\right)\Theta(s-(k+1)\tau)+\varepsilon\Theta(s-\tau)\right)ds}$$

$$e^{-\int_0^t(\alpha_s+\beta_s)ds} = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}$$

$$P_1(t) = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_1(0) + \int_0^t \left[\alpha_0 + \varepsilon\left(\Theta(\tau - s) - \Theta(s - \tau)\right)\right] e^{(\alpha_0+\beta_0)s}e^{\varepsilon\tau}ds\right]$$

$$-e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\int_0^t \left(2\sum_{k=1}^{n}(-1)^k\,\Theta\left(s - (k+1)\,\tau\right)\right) e^{(\alpha_0+\beta_0)s}e^{\varepsilon\tau}ds$$

Solving the integral:

$$P_1(t) = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_1(0) + \frac{\alpha_0 e^{\varepsilon\tau}}{\alpha_0+\beta_0}\left(e^{(\alpha_0+\beta_0)t} - 1\right) + \varepsilon e^{\varepsilon\tau}\int_0^\tau e^{(\alpha_0+\beta_0)s}\,ds\right] -$$

$$-\varepsilon e^{-(\alpha_0+\beta_0)t}\left[\int_\tau^t e^{(\alpha_0+\beta_0)s}\,ds + 2\sum_{k=1}^{n}(-1)^k\int_{(k+1)\tau}^t e^{(\alpha_0+\beta_0)s}\,ds\right]$$

Then:

$$P_1(t) = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_1(0) + \frac{\alpha_0 e^{\varepsilon\tau}}{(\alpha_0+\beta_0)}\left(e^{(\alpha_0+\beta_0)t} - 1\right) + \frac{\varepsilon e^{\varepsilon\tau}}{\alpha_0+\beta_0}\left(e^{(\alpha_0+\beta_0)\tau} - 1\right)\right] -$$

$$-\varepsilon e^{-(\alpha_0+\beta_0)t}\left[\frac{e^{(\alpha_0+\beta_0)t} - e^{(\alpha_0+\beta_0)\tau}}{\alpha_0+\beta_0} + \frac{2}{\alpha_0+\beta_0}\sum_{k=1}^{n}(-1)^k\left(e^{(\alpha_0+\beta_0)t} - e^{(\alpha_0+\beta_0)(k+1)\tau}\right)\right]$$

$$P_1(t) = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_1(0) - \frac{\alpha_0 e^{\varepsilon\tau} - 2\varepsilon e^{(\alpha_0+\beta_0+\varepsilon)\tau} + \varepsilon e^{\varepsilon\tau}}{\alpha_0+\beta_0}\right] + \frac{1}{\alpha_0+\beta_0}\left(\alpha_0 - \varepsilon - 2\varepsilon\sum_{k=1}^{n}(-1)^k\right) +$$

$$+\frac{2\varepsilon}{\alpha_0+\beta_0}e^{(\alpha_0+\beta_0)(\tau-t)}\sum_{k=1}^{n}(-1)^k\,e^{(\alpha_0+\beta_0)k\tau}$$

The second contribution depends on n:

- n even $\rightarrow \sum_{k=1}^{n}(-1)^k = 0 \implies \frac{\alpha_0-\varepsilon}{\alpha_0+\beta_0}$
- n odd $\rightarrow \sum_{k=1}^{n}(-1)^k = -1 \implies \frac{\alpha_0+\varepsilon}{\alpha_0+\beta_0}$

The third contribution:

$$\frac{2\varepsilon e^{(\alpha_0+\beta_0)(\tau-t)}}{\alpha_0+\beta_0}\sum_{k=1}^{n}(-1)^k\,e^{(\alpha_0+\beta_0)k\tau} = \frac{2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{\alpha_0+\beta_0}\frac{e^{-(\alpha_0+\beta_0)t}}{e^{(\alpha_0+\beta_0)k\tau}+1}\left((-1)^n e^{(\alpha_0+\beta_0)t} - 1\right)$$

$$\frac{2\varepsilon e^{(\alpha_0+\beta_0)(\tau-t)}}{\alpha_0+\beta_0}\sum_{k=1}^{n}(-1)^k\,e^{(\alpha_0+\beta_0)k\tau} = \frac{2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{\alpha_0+\beta_0}\left[\frac{(-1)^n - e^{-(\alpha_0+\beta_0)t}}{e^{(\alpha_0+\beta_0)\tau}+1}\right]$$

Finally:

$$P_1(t) = e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_1(0) - \frac{\alpha_0 e^{\varepsilon\tau} - 2\varepsilon e^{(\alpha_0+\beta_0+\varepsilon)\tau} + \varepsilon e^{\varepsilon\tau}}{\alpha_0+\beta_0} - \frac{2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{\alpha_0+\beta_0}\frac{1}{e^{(\alpha_0+\beta_0)\tau}+1}\right] +$$

$$+\frac{1}{\alpha_0+\beta_0}\left(\alpha_0-\varepsilon-2\varepsilon\sum_{k=1}^{n}(-1)^k+\frac{(-1)^n\ 2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{e^{(\alpha_0+\beta_0)\tau}+1}\right)$$

$$P_0(t)=e^{-(\alpha_0+\beta_0)t}e^{-\varepsilon\tau}\left[P_0(0)-\frac{\beta_0 e^{\varepsilon\tau}-\varepsilon e^{(\alpha_0+\beta_0+\varepsilon)\tau}}{\alpha_0+\beta_0}+\frac{2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{\alpha_0+\beta_0}\frac{1}{e^{(\alpha_0+\beta_0)\tau}+1}\right]+$$

$$+\frac{1}{\alpha_0+\beta_0}\left(\beta_0+\varepsilon+2\varepsilon\sum_{k=1}^{n}(-1)^k-\frac{(-1)^n\ 2\varepsilon e^{2(\alpha_0+\beta_0)\tau}}{e^{(\alpha_0+\beta_0)\tau}+1}\right)$$

The dependence on time is in the n. The g and f are periodic of period 2τ. We can note that also the probabilities are periodic:

$$t+2\tau=n\tau+2\tau\ \ \Rightarrow\ \ n+2$$

In fact, add two terms in the sum does not contribute because the result is zero. And in the last term there would be an irrelevant factor 1.

2.1.3.3 Example: covariance in the long time-limit

Now we want to study the correlation of the process at different time. It will be useful in the following. If we consider a two states system (0,1) with periodic transition rates:

$$\alpha_t=k_t(0\to1)\qquad\qquad\beta_t=k_t(1\to0)$$

such that:

$$\alpha_t=\alpha_0+\varepsilon\cos\omega t\qquad\qquad\beta_t=\beta_0-\varepsilon\cos\omega t$$

where ε is a small parameter in order to have positive transition rates. The solution of the associated master equation is (2.1.10). In the long-time limit the solution converges to a periodic state given by (2.1.11). Here the long-time limit has to be physically thought. In fact this limit for a trigonometric function does not exist. To avoid this mathematical difficulty we consider a time long enough (related to characteristic time $\tau=(\alpha_0+\beta_0)^{-1}$) to make the exponential go to zero. Now consider a stochastic process $x_t\in\{0,1\}$. We want to evaluate $\langle x_0;x_t\rangle$.

$$\langle x_0;x_t\rangle=\sum_{x,y}xP_0(x)\,yP(y,t\mid x,0)-\sum_{x}xP_0(x)\sum_{y}yP(y,t\mid x,0)=P_0(1)\,P(1,t\mid1,0)$$

$$\langle x_0;x_t\rangle=P_0(1)\,P(1,t\mid1,0)-P_0(1)\,P_t(1)$$

This covariance is zero if the conditional probability $P(1,t\mid1,0)$ converges to $P(1,t)$.

$$P(1,t\mid1,0)=e^{-(\alpha_0+\beta_0)t}\left(1-\frac{\alpha_0}{\alpha_0+\beta_0}-\varepsilon\frac{(\alpha_0+\beta_0)}{(\alpha_0+\beta_0)^2+\omega^2}\right)+\frac{\alpha_0}{\alpha_0+\beta_0}+\varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2}$$

$$P(1,t\mid1,0)\to\frac{\alpha_0}{\alpha_0+\beta_0}+\varepsilon\frac{(\alpha_0+\beta_0)\cos\omega t+\omega\sin\omega t}{(\alpha_0+\beta_0)^2+\omega^2}=P(1,t)$$

Even if the dynamics is periodic in the long-time limit the covariances tend to zero. It could seem strange since for the periodic dynamics any time interval has a superior extreme given by the period. Here the independence of the average values is a property of the periodic steady state that after many periods produces a kind of harmonization.

2.1.4 Trajectories

The evolution of x_s is described as a sequence of configurations in a time interval $[0,t]$. Such sequence is called a trajectory $\omega : [0,t] \to S$. Obviously it is stochastic given that:

- the transition times are exponentially distributed and they depend on escape times
- the value that the system assumes after a transition is probabilistic and it depends on the transition rates. In fact from the backward generator we can obtain the jump matrix which has zero in the diagonal and the probability of making a jump in each of the off-diagonal elements.

Now we want to write the probability for a generic trajectory. Since the dynamics is Markovian the probability of a trajectory is given as a product of the probability of the individual transitions:

$$\mathcal{P}(\omega) \propto \mu(C_0)\, e^{-\lambda_{t_1}(C_0)t_1} k_{t_1}(C_0, C_1)\; e^{-\lambda_{t_2}(C_1)(t_2-t_1)} k_{t_2}(C_1, C_2) \ldots k_{t_n}(C_{n-1}, C_n)\; e^{-\lambda_t(C_n)(t-t_n)}$$

where for C_i we mean the configurations. C_0 is the initial configuration, so $\mu(C_0)$ is the initial distribution that gives the probability that the trajectory starts from a particular state at time $t = 0$. In addition, the times t_i are the moments in which there is a transition, or rather a change of configuration. In this notation we have assumed that during the interval $[0,t]$ there would be n jumps. Obviously this number is stochastic (Poisson) and function of time. The right continuity assures that after a jump the system is in the new state. The trajectory probability can be written as:

$$\mathcal{P}(\omega) = \prod_{0 \le s \le t}^{N(t)} k_s(x_{s^-}, x_s)\; e^{-\int_0^t \lambda_s\left(x_{s^-}\right) ds} \tag{2.1.12}$$

where s represents the jumping times in the interval $[0,t]$. Now we want to explain why we have introduced an integral. If we consider all the exponentials:

$$\exp\left[-\left[\lambda_{t_1}(C_0)\, t_1 + \lambda_{t_2}(C_1)(t_2 - t_1) + \lambda_{t_3}(C_2)(t_3 - t_2) + \ldots + \lambda_t(C_n)(t - t_n)\right]\right]$$

In each term there is a difference between two jumping times (except for initial time). If we sum all the contributions, through differences we will gather all the time interval $[0,t]$, for this reason this sum can be written as an integral. We used x_{s^-} for the value of the variable before the jump because we assumed the right continuity of the trajectory. If fact, since the trajectory is a sequence of discrete configurations, it cannot be a smooth and a continuous curve. So we assumed that, if at time $t = s$ there is a transition:

$$x_{s^-} \neq x_s \qquad x_s = x_{s^+}$$

Note that we have indicated the probability of being in x at time t as $P_t(x)$, while the trajectory probability with $\mathcal{P}(\omega)$. They are different since the first one does not take into account how the system arrives in x at t.

2.2 Entropy

2.2.1 Shannon entropy

Since the rates are time-dependent, the system is out of equilibrium (even without a perturbation), there will be an entropy production. To understand it, consider a solution $P_t(x)$ of the master equation (2.1.2), for any state $x \in S$ and for any time t. We introduce the probability current between two states x and y:

$$J_t(x,y) = [P_t(x)\, k_t(x,y) - P_t(y)\, k_t(y,x)] \tag{2.2.1}$$

The Shannon entropy at time t is:

$$S_t = -\sum_x P_t(x) \ln P_t(x) \tag{2.2.2}$$

For now this is only a mathematical definition. But first of all we have to understand why we used the Shannon entropy in order to describe the system entropy. We will give an answer for equilibrium regime towards extending to nonequilibrium. In (2.2.2) a probability appears, to interpret it we suppose there are N independent copies of the system we want to study described by the processes $\left\{X_t^j\right\}_{j=1,\dots,N}$. We are interested in how many of those copies are in a particular state $x \in S$. To determine it we have to sum a delta function over all the copies. If the j-th copy is in x therefore that system contributes to the sum. If we divide it by the number of copies we obtain a probability distribution.

$$\nu(x) = \frac{1}{N}\sum_{j=1}^{N} \delta_{X^j,x}$$

The probability $P_t(x)$ in (2.2.2) must be thought in this sense. Since the system is at equilibrium, if N tends to infinite, we expect that $\nu(x)$ will converge to ρ_{eq}, the equilibrium distribution for the law of large numbers. Now we can ask what is the probability to find a certain distribution $\mu(x)$. In order to determine it we can use the large deviation principle:

$$\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N} \delta_{X^j,x} = \mu(x)\right] \sim e^{-NS(\mu|\nu)} \tag{2.2.3}$$

where the rate is given by the relative entropy between probability distributions ν and μ on S, set of states of the processes. The relative entropy has a particular physical meaning. Suppose a thermodynamic system is at equilibrium, if we perturb it in any way, it will relax to a new equilibrium, producing an amount of entropy. This amount is given by the relative entropy. Therefore here ν and μ are invariant distributions.

$$S(\mu \mid \nu) = \sum_{x\in S} \mu(x) \ln\left(\frac{\mu(x)}{\nu(x)}\right) \tag{2.2.4}$$

Now we want to demonstrate that the relative entropy has this expression. Since we are considering equilibrium system, $\nu(x)$ is a stationary distribution. We consider N repetition of the process X_t^j, at time t, by definition the invariant distribution does not depend on time, therefore we can forget about the time. It is heuristically possible to demonstrate (2.2.4) using a combinatory calculation. In fact, this problem is equivalent to answer the question "In how many ways can I put N particles

in M boxes?" where now the N is the repetition, and M is the number of states. This problem was solved by Boltzmann in order to obtain a statistical mechanics interpretation of entropy - see [10]. Now instead of evaluating the volume in the phase space we have to calculate the probability referred to the distribution $\nu(x)$, for this reason instead of the cells volume ω_j in which is divided the phase space, we use the probability of being in a certain state (in analogy with the cells). Therefore we can say:

$$\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]=\frac{N!}{(N\mu(x_1))!\dots(N\mu(x_k))!}\,\nu(x_1)^{N\mu(x_1)}\dots\nu(x_k)^{N\mu(x_k)}$$

Here $N\mu(x_1)$ gives the number of system copies that are in the first state (x_1). If we apply the logarithm

$$\ln\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]=\ln\frac{N!}{(N\mu(x_1))!\dots(N\mu(x_k))!}+N\sum_{x}\mu(x)\ln\nu(x)$$

Since N is big we can use the Stirling approximation:

$$\ln m!\simeq m\ln m-m$$

Therefore:

$$\ln\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]\simeq\ln\frac{N!}{(N\mu(x_1))!\dots(N\mu(x_k))!}+N\sum_{x}\mu(x)\ln\nu(x)$$

$$\ln\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]\simeq\ln N!-\sum_{x}\ln(N\mu(x))!+N\sum_{x}\mu(x)\ln\nu(x)$$

$$\ln\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]\simeq N\ln N-N-N\sum_{x}\mu(x)\ln(N\mu(x))+\sum_{x}N\mu(x)+N\sum_{x}\mu(x)\ln\nu(x)$$

Using the distribution normalization the two couples of terms cancel out and it remains:

$$\ln\mathbb{P}\left[\frac{1}{N}\sum_{j=1}^{N}\delta_{X^j,x}=\mu(x)\right]\simeq-N\sum_{x}\mu(x)\ln\frac{\mu(x)}{\nu(x)}$$

If we divide by N we obtain (2.2.3) with (2.2.4). $S(\mu\mid\nu)$ measures the discrepancy between μ and ν. It is always not negative and it is zero if and only if $\mu=\nu$. In order to demonstrate that $S(\mu\mid\nu)\geq 0$, we can write it as:

$$S(\mu\mid\nu)=\sum_{x\in S}\nu(x)\,\phi\left(\frac{\mu(x)}{\nu(x)}\right)=\left\langle\phi\left(\frac{\mu(x)}{\nu(x)}\right)\right\rangle_{\nu}$$

where $\phi(y)=y\ln y$ and the average value is made with respect to ν. If we use the Jensen's inequality (since $\phi(y)$ here is a convex function):

$$\langle\phi\rangle\geq\phi(\langle x\rangle)$$

But:

$$\left\langle \frac{\mu(x)}{\nu(x)} \right\rangle_{\nu} = \sum_{x \in S} \nu(x) \frac{\mu(x)}{\nu(x)} = 1$$

For the normalization condition of the probability distributions. Therefore $\phi\left(\langle x \rangle_{\nu}\right) = 0$. This result does not depend on μ and ν. In order to obtain (2.2.2) we are interested in the entropy due to the evolution with respect to the probability $\mu(x)$. We can derive it from the relative entropy if we assume that ν is the uniform distribution. If $\nu(x) = \frac{1}{N},\ \forall x \in S$ then:

$$S(\mu \mid \nu) = \sum_{x \in S} \mu(x) \ln \mu(x) - \frac{1}{N} \sum_{x \in S} \mu(x)$$

$$S(\mu) \simeq \sum_{x \in S} \mu(x) \ln \mu(x)$$

since in the N big limit the constant contribution tends to zero. Note that if ν converges to the Maxwell-Boltzmann equilibrium distribution $\rho_{eq} = \frac{e^{-\beta U(x)}}{Z}$, with system potential energy $U(x)$ and partition function Z, in the $N \to \infty$ limit we expect:

$$\mathbb{P}\left[\frac{1}{N} \sum_{j=1}^{N} \delta_{X^j, x} = \mu(x)\right] \sim e^{-NS(\mu \mid \rho_{eq})}$$

Therefore:

$$S(\mu \mid \rho_{eq}) = \sum_{x \in S} \mu(x) \ln \mu(x) - \beta \sum_{x \in S} \mu(x) U(x) + \sum_{x \in S} \mu(x) \ln Z$$

$$S(\mu \mid \rho_{eq}) = \sum_{x \in S} \mu(x) \ln \mu(x) + \beta \left[\sum_{x \in S} \mu(x) U(x) + k_B T \ln Z\right]$$

$$S(\mu \mid \rho_{eq}) = \beta \left[\sum_{x \in S} \mu(x) U(x) + k_B T \sum_{x \in S} \mu(x) \ln \mu(x) - \mathcal{F}^{eq}\right] \tag{2.2.5}$$

The first term in the braket is the average energy of the system with respect to the distribution μ, the second is minus the Shannon entropy due to (2.2.2). Therefore the first two terms are $\langle U \rangle_{\mu} - k_B T S(\mu)$ that is the free energy of the system with respect to the distribution μ (here the Boltzmann constant appears because the entropy defined in (2.2.2) is dimensionless). This shows that the decrease in free energy towards its minimum $\mathcal{F}^{eq}$ is equivalent to the decrease of relative entropy in the relaxation towards equilibrium. If we insert (2.2.5) in (2.2.3) we obtain:

$$\mathbb{P}\left[\frac{1}{N} \sum_{j=1}^{N} \delta_{X^j, x} = \mu(x)\right] \sim e^{-N\beta[\mathcal{F}(\mu) - \mathcal{F}^{eq}]}$$

We have demonstrated that $S(\mu \mid \nu) \geq 0$, therefore:

$$\mathcal{F}(\mu) \geq \mathcal{F}^{eq}$$

$\mathcal{F}^{eq}$ represents the minimal free energy possible for the system, according to the second law of thermodynamics. Using many independent copies of the system (the independence is necessary for the law of large numbers application) we have defined an entropy for the system at equilibrium.

The extension to nonequilibrium is quite easy since we can take the independent copies of the system despite of equilibrium or nonequilibrium. Evidently in this case the probability distribution μ could depend on time. Furthermore if the transition rates are time-dependent a stationary distribution does not exist, therefore it could be meaningless to study the law of large numbers for ν. As we have seen for the two states system even a time-dependent not stationary dynamics (periodic) could converge to a particular regime. In this sense the relative entropy has still sense. If for example we consider a periodic dynamics, we can measure the relative entropy between two different "stationary" periodic state.

Taking the time-derivative of (2.2.2) we get:

$$\frac{dS_t}{dt} = -\sum_x \frac{dP_t(x)}{dt} \ln P_t(x) - \sum_x \frac{dP_t(x)}{dt}$$

Using (2.1.2), the second term is zero for the conservation of probability, so:

$$\frac{dS_t}{dt} = \sum_{x,y} J_t(x,y) \ln P_t(x)$$

Using the antisymmetry of the current and the freedom of changing the name of the variable, we can rewrite it as:

$$\frac{dS_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{P_t(x)}{P_t(y)}$$

$$\frac{dS_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{P_t(x)\, k_t(x,y)}{P_t(y)\, k_t(y,x)} - \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{k_t(x,y)}{k_t(y,x)}$$

Here we have multiplied and divided by the ratio of rates. Now we can use (2.1.9) in the second term:

$$\frac{dS_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{P_t(x)\, k_t(x,y)}{P_t(y)\, k_t(y,x)} - \frac{1}{2}\sum_{x,y} J_t(x,y)\, F_t(x,y)$$

2.2.2 Local detailed balance

To give a physical meaning to this formula we have to introduce the local detailed balance. The detailed balance is a characteristic of systems at thermodynamic equilibrium. In fact it is related to the time reversal and it requires the existence of an invariant distribution. Its expression is, for each couple $x, y \in S$:

$$\rho_{eq}(y)\, k(y,x) = \rho_{eq}(x)\, k(x,y) \tag{2.2.6}$$

where ρ_{eq} is the invariant distribution. Evidently we have to consider time-independent rates for an equilibrium system. According to the Markov processes theory the link between the time-reversal property and the detailed balance relation is made by the invariant distribution existence. Therefore, first of all, we demonstrate that if the distribution $\lambda(x)$, $x \in S$ and L, backward generator, are in detailed balance then λ is invariant for L.

$$(\lambda L)_x = \sum_{y \in S} \lambda(y)\, L(y,x)$$

Using (2.2.6):

$$(\lambda L)_x = \sum_{y \in S} \lambda(x) L(x,y) = \lambda(x) \sum_{y \in S} L(x,y) = 0$$

By definition of backward generator. If a Markov process x_t admits a stationary distribution λ then the reverse process $\hat{x}_t = x_{T-t}$ is Markov too with the same invariant distribution and a backward generator $\hat{L}$, that can be obtained from L with:

$$\lambda(y) \hat{L}(y,x) = \lambda(x) L(x,y)$$

for each couple $x, y \in S$. The demonstration presents many technical issues and it can be found is Section 3.7 of [11]. Note that the theorem requires two more assumptions:

- the process must be irreducible. In other words there is no absorption state, from which the escape probability is zero once arrived here (in this case, the backward generator would have a row of zeros in correspondence to that state). Since we are considering the convergence to equilibrium it would be meaningless to consider not irreducible process.
- the process must be not-explosive. This condition is more subtle since it requires that in a finite time the process could not make infinite jumps. According to a theorem that can be found again in [11] any process with a finite and countable set of states cannot explode. Therefore in this case we can ignore this assumption.

According to what we have said if a distribution satisfies the detailed balance relation the process is reversible. The expression of ρ_{eq} in (2.2.6) is known since the system is described at equilibrium by a Maxwell-Boltzmann distribution, then:

$$\rho_{eq}(x) = \frac{e^{-\beta U(x)}}{\mathcal{Z}}$$

where $\mathcal{Z}$ is the partition function obtained by:

$$\mathcal{Z} = \sum_x \rho_{eq}(x)$$

Then the ratio of rates:

$$\frac{k(x,y)}{k(y,x)} = e^{-\beta \Delta U} = e^{\beta Q} = e^{\frac{\Delta S}{k_B}} \tag{2.2.7}$$

where Q is the heat exchanged from the system to the environment (for this reason it has the opposite sign respect to the energy difference) and ΔS is the change in entropy of the reservoir due to the transition $x \to y$. This equation describes the principle of maximum entropy for equilibrium systems (second principle of thermodynamics) because it says that the transition producing an entropic increase is probabilistically favorite. Note that, using (2.1.9) for time-independent rates:

$$\Delta S = k_B \ln \frac{k(x,y)}{k(y,x)} = k_B F(x,y)$$

we can say that the driving force of the transition multiplied by k_B is actually the entropy. What we have written is valid only at equilibrium where ρ_{eq} is the Maxwell-Boltzmann distribution. Therefore, it is clear that it can be no longer valid for out-of-equilibrium systems.

In this case, an extension exists and it is properly called local detailed balance since it is based on the assumption that locally in time and in space the system has a dynamics that is detailed

balanced. The locality is referred to the way of studying thermodynamically an out-of-equilibrium system. Consider for example a system in which the temperature is not constant. It can be seen as a system in contact with two reservoirs which are themselves in equilibrium at different temperatures T_1 and T_2. This assumption is restricted to the case in which the reservoirs only interact with the system, not between each others. Moreover the coupling between system and reservoirs should be sufficiently weak and the reservoirs sufficiently big, such that the reservoirs stay at equilibrium throughout the process. Microscopically the system never interacts with the two baths at the exact same time. Therefore we can imagine that during the transition it will interact before with the first reservoir and later with the second one. Until the system interacts with the first reservoir it satisfies the detailed balance relation since there is interaction with only one heat bath at a fixed temperature T_1. And the same is valid for the second reservoir. Therefore time by time the system satisfies a detailed balance relation like (2.2.7) that must be local since it depends parametrically on time:

$$\frac{k_t(x,y)}{k_t(y,x)} = e^{\frac{\Delta S_t}{k_B}} \tag{2.2.8}$$

Given that we are interested in considering inhomogeneous Markov processes, we have put the time dependence on the rates as done the in the previous Section. Therefore:

$$\Delta S_t = k_B \ln \frac{k_t(x,y)}{k_t(y,x)} = k_B F_t(x,y)$$

Locally the driving force is the entropic flux from the system to the environment due to transition $x \to y$ divided by k_B. Now, it is interesting to note that (2.2.8) can be thought as a contribution to a trajectory with respect to the opposite one. According to (2.1.12) the trajectory probability can be written as the product of all the transitions. If we consider the ratio of (2.1.12) over the probability of making the opposite trajectory we will have a product of terms like (2.2.8). Since the entropic flux contribution for each step appears in the exponential from this ratio we will obtain the total entropic flux exchanged from the system to the environment during the trajectory ω. Evidently it does not describe all the trajectory probability. In fact equation (2.1.12) says that also the exponentials of escape rates contribute to $\mathcal{P}(\omega)$, but this contribution does not appears in the ratio of the trajectory probability over the probability of the opposite trajectory, because it is a symmetric contribution. In fact in $e^{-\int_0^t \lambda_s(x_{s^-})ds}$ we can substitute x_{s^-} with x_s without any problem. The local detailed balance does not allow to understand all the dynamics, but gives an important contribution to understand the physical meaning.

In conclusion, we do a consideration. We have described a locally condition of detailed balance considering a system in contact with a several reservoirs at different temperatures in order to describe a not-constant temperature environment. Obviously, this is not the only possibility of considering a nonequilibrium system, therefore we expect there will be a local detailed balance also for nonequilibrium system in which the temperature is constant. The detailed balance condition is equivalent the thermodynamic equilibrium that is given by thermal, mechanical and chemical equilibrium. The system is no longer at equilibrium if just one of these three equilibrium conditions is not satisfied. Under the already explained considerations we can consider a not constant chemical potential system as if it is interacting with different probe reservoirs. For the pressure this interpretation is stranger, because it is meaningless speaking about a pressure reservoir. We can go through this problem assuming that all the mechanical work made by the environment on the system is automatically transformed in heat exchanged.

2.2.3 Entropy contributions

According to these considerations, if we consider the expression of the transition rates (2.1.7), we can interpret - as for the equilibrium system - the $F_t(x,y)$ in the ratio rates (2.1.9) as the entropy flux $S_t^{(e)}(x,y)$ during the transition $x \to y$ at time t from the system to the environment. Then:

$$\frac{dS_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{P_t(x)\, k_t(x,y)}{P_t(y)\, k_t(y,x)} - \frac{1}{2}\sum_{x,y} J_t(x,y)\, \beta_t Q_t(x,y) \tag{2.2.9}$$

where we have introduced the heat flux from the system to the environment. Now we want to understand the meaning of these two contributions:

- The first term is always not negative because it is like $(A-B)\ln\frac{A}{B}$, which is positive for any A and B, given that $A \geq 0$ and $B \geq 0$, by definition. These terms can be interpreted as the production of entropy. It gives the irreversible contribution to the entropy change.

$$\frac{d_i S_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y) \ln \frac{P_t(x)\, k_t(x,y)}{P_t(y)\, k_t(y,x)} \tag{2.2.10}$$

- According to the first principle of thermodynamics, heat flux is related to energy difference $\Delta U = U_t(y) - U_t(x)$ of the system before and after the transition and to the work done on the system $W_t(x,y)$:

$$Q_t = U_t(x) - U_t(y) + W_t(x,y)$$

  Conventionally we impose that Q_t is positive when it goes from the system to the environment. Therefore it must have the opposite sign respect to the energy difference. The work can be thought as an antisymmetric external force. Since the heat is multiplied for β_t - that is the inverse of the temperature - we have an entropy flux. The current multiplied for the entropy flux gives a probabilistic interpretation of the entropy flux. This term can be interpreted as the entropy exchange between the system and the environment and it is positive when the heat flux is from the system to the environment.

$$\frac{d_e S_t}{dt} = \frac{1}{2}\sum_{x,y} J_t(x,y)\, \beta_t \left[U_t(x) - U_t(y) + W_t(x,y)\right] \tag{2.2.11}$$

Now we want to manipulate the entropy flux term.

$$\frac{d_e S_t}{dt} = \frac{1}{2}\sum_{x,y} P_t(x)\, k_t(x,y)\, \beta_t \left[U_t(x) - U_t(y)\right] - \frac{1}{2}\sum_{x,y} P_t(y)\, k_t(y,x)\, \beta_t \left[U_t(x) - U_t(y)\right] +$$

$$+\frac{1}{2}\sum_{x,y} P_t(x)\, k_t(x,y)\, \beta_t W_t(x,y) - \frac{1}{2}\sum_{x,y} P_t(y)\, k_t(y,x)\, \beta_t W_t(x,y)$$

If we change the sign of the first term of difference energy it is easy to see that the two energy contributions are equal. If we use the antisymmetry of work we will find that also the work terms are equal. Then:

$$\frac{d_e S_t}{dt} = -\beta_t \sum_{x,y} P_t(x)\, k_t(x,y) \left[U_t(y) - U_t(x)\right] + \beta_t \sum_{x,y} P_t(x)\, k_t(x,y)\, W_t(x,y)$$

By definition, for any function $f_t(x)$:

$$L_t f_t(x) = \sum_y k_t(x,y)\left[f_t(y) - f_t(x)\right] \tag{2.2.12}$$

Then the entropy flux can be written as:

$$\frac{d_e S_t}{dt} = -\beta_t \sum_x P_t(x)\, L_t U_t(x) + \beta_t \sum_{x,y} P_t(x)\, k_t(x,y)\, W_t(x,y) \tag{2.2.13}$$

Since the average value of a function $f_t(x)$ at time t is

$$\langle f_t \rangle_\mu = \sum_x P_t(x)\, f_t(x) \tag{2.2.14}$$

we have

$$\frac{d_e S_t}{dt} = -\beta_t \langle L_t U_t \rangle_\mu + \beta_t \sum_x \langle k_t(x_t,x)\, W_t(x_t,x) \rangle_\mu \tag{2.2.15}$$

The average value is made with respect to the probability $P_t(x)$ summing on all the states and μ is the initial distribution P_0. If we multiple equation (2.1.3) by the function U_t and sum over all the states:

$$\sum_x \frac{d}{dt}\left(P_t(x)\, U_t(x)\right) = \sum_x \left[\frac{dP_t(x)}{dt}\, U_t(x) + \frac{\partial U_t(x)}{\partial t}\, P_t(x)\right] = \sum_x \left[P_t(x)\, L_t U_t(x) + \frac{\partial U_t(x)}{\partial t}\, P_t(x)\right]$$

We obtain the average value at time t:

$$\frac{d}{dt}\langle U_t \rangle_\mu = \langle L_t U_t \rangle_\mu + \left\langle \frac{\partial U_t}{\partial t} \right\rangle_\mu \tag{2.2.16}$$

because we have to take into account the explicit dependence on time of the energy. So the changing of average energy with respect to the time is given by two contributions: the first describes the variation due to the transitions, while the second describes the variation due to the explicit time dependence. Then the entropy flux will become:

$$\frac{d_e S_t}{dt} = \beta_t \left[-\frac{d}{dt}\langle U_t \rangle_\mu + \left\langle \frac{\partial U_t}{\partial t} \right\rangle_\mu + \sum_x \langle k_t(x_t,x)\, W_t(x_t,x) \rangle_\mu\right] \tag{2.2.17}$$

What we have found is the change in entropy of the heat bath. If we want the system entropy flux variation, we just need to take the opposite of what we have found because we have assumed that the sum of system and environment is a close system and then the outgoing energy flux is zero. Since the first contribution (2.2.10) is always positive, we can say:

$$\frac{dS_t}{dt} \geq \beta_t \left[\frac{d}{dt}\langle U_t \rangle_\mu - \left\langle \frac{\partial U_t}{\partial t} \right\rangle_\mu - \sum_x \langle k_t(x_t,x)\, W_t(x_t,x) \rangle_\mu\right] \tag{2.2.18}$$

Here, he first term is the change in energy, the last two terms in the bracket can be interpreted as the work made on the system by the environment. Note that if we integrate the entropy, the change in energy will depend only on initial and final time, as we expect. In the bracket there is the heat flux. For this reason (2.2.18) can be thought as a nonequilibrium extension to Clausius

theorem. If the work could be written as a potential the expression would be easier since the work contribution would be of the same form as the energy one using (2.2.12). We would just need to define a new potential function $\mathcal{U}_t = U_t - W_t$ and the entropy production would be:

$$\frac{dS_t}{dt} \geq \beta_t \left[\frac{d}{dt} \langle \mathcal{U}_t \rangle_\mu - \left\langle \frac{\partial \mathcal{U}_t}{\partial t} \right\rangle_\mu \right]$$

Therefore note that the time-derivative of the Shannon entropy is:

$$\frac{dS_t}{dt} = \frac{d_i S_t}{dt} + \frac{d_e S_t}{dt}$$

where here $\frac{d_e S_t}{dt}$ is the change in entropy of the system due to the environment. The Shannon entropy gives the entropy of the system. If the system reaches a stationary solution the Shannon entropy is constant (given that the probability of the process is no longer time-dependent). But this condition does not assure that the other terms are zero. It is true if and only if the system is isolated, in this case the entropy flux is zero and the system is at equilibrium. Otherwise the system reaches a nonequilibrium stationary state in which all the entropy produced (represented by $\frac{d_i S_t}{dt}$) is taken out from the system under the shape of entropy flux.

2.2.4 Quasi-static limit

If the transition rates change very slowly there is a characteristic time τ over which they are almost constant and then, time-independent. If the time τ is bigger than the relaxation time of the system to equilibrium that depends on the rates:

$$\tau \gg \max_t \left\{ \frac{1}{\lambda_t} \right\}$$

the system can relax to equilibrium and it is possible to describe it approximately with the invariant distribution corresponding to a fixed time. The time τ is strictly related to the changing of the rates, in fact to describe the slowness of the changing we have to parameterize the rates introducing a small parameter ε.

$$k_t^\varepsilon (x, y) := k_{\varepsilon t} (x, y) \qquad\qquad \varepsilon = \frac{1}{\tau}$$

When ε is small we are considering the quasi-static limit. The advantage of studying it is that at any fixed time t the probability of being in a state can be approximated by the invariant distribution ρ_t at that time plus a correction $\mathcal{O}(\varepsilon)$.

$$P_t (y) = \rho_t (y) + \mathcal{O}(\varepsilon) \tag{2.2.19}$$

This expression does not describe an evolution of the probability, it must be thought as an infinite and dense sequence of equilibrium states. Note that ρ_t is the solution:

$$\rho_t L_t = 0$$

If we substitute (2.2.19) in the current expression (2.2.1) we obtain:

$$J_t (x, y) = (\rho_t (x) + \mathcal{O}(\varepsilon)) k_t (x, y) - (\rho_t (y) + \mathcal{O}(\varepsilon)) k_t (y, x)$$

$$J_t (x, y) = \rho_t (x) k_t (x, y) - \rho_t (y) k_t (y, x) + \mathcal{O}(\varepsilon) (k_t (x, y) - k_t (y, x))$$

Given that the invariant distribution satisfies detailed balance.

$$J_t(x,y) = \mathcal{O}(\varepsilon)\left(k_t(x,y) - k_t(y,x)\right) \tag{2.2.20}$$

The first contribution to the current is of order ε, therefore for each couple of state x and y the current between them is zero plus a correction. This is a characteristic of the equilibrium solution of the stationary master equation (2.1.3). Now, if we consider (2.2.9)

$$\frac{d_i S_t}{dt} = \frac{1}{2}\sum_{x,y}\mathcal{O}(\varepsilon)\left[k_t(x,y) - k_t(y,x)\right]\cdot \ln\left[\frac{\left(\rho_t(x) + \mathcal{O}(\varepsilon)\right)k_t(x,y)}{\left(\rho_t(y) + \mathcal{O}(\varepsilon)\right)k_t(y,x)}\right]$$

$$\frac{d_i S_t}{dt} = \frac{1}{2}\sum_{x,y}\mathcal{O}(\varepsilon)\left[k_t(x,y) - k_t(y,x)\right]\cdot \left[\ln\left(1 + \frac{\mathcal{O}(\varepsilon)}{\rho_t(x)}\right) - \ln\left(1 + \frac{\mathcal{O}(\varepsilon)}{\rho_t(y)}\right)\right]$$

Now if we expand the logarithms:

$$\frac{d_i S_t}{dt} = \frac{1}{2}\sum_{x,y}\mathcal{O}\left(\varepsilon^2\right)\left[k_t(x,y) - k_t(y,x)\right]\cdot \left[\frac{1}{\rho_t(x)} - \frac{1}{\rho_t(y)}\right] \tag{2.2.21}$$

By definition the invariant distribution cannot be zero for any state, otherwise there would be a state in which it is impossible to arrive. Then the chain will be no longer irreducible, but this is a necessary condition for the invariant distribution existence.

We can observe that the irreversible contribution to entropy production is of order ε^2. Instead the second contribution, the reversible one, is of order ε. Then the first term is negligible compared to the second one. This is what we would expect in the quasi-static limit. If the dynamics changes slowly at any time the system can relax to equilibrium and then there will not be an irreversible contribution due to the fact that for an infinitesimal transformation from a equilibrium state the entropy production is zero. This stochastic result is an approximation because ε cannot be zero, otherwise the system would be in equilibrium and then there would not be entropy production at all. Note that this result is in agreement with the Clausius theorem (2.2.18). In thermodynamics a quasi-static transformation assures that $TdS = \delta Q$ that is what we have found up to order ε^2.

In thermodynamics a quasi-static transformation is ideal, but it is an useful tool since it allows to approximate, almost always, a real transformation with an reversible one. The "almost" is due to the fact that all the reversible processes are quasi-static, but not every quasi-static process is also reversible. If, for example, a dissipative force acts on the system, despite the evolution may be slow, however there will be energy dissipation and therefore irreversibility. The quasi-static limit approximation, or rather equation (2.2.19) can be demonstrated, we will do for a two states system, since it is more explicit.

2.2.4.1 Example: two states system

We have seen that the probabilities at time t for a two states system are:

$$\begin{cases} P_t(0) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_0(0) + \int_0^t \beta_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\,ds\right) \\ P_t(1) = e^{-\int_0^t(\alpha_s+\beta_s)ds}\left(P_0(1) + \int_0^t \alpha_s\, e^{\int_0^s(\alpha_\tau+\beta_\tau)d\tau}\,ds\right) \end{cases} \tag{2.2.22}$$

Consider now the transition rates depending on the parameter ε:

$$\alpha_t^\varepsilon := \alpha(\varepsilon t) \qquad\qquad \beta_t^\varepsilon := \beta(\varepsilon t)$$

Using (2.2.19) we want to approximate the probability of being in 0 at time t:

$$P_t^\varepsilon(0) = \rho_t(0) + \mathcal{O}(\varepsilon) = \frac{\beta_t}{\alpha_t + \beta_t} + \mathcal{O}(\varepsilon) \tag{2.2.23}$$

for any fixed time t and with the assumption that at time $t = 0$:

$$P_0^\varepsilon(0) = \rho_0(0) = \frac{\beta_0}{\alpha_0 + \beta_0} \tag{2.2.24}$$

For simplicity, we are going to call $\alpha_t^\varepsilon + \beta_t^\varepsilon = f_t^\varepsilon$. Then we want to obtain at the first order:

$$P_t^\varepsilon(0) = \frac{\beta_0 + \dot{\beta}_0 \varepsilon t}{f_0 + \dot{f}_0 \varepsilon t} + \mathcal{O}(\varepsilon)$$

Starting from the (2.2.22):

$$P_t^\varepsilon(0) = e^{-\int_0^t f_s^\varepsilon ds} \left(P_0^\varepsilon(0) + \int_0^t \beta_s \, e^{\int_0^s f_\tau^\varepsilon d\tau} \, ds \right)$$

Now we can expand the rates to the first order

$$P_t^\varepsilon(0) = e^{-\int_0^t (f_0 + \varepsilon s \dot{f}_0) ds} \left(P_0^\varepsilon(0) + \int_0^t \left(\beta_0 + \dot{\beta}_0 \varepsilon s \right) e^{\int_0^s (f_0 + \varepsilon \tau \dot{f}_0) d\tau} \, ds \right)$$

$$P_t^\varepsilon(0) = e^{-f_0 t} e^{-\frac{\varepsilon t^2}{2} \dot{f}_0} \left(P_0^\varepsilon(0) + \int_0^t \left(\beta_0 + \dot{\beta}_0 \varepsilon s \right) e^{f_0 s} e^{\frac{\varepsilon s^2}{2} \dot{f}_0} \, ds \right)$$

Now we can expand the second exponential to the first order using the smallness of ε

$$P_t^\varepsilon(0) = e^{-f_0 t} \left(1 - \frac{\varepsilon t^2}{2} \dot{f}_0 \right) \left(P_0^\varepsilon(0) + \int_0^t \left(\beta_0 + \dot{\beta}_0 \varepsilon s \right) e^{f_0 s} \left(1 + \frac{\varepsilon s^2}{2} \dot{f}_0 \right) ds \right) \tag{2.2.25}$$

Solving the integrals we obtain

$$\beta_0 \int_0^t e^{f_0 s} ds + \varepsilon \dot{\beta}_0 \int_0^t s \, e^{f_0 s} ds + \varepsilon \frac{\dot{f}_0 \beta_0}{2} \int_0^t s^2 e^{f_0 s} ds + \mathcal{O}(\varepsilon^2) =$$

$$= \frac{\beta_0}{f_0} \left(e^{f_0 t} - 1 \right) + \frac{\varepsilon \dot{\beta}_0}{f_0^2} e^{f_0 t} (f_0 t - 1) + \frac{\varepsilon \dot{\beta}_0}{f_0^2} + \varepsilon \frac{\dot{f}_0 \beta_0}{2 f_0^3} e^{f_0 t} \left[f_0 t (f_0 t - 2) + 2 \right] - \varepsilon \frac{\dot{f}_0 \beta_0}{f_0^3} + \mathcal{O}(\varepsilon^2)$$

If we insert the result of integral in (2.2.25):

$$P_t^\varepsilon(0) = e^{-f_0 t} \left(1 - \frac{\varepsilon t^2}{2} \dot{f}_0 \right) P_0^\varepsilon(0) + e^{-f_0 t} \left(1 - \frac{\varepsilon t^2}{2} \dot{f}_0 \right) \left\{ \frac{\beta_0}{f_0} \left(e^{f_0 t} - 1 \right) + \frac{\varepsilon \dot{\beta}_0}{f_0^2} e^{f_0 t} (f_0 t - 1) \right\} +$$

$$+ e^{-f_0 t} \left(1 - \frac{\varepsilon t^2}{2} \dot{f}_0 \right) \left\{ \frac{\varepsilon \dot{\beta}_0}{f_0^2} + \varepsilon \frac{\dot{f}_0 \beta_0}{2 f_0^3} e^{f_0 t} \left[f_0 t (f_0 t - 2) + 2 \right] - \varepsilon \frac{\dot{f}_0 \beta_0}{f_0^3} + \mathcal{O}(\varepsilon^2) \right\}$$

Then:

$$P_t^\varepsilon(0) = e^{-f_0 t} \left[P_0^\varepsilon(0) - \frac{\beta_0}{f_0} + \frac{\varepsilon}{f_0^3} \left(\dot{\beta}_0 f_0 - \dot{f}_0 \beta_0 \right) - \frac{\varepsilon t^2}{2} \dot{f}_0 \left(P_0^\varepsilon(0) - \frac{\beta_0}{f_0} \right) \right] +$$

$$+\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0}+\varepsilon\left[\frac{1}{f_0^3}\left(\dot{f}_0\beta_0-\dot{\beta}_0 f_0\right)-\frac{\beta_0\dot{f}_0}{f_0^2}t\right]+\mathcal{O}\left(\varepsilon^2\right)$$

Using the initial condition (2.2.24):

$$P_t^{\varepsilon}(0)=\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0}+\varepsilon\left[\left(\frac{1-e^{-f_0 t}}{f_0^3}\right)\left(\dot{f}_0\beta_0-\dot{\beta}_0 f_0\right)-\frac{\beta_0\dot{f}_0}{f_0^2}t\right]+\mathcal{O}\left(\varepsilon^2\right)$$

As we can see the expression found is different from the desired one. But if we consider the stationary distribution for the state 0 (2.2.23) expanded to the first order:

$$\rho_t(0)\simeq\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0+\dot{f}_0\varepsilon t}=\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0\left(1+\frac{\dot{f}_0}{f_0}\varepsilon t\right)}=\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0}\left(1-\frac{\dot{f}_0}{f_0}\varepsilon t\right)+\mathcal{O}\left(\varepsilon^2\right)$$

If we consider terms to order ε:

$$\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0+\dot{f}_0\varepsilon t}=\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0}-\frac{\beta_0\dot{f}_0}{f_0^2}\varepsilon t+\mathcal{O}\left(\varepsilon^2\right)$$

It is easy to note that the last term just found appears in the bracket in the probability expression. Finally:

$$P_t^{\varepsilon}(0)=\frac{\beta_0+\dot{\beta}_0\varepsilon t}{f_0+\dot{f}_0\varepsilon t}+\varepsilon\left[\left(\frac{1-e^{-f_0 t}}{f_0^3}\right)\left(\dot{f}_0\beta_0-\dot{\beta}_0 f_0\right)\right]+\mathcal{O}\left(\varepsilon^2\right)$$

Consider now, the entropy production in the quasi-static limit approximation for a two states system. If we use (2.2.23) we obtain:

$$\frac{dS_t}{dt}=\frac{1}{2}\mathcal{O}\left(\varepsilon^2\right)(\alpha_t-\beta_t)\cdot\left[\frac{(\alpha_t-\beta_t)(\alpha_t+\beta_t)}{\alpha_t\beta_t}\right]+\mathcal{O}(\varepsilon)(\alpha_t-\beta_t)\left[\mathcal{U}_t(1)-\mathcal{U}_t(0)\right]\qquad(2.2.26)$$

Note that there is $\mathcal{U}_t$ since for a two states system any function $W_t(x,y)$ can be written as a potential. For a two states system cannot exist a nonequilibrium steady state, therefore the invariant distribution can be only an equilibrium one. In fact equation (2.2.23) can be written as a Maxwell-Boltzmann equilibrium distribution using (2.1.9):

$$\rho_t(0)=\frac{\beta_t}{\alpha_t+\beta_t}=\frac{1}{\beta_t}\frac{\beta_t}{\left(1+\frac{\alpha_t}{\beta_t}\right)}=\frac{1}{1+e^{-\beta_t[U_t(1)-U_t(0)]}}=\frac{e^{-\beta_t U_t(0)}}{e^{-U_t(0)}+e^{-\beta_t U_t(1)}}=\frac{e^{-\beta_t U_t(0)}}{Z_t}$$

where the Z_t is the partition function at fixed time t. This is true only in the two states system since only in this situation the $F_t(x,y)$ of equation (2.1.9) can be always written as a potential.

Chapter 3

Linear response theory

Usually, detailed balance or time-independence are not enough to describe properly the physical phenomena. Consider for example the brownian motion of a probe. If we suppose that its evolution is memoryless we can describe it with a random walk model. If the motion is purely diffusive we expect that the transition rates of going in one direction or in the opposite one will be the same. In this case the problem is analytically solvable. But, if we suppose that the probe feels the effect of an external force, the transition rates will depend on this force and generally on time. Now the problem has became more difficult and usually not solvable.

Under the assumption that the external force is small, we can consider it as a perturbation to the initial system. This procedure allows to relate the perturbed system to the unperturbed one starting from the probability:

$$\mathcal{P}^h(\omega) = e^{-\mathcal{A}(\omega)}\,\mathcal{P}(\omega) \tag{3.0.1}$$

where $\mathcal{P}^h(\omega)$ and $\mathcal{P}(\omega)$ are respectively the probabilities that describe the perturbed and the unperturbed trajectories and $\mathcal{A}(\omega)$ is the relation between them, called excess action. We introduce the "excess" because it takes into account only the contributions due to the perturbation. Using (3.0.1), we can solve the average values of quantities for the system perturbed as average values for the initial one. Therefore, the key point of the perturbation theory is the excess action. We are going to expand it to the first (or linear) order to describe how the average values change with the perturbation. From the modification of average values we will deduce how the system responds to the perturbation. This approach is called linear response theory.

There are different types of perturbation and to understand the differences we are going to explain how a perturbation modifies the transition rates. Many aspects and assumptions will be introduced in the following Sections, but at this level we expect that the transition rates for the perturbed system can be written as a function of the old ones. Then:

$$k_t^h(x,y) = k_t(x,y)\, e^{\frac{\beta_t h_t}{2}\mathcal{V}_t(x,y)} \tag{3.0.2}$$

Where $\mathcal{V}_t(x,y)$ is a generic function of time and a pair of states. This function can be:

- antisymmetric $\mathcal{V}_t(y,x) = -\mathcal{V}_t(x,y)$
  we have said that a generic transition rate can be written as the product of a symmetric term called reactivities $a_t(x,y)$ and an antisymmetric one called drift $F_t(x,y)$. If the perturbation is antisymmetric it modifies the drift contribution:

$$F_t^h(x,y) = F_t(x,y) + \beta_t h_t \mathcal{V}_t(x,y) \tag{3.0.3}$$

This kind of perturbation tends to facilitate some transitions and to obstruct the opposite ones. Physically it can be interpreted as an external field, for example a magnetic field in the Ising model.

- symmetric $\mathcal{V}_t(y,x) = \mathcal{V}_t(x,y)$
  similarly, if the perturbation is symmetric it modifies the reactivity contribution:

$$a_t^h(x,y) = a_t(x,y)\, e^{\frac{\beta_t h_t}{2}\mathcal{V}_t(x,y)} \tag{3.0.4}$$

  Given the transitions $x \to y$ and $y \to x$, this type of perturbation acts in the same way on both. Therefore it must be a perturbation without a preferential direction. A physical example can be the increasing of the pressure or the temperature of a gas in a volume.

- mixed symmetry
  This kind of perturbation can be viewed as the sum of a symmetric part $f_t(x,y)$ and a antisymmetric part $g_t(x,y)$. Then it will modify both the reactivities and the drift. This is the most general kind of perturbation, in fact:

$$\mathcal{V}_t(x,y) = g_t(x,y) + f_t(x,y) \tag{3.0.5}$$

  Then:

$$\frac{k_t^h(x,y)}{k_t(x,y)} = e^{\frac{\beta_t h_t}{2} f_t(x,y)} e^{\frac{\beta_t h_t}{2} g_t(x,y)} \tag{3.0.6}$$

  where:

$$a_t^h(x,y) = a_t(x,y) \cdot e^{\frac{\beta_t h_t}{2} f_t(x,y)}$$
$$F_t^h(x,y) = F_t(x,y) + \beta_t h_t g_t(x,y)$$

A special type of perturbation that we are going to study is the potential one. In this situation the perturbation can be written as a potential that depends only on one state at a time:

$$\mathcal{V}_t(x,y) = V_t(y) - V_t(x)$$

Also for a potential perturbation we can have the three situations above. Since the potential perturbation is the most common, we will treat it in depth. We are going to start with the antisymmetric potential perturbation.

3.1 Antisymmetric potential perturbation

3.1.1 Rates modification

Suppose to apply at time $t = 0$ a potential time-dependent perturbation $h_t V_t(x_t)$ to the system with h_t small. Due to it, the system will no longer evolve with L_t and $P_t(x)$ since the transition rates will be modified. Then:

$$F_t(x,y) \longrightarrow F_t^h(x,y) = F_t(x,y) + \beta_t h_t V_t(y) - \beta_t h_t V_t(x) \tag{3.1.1}$$

$$F_t(y,x) \longrightarrow F_t^h(y,x) = -F_t(x,y) + \beta_t h_t V_t(x) - \beta_t h_t V_t(y) \tag{3.1.2}$$

Here $V_t(x_t)$ is an observable generally depending on time and on set of states. If we choose this kind of perturbation, $F_t(x,y)$ - that is antisymmetric - remains antisymmetric. In fact, $F_t^h(y,x) = -F_t^h(x,y)$. The transition rates become:

$$k_t^h(x,y) = a_t(x,y)\, e^{\frac{1}{2}[F_t(x,y)+\beta_t h_t V_t(y)-\beta_t h_t V_t(x)]}$$

$$k_t^h(y,x) = a_t(x,y)\, e^{-\frac{1}{2}[F_t(x,y)+\beta_t h_t V_t(y)-\beta_t h_t V_t(x)]}$$

We assumed that the perturbation could be potential and antisymmetric, so it does not affect the reactivities $a_t(x,y)$, but only the drift $F_t(x,y)$. If we consider the ratio:

$$\frac{k_t^h(x,y)}{k_t^h(y,x)} = \frac{a_t(x,y)\, e^{\frac{1}{2}[F_t(x,y)+\beta_t h_t V_t(y)-\beta_t h_t V_t(x)]}}{a_t(x,y)\, e^{-\frac{1}{2}[F_t(x,y)+\beta_t h_t V_t(y)-\beta_t h_t V_t(x)]}} = e^{F_t(x,y)+\beta_t h_t[V_t(y)-V_t(x)]}$$

$$\frac{k_t^h(x,y)}{k_t^h(y,x)} = \frac{k_t(x,y)}{k_t(y,x)} e^{\beta_t h_t[V_t(y)-V_t(x)]} \tag{3.1.3}$$

It is interesting to note that in the bracket there is the difference of the perturbation before and after the transition that can be thought as a heat flux from the reservoir to the system due to the perturbation. Since it is divided by the temperature of the reservoir it can be interpreted as an entropic flux. We can think at this perturbation as an external drift. So we can say:

$$k_t^h(x,y) = k_t(x,y)\, e^{\frac{\beta_t h_t}{2}[V_t(y)-V_t(x)]} \tag{3.1.4}$$

$$k_t^h(y,x) = k_t(y,x)\, e^{-\frac{\beta_t h_t}{2}[V_t(y)-V_t(x)]} \tag{3.1.5}$$

From now on we are going to call $\beta_s h_s = \gamma_s$. The transition rates ratio depends only on the difference of the values of the perturbation before and after the transition, for this reason it is called a potential perturbation. The probability of the trajectory will be modified:

$$\mathcal{P}^h(\omega) = \prod_{0\le s\le t}^{N(t)} k_s^h(x_{s^-}, x_s)\; e^{-\int_0^t \lambda_s^h(x_{s^-})ds} \tag{3.1.6}$$

3.1.2 Excess action

We are interested in the ratio of the two probabilities:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} = \prod_{0\le s\le t}^{N(t)} \frac{k_s^h(x_{s^-}, x_s)}{k_s(x_{s^-}, x_s)} e^{-\int_0^t[\lambda_s^h(x_{s^-})-\lambda_s(x_{s^-})]ds}$$

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} = \prod_{0\le s\le t}^{N(t)} e^{\frac{\gamma_s}{2}[V_s(x_s)-V_s(x_{s^-})]} e^{-\int_0^t[\lambda_s^h(x_{s^-})-\lambda_s(x_{s^-})]ds}$$

With (3.0.1) we can study the perturbed system with the unperturbed probability given by solving the master equation. If we apply the logarithm we obtain the Girsanov formula for excess action:

$$-\mathcal{A}(\omega) = \sum_{0\le s\le t}^{N(t)} \frac{\gamma_s}{2}[V_s(x_s) - V_s(x_{s^-})] - \int_0^t \left[\lambda_s^h(x_{s^-}) - \lambda_s(x_{s^-})\right] ds$$

Since we are going to take its average value we can substitute $\lambda_s^{(h)}(x_{s^-})$ with $\lambda_s^{(h)}(x_s)$ without changing the result. Then:

$$-\mathcal{A}(\omega) = \sum_{0\le s\le t}^{N(t)} \frac{\gamma_s}{2}\left[V_s(x_s) - V_s(x_{s^-})\right] - \int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds \tag{3.1.7}$$

$\mathcal{A}(\omega)$ is called excess action at time t because it takes into account how the probability of a trajectory ω changes by adding a small perturbation. Using the expression of the transition rates we want to manipulate the second term:

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} \left[k_s^h(x_s,x) - k_s(x_s,x)\right] ds$$

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} k_s(x_s,x)\left[\frac{k_s^h(x_s,x)}{k_s(x_s,x)} - 1\right] ds$$

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} k_s(x_s,x)\left[e^{\frac{\gamma_s}{2}[V_s(x)-V_s(x_s)]} - 1\right] ds$$

If we expand the exponential to the first order:

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \frac{1}{2}\int_0^t \gamma_s \sum_{x\neq x_s} k_s(x_s,x)\left[V_s(x) - V_s(x_s)\right] ds + \mathcal{O}(\gamma_t)$$

Finally the excess action to the first order:

$$\mathcal{A}^{(1)}(\omega) = -\frac{1}{2}\sum_{0\le s\le t}^{N(t)} \gamma_s\left[V_s(x_s) - V_s(x_{s^-})\right] + \frac{1}{2}\int_0^t \gamma_s \sum_{x\neq x_s} k_s(x_s,x)\left[V_s(x) - V_s(x_s)\right] ds$$

We note that the sum over the states excludes the state before the jump at time $t = s$. We can add also the contribution $x = x_s$ in the second sum since we have to take into account also the $V_s(x) - V_s(x_s)$, that vanishes if $x = x_s$. Then:

$$\mathcal{A}^{(1)}(\omega) = -\frac{1}{2}\sum_{0\le s\le t}^{N(t)} \gamma_s\left[V_s(x_s) - V_s(x_{s^-})\right] + \frac{1}{2}\int_0^t \gamma_s \sum_{x} k_s(x_s,x)\left[V_s(x) - V_s(x_s)\right] ds \tag{3.1.8}$$

3.1.3 Average values

If the perturbation modifies the probability we expect that also the average values made on the trajectory will change. For a general observable $Q_t(x_t)$:

$$\delta\langle Q_t(x_t)\rangle^h = \langle Q_t(x_t)\rangle_\mu^h - \langle Q_t(x_t)\rangle_\mu = \sum_x P_t^h(x)\,Q_t(x) - \sum_x P_t(x)\,Q_t(x)$$

$$\delta\langle Q_t(x_t)\rangle^h = \sum_x P_t(x)\,Q_t(x)\left(e^{-\mathcal{A}(x)} - 1\right)$$

$$\delta\langle Q_t(x_t)\rangle^h \simeq -\left\langle \mathcal{A}^{(1)}(x_t)\,Q_t(x_t)\right\rangle_\mu \tag{3.1.9}$$

$\delta \langle Q_t(x_t)\rangle^h$ is called the generalized susceptibility. In this way we can write the perturbed average values in function of the unperturbed ones. In fact, with $\langle . \rangle_\mu$ we mean the average value made with the probability $P_t(x)$ with initial distribution μ. Note that the perturbed and unperturbed average values have the same initial distribution. Then:

$$\delta \langle Q_t(x_t)\rangle^h \simeq \left\langle Q_t(x_t) \sum_{0\leq s\leq t}^{N(t)} \frac{\gamma_s}{2} \left[V_s(x_s) - V_s(x_{s^-})\right] \right\rangle_\mu -$$

$$- \left\langle Q_t(x_t) \int_0^t \frac{\gamma_s}{2} \sum_x k_s(x_s, x) \left[V_s(x) - V_s(x_s)\right] ds \right\rangle_\mu$$

3.1.3.1 First contribution

There is a general identity that allows the rewrite the sum in the first contribution:

$$\gamma_t V_t(x_t) - \gamma_0 V_0(x_0) = \sum_{0\leq s\leq t}^{N(t)} \gamma_s \left[V_s(x_s) - V_s(x_{s^-})\right] + \int_0^t \frac{d\gamma_s}{ds} V_s(x_s)\, ds + \int_0^t \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds \quad (3.1.10)$$

We are going to demonstrate it in the Appendices. The origin of the last term is the explicit dependence on time of the potential, for this reason we use a partial derivative. It does not act on the trajectory. This identity allows to rewrite the first term of the susceptibility as:

$$\left\langle Q_t(x_t) \sum_{0\leq s\leq t}^{N(t)} \frac{\gamma_s}{2} \left[V_s(x_s) - V_s(x_{s^-})\right] \right\rangle_\mu = \frac{1}{2} \left\langle Q_t(x_t) \left[\gamma_t V_t(x_t) - \gamma_0 V_0(x_0)\right] \right\rangle_\mu -$$

$$-\frac{1}{2} \left\langle Q_t(x_t) \int_0^t \frac{d\gamma_s}{ds} V_s(x_s)\, ds \right\rangle_\mu - \frac{1}{2} \left\langle Q_t(x_t) \int_0^t \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds \right\rangle_\mu$$

If we introduce:

$$\mathcal{S}(\omega) = \gamma_t V_t(x_t) - \gamma_0 V_0(x_0) - \int_0^t \frac{d\gamma_s}{ds} V_s(x_s)\, ds - \int_0^t \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds \quad (3.1.11)$$

Then:

$$\left\langle Q_t(x_t) \sum_{0\leq s\leq t}^{N(t)} \frac{\gamma_s}{2} \left[V_s(x_s) - V_s(x_{s^-})\right] \right\rangle_\mu = \frac{1}{2} \left\langle Q_t(x_t)\, \mathcal{S}(\omega) \right\rangle_\mu \quad (3.1.12)$$

$\mathcal{S}(\omega)$ is the entropy flux produced by the perturbation during the time interval $[0, t]$ along the trajectory ω, it does not take into account the entropic production due to the nonequilibrium dynamics. For this reason it is also called excess entropy flux. The first two terms in the entropy flux describe the reversible contribution, because they depend only on the initial and final values in relation to the trajectory. If we exclude the temperature β_t, it can be thought as an excess of energy difference of the system. Instead the last two terms in $\mathcal{S}(\omega)$ are irreversible work and it depends on the path via the integral. Again, by the first principle of thermodynamics we obtain the excess heat flux (from the environment to the system) given by the excess difference energy minus the excess work made by the environment.

3.1.3.2 Second contribution

If we recall (2.2.12) we can note that it is exactly what is written in the average value of the second contribution, so:

$$\left\langle Q_t(x_t) \int_0^t \sum_x k_s(x_s, x) \frac{\gamma_s}{2} \left[V_s(x) - V_s(x_s)\right] ds \right\rangle_\mu = \frac{1}{2} \left\langle Q_t(x_t) \int_0^t \gamma_s L_s V_s(x_s)\, ds \right\rangle_\mu$$

Usually this contribution is called frenetic excess or dynamical activity, because it describes how much the system is inclined to make transitions (in fact it depends explicitly on transition rates via the matrix L_s). As we saw, the application of L_s to a function describes how it changes during a transition in relation to the rates. Finally we obtain:

$$\delta \langle Q_t(x_t) \rangle^h \simeq \frac{1}{2} \langle Q_t(x_t)\, \mathcal{S}(\omega) \rangle_\mu - \frac{1}{2} \left\langle Q_t(x_t) \int_0^t \gamma_s L_s V_s(x_s)\, ds \right\rangle_\mu \tag{3.1.13}$$

It is interesting to note that these two contributions behave differently under time reversal. In fact, if we consider the trajectory x_{t-s} during the interval $[t, 0]$ the entropic contribution would be opposite (antisymmetric), instead the frenetic one would be the same (symmetric):

- Consider the entropic term

$$\mathcal{S}(\omega) = \gamma_t V_t(x_t) - \gamma_0 V_0(x_0) - \int_0^t \frac{d\gamma_s}{ds} V_s(x_s)\, ds - \int_0^t \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds$$

  Now we introduce dynamical time reversal operator θ, it acts on the trajectory in the following way:

$$(\theta\omega)_s = \omega_{t-s}$$

  using it, we reverse the time:

$$\mathcal{S}(\theta\omega) = \gamma_{-t} V_{-t}(x_{-t}) - \gamma_0 V_0(x_0) + \int_{-t}^0 \frac{d\gamma_s}{ds} V_s(x_s)\, ds + \int_{-t}^0 \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds$$

$$\mathcal{S}(\theta\omega) = -\left[\gamma_0 V_0(x_0) - \gamma_{-t} V_{-t}(x_{-t}) - \int_{-t}^0 \frac{d\gamma_s}{ds} V_s(x_s)\, ds - \int_{-t}^0 \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds\right]$$

  So, if we consider the average value with the observable evaluated at the end of time interval (and then $t = 0$):

$$-\left\langle Q_0(x_0) \left[\gamma_0 V_0(x_0) - \gamma_{-t} V_{-t}(x_{-t}) - \int_{-t}^0 \frac{d\gamma_s}{ds} V_s(x_s)\, ds - \int_{-t}^0 \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds\right] \right\rangle_\mu$$

  The average value is equal to the one calculated from ω except for the minus. Thus we can say:

$$\langle Q_0(x_0)\, \mathcal{S}(\theta\omega) \rangle = -\langle Q_t(x_t)\, \mathcal{S}(\omega) \rangle$$

- consider the frenetic term. If we reverse the time the integral does not change sign. In fact:

$$\left\langle Q_t(x_t) \int_0^t \gamma_s L_s V_s(x_s)\, ds \right\rangle_\mu = \frac{1}{2} \left\langle Q_0(x_0) \int_{-t}^0 \gamma_s L_s V_s(x_s)\, ds \right\rangle_\mu$$

$$\langle Q_0(x_0)\, \mathcal{T}(\theta\omega) \rangle = \langle Q_t(x_t)\, \mathcal{T}(\omega) \rangle$$

Therefore the excess action is made by a symmetric contribution and an antisymmetric one. Therefore:

$$\mathcal{A}(\omega) = \frac{\mathcal{T}(\omega) - \mathcal{S}(\omega)}{2}$$

with:

$$\mathcal{T}(\omega) = \frac{\mathcal{A}(\omega) + \mathcal{A}(\theta\omega)}{2}$$

$$\mathcal{S}(\omega) = \frac{\mathcal{A}(\theta\omega) - \mathcal{A}(\omega)}{2}$$

And then:

$$\delta \langle Q_t(x_t) \rangle^h \simeq \frac{1}{2} \langle Q_t(x_t)\, \mathcal{S}(\omega) \rangle_\mu - \frac{1}{2} \langle Q_t(x_t)\, \mathcal{T}(\omega) \rangle_\mu \tag{3.1.14}$$

3.1.3.3 Local detailed balance

The interpretation of the action antisymmetric contribution as entropic flux is due to the local detailed balance. In the entropy dissertation we have introduced it as a tool to give a physical meaning to the Shannon entropy. Here we can use it starting from the trajectories probability ratio. In fact considering the trajectory ω and its opposite $\theta\omega$:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} = \prod_{0\le s\le t}^{N(t)} \frac{k_s^h(x_{s^-}, x_s)}{k_s(x_{s^-}, x_s)} e^{-\int_0^t \left[\lambda_s^h\left(x_{s^-}\right) - \lambda_s\left(x_{s^-}\right)\right] ds}$$

$$\frac{\mathcal{P}^h(\theta\omega)}{\mathcal{P}(\theta\omega)} = \prod_{0\le s\le t}^{N(t)} \frac{k_s^h(x_s, x_{s^-})}{k_s(x_s, x_{s^-})} e^{-\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds}$$

If we consider the ratio between them:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} \cdot \frac{\mathcal{P}^h(\theta\omega)}{\mathcal{P}(\theta\omega)} = \prod_{0\le s\le t}^{N(t)} \frac{k_s^h(x_{s^-}, x_s)}{k_s(x_{s^-}, x_s)} \frac{k_s(x_s, x_{s^-})}{k_s^h(x_s, x_{s^-})}$$

Using the definition of the perturbed transition rates:

$$\frac{k_s^h(x_{s^-}, x_s)}{k_s^h(x_s, x_{s^-})} = \frac{k_s(x_s, x_{s^-})}{k_s(x_{s^-}, x_s)} e^{\gamma_s\left[V_s(x_s) - V_s\left(x_{s^-}\right)\right]}$$

we obtain:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} \cdot \frac{\mathcal{P}^h(\theta\omega)}{\mathcal{P}(\theta\omega)} = \prod_{0\le s\le t}^{N(t)} e^{\gamma_s\left[V_s(x_s) - V_s\left(x_{s^-}\right)\right]}$$

The local detailed balance assures:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} \cdot \frac{\mathcal{P}^h(\theta\omega)}{\mathcal{P}(\theta\omega)} = e^{\mathcal{S}(\omega)}$$

where $\mathcal{S}(\omega)$ is the entropic flux from the system to the environment divided by k_B. Therefore:

$$\mathcal{S}(\omega) = \sum_{0\le s\le t}^{N(t)} \gamma_s \left[V_s(x_s) - V_s(x_{s^-})\right]$$

3.1.4 Response

The linear response is defined from

$$\delta \langle Q_t(x_t)\rangle^h \simeq \int_0^t \gamma_s R_{Q,V}(t,s)\, ds \tag{3.1.15}$$

with $t > s$. Consider first the entropic term:

$$Ent[\omega] = \frac{1}{2}\left\langle Q_t(x_t)\left[\gamma_t V_t(x_t) - \gamma_0 V_0(x_0) - \int_0^t \frac{d\gamma_s}{ds} V_s(x_s)\, ds - \int_0^t \gamma_s \frac{\partial V_s(x_s)}{\partial s} ds\right]\right\rangle_\mu$$

Now we want to obtain the expression of the response for our system. We can rewrite it as:

$$Ent[\omega] = \frac{1}{2}\int_0^t ds \frac{d}{ds}\left[\gamma_s \langle Q_t(x_t) V_s(x_s)\rangle_\mu\right] -$$

$$-\frac{1}{2}\int_0^t \frac{d\gamma_s}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu\, ds - \frac{1}{2}\int_0^t \gamma_s \left\langle Q_t(x_t)\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu ds$$

Taking the time-derivative of the first term:

$$Ent[\omega] = \frac{1}{2}\int_0^t ds\, \gamma_s \frac{d}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu + \frac{1}{2}\int_0^t ds\, \langle Q_t(x_t) V_s(x_s)\rangle_\mu \frac{d\gamma_s}{ds} -$$

$$-\frac{1}{2}\int_0^t \frac{d\gamma_s}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu\, ds - \frac{1}{2}\int_0^t \gamma_s \left\langle Q_t(x_t)\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu$$

And then:

$$Ent[\omega] = \frac{1}{2}\int_0^t ds\, \gamma_s \left[\frac{d}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu - \left\langle Q_t(x_t)\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu\right]$$

Finally:

$$\delta \langle Q_t(x_t)\rangle^h \simeq \frac{1}{2}\int_0^t ds\, \gamma_s \left[\frac{d}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu - \left\langle Q_t(x_t)\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu - \langle Q_t(x_t) L_s V_s(x_s)\rangle_\mu\right] \tag{3.1.16}$$

The final result for the response is:

$$R_{Q,V}(t,s) = \frac{1}{2}\left[\frac{d}{ds}\langle Q_t(x_t) V_s(x_s)\rangle_\mu - \left\langle Q_t(x_t)\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu\right] - \frac{1}{2}\langle Q_t(x_t) L_s V_s(x_s)\rangle_\mu \tag{3.1.17}$$

The response is a correlation between an observable and the perturbation at different times. If the two variables are very correlated the response is bigger. The time t is fixed and it is the ending time of the trajectory. Instead the time s is a generic time during the evolution in which we evaluate the perturbation (not necessarily the initial one).

3.1.4.1 Comments

For $s < t$ in the frenetic term, it is not possible to apply a time derivative with respect to s if there is a function that depends on a time $t > s$. Instead, if $s > t$:

$$\frac{1}{2}\left\langle Q_t\left(x_t\right) L_s V_s\left(x_s\right)\right\rangle_\mu = \frac{1}{2}\frac{d}{ds}\left\langle Q_t\left(x_t\right) V_s\left(x_s\right)\right\rangle_\mu - \frac{1}{2}\left\langle Q_t\left(x_t\right)\frac{\partial V_s\left(x_s\right)}{\partial s}\right\rangle_\mu$$

The second term would be equal to the first since the response is zero if evaluated for a time preceding the perturbation one for the causality condition. So we can introduce the L_s operator, but it cannot be interpreted as a time derivative.

$$L_s V_s\left(x_s\right) = \sum_x k_s\left(x_s, x\right)\left[V_s\left(x\right) - V_s\left(x_s\right)\right]$$

It is interesting to note that the explicit time-dependence of the potential seems to give another contribution in the response. But it is not true. In fact in both cases only the dependence on time of the trajectory gives a contribution. So if there is also an explicit time dependence we must subtracting it. Actually the importance of this time dependence appears in the entropy flux under the form of irreversible work done on the system.

In addition also the time-dependence of the transition rates does not modify the structure of the response formula. Nevertheless it completely changes the reference process without the perturbation. In fact in the response formula found for time independent processes in [15], the average values are made on the stationary state. Instead if the rates are time-dependent the invariant distribution does not exist. Due to it, the problem becomes really more difficult since usually we do not know the $P_t\left(x\right)$ for a not stationary dynamics. There is an approximation that makes the problem easier. It is the quasi-static limit.

3.1.5 Response close to equilibrium

We want to show that if the system before being perturbed is at equilibrium the response formula can be manipulated to give the Kubo fluctuation-response theorem. In fact if the system is in thermodynamic equilibrium we can say:

- the system does not break symmetry of time reversal
- the system is in detailed balance (2.2.6)
- the system is invariant under time translations (note that it would be true also for nonequilibrium stationary state)
- the rates do not depend on time and neither the backward generator (homogeneous Markov chain)
- there are no currents between the states

If the system is at equilibrium the average values are made on the invariant distribution ρ_{eq} that can be found from the backward generator solving the linear system $\rho_{eq} L = 0$. If the system is at equilibrium the trajectory can be interpreted as how the perturbation takes the system out of equilibrium, obviously remaining close to it, since we consider small perturbations. So the opposite trajectory describes the converging to equilibrium. Due to Onsager regression principle these two

evolutions are physically equivalent to spontaneous fluctuation of the system at the equilibrium. For this reason we have time-reversal symmetry. There are two ways to obtain the Green-Kubo formula, we are going to explain both. The first is based on the properties of the equilibrium probability, while the second uses the symmetry of the excess action.

3.1.5.1 First method

Since the system is at equilibrium, the backward generator can no longer depend on time otherwise there will not be the invariant distribution. And even the observable cannot depend explicitly on time. Using time reversal symmetry we can write:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \langle Q(x_s)\, LV(x_t)\rangle_{eq}$$

Here the average values are made on the invariant distribution ρ_{eq}. In fact:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \sum_{x,y,z} \rho_{eq}(x)\, \mathbb{P}[x_s = y \mid x_0 = x]\, LV(y)\, \mathbb{P}[x_t = z \mid x_s = y]\, Q(z)$$

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \sum_{y,z} \rho_{eq}(y)\, LV(y)\, \mathbb{P}[x_t = z \mid x_s = y]\, Q(z)$$

Here we have used the definition of invariant distribution:

$$\sum_{x} \rho_{eq}(x)\, \mathbb{P}[x_s = y \mid x_0 = x] = \rho_{eq}(y) \tag{3.1.18}$$

Then:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \sum_{y,z} \rho_{eq}(y)\, LV(y)\, Q(z)\, \mathbb{P}[x_{t-s} = z \mid x_0 = y] = \langle Q(x_{t-s})\, LV(x_0)\rangle_{eq}$$

We have demonstrated the invariance under time translations. Now, if we use detailed balance:

$$\rho_{eq}(x)\, \mathbb{P}[x_s = y \mid x_0 = x] = \rho_{eq}(y)\, \mathbb{P}[x_s = x \mid x_0 = y] \tag{3.1.19}$$

Then:

$$\langle Q(x_{t-s})\, LV(x_0)\rangle_{eq} = \sum_{y,z} LV(y)\, Q(z)\, \rho_{eq}(z)\, \mathbb{P}[x_{t-s} = y \mid x_0 = z]$$

$$\langle Q(x_{t-s})\, LV(x_0)\rangle_{eq} = \sum_{y,z} Q(z)\, \rho_{eq}(z)\, LV(y)\, \mathbb{P}[x_{t-s} = y \mid x_0 = z] = \langle Q(x_0)\, LV(x_{t-s})\rangle_{eq} \tag{3.1.20}$$

Finally, if we use again the invariance under time translations:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \langle Q(x_0)\, LV(x_{t-s})\rangle_{eq} = \langle Q(x_s)\, LV(x_t)\rangle_{eq}$$

But since $t > s$ we can extract a time derivative due to the definition of L:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \frac{d}{dt} \langle Q(x_s)\, V(x_t)\rangle_{eq}$$

Now we can use the invariance under time translations:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = \frac{d}{dt}\langle Q(x_0)\, V(x_{t-s})\rangle_{eq}$$

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = -\frac{d}{ds}\langle Q(x_0)\, V(x_{t-s})\rangle_{eq}$$

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = -\frac{d}{ds}\langle Q(x_s)\, V(x_t)\rangle_{eq}$$

Finally, using again the time reversal symmetry:

$$\langle Q(x_t)\, LV(x_s)\rangle_{eq} = -\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq}$$

Now the response is:

$$R_{Q,V}(t,s) = \frac{\beta}{2}\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq} + \frac{\beta}{2}\frac{d}{ds}\langle Q(x_t)\, V_s(x_s)\rangle_{eq} = \beta\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq}$$

$$R_{Q,V}(t-s) = \beta\frac{d}{ds}\langle Q(x_{t-s})\, V(x_0)\rangle_{eq}$$

Obviously the response depends on the difference of the two times due to the translational symmetry. As we can see, for a perturbation near equilibrium the frenetic contribution is equal to the entropic. The dynamical activity appears only out of equilibrium because, moving away from equilibrium, the time reversal symmetry breaking is manifest (the detailed balance formula 3.1.19 is no longer valid). Since the dynamical term is symmetric with respect to time-reversal, it can give a contribution only if this symmetry is broken. According to it we should expect that the frenetic would be zero.

3.1.5.2 Second method

We have to start from (3.1.14). Suppose that the perturbation starts to act at time $t = 0$ on an equilibrium system. We expect that at time $t = 0$ the perturbed system will be equal to the unperturbed one. We can write the susceptivity:

$$\delta\langle Q(x_t)\rangle^h = \langle Q(x_t)\rangle^h - \langle Q(x_t)\rangle_{eq}$$

we can add and subtract $\langle Q(x_0)\rangle^h$. Then:

$$\langle Q(x_t)\rangle^h - \langle Q(x_t)\rangle_{eq} \pm \langle Q(x_0)\rangle^h = \langle Q(x_t) - Q(x_0)\rangle^h + \langle Q(x_0)\rangle^h - \langle Q(x_t)\rangle_{eq} \tag{3.1.21}$$

This is due to the independence on time of the observable at equilibrium. At equilibrium the average value are time independent. Furthermore since the perturbation acts from time $t = 0$ we can say:

$$\langle Q(x_0)\rangle^h = \langle Q(x_0)\rangle$$

Using these two properties we can eliminate the two average values in (3.1.21). Therefore:

$$\langle Q(x_t)\rangle^h - \langle Q(x_t)\rangle_{eq} = \langle Q(x_t) - Q(x_0)\rangle^h = -\left\langle [Q(x_t) - Q(x_0)]\, \mathcal{A}^{(1)}(\omega)\right\rangle_{eq}$$

Note that the observable in the bracket is antisymmetric under time reversal. Now we can study separately the two contributions:

- symmetric contribution

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{T}\left(\omega\right)\right\rangle_{eq}=\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{T}\left(\omega\right)\right\rangle_{eq}-\frac{1}{2}\left\langle Q\left(x_0\right)\mathcal{T}\left(\omega\right)\right\rangle_{eq}$$

  In the first term we calculate the average value between the observable evaluated at the final time of the the trajectory ω with the frenetic action contribution, while in the second we do the same for the observable evaluated at the initial time of the the trajectory ω, that is the final time of the opposite $\theta\omega$ during the interval $[t,0]$. Therefore, we can write:

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{T}\left(\omega\right)\right\rangle_{eq}=\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{T}\left(\omega\right)\right\rangle_{eq}-\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{T}\left(\theta\omega\right)\right\rangle_{eq}$$

  obtaining an equivalent expression, but $\mathcal{T}\left(\omega\right)=\mathcal{T}\left(\theta\omega\right)$ and then the two terms cancel out. Therefore the symmetric contribution is zero:

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{T}\left(\omega\right)\right\rangle_{eq}=0$$

- antisymmetric contribution

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{S}\left(\omega\right)\right\rangle_{eq}=\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{S}\left(\omega\right)\right\rangle_{eq}-\frac{1}{2}\left\langle Q\left(x_0\right)\mathcal{S}\left(\omega\right)\right\rangle_{eq}$$

  If we do the same we obtain:

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{S}\left(\omega\right)\right\rangle_{eq}=\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{S}\left(\omega\right)\right\rangle-\frac{1}{2}\left\langle Q\left(x_t\right)\mathcal{S}\left(\theta\omega\right)\right\rangle$$

  But $\mathcal{S}\left(\omega\right)$ is antisymmetric under time reversal $\mathcal{S}\left(\theta\omega\right)=-\mathcal{S}\left(\omega\right)$. Therefore:

$$\frac{1}{2}\left\langle \left[Q\left(x_t\right)-Q\left(x_0\right)\right]\mathcal{S}\left(\omega\right)\right\rangle_{eq}=\left\langle Q\left(x_t\right)S\left(\omega\right)\right\rangle$$

If we consider again the susceptivity:

$$\left\langle Q\left(x_t\right)\right\rangle^{h}-\left\langle Q\left(x_t\right)\right\rangle_{eq}=\left\langle Q\left(x_t\right)\mathcal{S}\left(\omega\right)\right\rangle_{eq}$$

from which we can obtain the Green-Kubo formula. In conclusion we can say that near to equilibrium the entropy flux describes completely the linear response to a perturbation.

3.1.6 Response in quasi-static limit

As we have said the probability $P_t\left(x\right)$ does not describe a system at equilibrium and usually it is difficult to calculate since we should solve the master equation for each state. There is a situation in which it can be well approximated. It is the quasi-static limit. In this limit we can approximate the probability to be in a state at time t with the stationary distribution at fixed time t plus a correction. It is equivalent to say that for each fixed time t the dynamics is detailed balance with corresponding distribution ρ_t. Or, in other words, ρ_t satisfies (3.1.19) at time t. We can interpret it as an instantaneous equilibrium distribution. In the quasi-static limit the solution to

the time-dependent Master equation converges at each time to the instantaneous ρ_t. It can be easily calculated solving the linear system:

$$\rho_t L_t = 0$$

Practically we write:

$$P_t(x) = \rho_t(x) + \mathcal{O}(\varepsilon)$$

This approximation, as we said in 2.2.4, is of order $\mathcal{O}(\varepsilon)$. Now we consider the response formula making explicit the average values. If we make this substitution in the response formula:

$$R_{Q,V}(t,s) = \frac{1}{2}\frac{d}{ds}\sum_{x,y} P_s(x) V_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y) - \sum_{x,y} P_s(x) \frac{\partial V_s(x)}{\partial s} \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y) -$$

$$-\sum_{x,y} P_s(x) L_s V_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y)$$

we obtain:

$$R_{Q,V}(t,s) = \frac{1}{2}\frac{d}{ds}\sum_{x,y} \rho_s(x) V_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y) - \sum_{x,y} \rho_s(x) \frac{\partial V_s(x)}{\partial s} \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y) -$$

$$-\sum_{x,y} \rho_s(x) L_s V_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y) + \mathcal{O}(\varepsilon)$$

Now the average values are made on the invariant distribution at time s:

$$R_{Q,V}(t,s) = \frac{1}{2}\left[\frac{d}{ds}\langle V_s(x_s) Q_t(x_t)\rangle_{\rho_s} - \left\langle \frac{\partial V_s(x_s)}{\partial s} Q_t(x_t)\right\rangle_{\rho_s} - \langle L_s V_s(x_s) Q_t(x_t)\rangle_{\rho_s}\right] + \mathcal{O}(\varepsilon)$$

Now the response is easily calculable because we know the invariant distribution. The response formula is formally equal to the one for time-independent reference process. But there is a deep difference due to the fact that ρ_s cannot be thought as an evolution. This formula is correct for time s fixed. For this reason we cannot use a time translation. In fact consider:

$$\langle V_s(x_s) Q_t(x_t)\rangle_{\rho_s} = \sum_{x,y} \rho_s(x) V_s(x) \mathbb{P}_t[x_t = y \mid x_s = x] Q_t(y)$$

If we do a time translation:

$$\langle V_s(x_s) Q_t(x_t)\rangle_{\rho_s} = \sum_{x,y} \rho_0(x) V_0(x) \mathbb{P}_0[x_{t-s} = y \mid x_0 = x] Q_{t-s}(y) = \langle V_0(x_0) Q_{t-s}(x_{t-s})\rangle_{\rho_0}$$

The problem is that $\rho_s \neq \rho_{s'}$ with $s' \neq s$. Therefore if we do a time translation we have changed the initial distribution. Even in the quasi-static limit the response depends on the two times s and t independently. We have said that in the quasi-static limit the system is detailed balance at any fixed time, therefore we expect it satisfies the global detailed balance (3.1.19) time by time. This consideration is interesting since we want to know if under quasi-static limit approximation the response formula can be led back to the Kubo one. If we consider again:

$$\langle V_s(x_s)\, Q_t(x_t)\rangle_{\rho_s} = \sum_{x,y} \rho_s(x)\, V_s(x)\, \mathbb{P}_s[x_t = y \mid x_s = x]\, Q_t(y)$$

The detailed balance at time s allows:

$$\langle V_s(x_s)\, Q_t(x_t)\rangle_{\rho_s} = \sum_{x,y} \rho_s(y)\, V_s(x)\, \mathbb{P}_s[x_t = x \mid x_s = y]\, Q_t(y)$$

Now we would to exchange the role of $Q_t(x_t)$ and $V_s(x_s)$ as in (3.1.20). The problem is that now the observables and the backward generator depend explicitly on time. Otherwise it would be possible to rewrite the frenetic term as the entropic one with the opposite sign and obtain a Kubo formula at fixed time. Therefore we conclude that, if the reference Markov process is inhomogeneous, in the quasi-static limit the probability can be approximated with nonequilibrium stationary state probability and not with equilibrium one because the response cannot be led back to Green-Kubo formula.

Furthermore, what we have said does not depend on the time-symmetry of the potential perturbation. Then we will obtain the same results in the following Section in which we are going to study a potential perturbation with generic time symmetry.

3.1.7 Appendix: demonstration of the general identity

To understand the idea of this demonstration it is useful to consider first a simpler trajectory with two jumps in the interval $[0, t]$. The jumps happen at time $t = t_1$ and $t = t_2$. So we can write:

$$\gamma_t V_t(x_t) - \gamma_0 V_0(x_0) = \gamma_{t_1}\left[V_{t_1}(x_{t_1}) - V_{t_1}\left(x_{t_1^-}\right)\right] + \gamma_{t_2}\left[V_{t_2}(x_{t_2}) - V_{t_2}\left(x_{t_2^-}\right)\right] +$$

$$+\gamma_t V_t(x_t) - \gamma_{t_2} V_{t_2}(x_{t_2}) + \gamma_{t_2} V_{t_2}\left(x_{t_{2^-}}\right) - \gamma_{t_1} V_{t_1}(x_{t_1}) + \gamma_{t_1} V_{t_1}\left(x_{t_{1^-}}\right) - \gamma_0 V_0(x_0)$$

We have only added and subtracted some terms. Now we can rearrange them:

$$\gamma_t V_t(x_t) - \gamma_0 V_0(x_0) = \gamma_{t_1}\left[V_{t_1}(x_{t_1}) - V_{t_1}\left(x_{t_1^-}\right)\right] + \gamma_{t_2}\left[V_{t_2}(x_{t_2}) - V_{t_2}\left(x_{t_2^-}\right)\right] +$$

$$+ (\gamma_{t_1} - \gamma_0) V_0(x_0) + (\gamma_{t_2} - \gamma_{t_1}) V_{t_1}(x_{t_1}) + (\gamma_t - \gamma_{t_2}) V_{t_2}(x_{t_2})$$

$$+\gamma_{t_1}\left[V_{t_1}\left(x_{t_1^-}\right) - V_0\left(x_{t_1^-}\right)\right] + \gamma_{t_2}\left[V_{t_2}\left(x_{t_2^-}\right) - V_{t_1}\left(x_{t_2^-}\right)\right] + \gamma_t\left[V_t(x_{t^-}) - V_{t_2}(x_{t^-})\right]$$

We have added and subtracted the terms:

$$\pm\gamma_{t_1} V_0\left(x_{t_1^-}\right) \pm \gamma_{t_2} V_{t_1}\left(x_{t_2^-}\right) \pm \gamma_t V_{t_2}(x_{t^-})$$

Note also that: $V\left(x_{t_1^-}\right) = V(x_0)$. In this way we have three groups of terms:

- $\gamma_s\left[V_s(x_s) - V_s(x_{s^-})\right]$
- $(\gamma_s - \gamma_{s^-})\, V_{s^-}(x_{s^-})$

- $\gamma_s \left[V_s \left(x_{s^-}\right) - V_{s^-} \left(x_{s^-}\right)\right]$

We can generalize it to a generic number of jumps during the time interval, then:

$$\gamma_t V_t \left(x_t\right) - \gamma_0 V_0 \left(x_0\right) = \sum_{0 \leq s \leq t}^{N(t)} \gamma_s \left[V_s \left(x_s\right) - V_s \left(x_{s^-}\right)\right] +$$

$$+ \sum_{0 \leq s \leq t}^{N(t)} \left(\gamma_s - \gamma_{s^-}\right) V_{s^-} \left(x_{s^-}\right) + \sum_{0 \leq s \leq t}^{N(t)} \gamma_s \left[V_s \left(x_{s^-}\right) - V_{s^-} \left(x_{s^-}\right)\right]$$

Every group of terms describes the variation of a variable during the jumps. The first term of the potential is related to its dependence on time of the trajectory, instead the second one is related to its explicit dependence on time. It is important to note that the first sum is different from the other two because it takes into account the dependence on time of the trajectory that is discontinuous; instead the other two sums take into account a continuous dependence on time. So we can write the last two sums as an integral exactly as we did for the escape rates. So in this case, s, that indices the transition times, tends to a continuous variable, the sum tends to an integral and the bracket tends to an incremental ratio of the average value.

$$\gamma_t V_t \left(x_t\right) - \gamma_0 V_0 \left(x_0\right) = \sum_{0 \leq s \leq t}^{N(t)} \gamma_s \left[V_s \left(x_s\right) - V_s \left(x_{s^-}\right)\right] + \int_0^t ds \, \frac{d\gamma_s}{ds} V_s \left(x_s\right) + \int_0^t ds \, \gamma_s \frac{\partial V_s \left(x_s\right)}{\partial s}$$

3.2 Mixed-symmetry potential perturbation

In the previous Section we have studied the particular case of a time-dependent potential perturbation: the antisymmetric case. In fact after applying the perturbation, both $F_t \left(x, y\right)$ and $F_t^h \left(x, y\right)$ are antisymmetric. Now we want to extend it to a more general situation:

$$F_t \left(x, y\right) \longrightarrow F_t^h \left(x, y\right) = F_t \left(x, y\right) + 2\beta_t h_t \left[\mathfrak{b} V_t \left(y\right) - \mathfrak{a} V_t \left(x\right)\right] \tag{3.2.1}$$

$$F_t \left(y, x\right) \longrightarrow F_t^h \left(y, x\right) = -F_t \left(x, y\right) + 2\beta_t h_t \left[\mathfrak{b} V_t \left(x\right) - \mathfrak{a} V_t \left(y\right)\right] \tag{3.2.2}$$

where $\mathfrak{a}$ and $\mathfrak{b}$ are some constants, by convection we assume that $\mathfrak{a} + \mathfrak{b} = 1$.

3.2.1 Rates modification

Due to the perturbation there is a modification of the transition rates:

$$k_t^h \left(x, y\right) = a_t \left(x, y\right) e^{\frac{F_t(x,y)}{2}} e^{\beta_t h_t [\mathfrak{b} V_t(y) - \mathfrak{a} V_t(x)]} = k_t \left(x, y\right) e^{\beta_t h_t [\mathfrak{b} V_t(y) - \mathfrak{a} V_t(x)]}$$

$$k_t^h \left(y, x\right) = a_t \left(x, y\right) e^{-\frac{F_t(x,y)}{2}} e^{\beta_t h_t [\mathfrak{b} V_t(x) - \mathfrak{a} V_t(y)]} = k_t^h \left(y, x\right) e^{\beta_t h_t [\mathfrak{b} V_t(x) - \mathfrak{a} V_t(y)]}$$

And:

$$\frac{k_t^h \left(x, y\right)}{k_t \left(x, y\right)} = e^{\beta_t h_t [\mathfrak{b} V_t(y) - \mathfrak{a} V_t(x)]} \tag{3.2.3}$$

Now the $F_t^h \left(x, y\right)$ is no longer purely antisymmetric and there will be also a symmetric contribution. It is easy to see it using an equivalent expression:

$$k_t^h(x,y) = k_t(x,y)\, e^{\frac{(\mathfrak{a}+\mathfrak{b})\beta_t h_t}{2}[V_t(y)-V_t(x)]} e^{\frac{(\mathfrak{b}-\mathfrak{a})\beta_t h_t}{2}[V_t(y)+V_t(x)]} \tag{3.2.4}$$

$$k_t^h(y,x) = k_t(y,x)\, e^{-\frac{(\mathfrak{a}+\mathfrak{b})\beta_t h_t}{2}[V_t(y)-V_t(x)]} e^{\frac{(\mathfrak{b}-\mathfrak{a})\beta_t h_t}{2}[V_t(y)+V_t(x)]} \tag{3.2.5}$$

Remembering that $\mathfrak{a}+\mathfrak{b}=1$ we note that there are two modifications of the rates:

- antisymmetric: the first exponential is exactly the same as studied in the previous Section. If $\mathfrak{a}=-\mathfrak{b}$ the perturbation is completely symmetric and this contribution is zero.
- symmetric: the second exponential is new and it depends on the sum of the perturbation evaluated in the states of the transition, for this reason is symmetric. A symmetric perturbation is going to increase or decrease in the same way a transition rate and its opposite, then this kind of perturbation acts on the reactivities of the transition rates. Therefore we can consider this exponential as related to $a_t(x,y)$:

  $$a_t^h(x,y) = a_t(x,y)\, e^{\frac{(\mathfrak{b}-\mathfrak{a})\beta_t h_t}{2}[V_t(y)+V_t(x)]}$$

  Obviously if $\mathfrak{a}=\mathfrak{b}$ the perturbation will be completely antisymmetric and we will obtain the same as already seen. In fact adding the condition $\mathfrak{a}+\mathfrak{b}=1$ we will find $\mathfrak{a}=\mathfrak{b}=\frac{1}{2}$.

If we consider the ratio of the transition rates we will obtain the same as the antisymmetric case since the symmetric contribution cancels in the ratio:

$$\frac{k_t^h(x,y)}{k_t^h(y,x)} = \frac{a_t(x,y)\, e^{\frac{F_t(x,y)}{2}} e^{\beta_t h_t[\mathfrak{b}V_t(y)-\mathfrak{a}V_t(x)]}}{a_t(x,y)\, e^{-\frac{F_t(x,y)}{2}} e^{\beta_t h_t[\mathfrak{b}V_t(x)-\mathfrak{a}V_t(y)]}} = e^{F_t(x,y)+\beta_t h_t[V_t(y)-V_t(x)]}$$

Then:

$$\frac{k_t^h(x,y)}{k_t^h(y,x)} = \frac{k_t(x,y)}{k_t(y,x)} e^{\beta_t h_t[V_t(y)-V_t(x)]} \tag{3.2.6}$$

All what we have said about the trajectory is still valid. We continue to call $\beta_t h_t = \gamma_t$. The transition rates ratio depends only on the difference of the values of the perturbation before and after the transition, for this reason it is still called a potential perturbation. Due to the perturbation, the probability of trajectories also gets modified:

$$\mathcal{P}^h(\omega) = \prod_{0\le s\le t}^{N(t)} k_s^h(x_{s^-}, x_s)\, dt e^{-\int_0^t \lambda_s^h(x_{s^-})ds} \tag{3.2.7}$$

3.2.2 Excess action

We are interested in the ratio of the two probabilities:

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} = \prod_{0\le s\le t}^{N(t)} \frac{k_s^h(x_{s^-}, x_s)}{k_s(x_{s^-}, x_s)} e^{-\int_0^t \left[\lambda_s^h(x_s)-\lambda_s(x_s)\right]ds}$$

$$\frac{\mathcal{P}^h(\omega)}{\mathcal{P}(\omega)} = \prod_{0\le s\le t}^{N(t)} e^{\gamma_s\left[\mathfrak{b}V_s(x_s)-\mathfrak{a}V_s\left(x_{s^-}\right)\right]} e^{-\int_0^t \left[\lambda_s^h(x_s)-\lambda_s(x_s)\right]ds}$$

Also in this case we can substitute $\lambda_s^{(h)}(x_{s^-})$ with $\lambda_s^{(h)}(x_s)$. If we use (3.0.1):

$$-\mathcal{A}(\omega) = \sum_{0\le s\le t}^{N(t)} \gamma_s \left[\mathfrak{b} V_s(x_s) - \mathfrak{a} V_s(x_{s^-})\right] - \int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds \tag{3.2.8}$$

we found the excess action expression. Using equation (3.2.3) we next investigate the second term:

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} \left[k_s^h(x_s,x) - k_s(x_s,x)\right] ds$$

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} k_s(x_s,x) \left[\frac{k_s^h(x_s,x)}{k_s(x_s,x)} - 1\right] ds$$

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} k_s(x_s,x) \left[e^{\gamma_s[\mathfrak{b}V_s(x) - \mathfrak{a}V_s(x_s)]} - 1\right] ds$$

If we expand the exponential to first order:

$$\int_0^t \left[\lambda_s^h(x_s) - \lambda_s(x_s)\right] ds = \int_0^t \sum_{x\neq x_s} k_s(x_s,x)\, \gamma_s \left[\mathfrak{b} V_s(x) - \mathfrak{a} V_s(x_s)\right] ds + \mathcal{O}(\gamma_t)$$

Finally, the excess action to first order is:

$$-\mathcal{A}_t^{(1)}(\omega) = \sum_{0\le s\le t}^{N(t)} \gamma_s \left[\mathfrak{b} V_s(x_s) - \mathfrak{a} V_s(x_{s^-})\right] - \int_0^t \gamma_s \sum_{x\neq x_s} k_s(x_s,x) \left[\mathfrak{b} V_s(x) - \mathfrak{a} V_s(x_s)\right] ds \tag{3.2.9}$$

We are going to connect this action to the one studied in the antisymmetric case, summing and subtracting some contributions. Then:

$$-\mathcal{A}^{(1)}(\omega) = \mathfrak{a} \sum_{0\le s\le t}^{N(t)} \gamma_s \left[V_s(x_s) - V_s(x_{s^-})\right] + \sum_{0\le s\le t}^{N(t)} (\mathfrak{b}-\mathfrak{a})\, \gamma_s V_s(x_s) -$$

$$-\mathfrak{b} \int_0^t \gamma_s \sum_x W_s(x_s,x) \left[V_s(x) - V_s(x_s)\right] ds - (\mathfrak{b}-\mathfrak{a}) \int_0^t \gamma_s \sum_{x\neq x_s} k_s(x_s,x)\, V_s(x_s)\, ds$$

$$-\mathcal{A}^{(1)}(\omega) = \mathfrak{a} \sum_{0\le s\le t}^{N(t)} \gamma_s \left[V_s(x_s) - V_s(x_{s^-})\right] - \mathfrak{b} \int_0^t \gamma_s L_s V_s(x_s)\, ds +$$

$$+ (\mathfrak{b}-\mathfrak{a}) \left\{ \sum_{0\le s\le t}^{N(t)} \gamma_s V_s(x_s) - \int_0^t \gamma_s \sum_{x\neq x_s} k_s(x_s,x)\, V_s(x_s)\, ds \right\} \tag{3.2.10}$$

3.2.3 Average values

Recall (3.1.9), if we use the excess action expression the susceptibility at first order we get:

$$\delta \langle Q_t(x_t)\rangle^h = \mathfrak{a}\sum_{0\le s\le t}^{N(t)} \gamma_s \langle [V_s(x_s) - V_s(x_{s^-})]\, Q_t(x_t)\rangle_\mu - \mathfrak{b}\int_0^t \gamma_s \langle L_s V_s(x_s)\, Q_t(x_t)\rangle_\mu ds +$$

$$+ (\mathfrak{b}-\mathfrak{a})\left[\sum_{0\le s\le t}^{N(t)} \gamma_s \langle V_s(x_s)\, Q_t(x_t)\rangle_\mu - \int_0^t \gamma_s \sum_{x\neq x_s} \langle k_s(x_s,x)\, V_s(x_s)\, Q_t(x_t)\rangle_\mu ds\right]$$

The first two contributions are equal to what we have studied in the previous Sections, with the only difference that the entropic and frenetic terms do not have the same factor. But, we remember the antisymmetric case, $\mathfrak{a} = \mathfrak{b} = \frac{1}{2}$.

$$\delta \langle Q_t(x_t)\rangle^h = \mathfrak{a}\langle S_t(\omega)\, Q_t(x_t)\rangle_\mu - \mathfrak{b}\int_0^t \gamma_s \langle L_s V_s(x_s)\, Q_t(x_t)\rangle_\mu ds +$$

$$+ (\mathfrak{b}-\mathfrak{a})\left[\left\langle \sum_{0\le s\le t}^{N(t)} \gamma_s V_s(x_s)\, Q_t(x_t)\right\rangle_\mu - \int_0^t \gamma_s \sum_{x\neq x_s} \langle k_s(x_s,x)\, V_s(x_s)\, Q_t(x_t)\rangle_\mu ds\right] \tag{3.2.11}$$

Now we want to write the first contribution in the bracket as an integral. Since it is a finite sum over the jump times it cannot be written as an integral. In fact it is as if during the time interval $[0,t]$ we consider only some points corresponding to the jumping times. Then we can introduce a stochastic integral over Poisson events. We need to define a stochastic measure $dk_s(x,y)$ - that depends on time and on set of states - over the time interval $[0,t]$ and over the trajectory ω that is equal to 1 when there is the transition $x \to y$ at time s and it is zero otherwise. Since there is a average value in the contribution, we will be interested in the average value of this measure with the observable $Q_t(x_t)$ over all the possible trajectories:

$$\left\langle \sum_{0\le s\le t}^{N(t)} \gamma_s V_s(x_s)\, Q_t(x_t)\right\rangle_\mu = \int_0^t \gamma_s \langle dk_s(x_{s^-}, x_s)\, V_s(x_s)\, Q_t(x_t)\rangle_\mu \tag{3.2.12}$$

Now we want to calculate the average value in the integral. So, by definition of average value we have to sum over all the states. In fact, generally:

$$\langle A_t(x_t)\, B_s(x_s)\rangle_\mu = \sum_{x,y,x_0} \mu(x_0)\, \mathbb{P}_s[x_s = x \mid x_0]\, B_s(x)\, \mathbb{P}_t[x_t = y \mid x_s = x]\, A_t(y)$$

Using equation (2.1.4):

$$\langle A_t(x_t)\, B_s(x_s)\rangle_\mu = \sum_{x,y} P_s(x)\, B_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} A_t(y)$$

Then:

$$\langle dk_s(x_{s^-}, x_s)\, V_s(x_s)\, Q_t(x_t)\rangle_\mu = \sum_{\substack{x,y \\ x'\neq x}} P_s(x')\, k_s(x',x)\, ds\, V_s(x) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t(y)$$

Since in the average value there are three elements we must have three sums. The sum indexed by x' is referred to the transition at time s because of which the system jumps from x_{s^-} to x_s. Then:

$$\left\langle \sum_{0\leq s\leq t}^{N(t)} \gamma_s V_s\left(x_s\right) Q_t\left(x_t\right) \right\rangle_\mu = \int_0^t ds\, \gamma_s \sum_{\substack{x,y \\ x'\neq x}} P_s\left(x'\right) k_s\left(x',x\right) V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right) \tag{3.2.13}$$

Therefore the susceptibility is:

$$\delta \left\langle Q_t\left(x_t\right)\right\rangle^h = \mathfrak{a} \left\langle S_t\left(\omega\right) Q_t\left(x_t\right)\right\rangle_\mu - \mathfrak{b} \int_0^t \gamma_s \left\langle L_s V_s\left(x_s\right) Q_t\left(x_t\right)\right\rangle_\mu ds +$$

$$+ \left(\mathfrak{b}-\mathfrak{a}\right) \int_0^t ds\, \gamma_s \left[\sum_{\substack{x,y \\ x'\neq x}} P_s\left(x'\right) k_s\left(x',x\right) V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right) - \sum_{x\neq x_s} \left\langle k_s\left(x_s,x\right) V_s\left(x_s\right) Q_t\left(x_t\right)\right\rangle_\mu \right]$$

3.2.4 Response

Recall (3.1.15), we find the response:

$$R_{Q,V}\left(t,s\right) = \mathfrak{a} \left[\frac{d}{ds} \left\langle Q_t\left(x_t\right) V_s\left(x_s\right)\right\rangle_\mu - \left\langle Q_t\left(x_t\right) \frac{\partial V_s\left(x_s\right)}{\partial s} \right\rangle_\mu \right] - \mathfrak{b} \left\langle Q_t\left(x_t\right) L_s V_s\left(x_s\right)\right\rangle_\mu +$$

$$+ \left(\mathfrak{b}-\mathfrak{a}\right) \left[\sum_{\substack{x,y \\ x'\neq x}} P_s\left(x'\right) k_s\left(x',x\right) V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right) - \sum_{x\neq x_s} \left\langle k_s\left(x_s,x\right) V_s\left(x_s\right) Q_t\left(x_t\right)\right\rangle_\mu \right]$$

The first two terms of susceptibility give the response studied in the antisymmetric case. Now if we make explicit the last average value in the bracket:

$$\sum_{x\neq x_s} \left\langle k_s\left(x_s,x\right) V_s\left(x_s\right) Q_t\left(x_t\right)\right\rangle_\mu = \sum_{\substack{x,y \\ x'\neq x}} P_s\left(x\right) k_s\left(x,x'\right) V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right)$$

We note that it is similar to the other contribution in the bracket. Then:

$$\sum_{\substack{x,y \\ x'\neq x}} P_s\left(x'\right) k_s\left(x',x\right) V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right) - \sum_{x\neq x_s} \left\langle k_s\left(x_s,x\right) V_s\left(x_s\right) Q_t\left(x_t\right)\right\rangle_\mu =$$

$$= \sum_{\substack{x,y \\ x'\neq x}} \left[P_s\left(x'\right) k_s\left(x',x\right) - P_s\left(x\right) k_s\left(x,x'\right)\right] V_s\left(x\right) \left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy} Q_t\left(y\right)$$

We can recognize the master equation. Then using (2.1.2):

$$(\mathfrak{b}-\mathfrak{a})\left[\sum_{\substack{x,y\\x'\neq x}}P_s\left(x'\right)k_s\left(x',x\right)V_s\left(x\right)\left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy}Q_t\left(y\right)-\sum_{x\neq x_s}\left\langle k_s\left(x_s,x\right)V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu\right]=$$

$$=(\mathfrak{b}-\mathfrak{a})\sum_{x,y}\frac{dP_s\left(x\right)}{ds}V_s\left(x\right)\left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy}Q_t\left(y\right)$$

At this point, the following identity is useful:

$$\frac{d}{dt}\left\langle V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu-\left\langle V_s\left(x_s\right)\frac{\partial Q_t\left(x_t\right)}{\partial t}\right\rangle_\mu=-\left[\frac{d}{ds}\left\langle V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu-\left\langle\frac{\partial V_s\left(x_s\right)}{\partial s}Q_t\left(x_t\right)\right\rangle_\mu\right]+$$

$$+\sum_{x,y}\frac{dP_s\left(x\right)}{ds}V_s\left(x\right)\left(e^{\int_s^t d\tau\, L_\tau}\right)_{xy}Q_t\left(y\right)+\left\langle V_s\left(x_s\right)\left[k_t\left(x_s,x_t\right)-k_s\left(x_s,x_t\right)\right]Q_t\left(x_t\right)\right\rangle_\mu$$

that we are going to demonstrate in the appendix 1. Then, the response:

$$R_{Q,V}\left(t,s\right)=\mathfrak{a}\left[\frac{d}{ds}\left\langle Q_t\left(x_t\right)V_s\left(x_s\right)\right\rangle_\mu-\left\langle Q_t\left(x_t\right)\frac{\partial V_s\left(x_s\right)}{\partial s}\right\rangle_\mu\right]-\mathfrak{b}\left\langle Q_t\left(x_t\right)L_sV_s\left(x_s\right)\right\rangle_\mu+$$

$$+(\mathfrak{b}-\mathfrak{a})\left[\frac{d}{dt}\left\langle V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu-\left\langle V_s\left(x_s\right)\frac{\partial Q_t\left(x_t\right)}{\partial t}\right\rangle_\mu+\frac{d}{ds}\left\langle V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu-\left\langle\frac{\partial V_s\left(x_s\right)}{\partial s}Q_t\left(x_t\right)\right\rangle_\mu\right]-$$

$$-(\mathfrak{b}-\mathfrak{a})\left\langle V_s\left(x_s\right)\left[k_t\left(x_s,x_t\right)-k_s\left(x_s,x_t\right)\right]Q_t\left(x_t\right)\right\rangle_\mu$$

Finally the response formula for $t\geq s$:

$$R_{Q,V}\left(t,s\right)=\mathfrak{b}\left[\frac{d}{ds}\left\langle Q_t\left(x_t\right)V_s\left(x_s\right)\right\rangle_\mu-\left\langle Q_t\left(x_t\right)\frac{\partial V_s\left(x_s\right)}{\partial s}\right\rangle_\mu\right]-\mathfrak{a}\frac{d}{dt}\left\langle V_s\left(x_s\right)Q_t\left(x_t\right)\right\rangle_\mu+$$

$$+\mathfrak{a}\left\langle V_s\left(x_s\right)\frac{\partial Q_t\left(x_t\right)}{\partial t}\right\rangle_\mu+\mathfrak{b}\left[\left\langle V_s\left(x_s\right)L_tQ_t\left(x_t\right)\right\rangle_\mu-\left\langle Q_t\left(x_t\right)L_sV_s\left(x_s\right)\right\rangle_\mu\right]-$$

$$-(\mathfrak{b}-\mathfrak{a})\left\langle V_s\left(x_s\right)\left[k_t\left(x_s,x_t\right)-k_s\left(x_s,x_t\right)\right]Q_t\left(x_t\right)\right\rangle_\mu \tag{3.2.14}$$

3.2.4.1 Comments

In the last two Sections we have studied the response formula when the transition rates depend on time. Our purpose is to understand how the response will be modified if the reference process (or rather the unperturbed system) is time-dependent compared with the case in which the reference is time-independent and therefore a stationary distribution exists. We have seen that if the perturbation is only antisymmetric (in other words, if it modifies only the transition rate drift)

the structure of the response formula does not change at all. The time-dependence affects only the reference process and therefore the probability over which we average. Instead, now, we have found out that, if the perturbation has also a time symmetric contribution, the response presents a new term. It takes into account in the correlation also how a transition rate changes between the two times considered in the response. This contribution is considerable if the rates change much in the interval $[s,t]$. It depends on the intensity of the transition rates and not on the drift (in fact it is evaluated for the same transition at different time), for this reason it can be associated to the reactivities contribution. This is the reason why it appears only if the perturbation is also symmetric. Furthermore, it depends only on the initial and final values, then, if $k_t(x_s,x_t)=k_s(x_s,x_t)$ it will be zero. For example, this could be the case of periodic time-dependence of the transition rates. Now we want to show that

- if $\mathfrak{a}=\mathfrak{b}$, antisymmetric perturbation:

$$R_{Q,V}(t,s)=\mathfrak{b}\left[\frac{d}{ds}\left\langle Q_t(x_t)\,V_s(x_s)\right\rangle_\mu-\left\langle Q_t(x_t)\,\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu-\left\langle Q_t(x_t)\,L_sV_s(x_s)\right\rangle_\mu\right]$$

  We obtain the response studied in the previous Section with $\mathfrak{b}=\frac{1}{2}$. In fact for $t>s$:

$$\frac{d}{dt}\left\langle V_s(x_s)\,Q_t(x_t)\right\rangle_\mu=\left\langle V_s(x_s)\,L_tQ_t(x_t)\right\rangle_\mu+\left\langle V_s(x_s)\,\frac{\partial Q_t(x_t)}{\partial t}\right\rangle_\mu$$

- if $\mathfrak{a}=-\mathfrak{b}$, symmetric perturbation:

$$R_{Q,V}(t,s)=\mathfrak{b}\left[\frac{d}{ds}\left\langle Q_t(x_t)\,V_s(x_s)\right\rangle_\mu-\left\langle Q_t(x_t)\,\frac{\partial V_s(x_s)}{\partial s}\right\rangle_\mu-\left\langle Q_t(x_t)\,L_sV_s(x_s)\right\rangle_\mu\right]+$$

$$+2\mathfrak{b}\left[\left\langle V_s(x_s)\,L_tQ_t(x_t)\right\rangle_\mu-\left\langle V_s(x_s)\left[k_t(x_s,x_t)-k_s(x_s,x_t)\right]Q_t(x_t)\right\rangle_\mu\right]$$

  We obtain a response for an antisymmetric perturbation plus another contribution. It is reasonable that in the symmetric case there is also the antisymmetric contribution since we can consider the symmetric perturbation

$$h_t\left[V_t(y)+V_t(x)\right]$$

  as an antisymmetric one plus another contribution

$$h_t\left[V_t(y)-V_t(x)\right]+2h_tV_t(x)$$

3.2.5 Appendices

3.2.5.1 Appendix 1: demonstration of the identity

$$\frac{d}{dt}\left\langle V_s(x_s)\,Q_t(x_t)\right\rangle_\mu-\left\langle V_s(x_s)\,\frac{\partial Q_t(x_t)}{\partial t}\right\rangle_\mu=-\left[\frac{d}{ds}\left\langle V_s(x_s)\,Q_t(x_t)\right\rangle_\mu-\left\langle\frac{\partial V_s(x_s)}{\partial t}Q_t(x_t)\right\rangle_\mu\right]+$$

$$+\sum_{x,y}\frac{dP_s(x)}{ds}\,V_s(x)\left(e^{\int_s^t d\tau\,L_\tau}\right)_{xy}Q_t(y)+\left\langle V_s(x_s)\left[k_t(x_s,x_t)-k_s(x_s,x_t)\right]Q_t(x_t)\right\rangle_\mu$$

If we calculate the contribution with respect to t:

$$\sum_{x,y}\left[\frac{d}{dt}\left(P_s(x)V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)\right)-P_s(x)V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}\frac{\partial Q_t(y)}{\partial t}\right]=$$

$$=\sum_{x,y}P_s(x)V_s(x)k_t(x,y)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)=\langle V_s(x_s)k_t(x_s,x_t)Q_t(x_t)\rangle_\mu$$

If we do the same with the contribution for the derivative with respect to s:

$$\sum_{x,y}\left[\frac{d}{ds}\left(P_s(x)V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)\right)-P_s(x)\frac{\partial V_s(x)}{\partial s}\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)\right]=$$

$$=\sum_{x,y}\left[\frac{dP_s(x)}{ds}V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)-P_s(x)V_s(x)k_s(x,y)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)\right]=$$

$$=\sum_{x,y}\frac{dP_s(x)}{ds}V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)-\langle V_s(x_s)k_s(x_s,x_t)Q_t(x_t)\rangle_\mu$$

Then, if we sum the two terms we obtain:

$$\frac{d}{dt}\langle V_s(x_s)Q_t(x_t)\rangle_\mu-\left\langle V_s(x_s)\frac{\partial Q_t(x_t)}{\partial t}\right\rangle_\mu+\left[\frac{d}{ds}\langle V_s(x_s)Q_t(x_t)\rangle_\mu-\left\langle\frac{\partial V_s(x_s)}{\partial t}Q_t(x_t)\right\rangle_\mu\right]=$$

$$=\sum_{x,y}\left[P_s(x)V_s(x)k_t(x,y)+\frac{dP_s(x)}{ds}V_s(x)-P_s(x)V_s(x)k_s(x,y)\right]\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)=$$

$$=\sum_{x,y}\frac{dP_s(x)}{ds}V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)+\sum_{x,y}P_s(x)V_s(x)\left[k_t(x,y)-k_s(x,y)\right]\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)=$$

$$=\sum_{x,y}\frac{dP_s(x)}{ds}V_s(x)\left(e^{\int_s^t d\tau L_\tau}\right)_{xy}Q_t(y)+\langle V_s(x_s)\left[k_t(x_s,x_t)-k_s(x_s,x_t)\right]Q_t(x_t)\rangle_\mu$$

It is interesting to note that the last average value is due to the transition rates time-dependence. In fact if they would not depend on time it would be zero. Therefore this contribution appears only out of equilibrium if the reference process in time-dependent.

3.2.5.2 Appendix 2: Close to equilibrium

Now we want to study what happens to the response formula if the system is near the equilibrium. All what we have said for the antisymmetric case is still valid. Then:

$$R_{Q,V}(t,s)=\mathfrak{b}\left[\frac{d}{ds}\langle Q(x_t)V(x_s)\rangle_{eq}-\langle Q(x_t)LV(x_s)\rangle_{eq}\right]+(\mathfrak{b}-\mathfrak{a})\frac{d}{dt}\langle V(x_s)Q(x_t)\rangle_{eq}$$

The last contribution in the response formula must be zero since the transition rates are time-independent. We can rewrite it as:

$$R_{Q,V}(t,s) = \mathfrak{a}\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq} - \mathfrak{b}\,\langle Q(x_t)\, LV(x_s)\rangle_{eq} + \\ + (\mathfrak{b}-\mathfrak{a})\left[\frac{d}{ds}\langle V(x_s)\, Q(x_t)\rangle_{eq} + \frac{d}{dt}\langle V(x_s)\, Q(x_t)\rangle_{eq}\right]$$

Now if we use invariance under time translations as we have done in the antisymmetric case the bracket will cancel since we can substitute the derivative with respect to s with minus the one with respect to t. Then

$$R_{Q,V}(t,s) = \mathfrak{a}\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq} - \mathfrak{b}\,\langle Q(x_t)\, LV(x_s)\rangle_{eq}$$

We can use again the same procedure to get:

$$R_{Q,V}(t,s) = (\mathfrak{a}+\mathfrak{b})\frac{d}{ds}\langle Q(x_t)\, V(x_s)\rangle_{eq}$$

As we expect near the equilibrium the response is given only by the antisymmetric contribution since near equilibrium the system is invariant under time reversal and then a symmetric perturbation that acts on reactivities cannot modify the system.

Part II

Diffusion processes

Chapter 4

Continuous Markov processes

4.1 General Features

4.1.1 Stochastic processes

Consider a stochastic process x_t that can assume values from a continuous set $S \subset \mathbb{R}^n$. Its evolution leads to a probability density $P_t(x)$ with respect to dx, measure on S. At any time, it gives the probability of assuming a certain value. The $P_t(x)$ must satisfy:

- $P_t(x) \geq 0 \qquad \forall x \in S$
- $\int_S dx\, P_t(x) = 1 \qquad \forall t$
- it must be differentiable and integrable with respect to x and t

Again we will consider the Markov approximation. A dynamics is called Markovian if, given where the probe is at time s, the future evolution ($t > s$) depends only on the system at time s and it does not depend on its previous history. In other words, once known the present, the future is independent of the past. A system that satisfies this condition is said memoryless. In fact, consider n values $x_1 \dots x_n$ assumed by x_t at time $t_1 \dots t_n$ chronologically arranged. The probability that x_t, using the Markov approximation, assumes all these values during its evolution is given by:

$$P(x_1, t_1; x_2, t_2; \dots; x_n, t_n \mid x_0, t_0) = P(x_1, t_1 \mid x_0, t_0)\, P(x_2, t_2 \mid x_1, t_1) \dots P(x_n, t_n \mid x_{n-1}, t_{n-1})$$

where the conditional probability is defined by:

$$P(x_2, t_2 \mid x_1, t_1)\, dx_2 = Prob\{x_{t_2} \in [x_2, x_2 + dx_2],\ given\, x_{t_1} = x_1\} \tag{4.1.1}$$

A Markov process can be either deterministic, meaning that its future is precisely determined by its present, or stochastic, meaning that its future is only probabilistically determined by its present. Or more generally it can be a combination of both.

4.1.2 Chapman-Kolmogorov equation

We require some equations to study the Markov dynamics. One of these is the Chapman-Kolmogorov equation. This equation is valid only under the Markov approximation.

$$P(x_3,t_3 \mid x_1,t_1) = \int_S dx_2\, P(x_3,t_3 \mid x_2,t_2)\, P(x_2,t_2 \mid x_1,t_1) \tag{4.1.2}$$

In fact:

$$P(x_3,t_3 \mid x_1,t_1) = \int_S dx_2\, P(x_3,t_3;x_2,t_2 \mid x_1,t_1)$$

we have conditioned on intermediate value x_2 at time $t_1 < t_2 < t_3$. Now we can use the definition of conditional probability:

$$P(x_3,t_3 \mid x_1,t_1) = \int_S dx_2\, P(x_3,t_3 \mid x_2,t_2;x_1,t_1)\, P(x_2,t_2 \mid x_1,t_1)$$

Now if we use the Markov property, we can ignore the condition on x_1 in the first probability to obtain (4.1.2). This equation is important because it gives a criterion to choose the probability $P_t(x)$ such that it satisfies the Markov property. And when the probability is known the Markov process is completely determined. There is another expression of the Chapman-Kolmogorov equation that is going to be useful in the following:

$$P(x,t+\Delta t \mid x_0,t_0) = \int_S d\xi\, P(x,t+\Delta t \mid x-\xi,t)\, P(x-\xi,t \mid x_0,t_0) \tag{4.1.3}$$

where $\xi \in S$ and Δt is a time interval (not necessarily infinitesimal). It is called forward time evolution since it studies the behavior of $P(x,t \mid x_0,t_0)$ for fixed x_0 and t_0. Here we are considering not infinitesimal time, but we will do it in the following Section since we are interested in studying continuous Markov process for which the dynamics evolves continuously. A possible procedure is to consider processes that assume different values at each time interval dt (that is thought as an infinitesimal parameter) and then to study the limit $dt \to 0$. This assumption will put some condition on the process evolution that we are going to explain.

4.1.3 The Markov Propagator

Suppose that the random variable x_t is in x at time t. Then, at a later time $t+\Delta t$ (not necessarily infinitesimal) the system will be evolved to some new state. Since the dynamics is Markovian, the displacement will depend only on x_t. Therefore we can define it as:

$$\Xi(\Delta t; x_t, t) = x_{t+\Delta t} - x_t \tag{4.1.4}$$

It is also called update relation and Δt is the time scale of the update (it can be thought as its sensibility). Obviously $\Xi(\Delta t; x_t, t)$ is a random variable and it is called the propagator of the process. Like any random variable it is completely determined by its probability density $\Pi(\xi \mid \Delta t; x, t)$, that by definition is:

$$\Pi(\xi \mid \Delta t; x, t)\, \Delta\xi = Prob\{\Xi(\Delta t; x, t) \in [\xi, \xi+\Delta\xi]\}$$

Now we are going to study some properties of the propagator and its probability density:

4.1.3.1 Moments

By definition the moments are the average values of a random variable powers. For the propagator:

$$\langle \Xi (\Delta t; x, t)^n \rangle = \int_S d\xi \, \xi^n \, \Pi (\xi \mid \Delta t; x, t) = \mathcal{B}_n (x, t) \, \Delta t + \mathcal{O} (\Delta t)$$

Since $\Xi (dt; x, t)$ is a continuous random variable, its probability density must be differentiable and also integrable, therefore all the moments are well defined functions. The $\mathcal{O} (\Delta t)$ is referred to the fact that the update formula is correct up to order Δt. Note that the moments depend on the value at time t. From what happens at time t we can determine the average displacement at time $t + \Delta t$. Note also that the propagator moments describe the fluctuations of the stochastic process.

4.1.3.2 Connection with $P_t (x)$

There is a very important relation between the probability density of the propagator and the probability density of the Markov process. By definition (4.1.1):

$$P (x + \xi, t + \Delta t \mid x, t) \, \Delta \xi = Prob \{ x_{t+\Delta t} \in [x + \xi, x + \xi + \Delta \xi] , \; given \, x_t = x \}$$

If we subtract the conditional value x:

$$P (x + \xi, t + \Delta t \mid x, t) \, \Delta \xi = Prob \{ x_{t+\Delta t} - x \in [\xi, \xi + \Delta \xi] , \; given \, x_t = x \}$$

we use the condition $x_t = x$ and via the definition (4.1.4) we obtain:

$$P (x + \xi, t + \Delta t \mid x, t) \, \Delta \xi = Prob \{ \Xi (\Delta t; x, t) \in [\xi, \xi + \Delta \xi] \}$$

The last equation is the definition of the propagator probability density. Therefore:

$$\Pi (\xi \mid \Delta t; x, t) = P (x + \xi, t + \Delta t \mid x, t) \tag{4.1.5}$$

Therefore $\Pi (\xi \mid \Delta t; x, t)$ is just the Markov probability density of moving by ξ in time Δt. This is meaningful since the $\Pi (\xi \mid \Delta t; x, t)$ is the probability density of the displacement. Furthermore the propagator density function is very important because it determines completely the probability $P_t (x)$ of the process. The moments can be written as:

$$\mathcal{B}_n (x, t) \, \Delta t = \int_S d\xi \, \xi^n \, P (x + \xi, t + \Delta t \mid x, t)$$

4.1.3.3 Connection with C-K equation

Using (4.1.5) and the Chapman-Kolmogorov equation (4.1.2) we can obtain an interesting relation that allows to put in evidence the Markovian nature of the displacement. Consider the probability:

$$P (x + \xi, t + \Delta t \mid x, t) = \int_S d\xi_1 P (x + \xi, t + \Delta t \mid x + \xi_1, t + a \Delta t) \, P (x + \xi_1, t + a \Delta t \mid x, t)$$

We have in fact demonstrated then the probability $P_t (x)$ satisfies the Chapman-Kolmogorov equation. Then:

$$P (x + \xi, t + \Delta t \mid x, t) = \int_S d\xi_1 P (x + \xi_1 + \xi - \xi_1, t + a \Delta t + (1 - a) \, \Delta t \mid x + \xi_1, t + a \Delta t) \cdot$$

$$\cdot P\left(x+\xi_1, t+a\Delta t \mid x, t\right)$$

Now, using (4.1.5) we can substitute:

$$P\left(x+\xi_1+\xi-\xi_1, t+a\Delta t+(1-a)\Delta t \mid x+\xi_1, t+a\Delta t\right)=\Pi\left(\xi-\xi_1 \mid (1-a)\Delta t; x+\xi_1, t+a\Delta t\right)$$

And finally:

$$\Pi\left(\xi \mid \Delta t; x, t\right)=\int_S d\xi_1 \Pi\left(\xi-\xi_1 \mid (1-a)\Delta t;\ x+\xi_1, t+a\Delta t\right)\cdot\Pi\left(\xi_1 \mid a\Delta t; x, t\right)$$

In this way we have obtained a Chapman-Kolmogorov equation also for the displacement probability density. And, as we have said, it gives a criterion to choose the expression of $\Pi\left(\xi \mid \Delta t; x, t\right)$. This result can be written also in function of the displacement:

$$\Xi\left(\Delta t; x_t, t\right)=\Xi\left(a\Delta t;\ x_t, t\right)+\Xi\left((1-a)\Delta t; x_t+\Xi\left(a\Delta t; x_t, t\right), t+a\Delta t\right) \tag{4.1.6}$$

This equation says that the change in the process during a interval $(t, t+\Delta t)$ must be equal to the change during the interval $(t, t+a\Delta t)$ plus the change during the interval $(t+a\Delta t, t+\Delta t)$ for any $0<a<1$. For this reason it is also called the self-consistency equation.

4.1.3.4 Homogeneity

If the Markov process is homogeneous with respect to time and space, it will affect also the propagator probability density. In fact:

- if x_t is temporally homogeneous the propagator probability will not depend on time
  $\Pi\left(\xi \mid \Delta t; x, t\right)=\Pi\left(\xi \mid \Delta t; x\right)$
- if x_t is spatially homogeneous the propagator probability will not depend on position
  $\Pi\left(\xi \mid \Delta t; x, t\right)=\Pi\left(\xi \mid \Delta t; t\right)$
- if x_t is temporally and spatially homogeneous the propagator probability will not depend on time and position
  $\Pi\left(\xi \mid \Delta t; x, t\right)=\Pi\left(\xi \mid \Delta t\right)$

There is no situation in which the $\Pi\left(\xi \mid dt; x, t\right)$ will not depend on Δt since it is referred to time interval during which there is the displacement. For this reason the Δt is isolated from x and t by an ;

4.1.4 Kramers-Moyal expansion

We know that the $P_t\left(x\right)$ must satisfy the Chapman-Kolmogorov equation, that is an integral equation. Now we want to find a differential equation. The starting point is (4.1.3). We define the infinitely differentiable function:

$$f\left(x\right)=P\left(x+\xi, t+\Delta t \mid x, t\right)P\left(x, t \mid x_0, t_0\right)$$

We can evaluate it in $x-\xi$. Then:

$$f\left(x-\xi\right)=P\left(x, t+\Delta t \mid x-\xi, t\right)P\left(x-\xi, t \mid x_0, t_0\right)$$

Now we want to expand it around $\xi = 0$. To do it we can define $y = x - \xi$ and then expand $f(y)$ around $y = x$. Therefore:

$$f(x-\xi) = f(x) + \sum_{n=1}^{\infty} \frac{(-\xi)^n}{n!} \nabla^n f(x)$$

But $f(x-\xi)$ appears in (4.1.3). Therefore we can substitute the expansion of $f(x-\xi)$ in the integral of equation (4.1.3):

$$P(x, t+\Delta t \mid x_0, t_0) = \int_S d\xi\, P(x+\xi, t+\Delta t \mid x, t)\, P(x, t \mid x_0, t_0) +$$

$$+\sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \nabla^n \int_S d\xi\, \xi^n P(x+\xi, t+\Delta t \mid x, t)\, P(x, t \mid x_0, t_0)$$

In the first term we can extract $P(x, t \mid x_0, t_0)$ and the integral gives 1 since the $P_t(x)$ is a probability density. Then:

$$P(x, t+\Delta t \mid x_0, t_0) - P(x, t \mid x_0, t_0) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \nabla^n \left[\int_S d\xi\, \xi^n P(x+\xi, t+\Delta t \mid x, t) \right] P(x, t \mid x_0, t_0)$$

We can use (4.1.5) and:

$$P(x, t+\Delta t \mid x_0, t_0) - P(x, t \mid x_0, t_0) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \nabla^n \left[\int_S d\xi\, \xi^n \Pi(\xi \mid \Delta t; x, t) \right] P(x, t \mid x_0, t_0)$$

Now, in the integral there are the moments and we know that:

$$P(x, t+\Delta t \mid x_0, t_0) - P(x, t \mid x_0, t_0) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \nabla^n \left[\mathcal{B}_n(x, t)\, P(x, t \mid x_0, t_0) \right] \Delta t$$

If we divide by time interval Δt and we take the limit $\Delta t \to 0$, in the left-hand side there is an incremental ratio. Therefore:

$$\frac{\partial}{\partial t} P(x, t \mid x_0, t_0) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \nabla^n \left[\mathcal{B}_n(x, t)\, P(x, t \mid x_0, t_0) \right] \tag{4.1.7}$$

Again we can see that, if the propagator and its probability density are given, it is known also the evolution of the probability $P_t(x)$ and then the random variable evolution. For the first time here we have used a infinitesimal time limit, but we have not said anything about the propagator and the moments yet. We will expect that if we let evolve the system for an infinitesimal time, the displacement will be small and close to zero. This should be a property of the Markov propagator, and it does not appear in what we have said till now. In the following chapter we will give some assumption on the propagator in order to do a meaningful $\Delta t \to 0$ limit.

4.2 The propagator

In the previous general treatment we have not said anything about the propagator probability. Now we want to study its property in order to describe continuous stochastic processes. Again

we consider the update equation (4.1.4), but now we are interested in infinitesimal update time. Therefore we consider, $\Pi(\xi \mid dt; x, t)$, where now dt is an infinitesimal time interval. To obtain an expression for it, we have to make some assumptions on the Markov process and therefore to consider a particular kind of processes. In this Section we are going to study the continuous Markov process with respect to time and position evolution. To do it we have to assume that:

- $\Pi(\xi \mid dt; x, t)$ is a smooth function for all its arguments (dt, x, t).
- $\Pi(\xi \mid dt; x, t)$ is practically zero everywhere outside of an infinitesimally small neighborhood of $\xi = 0$.
- We want to introduce the Markovian property in the noise. In other words, we expect that the average value of the stochastic contribution at two times t and t' is not zero if and only if $t = t'$.

4.2.1 Self-consistency of the propagator

Under these conditions the displacement $\Xi(dt; x_t, t)$ during the time dt must be infinitesimally small. Note that till now we have not assumed anything about its values. Assume that at time t the process is in the state x. We want to study its evolution during the interval $[t, t + dt]$. Suppose now that this interval could be divided in n subinterval of equal length $\frac{dt}{n}$. Therefore:

$$t_i = t_{i-1} + \frac{dt}{n}$$

with $t_0 = t$ and $t_n = t + dt$. Using (4.1.4):

$$x_{t_i} - x_{t_{i-1}} = \Xi_i\left(\frac{dt}{n};\, x_{t_{i-1}}, t_{i-1}\right)$$

If we take a sum over all the subintervals, in the left-hand side we recognize a telescopic series:

$$\sum_{i=1}^{n} x_{t_i} - x_{t_{i-1}} = x_{t_n} - x_{t_0} = x_{t+dt} - x_t = \sum_{i=1}^{n} \Xi_i\left(\frac{dt}{n};\, x_{t_{i-1}}, t_{i-1}\right)$$

Therefore:

$$\Xi(dt; x_t, t) = \sum_{i=1}^{n} \Xi_i\left(\frac{dt}{n};\, x_{t_{i-1}}, t_{i-1}\right) \tag{4.2.1}$$

This equation says that the displacement during the interval $[t, t + dt]$ is given by the sum of all the displacement during the subintervals. It is a consequence of the Markov dynamics since it derives from (4.1.6). The propagators Ξ_i are different random variables since they describe the displacement in each subinterval. They are not statistically independent since each Ξ_i depends on $x_{t_{i-1}}$. Now we use the smoothness condition of the propagator probability density $\Pi\left(\xi \mid \frac{dt}{n}; x_{t_i}, t_i\right)$. If we displace the values of x and t by arbitrary infinitesimal amounts, then there will be only small changes in the random variable $\Xi(dt; x_t, t)$. Therefore in each Ξ_i we can replace t_{i-1} by the infinitesimally close t. Nevertheless there could be a big displacement in the interval of width $\frac{dt}{n}$, but this possibility is practically zero due to the condition imposed on the $\Pi\left(\xi \mid \frac{dt}{n}; x_{t_i}, t_i\right)$. Therefore:

$$\Xi\left(dt; x_t, t\right) = \sum_{i=1}^{n} \Xi_i\left(\frac{dt}{n};\, x_t, t\right) \tag{4.2.2}$$

4.2.2 Propagator average value

Now the $\Xi_i\left(\frac{dt}{n};\, x_t, t\right)$ are n statistically independent variables. By definition, for any succession $(X_i)_{i\in\mathbb{N}}$ of random variables, not necessarily statistical independent:

$$\left\langle \sum_{i=1}^{n} a_i X_i \right\rangle = \sum_{i=1}^{n} a_i \left\langle X_i \right\rangle$$

$$Var\left[\sum_{i=1}^{n} a_i X_i\right] = \sum_{i=1}^{n} a_i^2 Var\left[X_i\right] + \sum_{i\neq j}^{n} a_i a_j \left\langle X_i; X_j \right\rangle$$

with $\left\langle\,;\right\rangle$ we mean the covariance. Obviously if the variables are statistically independent the variance expression becomes simpler, since the covariance is zero. Therefore if we consider (4.2.2):

$$\sum_{i=1}^{n} \left\langle \Xi_i\left(\frac{dt}{n};\, x_t, t\right)\right\rangle = \left\langle \Xi\left(dt; x_t, t\right)\right\rangle$$

$$\sum_{i=1}^{n} Var\left[\Xi_i\left(\frac{dt}{n};\, x_t, t\right)\right] = Var\left[\Xi\left(dt; x_t, t\right)\right]$$

Though the $\Xi_i\left(\frac{dt}{n};\, x_t, t\right)$ act on different intervals, they have the same probability distribution. Therefore they have the same average value and variance.

$$n\left\langle \Xi_i\left(\frac{dt}{n};\, x_t, t\right)\right\rangle = \left\langle \Xi\left(dt; x_t, t\right)\right\rangle$$

$$n\, Var\left[\Xi_i\left(\frac{dt}{n};\, x_t, t\right)\right] = Var\left[\Xi\left(dt; x_t, t\right)\right]$$

Now we need a lemma. Given a set, if $h\left(z\right)$ is a smooth function of $z \in S$ satisfying

$$h\left(z\right) = nh\left(\frac{z}{n}\right) \tag{4.2.3}$$

for any positive integer n, then it must be true that $h\left(z\right) = Cz$, where C is independent of z. To demonstrate it we have to consider two aspects:

- If we derive (4.2.3) with respect to z

  $$h'\left(z\right) = nh'\left(\frac{z}{n}\right)\frac{1}{n} = h'\left(\frac{z}{n}\right)$$

  This must be true for any n, even if $n \to \infty$. In fact

  $$\lim_{n\to\infty} h'\left(z\right) = \lim_{n\to\infty} h'\left(\frac{z}{n}\right) = h'\left(0\right)$$

  given that $h\left(z\right)$ is continuous. Meanwhile the left-hand side is not changed by the limit. Therefore:

  $$h'\left(z\right) = h'\left(0\right) = C \qquad \forall z \in S$$

- If we consider the limit

$$\lim_{n\to\infty}\frac{h(z)}{n}=\lim_{n\to\infty}h\left(\frac{z}{n}\right)\implies h(0)=0$$

A smooth function that satisfies these two properties must be of the form $h(z)=Cz$.

We cannot use the lemma for $\Xi_i\left(\frac{dt}{n};x_t,t\right)$ since the propagators of each subintervals are different functions, but the average values are the same. If we apply the lemma to the average values, function of dt, we obtain:

$$\langle\Xi(dt;x_t,t)\rangle=A_t(x_t)\,dt+\mathcal{O}(dt)$$

$$Var\left[\Xi(dt;x_t,t)\right]=B_t(x_t)\,dt+\mathcal{O}(dt)$$

The correction $\mathcal{O}(dt)$ derives from the replacement of t_i by t in the propagator. In conclusion:

- by the lemma $A_t(x_t)$ and $B_t(x_t)$ are independent of dt functions
- by definition of variance $B_t(x_t)\geq 0$

4.2.3 The propagator expression

To say more about these two functions we need to find out the expression of $\Pi(\xi\mid dt;x,t)$. We will start from (4.2.2). We have written the propagator as a sum of random variables. We can use the central limit theorem. Consider a succession of statistically independent random variables $X_1\ldots X_n$, each distributed according to a common density function which has finite mean and variance. Consider the variable:

$$Y=\sum_{i=1}^{n}X_i$$

In the limit $n\to\infty$, the distribution of Y converges to a Gaussian one. Therefore:

$$\Xi(dt;x_t,t)=N\left(A_t(x_t)\,dt,B_t(x_t)\,dt\right)\tag{4.2.4}$$

And the probability distribution $\Pi(\xi\mid dt;x,t)$ becomes:

$$\Pi(\xi\mid dt;x_t,t)=\frac{1}{\sqrt{2\pi B_t(x_t)\,dt}}e^{-\frac{(\xi-A_t(x_t)dt)^2}{2B_t(x_t)dt}}+\mathcal{O}(dt)\tag{4.2.5}$$

It is interesting to note that all the physics is in $A_t(x_t)$ and $B_t(x_t)$. Therefore, choosing them properly we can have a nonequilibrium system. But, even in this case, the distribution of the displacement is given by a Gaussian.

4.2.4 Consequences on Markov process

We want to put into evidence two properties of Gaussian variables:

- $N(m_1,\sigma_1^2)=N(m_1,0)+N(0,\sigma_1^2)$
  in which the first contribution is deterministic since the variance is zero.
- $\beta N(m_1,\sigma_1^2)=N(\beta m_1,\beta^2\sigma_1^2)$

Therefore from (4.2.4):

$$\Xi\left(dt; x_t, t\right) = N\left(A_t\left(x_t\right) dt, 0\right) + N\left(0,\, B_t\left(x_t\right) dt\right)$$

$$\Xi\left(dt; x_t, t\right) = A_t\left(x_t\right) dt\, N\left(1, 0\right) + \sqrt{B_t\left(x_t\right) dt}\, N\left(0,\, 1\right)$$

$$\Xi\left(dt; x_t, t\right) = A_t\left(x_t\right) dt + \sqrt{B_t\left(x_t\right) dt}\, N\left(0,\, 1\right) \tag{4.2.6}$$

The average values of the propagator probability density allow to comprehend the propagator itself. Furthermore we can see that it is made by two contributions. The first, depending on the mean value is deterministic, instead the second is stochastic. In fact, if $B_t\left(x_t\right)$ would be zero, the process would be deterministic.

For what we have said, the average values describe also the Markov process, for this reason $A_t\left(x_t\right)$ and $B_t\left(x_t\right)$ are also called characterizing functions of the process. $A_t\left(x_t\right)$ is properly called drift function because it controls the "drifting of the Gaussian peak. Instead $B_t\left(x_t\right)$ is called diffusion function because it controls the "diffusion spreading" of the peak, or in other words, its width. They depend differently on dt. In fact we expect that the random component, though infinitesimally small, will be much bigger than the deterministic one. Therefore, why does this contribution make any difference in the process evolution? The answer lies in the random variable N that multiplies $\sqrt{dt}$. Since N is equally positive and negative (the Gaussian distribution is even), the contributions order $\sqrt{dt}$ of the fluctuating term over a succession of dt-intervals tend to cancel each others out. Therefore averagely only the deterministic contribution influences the dynamics.

4.3 Fokker-Planck equation

Starting from equation (4.2.6) we want to find the moments $B_n\left(x, t\right)$ of the propagator:

$$\Xi^n\left(dt; x_t, t\right) = \left[A_t\left(x_t\right) dt + \sqrt{B_t\left(x_t\right) dt}\, N\left(0,\, 1\right)\right]^n$$

Using the binomial formula:

$$\left\langle \Xi^n\left(dt; x_t, t\right)\right\rangle = n! \sum_{\substack{k=0 \\ (k\, even)}}^{n} \frac{\left[A_t\left(x_t\right) dt\right]^{n-k} \left[B_t\left(x_t\right) dt\right]^{\frac{k}{2}}}{(n-k)!\left(\frac{k}{2}\right)! \, 2^{\frac{k}{2}}} + \mathcal{O}\left(dt\right)$$

$$\left\langle \Xi^n\left(dt; x_t, t\right)\right\rangle = n! \sum_{\substack{k=0 \\ (k\, even)}}^{n} \frac{A_t^{n-k}\left(x_t\right) B_t^{\frac{k}{2}}\left(x_t\right) \left(dt\right)^{n-\frac{k}{2}}}{(n-k)!\left(\frac{k}{2}\right)! \, 2^{\frac{k}{2}}} + \mathcal{O}\left(dt\right)$$

Since the power of dt is $n - \frac{k}{2}$, it is evident that if $n > 2$ there is no contribution of order dt. Therefore we can say that:

$$\mathcal{B}_1\left(x_t, t\right) = A_t\left(x_t\right) + \mathcal{O}\left(dt\right)$$

$$\mathcal{B}_2\left(x_t, t\right) = B_t\left(x_t\right) + \mathcal{O}\left(dt\right)$$

$$\mathcal{B}_n(x_t, t) = \mathcal{O}(dt) \qquad n \geq 3$$

Evidently, this result will simplify the Kramers-Moyal expansion (4.1.7) since only the first two contributions are not of order $\mathcal{O}(dt)$. Therefore:

$$\frac{\partial}{\partial t} P(x, t \mid x_0, t_0) = -\nabla \left[A_t(x) P(x, t \mid x_0, t_0) \right] + \frac{1}{2} \nabla^2 \left[B_t(x) P(x, t \mid x_0, t_0) \right] \tag{4.3.1}$$

with the condition $x_t = x$. This is called Fokker-Planck equation. Note that this equation is an approximation due to the sensibility of the update equation. If we write it via components:

$$\frac{\partial}{\partial t} P(x, t \mid x_0, t_0) = -\sum_{i=1}^{n} \frac{\partial}{\partial x_i} \left[A_i(x, t) P(x, t \mid x_0, t_0) \right] + \frac{1}{2} \sum_{i,j=1}^{n} \frac{\partial^2}{\partial x_i \partial x_j} \left[B_{ij}(x, t) P(x, t \mid x_0, t_0) \right]$$

The coefficient A_i and B_{ij} may be any real differentiable functions with the sole restriction that the matrix B_{ij} is taken to be symmetric and must be positive definite. Therefore if we consider $S = \mathbb{R}$:

$$\frac{\partial}{\partial t} P(x, t \mid x_0, t_0) = -\frac{\partial}{\partial x} \left[A(x, t) P(x, t \mid x_0, t_0) \right] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \left[B(x, t) P(x, t \mid x_0, t_0) \right]$$

4.3.1 Backward generator

We can rewrite the Fokker-Planck equation as:

$$\frac{\partial}{\partial t} P(x, t \mid x_0, t_0) = L_t^+ P(x, t \mid x_0, t_0) \tag{4.3.2}$$

Introducing the forward generator L_t^+. Its adjoint, the backward generator L_t is an operator acting on functions of the process and of the time. It is defined as:

$$L_t f_t(x) = A_t(x) \nabla f_t(x) + \frac{B_t(x)}{2} \nabla^2 f_t(x)$$

The expression of the backward generator can be easily got by (4.3.1) using partial integration. In 1-dimensional notation (with $S = \mathbb{R}$):

$$f_t(x_t) \left(L_t g_t(x_t) \right) = \int_{\mathbb{R}} dx\, f_t(x) A_t(x) \frac{\partial g_t(x)}{\partial x} + \int_{\mathbb{R}} dx\, f_t(x) \frac{B_t(x)}{2} \frac{\partial^2 g_t(x)}{\partial x^2}$$

$$f_t(x_t) \left(L_t g_t(x_t) \right) = f_t(x) A_t(x) g_t(x)_{|\mathbb{R}} - \int_{\mathbb{R}} dx\, g_t(x) \frac{\partial}{\partial x} \left(f_t(x) A_t(x) \right) +$$

$$+ f_t(x) \frac{B_t(x)}{2} \frac{\partial g_t(x)}{\partial x}_{|\mathbb{R}} - \frac{1}{2} \frac{\partial}{\partial x} \left(B_t(x) f_t(x) \right) g_t(x)_{|\mathbb{R}} + \frac{1}{2} \int_{\mathbb{R}} dx\, g_t(x) \frac{\partial^2}{\partial x^2} \left(B_t(x) f_t(x) \right)$$

With some boundary conditions we can eliminate the boundary terms and obtain:

$$f_t(x_t) \left(L_t g_t(x_t) \right) = -\int_{\mathbb{R}} dx\, g_t(x) \frac{\partial}{\partial x} \left(f_t(x) A_t(x) \right) + \frac{1}{2} \int_{\mathbb{R}} dx\, g_t(x) \frac{\partial^2}{\partial x^2} \left(B_t(x) f_t(x) \right)$$

Therefore, for a general manifold S:

$$f_t(x_t)\left(L_t g_t(x_t)\right) = \int_S dx\, f_t(x)\left(L_t g_t(x)\right) = \int_S dx\left(L_t^+ f_t(x)\right) g_t(x) = \left(L_t^+ f_t(x_t)\right) g_t(x_t)$$

For the L_t just written we have:

$$L_t^+ f_t(x) = -\nabla\left[A_t(x) f_t(x)\right] + \frac{1}{2}\nabla^2\left[B_t(x) f_t(x)\right]$$

in agreement with the Fokker-Planck equation.

4.3.2 Density current

If we define the current:

$$J(x,t \mid x_0,t_0) = A_t(x) P(x,t \mid x_0,t_0) - \frac{1}{2}\nabla\left[B_t(x) P(x,t \mid x_0,t_0)\right] \tag{4.3.3}$$

We can write the (4.3.1) as a continuity equation:

$$\frac{\partial}{\partial t} P(x,t \mid x_0,t_0) = -\nabla \cdot J(x,t \mid x_0,t_0) \tag{4.3.4}$$

that describes the conservation of the probability. If we integrate (4.3.4) with respect to dx:

$$\frac{\partial}{\partial t}\int_S dx\, P(x,t \mid x_0,t_0) = -\int_S dx\, \nabla \cdot J(x,t \mid x_0,t_0)\, dx = 0$$

Using the divergence theorem we can write the integral over S as an integral over the border of S ($\Sigma = \partial S$):

$$\int_{\partial S} d\Sigma\, J(x,t \mid x_0,t_0) = 0 \tag{4.3.5}$$

The flow of the current is zero as we expect by a continuity equation. This is due to the convergence of the probability. For this reason it is not a local conservation of the probability. The flow through an arbitrary surface is not necessarily zero. In addition, this does not imply that the current must be zero.

4.3.3 Stationarity

If $A_t(x_t)$ and $B_t(x_t)$ do not depend directly on time, it is possible to find a stationary solution:

$$\lim_{t\to\infty} P_t(x \mid x_0) = \rho(x)$$

In this case the left-hand side of (4.3.4) is zero and therefore:

$$\nabla \cdot J(x \mid x_0) = 0$$

This condition is different from (4.3.5) because it says that the current flow is zero through an arbitrary surface in S (even a finite one) and not necessarily through ∂S, therefore it is a local condition and it assures the local conservation of probability. If S is a simply connected manifold we can define a potential vector for the probability current:

$$\nabla \times C(x) = J(x)$$

An important consideration is that the current has not to be necessarily constant to assure stationarity of the probability. Instead, if $S = \mathbb{R}$, the current must be constant. In order to satisfy the Fokker-Planck equation there are two possibilities:

- the current is a not-zero constant

$$J = A(x)\rho(x) - \frac{1}{2}\frac{\partial}{\partial x}\left[B(x)\rho(x)\right]$$

  and the process x_t admits a nonequilibrium stationary state with a nonzero current.

- the current is zero

$$A(x)\rho(x) - \frac{1}{2}\frac{\partial}{\partial x}\left[B(x)\rho(x)\right] = 0 \tag{4.3.6}$$

  and the process x_t admits an equilibrium stationary state. It satisfies the detailed balance relation, that is the one just written. It is the equivalent of (2.2.6) for the jump processes. In this case x_t is a reversible process. Note that the detailed balance expression remind the balance between two currents acting on a system: the first is deterministic and is produced by an external force (for example the gravity), the second is stochastic and describes the diffusion flux due to the external force that tends to restore the balance.

4.4 Average dynamics of x_t

The best way of considering the moments of the process is using equation (4.1.4). In fact,

$$x_{t+dt}^n = \left[x_t + \Xi(dt; x_t, t)\right]^n$$

Via the binomial formula,

$$x_{t+dt}^n = x_t^n + \sum_{k=1}^{n} \frac{n!}{(n-k)!\,k!} x_t^{n-k} \Xi^k(dt; x_t, t)$$

Taking the average value:

$$\left\langle x_{t+dt}^n \right\rangle = \left\langle x_t^n \right\rangle + \sum_{k=1}^{n} \frac{n!}{(n-k)!\,k!} \left\langle x_t^{n-k} \Xi^k(dt; x_t, t) \right\rangle$$

Now we want to evaluate the average value:

$$\left\langle x_t^{n-k} \Xi^k(dt; x_t, t) \right\rangle = \int_S dx \int_S d\xi\, x^{n-k} \xi^k \Pi(\xi \mid dt; x, t) P(x, t \mid x_0, t_0)$$

$$\left\langle x_t^{n-k} \Xi^k(dt; x_t, t) \right\rangle = \int_S dx\, x^{n-k} \left[\int_S d\xi\, \xi^k \Pi(\xi \mid dt; x, t) \right] P(x, t \mid x_0, t_0)$$

In the bracket there are the moments of the propagator:

$$\left\langle x_t^{n-k} \Xi^k(dt; x_t, t) \right\rangle = \int_S dx\, x^{n-k} \mathcal{B}_k(x, t)\, dt\, P(x, t \mid x_0, t_0) + \mathcal{O}(dt)$$

Now we can solve the integral in dx since it is an average value:

$$\left\langle x_t^{n-k}\Xi^k\left(dt;X\left(t\right),t\right)\right\rangle = \left\langle x_t^{n-k}\mathcal{B}_k\left(x_t,t\right)\right\rangle dt + \mathcal{O}\left(dt\right)$$

Therefore:

$$\left\langle x_{t+dt}^n\right\rangle = \left\langle x_t^n\right\rangle + \sum_{k=1}^{n}\frac{n!}{(n-k)!\,k!}\left\langle x_t^{n-k}\mathcal{B}_k\left(x_t,t\right)\right\rangle dt + \mathcal{O}\left(dt\right)$$

Again if we know the propagator and its distribution we know also the process. Now we want to consider some special cases:

4.4.1 Mean value

If we consider $n = 1$:

$$\left\langle x_{t+dt}\right\rangle = \left\langle x_t\right\rangle + \left\langle \Xi\left(dt;x_t,t\right)\right\rangle$$

where:

$$\left\langle \Xi\left(dt;x_t,t\right)\right\rangle = \int_S dx\,\Xi\left(dt;x,t\right)P\left(x,t\mid x_0,t_0\right)$$

We have conditioned on $x_t = x$. Now we condition on the propagator $\Xi_t\left(dt;x,t\right) = \xi$:

$$\left\langle \Xi\left(dt;x_t,t\right)\right\rangle = \int_S dx\,\left[\int_S d\xi\,\xi\,\Pi\left(\xi\mid dt;x,t\right)\right]P\left(x,t\mid x_0,t_0\right) = \int_S dx\,A_t\left(x\right)dtP\left(x,t\mid x_0,t_0\right)+\mathcal{O}\left(dt\right)$$

Finally:

$$\left\langle x_{t+dt}\right\rangle = \left\langle x_t\right\rangle + \left\langle A_t\left(x_t\right)\right\rangle dt + \mathcal{O}\left(dt\right)$$

Therefore, since dt is infinitesimal we can expand the process and get an incremental ratio:

$$\frac{d}{dt}\left\langle x_t\right\rangle = \left\langle A_t\left(x_t\right)\right\rangle \tag{4.4.1}$$

as we expect the average value of the process is controlled by the deterministic contribution.

4.4.2 Correlation

By definition the covariance, or the two-times correlation function, is:

$$\left\langle x_{t_1};x_{t_2}\right\rangle = \left\langle x_{t_1}x_{t_2}\right\rangle - \left\langle x_{t_1}\right\rangle\left\langle x_{t_2}\right\rangle$$

If we take the time-derivative with respect to t_2

$$\frac{d}{dt_2}\left\langle x_{t_1};x_{t_2}\right\rangle = \frac{d}{dt_2}\left\langle x_{t_1}x_{t_2}\right\rangle - \left\langle x_{t_1}\right\rangle\frac{d}{dt_2}\left\langle x_{t_2}\right\rangle$$

Using (4.4.1) we obtain:

$$\frac{d}{dt_2}\left\langle x_{t_1};x_{t_2}\right\rangle = \frac{d}{dt_2}\left\langle x_{t_1}x_{t_2}\right\rangle - \left\langle x_{t_1}\right\rangle\left\langle A_{t_2}\left(x_{t_2}\right)\right\rangle$$

Now we have to calculate the first average value. Consider equation (4.1.4) for x_{t_2} and multiple it by x_{t_1} and take its average value. Then:

$$\left\langle x_{t_1}x_{t_2+dt_2}\right\rangle = \left\langle x_{t_1}x_{t_2}\right\rangle + \left\langle x_{t_1}\Xi\left(dt;x_{t_2},t_2\right)\right\rangle$$

Now we want to evaluate the last average value

$$\langle x_{t_1}\Xi\left(dt;x_{t_2},t_2\right)\rangle=\int_S dx_1\int_S dx_2\int_S d\xi\, x_1\,\xi\,P\left(x_1,t_1\mid x_0,t_0\right)P\left(x_2,t_2\mid x_1,t_1\right)\Pi\left(\xi\mid dt_2;x_2,t_2\right)$$

We have to introduce two values of the process since the system must evolve from x_0 to x_1 then from x_1 to x_2 and the from x_2 to $x_2+\xi$.

$$\langle x_{t_1}\Xi\left(dt;x_{t_2},t_2\right)\rangle=\int_S dx_1\,x_1\,P\left(x_1,t_1\mid x_0,t_0\right)\int_S dx_2\left[\int_S d\xi\,\xi\,\Pi\left(\xi\mid dt_2;x_2,t_2\right)\right]P\left(x_2,t_2\mid x_1,t_1\right)$$

Using the moments definition

$$\langle x_{t_1}\Xi\left(dt;x_{t_2},t_2\right)\rangle=\int_S dx_1\,x_1\,P\left(x_1,t_1\mid x_0,t_0\right)\int_S dx_2 A_{t_2}\left(x_{t_2}\right)dt_2\,P\left(x_2,t_2\mid x_1,t_1\right)+\mathcal{O}\left(dt_2\right)$$

The last two integrals describe a compound average value. Therefore:

$$\langle x_{t_1}\Xi\left(dt;x_{t_2},t_2\right)\rangle=\langle x_{t_1}A_{t_2}\left(x_{t_2}\right)\rangle\,dt_2+\mathcal{O}\left(dt_2\right)$$

And then:

$$\langle x_{t_1}x_{t_2+dt_2}\rangle=\langle x_{t_1}x_{t_2}\rangle+\langle x_{t_1}A_{t_2}\left(x_{t_2}\right)\rangle\,dt_2+\mathcal{O}\left(dt_2\right)$$

Dividing by dt_2 and taking the limit $dt_2\to 0$

$$\frac{d}{dt_2}\langle x_{t_1}x_{t_2}\rangle=\langle x_{t_1}A_{t_2}\left(x_{t_2}\right)\rangle \tag{4.4.2}$$

Finally:

$$\frac{d}{dt_2}\langle x_{t_1};x_{t_2}\rangle=\langle x_{t_1}A_{t_2}\left(x_{t_2}\right)\rangle-\langle x_{t_1}\rangle\langle A_{t_2}\left(x_{t_2}\right)\rangle$$

4.4.3 Variance

If we consider $n=2$:

$$\left\langle x_{t+dt}^2\right\rangle=\left\langle x_t^2\right\rangle+\left\langle\Xi^2\left(dt;x_t,t\right)\right\rangle+2\left\langle x_t\Xi\left(dt;x_t,t\right)\right\rangle$$

We have already evaluated the last average value, therefore:

$$\left\langle x_{t+dt}^2\right\rangle=\left\langle x_t^2\right\rangle+\left\langle\Xi^2\left(dt;x_t,t\right)\right\rangle+2\left\langle x_tA_t\left(x_t\right)\right\rangle dt+\mathcal{O}\left(dt\right)$$

Now we want to evaluate:

$$\left\langle\Xi^2\left(dt;x_t,t\right)\right\rangle=\int_S dx\,\Xi^2\left(dt;x,t\right)P\left(x,t\mid x_0,t_0\right)=\int_S dx\int_S d\xi\,\xi^2\,\Pi\left(\xi\mid dt;x,t\right)P\left(x,t\mid x_0,t_0\right)$$

Again we can substitute the expression of the second moment:

$$\left\langle\Xi^2\left(dt;x_t,t\right)\right\rangle=\int_S dx\,B_t\left(x\right)dtP\left(x,t\mid x_0,t_0\right)+\mathcal{O}\left(dt\right)$$

And therefore

$$\left\langle\Xi^2\left(dt;x_t,t\right)\right\rangle=\left\langle B_t\left(x_t\right)\right\rangle dt+\mathcal{O}\left(dt\right)$$

And then:

$$\left\langle x_{t+dt}^2 \right\rangle = \left\langle x_t^2 \right\rangle + \left\langle B_t\left(x_t\right)\right\rangle dt + 2\left\langle x_t A_t\left(x_t\right)\right\rangle dt + \mathcal{O}\left(dt\right)$$

since dt is infinitesimal:

$$\frac{d}{dt}\left\langle x_t^2 \right\rangle = \left\langle B_t\left(x_t\right)\right\rangle + 2\left\langle x_t A_t\left(x_t\right)\right\rangle \tag{4.4.3}$$

To obtain the variance:

$$\frac{d}{dt}Var\left[x_t\right] = \frac{d}{dt}\left[\left\langle x_t^2\right\rangle - \left\langle x_t\right\rangle^2\right] = \left\langle B_t\left(x_t\right)\right\rangle + 2\left\langle x_t A_t\left(x_t\right)\right\rangle - 2\left\langle x_t\right\rangle\left\langle A_t\left(x_t\right)\right\rangle$$

$$\frac{d}{dt}Var\left[x_t\right] = \left\langle B_t\left(x_t\right)\right\rangle + 2\left[\left\langle x_t A_t\left(x_t\right)\right\rangle - \left\langle x_t\right\rangle\left\langle A_t\left(x_t\right)\right\rangle\right] \tag{4.4.4}$$

Note that using the moments we can know the average dynamics of the process. This is the evidence of the propagator importance and a consequence of the Markov approximation.

4.4.4 Integral of the process

Usually it is interesting also to evaluate the integral of a process. For example:

$$y_t = y_0 + \int_0^t x_s\, ds$$

In which the process y_t is determined by the update equation

$$y_{t+dt} = y_t + x_t\, dt$$

But note that the update relation does not have the canonical Langevin form: its right side involves not only y_t but also x_t. Therefore even if we know y_t we cannot say anything about x_t. Therefore, y_t by itself, although obviously continuous, is not a Markov process. But since x_t and y_t together suffice to determine x_{t+dt} and y_{t+dt}, then the bivariate continuous process (x_t, y_t) is Markov. If we consider the average value we can define an ordinary derivative:

$$\frac{d\left\langle y_t\right\rangle}{dt} = \left\langle x_t\right\rangle \tag{4.4.5}$$

From which, using a classical integration we can obtain $\langle y_t\rangle$. For the variance:

$$\frac{d}{dt}Var\left[y_t\right] = \frac{d\left\langle y_t^2\right\rangle}{dt} - 2\left\langle y_t\right\rangle\frac{d\left\langle y_t\right\rangle}{dt} = \frac{d\left\langle y_t^2\right\rangle}{dt} - 2\left\langle y_t\right\rangle\left\langle x_t\right\rangle$$

To obtain the first average value we can take:

$$y_{t+dt}^2 = y_t^2 + 2y_t x_t dt + \mathcal{O}\left(dt\right) \tag{4.4.6}$$

We have considered terms up to order dt, because it is the limit of the update equation sensibility. If we take the average value of (4.4.6)

$$\frac{d\left\langle y_t^2\right\rangle}{dt} = 2\left\langle y_t x_t\right\rangle + \mathcal{O}\left(dt\right)$$

And finally:

$$\frac{d}{dt}Var\left[y_t\right] = 2\left\langle y_t x_t\right\rangle - 2\left\langle y_t\right\rangle\left\langle x_t\right\rangle = 2\left\langle x_t; y_t\right\rangle$$

Note that we have considered only the average process, and therefore without the stochastic contribution. To study the integral of processes without necessarily taking the average value we have to introduce the stochastic integration, and we are going to do it in Section 6. In physics, considering the integral process is very important, an example could be the process v_t that describes the velocity of the probe and x_t that describes its position.

4.5 The Langevin equation

4.5.1 The Wiener process

The Fokker-Planck (4.3.1) is a differential equation for the probability of the process. Now we want to obtain a differential equation for the continuous process itself. It is called Langevin equation and it is complementary to the Fokker-Planck one.

$$\Xi\left(dt; x_t, t\right) = dx_t\left(dt; x_t, t\right)$$

Therefore equation (4.1.4) becomes:

$$dx_t\left(dt; x_t\right) = x_{t+dt} - x_t$$

According to (4.2.6):

$$dx_t\left(dt; x_t\right) = A_t\left(x_t\right) dt + \sqrt{B_t\left(x_t\right) dt}\, N\left(0,\, 1\right)$$

The variation of the process is given by a deterministic contribution and by a randomly fluctuating one. If we unify the last two equations:

$$x_{t+dt} - x_t = A_t\left(x_t\right) dt + \sqrt{B_t\left(x_t\right) dt}\, N\left(0,\, 1\right) \tag{4.5.1}$$

Here x_t and $N\left(0, 1\right)$ are statistically independent. From (4.5.1) we can note that x_t is continuous but nowhere differentiable. In fact if we consider the limit $dt \to 0$, then $x_{t+dt} \to x_t$ assuring the continuity. While, if we consider:

$$\frac{x_{t+dt} - x_t}{dt} = A_t\left(x_t\right) + \sqrt{\frac{B_t\left(x_t\right)}{dt}}\, N\left(0,\, 1\right)$$

it is evident that, if $B \neq 0$, the second term in the right-hand side is divergent in the limit $dt \to 0$ and $\frac{dx_t}{dt}$ does not exist. Due to the fluctuating term the Langevin equation is not an ordinary differential equation, but it is a stochastic one. Now we are going to define a:

$$dW_t = N\left(0, 1\right)\sqrt{dt}$$

where W_t is a stochastic process called Wiener process. It is a process with $A_t\left(x_t\right) = 0$ and $B_t\left(x_t\right) = 1$. Its properties are:

- it is completely homogeneous
- $\langle W_t \rangle = x_0$
  there is no exponential decay because there is no friction contribution
- its distribution is a Gaussian with zero mean and dt variance (with $B = 1$)
- $Var\left[W_t\right] = t - t_0$
  this is equivalent to say that $\left(dx_t\right)^2 \propto dt$ according to its diffusive nature
- dW_t and x_t are statistically independent

As we have done for x_t we can write dW_t as an increment in dt:

$$dW_t = W_{t+dt} - W_t \sim N(0,\, dt) \tag{4.5.2}$$

If we divide by dt:

$$\frac{x_{t+dt} - x_t}{dt} = A_t(x_t) + \sqrt{B_t(x_t)}\,\frac{dW_t}{dt}$$

If we apply the limit $dt \to 0$:

$$\frac{dx_t}{dt} = A_t(x_t) + \sqrt{B_t(x_t)}\lim_{dt\to 0}\frac{dW_t}{dt}$$

Now we define the white noise form of the Langevin equation

$$\lim_{dt\to 0}\frac{dW_t}{dt} = \xi_t \tag{4.5.3}$$

In this way we have defined a differential equation:

$$\frac{dx_t}{dt} = A_t(x_t) + \xi_t\sqrt{B_t(x_t)}$$

The white noise satisfies two properties:

- zero average value
  $\langle \xi_t \rangle = 0$
- $\langle \xi_{t_1}\xi_{t_2} \rangle = \delta(t_1 - t_2)$

"White" means that the Fourier transform of the correlation function of the noise, or its spectral density, is independent of frequency. Defining the white noise, we have formally escaped the divergence of the stochastic term in the limit $dt \to 0$. But nevertheless $\frac{dx_t}{dt}$ cannot be formally thought as a derivative. The reason why this derivative is not mathematical well-defined is because it considers the variation of the process x_t in an interval dt, but we know that the stochastic term change is proportional to $\sqrt{dt}$. Therefore during the time in which we consider the incremental ratio the process randomly evolves. Since dx_t represents the variation of the process during an infinitesimally small time interval we are going to work with the formally correct:

$$dx_t = A_t(x_t)\,dt + \sqrt{B_t(x_t)}\,dW_t \tag{4.5.4}$$

Note that $B_t(x_t)$ describes the intensity of the random process fluctuations. Note that, due the markovian nature of the Langevin equation, it is presented as a discrete increment of the process value x_t controlled by the parameter dt that describes the sensibility of the evolution. This equation can naturally be numerically simulated without introducing other errors of computational approximation. The only approximation is due to the Markovianity and to the dt finite size.

4.5.2 Considerations on the Langevin equation

4.5.2.1 Degrees of freedom reduction

The Langevin equation is an useful tool to study a stochastic system x_t, since it derives from Newton equation and it depends only on the system degrees of freedom. In fact if there would be

also the degrees of freedom of the environment interacting with the system, the solution would be much more difficult. Therefore, the obvious question is why can we exclude the environment degrees of freedom? This procedure is called dynamics reduction and it is based on taking into account the environment presence as a global interaction with the system. Therefore in the Langevin equation there will be a term depending on the system degrees of freedom that takes into account all the environment interaction, instead of a huge number of contributions. The basic idea is to consider the presence of the system as a perturbation to the environment dynamics. Its response to that perturbation will be a global contribution that does no longer depend on all the environment degrees of freedom. We will develop it better in the following Sections.

4.5.2.2 Trajectories

If we consider a stochastic process x_t during the interval $[0, t]$, it defines a continuous path ω in the set of states S. Evidently, the probability of an entire path is different from the probability $P_t(x)$ that we have introduced in the previous Sections. In fact, $P_t(x)$ gives at any time the probability of being in state x, but it does not take into account how the system arrives in x at t. The path probability $\mathcal{P}(\omega)$ must depend on all the states the system goes through during the time interval. Evaluating this probability is very difficult and here we use the Markovian approximation. In fact, if we suppose to divide the interval $[0, t]$ in n subintervals of width dt, we could study each increment with the Langevin equation. The probability of going from x_t to x_{t+dt} is given by the Wiener process that is the stochastic contribution of the Langevin equation. Since the Wiener process at time t is statistically independent by its values assumed in the previous times, we can obtain the probability $\mathcal{P}(\omega)$ multiplying all the contributions of order dt. We are going to explain it better in the following Sections. Note that we have found the concept of trajectory also in the jump processes. The difference is that now S is continuous and therefore the trajectory will no longer be a discrete sequence of configuration, but indeed a continuous path.

4.5.2.3 Conclusions

In conclusion, the formalism of the continuous Markov process is the most useful to go beyond the simplest systems, like nonequilibrium ones. We are interested in nonequilibrium systems for which an invariant distribution does not exist because of an time-dependence in the dynamics. We have studied it in the context of the jump processes. Now we want to study it in the context of the diffusion processes. Since in the introduction to Langevin equation we have not had to make any distinction, we expect that it is valid both for equilibrium and nonequilibrium systems. In fact, the difference and all the physical meaning is in the two moments $A_t(x_t)$ and $B_t(x_t)$.

4.6 Stochastic integrals

In the last Section we have introduced the Langevin equation. It is not an ordinary differential equation since there is a rapidly and irregularly fluctuating function of time. Therefore it cannot be solved with the usual tools. Note also that the stochastic contribution is proportional to $\sqrt{dt}$ and, due to it, a time-derivative of the process cannot be defined as we have said in Section 4.5.1. There are two ways to study the dynamics described by the Langevin equation:

- if we consider the average value of the process, the Langevin equation will become an ordinary differential equation and we can solve it as we have done in Section 4.4.

- starting from (4.5.4) we can introduce a stochastic integration that takes into account also the fluctuating term.

Now we want to treat the second point introducing the stochastic integrals. First of all we want to explain why they are different from the Riemann ones. Consider $f_t(x_t)$, function of time and space. For now x_t is not a stochastic process. We want to evaluate the integral:

$$\int_0^t f_s(x_s)\, dx_s$$

More correctly, it is a Riemann-Stieltjes integral since it depends on x_s function of time but it can be written easily as a Riemann integral:

$$\int_0^t ds\, f_s(x_s)\, \dot{x}_s$$

To solve this integral we subdivide the interval $[0,t]$ in n subintervals. In each one the function is constant and then it does not depend on which point it is evaluated along the subinterval. Therefore, in the limit $n \to \infty$, we approximate with rectangles the area under the curve defining subintervals of width dt. Now suppose that x_t is a stochastic process, for example:

$$dx_t = A_t(x_t)\, dt + \sqrt{B_t(x_t)} dW_t$$

First of all we cannot define $\dot{x}_s$ because it is not an ordinary time-derivative. The process x_t is continuous but not differentiable. Furthermore, we can note that the first term is proportional to dt, instead the second one is proportional to $\sqrt{dt}$. Therefore if we subdivide the interval $[0,t]$ in n subintervals, now the function is no longer constant in a subinterval, because the subinterval has width dt in the limit $n \to \infty$, but the process variation is proportional to $\sqrt{dt}$ that is much bigger than dt. The stochastic term changes too quickly to assume that the function is constant in a subinterval. The diffusive nature of the process does not allow to define neither a velocity $\dot{x}_t$ nor an ordinary integration. Using (4.5.4):

$$(dx_t)^2 = \left(A_t(x_t)\, dt + \sqrt{B_t(x_t)} dW_t\right)^2 = (A_t(x_t)\, dt)^2 + B_t(x_t)\,(dW_t)^2 + 2A_t(x_t)\, dt \sqrt{B_t(x_t)}\, dW_t$$

$$(dx_t)^2 = B_t(x_t)\,(dW_t)^2 + \mathcal{O}(dt) = B_t(x_t)\, dt + \mathcal{O}(dt)$$

for the properties of the Wiener process. The increment of position is proportional to the square root of the time, for this reason the process x_t is called diffusive. Note that this result does not depend on $A_t(x_t)$ and $B_t(x_t)$. A way to go beyond this difficulty is to introduce a process dependence in the function. In this way also $f_s(x_s)$ is stochastic and its values are probabilistically determined by the Wiener process at time s. It is now evident that since the stochastic term can change in a subinterval, the integration depends on the particular choice of the intermediate point of each subinterval in which we evaluate the function. There are two possible choices:

Itô integral

If we evaluate the function at the beginning of the interval

$$\int_0^t f_s(x_s)\, dx_s = \lim_{n\to\infty} \sum_{i=0}^{n-1} f_{t_i}(x_{t_i}) \left(x_{t_{i+1}} - x_{t_i}\right) \tag{4.6.1}$$

where $t_0 = 0$ and $t_n = t$. This kind of integration is the most straightforward because it is consistent with how we have defined the Langevin equation. Now we want to derive a property of the Itô integration. Consider a function $f = \nabla g$. Its Itô integral is:

$$\int_0^t \nabla g_s(x_s)\, dx_s = \lim_{n\to\infty} \sum_{i=0}^{n-1} \nabla g_{t_i}(x_{t_i}) \left(x_{t_{i+1}} - x_{t_i}\right)$$

Consider the interval $x_{t_{i+1}} - x_{t_i}$, and consider the function $g_t(x_t)$ evaluated at the end of the interval. Using a Taylor-expansion we can connect it to the Itô case. Then, up to contributions $\mathcal{O}(dt)$:

$$g_{t_{i+1}}\left(x_{t_{i+1}}\right) = g_{t_i}(x_{t_i}) + \frac{\partial g_{t_i}(x_{t_i})}{\partial t}(t_{i+1} - t_i) + \nabla g_{t_i}(x_{t_i})\left(x_{t_{i+1}} - x_{t_i}\right) + \frac{1}{2}\nabla^2 g_{t_i}(x_{t_i})\left(x_{t_{i+1}} - x_{t_i}\right)^2$$

Note that:

$$\left(x_{t_{i+1}} - x_{t_i}\right)^2 = \left(dx_{t_i}\right)^2$$

But we have seen that it is proportional to dt. Therefore:

$$g_{t_{i+1}}\left(x_{t_{i+1}}\right) = g_{t_i}(x_{t_i}) + \frac{\partial g_{t_i}(x_{t_i})}{\partial t}(t_{i+1} - t_i) + \nabla g_{t_i}(x_{t_i})\left(x_{t_{i+1}} - x_{t_i}\right) + \frac{B_{t_i}(x_{t_i})}{2}\nabla^2 g_{t_i}(x_{t_i})(t_{i+1} - t_i)$$

Then:

$$\nabla g_{t_i}(x_{t_i})\left(x_{t_{i+1}} - x_{t_i}\right) = g_{t_{i+1}}\left(x_{t_{i+1}}\right) - g_{t_i}(x_{t_i}) - \frac{\partial g_{t_i}(x_{t_i})}{\partial t}(t_{i+1} - t_i) - \frac{B_{t_i}(x_{t_i})}{2}\nabla^2 g_{t_i}(x_{t_i})(t_{i+1} - t_i)$$

If we substitute it in the Itô integral ignoring the $\mathcal{O}(dt)$ contributions:

$$\int_0^t \nabla g_s(x_s)\, dx_s = \lim_{n\to\infty} \sum_{i=0}^{n-1} \left[g_{t_{i+1}}\left(x_{t_{i+1}}\right) - g_{t_i}(x_{t_i}) - \frac{\partial g_{t_i}(x_{t_i})}{\partial t}(t_{i+1} - t_i) - \frac{B_{t_i}(x_{t_i})}{2}\nabla^2 g_{t_i}(x_{t_i})(t_{i+1} - t_i) \right]$$

The first two terms in the right-hand side describe a telescopic series. In fact:

$$\sum_{i=0}^{n-1} g_{t_{i+1}}\left(x_{t_{i+1}}\right) - g_{t_i}(x_{t_i}) = g_{t_1}(x_{t_1}) - g_{t_0}(x_{t_0}) + g_{t_2}(x_{t_2}) - g_{t_1}(x_{t_1}) + \dots$$

$$\sum_{i=0}^{n-1} g_{t_{i+1}}\left(x_{t_{i+1}}\right) - g_{t_i}(x_{t_i}) = g_t(x_t) - g_{t_0}(x_{t_0})$$

Instead the other contributions are by definition Itô integrals. Therefore:

$$\int_0^t \nabla g_s(x_s)\, dx_s = g_t(x_t) - g_{t_0}(x_{t_0}) - \int_0^t ds\, \frac{\partial g_s(x_s)}{\partial s} - \int_0^t ds\, \frac{B_s(x_s)}{2}\nabla^2 g_s(x_s)$$

Given that:

$$g_t(x_t) - g_{t_0}(x_{t_0}) = \int_0^t dg_s(x_s)$$

Finally we can write:

$$dg_s(x_s) = \nabla g_s(x_s)\, dx_s + \frac{\partial g_s(x_s)}{\partial s} ds + \frac{B_s(x_s)}{2}\nabla^2 g_s(x_s)\, ds$$

This result is called Itô Lemma and it is useful to compute the stochastic differential of a function. It is a kind of chain rule for the ordinary calculus in which the first two terms are the ones expected, instead the last one is due to the diffusive nature of the process x_s.

Stratonovitch integral

If we evaluate the function in the middle point of the interval

$$\int_0^t f_s(x_s) \circ dx_s = \lim_{n\to\infty} \sum_{i=0}^{n-1} f_{\frac{t_i+t_{i+1}}{2}} \left(\frac{x_{t_i} + x_{t_{i+1}}}{2} \right) \left(x_{t_{i+1}} - x_{t_i} \right) \tag{4.6.2}$$

An interesting property of the Stratonovitch integral is its antisymmetry with respect to time reversal, if the process only describes positions and not velocities. When velocities are involved, we also have to reverse the signs of the velocities, and the Stratonovitch integral may not be time-antisymmetric in this case. There is a connection between Itô and Stratonovitch integral. In fact, consider the sum in (4.6.2), if we expand the function f around x_{t_i} (that is the beginning of the interval):

$$\sum_{i=0}^{n-1} \left[f_{t_i}(x_{t_i}) + \nabla f_{t_i}(x_{t_i}) \left(\frac{x_{t_{i+1}} - x_{t_i}}{2} \right) + \ldots \right] \left(x_{t_{i+1}} - x_{t_i} \right)$$

Now in the bracket there are only Itô integrals. Again we can use $(dx_{t_i})^2 \propto dt$. Therefore:

$$\int_0^t f_s(x_s) \circ dx_s = \int_0^t f_s(x_s)\, dx_s + \frac{1}{2} \int_0^t ds\, B_s(x_s)\, \nabla f_s(x_s) \tag{4.6.3}$$

And if we consider again $f = \nabla g$:

$$\int_0^t \nabla g_s(x_s) \circ dx_s = \int_0^t \nabla g_s(x_s)\, dx_s + \frac{1}{2} \int_0^t ds\, B_s(x_s)\, \nabla^2 g_s(x_s)$$

But we have seen:

$$\int_0^t \nabla g_s(x_s)\, dx_s = g_t(x_t) - g_{t_0}(x_{t_0}) - \int_0^t ds\, \frac{\partial g_s(x_s)}{\partial s} - \int_0^t ds\, \frac{B_s(x_s)}{2} \nabla^2 g_s(x_s)$$

Therefore:

$$\int_0^t \nabla g_s(x_s) \circ dx_s = g_t(x_t) - g_{t_0}(x_{t_0}) - \int_0^t ds\, \frac{\partial g_s(x_s)}{\partial s} \tag{4.6.4}$$

From mechanics we know that work should be equal to the integral over a path of the force times the displacement. But in diffusion systems this definition does not completely specify work, as one has to choose which stochastic integral to use. However, we also know that the work should be antisymmetric under time-reversal. Because of this, the work performed by a force $F_t(x_t)$ during ω is defined with a Stratonovitch integral.

Chapter 5

Diffusion processes

5.1 Equilibrium Brownian Motion

Now we want to use the continuous Markov processes theory for a particular case: the nonequilibrium Brownian motion. Before doing it, we will present the equilibrium case to take confidence with the formalism. Consider a probe with mass M and velocity v_t at time t, it is embedded in an equilibrium fluid of relatively small particles with mass m with which it can interact ($M \gg m$). We are going to study its extension to nonequilibrium case (especially the not-stationary one). To do it, we will use the formalism just introduced since the physical aspects depend on $A_t(v_t)$ and $B_t(v_t)$. Therefore to consider a nonequilibrium system we only have to choose the correct moments. Note that here we have written v_t instead of x_t since we want to study the velocity of the probe as a stochastic process.

5.1.1 Langevin equation

The equilibrium Brownian motion is solution of the Fokker-Planck equation with:

$$A(v_t) = -M\gamma v_t \qquad\qquad B = 2D_v$$

The term $-M\gamma v_t$ is the frictional force the probe feels, with γ the friction coefficient. Eventually in A_t there could be also a conservative potential, for the moment we suppose it zero. Indeed, when the probe has a velocity, the interaction with particles is not balanced and the probe perceives a bigger interaction in one direction. The net effect is equal to $-M\gamma v_t$. The probe feels also a stochastic interaction due to the thermal agitation of the particles that depends on the fluid temperature in the mesoscopic description. The intensity of this interaction is given by the diffusion coefficient. Note that the subscript v means that this diffusion coefficient is referred to the velocity. The reason for it will be clear in the following. Therefore, the Langevin equation is:

$$M dv_t = -M\gamma v_t dt + \sqrt{2D_v}\,\xi_t dt \tag{5.1.1}$$

Note that ξ_t is a Gaussian random variable with variance $\sqrt{dt}$ and it describes the white noise perceived by the probe. D_v is the proportionality coefficient between the gradient of the probe density and the current produced by it, therefore a question would be: if the system is at equilibrium, why are we talking about density gradient and current? The answer allows to understand the meaning of the Langevin equation. It is the result of a perturbation theory. In fact, it describes the motion of a probe in a system of particles, in this case, at equilibrium. Therefore the probe is

a perturbation to the particles motion. Using the response to this perturbation we can evaluate the properties of the probe motion as the friction and the diffusion coefficient that affect the probe dynamics during the transient before the convergence to equilibrium. Since the response takes into account all the particles, it can be thought as a macroscopic variable with respect to the particles scale. We will describe it in Section 5.1.2 using a mesoscopic description.

5.1.1.1 Average dynamics

Now we want to study the average dynamics of the Langevin equation (5.1.1). We can proceed in two ways.

- Using (4.4.1) and (4.4.3):

$$\frac{d}{dt}\langle v_t\rangle = -\gamma\langle v_t\rangle$$
$$\frac{d}{dt}\langle v_t^2\rangle = \frac{2D_v}{M^2} - 2\gamma\langle v_t^2\rangle$$

  And their solution is:

$$\langle v_t\rangle = v_0 e^{-\gamma t}$$
$$\langle v_t^2\rangle = v_0^2 e^{-2\gamma t} + \frac{D_v}{M^2\gamma}$$

  where v_0 is the initial velocity of the probe. As we expect, since the fluid is at equilibrium, in long-time limit the average velocity of the probe is zero and the square average tends to a constant value. In other words, after a long time the probe is in equilibrium with the fluid. This value is given by the physical nature of the equilibrium fluid that satisfies the equipartition theorem. According to it:

$$\langle v_\infty^2\rangle = \frac{k_B T}{M}$$

  where T is the fluid temperature. From this result we conclude that D_v and γ satisfy the relation:

$$D_v = \gamma M k_B T \tag{5.1.2}$$

  Therefore, according to it, the Langevin equation for the velocity:

$$\frac{dv_t}{dt} = -\gamma v_t + \sqrt{\frac{2\gamma k_B T}{M}}\xi_t$$

  Instead for the average value of the position we can use (4.4.5):

$$\langle x_t\rangle = \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right)$$

  We note that in the long time limit the average position does not depend on time.

- If we do in (5.1.1) the substitution:

$$v_t = e^{-\gamma t}\phi_t$$

  In this way we obtain a formal solution:

$$v_t = v_0 e^{-\gamma t} + \sqrt{\frac{2\gamma k_B T}{M}}\int_0^t ds\, e^{-\gamma(t-s)}\xi_s$$

This procedure is more useful since we are also interested in the Langevin equation for the probe position. In fact, from it we can obtain:

$$\langle v_{t_1} v_{t_2} \rangle = \frac{k_B T}{M} \left(e^{-\gamma |t_2 - t_1|} - e^{-\gamma (t_1 + t_2)} \right) + v_0^2 e^{-\gamma (t_1 + t_2)}$$

From which:

$$\left\langle x_t^2 \right\rangle = \int_0^t dt_1 \int_0^t dt_2 \, \langle v_{t_1} v_{t_2} \rangle \tag{5.1.3}$$

Solving these integrals:

$$\left\langle x_t^2 \right\rangle = \frac{2 k_B T}{M \gamma} t + \frac{k_B T}{M \gamma^2} \left(4 e^{-\gamma t} - 2 e^{-2 \gamma t} - 3 \right) + \frac{v_0^2}{\gamma^2} \left(e^{-\gamma t} - 1 \right)^2$$

Note that in this equation there is also a constant term. Since we will consider the long-time limit, this contribution is irrelevant compared to the one increasing with time. Differently by the average value, the square average value is linear in time and it is proportional to a constant called position diffusion coefficient that satisfies the Einstein-Smoluchowski relation:

$$D_x = \frac{k_B T}{M \gamma} \tag{5.1.4}$$

If the fluid particles are hard spheres of radius R, the drag is $\gamma = 6 \pi \eta R$, where η is the fluid viscosity. These results are characteristic of the diffusive motion. From equation (5.1.3) we can relate the diffusion coefficient D_x to the velocity fluctuation:

$$D_x = \lim_{t \to \infty} \frac{1}{2} \frac{\partial}{\partial t} \int_0^t dt_1 \int_0^t dt_2 \, \langle v_{t_1} v_{t_2} \rangle$$

Solving the derivative:

$$D_x = \lim_{t \to \infty} \frac{1}{2} \left[\int_0^t dt_2 \, \langle v_t v_{t_2} \rangle + \int_0^t dt_1 \, \langle v_{t_1} v_t \rangle \right]$$

Since the two integrals are equivalent:

$$D_x = \lim_{t \to \infty} \int_0^t dt' \, \langle v_t v_{t'} \rangle$$

There is a relation between D_x and D_v, it is:

$$D_x = \frac{D_v}{M^2 \gamma^2} \tag{5.1.5}$$

Under these considerations, equation (5.1.4) is known as the second fluctuation-dissipation theorem for equilibrium systems. In fact it relates the friction that describes the energy dissipation and the diffusion coefficient that describes the fluctuation of the process. In fact, if x_t is the probe position at time t:

$$\left\langle (x_t - x_0)^2 \right\rangle \underset{t \to \infty}{\sim} 2 D_x t$$

D_x and γ are properties of the fluid in which the probe is embedded, they derive from average values over the fluid dynamic and therefore they do not depend on particles position, they could

depend on the probe position but in this case the Langevin equation for the probe will be no longer (5.1.1) and the dynamics will be no longer of equilibrium. Equation (5.1.4) is valid only if the fluid is at equilibrium since it is based on equipartition theorem. The Fokker-Planck equation associated to this Langevin equation is:

$$\frac{\partial P_t(v)}{\partial t} = \gamma \frac{\partial}{\partial v}\left(v P_t(v)\right) + \frac{D_v}{M^2}\frac{\partial^2 P_t(v)}{\partial v^2}$$

This equation admits a stationary solution, and if we use (5.1.4), it is:

$$\rho(v) = \sqrt{\frac{\beta M}{2\pi}} e^{-\frac{\beta M v^2}{2}}$$

which is a Maxwellian distribution. To obtain this solution we have used the detailed balance relation (4.3.6). Since this relation is valid only at equilibrium, or rather when the velocity is distributed as a Maxwell-Boltzmann we can say that (5.1.4) is at equilibrium equivalent to the detailed balance relation. Furthermore, if in (5.1.1) there would have been an external force, the system could still have been of equilibrium. This is true if and only if the external force is conservative. In this case in the Maxwell-Boltzmann distribution there would have been another contribution depending on the potential that produces that force.

5.1.1.2 Over-damped limit

Consider the Langevin equation (5.1.1). Now, we consider a special situation. If the drag coefficient γ is big enough, the magnitude of the friction force is much bigger than the magnitude of inertia force:

$$\left|\gamma(x_t)\frac{dx_t}{dt}\right| \gg \left|M\frac{d^2x_t}{dt^2}\right|$$

In other words we are considering the limit $\gamma \to \infty$ and $M \to 0$ with fixed product $M\gamma$. Under this condition we can ignore the acceleration term. Therefore:

$$\frac{dx_t}{dt} = \frac{1}{M\gamma}\sqrt{2D_v}\,\xi_t$$

Using (5.1.5) we obtain D_x. According to it the difference between D_x and D_v is evident: D_x is the position fluctuation intensity, D_v is the velocity fluctuation intensity. By definition, the mobility is

$$\nu = \frac{1}{M\gamma} \tag{5.1.6}$$

It is possible to adopt the over-damped limit for both equilibrium or nonequilibrium dynamics. We will use it many times in the following.

5.1.2 Equilibrium fluctuation-dissipation relation

As we have said at the end of the previous chapter the Langevin equation is the result of "integrating out" the degrees of freedom of the environment surrounding the system. In the Section we will derive, using equilibrium linear response theory, the Langevin equation for a probe embedded in a equilibrium fluid of interacting particles. We want to describe the probe position with a Langevin equation. To do this, we need to know how to ignore the particles degrees of freedom and then to consider the reduced system. We want to find out:

- the properties of the noise perceived by the probe.
- the expression of the friction in function of particles dynamics. This is also called second fluctuation-dissipation theorem.

The treatment we will present in this Section is an extension for interacting particle of the Model presented in Section 1.6 of Zwanzig's book, [1] for independent particles.

5.1.2.1 Newton equations

We suppose that an external conservative force acts on the probe and that the interaction between fluid and probe is harmonic (and therefore conservative). The external force can be written as a potential $V(x_t)$ where x_t is the position of the probe. We assume that $x_0 = y$ and $V'(y) = 0$. Then y is the equilibrium position (in absence of interaction with the fluid) of the probe in the long-time limit since it corresponds to the potential minimum. The fluid particles can interact with each others and with the probe. Then the potential energy for the fluid must take into account both contributions. Then, if we indicate with X_t^j the position of the j-th probe:

$$U(X_t, x_t) = \sum_{j<j'} \Phi\left(X_t^j - X_t^{j'}\right) + \sum_j \frac{\omega_j^2}{2}\left(X_t^j - \frac{\lambda_j}{\omega_j^2} x_t\right)^2$$

where $X = \{X^j\}$ is the set of all the particles coordinates, it is a N-dimensional stochastic process, if N is the number of particles in the fluid. The energy is time-dependent due to the coupling with the probe. This coupling modifies also the particles position X_t^j. Here λ_j is the coupling coefficient of the j-th degrees of freedom with the probe (generally they can be different for each degree) and ω_j is the oscillation frequency of the j-th particle. We are adopting the weak coupling limit (it is necessary for the linear response theory), therefore we are assuming the λ_j are small parameters. Since the fluid is at equilibrium at temperature T, there is a thermal agitation perceived by the particles, we are going to indicate it as ξ_t^j. Therefore in a mesoscopic description the noise describes the interaction with the environment surrounding the fluid.

$$M\ddot{x}_t = -V'(x_t) - \frac{\partial U(X_t, x_t)}{\partial x}$$

$$\dot{X}_t^j = -\gamma_j \dot{X}_t^j - \frac{\partial U(X_t, x_t)}{\partial X^j} + \sqrt{2\gamma_j k_B T}\xi_t^j$$

where γ_j is the friction for the j-th probe. For simplicity we assume $m = 1$. Since we assumed the over-damped limit we have $\ddot{X}_t^j = 0$. Therefore we can rewrite the equation for the fluid particles as:

$$\dot{X}_t^j = -\frac{1}{\gamma_j}\frac{\partial U(X_t, x_t)}{\partial X^j} + \sqrt{\frac{2k_B T}{\gamma_j}}\xi_t^j$$

The forces acting on the fluid particles are conservative, necessary condition to be at equilibrium. Therefore if we take the derivative of the energy we get the equation

- for the probe:

$$M\ddot{x}_t = -V'(x_t) - \sum_j \lambda_j\left(X_t^j - \varepsilon_j x_t\right) \tag{5.1.7}$$

we have defined the parameter $\varepsilon_j = \frac{\lambda_j}{\omega_j^2}$. Since the coupling is weak, the ε_j is small for any particle. The only case in which it could be big is when the frequencies are small, but the time scale of the particles is much bigger than the probe one, therefore we are excluding this case.

- for the fluid particles is:

$$\dot{X}_t^j = -\sum_{j<j'} \frac{1}{\gamma_j} \Phi' \left(X_t^j - X_t^{j'} \right) - \frac{\omega_j^2}{\gamma_j} \left(X_t^j - \varepsilon_j x_t \right) + \sqrt{\frac{2k_B T}{\gamma_j}} \xi_t^j \tag{5.1.8}$$

The first contribution between the j-th particle and all the others, the second is the interaction with the probe and the third is its stochastic noise.

We will use the linear response to study how the particles react to the probe motion.

5.1.2.2 Expansion of energy

The time scale of probe dynamics is really slower than the particles one, due to the condition $M \gg m$. After a probe position changing x_t, the fluid has enough time to equilibrate before the probe changes again its position. In this way, for each probe position, the fluid will be always at equilibrium described by a Maxwellian distribution that will depend on x_t at fixed time t. Then, in the ensemble of the fluid, the probe position can be thought as a parameter. This situation is due also the the weak coupling assumption since it lets us suppose the probe motion evolution will not affect the fluid so much. Under these considerations, in the energy, the dependence on x_t is not meant as an evolution otherwise the fluid will not be at equilibrium, but as a fixed parameter. Due to the masses condition and the weak coupling assumption (ε_j is small) it is reasonable that the probe position will be close to y for each time. Therefore we can expand the energy around $x = y$:

$$U\left(X_t, x_t\right) \simeq U\left(X, y\right) + \left(x_t - y\right) \frac{\partial U\left(X, x_t\right)}{\partial x} \mid_{x_t = y}$$

Here we are going to introduce time dependence of the x, but as we have said, it has been interpreted as a fixed time parameter. For simplicity we are going to call:

$$-\frac{\partial U\left(X_t, x_t\right)}{\partial x} = g\left(X_t,\, x_t\right) = \sum_j \lambda_j X_t^j - \frac{\lambda_j^2}{\omega_j^2} x_t$$

The energy evaluated in $x_t = y$ is time-independent. We can expand the particles equation.

$$\dot{X}_t^j = -\frac{1}{\gamma_j} \frac{\partial U\left(X, y\right)}{\partial X_j} + \left(x_t - y\right) \frac{1}{\gamma_j} \frac{\partial g\left(X, y\right)}{\partial X_j} + \sqrt{\frac{2k_B T}{\gamma_j}} \xi_t^j + \mathcal{O}\left(x_t - y\right) \tag{5.1.9}$$

due to the possibility of exchanging the derivatives with respect to X and x. Therefore:

$$M \ddot{x}_t = -V'\left(x_t\right) + \sum_j \lambda_j \left(X_t^j - \varepsilon_j x_t \right) \tag{5.1.10}$$

$$\dot{X}_t^j = -\sum_{j<j'} \frac{1}{\gamma_j} \Phi' \left(X_t^j - X_t^{j'} \right) - \frac{\omega_j^2}{\gamma_j} \left(X_t^j - \varepsilon_j y \right) + \frac{\lambda_j}{\gamma_j} \left(x_t - y \right) + \sqrt{\frac{2k_B T}{\gamma_j}} \xi_t^j \tag{5.1.11}$$

Now the first two contributions describe the motion of the particles: they oscillate around the probe equilibrium position y interacting with the others. Instead the third term depends on the probe and it represents the coupling. It can be thought as a small perturbation (small due to the parameter λ_j). We are going to use the linear response theory to study the perturbation of the probe on the particles.

5.1.2.3 Statistical ensemble

The energy is necessary to study the particles using statistical mechanics. In fact, consider the macroscopic observable:

$$X^\lambda = \sum_j \lambda_j X^j \tag{5.1.12}$$

that takes into account all the particles. From energy expression:

$$g\left(X, y\right) = \sum_j \lambda_j \left(X^j - \varepsilon_j y\right) = X^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} y \tag{5.1.13}$$

Therefore X^λ is the potential from which is defined the perturbation. As we know in the response formula the potential appears rather then the perturbation. For the moment we are considering the static case in which $x_t \equiv x$. The $g\left(X, x_t\right)$ already appears in the Newton equation for the probe via the derivative of energy with respect to x. Due to this contribution, the fluid dynamics affects the probe one, but it is difficult to study it since it is stochastic via the fluid noise. For this reason we are interested in its average value:

$$\left\langle X^\lambda \right\rangle = \frac{\int dX\, e^{-\beta U(X,x)} X^\lambda}{\int dX\, e^{-\beta U(X,x)}} = \frac{1}{Z_x} \int dX\, e^{-\beta U(X,x)} X^\lambda$$

Obviously it depends on the probe position, it is like a parameter in the ensemble integration. Only if x_t is constant it is possible to define a partition function, otherwise the energy would be time-dependent, and the fluid would be out of equilibrium. We will study the dynamic case using the considerations about the difference between the two time scales presented at the beginning of Section 5.1.2.2.

The $g\left(X, y\right)$ can be interpreted as the potential perturbation to the dynamics of fluid and of probe. It is small since it depends on λ. The dynamics not perturbed is the one in which the probe is at equilibrium in y and the fluid's particles oscillates around y interacting with each others.

5.1.2.4 Expansion of partition function

We can expand also the partition function:

$$Z_x = Z_y + \frac{\partial Z\left(X, x\right)}{\partial x} \mid_{x=y} \left(x - y\right)$$

Then:

$$\frac{\partial Z\left(X, x\right)}{\partial x}_{\mid_{x=y}} = \frac{\partial}{\partial x} \left[\int dX\, e^{-\beta U(X,x)}\right]_{\mid_{x=y}} = \int dX\, e^{-\beta U(X,y)} \beta\, g\left(X, y\right)$$

$$Z_x = Z_y \left[1 + \beta \left\langle g\left(X, y\right)\right\rangle_y \left(x - y\right)\right]$$

The average values $\langle\rangle_y$ are made with respect to Z_y, here $dX = \prod_j dX^j$. Since we have $x = y$, we obtain an average value with the equilibrium value of the parameter. Using (5.1.13):

$$Z_x = Z_y \left[1 + \beta \left\langle X^\lambda \right\rangle_y (x - y) - \beta (x - y) \sum_j \frac{\lambda_j^2}{\omega_j^2} y\right]$$

And finally

$$\frac{1}{Z_x} \simeq \frac{1}{Z_y} \left[1 - \beta \left\langle X^\lambda \right\rangle_y (x - y) + \beta (x - y) \sum_j \frac{\lambda_j^2}{\omega_j^2} y\right]$$

given that $\frac{1}{1-\varepsilon} \simeq 1 + \varepsilon$. Instead, for the numerator

$$\int dX\, e^{-\beta U(X,x)} X^\lambda = \int dX\, e^{-\beta U(X,y)} X^\lambda e^{\beta g(X,y)(x-y)}$$

Expanding the exponential to the first order

$$\int dX\, e^{-\beta U(X,x)} X^\lambda = \int dX\, e^{-\beta U(X,y)} X^\lambda \left[1 + \beta g(X, y)(x - y)\right]$$

Using (5.1.13)

$$\int dX\, e^{-\beta U(X,x)} X^\lambda = \int dX\, e^{-\beta U(X,y)} X^\lambda \left[1 + \beta \left(X^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} y\right)(x - y)\right]$$

$$\int dX\, e^{-\beta U(X,x)} X^\lambda = \int dX\, e^{-\beta U(X,y)} X^\lambda + \beta (x - y) \int dX\, e^{-\beta U(X,y)} \left(X^\lambda\right)^2 -$$

$$-\beta (x - y) \sum_j \frac{\lambda_j^2}{\omega_j^2} y \int dX\, e^{-\beta U(X,y)} X^\lambda$$

Therefore:

$$\frac{1}{Z_x} \int dX\, e^{-\beta U(X,x)} X^\lambda = \left[\left\langle X^\lambda \right\rangle_y - \beta \left\langle X^\lambda \right\rangle_y^2 (x - y) + \beta \left\langle \left(X^\lambda\right)^2 \right\rangle_y (x - y)\right] + \mathcal{O}\left(\beta^2\right)$$

Finally:

$$\frac{1}{Z_x} \int dX\, e^{-\beta U(X,x)} X^\lambda = \left\langle X^\lambda \right\rangle = \left\langle X^\lambda \right\rangle_y + \beta Var\left[X^\lambda\right]_y (x - y) \tag{5.1.14}$$

5.1.2.5 Kubo Formula

We want to know how the average value of X^λ will change under this perturbation. Given that the fluid is at equilibrium we can use the Kubo formula:

$$\langle A_t \rangle^h - \langle A_t \rangle = \beta \int_0^t ds\, h_s \frac{d}{ds} \langle V(x_s) A(x_t) \rangle \tag{5.1.15}$$

where h_s is a small time dependent parameter that gives the intensity of the perturbation described by the observable, potential perturbation. In 5.1.11 does not appear explicitly a potential perturbation, but we can easily write it as:

$$\dot{X}_t^j = -\sum_{j<j'} \frac{1}{\gamma_j} \Phi' \left(X_t^j - X_t^{j'} \right) - \frac{\omega_j^2}{\gamma_j} \left(X_t^j - \varepsilon_j y \right) + (x_t - y) \frac{1}{\gamma_j} \frac{\partial}{\partial X_j} \sum_j \lambda_j X_t^j + \sqrt{\frac{2k_B T}{\gamma_j}} \xi_t^j$$

In our situation:

$$h_s = x_s - y \qquad\qquad V(x_s) = X_s^\lambda$$

given that the perturbation is $g(X, x_t)$. The reference process is the one with $x_t = y$. Now the observable X^λ depends on time. So:

$$\left\langle X_t^\lambda \right\rangle - \left\langle X^\lambda \right\rangle_y = \beta \int_0^t ds \; (x_s - y) \; \frac{d}{ds} \left\langle X_s^\lambda X_t^\lambda \right\rangle_y$$

There should be also the contribution of order λ^2 in the $g(X, x_t)$, but in the product it would be order λ^4 and therefore we can ignore it. Note that we obtain the autocorrelation without changing the equation, in fact:

$$\frac{d}{ds} \left\langle X_s^\lambda X_t^\lambda \right\rangle = \frac{d}{ds} \left[\left\langle X_s^\lambda X_t^\lambda \right\rangle_y - \left\langle X_s^\lambda \right\rangle_y \left\langle X_t^\lambda \right\rangle_y \right] + \frac{d}{ds} \left\langle X_s^\lambda \right\rangle_y \left\langle X_t^\lambda \right\rangle_y$$

$$\frac{d}{ds} \left\langle X_s^\lambda X_t^\lambda \right\rangle = \frac{d}{ds} \left\langle X_s^\lambda ; X_t^\lambda \right\rangle_y + \left\langle X_t^\lambda \right\rangle_y \frac{d}{ds} \left\langle X_s^\lambda \right\rangle_y$$

The last derivative is zero, since the average value at the equilibrium does not depend on time. Then:

$$\left\langle X_t^\lambda \right\rangle - \left\langle X^\lambda \right\rangle_y = \beta \int_0^t ds \; (x_s - y) \; \frac{d}{ds} \left\langle X_s^\lambda ; X_t^\lambda \right\rangle_y \tag{5.1.16}$$

5.1.2.6 Langevin Equation

If we integrate (5.1.16) by partial integration:

$$\left\langle X_t^\lambda \right\rangle - \left\langle X^\lambda \right\rangle_y = \beta (x_s - y) \left\langle X_s^\lambda ; X_t^\lambda \right\rangle_y \Big|_0^t - \beta \int_0^t ds \, \dot{x_s} \left\langle X_s^\lambda ; X_t^\lambda \right\rangle_y$$

Since $x_0 = y$, we have:

$$\left\langle X_t^\lambda \right\rangle = \left\langle X^\lambda \right\rangle_y + \beta (x_t - y) \, Var \left[X_t^\lambda \right]_y - \beta \int_0^t ds \, \dot{x_s} \left\langle X_s^\lambda ; X_t^\lambda \right\rangle_y$$

Now we can use (5.1.14). But it is valid only if x_t is constant, otherwise is not possible to define a partition function, instead in this case x_t is a time-dependent stochastic process. Now we remind the considerations introduced in Section 5.1.2.2. Since the probe time scale is much slower, it is reasonable to assume that at each time the fluid relaxes to a new equilibrium characterized by the value x_t of the probe. Therefore we can define a equilibrium partition function for each time. Practically we can add the subscript t in (5.1.14).

$$\frac{1}{Z_{x_t}}\int dX\, e^{-\beta U(X,x_t)} X_t^\lambda = \left\langle X^\lambda \right\rangle_y + \beta Var\left[X^\lambda\right]_y (x_t - y)$$

In this context we can define:

$$X_t^\lambda = \left\langle X_t^\lambda \right\rangle + \eta_t \tag{5.1.17}$$

where η_t measures the fluctuation of this average value and it describes the noise perceived by the probe produced by all the particles. Now from (5.1.10):

$$M\ddot{x}_t = -V'(x_t) + X_t^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} x_t = -V'(x_t) + \left\langle X_t^\lambda \right\rangle + \eta_t - \sum_j \frac{\lambda_j^2}{\omega_j^2} x_t$$

Now we can substitute the average value of X^λ expression:

$$M\ddot{x}_t = -V'(x_t) + \frac{1}{Z_{x_t}}\int dX\, e^{-\beta U(X,x_t)} X_t^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} x_t - \beta \int_0^t ds\, \dot{x}_s \left\langle X_s^\lambda; X_t^\lambda \right\rangle_y + \eta_t$$

Now we want to calculate:

$$\frac{1}{\beta}\frac{\partial}{\partial x}\ln Z_{x_t} = \frac{1}{\beta}\frac{1}{Z_{x_t}}\int dX\, e^{-\beta U(X,x_t)}\left(-\beta \frac{\partial U(X,x_t)}{\partial x}\right)$$

$$\frac{1}{\beta}\frac{\partial}{\partial x}\ln Z_{x_t} = \frac{1}{Z_{x_t}}\int dX\, e^{-\beta U(X,x_t)}\left(X^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} x_t\right) = \frac{1}{Z_{x_t}}\int dX\, e^{-\beta U(X,x_t)} X_t^\lambda - \sum_j \frac{\lambda_j^2}{\omega_j^2} x_t$$

Where the free energy

$$\mathcal{F}(x_t) = -k_B T \ln Z_{x_t}$$

Finally:

$$M\ddot{x}_t = -\frac{\partial \mathcal{F}(x_t)}{\partial x} - V'(x_t) - \beta \int_0^t ds\, \dot{x}_s \left\langle X_s^\lambda; X_t^\lambda \right\rangle_y + \eta_t \tag{5.1.18}$$

that is the Langevin equation for the reduced dynamics. In fact we have eliminated integrating out all the degrees of freedom related to the fluid.

5.1.2.7 Second F-D theorem

It is interesting to note that from $X_t^\lambda = \left\langle X_t^\lambda \right\rangle + \eta_t$ we can obtain some information on the noise:

$$\langle \eta_t \rangle = \left\langle X_t^\lambda \right\rangle - \left\langle X_t^\lambda \right\rangle = 0$$

The mean in zero as we expect from a noise. Instead the correlation:

$$\langle \eta_s \eta_t \rangle = \left\langle \left[X_s^\lambda - \left\langle X_s^\lambda \right\rangle\right]\left[X_t^\lambda - \left\langle X_t^\lambda \right\rangle\right] \right\rangle = \left\langle X_s^\lambda; X_t^\lambda \right\rangle$$

We have found a relation between the friction and the correlation over the perturbed average value, but we can solve only the unperturbed ones. Using the smallness of λ we can approximate the perturbed average values. This is easily understandable using linear response theory given that

the perturbation depends on X_t^λ and, then, on λ. Therefore the correction would be of order λ^3. We can ignore it.

$$\langle \eta_s \eta_t \rangle \simeq \left\langle X_s^\lambda; X_t^\lambda \right\rangle_y \tag{5.1.19}$$

Since the integral in the Langevin equation depends on the velocity we can say that:

$$\left\langle X_s^\lambda; X_t^\lambda \right\rangle_y = \gamma\left(t-s\right)$$

where $\gamma\left(t-s\right)$ is the macroscopic friction perceived by the probe. Note that it does not depends only on time t, therefore the integral term in (5.1.18) is not memoryless. We call it memory kernel. Using (5.1.19) we obtain a relation between the friction and the noise:

$$\beta \left\langle \eta_s \eta_t \right\rangle = \gamma\left(t-s\right) \tag{5.1.20}$$

that is the second fluctuation-dissipation relation for a system at equilibrium. Note that using (5.1.4) we can derive the diffusion coefficient perceived by the probe. Therefore integrating out the fluid degrees of freedom we know all the probe motion properties.

5.1.2.8 No interacting particles

The Langevin equation (5.1.18) is different from (5.1.1). Evidently in (5.1.18) there are also conservative forces acting on the probe, but the most important difference is that the latter is not memoryless. In fact the noise correlation is not a delta function as we would expect from a white noise. Now we want to demonstrate that (5.1.1) is a not-interacting particles approximation of (5.1.18). If we consider the expression of X_t^λ in (5.1.19) two sums over the particles appear.

$$\langle \eta_s \eta_t \rangle \simeq \sum_j \sum_{j'} \lambda_j \lambda_{j'} \left\langle X_s^j; X_t^{j'} \right\rangle_y$$

Since the particles are interacting, the two sums are not independent. Suppose that there is no interaction. In this case there is no correlation between different particles, therefore we can eliminate one of the sum.

$$\langle \eta_s \eta_t \rangle \simeq \sum_j \lambda_j^2 \left\langle X_s^j; X_t^j \right\rangle_y \tag{5.1.21}$$

At this level there are two ways in order to demonstrate that the correlation $\langle \eta_s \eta_t \rangle$ is not zero practically only if $s = t$:

- Consider equation (5.1.8) with $x_t = y$ and not interacting particles. If we calculate X_t^j as we did in the second point of the Section 5.1.1.1. We obtain:

$$\left\langle X_s, X_t \right\rangle_y = e^{-\frac{\omega_j^2}{\gamma_j}(t+s)} \left[X_0^2 - 2yX_0 \frac{\lambda_j}{\omega_j^2} + y^2 \left(\frac{\lambda_j}{\omega_j^2}\right)^2 - \sqrt{\frac{2k_BT}{\gamma_j}} \right] +$$

$$+ \left(e^{-\frac{\omega_j^2}{\gamma_j}s} + e^{-\frac{\omega_j^2}{\gamma_j}t} \right) \left(yX_0 \frac{\lambda_j}{\omega_j^2} - y^2 \left(\frac{\lambda_j}{\omega_j^2}\right)^2 \right) + y^2 \left(\frac{\lambda_j}{\omega_j^2}\right)^2 + \left(\frac{2k_BT}{\gamma_j}\right) e^{-\frac{\omega_j^2}{\gamma_j}|s-t|}$$

  Note that the first two couples of terms go to zero exponentially fast if $t \neq s$ and the last one is equal to the one found in Section 5.1.1.1. Note that there is also a constant term, but it is of order λ^2, therefore we can ignore it.

- If the particles are not interacting all the average values in (5.1.21) are the same for all the particles. If N is big the noise correlation is a sum of independent term equally distributed. We can apply the central limit theorem and approximate the noise with a gaussian distribution. This result in the weak coupling limit assures that there is no memory in the noise correlation and using (5.1.20) we can obtain a memoryless friction kernel.

5.1.3 Mobility

From the model described in the previous Section we have understood that the Langevin equation, that is based on the environment degrees of freedom reduction, is derived from the linear response theory. The parameters that appear in the Langevin equation, the friction and the diffusion coefficient perceived by the probe, are properties of the fluid, and not of the probe. Therefore if we know how to integrate out the degrees of freedom of the environment we know everything about the probe motion, even the mobility that is related to the friction via (5.1.6). But, is it actually true? There is another way to derive the mobility of a particle, using the linear response theory. Consider a process v_t that describes the velocity of a probe particle embedded in an equilibrium fluid. Suppose to add a constant force E acting only on the probe, for example an electric field if the probe is electrically charged. The mobility is defined via:

$$\nu = \frac{\partial}{\partial E} \langle v_t \rangle^E \tag{5.1.22}$$

where $\langle\rangle^E$ is the average value made the probability, solution of the Fokker-Plank equation with also the constant force. This mobility definition is more intuitive and it is actually a property of the particle since we perturb it in order to see how it responds to the perturbation. We can demonstrate that this mobility is proportional to the friction that appears in the Langevin equation using (5.1.1). In fact:

$$M\frac{dv_t}{dt} = -M\gamma v_t + \sqrt{2D_v}\,\xi_t + E$$

If we proceed as in Section 5.1.1.1, we obtain:

$$Mv_t = Mv_0 e^{-\gamma t} + \int_0^t ds\, e^{-\gamma(t-s)} \left(E + \sqrt{2D_v}\xi_s\right)$$

Taking the average value

$$\langle v_t \rangle^E = v_0 e^{-\gamma t} + \frac{E}{M}\int_0^t ds\, e^{-\gamma(t-s)}$$

$$\frac{\partial}{\partial E}\langle v_t \rangle^E = \frac{1}{M\gamma}\left(1 - e^{-\gamma t}\right)$$

After few $\frac{1}{\gamma}$ relaxing times the mobility converges to $\frac{1}{M\gamma}$, that is the one due to the fluid, as we expect. Nevertheless, this result is valid only at equilibrium. In fact if we consider a nonequilibrium system the linear response formula is not the Kubo one, used in Section 5.1.2.5, but it depends also on a frenetic term. Due to this contribution the mobility given by (5.1.22) is different from the one given by the fluid. We are going to explain it better in the next Section. In conclusion we present another definition of the mobility that will be more useful in the over-damped limit:

$$\nu = \lim_{t\to\infty} \frac{1}{t} \frac{\partial}{\partial E} \langle x_t \rangle^E$$

It is equivalent, in fact using (5.1.1) in the over-damped limit:

$$\frac{dx_t}{dt} = \sqrt{2D_x}\,\xi_t + \frac{E}{M\gamma}$$

$$\langle x_t \rangle^E = x_0 + \frac{E}{M\gamma} t$$

$$\nu = \lim_{t\to\infty} \frac{1}{t} \frac{\partial}{\partial E} \langle x_t \rangle^E = \frac{1}{M\gamma}$$

5.2 Nonequilibrium Brownian Motion

If we want to describe the motion of a probe in a nonequilibrium fluid we have to introduce an external nonequilibrium force acting on the particles. Here the matter is much more difficult because we want to consider the probe as a perturbation to a reference process that is out of equilibrium. Evidently we need to obtain a Langevin equation for the fluid in contact with a reservoir that depends on its external force and then we should use it to obtain a Langevin equation for the probe. We are going to present the first step in Section 5.2.3 in which we will present the Langevin equation for a nonequilibrium system embedded in an equilibrium fluid. After that, we are going to study the second step in Section 6.

5.2.1 Going beyond equilibrium

For now, we are going to study how the Langevin equation and the moments change in a nonequilibrium context. We will consider a generic system kept out of equilibrium interacting with the environment. If we want to take the system out of equilibrium, we have to modify the deterministic contribution. In fact we can imagine that an external and deterministic force $F_t(x_t)$ acting on the system takes it out of equilibrium. Here we are assuming the force depends on time via the process and explicitly. This is not necessary in order to describe nonequilibrium systems, but for this treatment we consider the most general situation. If we want to consider a system with not-constant temperature we would have to modify also the stochastic term, since the noise depends on temperature. In contrast with the equilibrium case, now we suppose that the moments can depend directly on time. Usually we are interested in a position-dependent force, for this reason we define a new process x_t that describes the probe position and that is related to v_t by:

$$dx_t = v_t dt \tag{5.2.1}$$

Since neither x_t nor v_t are differentiable, it is not possible to determine a time-derivative. Note that if the force depends directly on time, it is no longer necessary that the force is not-conservative to avoid the equilibrium case, since there cannot even exist a stationary distribution. Note that, conceptually, it is similar to consider time-dependent transition rates for the jump processes. Therefore the moments become:

$$A_t(x_t, v_t) = F_t(x_t) - \frac{\partial U(x_t)}{\partial x} - M\gamma v_t$$

$$B(x_t) = 2D_v$$

We have supposed that the diffusion coefficient and the friction are still constant. Note that this is not the most general case. In fact due to the external force they could be no longer constant. There would be a diffusion gradient, in other words another external and deterministic force that should appear in $A_t(x_t)$. If we assume that the friction and the diffusion coefficient are not-constant, they can create interactions that are not found in the equilibrium process. We suppose that these interactions are consequence of a nonequilibrium force $F_t(x_t)$. Therefore if $F_t(x_t)$ would be zero the friction and the diffusion coefficient would be constant. Note that the friction and the diffusion coefficient can be not-constant even if $F_t(x_t) = 0$, but in this case the temperature must be not constant.

5.2.2 Einstein-Smoluchowski relation

We have said that the Einstein-Smoluchowski relation is valid only at equilibrium with constant diffusion coefficient and friction. Nevertheless to define $B(x_t)$ we have used it. In fact we can find a generalization that is meaningful also if the fluid is out of equilibrium:

$$D_x(x_t) = \frac{k_B T}{M\gamma(x_t)} \tag{5.2.2}$$

that is valid point by point (locally). This relation is a consequence of local detailed balance. We have introduced it for jump processes and we have described it as the contact between the mathematical transition rates and the physics. In fact we have shown that the ratio of making a transition with respect to the opposite one depends on the entropic flux exchanged during the transition. For the continuous Markov process there are no longer transition rates. Then, to introduce the local detailed balance, we have to understand how to define the trajectories probability and even the trajectories themselves. We are going to do it in the following.

But, for now we want to give an intuitive reason for the validity of (5.2.2). The local detailed balance physical meaning is related to the thermodynamical way of describing nonequilibrium systems. In fact if a system is out of equilibrium (for example because the temperature or the pressure is not homogeneous) it can be thought as a sum of two or more subsystems each one at equilibrium that weakly interacts with each other. Since each part of the system is detailed balance, or rather, at equilibrium, the equilibrium relations like (5.1.4) are satisfied. Therefore we can talk about local equilibrium with local equilibrium properties. In this way, we give a physical meaning to the stochastic contribution in the Langevin equation for a nonequilibrium system. The new Einstein-Smoluchowski relation is physically different from (5.1.4) because it is no longer the second fluctuation-dissipation theorem. We will obtain a new expression for it, that will be more complicated, in the last Section in which we are going to obtain an expression for the drag coefficient $\gamma(x_t)$. Note that this is true only if the local detailed balance is valid. Otherwise a correction to Einstein-Smoluchowski relation is necessary.

In order to obtain nonequilibrium we have said that it is not necessary a not-constant diffusion coefficient and friction. Therefore a constant coefficients version of (5.2.2) exists. Even with constant parameter the Einstein-Smoluchowski relation is not equal to the second fluctuation-dissipation relation. In fact the mobility that appears in (5.2.2) is not the mobility of the system described by the Langevin equation. The mobility is given by (5.1.22) via linear response theory, but in a nonequilibrium regime the response formula depends also on the frenetic contribution.

According to it, out of equilibrium the mobility is indeed a property of the probe and it cannot be derived only by the environment. The interaction with the environment, according to the local detailed balance, gives the entropy flux from the system to the environment. But it does not say anything about the dynamical activity that gives its contribution only when the time-reversal symmetry is broken.

Furthermore, equation (5.2.2) tells us another important aspect of nonequilibrium dynamics satisfying local detailed balance: the diffusion coefficient and friction fates are related. Note that the diffusive force does not depend directly on time. Instead the dependence on the process of the friction is indeed a nonequilibrium aspect. Therefore we could have a system at equilibrium with a diffusive force if the friction would be constant. But this is impossible because according to (5.2.2) or they are both constant (equilibrium) or they are both not-constant (nonequilibrium). In addition if the temperature is time-dependent, according to (5.2.2) the diffusion coefficient and the friction must depend explicitly on time. The contrary is not true: if the diffusion coefficient and friction explicit dependence on time is the same, it could be cancelled out causing a time-independent temperature.

5.2.3 Langevin equation

In this Section we want to obtain a Langevin equation that describes a nonequilibrium system interacting with an equilibrium environment under the local detailed balance assumption. In Section 2.2.2 we have said that the local detailed balance could concern any of the three equilibrium properties (thermal, chemical, mechanics). Therefore even if the temperature is constant, since the nonequilibrium regime is produced by an external force, the local detailed balance must be referred to the heat exchanged between system and environment due to the nonequilibrium force. We suppose that the noise perceived by the system is Gaussian. Furthermore for simplicity we will work in the over-damped limit. Under these considerations the required Langevin equation is presented in [2]:

$$dx_t = \frac{1}{M\gamma\left(x_t\right)}\left[F_t\left(x_t\right) - \nabla U\left(x_t\right)\right]dt + \nabla D_x\left(x_t\right) + \sqrt{2D\left(x_t\right)}dW_t$$

We are considering the most general case with not-constant friction and diffusion coefficient. Since the external force $F_t\left(x_t\right)$ continues to keep the system out of equilibrium we expect that there will be no relaxation to equilibrium (in general not even to a nonequilibrium stationary state). Here we require that the external force does not act on the environment degrees of freedom, otherwise the fluid will be modified not also by the presence of the probe (that we consider as a perturbation) but also by the external force. It is a necessary condition to determine the Langevin equation, because the interaction with the environment degrees of freedom is in the noise term that as we have said is obtained through the linear response theory. This condition is necessary only out equilibrium, while at equilibrium only the assumption on the different time scales was necessary. As the explanation about the nonequilibrium mobility this is a consequence of the frenetic term that makes more difficult to understand the energy exchange between system and environment.

Since the dynamics of the system is detailed balance with the environment, there is a relation between $D_x\left(x_t\right)$ and $\gamma\left(x_t\right)$ given by (5.2.2). If we introduce the mobility:

$$dx_t = \nu\left(x_t\right)\left[F_t\left(x_t\right) - \nabla U\left(x_t\right)\right]dt + \nabla D_x\left(x_t\right)dt + \sqrt{2D_x\left(x_t\right)}dW_t \tag{5.2.3}$$

This is the Langevin equation for the over-damped limit. In this limit the velocity is proportional

to the external force via the mobility. In this case we have eliminated a process from the equation, therefore we can study it with (4.3.1). The Fokker-Planck equation associated to (5.2.3) is:

$$\frac{\partial P_t(x)}{\partial t} = -\frac{\partial}{\partial x}\left[\nu(x) F_t(x) P_t(x) - \nu(x)\frac{\partial U(x)}{\partial x}P_t(x) + \frac{\partial D_x(x)}{\partial x}P_t(x) - \frac{\partial D_x(x) P_t(x)}{\partial x}\right]$$

$$\frac{\partial P_t(x)}{\partial t} = -\frac{\partial}{\partial x}\left[\nu(x) F_t(x) P_t(x) - \nu(x)\frac{\partial U(x)}{\partial x}P_t(x) - D_x(x)\frac{\partial P_t(x)}{\partial x}\right]$$

Note that the inhomogeneity of the diffusion coefficient does not produce new terms in the Fokker-Planck equation. According to (4.3.2) we have introduced the forward generator L_t^+. Here Its adjoint is called backward generator and it is an operator defined as:

$$L_t = \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]\cdot\nabla + \nabla D_x(x_t)\cdot\nabla + D_x(x_t)\cdot\nabla^2 \tag{5.2.4}$$

Or analogously:

$$L_t = \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]\cdot\nabla + \nabla\left(D_x(x_t)\cdot\nabla\right)$$

Therefore the moments of the over-damped process are:

$$A_t(x_t) = \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right] + \nabla D_x(x_t)$$

$$B(x_t) = 2D_x(x_t)$$

5.3 Entropy

The Langevin and Fokker-Planck equations are useful tools in order to study continuous stochastic processes. In fact their structure does not change if we consider more difficult or more general situations. If we describe the position of a probe with the process x_t we can describe both equilibrium or nonequilibrium condition, we have only to modify the moments. But they are mathematical equations and then, in order to make the models that we are going to describe with these equations physically consistent, we have to introduce more physics in them. For this reason we will obtain a stochastic entropy depending on the trajectories from the Langevin equation. The entropy is the most useful physical instrument in order to study and understand nonequilibrium. Consider a system that can interact thermally with the environment at constant temperature T. Generally, such a system can be at equilibrium or out of equilibrium. A nonequilibrium system differs from an equilibrium one for many aspects. Two of the most important are:

- it dissipates continuously energy to maintain the nonequilibrium condition.
- there is no longer invariance under time-reversal

Therefore we have to introduce a quantity that measures the amount of time-reversal breaking starting from the trajectories.

$$S_\mu(\omega) = \ln\frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}_{\mu_t}(\theta\omega)} \tag{5.3.1}$$

where θ is the time reversal operator acting on trajectories in the following way:

$$(\theta\omega)_s = \omega_{t-s}$$

and μ is the initial distribution for process x_s while μ_t is the initial distribution for the opposite process x_{t-s}. $S_\mu(\omega)$ depends on the initial distribution μ and on the trajectory ω. We are interested in the average values over all the trajectories starting from μ:

$$\langle S_\mu(\omega)\rangle_\mu = \left\langle \ln \frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}_{\mu_t}(\theta\omega)} \right\rangle_\mu$$

Now it is interesting to note:

$$\left\langle \frac{\mathcal{P}_{\mu_t}(\theta\omega)}{\mathcal{P}_\mu(\omega)} \right\rangle_\mu = \int_S d\omega\, \mathcal{P}_\mu(\omega) \frac{\mathcal{P}_{\mu_t}(\theta\omega)}{\mathcal{P}_\mu(\omega)}$$

$$\left\langle \frac{\mathcal{P}_{\mu_t}(\theta\omega)}{\mathcal{P}_\mu(\omega)} \right\rangle_\mu = \int_S d\omega\, \mathcal{P}_{\mu_t}(\theta\omega) = 1$$

Because $\mathcal{P}_{\mu_t}(\theta\omega)$ is a probability over the trajectories and it is normalized. Therefore:

$$\left\langle e^{-S_\mu(\omega)} \right\rangle_\mu = \left\langle \frac{\mathcal{P}_{\mu_t}(\theta\omega)}{\mathcal{P}_\mu(\omega)} \right\rangle_\mu = 1$$

Now, if we use the Jensen inequality (due to the exponential convexity)

$$\left\langle e^{-S_\mu(\omega)} \right\rangle_\mu \geq e^{-\langle S_\mu(\omega)\rangle_\mu}$$

And finally:

$$\langle S_\mu(\omega)\rangle_\mu \geq 0$$

Under this consideration we can give a physical meaning to the amount of time-reversal breaking: it is the entropy production during the time interval $[0, t]$. We are interested also in the entropy production rate. In other words, the instantaneous average entropy production.

$$\frac{dS_t}{dt} = \lim_{t\to 0} \frac{1}{t} \left\langle \ln \frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}_{\mu_t}(\theta\omega)} \right\rangle_\mu$$

If we consider again (5.3.1) we can separate the dependence on the initial distribution:

$$S_\mu(\omega) = \ln \frac{\mu(x_0)}{\mu_t(x_t)} \frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)}$$

where x_0 is the value assumed by the process at time $t = 0$ and x_t is the one assumed at the end of the trajectory. Then:

$$S_\mu(\omega) = \ln \frac{\mu(x_0)}{\mu_t(x_t)} + \ln \frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)}$$

If we take the average values:

$$\langle S_\mu(\omega)\rangle_\mu = \left\langle \ln \frac{\mu(x_0)}{\mu_t(x_t)} \right\rangle_\mu + \left\langle \ln \frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)} \right\rangle_\mu$$

It is easy to note that the first contribution in the left-hand side is the Shannon entropy:

$$\left\langle \ln \frac{\mu\left(x_0\right)}{\mu_t\left(x_t\right)} \right\rangle_\mu = -\left[\int_S dx\, \mu_t\left(x\right) \ln \mu_t\left(x\right) - \int_S dx\, \mu\left(x\right) \ln \mu\left(x\right) \right]$$

Now, if we consider the instantaneous entropy production this contribution becomes the Shannon entropy change. Starting from the entropy production we have found two contributions, now we want to give them a physical meaning. Consider a system that can interact thermally with the environment at constant temperature T. In order to study it, we can define two entropies:

- system entropy ($d_i S$): this contribution describes the entropy change in the system. Statistically it is represented by the Shannon entropy via the process probability $P_t\left(x\right)$:

$$S_i\left(t\right) = -\int dx\, P_t\left(x\right) \ln P_t\left(x\right) \tag{5.3.2}$$

  We have already explained why the system entropy can be described by the Shannon entropy in Section 2.2.1. Therefore the system entropy corresponds to the first contribution found from (5.3.1).

- environment entropy ($d_e S$): this contribution describes the entropy flux from the system to the environment. Evidently if the system is isolated this contribution is zero. According to what we have said we expect that the environment entropy is described by the second contribution in (5.3.1). A priori this is not evident, we are going to demonstrate it in the following Section with the local detailed balance assumption.

Summing them we can define the total change of entropy that we have called entropy production:

$$\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_e S}{dt}$$

What we have said about entropy is equivalent to (2.2.9) as we expect. Note that all these entropies are adimensional.

5.3.1 Stationarity

A system is in a stationary condition if its probability $P_t\left(x\right)$ does not depend on time. But this is a mathematical definition. A possible physical definition is by the time-independence of the physical quantities (i.e. currents and entropy). A stationary condition can be of equilibrium or nonequilibrium, but this distinction is not completely evident from the Fokker-Planck equation. In fact stationarity condition implies that the current must be constant, but the constant can be arbitrarily zero or not. Now we are going to explain the distinction between equilibrium or nonequilibrium stationarity using the entropy. First of all we note that the equilibrium state for a system is unique because it derives from imposing the maximum entropy condition. Instead there could exist more than one nonequilibrium stationary states with different entropy values. According to (5.3.2) the change of system entropy is:

$$\frac{dS_i\left(t\right)}{dt} = -\int dx\, \frac{dP_t\left(x\right)}{dt} \ln P_t\left(x\right) - \int dx\, \frac{dP_t\left(x\right)}{dt} = -\int dx\, \frac{dP_t\left(x\right)}{dt} \ln P_t\left(x\right)$$

Using the probability conservation the last term is zero. Then:

$$\frac{dS_i(t)}{dt} = -\int dx \frac{dP_t(x)}{dt} \ln P_t(x)$$

It is evident that if:

$$\frac{dP_t(x)}{dt} = 0 \quad \Longrightarrow \quad \frac{dS_i(t)}{dt} = 0$$

This condition says that all the entropy produced by the system goes away from the system. But it does not tells if this entropy is zero or not. If the system is isolated this condition is sufficient to assure the equilibrium. But in general we have to consider the entropy flux that goes away from the system. If it is zero the system is at equilibrium with the environment and the total entropy does not change (the system has reached the maximum value of entropy), otherwise it is in a nonequilibrium stationary state and the total entropy changes due to the environment entropy change. Therefore the key is to find the environment entropy expression.

$$S_e(\omega) = \ln \frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)} \tag{5.3.3}$$

Evidently if the two probabilities are equal, the process is invariant under time reversal and the system satisfies detailed balance relation (4.3.6). Equation (5.3.3) depends on the trajectory, for this reason we will take the average value over all the trajectories with initial distribution μ. Furthermore this result gives the average entropic flux during the interval $[0, t]$, therefore if we divide it by t and we take the limit $t \to 0$ we obtain an instantaneous average entropy:

$$\frac{d_e S(t)}{dt} = \lim_{t\to 0} \frac{1}{t} \left\langle \ln \frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)} \right\rangle_\mu$$

5.3.1.1 Equilibrium or nonequilibrium

Now we want to determine $\mathcal{P}_{x_0}(\omega)$. Consider the Langevin equation:

$$M dv_t = F(x_t)\, dt - M\gamma v_t dt + \sqrt{2D_v}\, dW_t$$

To have a stationary state the external force must not depend directly on time. This equation is an update relation that describes the evolution of the process for each infinitesimal interval dt. All the terms that appear in the Langevin equation are deterministic except for the white noise. In (4.5.3) we have defined the noise, therefore we can obtain from it the Wiener process dW_t. The equation (5.3.8) is an update relation that describes the evolution of the process for each infinitesimal interval dt. Evidently, it is in analogy with the sequence of configuration for the jump processes. Therefore the probability of going from x_t to x_{t+dt} and from v_t to v_{t+dt} during dt

$$P(x_{t+dt}, v_{t+dt} \mid v_t, x_t)\, dx_t dv_t$$

is determined by:

$$dW_t = \frac{1}{\sqrt{2D_v}} \left[M dv_t - F(x_t)\, dt + M\gamma v_t dt \right]$$

Now we can use (4.5.2). We know that the Wiener process follows a Gaussian distribution:

$$P(dW_t) = \frac{1}{N} e^{-\frac{(dW_t)^2}{2dt}}$$

where N is a normalization constant. If we substitute the expression of dW_t:

$$P\left(dW_t\right) = \frac{1}{N}\, e^{-\mathcal{L}(v_t, x_t, dv_t)} dv_t dx_t$$

where:

$$\mathcal{L}\left(x_t, v_t, dv_t\right) = \frac{1}{4D_v dt}\left[dv_t - F\left(x_t\right) dt + \gamma v_t dt\right]^2$$

Or equivalently

$$\mathcal{L}\left(x_t, v_t, dv_t\right) = \frac{dt}{4D_v}\left[M\frac{dv_t}{dt} - F\left(x_t\right) + M\gamma v_t\right]^2$$

$P\left(dW_t\right)$ describes only the probability during the infinitesimal time dt. If we subdivide the time interval $[0, t]$ in n infinitesimally small time intervals dt we can describe the probability of the trajectory ω using the probability over each subinterval dt. Here we have to introduce Markov approximation. In this way, as we have done for the jump processes, the probability $\mathcal{P}_\mu\left(\omega\right)$ is given by a product of probabilities $P\left(dW_t\right)$. As a consequence of the product we obtain a sum in the exponential of all the small contributions along the trajectory. Therefore:

$$\mathcal{P}_{x_0}\left(\omega\right) = \frac{1}{N^n}\, \exp\left\{-\frac{1}{4D_v}\sum_{i=0}^{n-1}\left[M\frac{\left(v_{t_{i+1}} - v_{t_i}\right)}{dt} - F\left(x_{t_i}\right) + M\gamma v_{t_i}\right]^2 dt\right\} \tag{5.3.4}$$

By definition of Itô integral we can write:

$$\mathcal{P}_{x_0}\left(\omega\right) = \frac{1}{\mathcal{N}}\, \exp\left\{-\frac{1}{4D_v}\int_0^t \left[M\dot{v}_s - F\left(x_s\right) + M\gamma v_s\right]^2 ds\right\}$$

where $\mathcal{N}$ is a new normalization coefficient obtained in the limit $n \to \infty$. If we make explicit the square:

$$\mathcal{P}_{x_0}\left(\omega\right) = \frac{1}{\mathcal{N}}\, \exp\left\{-\frac{1}{4D_v}\int_0^t \left[\left(M\dot{v}_s\right)^2 + F\left(x_s\right)^2 + \left(M\gamma v_s\right)^2 + 2M^2\gamma v_s\dot{v}_s\right] ds\right\} \cdot$$

$$\cdot \exp\left\{-\frac{1}{4D_v}\int_0^t \left[-2F\left(x_s\right) M\dot{v}_s - 2F\left(x_s\right) M\gamma v_s\right] ds\right\}$$

We can rewrite it as:

$$\mathcal{P}_{x_0}\left(\omega\right) = \frac{1}{\mathcal{N}}\, \exp\left\{-\frac{1}{4D_v}\int_0^t \left[\left(M\dot{v}_s\right)^2 + F\left(x_s\right)^2 + \left(M\gamma v_s\right)^2 - 2F\left(x_s\right) M\dot{v}_s\right] ds\right\} \cdot$$

$$\cdot \exp\left\{-\frac{1}{4D_v}\int_0^t 2M^2\gamma v_s dv_s + \frac{1}{4D_v}\int_0^t 2F\left(x_s\right) M\gamma dx_s\right\}$$

Since we are interested in studying the time symmetry, we have to pass from Itô to Stratonovitch integral using (4.6.3). Evidently all the integrals are ds are time symmetric. Instead:

$$\frac{1}{4D_v}\int_0^t 2M^2\gamma v_s dv_s = \frac{1}{4D_v}\int_0^t 2\gamma M^2 v_s \circ dv_s - \frac{\gamma M^2}{2}\int_0^t ds$$

For the last integral in dx_s:

$$\frac{1}{4D_v}\int_0^t 2MF(x_s)\,\gamma dx_s = \frac{1}{4D_v}\int_0^t 2M\gamma F(x_s)\circ dx_s - \frac{M\gamma}{2}\int_0^t \nabla F(x_s)\,ds$$

We can therefore rewrite the trajectory probability:

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{\mathcal{N}}\exp\left\{-\frac{1}{4D_v}\int_0^t\left[(M\dot{v}_s)^2 + F(x_s)^2 + (M\gamma v_s)^2 - 2\frac{F(x_s)}{M}\dot{v}_s - 2D_v\gamma M^2\right]ds\right\}\cdot$$

$$\cdot\exp\left\{\frac{\gamma M}{2}\int_0^t \nabla F(x_s)\,ds\right\}\cdot\exp\left\{-\frac{\beta M}{2}\int_0^t v_s\circ dv_s + \frac{\beta}{2}\int_0^t F(x_s)\circ dx_s\right\}$$

We have also used (5.1.2). Now we want to consider the opposite trajectory. The $\theta\omega$ initial time is obviously 0. But if we want to refer x_{t-s} to x_s evidently the initial time will be t. Therefore the first time interval of width dt is $t_{n-1} - t_n$. It is evident that if we gather a minus for all the contributions $x_{t_{i+1}} - x_{t_i}$ we can obtain the first term in (5.3.4). The difference $x_{t_{i+1}} - x_{t_i}$ is antisymmetric under time reversal. This is not true for the difference $v_{t_{i+1}} - v_{t_i}$ because we have to take into account that if we reverse the trajectory also the velocity values must change. Therefore this difference is time-symmetric.

$$\mathcal{P}_{x_t}(\theta\omega) = \frac{1}{\mathcal{N}}\exp\left\{-\frac{1}{4D_v}\int_0^t\left[(M\dot{v}_s)^2 + F(x_s)^2 + (M\gamma v_s)^2 - 2\frac{F(x_s)}{M}\dot{v}_s - 2D_v\gamma M^2\right]ds\right\}\cdot$$

$$\cdot\exp\left\{-\frac{\gamma M}{2}\int_0^t \nabla F(x_s)\,ds\right\}\cdot\exp\left\{\frac{\beta M}{2}\int_0^t v_s\circ dv_s - \frac{\beta}{2}\int_0^t F(x_s)\circ dx_s\right\}$$

We can say that the integral in dx_s is antisymmetric just because we have considered the Stratonovitch interpretation, in fact the force in each subinterval $[t_i, t_{i+1}]$ is evaluated in the middle point. Then, only the last term has changed sign, in fact the force does not change if we invert the time. If we consider the ratio of $\mathcal{P}_{x_0}(\omega)$ over $\mathcal{P}_{x_t}(\theta\omega)$ we obtain:

$$\frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)} = \exp\left\{\beta\int_0^t F(x_s)\circ dx_s - \beta M\int_0^t v_s\circ dv_s\right\}$$

By definition (5.3.3):

$$S_e(\omega) = \beta\int_0^t F(x_s)\circ dx_s - \beta M\int_0^t v_s\circ dv_s$$

The entropy flux depends on two terms. The first can be seen as the work made by the external force. The second one, instead, given the kinetic energy difference of the system between the initial and the final step of the trajectory. It is a boundary term that depends only on the v_t and v_0, therefore choosing the trajectory it could be zero. Therefore the external force is the responsible of time-reversal symmetry breaking. Now we want to consider some cases:

- If $F(x_s) = 0$, the entropy flux is zero and therefore the system is at equilibrium. This is meaningful because this case coincides with the Ornstein-Uhlenbeck process in the over-damped limit. We can conclude that:

$$\mathcal{P}_{x_0}(\omega) = \mathcal{P}_{x_t}(\theta\omega)$$

There is no time-reversal symmetry breaking and the probability $P_t(x)$ satisfies detailed balance (4.3.6) from the Fokker-Planck equation. Evidently if we have to consider a trajectory that produces a change in the kinetic energy, there would be a not-zero entropy flux. But only the average entropy flux has a physically meaning. If we take the average values we have to take into account all the trajectories and surely there would be one that produces the opposite change in the kinetic energy. Therefore if $F(x_s) = 0$ then $\langle S_e(\omega)\rangle_\mu = 0$.

- if $F(x_s) = -\nabla U(x_s)$ is a conservative force, then:

$$S_e(\omega) = -\beta \int_0^t \nabla U(x_s) \circ dx_s - \beta M \int_0^t v_s \circ dv_s = -\beta \left[U(x_t) - U(x_0)\right] - \frac{\beta M}{2}\left[v_t^2 - v_0^2\right]$$

The entropy flux depends only on the initial and final value of the potential (and of the kinetic energy). Evidently if we consider $U(x_t) = U(x_0)$, the entropy flux will be zero and the system will be at equilibrium. Note that it is in agreement with Fokker-Planck equation. If the external force in the moment $A(x_t)$ can be written as a potential the stationary equation is solved by a Maxwell-Boltzmann solution. This is not a sufficient condition to assure equilibrium, but it becomes sufficient if $F(x_s)$ is a conservative force.

- If $F(x_s)$ is not a conservative force generally we can write it as the sum of a conservative contribution and a nonconservative one. Therefore using (4.6.4):

$$S_e(\omega) = -\beta \int_0^t \left[-\nabla U(x_s) + W(x_s)\right] \circ dx_s - \beta M \int_0^t v_s \circ dv_s$$

$$S_e(\omega) = -\beta \left[U(x_t) - U(x_0)\right] - \frac{\beta M}{2}\left[v_t^2 - v_0^2\right] + \beta \int_0^t W(x_s) \circ dx_s$$

The first contribution is the system energy change due to the external force, the second one is always the change in kinetic energy, instead the integral (that is antisymmetric since it is in the Stratonovitch sense) describes the work made on the system by the environment. As we can expect $S_e(\omega)$ is, via the first principle of thermodynamics, the heat exchanged from the system to the environment multiplied by β. The nonequilibrium force does not act directly on the environment degrees of freedom, instead it acts indirectly due to the energy exchange via the entropy flux.

We want to treat the case in which $F(x_s) = F$. A constant force can be derived by a linear potential and therefore it is conservative, but it is not always true, it depends on the kind of system we are describing. For example if we consider the diffusion on a circle, F cannot be a conservative force due to the fact that the manifold (S^1) is not simply connected. In this case the entropy flux is not zero and we are considering a nonequilibrium stationary state with entropy flux:

$$S_e(\omega) = \beta F \int_0^t dx_s = \beta F (x_t - x_0)$$

In fact, if we consider, as a trajectory, a whole circle the entropy flux would be $2\beta F\pi$. Note that this is strictly due to the manifold S^1. For example we consider as constant force the gravity acting on a probe in a box filled by particles. We expect that the probability of finding the particles at the bottom of the box will be greater. According to the current expression there will be a diffusion force proportional to probability gradient that tends to equilibrate the probability through a stochastic

current from the bottom to the top. In the long-time limit these two contributions tend to balance each others assuring equilibrium and then, no entropic flux. In this example we have supposed that the external force acts on the probe will not affect the fluid dynamics. As we have said this is an important requirement. Physically, it is reasonable that the gravity does not act on the particles because the probe mass is much bigger than the particles one ($M \gg m$).

5.3.2 Entropy flux and local detailed balance

In this Section we demonstrate that (5.2.2) is a consequence of assuming local detailed balance validity. We will proceed in the same way explained in the previous Section, but now we are considering a Langevin equation like

$$dx_t = \nu_t(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]dt + \nabla D_t(x_t)\,dt + \sqrt{2D_t(x_t)}dW_t$$

The probability of going from x_t to x_{t+dt} during dt

$$P(dW_t) = \frac{1}{N}\,e^{-\frac{(dW_t)^2}{2dt}}$$

where N is a normalization constant. If we substitute the expression of dW_t:

$$P(dW_t) = \frac{1}{N}\,e^{-\mathcal{L}(x_t,dx_t)}dx_t$$

where:

$$\mathcal{L}(x_t, dx_t) = \frac{dt}{4D_t(x_t)}\left[\frac{dx_t}{dt} - \nu_t(x_t)\left[F_t(x_t) - \nabla U(x_t)\right] - \nabla D_t(x_t)\right]^2$$

$P(dW_t)$ describes only the probability during the infinitesimal time dt. If we subdivide the time interval $[0,t]$ in n infinitesimally small time intervals dt we can describe the probability of the trajectory ω using the probability over each subinterval dt. Since the dynamics is Markovian the probability $\mathcal{P}_{x_0}(\omega)$ is given by a product of probabilities $P(dW_t)$ over each independent subinterval. As a consequence of the product we obtain a sum in the exponential of all the small contributions along the trajectory.

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{N^n}\,exp{-}\left\{\sum_{i=0}^{n-1}\frac{1}{4D_{t_i}(x_{t_i})}\left[\frac{\left(x_{t_{i+1}} - x_{t_i}\right)}{dt} - \nu_{t_i}(x_{t_i})\left[F_{t_i}(x_{t_i}) - \nabla U(x_{t_i})\right] - \nabla D_{t_i}(x_{t_i})\right]^2 dt\right\} \tag{5.3.5}$$

By definition of Itô integral

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{\mathcal{N}}\,\exp\left\{-\int_0^t ds\,\frac{1}{4D_s(x_s)}\left[\dot{x}_s - \nu_s(x_s)\left[F_s(x_s) - \nabla U(x_s)\right] - \nabla D(x_s)\right]^2\right\} \tag{5.3.6}$$

where $\mathcal{N}$ is a new normalization constant. Since we are going to consider only the ratio of probabilities of trajectories we are not interested in finding $\mathcal{N}$. We are interested in studying the time symmetry, then we have to pass from Itô to Stratonovitch integral. Using (4.6.3):

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{\mathcal{N}}\,\exp\left\{\int_0^t dx_s \circ \frac{\nu_s(x_s)}{2D_s(x_s)}\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_s(x_s)}{\nu_s(x_s)}\right]\right\}\exp\left\{\int_0^t ds\,\mathscr{G}_s(x_s)\right\}$$

we can separate the integral in one antisymmetric under time reversal contribution plus a symmetric one depending on $\mathscr{G}_s(x_s)$ function of time and of the process. We do not need to write explicitly the $\mathscr{G}_s(x_s)$ since in the ratio of probabilities this contribution cancels out. Now we consider the opposite trajectory. The $\theta\omega$ initial time is obviously 0. But, if we want to refer it to the trajectory ω, evidently the initial time will be t. Therefore the first time interval of width dt is $t_{n-1} - t_n$. It is evident that if we gather a minus for all the contributions $x_{t_{i+1}} - x_{t_i}$ we can obtain the first term in (5.3.5). The difference $x_{t_{i+1}} - x_{t_i}$ is antisymmetric under time reversal.

$$\mathcal{P}_{x_t}(\theta\omega) = \frac{1}{\mathcal{N}} \exp\left\{-\int_0^t dx_s \circ \frac{\nu_s(x_s)}{2D_s(x_s)}\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_s(x_s)}{\nu_s(x_s)}\right]\right\} \exp\left\{\int_0^t ds\, \mathscr{G}_s(x_s)\right\}$$

If we consider the ratio:

$$\frac{\mathcal{P}_{x_0}(\omega)}{\mathcal{P}_{x_t}(\theta\omega)} = \exp\left\{\int_0^t dx_s \circ \frac{\nu_s(x_s)}{D_s(x_s)}\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_s(x_s)}{\nu_s(x_s)}\right]\right\} \tag{5.3.7}$$

If local detailed balance is satisfied, the logarithm of 5.3.7 must be equal to the entropy flux $S_e(\omega)$ from the system to the environment along the trajectory ω. Therefore in the exponential there must be forces divided by $k_B T$. Therefore:

$$S_e(\omega) = \int_0^t dx_s \circ \beta_s\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_s(x_s)}{\nu_s(x_s)}\right]$$

This implies the validity of (5.2.2).

5.3.3 Entropy excess

5.3.3.1 Beyond stationarity

A nonequilibrium system dissipates continuously energy to maintain the nonequilibrium condition. In fact the energy to keep the system out of equilibrium is supplied by an external force as work made on the system. During the time-interval $[0, t]$ the energy input in the system is:

$$W_t = \int_0^t F_s(x_s) \circ dx_s$$

This energy will cause an entropy production into the system that we are going to call dS. Evidently this contribution is irreversible and therefore it breaks the time-reversal symmetry of the system. It corresponds to (5.3.1). An obvious question would be: where does the energy given to the system go? The answer is heat exchanged from the system to the environment. This heat divided by the temperature produces an entropic flux $d_e S$. Is this contribution representing all the energy input in the system? Generally it does not, but this question gives origin to an important distinction for nonequilibrium systems:

- if the entropic flux balances the entropy production the system is in a stationary condition. All the entropy produced is taken out of the system and the system entropy does not change in time:
$$\frac{d_i S}{dt} = 0 \qquad \frac{d_e S}{dt} > 0$$
The stationary state is a particular regime in which there is no dependence on time as in equilibrium, therefore there is invariance under time-translations. But, nevertheless there is

no time-reversal symmetry due to irreversible entropy production and to the currents. In this case all the energy input into the system will go out as heat exchange and it increases the environment entropy.

- if the entropic flux does not balance the entropy production the system we cannot talk about a stationary condition. The system continues to evolve with increasing time and therefore there is no invariance under time translations. It is evident that since not all the energy put in the system goes out in the form of entropic flux there will be a variation in the system energy according to the first principle of thermodynamics. But it could be even more difficult, for example the excess energy could be used for chemical reactions or phase transitions.

This distinction will be the starting point. In fact, the stationary state has already been studied. In contrast, what happens far from the stationarity is almost unknown. Therefore, using a Markov process, we are going to study some properties of the not-stationary dynamics because, as we have said, the physical opportunities are numerous. We are going to start from the entropic aspect. We are interested in evaluating the entropy variation due to the presence of an external force in a system at equilibrium. The way of proceeding is to refer the dynamics with the force to one without the force and it is similar to what we have done in the last Section. In this Section we will also demonstrate that (5.2.2) is a consequence of local detailed balance condition for the entropy flux.

5.3.3.2 Trajectories probability

The starting point is the Langevin equation in the over-damped limit with the external nonequilibrium force:

$$dx_t = \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]dt + \nabla D_x(x_t)\,dt + \sqrt{2D_x(x_t)}dW_t \tag{5.3.8}$$

Now the temperature is constant. We are interested in the entropy production due to the external force $F_t(x_t)$ that brings the system out of equilibrium. In fact we suppose that the initial system is at equilibrium and at time $t = 0$ the external force starts to act on the system. The energy input into the system by the environment divided by its temperature is not generally the flux entropy from the environment to the system (in other words there is no stationary condition). Therefore we are interested in finding the entropy flux expression. Generally at equilibrium there could be also an external conservative force produced by the potential $U(x_t)$. The probability of going from x_t to x_{t+dt} during dt is determined by:

$$dW_t = \frac{1}{\sqrt{2D_x(x_t)}}\left[dx_t - \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]dt - \nabla D_x(x_t)\,dt\right]$$

As we have done we can define the $P(dW_t)$ with

$$\mathcal{L}(x_t, dx_t) = \frac{dt}{4D_x(x_t)}\left[\frac{dx_t}{dt} - \nu(x_t)\left[F_t(x_t) - \nabla U(x_t)\right] - \nabla D_x(x_t)\right]^2$$

As we have done in the previous Section we can obtain $\mathcal{P}_\mu(\omega)$:

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{N^n}\,exp\left\{-\sum_{i=0}^{n-1}\frac{1}{4D_x(x_{t_i})}\left[\frac{\left(x_{t_{i+1}} - x_{t_i}\right)}{dt} - \nu(x_{t_i})\left[F_{t_i}(x_{t_i}) - \nabla U(x_{t_i})\right] - \nabla D_x(x_{t_i})\right]^2 dt\right\} \tag{5.3.9}$$

By definition of Itô integral:

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\int_0^t ds \frac{1}{4D_x(x_s)} \left[\dot{x}_s - \nu(x_s)\left[F_s(x_s) - \nabla U(x_s)\right] - \nabla D_x(x_s)\right]^2 \right\} \quad (5.3.10)$$

Since we are going to consider only the ratio of probabilities of trajectories we are not interested in finding $\mathcal{N}$. We can rewrite the exponential argument expanding the square:

$$Arg[x_s] = \int_0^t ds \frac{\dot{x}_s^2 + \nu^2(x_s)\left[F_s(x_s) - \nabla U(x_s)\right]^2 + (\nabla D_x(x_s))^2 + 2\nu(x_s) F_s(x_s) \nabla D_x(x_s)}{4D_x(x_s)} -$$

$$- \int_0^t ds \frac{2\nu(x_s)\nabla U(x_s)\nabla D_x(x_s)}{4D_x(x_s)} - \int_0^t dx_s \frac{\nu(x_s)}{D_x(x_s)}\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_x(x_s)}{\nu(x_s)}\right]$$

Here we can use (5.2.2):

$$Arg[x_s] = \int_0^t ds \frac{\left[\dot{x}_s^2 + \nu^2(x_s)\left[F_s(x_s) - \nabla U(x_s)\right]^2 + (\nabla D_x(x_s))^2\right]}{4D_x(x_s)} + \frac{\beta}{2}\int_0^t ds\, F_s(x_s)\nabla D_x(x_s) -$$

$$-\frac{\beta}{2}\int_0^t ds\, \nabla U(x_s)\nabla D_x(x_s) - \frac{\beta}{2}\int_0^t dv_s\, \dot{x}_s\left[F_s(x_s) - \nabla U(x_s) + \frac{\nabla D_x(x_s)}{\nu(x_s)}\right]$$

5.3.3.3 Action

Now we want to compare this probability to the one for the equilibrium dynamics; in other words, when $F = 0$. For the equilibrium dynamics as $\mathcal{P}^0_{x_0}(\omega)$:

$$\mathcal{P}^0_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\frac{1}{4D_x}\int_0^t ds\, \left[\dot{x}_s + \nu\nabla U(x_s)\right]^2 \right\}$$

At equilibrium condition we have to assume D and ν constant. Also for $\mathcal{P}^0_\mu(\omega)$ we can rewrite the exponential argument:

$$\mathcal{P}^0_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\frac{1}{4D_x}\int_0^t ds\, \left[\dot{x}_s^2 + (\nu\nabla U(x_s))^2\right] \right\} \cdot \exp\left\{ -\frac{\nu}{2D_x}\int_0^t ds\, \dot{x}_s \nabla U(x_s) \right\}$$

If we use (5.1.4):

$$\mathcal{P}^0_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\frac{1}{4D_x}\int_0^t ds\, \left[\dot{x}_s^2 + (\nu\nabla U(x_s))^2 + 2\dot{x}_s\nu\nabla U(x_s)\right] \right\} \cdot \exp\left\{ -\frac{\beta}{2}\int_0^t ds\, \dot{x}_s \nabla U(x_s) \right\}$$

Now if we consider the ratio there are some terms equal in both probabilities of trajectories that can be cancelled out. Therefore:

$$\frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}^0_\mu(\omega)} = \exp\left\{ \int_0^t ds\, \dot{x}_s \left[\frac{\nabla D(x_s)}{\nu(x_s)} + F_s(x_s)\right] - \int_0^t ds\, \mathscr{G}_s(x_s) \right\}$$

where:

$$\mathscr{G}_s(x_s) = \frac{\dot{x}_s^2 + \nu^2(x_s)\left[F_s(x_s) - \nabla U(x_s)\right]^2 + (\nabla D_x(x_s))^2}{4D_x(x_s)} +$$

$$+\frac{2\nu\left(x_s\right)\left[F_s\left(x_s\right)-\nabla U\left(x_s\right)\right]\nabla D_x\left(x_s\right)}{4D_x\left(x_s\right)}-\frac{\dot{x}_s^2+\left(\nu\nabla U\left(x_s\right)\right)^2}{4D_x}$$

Now we can define the action $\mathcal{A}(\omega)$ as:

$$\frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}_\mu^0(\omega)}=e^{-\mathcal{A}(\omega)} \tag{5.3.11}$$

In this way:

$$\mathcal{A}(\omega)=-\frac{\beta}{2}\int_0^t ds\,\dot{x}_s\left[\frac{\nabla D\left(x_s\right)}{\nu\left(x_s\right)}+F_s\left(x_s\right)\right]+\frac{\beta}{2}\int_0^t ds\,\mathscr{G}_s\left(x_s\right) \tag{5.3.12}$$

Note that we can rewrite is as:

$$\mathcal{A}(\omega)=-\frac{\beta}{2}\int_0^t dx_s\left[\frac{\nabla D\left(x_s\right)}{\nu\left(x_s\right)}+F_s\left(x_s\right)\right]+\frac{\beta}{2}\int_0^t ds\,\mathscr{G}_s\left(x_s\right)$$

In the action we have Itô integrals. Since we want to write the action as the sum of a symmetric part and an antisymmetric one, we have to use the Stratonovitch integral. Though the first integral in the action (5.3.12) seems antisymmetric under time-reversal this is not true. The mistake is to consider v_s as a time-derivative, but we have seen that it is not right. If we write the integral (in the Itô sense) as done in (4.6.1) we can easily to understand that its symmetry is not defined. In fact if for ω we have considered the subinterval $[t_i, t_{i+1}]$, for $\theta\omega$ we should consider the the subinterval $[t_{i+1}, t_i]$. Therefore the initial value of the function in each subinterval would be different. This is not true for the Stratonovitch sense because the middle point is the same despite of the direction in which we go through the subinterval. Using (4.6.3):

$$\int_0^t f_s\left(x_s\right)dx_s=\int_0^t f_s\left(x_s\right)\circ dx_s-\frac{1}{2}\int_0^t ds\,B_s\left(x_s\right)\nabla f_s\left(x_s\right)$$

Therefore:

$$\begin{aligned}\mathcal{A}(\omega)=-\frac{\beta}{2}\int_0^t dx_s\circ\left[\frac{\nabla D\left(x_s\right)}{\nu\left(x_s\right)}+F_s\left(x_s\right)\right]+\frac{\beta}{2}\int_0^t ds\,\mathscr{G}_s\left(x_s\right)-\\-\int_0^t ds\,D_x\left(x_s\right)\nabla\cdot\left(\frac{\nabla D\left(x_s\right)}{\nu\left(x_s\right)}+F_s\left(x_s\right)\right)\end{aligned}$$

Now the first integral is antisymmetric. If we introduce the time-reversal operator θ we can note that the last two integrals are time-symmetric. Therefore we can divide the action in two contributions:

- time-symmetric $\mathcal{T}(\omega)=\frac{\mathcal{A}(\omega)+\mathcal{A}(\theta\omega)}{2}$
- time-antisymmetric $\mathcal{S}(\omega)=\frac{\mathcal{A}(\theta\omega)-\mathcal{A}(\omega)}{2}$

Therefore the action:

$$\mathcal{A}(\omega)=\frac{\mathcal{T}(\omega)-\mathcal{S}(\omega)}{2}$$

with:

$$\mathcal{T}(\omega)=\frac{\beta}{2}\int_0^t ds\,\left[\mathscr{G}_s\left(x_s\right)-D_x\left(x_s\right)\nabla\cdot\left(\frac{\nabla D\left(x_s\right)}{\nu\left(x_s\right)}+F_s\left(x_s\right)\right)\right]$$

$$\mathcal{S}(\omega) = \frac{\beta}{2}\int_0^t dx_s \circ \mathcal{F}_s(x_s)$$

Where we have defined the effective force:

$$\mathcal{F}_s(x_s) = \frac{\nabla D(x_s)}{\nu(x_s)} + F_s(x_s)$$

that takes into account also the diffusion gradient contribution.

5.3.3.4 Local detailed balance

In the last subsection we have found the functional of the trajectory, depending on the dynamics with different behavior with respect to time-reversal. Now we want to give them a physical meaning. We have obtained the action referred to a trajectory ω as the ratio between the probability of the two different dynamics. If we do the same but evaluated for the opposite trajectory and we calculate the ratio between them:

$$\frac{\mathcal{P}_\mu(\omega)}{\mathcal{P}^0_\mu(\omega)} \cdot \frac{\mathcal{P}^0_\mu(\theta\omega)}{\mathcal{P}_\mu(\theta\omega)} = e^{\mathcal{S}(\omega)}$$

where $\mathcal{S}(\omega)$ is the antisymmetric functional in the action. Then the ratio depends only on $\mathcal{S}(\omega)$. The assumption of local detailed balance assures that $\mathcal{S}(\omega)$ is the entropic flux from the system to the environment due to the nonequilibrium external force. Note that it represents only the external contribution to the entropy that we have called d_eS.

$$\mathcal{S}(\omega) = \frac{\beta}{2}\int_0^t dx_s \circ \mathcal{F}_s(x_s)$$

Generally we can write $\mathcal{F}_s(x_s)$ as:

$$\mathcal{F}_s(x_s) = -\nabla U(x_s) + W_s(x_s).$$

where the first contribution is conservative contribution and the second is not-conservative. Therefore $\mathcal{S}(\omega)$:

$$\mathcal{S}(\omega) = -\frac{\beta}{2}\int_0^t dx_s \circ \nabla U(x_s) + \frac{\beta}{2}\int_0^t dx_s \circ W_s(x_s)$$

Using (4.6.4) for function that does not depend directly on time:

$$\mathcal{S}(\omega) = -\frac{\beta}{2}\left[U(x_t) - U(x_0)\right] + \frac{\beta}{2}\int_0^t dx_s \circ W_s(x_s) \tag{5.3.13}$$

Where the first contribution depends only on the initial and final values of the trajectory and it describes the variation of the system energy due to the presence of external force. Instead the second contribution depends on the path via the integral and it describes the work made by the environment on the system. According to the first principle of thermodynamics, in the right-hand side of (5.3.13) there is the heat exchanged from the system to the environment divided by the temperature, that is actually the change in entropy of the environment. Note that the local detailed balance allows to give a physical meaning to the stochastic evolution, but only for the antisymmetric contribution.

In this dissertation we have supposed β constant, but the extension to time-dependent temperature would be straightforward. In fact there would be another work term related to temperature variation. In conclusion it is interesting to note that to obtain this result we have used (5.2.2). Equivalently, we can say that, in order to satisfy local detailed balance, the (5.2.2) must be valid. Therefore equation (5.2.2) is a consequence of the local detailed balance, as we have introduced in the previous Section.

5.4 Linear response theory

5.4.1 Backward generator

As we have done for the jump processes, now we are interested in studying the perturbation theory for a diffusive one. In other words, we will apply a potential time-dependent perturbation $h_t V_t(x_t)$ to the system in order to comprehend how it responds. Here $V_t(x_t)$ is a time-dependent observable and h_t describes the amplitude of the perturbation. In the jump processes context we have changed the transition rates (and therefore the backward generator) writing them as function of the not-perturbed ones. For the diffusive process the perturbation will modify the moments of the propagator $A_t(x_t)$ and $B_t(x_t)$ and consequently also the backward generator. As we can see the procedure is equivalent. Then we have to write the new backward generator in function of the old one. In order to do this, we consider the new moments starting from the ones introduced in 4.1:

$$A_t^h(x_t) = A_t(x_t) + \nu_t(x_t)\, h_t \nabla V_t(x_t)$$

$$B_t^h(x_t) = B_t(x_t)$$

A potential perturbation like this is equivalent to the antisymmetric one studied for jump processes. In fact we have seen that the perturbed transition rates depend on the perturbation by the difference $V_s(x_s) - V_s(x_{s^-})$. But, since now the dependence on trajectory is continuous this difference can be expanded and the first not-zero contribution is exactly the space-derivative of $V_s(x_s)$. Furthermore this kind of perturbation does not affect the reactivity (the mobility and diffusion coefficient in the continuous Markov process) but only the energy. And, since in the Langevin equation there is a space-derivative of energy, it is clear why there is the gradient of $V_s(x_s)$. Then, the stochastic moment is not modified since we suppose that the perturbation will not affect the diffusion coefficient and the mobility. Therefore, the perturbed backward generator:

$$L_t^h = \nu_t(x_t)\left[F_t(x_t) - \nabla U(x_t)\right]\cdot\nabla + \nabla D_t(x_t)\cdot\nabla + \nu_t(x_t)\, h_t \nabla V_t(x_t)\cdot\nabla + D_t(x_t)\,\nabla^2$$

$$L_t^h = L_t + \nu_t(x_t)\, h_t \nabla V_t(x_t)\cdot\nabla \tag{5.4.1}$$

Note that now the diffusion coefficient and the mobility depends directly on time. In fact, in order to consider a time-dependent temperature, it is necessary due to the local detailed balance:

$$\beta_t D_t(x_t) = \nu_t(x_t)$$

The perturbation appears in (5.2.3) as the gradient of the potential. For this reason it is a potential contribution. As we have done for the jump processes we are going to study the perturbed dynamics

compared with the not-perturbed one. The procedure is equivalent to the one already done for the entropy production.

5.4.2 Excess action

As we have done for the jump processes we are interested in the ratio of the perturbed probability over the non-perturbed one. Consider the trajectory probability for the unperturbed dynamics:

$$\mathcal{P}_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\int_0^t \frac{1}{4D_s(x_s)} \left[\dot{x}_s - \nu_s(x_s) F_s(x_s) + \nu_s(x_s) \nabla U(x_s) - \nabla D_s(x_s) \right]^2 ds \right\}$$

And the one for the perturbed dynamics:

$$\mathcal{P}^h_{x_0}(\omega) = \frac{1}{\mathcal{N}} \exp\left\{ -\int_0^t \frac{1}{4D_s(x_s)} \left[\dot{x}_s - \nu_s(x_s) \left(F_s(x_s) - \nabla U(x_s) + h_s \nabla V_s(x_s) \right) - \nabla D_s(x_s) \right]^2 ds \right\}$$

Now consider the ratio, using (5.2.2) with explicit time-dependence:

$$\frac{\mathcal{P}^h_{x_0}(\omega)}{\mathcal{P}_{x_0}(\omega)} = \exp\left\{ \int_0^t \frac{\beta_s h_s}{2} \left[\dot{x}_s - \nu_s(x_s) \left(F_s(x_s) - \nabla U(x_s) + \frac{h_s}{2} \nabla V_s(x_s) \right) - \nabla D_s(x_s) \right] \nabla V_s(x_s)\, ds \right\}$$

We are going to call $\varphi_s = \beta_s h_s$. Now using (5.3.11):

$$-\mathcal{A}(\omega) = \frac{1}{2} \int_0^t dx_s\, \varphi_s \nabla V_s(x_s) - \frac{1}{2} \int_0^t ds\, \varphi_s \left[\nu_s(x_s) \left(F_s(x_s) - \nabla U(x_s) \right) - \nabla D_s(x_s) \right] \nabla V_s(x_s) + \mathcal{O}(h_s) \tag{5.4.2}$$

We are going to ignore the contribution depending on $(\nabla V_s(x_s))^2$ because we consider only the linear terms in h_s. As we have done for entropy production we are interested in dividing the action in a symmetric part and in an antisymmetric one. But, to do it we have to pass from Itô to Stratonovitch integral. Therefore:

$$-\mathcal{A}(\omega) = \frac{1}{2} \int_0^t dx_s \circ \varphi_s \nabla V_s(x_s) - \frac{1}{2} \int_0^t ds\, \varphi_s \left[\nu_s(x_s) \left(F_s(x_s) - \nabla U(x_s) \right) \right] \nabla V_s(x_s) +$$

$$+ \frac{1}{2} \int_0^t ds\, \varphi_s \nabla \left(D_s(x_s) \nabla V_s(x_s) \right) + \mathcal{O}\left(h_s^2 \right)$$

We have also added the contribute:

$$\frac{1}{2} \int_0^t ds\, \varphi_s \nu_s(x_s) D_s(x_s) \nabla^2 V_s(x_s)$$

But we have included it in the action formula symmetric integral. Therefore we can write the action to the first order as:

$$\mathcal{A}^{(1)}(\omega) = -\frac{1}{2} \int_0^t \varphi_s \nabla V_s(x_s) \circ dx_s + \frac{1}{2} \int_0^t ds\, \varphi_s L_s V_s(x_s) \tag{5.4.3}$$

In which we have introduced the backward generator. Now we can use (4.6.4), but we have to modify it, since there is also φ_s is the integral. We can explain how it changes starting from the Itô integral:

$$\int_0^t \nabla g_s(x_s)\, \varphi_s dx_s = \lim_{n \to \infty} \sum_{i=0}^{n-1} \nabla g_{t_i}(x_{t_i})\, \varphi_{t_i} \left(x_{t_{i+1}} - x_{t_i} \right)$$

As we have done we can expand $g_{t_{i+1}}\left(x_{t_{i+1}}\right)$ and obtain an expression for $\nabla g_{t_i}\left(x_{t_i}\right)\left(x_{t_{i+1}}-x_{t_i}\right)$. Therefore:

$$\int_0^t \nabla g_s\left(x_s\right)\varphi_s dx_s = \lim_{n\to\infty}\sum_{i=0}^{n-1}\varphi_{t_i}\left[g_{t_{i+1}}\left(x_{t_{i+1}}\right)-g_{t_i}\left(x_{t_i}\right)-\frac{\partial g_{t_i}\left(x_{t_i}\right)}{\partial t}\left(t_{i+1}-t_i\right)\right]-$$

$$-\lim_{n\to\infty}\sum_{i=0}^{n-1}\varphi_{t_i}\frac{B_{t_i}\left(x_{t_i}\right)}{2}\nabla^2 g_{t_i}\left(x_{t_i}\right)\left(t_{i+1}-t_i\right)$$

The first two terms in the right-hand side should describe a telescopic series, but now there is also φ_{t_i}. In fact:

$$\sum_{i=0}^{n-1} g_{t_{i+1}}\left(x_{t_{i+1}}\right)-g_{t_i}\left(x_{t_i}\right)=\varphi_{t_0}g_{t_1}\left(x_{t_1}\right)-\varphi_{t_0}g_{t_0}\left(x_{t_0}\right)+\varphi_{t_1}g_{t_2}\left(x_{t_2}\right)-\varphi_{t_1}g_{t_1}\left(x_{t_1}\right)+\ldots$$

Now the terms do not cancel out. The solution is to add and subtract $\varphi_{t_i}g_{t_i}\left(x_{t_i}\right)$ in the series. In this way:

$$\sum_{i=0}^{n-1} g_{t_{i+1}}\left(x_{t_{i+1}}\right)-g_{t_i}\left(x_{t_i}\right)=\varphi_t g_t\left(x_t\right)-\varphi_{t_0}g_{t_0}\left(x_{t_0}\right)-\sum_{i=0}^{n-1}\left(\varphi_{t_{i+1}}-\varphi_{t_i}\right)g_{t_1}\left(x_{t_1}\right)$$

Therefore:

$$\int_0^t \nabla g_s\left(x_s\right)\varphi_s dx_s=\varphi_t g_t\left(x_t\right)-\varphi_{t_0}g_{t_0}\left(x_{t_0}\right)-\int_0^t ds\,\varphi_s\frac{\partial g_s\left(x_s\right)}{\partial s}-$$

$$-\int_0^t ds\,\frac{d\varphi_s}{ds}g_s\left(x_s\right)-\int_0^t ds\,\frac{B_s\left(x_s\right)}{2}\varphi_s\nabla^2 g_s\left(x_s\right)$$

Finally, to obtain a Stratonovitch integral:

$$\int_0^t \nabla g_s\left(x_s\right)\varphi_s\circ dx_s=\varphi_t g_t\left(x_t\right)-\varphi_0 g_0\left(x_0\right)-\int_0^t ds\,\varphi_s\frac{\partial g_s\left(x_s\right)}{\partial s}-\int_0^t ds\,g_s\left(x_s\right)\frac{d\varphi_s}{ds}$$

If we insert this result in (5.4.3):

$$\mathcal{A}^{(1)}\left(\omega\right)=-\frac{1}{2}\left[\varphi_t V_t\left(x_t\right)-\varphi_0 V_0\left(x_0\right)-\int_0^t\varphi_s\frac{\partial V_s\left(x_s\right)}{\partial s}ds-\int_0^t\frac{d\varphi_s}{ds}V_s\left(x_s\right)ds\right]+\frac{1}{2}\int_0^t ds\,\varphi_s\,L_s V_s\left(x_s\right)$$

With (5.2.4) the excess action for a continuous Markov process is:

$$\mathcal{A}^{(1)}\left(\omega\right)=-\frac{1}{2}\left[\varphi_t V_t\left(x_t\right)-\varphi_0 V_0\left(x_0\right)-\int_0^t\varphi_s\frac{\partial V_s\left(x_s\right)}{\partial s}ds-\int_0^t\frac{d\varphi_s}{ds}V_s\left(x_s\right)ds\right]+\frac{1}{2}\int_0^t ds\,\varphi_s\,L_s V_s\left(x_s\right)\tag{5.4.4}$$

Now it is evident that - as for the jump processes - the excess action is made by two contributions: the first one is entropic since it describes the excess entropic flux from the system to environment. We said excess entropy flux because in (5.4.4) there is only the entropic flux due to the perturbation. In fact, since the system is out of equilibrium even without the perturbation, there will be an entropy production to maintain the system far from equilibrium as we have seen. The nonequilibrium regime is assured by the external force $F_t\left(x_t\right)$. Now we want to show that the first bracket terms in (5.4.4) describe an entropic flux. In fact $\varphi_t V_t\left(x_t\right)-\varphi_0 V_0\left(x_0\right)$ describes the

energy difference of the system due to the perturbation between the initial and final time of the trajectory divided by the temperature (via the φ), instead the other two terms describe the work made on the system by the environment again due only to the perturbation, they depend on the path via the integral. Instead the second contribution, that has the opposite sign, describes the excess in dynamical activity. As for the jump processes it takes into account how much the system is inclined to change state. Therefore it depends on the backward generator and on the propagator moments.

5.4.3 Average values

If the perturbation modifies the probability we expect that also the average values will change. For a general observable $Q_t(x_t)$

$$\delta \langle Q_t(x_t)\rangle^h = \langle Q_t(x_t)\rangle^h - \langle Q_t(x_t)\rangle_\mu = \int dx\, P_t^h(x)\, Q_t(x) - \int dx\, P_t(x)\, Q_t(x)$$

$$\delta \langle Q_t(x_t)\rangle^h = \int dx\, P_t(x)\, Q_t(x)\left(e^{-\mathcal{A}_t(x)} - 1\right)$$

$$\delta \langle Q_t(x_t)\rangle^h \simeq -\left\langle \mathcal{A}_t^{(1)}(x_t)\, Q_t(x_t)\right\rangle_\mu \tag{5.4.5}$$

is called the generalized susceptibility. In this way we can write the perturbed average values in function of the unperturbed ones. In fact, with $\langle . \rangle_\mu$ we mean the average value made with the probability $P_t(x)$ with initial distribution μ. It is important to note that since the process is not homogeneous in time the initial distribution cannot be stationary at all. Then:

$$\delta \langle Q_t(x_t)\rangle^h = \frac{1}{2}\left\langle \left[\varphi_t V_t(x_t) - \varphi_0 V_0(x_0) - \int_0^t \varphi_s \frac{\partial V_s(x_s)}{\partial s} ds - \int_0^t \frac{d\varphi_s}{ds} V_s(x_s)\, ds\right] Q_t(x_t)\right\rangle_\mu -$$

$$-\frac{1}{2}\int_0^t ds\, \varphi_s \langle L_s V_s(x_s)\, Q_t(x_t)\rangle_\mu \tag{5.4.6}$$

5.4.4 Response

The linear response is defined by

$$\delta \langle Q_t(x_t)\rangle^h \simeq \int_0^t \varphi_s\, R_{Q,V}(t,s)\, ds$$

The frenetic term is already written as an integral over time, instead the entropic one does not. We can note that:

$$Ent[\omega] = \frac{1}{2}\left\langle Q_t(x_t)\left[\varphi_t V_t(x_t) - \varphi_0 V_0(x_0) - \int_0^t \varphi_s \frac{\partial V_s(x_s)}{\partial s} ds - \int_0^t \frac{d\varphi_s}{ds} V_s(x_s)\, ds\right]\right\rangle_\mu$$

If we note that:

$$\langle Q_t(x_t)\left[\varphi_t V_t(x_t) - \varphi_0 V_0(x_0)\right]\rangle_\mu = \int_0^t ds \frac{d}{ds}\langle Q_t(x_t)\, \varphi_s V_s(x_s)\rangle_\mu$$

Therefore:

$$Ent\left[\omega\right]=\frac{1}{2}\int_{0}^{t}ds\,\frac{d}{ds}\left\langle Q_{t}\left(x_{t}\right)\varphi_{s}V_{s}\left(x_{s}\right)\right\rangle_{\mu}-\frac{1}{2}\int_{0}^{t}\varphi_{s}\left\langle \frac{\partial V_{s}\left(x_{s}\right)}{\partial s}Q_{t}\left(x_{t}\right)\right\rangle_{\mu}ds-$$

$$-\frac{1}{2}\int_{0}^{t}\frac{d\varphi_{s}}{ds}\left\langle V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}ds$$

If we make the derivative in the first integral we get:

$$Ent\left[\omega\right]=\frac{1}{2}\left[\int_{0}^{t}\varphi_{s}\frac{d}{ds}\left\langle Q_{t}\left(x_{t}\right)V_{s}\left(x_{s}\right)\right\rangle_{\mu}ds-\int_{0}^{t}\varphi_{s}\left\langle \frac{\partial V_{s}\left(x_{s}\right)}{\partial s}Q_{t}\left(x_{t}\right)\right\rangle_{\mu}ds\right]$$

If we insert the entropic term in (5.4.6):

$$\delta\left\langle Q_{t}\left(x_{t}\right)\right\rangle^{h}=\frac{1}{2}\int_{0}^{t}ds\,\varphi_{s}\left[\frac{d}{ds}\left\langle Q_{t}\left(x_{t}\right)V_{s}\left(x_{s}\right)\right\rangle_{\mu}-\left\langle \frac{\partial V_{s}\left(x_{s}\right)}{\partial s}Q_{t}\left(x_{t}\right)\right\rangle_{\mu}\right]-\frac{1}{2}\int_{0}^{t}ds\,\varphi_{s}\left\langle L_{s}V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}$$

Therefore:

$$R_{Q,V}\left(t,s\right)=\frac{1}{2}\frac{d}{ds}\left\langle V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-\frac{1}{2}\left\langle \frac{\partial V_{s}\left(x_{s}\right)}{\partial s}Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-\frac{1}{2}\left\langle L_{s}V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}$$

And using the expression of the backward generator:

$$R_{Q,V}\left(t,s\right)=\frac{1}{2}\frac{d}{ds}\left\langle V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-\frac{1}{2}\left\langle \frac{\partial V_{s}\left(x_{s}\right)}{\partial s}Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-\frac{1}{2}\left\langle \nu_{s}\left(x_{s}\right)F_{s}\left(x_{s}\right)\cdot\nabla V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-$$

$$-\frac{1}{2}\left\langle \left[-\nu_{s}\left(x_{s}\right)\nabla U\left(x_{s}\right)+\nabla D_{s}\left(x_{s}\right)\right]\nabla V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}-\frac{1}{2}\left\langle D_{s}\left(x_{s}\right)\nabla^{2}V_{s}\left(x_{s}\right)Q_{t}\left(x_{t}\right)\right\rangle_{\mu}\qquad(5.4.7)$$

We can note that the first two terms are equal to the ones studied for the jump processes and they describe the entropic contribution. The other terms represent the frenetic part of the response, they depend on the mobility and on the diffusion coefficient as we expect. This kind of relation is also called nonequilibrium first fluctuation-dissipation theorem. In fact the response is related to the energy dissipated due to the perturbation.

5.4.5 Quasi-static limit

5.4.5.1 Stationary solution

Also for the continuous Markov process we are interested in the quasi-static limit. In fact, if the dynamics evolves slowly, it is possible to approximate the probability $P_{t}\left(x\right)$ with the invariant distribution at time t fixed, solution of $L_{t}^{+}\rho_{t}\left(x\right)=0$. Using equation (4.3.2) it is clear that the quasi-static limit acts on the backward generator. This is meaningful since in the jump processes context we have assumed that the transition rates change slowly and therefore also the L_{t} matrix. If the backward generator changes very slowly there is a characteristic time τ over which it is almost constant and then, time-independent. The time τ ($dt\ll\tau\ll t$, where t is the trajectory ending time) is strictly related to the changing of L_{t}, in fact to describe the slowness of the changing

we have to parameterize the moments $A_t(x_t)$ and $B_t(x_t)$ introducing a small parameter ε, with $\varepsilon = \frac{1}{\tau}$. Now we want to find the expression for this stationary distribution. We have to solve the Fokker-Planck equation with zero left-hand side. Then with the condition $x_t = x$:

$$\nabla \left[A_t(x) \rho(x, t \mid x_0, t_0) \right] = \frac{1}{2} \nabla^2 \left[B_t(x) \rho(x, t \mid x_0, t_0) \right]$$

$$\nabla \left[A_t(x) \rho(x, t \mid x_0, t_0) - \frac{1}{2} \nabla \left[B_t(x) \rho(x, t \mid x_0, t_0) \right] \right] = 0$$

The quantity in the bracket must be constant and in particular it must be zero. In fact the quasi-static limit says that at any fixed time the instantaneous stationary distribution must satisfy detailed balance (4.3.6):

$$A_t(x) \rho(x, t \mid x_0, t_0) = \frac{1}{2} \nabla \left[B_t(x) \rho(x, t \mid x_0, t_0) \right]$$

$$\nabla \rho(x, t \mid x_0, t_0) = \left[\frac{2A_t(x) - \nabla B_t(x)}{B_t(x)} \right] \rho(x, t \mid x_0, t_0)$$

$$\frac{\nabla \rho(x, t \mid x_0, t_0)}{\rho(x, t \mid x_0, t_0)} = f_t(x)$$

Its solution is:

$$\rho(x, t \mid x_0, t_0) = \left(e^{\int_0^t f_s(x_s) \circ dx_s} \right)_{x_t = x} \tag{5.4.8}$$

Here t is thought as a fixed parameter, the solution depends on the evolution until t. Consider, for example, the solution for the Ornstein-Uhlenbeck model in which $A_t(x_t) = -\gamma v_t$ and $B_t(x_t) = 2D\gamma^2$. This model describes a Brownian motion introduced at the beginning of Section 3. In this case we have $f(v_t) = -\frac{v_t}{\gamma D}$. And the probability will be:

$$\rho(v, t \mid v_0, t_0) = \left(e^{-\frac{1}{2\gamma D} \int_0^t v_s \circ dv_s} \right)_{v_t = v} = \frac{1}{\sqrt{2\pi D\gamma}} e^{-\frac{v^2 - v_0^2}{2D\gamma}}$$

And, given the Einstein-Smoluchowski relation $\frac{1}{D} = M\beta\gamma$, we obtain the stationary distribution presented in Section $VII.B$ of [1]. Therefore, (5.4.8) is the invariant distribution at time fixed for the diffusion process. The quasi-static limit allows to write the probability $P_t(x)$ as the invariant distribution plus a correction of order ε:

$$P_t(x) = \rho_t(x) + \mathcal{O}(\varepsilon) \tag{5.4.9}$$

where ε is a parameter introduced to describe the slowness of the dynamics changing and then it appears in the backward generator. This expression does not describe the evolution of the probability, it must be thought as an infinite and dense sequence of stationary states. The fact that the sequence is made by equilibrium or nonequilibrium states depends on the moments $A_t(x_t)$ and $B_t(x_t)$. In fact for the Ornstein-Uhlenbeck process the invariant distribution is the Maxwellian one and therefore it describes a equilibrium system. In general $\rho_t(x)$ is not a Gaussian distribution and then it describes a nonequilibrium stationary state.

5.4.5.2 Response formula

If we use (5.4.9) in (5.4.7) we obtain:

$$R_{Q,V}(t,s) = \frac{1}{2}\frac{d}{ds}\left\langle V_s(x_s)\, Q_t(x_t)\right\rangle_{\rho_s} - \frac{1}{2}\left\langle \frac{\partial V_s(x_s)}{\partial s} Q_t(x_t)\right\rangle_{\rho_s} - \frac{1}{2}\left\langle \nu_s(x_s)\, F_s(x_s)\cdot\nabla V_s(x_s)\, Q_t(x_t)\right\rangle_{\rho_s} -$$

$$-\frac{1}{2}\left\langle [-\nu_s(x_s)\,\nabla U(x_s) + \nabla D_s(x_s)]\,\nabla V_s(x_s)\, Q_t(x_t)\right\rangle_{\rho_s} - \frac{1}{2}\left\langle D_s(x_s)\,\nabla V_s(x_s)\, Q_t(x_t)\right\rangle_{\rho_s} + \mathcal{O}(\varepsilon)$$

Now the average values are made over the invariant distribution at time s. Since this distribution cannot be thought as an evolution, for the same reason explained in the jump processes dissertation, the response formula is not invariant under time-translations. Therefore it continues to depend separately on t and s, but in this approximation the average values are easier to solve. From (5.4.8) we can find the instantaneous stationary distribution for the Langevin equation (5.2.3):

$$\rho(x,t \mid x_0,t_0) = \left(e^{\int_0^t \beta_s[F_s(x_s)-\nabla U(x_s)]\circ dx_s}\right)_{x_t=x}$$

Chapter 6

Second fluctuation-dissipation theorem

6.1 Introduction

As we have briefly said in Section 4.5.2, the Langevin equation is the result of a dynamics reduction. To eliminate the environment degrees of freedom is not obvious, especially if the environment is maintained out of equilibrium by an external force. In Section 5.1.2 we have discussed the equilibrium case, in this Chapter we are going to explain how the reduction works when the environment is in a time-dependent nonequilibrium condition in order to obtain the Langevin equation for the system. In our case the system will be a probe embedded in a nonequilibrium fluid at constant temperature that will be the environment. We can do it in two steps. First, we have to obtain the Langevin equation for the nonequilibrium fluid interacting with a reservoir, in this case the system is the fluid and the reservoir is the environment. For it, we can use the local detailed balance principle and find a relation between the friction and the diffusion coefficient perceived by the fluid particles - we have done it in Section 5.2.3. Using it, we can determine the Langevin equation for the probe.

It must be thought as an extension to [5], in which the stationary state has been studied. Here we want to deal with the not-stationary case. In fact if the backward generator depends on time, a stationary distribution does not exist. But if this time-dependence is periodic the Markov process will asymptotically converge to a periodic process and its distribution will be periodic too. This is easily understandable considering equation (4.3.2), if the backward generator is periodic. The periodic regime can be thought as a kind of "stationary" state, even if it is not stationary at all, because it continues to repeat in the same way after a time $\mathcal{T}$, called period of the process.

If we consider a perturbation which is generally not-periodic, we expect that the system dynamics will be no longer periodic. But if the perturbation is small, it is reasonable to assume that the new dynamics is close to the initial one. Using the linear response theory we can study a generic time-dependent regime in function of the periodic unperturbed one. Nevertheless, there is a case in which the perturbed dynamics converges to a periodic one and it corresponds to the long-time limit approximation when h_t is constant. Because, if the perturbation is static, a relaxation to a new "stationary" state is possible. Obviously the new periodic state will be different from the initial one. This situation can be interpreted as the analogue of formula 2.3 in [5]. For this reason we are going to use it in the following. We will study a probe with mass M embedded in an out-of-equilibrium fluid made by n particles with mass m, under the condition $M \gg m$. We suppose the fluid is in a volume V and it can thermally interact with a reservoir at constant temperature T.

6.1.1 Fluid dynamics

The particles positions are described by n processes X_t^j; we are going to group them as $X_t = \left\{X_t^j\right\}_j$. This process gives at any time the position of all the particles. Therefore it takes values from a manifold S in the phase space whose dimension is n times the dimension of the single particle system and it is described by the probability $P_t(X)$. In this treatment we are going to use a 1-dimensional notation, but it is obvious how to extend it to a bigger manifold. If the fluid is out of equilibrium there will be an external and time-dependent force F_t acting on it. We suppose that it does not depend on X_t but only on time (for example we can imagine a piston that modifies the pressure of a gas in a volume V). another example is imagining a fluid driven by a constant force into a narrow tube with not-constant cross-Section. In other words, there are bottlenecks periodically disposed. We assume the force dependence on time is periodic and then we expect that in the long-time limit also the dynamics, described by the process X_t, of the fluid will be periodic.

For the moment we are ignoring the presence of the probe that, evidently, will produce a not-periodic dynamics for the fluid. We are going to treat it in the following. If we just consider the nonequilibrium fluid interacting with the reservoir, the local detailed balance relation is satisfied. As we have said the detailed balance condition takes into account the temperature, the pressure and the chemical potential. We have assumed that the temperature is constant and that the fluid cannot exchange particles with the reservoir. Therefore there is thermal and chemical equilibrium between fluid and reservoir. But there is no mechanical equilibrium since there is the external force, or in other words, there is work made on the fluid by the environment. If we assume that the work is automatically transformed in heat exchanged, it is reasonable to use the local detailed balance supposing that the fluid interacts with more than one heat reservoirs. We have also supposed that the reservoirs are enough big to not be affected by the heat exchange. Under these considerations, we can use local detailed balance and (5.2.2) in the fluid Langevin equation.

Due to the nonequilibrium force F_t the density of particles is no longer constant and generally it can produce a not-constant diffusion coefficient depending on X_t. Therefore there would be another force depending on the diffusion coefficient gradient. The same reasoning is valid also for the friction and the mobility. The dependence on the process of the friction and of the diffusion coefficient is a consequence of the nonequilibrium external force. In addition, we suppose that the fluid particles interact with each others via an attractive, time-independent and central potential Φ (it depends only on the relative distance between two particles). Finally since the fluid is at constant temperature T there will be thermal agitation described by a white Gaussian noise. To describe the motion of the fluid we will adopt the over-damped limit. We are going to explain the consequences of it in the next Section.

6.1.2 Probe dynamics

The probe position is described by a diffusion process x_t. It takes values from a continuous set of states whose dimension is equal to system dimension and it is described by the probability $p_t(x)$. The probe can interact weakly with the fluid particles via a conservative potential. We suppose there is no external forces acting on the probe. Therefore its motion is a random walk interacting with the fluid particles. Since the fluid is out of equilibrium the average position of the particles will not be zero, therefore, the probe will not oscillate around a fixed equilibrium position. Since in the nonequilibrium fluid there are currents, it is reasonable to assume that the probe follows these currents. According to it, the probe motion is related to the average position of the fluid X_t since

the currents are determined by the average velocity of the fluid. The average position determines a continuous and differentiable trajectory since we have averaged over the noise. Evidently this trajectory will not represent the motion of the probe. But, since the probe mass is much bigger if compared to the probe one and the coupling is weak, x_t will be not much different from this trajectory, that we are going to call y_t. Note that y_t is not a property of the probe but of the fluid. In the next Section we are going to present the equations of the motion for our system and we will say also how to determine y_t.

Note that the Chapter 6 must be thought as a nonequilibrium extension to what we have done for equilibrium Langevin equation in Section 5.1.2. There we supposed the existence of a minimum in the potential, instead here we suppose there is no external force acting on the probe. In fact it is not obvious how to conciliate the fluid trajectory y_t with the motion produced by the potential. Therefore for the moment we suppose there is no potential on the probe.

6.1.3 Dissertation objective

We want to describe the probe position with a Langevin equation. To do this, we need to know how to take into account the particles degrees of freedom and, then, how to consider the reduced system. We want to find out:

- the properties of the noise perceived by the probe.
- the expression of the friction in function of the particles dynamical fluctuations. This is also called second fluctuation-dissipation theorem for nonequilibrium systems.

The way of proceeding is the following. We will consider the probe presence and therefore the coupling with it as a small perturbation to the particles dynamics. We will obtain the linear response formula to this perturbation. Since the response takes into account all the particles via average values, it does not longer depend on X_t. Instead it depends on the probe position and therefore it can be interpreted as the global interaction between fluid and probe. It can be put in the Langevin equation representing the dynamics reduction. According to this description, it is obvious that we have to assume that the coupling is small in order to consider it as a perturbation. There is another more subtle assumption: if an external not-conservative force acts on the probe it cannot modify the fluid dynamics. Otherwise the perturbation theory studied in the previous Section will no longer be valid since it is for potential perturbation. Since we are supposing there is no external force on the probe, we can ignore this assumption.

6.2 Equations of motion

6.2.1 Fluid particles

As we have said, four forces act on the particles: the external nonequilibrium force, the interaction with other particles, the diffusion gradient and the coupling with the probe. Since it is conservative, it derives from a potential energy $\mathcal{U}(X_t - x_t)$. It takes into account the coupling of each particles with the probe, therefore it depends on λ_j that are the coupling coefficients for each degree of freedom (generally λ_j can be different for each degree). It is a small parameter for each particle. Though it is conservative it cannot be an equilibrium force for the fluid because it depends on the probe position that is time-dependent. Also the particles interaction is conservative, therefore its potential energy is:

$$U\left(X_t\right)=\sum_{j<j'}\Phi\left(X_t^j-X_t^{j'}\right)$$

If we take into account also the noise perceived by the particles we obtain a Langevin equation. It is important to note that this noise is different from what we are looking for. We assume the over-damped limit for the fluid. Deriving the energy we can obtain the Langevin equation for the particles:

$$\frac{dX_t^j}{dt}=\nu_j\left(X_t\right)\left[F_t^j-\frac{\partial U\left(X_t\right)}{\partial X_j}-\lambda_j\frac{\partial\mathcal{U}_j\left(X_t^j-x_t\right)}{\partial X_j}\right]+\frac{\partial D\left(X_t\right)}{\partial X_j}+\sqrt{2D\left(X_t\right)}\xi_t^j \tag{6.2.1}$$

where $\nu_j\left(X_t\right)$ is the mobility of the j-th particle. It depends on particle mass m, that for simplicity we assume equal to 1. Here we have make explicit the dependence on the coupling coefficient introducing $\lambda_j\mathcal{U}_j$, the coupling energy with the j-th particle such that:

$$\sum_{j=1}^{n}\lambda_j\mathcal{U}_j\left(X_t^j-x_t\right)=\mathcal{U}\left(X_t-x_t\right)$$

Following the notation introduced in the previous Sections, the moments are:

$$A_t^j\left(X_t\right)=\nu_j\left(X_t\right)\left[F_t^j-\frac{\partial U\left(X_t\right)}{\partial X_j}-\lambda_j\frac{\partial\mathcal{U}_j\left(X_t^j-x_t\right)}{\partial X_j}\right]+\frac{\partial D\left(X_t\right)}{\partial X_j}$$

$$B\left(X_t\right)=2D\left(X_t\right)$$

It is important to note that the process is $X_t=\left(X_t^1\ldots X_t^n\right)$, while x_t is a parameter of the process. The Fokker-Planck equation is:

$$\frac{\partial}{\partial t}P_t^{\{x_t\}}\left(X\right)=-\sum_{j=1}^{n}\frac{\partial}{\partial X_j}\left[\nu_j\left(X\right)\left(F_t^j-\frac{\partial U\left(X\right)}{\partial X_j}-\lambda_j\frac{\partial\mathcal{U}_j\left(X^j-x_t\right)}{\partial X_j}\right)P_t^{\{x_t\}}\left(X\right)\right]+$$

$$+\sum_{j=1}^{n}\frac{\partial}{\partial X_j}\left[D\left(X\right)\frac{\partial}{\partial X_j}P_t^{\{x_t\}}\left(X\right)\right]$$

where $P_t^{\{x_t\}}\left(X\right)$ is the probability of the process X_t. Generally, it does not depend only the probe position at time t, but on all the values assumed by x_t until time t. For this reason we use the notation $\{x_t\}$. Note that it is not-periodic due to x_t. The coupling with the probe is the perturbation. For this reason we have separated it by the Φ-potential. The process X_t is our reference process but it already contains the perturbation that we are going to study. Note that the mobility and the diffusion coefficient that appear in (6.2.1) are not referred to the probe but only to the fluid particles.

We do a consideration: here we are supposing the fluid is kept out of equilibrium by a time-dependent force, because we want to present the most general calculation. But, in order to obtain a time-dependent dynamics for the fluid, it is not necessary. For example we can consider a nonequilibrium stationary regime for the fluid without the coupling with the probe. Therefore if we add in the Langevin equation for the fluid this coupling, the equation will depend on a time-dependent contribution. In other words, the time-dependent regime is not necessarily a prerogative

of the fluid, but it can be a consequence of the probe presence. Nevertheless the dependence on time of the force could be necessary in order to obtain a periodic dynamic for the fluid. If the motion, with a constant force, is on a circle the motion will be periodic even if the force is not time-dependent. We will present it in Section 6.4.

6.2.2 Probe

The probe is affected by the coupling with the fluid:

$$M\frac{d^2x_t}{dt^2} = -\sum_{j=1}^{N}\lambda_j\frac{\partial\mathcal{U}_j\left(X_t^j - x_t\right)}{\partial x} \tag{6.2.2}$$

The probe is affected only by the coupling with the particles, therefore we consider the sum over all of them. Nevertheless, it is very difficult to calculate the interaction with all the particles. For this reason we calculate, via the linear response theory, a kind of mean interaction described by a statistical force that takes into account all of them. This statistical force will depend on the probe position and on the average particles position. Where the average values will be made over the fluid distribution. We are going to develop it in the following Section. But now we want to explain better y_t that we have previously introduced because it is strictly related to the perturbation theory we are going to do. In fact, the fluid particles, due to the nonequilibrium force produce a current. Therefore if we consider the probe it is reasonable to suppose that it will follow that current. Evidently this is not the real probe dynamics, but it can be a good approximation especially if the probe mass is much bigger than the particles one. Under these consideration we can obtain the trajectory y_t from the average Langevin equation for the fluid in absence of the probe:

$$\frac{dX_t^j}{dt} = \nu_j\left(X_t\right)\left[F_t^j - \frac{\partial U\left(X_t\right)}{\partial X_j}\right] + \frac{\partial D\left(X_t\right)}{\partial X_j} + \sqrt{2D\left(X_t\right)}\xi_t^j$$

The associated Fokker-Planck equation is:

$$\frac{\partial P_t}{\partial t} = -\sum_{j=1}^{n}\frac{\partial}{\partial X_j}\left[\nu_j\left(X\right)\left(F_t^j - \frac{\partial U\left(X\right)}{\partial X_j}\right)P_t\left(X\right) - D\left(X\right)\frac{\partial}{\partial X_j}P_t\left(X\right)\right]$$

from which we can extract the current:

$$J_t\left(X_t\right) = \sum_{j=1}^{n}\nu_j\left(X_t\right)\left(F_t^j - \frac{\partial U\left(X_t\right)}{\partial X_j}\right)P_t\left(X\right) - D\left(X_t\right)\frac{\partial}{\partial X_j}P_t\left(X\right)$$

If we divide it by the probability:

$$\frac{J_t\left(X_t\right)}{P_t\left(X\right)} = \sum_{j=1}^{n}\nu_j\left(X_t\right)\left(F_t^j - \frac{\partial U\left(X_t\right)}{\partial X_j}\right) - D\left(X_t\right)\frac{\partial}{\partial X_j}\ln P_t\left(X\right)$$

Dimensionally it is a velocity. It is the velocity of the fluid:

$$V_t\left(X_t\right) = \nu\left(X_t\right)\left(F_t - \nabla U\left(X_t\right)\right) - D\left(X_t\right)\nabla\ln P_t\left(X\right)$$

Here the gradient is a n-dimensional operator that takes into account all the particles. If we average over the probability $P_t\left(X\right)$ we obtain an equation for y_t:

$$\frac{dy_t}{dt} = \langle V_t(X_t)\rangle_\mu$$

where $\mu(X) = P_0(X)$ is the initial distribution. Note the y_t is not a stochastic process because it derives by an average value over the fluid degrees of freedom. Therefore, y_t is a continuous and differentiable trajectory. We suppose that $x_0 = y_0$. If y_t represents the average position of the probe at time t, $x_t - y_t$ can be thought as the fluctuation at time t between the probe position and its average value due to the interaction with the fluid. Physically, the probe oscillates around a time-dependent equilibrium position.

The external force F_t, that keeps the fluid out of equilibrium, does not affect the probe motion. We have already seen these requirements in the previous Sections, they are necessary in order to obtain a Langevin equation for the fluid that will be the starting point for a Langevin equation for the probe.

6.2.3 Energy expansion

If the coupling is small, we can suppose that the interaction with the particles will not modify largely the probe position. Since y_t is the instantaneous probe equilibrium position if there is no interaction with particles, it is reasonable to expand the coupling energy $\mathcal{U}$ around $x_t = y_t$ to linear order.

$$\lambda_j \mathcal{U}_j\left(X_t^j - x_t\right) \simeq \lambda_j \mathcal{U}_j\left(X_t^j - y_t\right) + \lambda_j \frac{\partial \mathcal{U}_j\left(X_t^j - x_t\right)}{\partial x}_{|_{x_t=y_t}} (x_t - y_t)$$

If we define:

$$g^j\left(X_t^j - x_t\right) = -\lambda_j \frac{\partial \mathcal{U}_j\left(X_t^j - x_t\right)}{\partial x}$$

This expansion is very important because it allows a relation between the particles equation and the probe one. In fact if we substitute the energy expansion in (6.2.1):

$$\frac{dX_t^j}{dt} = \nu_j(X_t)\left[F_t^j - \frac{\partial U(X_t)}{\partial X_j} - \lambda_j \frac{\partial \mathcal{U}_j\left(X_t^j - y_t\right)}{\partial X_j} + (x_t - y_t)\frac{\partial g^j\left(X_t^j - y_t\right)}{\partial X_j}\right] + \frac{\partial D(X_t)}{\partial X_j} + \sqrt{2D(X_t)}\xi_t^j \tag{6.2.3}$$

Now we can better understand the particles dynamics. In fact the zero order of the coupling potential can be thought as part of the unperturbed dynamics and it represents the coupling between particles and the probe in an instantaneous equilibrium position. They oscillate around y_t interacting with each others and diffusing. Therefore, the perturbation is described by the observable $g(X_t, y_t)$ and it is potential since in the Langevin equation appears its derivative with respect to X_j. Instead $x_t - y_t$ describes the intensity of the perturbation and it depends on time by the process x_t, it is analogous to h_t in the perturbation theory introduced in Section 5. Therefore $h_t = x_t - y_t$. The (6.2.3) is the perturbed process. According to it, we can define the new backward generator:

$$L_t^h = \sum_{j=1}^n \nu_j(X_t)\left[F_t^j + \frac{\partial D(X_t)}{\partial X_j} - \frac{\partial U(X_t)}{\partial X_j} - \lambda_j \frac{\partial \mathcal{U}_j\left(X_t^j - y_t\right)}{\partial X_j} + (x_t - y_t)\frac{\partial g^j\left(X_t^j - y_t\right)}{\partial X_j}\right] \cdot \frac{\partial}{\partial X_j} +$$

$$+ \sum_{j=1}^n \frac{\partial D(X_t)}{\partial X_j} \cdot \frac{\partial}{\partial X_j} + D(X_t) \cdot \frac{\partial^2}{\partial X_j^2}$$

$$L_t^h = L_t + (x_t - y_t) \sum_{j=1}^{n} \nu_j (X_t) \frac{\partial g^j \left(X_t^j - y_t\right)}{\partial X_j} \cdot \frac{\partial}{\partial X_j}$$

We suppose we know how to solve the Fokker-Plank equation for the unperturbed dynamics L_t. It is:

$$\frac{\partial}{\partial t} P_t^{\{y\}} (X) = -\sum_{j=1}^{n} \frac{\partial}{\partial X_j} \left[\nu_j (X) \left(F_t^j - \frac{\partial U (X)}{\partial X_j} - \lambda_j \frac{\partial \mathcal{U}_j \left(X^j - y_t\right)}{\partial X_j} \right) P_t^{\{y\}} (X) \right] +$$

$$+ \sum_{j=1}^{n} \frac{\partial}{\partial X_j} \left[D (X) \frac{\partial}{\partial X_j} P_t^{\{y\}} (X) \right] \tag{6.2.4}$$

Since y_t appears in the backward generator, we expect it will appear, as a time-dependent parameter, also in the probability $P_t (X)$. In general the probability at time t does not depend only on y_t, but it can depend also on all the values assumed by the process y_t from the initial time to time t. Since the unperturbed probability is periodic we expect that y_t will be periodic too. Therefore, generally, we suppose that the fluid probability can depend on all the values assumed by y_t in a period. We will indicate it with $\{y\}$. Then the probability of the fluid at time t will be $P_t^{\{y\}} (X)$. Now consider the equation of the motion for the probe. The $g \left(X_t - x_t\right)$ appears in it.

$$M \frac{d^2 x_t}{dt^2} = \sum_{j=1}^{n} g^j \left(X_t^j - x_t\right) \tag{6.2.5}$$

From this equation it is evident what we have described in the introduction. The $g \left(X_t - x_t\right)$ describes the interaction with the particles perceived by the probe. Instead, if it is evaluated in y_t, it produces the perturbation to the particles dynamics. We will use it as a perturbation in order to obtain the response. Since the $g \left(X_t - x_t\right)$ appears also in the equation for x_t we will use the response to obtain a Langevin equation for x_t. Under these considerations the difference between x_t and y_t is due to the noise. Therefore if the noise is too big it is not correct to use the linear response theory, because h_t would not be small. At the end of this Section we will obtain an expression for the noise, and we will check a posteriori if the assumption done was correct.

6.3 Linear response

Suppose that the potential perturbation $g^j \left(X_t^j - x_t\right)$ acts from time $t = 0$ under the condition $x_0 = y_0$. The perturbation depends on the process X_t and it is not periodic. We are interested in finding the response formula for the observable $g^j \left(X_t^j - x_t\right)$. We are going to use (5.4.7), but note that the perturbation depends on time via the process X_t and via the trajectory y_t. Therefore there will be two contributions to the entropic term:

$$\left\langle g^j \left(X_t^j - x_t\right) \right\rangle_\mu^{\{x_t\}} = \left\langle g^j \left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \frac{\beta}{2} \int_0^t ds\, h_s \left[\frac{d}{ds} \left\langle g^j \left(X_s^j - y_s\right) g^j \left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right] -$$

$$- \frac{\beta}{2} \int_0^t ds\, h_s \left[\left\langle \dot{y}_s \frac{\partial g^j \left(X_s^j - y_s\right)}{\partial y} g^j \left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \left\langle L_s g^j \left(X_s - y_s\right) g^j \left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right] \tag{6.3.1}$$

where μ is the initial distribution and it is the same for the unperturbed and the perturbed dynamics, $\mu = P_0^{\{y\}}$. The average values $\langle\cdot\rangle_\mu^{\{y\}}$ is made with respect to the unperturbed probability. In fact it depends on $\{y\}$. While, the average value $\langle\cdot\rangle_\mu^{\{x_t\}}$ is made over all the possible trajectories starting at time $t = 0$ from distribution μ and it depends on all the positions assumed by the probe until time t. In fact, x_t is not a periodic process. We are supposing that the temperature is constant. Furthermore, note that in the second term of the entropic contribution appears the derivative of the trajectory y_t since we are considering the time-derivative with respect to y_s in the perturbation. These average values are:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{x_t\}} = \int_S dX\, P_t^{\{x_t\}}(X)\, g^j\left(X^j - x_t\right)$$

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}} = \int_S dX\, P_t^{\{y\}}(X)\, g^j\left(X^j - x_t\right)$$

First of all we want to get the covariance in (6.3.1). Consider the first term in the integral in (6.3.1):

$$\frac{d}{ds}\left[\left\langle g^j\left(X_s^j - y_s\right) g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}} - \left\langle g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}}\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}}\right] +$$

$$+\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}}\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} = \frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}} +$$

$$+\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}}\left[\left\langle L_s g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} + \left\langle \dot{y}_s\frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}\right\rangle_\mu^{\{y\}}\right] \tag{6.3.2}$$

This is evident if we consider the average value:

$$\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} = \frac{d}{ds}\int_S dX\, P_s^{\{y\}}(X)\, g^j\left(X^j - y_s\right) = \int_S dX\,\frac{d}{ds}\left[P_s^{\{y\}}(X)\, g^j\left(X^j - y_s\right)\right]$$

Now we can use (4.3.2):

$$\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} = \int_S dX\, P_s^{\{y\}}(X)\, L_s g^j\left(X^j - y_s\right) + \int_S dX\, P_s^{\{y\}}(X)\,\frac{\partial g^j\left(X^j - y_s\right)}{\partial y}\dot{y}_s$$

And finally:

$$\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} = \left\langle L_s g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} + \left\langle\frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}\dot{y}_s\right\rangle_\mu^{\{y\}}$$

If we insert (6.3.2) in (6.3.1) we will obtain:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{x_t\}} = \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}} + \frac{\beta}{2}\int_0^t ds\, h_s\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}} +$$

$$+\frac{\beta}{2}\int_0^t ds\, h_s\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_\mu^{\{y\}}\left[\left\langle L_s g^j\left(X_s^j - y_s\right)\right\rangle_\mu^{\{y\}} + \left\langle\frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}\dot{y}_s\right\rangle_\mu^{\{y\}}\right] -$$

$$-\frac{\beta}{2}\int_0^t ds\, h_s \left[\left\langle \dot{y}_s \frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y} g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \left\langle L_s g^j\left(X_s^j - y_s\right) g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right]$$

And then:

$$\left\langle g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{x_t\}} = \left\langle g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \frac{\beta}{2}\int_0^t ds\, h_s \frac{d}{ds} \left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} -$$

$$-\frac{\beta}{2}\int_0^t ds\, h_s \left[\left\langle \dot{y}_s \frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \left\langle L_s g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right] \quad (6.3.3)$$

Now we want to integrate (6.3.3) by partial integration. But, first of all, we have to write also the last contribution as a derivative:

$$\left\langle L_s g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} = \frac{d}{ds}\int_{-\infty}^s du \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}}$$

$$\left\langle \dot{y}_s \frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} = \frac{d}{ds}\int_{-\infty}^s du \left\langle \dot{y}_u \frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}}$$

Then:

$$\left\langle g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{x_t\}} = \left\langle g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \frac{\beta}{2}\int_0^t ds\, h_s \frac{d}{ds} \left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} -$$

$$-\frac{\beta}{2}\int_0^t h_s \frac{d}{ds}\int_{-\infty}^s du \left[\left\langle \dot{y}_u \frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right]$$

Integrating by parts:

$$\frac{\beta}{2} h_s \left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \Bigg|_0^t - \frac{\beta}{2} h_s \int_{-\infty}^s \left\langle \dot{y}_u \frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} du \Bigg|_0^t -$$

$$-\frac{\beta}{2} h_s \int_{-\infty}^s \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} du \Bigg|_0^t - \frac{\beta}{2}\int_0^t ds \frac{dh_s}{ds} \left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} +$$

$$+\frac{\beta}{2}\int_0^t ds \frac{dh_s}{ds}\int_{-\infty}^s du \left[\left\langle \dot{y}_u \frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} + \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} \right]$$

Now, we have to evaluate the boundary terms, remembering that we have assumed $x_0 = y_0$. It is equivalent to say $h_0 = 0$. Then:

$$\frac{\beta}{2} h_t \left\langle g^j\left(X_t^j - y_t\right); g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} - \frac{\beta}{2} h_t \int_{-\infty}^t ds \left\langle \dot{y}_s \frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}; g^j\left(X_t^j - x_t\right) \right\rangle_\mu^{\{y\}} -$$

$$-\frac{\beta}{2}h_t\int_{-\infty}^{t}\left\langle L_s g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}ds-\frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\left\langle g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}+$$

$$+\frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\int_{-\infty}^{s}du\left[\left\langle \dot{y}_u\frac{\partial g^j\left(X_u^j-y_u\right)}{\partial y};g^j\left(X_t^j-x_t\right)\right\rangle+\left\langle L_u g^j\left(X_u^j-y_u\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}\right] \tag{6.3.4}$$

Therefore:

$$\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{x_t\}}=\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}+\frac{\beta}{2}h_t\left\langle g^j\left(X_t^j-y_t\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}-$$

$$-\frac{\beta}{2}h_t\left[\int_{-\infty}^{t}ds\,\dot{y}_s\left\langle\frac{\partial g^j\left(X_s^j-y_s\right)}{\partial y};g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}+\int_{-\infty}^{t}ds\left\langle L_s g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}\right]-$$

$$-\frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\left[\left\langle g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}-\int_{-\infty}^{s}du\left\langle\dot{y}_u\frac{\partial g^j\left(X_u^j-y_u\right)}{\partial y};g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}\right]+$$

$$+\frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\int_{-\infty}^{s}du\left\langle L_u g^j\left(X_u^j-y_u\right);g^j\left(X_t^j-x_t\right)\right\rangle_\mu^{\{y\}}$$

Now we want to understand the meaning of the boundary term that corresponds to the two contributions in the bracket. Note that the response formula must be valid for each initial distribution. According to it, we will use as initial distribution the periodic "stationary" distribution $\rho^{\{y\}}$. Generally it is not equal to $P_t^{\{y\}}$, solution of the Fokker-Planck equation (6.2.4). As seen for the two states system the probability solution of the master equation depends also on an exponentially decreasing term. In that case the periodic "stationary" distribution is given by the probability in the long-time limit, in which the exponential contribution goes to zero. This limit must be done carefully because any periodic function does not admit a limit for $t\to\infty$. For $P_t^{\{y\}}$ we have to do the same to determine $\rho_t^{\{y\}}$. After that, we consider $\rho^{\{y\}}=\rho_0^{\{y\}}$. First of all, it is interesting to note that:

$$\{x_t\}=\{y\}+\{h_t\}$$

where $\{y\}$ is periodic and h_t is small. If we suppose that h_t is constant even the probability depending on $\{x_t\}$ becomes periodic. Therefore if we consider the average value $\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}$ starting from the initial distribution $\rho^{\{y\}}$ in the unperturbed dynamics and we apply a constant perturbation $hg^j\left(X_t^j-x_t\right)$, the perturbed average value $\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}}$ with the same initial distribution will be periodic too. Using the linear response theory (6.3.3) we can find a relation between the two average values:

$$\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}}=\left\langle g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}+\frac{\beta h}{2}\int_0^t ds\,\frac{d}{ds}\left\langle g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}-$$

$$-\frac{\beta h}{2}\int_0^t ds\left\langle\dot{y}_s\frac{\partial g^j\left(X_s^j-y_s\right)}{\partial y};g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}-\frac{\beta h}{2}\int_0^t ds\left\langle L_s g^j\left(X_s^j-y_s\right);g^j\left(X_t^j-x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}$$

But equivalently we can say:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}} = \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} + \frac{\beta h}{2}\int_0^t ds\,\frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} -$$

$$-\frac{\beta h}{2}\int_0^t ds\,\frac{d}{ds}\int_{-\infty}^s du\,\left\langle \dot{y}_u\frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} -$$

$$-\frac{\beta h}{2}\int_0^t ds\,\frac{d}{ds}\int_{-\infty}^s du\,\left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}$$

For simplicity we can define an operator:

$$\dot{y}_u\frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y} + L_u g^j\left(X_u^j - y_u\right) = \mathcal{K}_u^j\left(X_u^j - y_u\right)$$

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}} = \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} + \frac{\beta h}{2}\int_0^t \frac{d}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} ds -$$

$$-\frac{\beta h}{2}\int_0^t \frac{d}{ds}\int_{-\infty}^s du\,\left\langle \mathcal{K}_u^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}$$

We can solve the integral in ds:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}} - \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} = \frac{\beta h}{2}\left\langle g^j\left(X_t^j - y_t\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} -$$

$$-\frac{\beta h}{2}\left\langle g^j\left(X_0^j - y_0\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} - \frac{\beta h}{2}\int_{-\infty}^t ds\,\left\langle \mathcal{K}_s^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} +$$

$$+\frac{\beta h}{2}\int_{-\infty}^0 ds\,\left\langle \mathcal{K}_s^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} \tag{6.3.5}$$

Note that on the left-hand side there is the difference between two average values with the same initial distribution and different dynamics. It is reasonable to assume that after a long time $\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}}$ evolves as if its initial distribution was $\rho^{\{y+h\}}$. This is due to the constancy of h. Therefore now we want to apply the limit $t \to \infty$ in (6.3.5). Note that this is equivalent to

$$\lim_{n\to\infty}\left(t + n\mathcal{T}\right)$$

where $\mathcal{T}$ is the period of any averaged function of the process X_t. In fact we can apply the limit $t \to \infty$ adding infinite period to time t. Note that:

$$\left\langle g^j\left(X_{t+n\mathcal{T}}^j - x_{t+n\mathcal{T}}\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} = \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}$$

Note that generally x_t is not a periodic process, therefore what we have just written is not correct. But now we are considering a static perturbation, then $x_t = y_t + h$. If y_t is periodic, also x_t must be periodic. Therefore:

$$\lim_{n\to\infty}\left[\left\langle g^j\left(X_{t+n\mathcal{T}}^j - x_{t+n\mathcal{T}}\right)\right\rangle_{\rho^{\{y\}}}^{\{y+h\}} - \left\langle g^j\left(X_{t+n\mathcal{T}}^j - x_{t+n\mathcal{T}}\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}\right] =$$

$$\lim_{n\to\infty}\frac{\beta h}{2}\left[\left\langle g^j\left(X^j_{t+n\mathcal{T}}-y_{t+n\mathcal{T}}\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}-\left\langle g^j\left(X^j_0-y_0\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}\right]-$$

$$-\lim_{n\to\infty}\frac{\beta h}{2}\int_{-\infty}^{t+n\mathcal{T}}ds\,\left\langle\mathcal{K}^j_s\left(X^j_s-y_s\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}+$$

$$+\lim_{n\to\infty}\frac{\beta h}{2}\int_{-\infty}^{0}ds\,\left\langle\mathcal{K}^j_s\left(X^j_s-y_s\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}$$

We already know what happens to the left-hand side. Now we have to understand what happens to the right hand side:

- In the first term we can use the periodicity of the average value. Therefore:

  $$\left\langle g^j\left(X^j_{t+n\mathcal{T}}-y_{t+n\mathcal{T}}\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}=\left\langle g^j\left(X^j_t-y_t\right);g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}$$

  is evident that it is not modified by the limit.

- In the second term we have to calculate the covariance between the same observable evaluated at infinite time-distance. This contribution reasonably tends to zero. Generally it is not easy to demonstrate. We have given a demonstration for the two states system in Section 2.1.3.3.

- In the third term we can do a variable change in the integral:

  $$s'=s-n\mathcal{T}$$

  Then:

  $$\int_{-\infty}^{t+n\mathcal{T}}ds\,\left\langle\mathcal{K}^j_s\left(X^j_s-y_s\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}=$$

  $$=\int_{-\infty}^{t}ds'\,\left\langle\mathcal{K}^j_{s'+n\mathcal{T}}\left(X^j_{s'+n\mathcal{T}}-y_{s'+n\mathcal{T}}\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}$$

  Again we can use the periodicity of the process:

  $$\int_{-\infty}^{t+n\mathcal{T}}ds\,\left\langle\mathcal{K}^j_s\left(X^j_s-y_s\right);g^j\left(X^j_{t+n\mathcal{T}}-x_{t+n\mathcal{T}}\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}=\int_{-\infty}^{t}ds'\,\left\langle\mathcal{K}^j_{s'}\left(X^j_{s'}-y_{s'}\right);g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}$$

- For the fourth term we can do the same the difference is that now the integral arrives till $s=0$, instead the covariance goes to infinite. For the same reason of the second term this contribution goes to zero.

Therefore after applying the long-time limit:

$$\left\langle g^j\left(X^j_t-x_t\right)\right\rangle^{\{y+h\}}_{\rho^{\{y+h\}}}-\left\langle g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}=\frac{\beta h}{2}\left\langle g^j\left(X^j_t-y_t\right);g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}-$$

$$-\frac{\beta h}{2}\int_{-\infty}^{t}ds\,\left\langle\dot{y}_s\frac{\partial g^j\left(X^j_s-y_s\right)}{\partial y};g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}-\frac{\beta h}{2}\int_{-\infty}^{t}ds\,\left\langle L_s g^j\left(X^j_s-y_s\right);g^j\left(X^j_t-x_t\right)\right\rangle^{\{y\}}_{\rho^{\{y\}}}\tag{6.3.6}$$

This is true if and only if the probe position is time-independent, or rather, when h_t is constant. To extend it to our case we will adopt an approximation. Whenever the probe changes position, it perturbs the fluid particles. Since $M \gg m$ and the coupling is small we expect that the probe moves much slower than the particles and then, the time-scale of x_t is much bigger than the one of X_t (for this reason we call the fast the fluid degrees of freedom, and slow the probe ones). Therefore, it is reasonable to assume that the particles can relax to a new periodic "stationary" state before the probe changes again position. In other words, the dynamics of the fluid is at any time described by periodic probability $P_t^{\{y+h_t\}}(X)$. We can write the response in this approximation considering (6.3.6) at fixed time t:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y+h_t\}}}^{\{y+h_t\}} - \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} = \frac{\beta h_t}{2}\left\langle g^j\left(X_t^j - y_t\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} -$$

$$-\frac{\beta h_t}{2}\int_{-\infty}^{t} ds\left\langle \dot{y}_s \frac{\partial g^j\left(X_s^j - y_s\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} - \frac{\beta h_t}{2}\int_{-\infty}^{t} ds\left\langle L_s g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} \tag{6.3.7}$$

Where now t is considered a fixed parameter. Now it is important to note that the right-hand side of (6.3.7) appears in (6.3.4). Therefore we can write:

$$\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{x_t\}} = \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y+h_t\}}}^{\{y+h_t\}} - \frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} +$$

$$+\frac{\beta}{2}\int_0^t ds\,\frac{dh_s}{ds}\int_{-\infty}^{s} du\left[\left\langle \dot{y}_u \frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} + \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}\right] \tag{6.3.8}$$

6.3.1 Langevin equation for the probe

In the last Section we have found an expression for the average value of the coupling $g^j\left(X_t^j - x_t\right)$. The observable $g^j\left(X_t^j - x_t\right)$, as we have said, appears in the equation of the motion for the probe and it describes the interaction of the probe with the particles. It is very difficult since it depends on the process X_t. But once averaged it over all the possible trajectories, $\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{x_t\}}$ will no longer depends on X_t, but only on x_t. We can interpret $g^j\left(X_t^j - x_t\right)$ as the fluctuation around its average value if we introduce a random variable η_t:

$$\sum_{j=1}^{n} g^j\left(X_t^j - x_t\right) - \left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{x_t\}} = \eta_t \tag{6.3.9}$$

where η_t will be the noise perceived by the probe. In the next Section we are going to study its properties. If we consider the equation (6.2.5)

$$M\frac{d^2x_t}{dt^2} = \sum_{j=1}^{n}\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{x_t\}} + \eta_t$$

Now, if we insert (6.3.8) in the equation of the motion:

$$M\frac{d^2x_t}{dt^2} = \sum_{j=1}^{n}\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y+h_t\}}}^{\{y+h_t\}} + \eta_t - \frac{\beta}{2}\sum_{j=1}^{n}\int_0^t ds\,\frac{dh_s}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} +$$

$$+\frac{\beta}{2}\sum_{j=1}^{n}\int_0^t ds\,\frac{dh_s}{ds}\int_{-\infty}^{s} du\,\left[\left\langle \dot{y}_u\frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} + \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}\right]$$

If we define:

$$G\left(x_t\right) = \sum_{j=1}^{n}\left\langle g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y+h_t\}}}^{\{y+h_t\}}$$

It is a statistical force (due to its dependence on x_t) that no longer depends on X_t since we have integrated out the degrees of freedom of the fluid. It can be thought as an external force acting on the probe. It takes into account all the particles and it is the result of the dynamical reduction. It describes the mean interaction with the fluid and it is considered at fixed time. We obtain a Langevin equation depending on:

$$M\frac{d^2x_t}{dt^2} = G\left(x_t\right) + \eta_t - \frac{\beta}{2}\sum_{j=1}^{n}\int_0^t ds\,\frac{dh_s}{ds}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} +$$

$$+\frac{\beta}{2}\sum_{j=1}^{n}\int_0^t ds\,\frac{dh_s}{ds}\int_{-\infty}^{s} du\,\left[\left\langle \dot{y}_u\frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} + \left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}}\right]$$

If we call:

$$\gamma\left(t,s\right) = \frac{\beta}{2}\sum_{j=1}^{n}\left\langle g^j\left(X_s^j - y_s\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} - \frac{\beta}{2}\sum_{j=1}^{n}\int_{-\infty}^{s} du\,\left\langle \dot{y}_u\frac{\partial g^j\left(X_u^j - y_u\right)}{\partial y}; g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} -$$

$$-\frac{\beta}{2}\sum_{j=1}^{n}\int_{-\infty}^{s} du\,\left\langle L_u g^j\left(X_u^j - y_u\right); g^j\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y\}}}^{\{y\}} \tag{6.3.10}$$

we have found the expression of the friction coefficient perceived by the probe. It does not depend on the particles dynamics. The Langevin equation for the probe will be:

$$M\frac{d^2x_t}{dt^2} = G\left(x_t\right) + \eta_t - \int_0^t \frac{dh_s}{ds}\,\gamma\left(t,s\right) ds$$

The last contribution describes the energy dissipation due to the presence of the particles and it depends on the derivative of $h_s = x_s - y_s$. It depends on the fluctuations of the probe position around the instantaneous equilibrium, therefore it can be thought as the probe velocity. This contribution is not memoryless since it depends on all the evolution. Using the linear response theory we have obtained one of the fundamental ingredient of the Langevin equation, the friction coefficient.

6.3.2 The Noise

By definition the noise is given by:

$$\eta_t = \sum_{j=1}^{n} \left[g^j \left(X_t^j - x_t \right) - \left\langle g^j \left(X_t^j - x_t \right) \right\rangle^{\{x_t\}} \right]$$

Then:

- $\langle \eta_t \rangle^{\{x_t\}} = 0$
- $\langle \eta_s \eta_t \rangle^{\{x_t\}} = \sum_{j=1}^{n} \left\langle g^j \left(X_s^j - x_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle^{\{x_t\}}$

Using the approximation of weak coupling (λ small) we relate these average values to the ones made over the periodic steady state $\{y\}$ Therefore:

$$\langle \eta_s \eta_t \rangle^{\{x_t\}} = \sum_{j=1}^{n} \left\langle g^j \left(X_s^j - x_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle^{\{y\}} + O\left(\lambda^2\right)$$

This is easily understandable using linear response theory given that the perturbation depends on $g^j \left(X_t^j - y_t \right)$ and, then, on λ. The noise perceived by the probe is not gaussian and it depends on the coupling between particle and probe. Note that:

- x_t differs from y_t (in absence of other external forces) for the fluctuations, or rather, for the noise. For the linear response theory we have assumed h_t small, but this is true if and only if the intensity of the fluctuation are not too big. This condition is assured by the weak coupling assumption.
- If there would be no interaction between the particles all the contributions of the sum over j in η_t would be independent and equal. Then, according to the central limit, η_t would converge to a gaussian distribution. Therefore, the memory is due to the interaction between the particles. This result is equal to the one found in the equilibrium case.

6.3.3 Second F-D theorem

First of all we are interested in the property of the noise perceived by the Brownian probe:

$$\eta_t = \sum_{j=1}^{n} g^j \left(X_t^j - x_t \right) - \left\langle g^j \left(X_t^j - x_t \right) \right\rangle_{\rho^{\{y\}}}^{\{x_t\}}$$

Then:

$$\langle \eta_t \rangle_{\rho^{\{y\}}}^{\{x_t\}} = \sum_{j=1}^{n} \left\langle g^j \left(X_t^j - x_t \right) \right\rangle_{\rho^{\{y\}}}^{\{x_t\}} - \left\langle g^j \left(X_t^j - x_t \right) \right\rangle_{\rho^{\{y\}}}^{\{x_t\}} = 0$$

$$\langle \eta_s \eta_t \rangle_{\rho^{\{y\}}}^{\{x_t\}} = \sum_{j=1}^{n} \left\langle \left[g^j \left(X_s^j - x_s \right) - \left\langle g^j \left(X_s^j - x_s \right) \right\rangle_{\rho^{\{y\}}}^{\{x_t\}} \right] \cdot \left[g^j \left(X_t^j - x_t \right) - \left\langle g^j \left(X_t^j - x_t \right) \right\rangle_{\rho^{\{y\}}}^{\{x_t\}} \right] \right\rangle_{\rho^{\{y\}}}^{\{x_t\}}$$

$$\langle \eta_s \eta_t \rangle_{\rho\{y\}}^{\{x_t\}} = \sum_{j=1}^{n} \left\langle g^j \left(X_s^j - x_s \right) g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{x_t\}} - \left\langle g^j \left(X_s^j - x_s \right) \right\rangle_{\rho\{y\}}^{\{x_t\}} \left\langle g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{x_t\}}$$

$$\langle \eta_s \eta_t \rangle_{\rho\{y\}}^{\{x_t\}} = \sum_{j=1}^{n} \left\langle g^j \left(X_s^j - x_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{x_t\}}$$

These results are true for each initial distribution. Note that η_t is not a white noise. We have found a relation between friction and covariance over the perturbed average value, but we can solve only the unperturbed ones. For what we have said in the previous Section we can write it as an unperturbed average value committing an error of order λ^2. Note that the noise correlation expression is close to the first term of the friction expression (6.3.10), but here we have $\left\langle g^j \left(X_s^j - x_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle$ instead of $\left\langle g^j \left(X_s^j - y_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle$. Using the weak coupling assumption we can expand it:

$$g^j \left(X_s^j - x_s \right) = g^j \left(X_s^j - y_s \right) + \left(x_s - y_s \right) \frac{\partial}{\partial x} g^j \left(X_s^j - x_s \right)_{|_{x_s = y_s}} + \mathcal{O}\left(h_s \right)$$

here h_s is small due to the weak coupling assumption and $g^j \left(X_s^j - x_s \right)$ with all its derivative is proportional to λ therefore, the linear order is proportional to λ^2. Due to it we can write:

$$\langle \eta_s \eta_t \rangle_{\rho\{y\}}^{\{x_t\}} = \left\langle g^j \left(X_s^j - y_s \right) ; g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{y\}} + \mathcal{O}\left(\lambda^2 \right) \tag{6.3.11}$$

Now the two expressions coincide. Therefore we can insert (6.3.11) in (6.3.10):

$$\gamma\left(t, s \right) = \frac{\beta}{2} \langle \eta_s \eta_t \rangle_{\rho\{y\}}^{\{y\}} - \frac{\beta}{2} \sum_j \int_{-\infty}^{s} du \left\langle \dot{y}_u \frac{\partial g^j \left(X_u^j - y_u \right)}{\partial y} ; g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{y\}} -$$

$$- \frac{\beta}{2} \sum_j \int_{-\infty}^{s} du \left\langle L_u g^j \left(X_u^j - y_u \right) ; g^j \left(X_t^j - x_t \right) \right\rangle_{\rho\{y\}}^{\{y\}}$$

The $\langle \eta_s \eta_t \rangle$ describes the fluctuation of the noise for the particles. Firstly we have to note that generally it is no longer white and it depends on the perturbation to the fluid. We have found a relation between the friction and the noise covariance. It is different from the second fluctuation-dissipation relation for equilibrium system studied in [4]. As for the equilibrium relation the first term is the entropic contribution, due to the nonequilibrium response theory there is a $\frac{1}{2}$ pre-factor and the last two terms are nonequilibrium corrections. The one depending on $\dot{y}_t$ is still an entropic contribution, while the last is due to the dynamical activity depending on the backward generator. Note that if $y_s \equiv y$ would be constant we would obtain the second fluctuation-dissipation relation found in [4] for stationary nonequilibrium dynamics. This formula paves the way to negative friction physical phenomena. The sum over j has a huge number of terms, then the convergence of the series is controlled by the covariances. This is indeed the second fluctuation-dissipation relation for a nonequilibrium system. It relates the fluctuation of the only random part in the Langevin equation for the probe to the drag contribution that is the dissipative contribution. As we expect it is different from the second fluctuation-dissipation relation for equilibrium system studied in [4] . The correction is due to the dynamical activity depending on the backward generator. This is in agreement with the nonequilibrium linear response theory.

6.4 Example

We consider time-homogeneous driven diffusion on the circle $X_t \in S^1$ with

$$\dot{X}_t = \nu E - \nu V'(X_t) + \sqrt{2D_x}\xi_t$$

where the potential V is periodic in x. For non-zero forcing $E > 0$ the particle will start to move around the circle, reaching a steady angular velocity

$$J = \frac{\nu E}{\oint dX\, \rho^{-1}(X)} > 0 \tag{6.4.1}$$

for probability density $\rho(x)$, $x \in S^1$ which solves the stationary Smoluchowski equation

$$(\nu(E - V')\rho)' - \beta^{-1}\rho'' = 0$$

The system converges to a nonequilibrium stationary regime. This current and probability density should be interpreted as follows. One considers a great many of such identical independent particles with positions x_t^j in the same toroidal trap and then ρ actually gives the real particle density in the steady regime. Similarly the mass center over all particles moves with angular velocity J.

Imagine now a probe inserted in that environment made up of the fluid particles (with positions denoted above by X_t^j). If the probe is sufficiently big compared to the fluid particles we expect that ignoring fluctuations the probe follows the motion $\dot{y}_t = J$ on S^1. The fluid particles interact with the probe position via some smooth potential U so that the new dynamics of the fluid becomes

$$\dot{X}_t^j = \nu E - \nu \sin\left(X_t^j\right) - \lambda\nu\partial_j U\left(X_t^j - y_t\right) + \sqrt{2D_x}\xi_t^j \tag{6.4.2}$$

which couples each X_t^j with y_t, defined as the solution of $\dot{Y}_t = J$ on S^1. In this example we ignore the interaction between the fluid particles. Here we see a driven motion with forcing $F\left(X_t^j\right) = E - \sin\left(X_t^j\right)$ and with a time-dependent periodic protocol y_t (rotation with angular velocity J). But the probe does not strictly be following the dynamics $\dot{y}_t = J$, as there will be fluctuations and perhaps extra forces acting on the probe. In other words, the probe has a position X_t not exactly equal to Y_t, but we expect that X_t more or less follows Y_t, especially when averaged over many runs or over many identical but independent particles. Therefore the complete Langevin equation for the fluid particles is

$$\dot{X}_t^j = \nu E - \nu \sin\left(X_t^j\right) - \lambda\nu\partial_j U\left(X_t^j - x_t\right) + \sqrt{2D_x}\xi_t^j \tag{6.4.3}$$

where X_t is generally not-periodic. The coupling with the probe produces a time-dependent nonequilibrium dynamics for the fluid. If $x_t - y_t$ is small we can expand the potential U around $x_t = y_t$. At the zero order we obtain (6.4.2). If we truncate the expansion to the first order we can use the linear response theory to study how the probe motion perturbs the fluid dynamics. We consider equation (6.4.3) making a choice for the potential

$$\dot{X}_t^j = \nu E - \nu \sin\left(X_t^j\right) - \lambda\nu \sin\left(X_t^j - y_t\right) + \sqrt{2D_x}\xi_t^j$$

Here we are ignoring the interaction between the fluid particles. If we expand the coupling around $X_t = Y_t$ and we write it as a potential perturbation for the fluid dynamics

$$\dot{X}_t^j = \nu E - \nu \sin\left(X_t^j\right) - \lambda\nu \sin\left(X_t^j - y_t\right) + \lambda\nu h_t \partial_j \sin\left(X_t^j - y_t\right) + \sqrt{2D_x}\xi_t^j$$

Following what we have done in Section 6.3, the equation for the probe is

$$M\ddot{x}_t = \sum_j \left\langle \sin\left(X_t^j - x_t\right)\right\rangle_{\rho^{\{y+h_t\}}}^{\{y+h_t\}} + \eta_t - \int_0^t ds\, \frac{dh_s}{ds}\gamma\left(t,s\right)$$

where:

$$\langle \eta_s \eta_t \rangle^{\{x_t\}} \simeq N \left\langle \sin\left(X_s - y_s\right); \sin\left(X_t - x_t\right)\right\rangle^{\{y\}}$$

$$\gamma\left(t,s\right) = \frac{\beta N \lambda}{2}\left\langle \sin\left(X_s - y_s\right); \sin\left(X_t - x_t\right)\right\rangle^{\{y\}} + \frac{\beta N \lambda J}{2}\int_{-\infty}^{s} du \left\langle \cos\left(X_u - y_u\right); \sin\left(X_t - x_t\right)\right\rangle^{\{y\}}$$

$$-\frac{\beta N \lambda}{2}\int_{-\infty}^{s} du \left\langle L_u \sin\left(X_u - y_u\right); \sin\left(X_t - x_t\right)\right\rangle^{\{y\}}$$

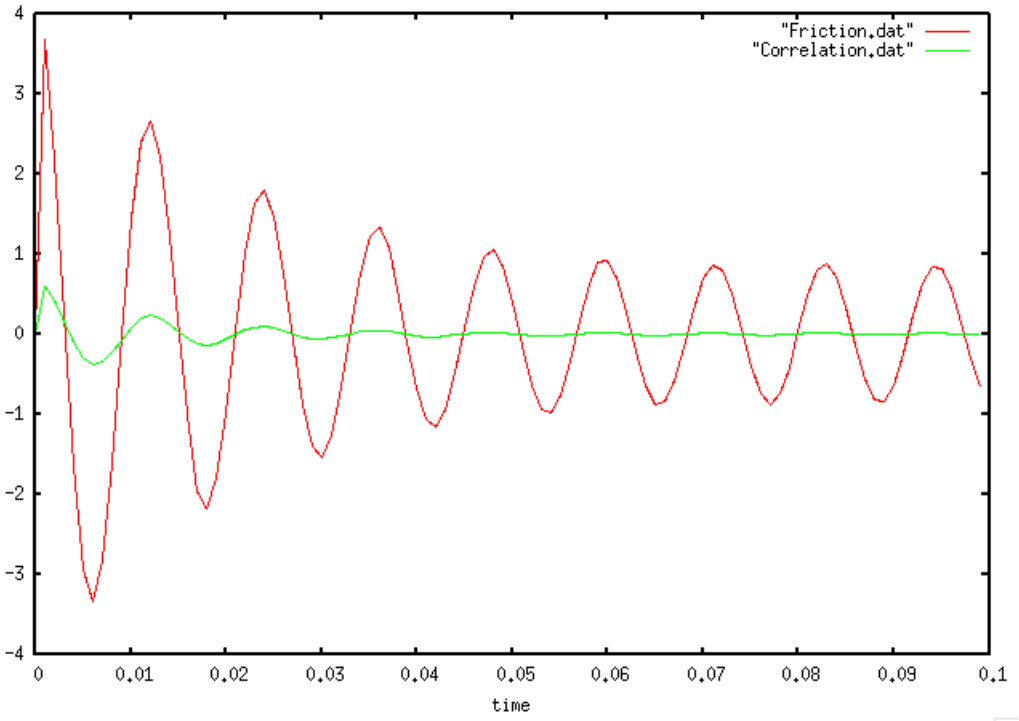
with:

$$L_s \sin\left(X_s - y_s\right) = \left[\nu E - \nu \sin\left(X_s\right) - \lambda\nu \sin\left(X_s - y_s\right)\right]\cos\left(X_s - y_s\right) - \beta^{-1}\sin\left(X_s - y_s\right)$$

we have used $\dot{y}_t = J$. Here it appears N because the particles are equally distributed due to their independence, therefore we can forget about the j index. We have done a numerical simulation in two steps:

- Simulate the fluid dynamics without the coupling with the probe in order to obtain the current J that is equal to $\dot{y}_t$ according to (6.4.1). Since there is no time-dependent force the dynamics relaxes to a nonequilibrium steady state (due to the nonconservative constant force). The current tends to a constant value.
- Simulate the perturbed dynamics (6.4.3). In order to do it we have to evolve at each step of width dt the trajectory y_t that is given by the current J (we take to stationary value obtained from the first simulation) multiplied by the time t and the probe position X_t. To determine it we solved the equation (6.2.2). The average value are made simulating many trajectories. The average value at a certain time is made summing the value of the process at that time for each trajectory and then dividing by the number of trajectory.

With a numerical simulation we have obtained $\langle \eta_0\, \eta_s \rangle^{\{x_t\}}$ and $\gamma\left(s\right)$:



As we can note the correlation goes quickly to zero. This is what we expect since without interacting particle the noise becomes white. Instead the friction, after a relaxing time, does not become constant, but it oscillate periodically around the same values.

6.4.1 Considerations

In this Chapter we have obtained an expression for the friction perceived by the probe, but we have not said anything about the diffusion coefficient. If local detailed balance is no longer satisfied the Einstein-Smoluchowski equation is no longer valid. Due to it, the diffusion coefficient perceived by the probe is not easily estimable. If the probe dynamics is slowly changing, it is possible to obtain an extension to Einstein-Smoluchowski relation adding a correcting contribution and then obtain the diffusion coefficient. In [17] it has been made for a stationary nonequilibrium fluid, but it is still unknown for a periodic steady state. A possible development of the presented theory would be to obtain the correction in the not-stationary regime in order to find the diffusion coefficient and to complete the understanding of the probe motion.

Furthermore, in this work we have supposed no external force acts directly on the probe, differently from [4]. In fact, in this case the h_t is not referred to a constant point y, minimum of the potential V, but it is referred to a trajectory, property of the fluid. If we would suppose the presence of a potential for the probe with a minimum, it would not be easy to conciliate the dynamics y_t with the tendency to stay close to the minimum. A possible development would be the understanding of this conciliation.

In this work we have presented a method to describe a generic nonequilibrium system. In fact proceeding by steps as just described we can obtain every needed Langevin equation and then using it for the following step. This method is general and the only requirements are the ones needed for the linear response theory. The description of nonequilibrium could then be viewed as a chain in which each step is related to the following one. The relation is given by the local detailed balance principle. Therefore, if for a step this principle is no longer satisfied, the chain is "broken".

It means that it is no longer possible to obtain the property of that system from the surrounding dynamics. An example is indeed the Einstein-We have obtained an expression for the friction perceived by the probe, but we have not said anything about the diffusion coefficient. If local detailed balance is no longer satisfied the Einstein-Smoluchowski equation is no longer valid. Due to it, the diffusion coefficient perceived by the probe is not easily estimable. If the probe dynamics is slowly changing, it is possible to obtain an extension to Einstein-Smoluchowski relation adding a correcting contribution and then obtain the diffusion coefficient. In [17] it has been made for a stationary nonequilibrium fluid, but it is still unknown for a periodic steady state. A possible development of the presented theory would be to obtain the correction in the not-stationary regime in order to find the diffusion coefficient and to complete the understanding of the probe motion.

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In this work we have presented a method to describe a generic nonequilibrium system. In fact proceeding by steps as just described we can obtain every needed Langevin equation and then using it for the following step. This method is general and the only requirements are the ones needed for the linear response theory. The description of nonequilibrium could then be viewed as a chain in which each step is related to the following one. The relation is given by the local detailed balance principle. Therefore, if for a step this principle is no longer satisfied, the chain is "broken". It means that it is not possible to obtain the property of that system from the surrounding dynamics. An example is indeed the Einstein-Smoluchowski equation. This kind of situations is really common for the nonequilibrium systems, especially for the not-stationary ones. Therefore it would be interesting to develop issues to go through the problem of the "broken" chain introducing reasonable approximations. equation. This kind of situations is really common for the nonequilibrium systems, especially for the not-stationary ones. Therefore it would be interesting to develop issues to go through the problem of the "broken" chain introducing reasonable approximations.

Chapter 7

Conclusions

7.1 Part I

In the first part of this thesis we have studied the time-dependent jump processes. In order to develop a general theory we have extended many properties of the jump processes to the time-dependent case, from the most obvious ones - as the backward generator - to the subtlest ones, as the entropy production. Since the transition rates are time-dependent, the probability of a time-dependent process does not have a stationary distribution. Nevertheless, the process converges to a particular regime in any case. To demonstrate it we have discussed the periodic regime evaluating the probability for a two states system and simulating a system with a generic number of states. In both cases, the probability depends on an exponentially decreasing term, therefore after a certain time, given by the transition rates of the process, the probability converges to a periodic regime that does not depend on the initial state.

This convergence is very important in order to explain the result obtained for entropy. In fact the Shannon entropy is based on the relative entropy between two equilibrium regimes of the process. Therefore if we consider a system at equilibrium and we perturb it, there will be a convergence to a new equilibrium, the relative entropy gives the amount of entropy produced during this relaxation in which the system is not at equilibrium. It can be extended to the nonequilibrium only if the relative entropy has still meaning and this is true only if it compares two stationary regimes. If the time-dependent probability converges to a "stationary" periodic regime, we can introduce a comparison in the long-time limit.

Furthermore we have discussed the linear response theory in the framework of the time-dependent processes. As in the time-independent situation, a perturbation can be of two types: if it facilitates or obstacles in the same way a transition or its opposite it is said symmetric for states exchange (this perturbation is thought as a global action as the variation of temperature). If it tends to facilitate a transition and to obstacle the opposite one it is said antisymmetric (usually it is associated to an external force). The symmetry for states exchange is very important because when we consider the trajectories, it is related to the time-reversal symmetry. We have seen that, if the perturbation is antisymmetric for states exchange the structure of the response is not changed respect to the time-independent case. While, it is not true if the perturbation is symmetric because, in this case, the perturbation acts also on the symmetric reactivities. The reactivities, that are the symmetric part of the transition rates, are related to the frenetic contribution that depends on the time-dependent backward generator.

7.2 Part II

In the second part we have studied the diffusive process introducing the Markov propagator. Imposing the Markov approximation we have derived the Fokker-Planck equation and the Langevin equation. After that, we have concentrated ourselves on the latter understanding its characteristics:

- The Langevin equation depends on two functions, the first represents the drift, it is deterministic and it depends on the forces. While the second represents the diffusion and it is stochastic. The structure of the equation is the same apart from the process is at equilibrium or not. In other words the Langevin equation formalism can be easily extended to nonequilibrium introducing not-conservative forces.

- The dynamics reduction, obtained by "integrating out" the fast variables related to the environment surrounding the system, and the two functions just recalled do not depend on the system scale. Therefore the Langevin equation can be used to study microscopic systems (e.g. a protein moving in a cell) as well as macroscopic systems (e.g. an air ballon moving in the atmosphere).

- The Langevin equation depends only on the system degrees of freedom via the dynamics reduction by integrating out the environment degrees of freedom. It can be done using the linear response theory for diffusive process. Therefore the Langevin equation can be thought as a consequence of linear response theory.

As an example of Langevin equation we have discussed the equilibrium Brownian motion. We have described the motion of a particle embedded in an equilibrium fluid depending on two parameters, the mobility and the diffusion coefficient. They are related via the so called Einstein-Smoluchowski equation. It depends also on the fluid temperature. Since the Langevin equation is a consequence of a dynamics reduction, it can be derived using the linear response theory. We have considered the probe as a perturbation to an equilibrium fluid. Proceeding in this way we have obtained those parameters (e.g. the mobility and the diffusion coefficient) as property of the fluid. Nevertheless, we have derived a way to determine those parameters as property of the system itself. These parameters are related via the fluctuation-dissipation relation, since the friction represents the energy dissipation and the diffusion coefficient gives the intensity of the fluctuation. Since at equilibrium the parameters obtained in the two ways coincide, the Einstein-Smoluchowski equation is equivalent to the fluctuation-dissipation relation.

After that, we have studied the nonequilibrium regime in order to obtain an extension of the Langevin equation. At the first step, our objective was to derive a Langevin equation for a nonequilibrium system in an equilibrium environment introducing not-conservative, or time-dependent external forces acting on the system. A nonequilibrium system can be seen as sum of subsystems that are locally at equilibrium. In each subsystem the equilibrium relations between mobility and diffusion coefficient (e.g. Einstein-Smoluchowski equation) are satisfied. If the system can be studied in this way it satisfies the local detailed balance principle. On the other hand, the local detailed balance principle, by definition, relates the action obtained by the trajectory probability to the entropy flux. These two definitions must be equivalent. In order to demonstrate it, we have studied a way to derive the entropy for a diffusive process.

We have shown how the mobility and the diffusion coefficient in the Langevin equation are not equal to the one derived as a property of the fluid. Out of equilibrium the system dynamics cannot be obtained as property of the fluid due to the nonequilibrium response theory. The

response depends on a frenetic term that is important only out of equilibrium. Due to it the Einstein-Smoluchowski equation does no longer represent also the fluctuation-dissipation theorem. In fact out of equilibrium the mobility and the diffusion coefficient that appear in this relation are properties of the fluid, and we have said that out of equilibrium they do not correspond to the ones properties of the system. In other words out of equilibrium the Einstein-Smoluchowski equation is only an useful relation between variables that appear in the Langevin equation.

Furthermore, we have studied the case in which the environment itself is out of equilibrium. This situation is very common in the biological physics under the name of active matter. We have developed the linear response theory for the diffusive processes using the stochastic integration in order to develop the necessary tools to obtain the Langevin equation for a probe embedded in a nonequilibrium fluid. This is what we have done in the last Chapter. The problem is divided in two steps:

- First, we have considered a Langevin equation for the fluid particles in contact with one (or more) reservoir. At this level the system is the fluid and the environment is the thermal bath. According to it, the system dynamics satisfies the local detailed balance condition. Note that even if the temperature is constant we cannot consider detailed balance due to the nonequilibrium force acting on the fluid.

- Second, we have used the Langevin equation for the fluid to obtain an equation for the probe. In this case the system is the probe and the environment is the fluid. Now it is no longer reasonable to assume the validity of the local detailed balance principle due to the not-stationary dynamics of the fluid.

In the last chapter we have presented the dynamics reduction for a not-stationary nonequilibrium system and we have seen how also in this context the noise and the friction are obtained by averaging the fluid dynamics. Since the fluid is made by interacting particles the friction and the noise correlation at different times depend on all the history of the fluid motion. We have demonstrated that if the fluid particle would be not-interacting the noise correlation will converge to zero assuring a memoryless or Markovian dynamics. To demonstrate it we have also done a numerical simulation. Therefore the not-Markovianity is a consequence of the particle interactions.

Relating the friction and the noise correlation expressions we have obtained the second fluctuation-dissipation relation for a nonequilibrium fluid in a periodic "stationary" state. As we can see, this expression is different from the equilibrium one, since it depends also on the frenetic contribution of the linear response. Once again the nonequilibrium regime produces new terms that affect the whole dynamics.

The obtained Langevin equation is very important due to its versatility. In fact we have not assumed anything about the system scale, therefore it could describe any system, from the microscopic to the macroscopic world. For this reason we have decided in this thesis to develop its meaning and to extend it to the most general situation. Nevertheless this equation is not complete. In fact we need to find also the diffusion coefficient perceived by the particle. In the equilibrium case we have derived the friction expression and then we have used the Einstein-Smoluchowski to find the diffusion coefficient. But, in this situation it is not possible since for the probe system it is no longer possible to use the local detailed balance relation. In this case the Einstein-Smoluchowski must be corrected adding another contribution. A possible development to this result would be to find the extension to Einstein-Smoluchowski for periodic "stationary" state and then find the diffusion coefficient expression. Furthermore, it would be interesting to consider more then one probe particles embedded in the fluid. In this case, in fact, they could interact

directly via a potential, or indirectly via the fluid perturbed by them. The possible applications of this theory are many. One example is the Superconductivity where the interaction between the Cooper's couple electrons is made via the phonons emitted by the ions lattice. As it is easily understandable, the potentiality of this theory is big and it is our interest to comprehend it.

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