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Non equilibrium statistical mechanics

Michel Le Bellac

Institut Non Linéaire de Nice

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Abstract

In part I of these lecture notes, I introduce the basic tools of non equilibrium statistical mechanics: linear response, Brownian motion, Langevin equation, (Pauli) master equation. Part II is devoted to a derivation of quantum master equations from the Schrödinger equation, and to some of their applications to quantum optics and to Brownian motion. Finally, in part III, I examine more recent developments: the Crooks and Jarzynski equalities and the Gallavotti-Cohen fluctuation theorem.

Contents

Chapter 1

Introduction: basic tools

In equilibrium statistical mechanics, all thermodynamics properties are derived from the partition function: once a physicist is given a Hamiltonian, his job is to compute as accurately as possible the partition function $Z = \mathrm{Tr}\,\exp[-\beta H]$, either by using exact analytic calculations, or perturbative expansions, or variational methods, or numerical methods etc. So, textbooks on equilibrium statistical mechanics all look more or less the same. The situation is very different in non equilibrium statistical mechanics: there one finds a variety of approaches, whose connections are far from evident, and seemingly of no universal validity. The purpose of this set of lectures is to show that there is nevertheless some underlying unity in this variety of approaches. In this first chapter, I'll review the basic tools of non equilibrium statistical mechanics.

1.1 Microscopic reversibility and macroscopic irreversibility

Our everyday world is clearly irreversible: you cannot put back your eggs together when you have begun an omelette and decide, that, after all, you would like them hard boiled, you can watch and ice cube melting in a glass of water at 20ºC, but ice cubes do not form spontaneously in the glass, and dead people do not rise and walk out of their graves (except in not so well documented cases...). However, for a physicist, this should be surprising, because a physicist knows that the basic equations of motion are invariant under time reversal, with the exception of a very weak interaction whose effects have been visible up to now only in some delicate experiments on the $K^0 - \overline{K^0}$ and $B^0 - \overline{B^0}$ meson systems. Although very difficult to detect, these time non invariant interactions have had an enormous importance in the early history of the Universe: without them, matter would not dominate over antimatter. However, they can be ignored for the purpose of these lectures, because the only interactions we shall be considering are electromagnetic interactions, which are known to be invariant under time reversal.

Let us examine invariance under time reversal in classical mechanics. Suppose we have an ensemble of interacting particles, for example, the molecules in a gas, and we look at the trajectory of particle i, $i = 1, \ldots, N$, which goes through the point $\vec{r}_i(0)$ at time $t = 0$ with momentum $\vec{p}_i = \vec{p}_i(0)$ (figure 1.1). At time τ, it is located at a point $\vec{r}_i(\tau)$ with momentum $\vec{p}_i(\tau)$. Let us assume that we are able to reverse the momenta (or the velocities) of all particles at $t = \tau$: $\vec{p}_i(\tau) \to -\vec{p}_i(\tau)$. This cannot be done in a real gas, but is easily implemented in a molecular dynamics numerical simulation. Then we wait for another time interval τ, and if invariance under time reversal is valid we shall have

$$\vec{r}_i(2\tau) = \vec{r}_i(0) \qquad \vec{p}_i(2\tau) = -\vec{p}_i(0) \tag{1.1}$$

Equation (1.1) leads us to an important definition: a dynamical variable such as a position $\vec{r}$ is *even under time reversal*, while a velocity $\vec{v}$ or a momentum $\vec{p}$ are *odd under time reversal*. The origin of (1.1) can be understood from an elementary example. Let us take the case of the one-dimensional motion of a particle submitted to a force $F(x(t))$

$$m\frac{\mathrm{d}^2 x(t)}{\mathrm{d}t^2} = F(x(t)) \tag{1.2}$$

and define the time reversed motion as $\overline{x}(t) = x(-t)$. We get from (1.2)

$$m\frac{\mathrm{d}^2\overline{x}(t)}{\mathrm{d}t^2} = m\frac{\mathrm{d}^2 x(-t)}{\mathrm{d}t^2} = F(x(-t)) = F(\overline{x}(t)) \tag{1.3}$$

so that the motion described by $\overline{x}(t)$ obeys Newton's law and is physically possible. If you were able to take a video of the molecules in a small volume of the gas and run it backwards, what you would see on the screen would appear as physically possible. This is very similar to parity invariance: if parity is conserved, the mirror image of an experiment appears physically possible: see Figure 1.2.
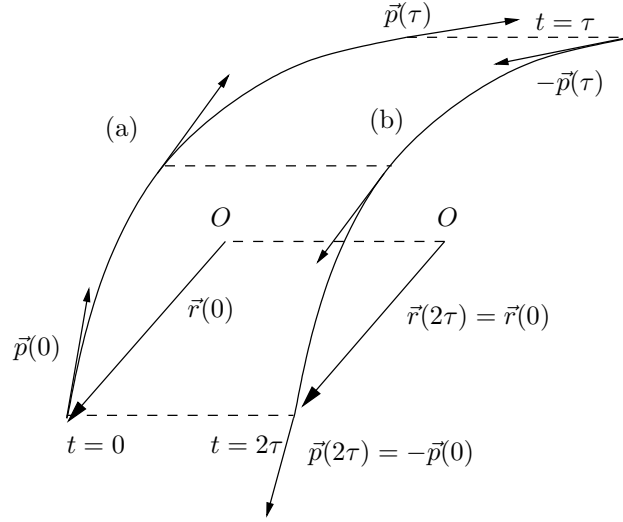

Figure 1.1: A trajectory (a) and the time reversed trajectory (b). In fact, the time reversed trajectory is superimposed on the original one, but it has been translated horizontally for clarity.

This is in sharp contrast with everyday life. If you run backwards a video of an everyday life event, you see your mistake at once! This is the irreversibility paradox: although the microscopic laws of nature are invariant under time reversal, macroscopic phenomena are not. But the paradox goes even deeper: as we shall see, microscopic reversibility has an important impact on the description of irreversible phenomena. For example, the fundamental property of detailed balance follows from time reversal invariance (§ 1.5.3), as well as the symmetry properties of the Onsager coefficients (§ 3.3.2).

The first physicist able to give an explanation of irreversibility was Ludwig Boltzmann, who understood that irreversibility could not be derived from purely mechanical arguments, and that statistical arguments had to be invoked: evolution goes from the less probable toward the more probable. Given macroscopic constraints, we can, at least in principle, count the number Ω of microscopic configurations compatible with these constraints: Ω is the phase space volume compatible with the constraints, also called the phase space volume of the macrostate. The probability that the system is found in a restricted volume Ω' of the phase space is simply Ω'/Ω. A standard example is that of a gas which is initially contained in the left compartment of a container divided into two halves. A hole is drilled in the wall between the two compartments. After some time, the gas will expand into the whole container, and it will never come back spontaneously in the left compartment. Following Boltzmann's line of thought, let us give the statistical explanation of this phenomenon. We know from statistical mechanics that the phase space volume $\Omega(E)$ for the energy E_r of the gas to lie in the range $E \le E_r \le E + \Delta E$ is

$$\Omega(E) = \frac{1}{N!h^N} \int_{E \le E_r \le E + \Delta E} \prod_{i=1}^{N} \mathrm{d}^3 r_i\, \mathrm{d}^3 p_i \tag{1.4}$$

where N is the number of molecules, h Planck's constant, $\vec{p}$ denotes the momentum and we have assumed that the gas obeys Maxwell-Boltzmann's statistics. If the gas is approximately an ideal gas, then the
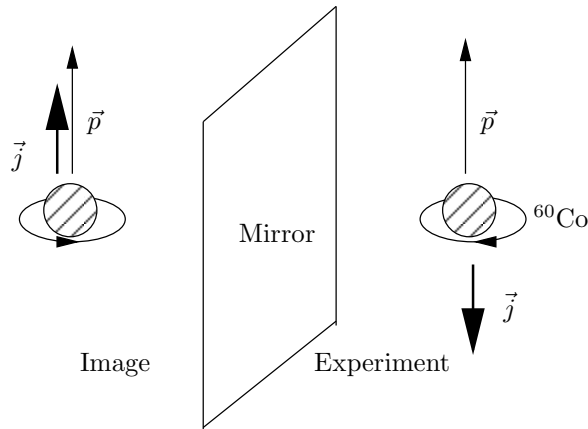
Figure 1.2: Parity non invariance in the Wu experiment. This experiment studies the decay of polarized ^{60}Cobalt, and shows that the electrons are emitted preferentially in the direction $\vec{p}$ opposite to that of the ^{60}Co angular momentum $\vec{j}$. The image of the experiment in the mirror does not correspond to a possible process.

ratio of the volumes in phase space is

$$\frac{\Omega_{\text{fin}}}{\Omega_{\text{in}}} \simeq \left(\frac{V_{\text{fin}}}{V_{\text{in}}}\right)^N = 2^N \tag{1.5}$$

so that the probability of finding all the molecules in the left compartment is $\sim 2^{-N}$.

This argument by Boltzmann was severely criticized by his contemporaries, and it may be that this criticism led him to commit suicide. The main two objections were made by Zermelo and Loschmidt. Zermelo used a theorem proved by Poincaré: a finite Hamiltonian system will come back arbitrarily close to its starting point in phase space if one waits long enough. This phenomenon is called a *Poincaré recurrence*. However, the time necessary to see a Poincaré recurrence, that is, Poincaré's recurrence time, grows as $\sim \text{e}^N$, and even for a small number of degrees of freedom you might have to wait for times of the order of the age of the Universe in order to see a recurrence (see e. g. Dorfman [1999], chapter 3). Loschmidt argued from time reversal invariance. Let us again take the expanding gas example, let the hole be drilled at time $t = 0$, and let us wait for a time τ. At time τ we reverse the velocities of all the molecules, and at time $t = 2\tau$ all molecules will be located in the left compartment. This behaviour is very easy to check on a numerical simulation. However, one notices that the slightest errors on the reversed velocities tend to destroy the phenomenon very rapidly. This is a consequence of the chaotic character of the dynamics, because chaotic dynamics implies extreme sensitivity to the initial conditions: two trajectories with almost identical initial conditions will diverge exponentially. To summarize: irreversibility is linked to the following properties.

1. The validity of a probabilistic reasoning which relates the probability of a macrostate to the occupied volume in phase space.

2. The existence of an enormous number ($\sim 10^{23}$) of degrees of freedom.

3. Initial conditions which fill only a very small volume of the available phase space: the probability of the initial macrostate becomes negligible when the initial constraints have been lifted.

4. The chaotic character of the dynamics.

However, although the preceding list certainly contains part of the truth, it is likely that we do not have at present a fully convincing picture of non-equilibrium statistical mechanics. As Maes and Netocny (Maes and Netocny [2003]) put it "Non equilibrium statistical mechanics is to a large extent still under construction".

1.2   The damped harmonic oscillator

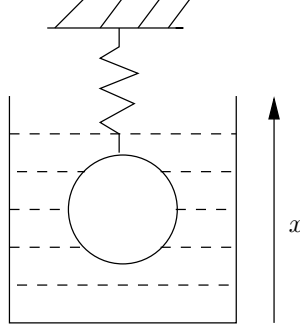### 1.2.1   Dynamical susceptibility

Figure 1.3: A damped harmonic oscillator.

A simple example of an irreversible system is the damped harmonic oscillator. To fix ideas, let us consider a mass m linked to a spring and oscillating in a viscous medium (Figure 1.3): it is submitted to the standard harmonic force $-m\omega_0^2 x$ and a viscous force $-m\gamma\dot{x}$. In addition we assume that the oscillator is forced

$$\boxed{\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{F(t)}{m} = f(t)} \tag{1.6}$$

Even in the absence of the external force $F(t)$, the equation of motion

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}x}{\mathrm{d}t} + \omega_0^2 x = 0 \tag{1.7}$$

is not invariant under time reversal, because of the term depending on the first order derivative, $\gamma\dot{x}$. If we set as previously $\overline{x}(t) = x(-t)$, the equation of motion for $\overline{x}$ is

$$\frac{\mathrm{d}^2\overline{x}}{\mathrm{d}t^2} - \gamma\frac{\mathrm{d}\overline{x}}{\mathrm{d}t} + \omega_0^2\overline{x} = 0$$

The viscosity accelerates the pendulum! Of course, it is to be understood that the expression for the viscous force $-m\gamma\dot{x}$ is a phenomenological expression, which takes into account in an effective way the complicated interactions between the mass and the fluid. When we consider the ensemble pendulum plus fluid (or reservoir), the full Hamiltonian is invariant under time reversal, but we get phenomenological time non invariant equations when we restrict ourselves to the pendulum. The viscous force $-m\gamma\dot{x}$ is not a fundamental force, but it gives an effective (and very useful!) description of viscosity. As we shall see in detail in these lectures, this effective description relies on the existence of two widely separated time scales, a microscopic one τ_c and a macroscopic one τ, with $\tau_c \ll \tau$: this is the reason which allows us to concentrate on the motion with the long time scale.

This preliminary remark being made, we now concentrate on our main goal, which is to describe the response of the oscillator to the external excitation $f(t)$. Since the equation of motion (1.6) is linear, $x(t)$ must be a linear functional of $f(t)$ in a stationary regime

$$\boxed{x(t) = \int_{-\infty}^{+\infty} \mathrm{d}t'\, \chi(t - t')f(t')} \tag{1.8}$$

The function $\chi(t)$ is called the *dynamical susceptibility*. We have implicitly assumed time translation invariance: this assumption would not hold when considering aging phenomena, in which case χ would

be a function of t *and* t'. Another way of writing (1.8) is to use a functional derivative

$$\frac{\delta x(t)}{\delta f(t')} = \chi(t - t')$$

Since (1.8) gives $x(t)$ as a convolution, it takes the form of a product in Fourier space

$$\tilde{x}(\omega) = \tilde{\chi}(\omega)\,\tilde{f}(\omega) \tag{1.9}$$

where $\tilde{x}$, $\tilde{\chi}$ and $\tilde{f}$ are Fourier transforms of x, χ and f (see the next subsection). As we shall see, equations (1.8) or (1.9) are valid not only for the forced harmonic oscillator, but also for general systems submitted to a weak perturbation. They are exactly valid for the harmonic oscillator, but only in the linear approximation in the more general case.

1.2.2 Analytical properties

One very important property of the dynamical susceptibility follows from *causality*: the effect should follow the cause, which means that $\chi(t) = 0$ if $t < 0$. This entails that we can define the Laplace transform $\tilde{\chi}(z)$ of $\chi(t)$ when z is located in the upper complex plane, $\mathrm{Im}\,z > 0$. Indeed, the integral giving $\chi(z)$

$$\tilde{\chi}(z) = \int_0^\infty \mathrm{e}^{\,\mathrm{i}zt}\,\chi(t)\mathrm{d}t \tag{1.10}$$

is certainly convergent when $\mathrm{Im}\,z > 0$. The Fourier transform $\tilde{\chi}(\omega)$ will be defined by the limiting procedure

$$\tilde{\chi}(\omega) = \lim_{\eta \to 0^+} \tilde{\chi}(\omega + \mathrm{i}\eta)$$

Since $\chi(t)$ is a real function, the real part $\tilde{\chi}'(\omega)$ and the imaginary part $\tilde{\chi}''(\omega)$ of $\tilde{\chi}(\omega)$ are even and odd functions of ω respectively

$$\tilde{\chi}'(\omega) = \lim_{\eta \to 0^+} \int_0^\infty \chi(t)\mathrm{e}^{-\eta t}\,\cos\omega t\,\mathrm{d}t \tag{1.11}$$

$$\tilde{\chi}''(\omega) = \lim_{\eta \to 0^+} \int_0^\infty \chi(t)\mathrm{e}^{-\eta t}\,\sin\omega t\,\mathrm{d}t \tag{1.12}$$

A useful formula is obtained by noticing that $\chi(t)$ may be decomposed into components which are even and odd in t,

$$\chi_{\mathrm{even}}(t) = \frac{1}{2}[\chi(t) + \chi(-t)] \qquad \chi_{\mathrm{odd}}(t) = \frac{1}{2}[\chi(t) - \chi(-t)]$$

and that

$$\chi(t) = 2\theta(t)\chi_{\mathrm{odd}}(t) = 2\mathrm{i}\theta(t)\chi''(t)$$

where $\theta(t)$ is the step function and $\chi''(t)$ the inverse Fourier transform of $\tilde{\chi}''(\omega)$. Then we get

$$\tilde{\chi}(z) = 2\mathrm{i} \int_0^\infty \mathrm{d}t\,\mathrm{e}^{\,\mathrm{i}zt} \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} \tilde{\chi}''(\omega)\mathrm{e}^{-\mathrm{i}\omega t}$$

and performing the t integration

$$\boxed{\tilde{\chi}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\tilde{\chi}''(\omega)}{\omega - z}\mathrm{d}\omega} \tag{1.13}$$

This is a *dispersion relation* for $\tilde{\chi}(z)$. It is instructive to write the explicit form of $\tilde{\chi}''(\omega)$ in the case of the damped harmonic oscillator. Because of our definition (1.10) of Fourier transforms, $\partial_t \to -\mathrm{i}\omega$, so that the Fourier transform of (1.6) reads

$$\tilde{x}(\omega)[-\omega^2 - \mathrm{i}\gamma\omega + \omega_0^2] = \tilde{f}(\omega)$$

and we immediately get $\chi(\omega)$

$$\tilde{\chi}(\omega) = \frac{\tilde{x}(\omega)}{\tilde{f}(\omega)} = \frac{-1}{\omega^2 + i\gamma\omega - \omega_0^2} \tag{1.14}$$

One checks that $\tilde{\chi}(\omega)$ is analytic in the upper half plane $\text{Im}\,\omega > 0$. Taking the imaginary part of (1.14), we obtain $\tilde{\chi}''(\omega)$

$$\tilde{\chi}''(\omega) = \frac{\omega\gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2} \geq 0 \tag{1.15}$$

1.2.3   Dissipation

If we want to maintain the damped oscillator in a state of stationary motion, we must provide it with energy, otherwise the motion would stop due to viscosity: our oscillator is then in a *stationary non equilibrium state*. The energy which is supplied to the oscillator is dissipated into heat in the reservoir. We are going to show that dissipation is governed by the function $\tilde{\chi}''(\omega)$. The proof given below applies to general linear response theory, and is not restricted to the harmonic oscillator. Assume that the force $f(t)$ is harmonic

$$f(t) = \text{Re}\left[f_0 e^{-i\omega t}\right] = f_0 \cos \omega t$$

where f_0 has been chosen real for simplicity. From (1.8) which we write, using causality, in the form

$$x(t) = \int_0^\infty dt'\, \chi(t') f(t - t')$$

we find that $x(t)$ is given by

$$
\begin{aligned}
x(t) &= \text{Re}\left[f_0 e^{-i\omega t} \int_0^\infty \chi(t') e^{i\omega t'}\, dt'\right] = \text{Re}\left[f_0 e^{-i\omega t}\tilde{\chi}(\omega)\right] \\
&= f_0\left[\tilde{\chi}'(\omega)\cos\omega t + \tilde{\chi}''(\omega)\sin\omega t\right]
\end{aligned}
\tag{1.16}
$$

$\tilde{\chi}'(\omega)$ governs the part of the response which is in phase with the excitation, and $\tilde{\chi}''(\omega)$ the part which is out of phase by $\pi/2$. The power dW/dt which is dissipated in the reservoir is equal to the work done on the oscillator

$$\frac{dW}{dt} = f_0\,\dot{x}(t)\cos\omega t = f_0\,\cos\omega t\left[-\omega\tilde{\chi}'(\omega)\sin\omega t + \omega\tilde{\chi}''(\omega)\cos\omega t\right]$$

whence the time average

$$\boxed{\left\langle\frac{dW}{dt}\right\rangle = \frac{1}{2}\,\omega f_0^2\,\tilde{\chi}''(\omega)} \tag{1.17}$$

Because of the second law, $\langle dW/dt\rangle \geq 0$, and we learn that $\omega\tilde{\chi}''(\omega) \geq 0$. We shall see later on that (1.17) is an elementary case of the *fluctuation-dissipation theorem*, because $\tilde{\chi}''(\omega)$ will be related to fluctuations. Given (1.15), we see that $\langle dW/dt\rangle$ has a resonant shape: as is well known, dissipation goes through a maximum at resonance.

1.3   Classical linear response theory

We are now going to examine systems which stay close to equilibrium. As the deviations from equilibrium remain small, we shall be able to work in the framework of linear response theory[1]. However, I wish to emphasize that the validity of linear response requires more than small deviations from equilibrium. Most dynamical variables of the system, called *fast modes*, will exhibit wild fluctuations on short time intervals, with a characteristic time scale called the microscopic characteristic time τ_c. However, a few peculiar combination of microscopic modes, called the *slow modes*,[2] will exhibit a behaviour characterized

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[1] Objections against linear response theory have been raised by van Kampen. For an account of van Kampen's arguments and possible answers, se e. g. Dorfman [1999], chapter 6.

[2] In many cases, the existence of slow modes may be related to conservation laws.

by long time scale τ. *Statistical mechanics close to equilibrium depends on the fact that we have been able to identify all the slow modes, whose characteristic macroscopic time scale $\tau \gg \tau_c$. Then, we may try to project the full dynamics on the dynamics of slow modes only.* The back action of the fast modes on the slow modes is then described by a stochastic force and memory effects. This strategy is called the projection method, which can be studied in full generality (see, for example, Balian [1991], chapter 15, or Le Bellac *et al* 2004, chapter 9, which give references to the original literature). However, the corresponding formalism is somewhat heavy going, and, in these lectures, I'll use only simple versions of this method. In what follows, all the dynamical variables $A(t), B(t) \cdots$ which will be considered will always correspond to slow modes.

1.3.1 The fluctuation-response theorem

There are some complications when dealing with quantum linear response theory, so that we limit ourselves to a classical treatment and refer to the literature for the quantum case. Let us consider a classical dynamical system with N degrees of freedom and $2N$ canonically conjugate variables: N positions $q_i(t)$ and N momenta $p_i(t)$, $i = 1, \cdots, N$, with the shorthand notation

$$\{p_i(t), q_i(t)\} = [p(t), q(t)]$$

For simplicity, we assume that these variables are governed by a time-independent Hamiltonian $H(p, q)$

$$\dot{q} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{\partial H}{\partial q} \tag{1.18}$$

The time evolution from $t = 0$ to t is

$$[p(0), q(0)] \equiv [p, q] \rightarrow [p(t), q(t)] \equiv [p', q'] \tag{1.19}$$

and from Liouville's theorem

$$\mathrm{d}p\,\mathrm{d}q = \mathrm{d}p'\mathrm{d}q' \tag{1.20}$$

In classical statistical mechanics, the probability distribution in phase space is described by a probability density $\rho(p, q; t)$ which obeys

$$\rho(p, q; t) \geq 0 \qquad \int \mathrm{d}p\,\mathrm{d}q\,\rho(p, q; t) = 1$$

The conservation of probability means that $\rho(p, q; t)$ is constant along a trajectory in phase space

$$\rho(p(t), q(t); t) = \rho(p, q; t = 0)$$

where $p(t)$ and $q(t)$ are deduced from p and q by the equations of motion (see (1.19)). This conservation law can be written in differential form

$$0 = \frac{\mathrm{d}}{\mathrm{d}t}\rho(p(t), q(t); t) = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial p}\dot{p} + \frac{\partial \rho}{\partial q}\dot{q} = \frac{\partial \rho}{\partial t} + \{\rho, H\} \tag{1.21}$$

where the Poisson bracket $\{A, B\}$ of two dynamical variables A and B is defined by[3]

$$\{A, B\} = \frac{\partial A}{\partial q}\frac{\partial B}{\partial p} - \frac{\partial A}{\partial p}\frac{\partial B}{\partial q} \tag{1.22}$$

and the partial derivative $\partial/\partial t$ is taken at a *fixed* point in phase space. The (classical) *Liouvillian* $\mathcal{L}$ is defined by its action on dynamical variables $A(t) \equiv A(p(t), q(t))$, $A(0) = A(p, q)$

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \mathcal{L}A = \{A, H\} \quad \text{so that} \quad \frac{\partial \rho}{\partial t} = -\mathcal{L}\rho \tag{1.23}$$

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[3]Beware that the overall sign in the definition of the Poisson bracket is author dpendent.

The differential equation for ρ can be integrated for a time-independent Hamiltonian

$$\rho(p, q; t) = \mathrm{e}^{-t\mathcal{L}}\, \rho(p, q; t = 0) \tag{1.24}$$

Let us now consider a dynamical variable $A(t)$. Then its time evolution is given by (1.23)

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \mathcal{L}\, A \Longrightarrow A(t) = \mathrm{e}^{t\mathcal{L}}\, A(0) = \mathrm{e}^{t\mathcal{L}}\, A(p, q) \tag{1.25}$$

The reader should notice the sign difference in (1.24) and (1.25). Indeed, as in quantum mechanics, there are two ways of dealing with time evolution. In the classical analogue of the Heisenberg picture, the probability distribution is given at some initial time, for example, $t = 0$, and dynamical variables evolve according to (1.25). The expectation value of a dynamical variable A is then

$$\langle A \rangle(t) = \int \mathrm{d}p\, \mathrm{d}q\, A(p(t), q(t))\rho(p, q; t = 0) \tag{1.26}$$

One can also use the analogue of the Schrödinger picture, where $\rho(p, q; t)$ is given by (1.24), and the expectation value by

$$\langle A \rangle(t) = \int \mathrm{d}p\, \mathrm{d}q\, A(p, q)\rho(p, q; t) \tag{1.27}$$

It is easy to prove directly the equivalence between (1.26) and (1.27) by making for example in (1.26) the change of variables (1.19), by using Liouville's theorem (1.20) and conservation of probability in phase space in the form $\rho(p(-t), q(-t); t = 0) = \rho(p, q; t)$.

After this brief review of classical statistical mechanics, let us now turn to linear response. Assume first that our system is in equilibrium at temperature T. The time-independent canonical distribution is, with $\beta = 1/k_{\mathrm{B}}T$

$$\rho(p, q) = \frac{1}{Z(H)}\, \mathrm{e}^{-\beta H(p, q)}$$
$$Z(H) = \int \mathrm{d}p\, \mathrm{d}q\, \mathrm{e}^{-\beta H(p, q)} \tag{1.28}$$

where $Z(H)$ is the partition function. In all what follows, $\langle \bullet \rangle$ will denote an average taken with the *equilibrium* distribution (1.28). If $A(p, q)$ is a dynamical variable, then its average value is

$$\langle A \rangle = \int \mathrm{d}p\, \mathrm{d}q\, A(p, q)\rho(p, q) \tag{1.29}$$

Let us now perturb H with a time-independent potential V

$$H \to H_1 = H + V \qquad V = -f A(p, q) \tag{1.30}$$

where f is a numerical coeffficient, which can be used to adjust the strength of the perturbation, and we limit ourselves to effects which are *linear* in f. The new partition function, is, to first order in f

$$Z(H + V) \simeq \frac{Z(H)}{Z(H)} \int \mathrm{d}p\, \mathrm{d}q\, \mathrm{e}^{-\beta H}(1 - \beta V) = Z(H)(1 - \beta\langle V \rangle) \tag{1.31}$$

We introduce a second dynamical variable $B(p, q)$ and compute its average value $\overline{B}$ to first order in f

$$\begin{aligned}
\overline{B} &\simeq \frac{1}{Z(H)(1 - \beta\langle V \rangle)} \int \mathrm{d}p\, \mathrm{d}q\, \mathrm{e}^{-\beta H}(1 - \beta V)B(p, q) \\
&\simeq (1 + \beta\langle V \rangle)(\langle B \rangle - \beta\langle V B \rangle) \\
&= \langle B \rangle + \beta[\langle V \rangle\langle B \rangle - \langle V B \rangle] = \langle B \rangle - \beta\langle V B \rangle_c
\end{aligned}$$

where we have defined the *connected part* $\langle VB \rangle_c$ of $\langle VB \rangle$ as $\langle VB \rangle - \langle V \rangle \langle B \rangle$, so that the variation of B, $\overline{\delta B}$ is

$$\overline{\delta B} = \overline{B} - \langle B \rangle = -\beta \langle VB \rangle_c = \beta f \langle BA \rangle_c \tag{1.32}$$

The *static susceptibility* χ_{BA} is the derivative of the response $\overline{\delta B}$ (or of $\overline{B}$) with respect to the force f

$$\boxed{\chi_{BA} = \frac{\partial \overline{B}}{\partial f} = \beta \langle BA \rangle_c} \tag{1.33}$$

This is the *fluctuation-response theorem*: the response of the system to a small perturbation, described by χ_{BA}, is governed by the *equilibrium* fluctuation $\langle BA \rangle_c$.

1.3.2 Dynamical susceptibility and the fluctuation-dissipation theorem

Let us now assume the following situation: the perturbation V is applied from $t = -\infty$ to $t = 0$ and switched off at $t = 0$

$$
\begin{aligned}
H_1(p, q) &= H(p, q) - f A(p, q) & t < 0 \\
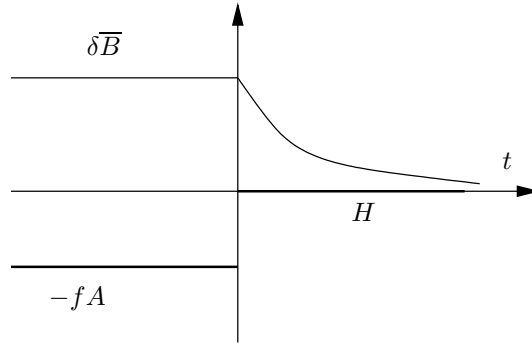&= H(p, q) & t > 0
\end{aligned}
\tag{1.34}
$$

Figure 1.4: Schematic picture of the time evolution.

Now, the average value of B, $\overline{B}$, is no longer time-independent for $t > 0$, because the distribution function $\rho(p, q)$ is determined by H_1, while A evolves with H. In order to evaluate $\overline{B}$, we work in the analogue of the Heisenberg picture: the probability distribution is given by its value at $t = 0$, $\exp(-\beta H_1)/Z(H_1)$. Then we get from (1.32) (see figure 1.4 for a schematic picture)

$$\boxed{\overline{\delta B}(t) = \overline{B}(t) - \langle B \rangle = \beta f \langle B(t) A(0) \rangle_c} \tag{1.35}$$

where, as usual, $A(0) = A(p, q)$. Note that the correct boundary condition (1.32) is ensured at $t = 0$

$$\overline{\delta B}(t = 0) = \beta f \langle B(0) A(0) \rangle_c$$

The function $\langle B(t) A(0) \rangle_c$ is the (connected) *equilibrium time correlation function* of B and A, also called the *Kubo function* $C_{BA}(t)$

$$\boxed{C_{BA}(t) = \langle B(t) A(0) \rangle_c} \tag{1.36}$$

The dynamical susceptibility is nothing other than the time-derivative of the Kubo function. To see, it let us write from linear response in the form (1.8)

$$\overline{\delta B}(t) = \int_{-\infty}^{t} \mathrm{d}t' \, \chi_{BA}(t - t') f(t')$$

Using the form (1.34) of the excitation so that $f(t') = f\theta(-t')$,

$$\overline{\delta B}(t) = f \int_{-\infty}^{0} dt' \, \chi_{BA}(t - t') = f \int_{t}^{\infty} dt' \, \chi_{BA}(t') \tag{1.37}$$

Then we can compare (1.37) and the time-derivative of (1.35)

$$\frac{d}{dt}\overline{\delta B}(t) = \beta f \dot{C}_{BA}(t) \quad = \quad -f\chi_{BA}(t) \quad t > 0$$
$$= \quad 0 \qquad\qquad t < 0$$

so that

$$\boxed{\chi_{BA}(t) = -\beta\theta(t)\,\dot{C}_{BA}(t)} \tag{1.38}$$

We are now in a position to discuss two very important results: Onsager's regression law and the fluctuation-dissipation theorem. Let us take $A = B$. The function $A(t)$ is a random function, due to thermal fluctuations, which means that at fixed t, $A(t)$ is a random variable. The equilibrium average $\langle A(t)\rangle$ is obtained by an ensemble average over a large number of realizations of $A(t)$. The connected *equilibrium autocorrelation function* $C_{AA}(t) \equiv C(t)$ is defined by

$$\boxed{C(t) = \langle A(t)A(0)\rangle_c} \tag{1.39}$$

Let us derive a few elementary properties of $C(t)$. From time translation invariance at equilibrium we get[4]

$$\langle A(t)A(0)\rangle_c = \langle A(0)A(-t)\rangle_c = \langle A(-t)A(0)\rangle_c$$

so that $C(t) = C(-t)$: $C(t)$ is an even function of t. Furthermore, it is easy to see that $|C(t)| \leq C(0)$, because

$$\langle (A(t) \pm A(0))^2 \rangle = 2\langle A \rangle^2 \pm 2\langle A(t)A(0)\rangle \geq 0$$

where we have made use of the fact that $\langle A(t)\rangle$ is time independent due to time-translation invariance. Finally, we expect a rough exponential dependence of $C(t)$ with respect to t, possibly with some oscillations

$$C(t) \simeq C(0)e^{-|t|/\tau} \tag{1.40}$$

where τ is the *relaxation time*. The relation

$$\chi_{AA}(t) \equiv \chi(t) = -\beta\frac{d}{dt}\langle A(t)A(0)\rangle_c$$

may now be understood as follows: the system can be brought out of equilibrium either by a small perturbation V, or by a spontaneous thermal fluctuation. In both cases, the return to equilibrium is governed by the equilibrium fluctuations: this is Onsager's regression law.

Now for the *fluctuation-dissipation theorem*, or FD theorem. The odd part $\chi''(t)$ of $\chi(t)$ is given by

$$\chi''(t) = -\chi''(-t) = \frac{i}{2}\beta\dot{C}(t)$$

which means, under a Fourier transformation, that

$$\boxed{\tilde{\chi}''(\omega) = \frac{1}{2}\beta\omega\tilde{C}(\omega)} \tag{1.41}$$

On the other hand, $\tilde{\chi}''(\omega)$ is linked to energy dissipation per unit of time through (1.17), which can then be written

$$\boxed{\left\langle \frac{dW}{dt} \right\rangle = \frac{\beta}{4}\,\omega^2 f_0^2 \tilde{C}(\omega)} \tag{1.42}$$

Thus, energy dissipation is linked to equilibrium fluctuations described by the Kubo function $C(t)$ or its Fourier transform $\tilde{C}(\omega)$.

---

[4]Commuting $A(t)$ and $A(0)$ is fine in classical mechanics, but not generally possible in quantum mechanics.

1.3.3 A simple application: Nyquist's theorem

As a simple application of the preceding considerations, let us derive the Nyquist theorem, which relates the electrical conductivity $\sigma_{\rm el}$ to the equilibrium fluctuations of the electrical current. Using time-translation invariance at equilibrium yields

$$\dot{C}_{BA}(t) = \langle \dot{B}(t)A(0) \rangle_c = -\langle B(t)\dot{A}(0) \rangle_c \tag{1.43}$$

From (1.9) and (1.35) we can write the Fourier transform $\overline{\delta B}(\omega)$ as

$$\overline{\delta B}(\omega) = \beta f_A(\omega) \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \langle B(t)\dot{A}(0) \rangle_c \tag{1.44}$$

As we have seen in § 1.2.2, ω should be understood as $\lim_{\eta \to 0^+}(\omega + {\rm i}\eta)$. Let us use this result in the following case: we consider charge carriers with charge q and mass m in a one-dimensional conductor and take as dynamical variables the following A and B

$$A = q \sum_i x_i \qquad B = \dot{A} = q \sum_i \dot{x}_i = \Omega j \tag{1.45}$$

where x_i is the position of carrier i, j the current density and Ω the volume of the conductor. The external force is an external (uniform) time dependent electric field $E(t)$ and the perturbation $V(t)$ is

$$V(t) = -qE(t) \sum_i x_i = -E(t)A$$

so that from (1.44)

$$
\begin{aligned}
\overline{\delta B}(\omega) = \Omega j(\omega) &= \beta \Omega^2 E(\omega) \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \langle j(t)j(0) \rangle|_{E=0} \\
&= \beta q^2 E(\omega) \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \sum_{i,k} \langle \dot{x}_i(t)\dot{x}_k(0) \rangle|_{E=0}
\end{aligned}
$$

Since the average equilibrium (or $E = 0$) current density vanishes, we may write j instead of δj. This equation is nothing other than the time dependent Ohm law $j(\omega) = \sigma_{\rm el}(\omega)E(\omega)$. We have thus shown that the electrical conductivity $\sigma_{\rm el}(\omega)$ is given by the Fourier transform of the time-correlation of the current density in the absence of an external electric field

$$\boxed{\sigma_{\rm el}(\omega) = \beta \Omega \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \langle j(t)j(0) \rangle|_{E=0}} \tag{1.46}$$

In the zero frequency limit $\omega = 0$ we get the following formula for the static conductivity $\sigma_{\rm el}$

$$\sigma_{\rm el} = \beta \Omega \int_0^\infty {\rm d}t\, \langle j(t)j(0) \rangle|_{E=0} \tag{1.47}$$

It may be necessary to include a factor $\exp(\eta t)$ in (1.47) in order to ensure the convergence of the integral. Equation (1.47) is one version of *Nyquist theorem*, and is typical of a *Green-Kubo formula*, which gives a transport coefficient (in the present case the static electrical conductivity) in terms of the integral of a time correlation function. Let us give a rough estimate of (1.46). Using the fact that velocities of different particles are uncorrelated in classical statistical mechanics, and introducing a microscopic relaxation (or collision) time $\tau_c \sim 10^{-14}\,{\rm s}$

$$\langle \dot{x}_i(t)\dot{x}_k(0) \rangle = \delta_{ik} \langle \dot{x}(t)\dot{x}(0) \rangle \sim \delta_{ik} \frac{kT}{m} {\rm e}^{-|t|/\tau_c}$$

leads to the familiar result

$$\boxed{\sigma_{\rm el}(\omega) = \frac{nq^2 \tau_c}{m(1 - {\rm i}\omega\tau_c)}} \tag{1.48}$$

where n is the density of carriers. Of course, (1.48) may be obtained by much more elementary methods, but the point is that (1.46) and (1.47) are *exact* results (within the linear response approximation!), and at least one knows where to start from if one wishes to derive better approximations.

1.3.4   Quantum linear response theory

The technical problem of quantum linear response theory is that we cannot expand an exponential of two operators when they do not commute, because, if H and V do not commute

$$\mathrm{e}^{H+fV} \neq \mathrm{e}^{H}\,\mathrm{e}^{fV}$$

so that we cannot write

$$\mathrm{e}^{H+fV} \simeq \mathrm{e}^{H}\,(I + fV)$$

and the perturbative expansion in powers of f is quite cumbersome. The function $\chi''_{BA}(t)$ of two observables A and B is defined through a commutator

$$\chi''_{BA}(t) = \frac{1}{2}\,\langle [B(t), A(0)] \rangle \tag{1.49}$$

so that the dynamical susceptibility $\chi_{BA}(t)$ is

$$\chi_{BA}(t) = \mathrm{i}\theta(t)\langle [B(t), A(0)] \rangle \tag{1.50}$$

In these equations, $A(t)$ is written in the Heisenberg picture

$$A(t) = \mathrm{e}^{\mathrm{i}Ht/\hbar}\,A(0)\,\mathrm{e}^{-\mathrm{i}Ht/\hbar} \tag{1.51}$$

As in the preceding subsections, $\langle \bullet \rangle$ is an equilibrium average taken with the Hamiltonian H

$$\langle A \rangle = \frac{1}{Z(H)}\,\mathrm{Tr}\,\left[A\mathrm{e}^{-\beta H}\right] \qquad Z(H) = \mathrm{Tr}\,\mathrm{e}^{-\beta H} \tag{1.52}$$

The relation between dissipation and correlations is different from that of the classical case

$$\boxed{\tilde{\chi}''_{BA}(\omega) = \frac{1}{2\hbar}\left(1 - \mathrm{e}^{-\hbar\omega/k_{\mathrm{B}}T}\right)\tilde{S}_{BA}(\omega)} \tag{1.53}$$

where the correlation $S_{BA}(t)$ is defined by

$$S_{BA}(t) = \langle B(t)A(0) \rangle_c$$

while χ'' is again given by the time-derivative of the Kubo function

$$\chi''_{BA}(t) = \frac{\mathrm{i}}{2}\,\beta\dot{C}_{BA}(t) \tag{1.54}$$

However, the expression of the Kubo function is somewhat complicated and will not be given here.

1.4   Brownian motion

1.4.1   The Caldeira-Leggett model

A Brownian particle is a "heavy" particle of mass M interacting with "light" particles of mass m_λ, with $m_\lambda/M \ll 1$. These light particles form a heat bath, or reservoir, in equilibrium a temperature T. The first effect one can think of is viscosity: if the heavy particle has a velocity $\vec{v}$ in the positive x direction, the fluid molecules coming from the right will appear to have a larger velocity than those coming from the left, and because of its collisions with the fluid molecules and of this simple Doppler effect, the particle will be submitted to a force directed toward the left

$$\vec{F}_{\mathrm{visc}} = -\alpha\vec{v}$$

where α is the friction coefficient; $\gamma = \alpha/M = 1/\tau$ defines a characteristic *macroscopic* time scale for the particle. However, there is another time scale in the problem, a *microscopic* time scale τ_c: due to

the random character of the collisions with the fluid molecules, one observes fluctuations of the force on a time scale $\sim 10^{-12} - 10^{-14}$ s on the order of the interval between two successive collisions. It can be shown that the separation of time scales relies on the inequality $m/M \ll 1$: compare on figure 1.5 the behaviour of the velocity of a Brownian particle and that of a tagged ^{17}O molecule in a gas of ^{16}O molecules. In the latter case the velocity changes suddenly on a time scale τ_c (it may even change sign), while in the case of the Brownian particle, the time scale for velocity changes is τ because of its large inertia, although a short time scale τ_c is superimposed on this average motion. Although the Brownian particle may suffer large accelerations, the mean velocity varies very little on a time scale τ_c, and the average motion is a smooth one. Thus, all the equations which will be written in what follows should be understood as *coarse grained equations*: choosing a time interval Δt such that $\tau_c \ll \Delta t \ll \tau$, a time derivative of the velocity, for example, will mean $\Delta v/\Delta t$, and one should *not* take the limit $\Delta t \to 0$. It is important to understand the connection with the introduction to section 1.3: here the the fast modes are dynamical variables of the molecules, the slow mode corresponds to those of the Brownian particle.
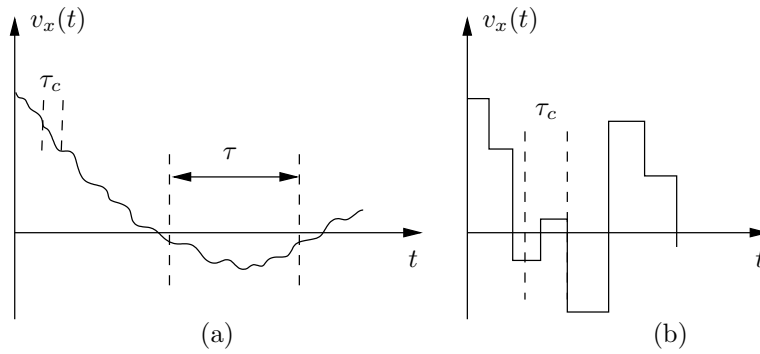

(a) (b)

Figure 1.5: x-component of the velocity: (a) Heavy (Brownian) particle in a bath of light particles (b) Tagged ^{17}O molecule in a gas of ^{16}O molecules.

A simple and much studied model of Brownian motion is the so-called Caldeira-Leggett model. Actually, many papers on the same model were published much before the Caldeira-Leggett paper, which became famous as a model of decoherence. This model is exactly solvable, because all the couplings, between the light particles and between the heavy particle and the light ones, are harmonic couplings. This means that the equations of motion are linear, and in principle exactly solvable, either in classical or in quantum mechanics. For the sake of simplicity, I'll limit myself to one-dimensional motion, without losing any essential physics. In this Chapter, I'll discuss the classical case, and the quantum version will be studied in the next Chapter. The Hamiltonian is given by

$$H = \frac{P^2}{2M} + \sum_{\lambda=1}^{N} \frac{p_\lambda^2}{2m_\lambda} + \frac{1}{2} \sum_{\lambda=1}^{N} m_\lambda \omega_\lambda^2 (X - x_\lambda)^2 \tag{1.55}$$

Here, X and P are the position and momentum of the heavy particles, m_λ, x_λ, p_λ and ω_λ the masses, positions, momenta and frequencies of the light particles. While preserving the linear character of the equations of motion, it is possible to add a harmonic potential $M\Omega^2 X^2/2$ for the heavy particle. We define

$$\kappa = \sum_\lambda m_\lambda \omega_\lambda^2 \tag{1.56}$$

and rewrite H in a form which looks superficially translation non invariant

$$H = \left[\frac{P^2}{2M} + \frac{1}{2} \kappa X^2 \right] + \left[\sum_\lambda \left(\frac{p_\lambda^2}{2m_\lambda} + \frac{1}{2} m_\lambda \omega_\lambda^2 x_\lambda^2 \right) \right] - \left[X \left(\sum_\lambda m_\lambda \omega_\lambda^2 x_\lambda \right) \right]$$
$$= H_A + H_R + V \tag{1.57}$$

H_A is the Hamiltonian of the system of interest (here the heavy particle), H_R that of the reservoir and V describes the system-reservoir interaction. The interaction between the particle and the reservoir may be written in a form encountered in linear response

$$V = -X(t)\mathcal{F}(t) \qquad \mathcal{F}(t) = \sum_\lambda m\omega_\lambda^2 x_\lambda(t) \tag{1.58}$$

where X plays the role of f in (1.34) and $\mathcal{F}$ plays the role of A, the dynamical variable of the bath coupled to X. From (1.57), the equation of motion of the particle is

$$\dot{P} = -\kappa X + \mathcal{F}(t) \tag{1.59}$$

If we neglect the influence of the particle on the bath, $\mathcal{F}(t)$ can be computed explicitly in terms of initial conditions $x_\lambda(0)$ and $p_\lambda(0)$

$$\mathcal{F}(t) = \sum_\lambda \left[m_\lambda \omega_\lambda^2 x_\lambda(0) \cos \omega_\lambda t + \omega_\lambda p_\lambda(0) \sin \omega_\lambda t \right] \tag{1.60}$$

Now, $\mathcal{F}(t)$ is modified by the presence of the particle,

$$\mathcal{F}(t) \to \mathcal{F}(t) + \overline{\delta\mathcal{F}}(t)$$

and this modification is given by linear response theory which is *exact* in the present context. Assuming that the interaction is switched on at $t = 0$, we get from (1.37) and (1.38)

$$\overline{\delta\mathcal{F}}(t) = \int_0^t \chi(t-t')X(t')\mathrm{d}t' = -\beta \int_0^t \dot{C}(t-t')X(t')\mathrm{d}t' \tag{1.61}$$

where $C(t)$ is the Kubo function (1.39), the time autocorrelation function of $\mathcal{F}$

$$C(t) = \langle \mathcal{F}(t)\mathcal{F}(0) \rangle \tag{1.62}$$

We emphasize that $\mathcal{F}(t)$ in (1.62) is given by the *unperturbed* bath variables (1.60). We make in (1.61) the change of variables $t' \to t - t'$ and integrate by parts to obtain

$$\dot{P} = -\kappa X(t) + \beta C(0)X(t) - \beta C(t)X(0) + \mathcal{F}(t) - \beta \int_0^t C(t')\dot{X}(t-t')\mathrm{d}t' \tag{1.63}$$

We shall show later on that the sum of the first three terms in (1.63) vanishes in the long time limit and concentrate on the last two terms. The force on the Brownian particle is then the sum of a fluctuating force $\mathcal{F}(t)$ and a velocity dependent force governed by the autocorrelation function of $\mathcal{F}$. The equations of motion (1.63) are not Markovian, as they depend not only on t, but also on times t' earlier than t, and for this reason $C(t)$ is also called a *memory kernel* in the present context. This is a nice illustration of the general theory briefly exposed at the beginning of section 1.3: the back action of the fast modes on the slow modes is described by a stochastic force (here $\mathcal{F}(t)$) and memory effects contained in the Kubo function $C(t)$. In order to get Markovian equations of motion, we must compare the characteristic time scale of the Brownian particle and the characteristic time scale of the reservoir. The equations of motion will be approximately Markovian only if $\tau = \gamma^{-1} \gg \tau_c$. This is a feature which we shall repeatedly encounter in what follows: in order to get Markovian equations, we need two widely separated time scales, a microscopic time scale τ_c, and a macroscopic one $\tau = 1/\gamma$, which obey

$$\boxed{\tau_c = \frac{1}{\omega_c} \ll \tau = \frac{1}{\gamma}} \tag{1.64}$$

where ω_c is a typical frequency range of the reservoir. Furthermore, it is easy to compute the memory kernel $C(t)$: remember that $C(t)$ is given by an equilibrium average, for a bath which is unperturbed by the particle. We then obtain

$$\begin{aligned} C(t) &= \left\langle \sum_{\lambda,\lambda'} \left(m_\lambda \omega_\lambda^2 x_\lambda(0) \cos \omega_\lambda t + \omega_\lambda p_\lambda(0) \sin \omega_\lambda t \right) m_{\lambda'} \omega_{\lambda'}^2 x_{\lambda'}(0) \right\rangle \\ &= k_\mathrm{B} T \sum_\lambda m_\lambda \omega_\lambda^2 \cos \omega_\lambda t \end{aligned} \tag{1.65}$$

where we have used

$$m_\lambda \omega_\lambda^2 \langle x_\lambda(0) x_{\lambda'}(0) \rangle = k_\mathrm{B} T \delta_{\lambda\lambda'} \qquad \langle x_\lambda(0) p_{\lambda'}(0) \rangle = 0$$

as the probability distributions[5] of $x_\lambda(0)$ and $p_\lambda(0)$ are independent Boltzmann distributions centered at $x_\lambda(0) = 0$ and $p_\lambda(0) = 0$. Note that

$$\beta C(t=0) = \sum_\lambda m_\lambda \omega_\lambda^2 = \kappa$$

so that the first two terms in (1.63) cancel out.

Let us now derive further properties of (1.63). First we observe that, for $t \gg \tau_c$, the third term in (1.63) is negligible, so that the initial conditions are forgotten. Then, if we can assume that $C(t)$ is a rapidly decreasing function of t with a time scale τ_c much smaller than that of X, τ: $\tau_c \ll \tau$, we can make the short memory approximation

$$-\beta \int_0^t C(t') \dot{X}(t-t') \mathrm{d}t' \simeq -\beta \dot{X}(t) \int_0^\infty C(t) \mathrm{d}t = -\beta \dot{X} \int_0^\infty \langle \mathcal{F}(t) \mathcal{F}(0) \rangle \mathrm{d}t$$

and this term can be identified with a viscous force

$$\boxed{F_\mathrm{visc} = -M\gamma \dot{X}(t) = -\gamma \dot{P}(t) \qquad \gamma = \frac{\beta}{M} \int_0^\infty \langle \mathcal{F}(t) \mathcal{F}(0) \rangle \mathrm{d}t} \tag{1.66}$$

This is a fluctuation-dissipation theorem: the viscosity coefficient, which describes dissipation, is related to the fluctuations of the force $\mathcal{F}(t)$. The final equation of motion for the Brownian particle is then

$$\boxed{\dot{P} = -\gamma \dot{P} + \mathcal{F}(t)} \tag{1.67}$$

We see explicitly on (1.67) that the characteristic time scale of the macroscopic motion is $\tau = 1/\gamma$ so that the consistency condition for the validity of the short memory approximation $\tau_c/\tau \ll 1$.

It is instructive to be a little more precise about the memory kernel $C(t)$ and to give an explicit model. We assume that the frequencies ω_λ form a continuum (with a finite number of frequencies, or even with an infinite number of discrete frequencies, we would encounter Poincaré recurrences), and that they follow a distribution characterized by a width $\sim \omega_c$. For $t \gg 1/\omega_c$, $C(t)$ will be a sum of a large number of terms oscillating with different frequencies, and the function $C(t)$ will be approximately zero. It is convenient to introduce a *spectral function* $J(\omega)$

$$J(\omega) = \frac{\pi}{2} \sum_\lambda m_\lambda \omega_\lambda^3 \delta(\omega - \omega_\lambda) \tag{1.68}$$

Defining $J(-\omega) = -J(\omega)$ allows us to rewrite $C(t)$ as

$$\frac{1}{2} \beta C(t) = \frac{1}{\pi} \int_0^\infty \frac{\mathrm{d}\omega}{\omega} J(\omega) \cos \omega t = \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi\omega} J(\omega) \mathrm{e}^{\mathrm{i}\omega t} \mathrm{d}\omega \tag{1.69}$$

$J(\omega)/\omega$ is the Fourier transform of $C(t)$, within a numerical factor $\beta/2$ which has been chosen for later convenience. The behaviour of the heavy particle depends in a crucial way on that of the spectral function when $\omega \to 0^+$: if $J(\omega) \propto \omega^\delta$, then the exponent δ will govern the behaviour of the Brownian particle. In what follows, we shall adopt the so-called *ohmic model*, in which $\delta = 1$, so that $J(\omega) \propto \omega$ when $\omega \to 0$. We shall write more precisely

$$\omega \to 0 \quad : \quad J(\omega) \simeq M\gamma\omega \tag{1.70}$$

---

[5]The probability distributions are

$$P[x_\lambda(0)] \propto \exp\left[-\frac{m_\lambda \omega_\lambda^2 x_\lambda^2(0)}{2k_\mathrm{B}T}\right] \qquad P[p_\lambda(0)] \propto \exp\left[-\frac{p_\lambda^2(0)}{2mk_\mathrm{B}T}\right]$$

The physical meaning of the coefficient γ can be deduced from dimensional analysis. Indeed, $J(\omega)$ is a mass times a frequency squared, so that γ has the dimension of a frequency, that is, the dimension of a friction coefficient as in (1.6). We must also take into account the finite width ω_c of the frequency distribution. The results do not depend in a qualitative way on the precise shape which is taken for $J(\omega)$, and a convenient choice for simple analytic calculations is that of a Lorentzian

$$J(\omega) = M\gamma\omega\,\frac{\omega_c^2}{\omega^2 + \omega_c^2} \tag{1.71}$$

Then we can write an explicit form for $C(t)$

$$\begin{aligned}
\frac{1}{2}\beta C(t) &= M\gamma \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi}\,\frac{\omega_c^2}{\omega^2+\omega_c^2}\,\mathrm{e}^{\mathrm{i}\omega t} \\
&= \frac{1}{2}M\gamma\omega_c\,\mathrm{e}^{-\omega_c|t|} = \frac{M\gamma}{2\tau_c}\,\mathrm{e}^{-|t|/\tau_c}
\end{aligned} \tag{1.72}$$

We have then identified the microscopic time scale $\tau_c = 1/\omega_c$. Note that γ is related to the zero frequency Fourier transform of $C(t)$, the so-called *power spectrum* of $\mathcal{F}(t)$

$$\tilde{C}(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t\, C(t)\mathrm{e}^{\mathrm{i}\omega t} = 2\int_0^\infty \mathrm{d}t\, C(t)\cos\omega t$$

where we have used the fact that $C(t)$ is an even function, and $\gamma = (\beta/2M)\tilde{C}(\omega = 0)$.

1.4.2   The Langevin equation

From its definition (1.69), $\mathcal{F}(t)$ is a sum over randomly distributed initial conditions $x_\lambda(0)$ and $p_\lambda(0)$, and it should be approximately a Gaussian random function. Defining $V = P/M$ and $f = \mathcal{F}/M$, we get from (1.67) a *Langevin equation* for the velocity V

$$\boxed{\dot{V}(t) = -\gamma V + f(t)} \tag{1.73}$$

Now we can forget the model and define precisely what we mean by Langevin equation. $V(t)$ is a *random function*, which we write with a capital letter V in order to make the distinction with the *number* $v(t)$, which is the value of the velocity for a particular realization of $f(t)$. The function $f(t)$ is a random function with zero average value, $\overline{f(t)} = 0$, and with a characteristic time scale τ_c much smaller than the characteristic time scale $\tau = 1/\gamma$ of the velocity: $\tau_c \ll \tau$. We shall define $\overline{X}$ as the average of the random variable X taken over all the realizations of the random function $f(t)$, while $\langle X \rangle$ denotes as before an equilibrium average. In the short memory approximation, $f(t)$ will be a *white noise*

$$\boxed{\overline{f(t)} = 0 \qquad \overline{f(t)f(t')} = 2A\,\delta(t-t')} \tag{1.74}$$

Moreover, it is customary to assume that $f(t)$ is a Gaussian random function. Equations (1.73), (1.74) and the Gaussian character of $f(t)$ define precisely what we mean by a Langevin equation as given *a priori*, and not derived from a model.

It is easy to write the solution of (1.73) with the initial condition $V(0) = v_0$

$$V(t) = v_0\,\mathrm{e}^{-\gamma t} + \mathrm{e}^{-\gamma t}\int_0^t \mathrm{d}t'\,\mathrm{e}^{\gamma t'} f(t') \tag{1.75}$$

From this solution and (1.74) we get the average velocity

$$\overline{V(t)} = v_0\,\mathrm{e}^{-\gamma t} = v_0\,\mathrm{e}^{-t/\tau} \tag{1.76}$$

Thus τ is the characteristic time scale of the velocity, and the initial conditions are forgotten if $t \gg \tau$. The dispersion of the velocity is easily computed

$$
\begin{aligned}
\overline{\left(V(t) - v_0\, \mathrm{e}^{-\gamma t}\right)^2} &= \mathrm{e}^{-2\gamma t} \int_0^t \mathrm{d}t'\, \mathrm{d}t''\, \mathrm{e}^{\gamma(t'+t'')}\, \overline{f(t')f(t'')} \\
&= 2A\, \mathrm{e}^{-2\gamma t} \int_0^t \mathrm{d}t'\, \mathrm{e}^{2\gamma t'} = \frac{A}{\gamma}\left(1 - \mathrm{e}^{-2\gamma t}\right)
\end{aligned}
\tag{1.77}
$$

If $t \gg 1/\gamma$ we reach an equilibrium situation

$$
\left\langle \left(V(t) - v_0 \mathrm{e}^{-\gamma t}\right)^2 \right\rangle \to \langle V^2 \rangle = \frac{A}{\gamma} = \frac{k_{\mathrm{B}}T}{M}
$$

and we obtain one form of Einstein's equation, that which gives the velocity diffusion coefficient A as a function of $k_{\mathrm{B}}T$ and γ

$$
\boxed{A = \gamma \frac{k_{\mathrm{B}}T}{M}}
\tag{1.78}
$$

This is nothing other than the fluctuation-dissipation theorem (1.66): A describes the fluctuations of the random force $f(t)$, while γ describes the viscosity, which is at the origin of dissipation in the reservoir. The Langevin equation is a convenient way to simulate the coupling of a system to a heat bath.

We can also compute the position $X(t)$ of the Brownian particle from

$$
X(t) = x_0 + \int_0^t \mathrm{d}t'\, V(t')
$$

An elementary, but somewhat tedious calculation, leads to

$$
\overline{(X(t) - x_0)^2} = \left(v_0^2 - \frac{k_{\mathrm{B}}T}{M}\right)\frac{1}{\gamma^2}\left(1 - \mathrm{e}^{-\gamma t}\right)^2 + \frac{2kT}{M\gamma}\left(t - \frac{1}{\gamma}\left[1 - \mathrm{e}^{-\gamma t}\right]\right)
$$

For $t \ll 1/\gamma$, one observes a ballistic behavior: $\overline{(X(t) - x_0)^2} = v_0^2 t^2$, but the interesting result is that giving the large time behaviour

$$
\langle X^2(t) \rangle \simeq \frac{2k_{\mathrm{B}}T}{M\gamma}
$$

A simple way to derive this long time behavior is to remark that the velocity autocorrelation function is easily computed if $t', t'' \gg \tau$ (exercise 1.6.4)

$$
\overline{V(t')V(t'')} = \frac{A}{\gamma}\, \mathrm{e}^{-\gamma|t'-t''|}
\tag{1.79}
$$

Actually, this is an idealization: numerical simulations show that time correlations have a small component decreasing as $|t|^{-d/2}$, where d is the dimension of space, owing to multiple collisions. Ignoring this component, we get for the dispersion of the position for long times (exercise 1.6.4)

$$
\overline{(X(t) - x_0)^2} = \int_0^t \mathrm{d}t'\mathrm{d}t''\, \overline{V(t')V(t'')} \simeq 2\frac{k_{\mathrm{B}}T}{M\gamma}\, t = 2Dt
\tag{1.80}
$$

This is characteristic of diffusive motion, with a *diffusion coefficient* D, given by another Einstein relation

$$
\boxed{D = \frac{k_{\mathrm{B}}T}{M\gamma}}
\tag{1.81}
$$

From Langevin's equation, we can obtain a simple equation of motion for the position X in the strong friction limit (exercises 1.6.2 or 1.6.8). As is shown in these exercises, in this limit, the momentum follows adiabatically the position and we get for X an equation of the form

$$
\dot{X} = -\frac{V'(x)}{M\gamma} + B(t)
\tag{1.82}
$$

where $-V'(x) = F(x)$ is the deterministic force and $b(t)$ a random force. In the absence of a deterministic force, X exhibits a diffusive behaviour

$$\overline{X^2(t)} = 2Dt$$

so that the random force obeys

$$\overline{B(t)} = 0 \qquad \overline{B(t)B(t')} = 2D\delta(t - t') \tag{1.83}$$

We shall write the equation of motion for X in the following form, with $a(x) = F(x)/M\gamma$

$$\boxed{\dot{X} = a(x) + B(t)} \tag{1.84}$$

From (1.84), one can derive a Fokker-Planck (FP) equation for the conditional probability $P(x, t|x_0)$ for finding the particle at x at time t, given that it was located at x_0 at time $t = 0$. As shown in exercise 1.6.5, this equation is

$$\boxed{\frac{\partial}{\partial t} P(x, t|x_0) = -\frac{\partial}{\partial x}\left[a(x)P(x, t|x_0)\right] + D\frac{\partial^2}{\partial x^2} P(x, t|x_0)} \tag{1.85}$$

The first term is called the *drift term*: in the absence of diffusion, since the velocity is then $\dot{x} = a(x)$, the FP equation is nothing other than a continuity equation

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{1.86}$$

where the current $j = \dot{x}P = a(x)P$. The second term in the RHS of (1.85) is a diffusive term, and the full expression of the current reads

$$j(x) = a(x)P - D\frac{\partial P}{\partial x} \tag{1.87}$$

When the diffusion coefficient depends on x, the Langevin equation becomes ambiguous: this is the Itô-Stratonovitch ambiguity which is studied in exercise 1.6.6. The Langevin equation is defined by

$$\dot{X} = a(x) + \sqrt{D(x_m)}\, b(t) \tag{1.88}$$

where $b(t)$ is the random function (1.83) with $D = 1$

$$\overline{b(t)} = 0 \qquad \overline{b(t)b(t')} = 2\delta(t - t') \tag{1.89}$$

x_m is the point which gives the argument of the diffusion coefficient, and it is chosen somewhere between the initial and final positions in an infinitesimal time interval $[t, t + \varepsilon]$; it is given as a function of a parameter q, $0 \leq q \leq 1$ by

$$x_m = y + (1 - q)[X(t + \varepsilon) - y] \tag{1.90}$$

where y is the position at time t: $y = x(t)$. The Itô prescription corresponds to $q = 1$, the Stratonovitch prescription to $q = 1/2$. In general, q depends on the problem and should be chosen from physical arguments. With the Itô prescription, the FP equation is (exercise 1.6.6)

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}[a(x)P] + \frac{\partial^2}{\partial x^2}[D(x)P] \tag{1.91}$$

It is also shown in exercise 1.6.6 that the ambiguity only affects the drift term. With respect to the Itô prescription, the drift term of (1.91) is changed into

$$a(y) \rightarrow a(y) + (1 - q)D'(y) \tag{1.92}$$

Thus, the Itô-Stratonovitch ambiguity will unimportant if $|D'/a| \ll 1$, which will be the case if the system is macroscopic (see the next subsection).

1.4.3   The long time limit revisited

Let us re-examine the long time limit without assuming a final thermal equilibrium; however, we assume that the fluctuations around the average trajectory are small. We write for the average trajectory $\overline{x}$ and the dispersion σ

$$X = \overline{x} + \delta x \qquad \sigma = \overline{(X - \overline{x})^2} \tag{1.93}$$

where $\mathrm{d}\overline{x}/\mathrm{d}t = a(\overline{x})$. The time derivative of δx is obtained from (1.84), with $D(x,t) = D^{1/2)}(x)b(t)$

$$\delta \dot{x} = a(x) - a(\overline{x}) + D(x,t) \tag{1.94}$$

where we have used Itô prescription, while that of σ is

$$\dot{\sigma} = 2\overline{\delta x \delta \dot{x}} = 2a'\sigma + 2\overline{D(x,t)\delta x} \tag{1.95}$$

Now, the component δx_c of δx which is correlated to $D(x,t)$ is given by

$$\delta x_c(t) = \int_{-\infty}^{t} \mathrm{d}t' \, D(x,t')$$

so that

$$\overline{D(x,t)\delta x(t)} = \overline{D(x,t)\delta x_c(t)} = \int_{-\infty}^{t} \mathrm{d}t' \, \overline{D(x,t)D(x,t')} = D(x)$$

The time evolution of $\overline{x}$ and σ is then

$$\begin{aligned} \frac{\mathrm{d}\overline{x}}{\mathrm{d}t} &= a(\overline{x}) \\ \frac{\mathrm{d}\sigma}{\mathrm{d}t} &= 2a'\sigma + D(x) \end{aligned} \tag{1.96}$$

We now assume that $a(x)$ has a zero at $x = x^*$: $a(x^*) = 0$, and that in the vicinity of x^*, $a(x) \simeq -\gamma(x-x^*)$. Then x^* is a fixed point of the trajectory, that is, a point where the velocity vanishes. The probability distribution $P(x,t)$ obeys a FP equation (1.91)

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0 \qquad j(x) = a(x)P - \frac{\partial(DP)}{\partial x}$$

Setting $D^* = D(x^*)$, the FP equation reduces in the vicinity of the fixed point to

$$-\gamma(x - x^*)P - D^* \frac{\partial P}{\partial x} = 0$$

so that P is a Gaussian

$$P(x) \propto \exp\left(-\frac{\gamma(x - x^*)^2}{2D^*}\right) \tag{1.97}$$

No thermal equilibrium was required to obtain this Gaussian form. However, we did require the fluctuations to be small. If the system is close to thermal equilibrium, the free energy F has the form

$$F = F_{\mathrm{eq}} + \frac{1}{2}A\left(x - x^*\right)^2 + \cdots \tag{1.98}$$

where A is a susceptibility because $A = \partial^2 F/\partial x^2|_{\mathrm{eq}}$. Then $P \propto \exp(-F/k_{\mathrm{B}}T)$, so that we recover a FD theorem

$$\frac{A}{k_{\mathrm{B}}T} = \frac{\gamma}{D^*} \tag{1.99}$$

The generalization to several degrees of freedom is interesting, but non trivial: see Nozières [1993].

1.5   Master equations from stochastic dynamics

This last section is devoted to master equations. We shall derive master equations by imposing specific conditions on random processes, but we shall not attempt to deduce them from fundamental equations, for example the Schrödinger equation. This derivation will be addressed in the next Chapter.

1.5.1   Markov processes and the Chapman-Kolmogorov equation

We shall call a *dynamical system* a collection of configurations C, for example cells in phase space, together with a set of rules, which, to each configuration C_0 at time t_0 associates a new configuration C_1 at time t_1. The dynamical law is then defined by a set of *conditional* probabilities $P_{1|1}(C_1, t_1|C_0, t_0)$, the probability for finding the system a time t_1 in configuration C_1, given that it was at time t_0 in configuration C_0. We can similarly define the conditional probabilities $P_{1|2}(C_2, t_2|C_1, t_1; C_0, t_0)$, with time ordering $t_2 > t_1 > t_0$, which is the probability for finding the system a time t_2 in configuration C_2, given that it was at time t_1 in configuration C_1 *and* at time t_0 in configuration C_0. Bayes's law allows us to write the conditional probabilities in terms of joint probabilities $P_n(C_k, t_k; \cdots; C_0, t_0)$

$$P_{1|2}(C_2, t_2|C_1, t_1; C_0, t_0) = \frac{P_3(C_2, t_2; C_1, t_1; C_0, t_0)}{P_2(C_1, t_1; C_0, t_0)} \tag{1.100}$$

We can write $P_2(C_2, t_2; C_0, t_0)$ as a sum over intermediate configurations C_1

$$\begin{aligned}
P_2(C_2, t_2; C_0, t_0) &= \sum_{C_1} P_3(C_2, t_2; C_1, t_1; C_0, t_0) \\
&= \sum_{C_1} P_{1|2}(C_2, t_2|C_1, t_1; C_0, t_0) P_{1|1}(C_1, t_1|C_0, t_0) P_1(C_0, t_0)
\end{aligned} \tag{1.101}$$

We now make the crucial assumption that the system is *Markovian*. Of course, one would like to be able to derive the Markovian dynamics from microscopic equations, such as Newton's laws or the Schrödinger equation, under well controlled approximations, as will be done in the next Chapter. For the time being, we limit ourselves to the following observation: it is believed that a dynamics will be Markovian if:

  (i) the system is in contact with a heat bath which is much larger that the system, so that the heat bath dynamics is affected in a negligible way by its coupling to the system;

 (ii) the dynamics of the heat bath is governed by a short microscopic time τ_c, so that memory effects are limited by τ_c.

(iii) Because of (ii), a coarse graining of the system evolution is possible, so that the master equation smoothes off fluctuations over times $\lesssim \tau_c$.

Under the assumption of a Markovian dynamics, the conditional probabilities depend only on the last but one time before t_2, so that

$$P_{1|2}(C_2, t_2|C_1, t_1; C_0, t_0) = P_{1|1}(C_2, t_2|C_1, t_1) \tag{1.102}$$

Then we get from (1.101) the Chapman-Kolmogorov equation, by dividing both sides by $P_1(C_0, t_0)$

$$\boxed{P_{1|1}(C_2, t_2; C_0, t_0) = \sum_{C_1} P_{1|1}(C_2, t_2|C_1, t_1) P_{1|1}(C_1, t_1|C_0, t_0)} \tag{1.103}$$

From now on we write simply P instead of $P_{1|1}$, as almost our probabilities will be conditional.

1.5.2 Derivation of the master equation

The master equation is the differential form of the Chapman-Kolmogorov equation. Let us start from (1.103) with $t_2 = t_1 + \tau$, $\tau \to 0$. Assuming that a Taylor expansion is valid for small τ, we write

$$P(C_2, t_1 + \tau | C_1, t_1) = [1 - a(C_1; t_1)\tau]\, \delta_{C_2, C_1} + \tau W(C_2, C_1; t_1) + O(\tau^2) \tag{1.104}$$

where $W(C_2, C_1; t_1)$ is a transition probability per unit of time. The normalization condition

$$\sum_{C_2} P(C_2, t_2 | C_1, t_1) = 1$$

entails

$$1 = [1 - a(C_1; t_1)\tau] + \tau \sum_{C_2} W(C_2, C_1; t_1) + O(\tau^2)$$

so that we find

$$a(C_1; t_1) = \sum_{C_2} W(C_2, C_1; t_1) \tag{1.105}$$

Clearly, $[1 - \tau a(C_1; t_1)]$ is the probability that no transition occurs from C_1 during the infinitesimal time interval τ. We get from (1.103), to first order in τ

$$
\begin{aligned}
P(C_2, t_1 + \tau; C_0, t_0) &= \sum_{C_1} \big[(1 - a(C_1; t_1)\tau)\, \delta_{C_2, C_1} + \tau W(C_2, C_1; t_1) \big] P(C_1, t_1 | C_0, t_0) \\
&= P(C_2, t_1; C_0, t_0) - a(C_2; t_1)\tau P(C_2, t_1; C_0, t_0) + \tau \sum_{C_1} W(C_2, C_1; t_1) P(C_1, t_1; C_0, t_0)
\end{aligned}
$$

Performing another Taylor expansion to order τ in the LHS of the preceding eqiuation, we transform the preceding equation into a differential equation, with $t_1 \to t$

$$\frac{\mathrm{d}}{\mathrm{d}t} P(C_2, t | C_0, t_0) = -a(C_2; t) P(C_2, t; C_0, t_0) + \sum_{C_1} W(C_2, C_1; t) P(C_1, t; C_0, t_0)$$

In most of the cases of physical interest, the coefficients W will be time independent: $W(C_1, C_2; t) = W(C_1, C_2)$, and we shall assume this to be true in all that follows. Remembering that

$$a(C_2) = \sum_{C_1} W(C_1, C_2)$$

and writing $P(C_2, t | C_0, t_0)$ as $P_t(C)$, we obtain the final from of the master equation

$$\boxed{\frac{\mathrm{d}P_t(C)}{\mathrm{d}t} = \sum_{C' \neq C} \big[W(C, C') P_t(C') - W(C', C) P_t(C) \big]} \tag{1.106}$$

The master equation describes a gain-loss situation: the first term between square brackets in the RHS of (1.106) is a gain term for $P_t(C)$, the second one is a loss term. It should be remembered that the dynamics is coarse grained: $\mathrm{d}P_t/\mathrm{d}t$ must be interpreted as $(P_{t+\Delta t} - P_t)/\Delta t$, where Δt is small, but not infinitesimal. In fact we have $\tau_c \ll \Delta t \ll \tau$.

It is often convenient to write the master equation in matrix form. Setting by convention $W(C, C) = 0$, we define

$$
\begin{aligned}
\mathcal{W}(C, C') &= W(C, C') + \delta_{CC'} \mathcal{W}(C, C) \tag{1.107} \\
\mathcal{W}(C, C) &= -\sum_{C' \neq C} W(C', C) \tag{1.108}
\end{aligned}
$$

so that the master equation (1.106) becomes

$$\frac{\mathrm{d}P_t(C)}{\mathrm{d}t} = \sum_{C'} \mathcal{W}(C,C')P_t(C') \tag{1.109}$$

As the transition probabilities $W(C,C')$ have been assumed to be time independent, this equation can be formally integrated

$$P_t(C) = \sum_{C'} \left[\mathrm{e}^{t\mathcal{W}}\right](C,C')P_{t=0}(C') \tag{1.110}$$

The matrix elements of $\mathcal{W}$ obey an interesting relation

$$\sum_C \mathcal{W}(C,C') = \sum_{C \neq C'} W(C,C') - \mathcal{W}(C',C') = \sum_{C \neq C'} W(C,C') - \sum_{C \neq C'} W(C,C') = 0 \tag{1.111}$$

which shows that the vector $\phi = (1,1,\cdots,1)$ is a left eigenvector of $\mathcal{W}$ with eigenvalue zero. Thus, there also exists a right eigenvector with eigenvalue zero.

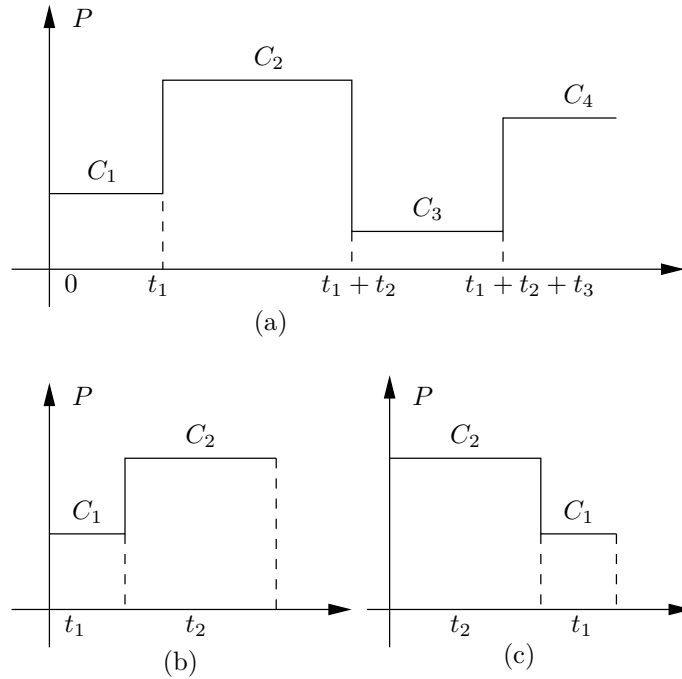### 1.5.3   Detailed balance and correlation functions

Figure 1.6: Trajectories and proof of detailed balance.

In the long time limit, we expect that the system reaches an equilibrium situation: $\lim_{t\to\infty} P_t(C) = P_{\mathrm{eq}}(C)$. If the dynamics is invariant under time reversal, the probability of a trajectory will be, in equilibrium, equal to that of the time reversed trajectory. A "trajectory" of the system is a sequence of time *intervals* during which the system stays is a given configuration: for example, starting at $t=0$ in configuration C_1, it stays t_1 in C_1, then jumps in C_2 at $t=t_1$ and stays t_2 in C_2, jumps in C_3 at time $t = t_1+t_2$ etc. It can be shown (Exercise 1.6.9) that the probability of a trajectory $(C_1,\cdots,C_k;t_1,\cdots,t_k)$ is

$$P(C_1,\cdots,C_k;t_1,\cdots t_k) = K\mathrm{e}^{t_k\mathcal{W}(C_k,C_k)}\cdots\mathrm{e}^{t_1\mathcal{W}(C_1,C_1)}W(C_k,C_{k-1})\cdots W(C_2,C_1)P_{\mathrm{eq}}(C_1) \tag{1.112}$$

where K is a normalization factor. Time reversal invariance in equilibrium implies

$$P(C_1, \cdots, C_k; t_1, \cdots t_k) = \overline{P}(\overline{C}_k, \cdots, \overline{C}_1; t_k, \cdots, t_1) \tag{1.113}$$

and if the cells are invariant under a change of sign of the momenta, $C_i = \overline{C}_i$, we get from (1.113)

$$P(C_1, \cdots, C_k; t_1, \cdots t_k) = \overline{P}(C_k, \cdots, C_1; t_k, \cdots, t_1) \tag{1.114}$$

We now make use of (1.112), for simplicity in the case of two configurations (Figure 1.6)

$$\mathrm{e}^{t_2 \mathcal{W}(C_2, C_2)} \, \mathrm{e}^{t_1 \mathcal{W}(C_1, C_1)} \, W(C_2, C_1) P_{\mathrm{eq}}(C_1) = \mathrm{e}^{t_1 \mathcal{W}(C_1, C_1)} \, \mathrm{e}^{t_2 \mathcal{W}(C_2, C_2)} \, W(C_1, C_2) P_{\mathrm{eq}}(C_2) \tag{1.115}$$

from which we deduce the detailed balance property

$$\boxed{W(C_i, C_j) P_{\mathrm{eq}}(C_j) = W(C_j, C_i) P_{\mathrm{eq}}(C_i)} \tag{1.116}$$

The master equation formalism allows us to give an explicit expression for the equilibrium time correlation functions. Let us compute, for example, the correlation of $B(t)$ and $A(t')$

$$\begin{aligned}
\langle B(t) A(t') \rangle &= \sum_{C', C} B(C) P(C, t | C', t') A(C') P_{\mathrm{eq}}(C') \\
&= \sum_{C', C} B(C) \left[\mathrm{e}^{(t-t') \mathcal{W}} \right] (C, C') A(C') P_{\mathrm{eq}}(C')
\end{aligned} \tag{1.117}$$

In the next subsection, we shall need the time derivative of this function $\langle \dot{B}(t) A(t') \rangle$

$$\langle \dot{B}(t) A(t') \rangle = \sum_{C, C', C''} B(C) \left[\mathrm{e}^{(t-t') \mathcal{W}} \right] (C, C') \mathcal{W}(C', C'') A(C'') P_{\mathrm{eq}}(C'') \tag{1.118}$$

1.5.4 The fluctuation-dissipation theorem

We are now in a position to give an alternative derivation of the fluctuation-dissipation theorem. For this derivation, it will be convenient to switch the perturbation on at $t = 0$, the energy of a configuration C being given by

$$\begin{aligned}
t < 0 \qquad & E_\varepsilon(C) = E_{\mathrm{eq}}(C) \\
t > 0 \qquad & E_\varepsilon(C) = E_{\mathrm{eq}}(C) - \varepsilon A(C)
\end{aligned} \tag{1.119}$$

Clearly, ε plays the role of f in Section 1.3. Let us call $W_\varepsilon(C, C')$ the transition probabilities for $t > 0$. Then $P_t(C)$ will obey the master equation

$$\frac{\mathrm{d} P_t(C)}{\mathrm{d} t} = \sum_{C'} \mathcal{W}_\varepsilon(C, C') P_t(C') \tag{1.120}$$

In order to estimate $\mathcal{W}_\varepsilon(C, C')$, we use detailed balance for $t > 0$

$$\frac{W_\varepsilon(C, C')}{W_\varepsilon(C', C)} = \frac{P_\varepsilon(C)}{P_\varepsilon(C')} = \frac{\mathrm{e}^{\beta \varepsilon A(C)} \, P_{\mathrm{eq}}(C)}{\mathrm{e}^{\beta \varepsilon A(C')} \, P_{\mathrm{eq}}(C')} \tag{1.121}$$

Let us define Q_t as the difference between P_t and P_{eq}. We get for Q_t the differential equation

$$\frac{\mathrm{d} Q_t(C)}{\mathrm{d} t} = \sum_{C'} \mathcal{W}_\varepsilon(C, C') Q_t(C') + \sum_{C' \neq C} \left[W_\varepsilon(C, C') P_{\mathrm{eq}}(C') - W_\varepsilon(C', C) P_{\mathrm{eq}}(C) \right]$$

Now, we use (1.121) to first order in ε

$$W_\varepsilon(C, C') P_{\mathrm{eq}}(C') = \left[1 + \beta \varepsilon [A(C) - A(C')] \right] W_\varepsilon(C', C) P_{\mathrm{eq}}(C)$$

To first order in ε we can write $W_\varepsilon = W_0$

$$
\begin{aligned}
W_\varepsilon(C,C')P_{\mathrm{eq}}(C') - W_\varepsilon(C',C)P_{\mathrm{eq}}(C) &= \beta\varepsilon[A(C) - A(C')]]\,W_0(C',C)P_{\mathrm{eq}}(C) \\
&= \beta\varepsilon A(C)W_0(C,C')P_{\mathrm{eq}}(C') - \beta\varepsilon A(C')W_0(C',C)P_{\mathrm{eq}}(C)
\end{aligned}
$$

where we have used detailed balance for $\varepsilon = 0$. As Q_t is first order in ε, we can make the approximation $\mathcal{W}_\varepsilon \to \mathcal{W}_0$. To order ε, the master equation for Q_t is then

$$
\begin{aligned}
\frac{\mathrm{d}Q_t(C)}{\mathrm{d}t} &= \sum_{C'} \mathcal{W}_0(C,C')Q_t(C') \\
&+ \beta\varepsilon \sum_{C' \neq C} W_0(C,C')[A(C) - A(C')]P_{\mathrm{eq}}(C')
\end{aligned}
\tag{1.122}
$$

The solution of (1.121) is easily seen to be

$$
Q_t(C) = -\beta\varepsilon \sum_{C,C''} \int_0^t \left[\mathrm{e}^{(t-t')\mathcal{W}_0}\right](C,C')\mathcal{W}_0(C',C'')A(C'')P_{\mathrm{eq}}(C'')
\tag{1.123}
$$

This equation leads immediately to the response of the system to the perturbation (1.118)

$$
\begin{aligned}
\overline{\delta B}(t) &= \overline{B}(t) - \langle B \rangle = \sum_C B(C)Q_t(C) \\
&= -\beta\varepsilon \sum_{C,C',C''} \int_0^t B(C) \left[\mathrm{e}^{(t-t')\mathcal{W}_0}\right](C,C')\mathcal{W}_0(C',C'')A(C'')P_{\mathrm{eq}}(C'')\mathrm{d}t' \\
&= -\beta\varepsilon \int_0^t \langle \dot{B}(t)A(t') \rangle \mathrm{d}t'
\end{aligned}
\tag{1.124}
$$

where we have used (1.118). By using (1.38), it is easily checked that this result is equivalent to those of § 1.3.2.

1.6   Exercises

1.6.1   Another derivation of Nyquist's theorem

1. Instead of the "Heisenberg picture", where the average values are given by (1.26), we now work in the "Schrödinger picture" (1.27), following Dorfman [1999], chapter 6. Show that to first order in the perturbation $V(t)$, the density distribution may be written as $\rho \simeq \rho_{\mathrm{eq}} + \rho_1$, where ρ_{eq} is the equilibrium distribution (1.28) and

$$
\rho_1(t) = \mathrm{e}^{-t\mathcal{L}}\rho_1(0) - \int_0^t \mathrm{e}^{-(t-\tau)\mathcal{L}}\{\rho_{\mathrm{eq}}, V(\Gamma:\tau)\}\mathrm{d}\tau
$$

with a Liouvillian defined by

$$
\mathcal{L}A = \{A, H\}
$$

We have used the following notation: a point in phase space is denoted by $\Gamma \equiv \{p_i, q_i\}$, while $\Gamma_t = \{p_i(t), q_i(t)\}$.

2. As in § 1.3.3, the system is a one-dimensional conductor of volume Ω, and the perturbation V is driven by an external time-dependent electric field $E(t)$

$$
V(\Gamma:t) = \left[-q\sum_i x_i\right]E(t)
$$

Note that $q_i \to x_i$ and that the t-dependence of V lies in the t-dependence of the external electric field $E(t)$. We assume that the electric field is switched on at $t = 0$. Compute the Poisson bracket $\{\rho_1, H\}$ and derive the following formula, valid within the linear response approximation

$$\rho(\Gamma, t) \simeq \rho_{\text{eq}} \left[1 + \beta \int_0^t d\tau\, E(\tau) j(t - \tau) \right]$$

where the current j is given by (1.45). Note that

$$j(\Gamma_t) = \frac{q}{\Omega} \sum_i \frac{p_i(t)}{m}$$

3. The average value of the current is given by (1.27)

$$\overline{j(t)} = \int d\Gamma\, \rho(\Gamma, t)\, j(\Gamma)$$

Using the expression of $\rho(\Gamma, t)$ derived in the preceding question, obtain that of $\overline{j(t)}$ as an integral of an equilibrium time autocorrelation function

$$\overline{j(t)} = \int_0^t \langle j(\Gamma) j(\Gamma_{-\tau}) \rangle\, E(t - \tau) d\tau$$

This is a typical Green-Kubo formula. From this expression of $\overline{j(t)}$, recover the results of § 1.3.3.

1.6.2 Strong friction limit: The harmonic oscillator

We consider the forced harmonic oscillator (1.6) , assuming that the external force $F(t)$ is a stationary random force

$$\ddot{X} + \gamma \dot{X} + \omega_0^2 X = \frac{F(t)}{m}$$

Let $C_{xx}(t)$ denote the position autocorrelation function

$$C_{xx}(t) = \overline{X(t' + t) X(t')}$$

and $C_{pp}(t)$ the momentum autocorrelation function

$$C_{pp}(t) = \overline{P(t' + t) P(t')}$$

τ_x and τ_p are the characteristic time scales for $C_{xx}(t)$ and $C_{pp}(t)$.

1. Using Wiener-Kinchin's theorem, compute the Fourier transform $C_{xx}(\omega)$ as a function of the autocorrelation of the force $C_{FF}(\omega)$. If $C_{FF}(t)$ is given by

$$C_{FF}(t) = \overline{F(t' + t) F(t')} = 2A\delta(t)$$

show that

$$C_{xx}(\omega) = \frac{1}{m^2} \frac{2A}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}$$

2. The strong friction limit corresponds to $\gamma \gg \omega_0$. Draw qualitatively $C_{xx}(\omega)$ in this limit, show that the width of the curve is $\simeq \omega_0^2/\gamma$ and estimate τ_x.

3. What is the relation between $C_{xx}(\omega)$ and $C_{pp}(\omega)$? Draw qualitatively $C_{pp}(\omega)$ in the strong friction limit and determine its witdth. Deduce from this width that $\tau_p \simeq 1/\gamma$ and that $\tau_x \gg \tau_p$. Discuss the physical significance of this result.

4. Show that taking the strong friction limit amounts to neglecting the inertial term $\ddot{X}$ in the equation of motion and recover the Ornstein-Uhlenbeck equation for $\dot{X}$

$$\dot{X}(t) = \frac{F(X)}{m\gamma} + b(t) \qquad \overline{b(t)b(t')} = 2D\delta(t - t')$$

as well as the value of τ_x.

1.6.3   Memory effects in Brownian motion

Let us consider a one-dimensional harmonic oscillator of frequency ω_0 and mass $m = 1$, in contact with a heat bath at temperature T. The oscillator is also coupled to an external oscillating electric field of frequency ω through a dipole moment proportional to $X(t)$. We work in the linear approximation.

1. What is, within a proportionality factor, the power $P(\omega)$ absorbed by the oscillator?

2. Let $C(t)$ be the autocorrelation function of the heat bath. Then $X(t)$ obeys (1.63) for $t \gg \tau_c$

$$\dot{P} = -\omega_0^2 X(t) + \beta C(0) X(t) + \mathcal{F}(t) - \beta \int_0^t C(t') \dot{X}(t - t') \mathrm{d}t'$$

Show that the coupling to the bath "renormalizes" the oscillator frequency

$$\omega_0^2 \to \overline{\omega}^2 = \omega_0^2 - \beta C(0)$$

Write a differential equation for the autocorrelation function

$$g(t) = \langle X(t) X(0) \rangle$$

of $X(t)$ in the limit $\tau_c \to 0$. What are the initial conditions?

3. Solve the differential equation for $g(t)$ by Laplace transformation

$$\tilde{g}(z) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}zt} g(t)$$

Let $\tau = 1/\gamma$ be the relaxation time of $g(t)$. What is the convergence domain of the integral? Write $\tilde{g}(z)$ as a function of $\langle X^2 \rangle$ and the Laplace transform $\tilde{C}(z)$ of $C(t)$.

4. Assume that $C(t) = B \exp(-t/\tau_c)$. what is, within a proportionality factor, the power $P(\omega)$ absorbed by the oscillator? Draw qualitatively $P(\omega)$ when $\tau_c \ll 1/\overline{\omega}$, while $B\beta/\overline{\omega} \sim 1$.

1.6.4   Simple derivation of the diffusion coefficient

1. Let us first compute the velocity autocorrelation function for $t, t' \gg 1/\gamma$. Show that

$$\overline{V(t)V(t')} = 2A \mathrm{e}^{-\gamma(t+t')} \int_0^t \mathrm{d}u \int_0^{t'} \mathrm{d}v\, \mathrm{e}^{\gamma(u+v)} \delta(u - v)$$

By examining separately the cases $t > t'$ and $t' > t$, show that

$$\overline{V(t)V(t')} = \frac{A}{\gamma} \mathrm{e}^{-\gamma|t-t'|}$$

2. Preliminary result: show that

$$I(T) = \int_{-T/2}^{T/2} \mathrm{d}t' \int_{-T/2}^{T/2} \mathrm{d}t''\, g(t' - t'') = T \int_{-T}^{T} \mathrm{d}t\, g(t) \left(1 - \frac{|t|}{T} \right)$$

If $g(t)$ tends to zero with a time scale $\tau \ll T$, show that the term $|t|/T$ in the integrand gives a negligible contribution of order τ/T.

3. Using this formula, show that a diffusive behaviour is obtained for X when $t \gg 1/\gamma$

$$\overline{(X - x_0)^2} = \int_0^t \mathrm{d}t'\, \mathrm{d}t''\, \overline{V(t')V(t'')} = 2 \frac{k_\mathrm{B} T}{M\gamma} t$$

1.6.5   Derivation of Fokker-Planck from Langevin equation

We wish to show that the conditional probability $P(x, t|x_0) \equiv P(x, t|x_0, t_0 = 0)$ of finding the particle a x at time t when it was at x_0 at time $t = 0$ obeys partial differential equation (PDE), when $X(t)$ obeys a Langevin equation of the form (1.84)

$$\dot{X}(t) = a(x) + B(t) \qquad \overline{B(t)B(t')} = 2D\delta(t - t')$$

To show it, we shall consider an initial position $y = x(t)$ at time t and examine the trajectory between times t and $t + \varepsilon$. Our goal is to prove that the moments $\overline{(X - y)^n}$ of the trajectory given by the PDE are identical to those computed from the Langevin equation.

1. *Moments from the Langevin equation.* Starting form an initial position $x(t) = y$, the trajectory $X_y^{[B]}(t + \varepsilon; t)$ is a random function, depending on the particular realization of the random force $B(t)$ and of the initial position y. Write

$$X_y^{[B]}(t + \varepsilon; t) = y + \varepsilon a(y) + \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t') = y + \varepsilon a(y) + B_\varepsilon$$

Show that $\overline{B_\varepsilon} = 0$ and that $\overline{B_\varepsilon^2} = 2\varepsilon$, so that B_ε is formally of order $\sqrt{\varepsilon}$. From this observation, derive the moments

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \overline{[X(t + \varepsilon; t) - y]} = a(y)$$

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \overline{[X(t + \varepsilon; t) - y]^2} = 2D$$

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \overline{[X(t + \varepsilon; t) - y]^n} = 0 \ \text{ for } \ n \geq 2$$

2. We now assume that $P(x, t|x_0) \equiv P$ obeys the FP equation (1.85). From

$$P(x, t + \varepsilon|y, t) \simeq \delta(x - y) - \varepsilon \frac{\partial}{\partial x}[a(x)P] + \varepsilon D \frac{\partial^2 P}{\partial x^2} + O(\varepsilon^{3/2})$$

compute the moments from P

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \overline{[X(t + \varepsilon; t) - y]^n} = \int \mathrm{d}x (x - y)^n \left[-\frac{\partial}{\partial x}(a(x)P) + D \frac{\partial^2 P}{\partial x^2} \right]$$

Integrating by parts and using the fact that

$$\lim_{|x| \to \infty} P(x, t|x_0) = 0$$

recover the results for the moments obtained from the Langevin equation.

1.6.6   The Itô versus Stratonovitch dilemma

1. *Itô prescription.* Show that the results of the preceding exercise are immediately generalized with the substitution $D \to D(y)$ in the Langevin equation, provided in the FP equation one makes also the substitution

$$D \frac{\partial^2 P}{\partial x^2} \to \frac{\partial^2 [D(x)P]}{\partial x^2}$$

Thus the FP equation is (1.91).

2. *General case.* Expanding to order ε and taking the average value in the general case, show that

$$\overline{X(t + \varepsilon) - y} = \varepsilon[a(y) + (1 - q)D'(y)]$$

so that, with respect to the preceding case, one has to make the substitution

$$a(y) \to a(y) + (1-q)D'(y)$$

Show that the term with the second order derivative is the same as that of the Itô prescription. Thus, only the drift term is modified. Show that the F-P equation for arbitrary q can be cast in the form

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}[a(x)P] + \frac{\partial}{\partial x}[D^{1-q}(x)\frac{\partial}{\partial x}D^q(x)P]$$

The Stratonovitch prescription corresponds to $q = 1/2$.

3. *Qualitative interpretation and orders of magnitude.* Writing $d(x,t) = D^{1/2}(x)b(t)$, let τ_c be the correlation time of $b(t)$ and Δx the typical length scale: $\Delta x \sim a/a' \sim D/D'$. Show that a necessary condition for the IS ambiguity to be negligible is that

$$\alpha = \frac{\tau_c \, d}{\Delta x} \ll 1$$

Define $\overline{d^2}$ as the average value of d^2 over a correlation time τ_c

$$\overline{d^2} = \frac{1}{\tau_c^2} \int_0^{\tau_c} \mathrm{d}t \, \mathrm{d}t' \, \overline{d(x,t)d(x,t')} = \frac{2}{\tau_c}D(x)$$

Show that the effective average noise is now different from zero: it is given by

$$\overline{d^*} \sim \overline{d(x - d\tau_c, t)} \sim (\overline{d^2 \tau_c})' \sim D'$$

The second condition is then $\beta = D'/a \ll 1$, in agreement with the results of question **2**. Show that it is in fact the important condition: if $\beta \ll 1$, then automatically $\alpha \ll 1$.

1.6.7   Backward velocity

Let v^+ be the forward velocity

$$v^+ = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon}\overline{X(t+\varepsilon) - x} = a(x)$$

for the Langevin equation

$$\frac{\mathrm{d}X}{\mathrm{d}t} = a(x) + b(t) \qquad \overline{b(t)b(t')} = 2D\delta(t-t')$$

Assume that one *knows* that the particle is at x at time t. One now wishes to determine the backward velocity

$$v^- = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon}\overline{[x - X(t-\varepsilon)]}$$

Show that

$$v^- = v^+ - 2D\frac{\partial \ln P(x,t|x_0)}{\partial x}$$

Hint: use $P(x,t|y,t-\varepsilon)$. This result shows clearly that the trajectory is not differentiable.

1.6.8   Kramers equation

Consider a particle of mass m, moving in one dimension, which is subjected to a deterministic force $F(x) = -\partial V/\partial x$, a viscous force $-\gamma p$ and a random force $f(t)$

$$\overline{f(t)f(t')} = 2A\,\delta(t-t')$$

The equations of motion are

$$\dot{P} = F(x) - \gamma P + f(t) \qquad \dot{X} = \frac{P}{m}$$

Note that X and P alone are not Markovian variables, but the set (X, P) is Markovian.

1. Write a Fokker-Planck equation for $P(x, p; t)$. By examining the moments $\overline{\Delta X}$, $\overline{\Delta P}$, $\overline{(\Delta P)^2}$, $\overline{(\Delta X)^2}$ and $\overline{\Delta P \Delta X}$, show that the probability distribution $P(x, p; t)$ obeys the *Kramers equation*

$$\left[\frac{\partial}{\partial t} + \frac{p}{m} \frac{\partial}{\partial x} + F(x) \frac{\partial}{\partial p} \right] P = \gamma \left[\frac{\partial}{\partial p}(pP) + mkT \frac{\partial^2 P}{\partial p^2} \right]$$

with $kT = A/(m\gamma)$. This equation can be simplified in the strong friction limit. Let us define the density

$$\rho(x, t) = \int dp \, P(x, p; t)$$

and the current

$$j(x, t) = \int dp \, \frac{p}{m} \, P(x, p; t)$$

2. From the $|p| \to \infty$ behaviour of $P(x, p; t)$, prove the (exact) continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0$$

In the strong friction limit, show that one expects

$$P(x, p; t) \simeq \rho(x, t) \sqrt{\frac{1}{2\pi mkT}} \exp\left(-\frac{[p - \overline{p}(x)]^2}{2mkT} \right)$$

with $\overline{p}(x) = F(x)/\gamma$.

3. Let us finally define

$$K(x, t) = \int dp \, \frac{p^2}{m} \, P(x, p; t)$$

What is the physical meaning of K? Prove the (exact) continuity equation

$$m \frac{\partial j}{\partial t} + \frac{\partial K}{\partial x} - F(x)\rho = -\gamma m j(x, t)$$

and show that in the strong friction limit

$$\left| \frac{\partial j}{\partial t} \right| \ll \gamma |j|$$

and that

$$K(x, t) \simeq \rho(x, t) \left[kT + \frac{\overline{p}^2(x)}{m} \right]$$

Using the continuity equation for $K(x, t)$, show that $\rho(x, t)$ obeys a Fokker-Planck equation when $kT \gg \overline{p}^2(x)/m$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} \left[\frac{F(x)}{m\gamma} \rho(x, t) - D \frac{\partial}{\partial x} \rho(x, t) \right] = 0$$

Give the explicit expression of the diffusion coefficient D for x-independent γ and A. Can you generalize to x dependent γ and A?

4. Show that for $F(x) = 0$, $X(t)$ obeys a diffusion equation with a space dependent diffusion coefficient. Write this diffusion equation in the form of a Langevin equation and find the prescrition (Itô, Stratonovitch or other, see Exercise??) which must be used in the following two cases (i) γ is x-independent and A is x-dependent and (ii) vice-versa.

1.6.9   Probability for a trajectory

Show that that the probability of a trajectory $(C_1, \cdots, C_k; t_1, \cdots, t_k)$ is

$$P(C_1, \cdots, C_k; t_1, \cdots t_k) = K \mathrm{e}^{t_k \mathcal{W}(C_k, C_k)} \cdots \mathrm{e}^{t_1 \mathcal{W}(C_1, C_1)} W(C_k, C_{k-1}) \cdots W(C_2, C_1) P_{\mathrm{eq}}(C_1)$$

where K is a normalization factor. Hint: consider first a simple case with two configurations C_1 and C_2 and compute $P(C_1, C_2; t_2, t_1)$.

1.7   Further reading

An elementary, but insightful introduction to linear response and to Brownian motion can be found in Chandler, chapter 8. For further developments, see Foerster [1975], chapter 6, Zwanzig [2001], chapters 1 and 7, Balian [1991], chapter 15 or Le Bellac *et al.* [2004], chapter 9. The derivation of master equations in section 5 follows that of Derrida and Brunet [2005]. Master equations are also derived and studied in van Kampen [2007], chapters IV and V. See also Zwanzig [2001], chapter 3.

Chapter 2

Quantum master equation

In the present Chapter, I would like to give a microscopic derivation of the master equation (1.111), starting from the Schrödinger equation. This derivation will rely on the existence of two widely separated times scales, a microscopic scale τ_c characteristic of the time evolution of the reservoir $\mathcal{R}$, and a macroscopic scale τ characteristic of that of the system $\mathcal{A}$, with $\tau_c \ll \tau$. In fact, there are two main kinds of quantum master equations, one which is used typically in quantum optics, and another one which is used for Brownian motion. In both cases we shall need one further assumption, which will however be different for each case.

2.1 Coupling to a thermal bath of oscillators

2.1.1 Exact evolution equations

In contrast to the first Chapter, we now work in a quantum mechanical framework. Our reservoir is thus a thermal bath of quantum harmonic oscillators, whose Hamiltonian H_R is

$$H_R = \sum_\lambda \hbar \omega_\lambda a_\lambda^\dagger a_\lambda. \tag{2.1}$$

It is important that the frequencies ω_λ form a quasi-continuuum in a large frequency interval $\omega_c \sim 1/\tau_c$. The statistical operator of the uncoupled reservoir is given by the Boltzmann law

$$\rho_R(t=0) = \frac{\mathrm{e}^{-H_R/k_{\mathrm{B}}T}}{\mathrm{Tr}\left(\mathrm{e}^{-H_R/k_{\mathrm{B}}T}\right)} \tag{2.2}$$

We shall need the following equilibrium average values, which are immediately derived from (2.2)

$$\langle a_\lambda \rangle = \langle a_\lambda^\dagger \rangle = 0, \qquad \langle a_\lambda^\dagger a_\mu \rangle = n_\lambda \delta_{\lambda\mu}, \qquad \langle a_\lambda a_\mu^\dagger \rangle = (n_\lambda + 1)\delta_{\lambda\mu} \tag{2.3}$$

where the average occupation number n_λ of oscillator λ is

$$n_\lambda = \frac{1}{\mathrm{e}^{\hbar\omega_\lambda/k_{\mathrm{B}}T} - 1} \tag{2.4}$$

The system–reservoir coupling V is assumed to be of the form

$$V = AR, \qquad R = R^\dagger = \sum_\lambda \left(g_\lambda a_\lambda + g_\lambda^* a_\lambda^\dagger \right) \tag{2.5}$$

where $A = A^\dagger$ is an operator acting in $\mathcal{H}_A$ and the total Hamiltonian H_{AR} is

$$H_{AR} = H_A + H_R + V = H_T + V, \qquad H_T = H_A + H_R \tag{2.6}$$

The evolution equation for the statistical operator, first written in the Schrödinger picture

$$\frac{\mathrm{d}\rho_{AR}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\left[H_{AR}, \rho_{AR}\right]$$

is transformed into the interaction picture, defined as usual by

$$\tilde{\rho}_{AR}(t) = \mathrm{e}^{\mathrm{i}H_T t/\hbar}\,\rho_{AR}\,\mathrm{e}^{-\mathrm{i}H_T t/\hbar}$$

In this picture the evolution equation reads

$$\frac{\mathrm{d}\tilde{\rho}_{AR}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\left[V(t), \tilde{\rho}_{AR}(t)\right] = -\frac{\mathrm{i}}{\hbar}\left[A(t)R(t), \tilde{\rho}_{AR}(t)\right] \tag{2.7}$$

where $A(t)$ and $R(t)$ are given by[1]

$$A(t) = \mathrm{e}^{\mathrm{i}H_T t/\hbar}\,A\,\mathrm{e}^{-\mathrm{i}H_T t/\hbar} = \mathrm{e}^{\mathrm{i}H_A t/\hbar}\,A\,\mathrm{e}^{-\mathrm{i}H_A t/\hbar},$$

$$R(t) = \mathrm{e}^{\mathrm{i}H_T t/\hbar}\,R\,\mathrm{e}^{-\mathrm{i}H_T t/\hbar} = \mathrm{e}^{\mathrm{i}H_R t/\hbar}\,R\,\mathrm{e}^{-\mathrm{i}H_R t/\hbar} = \sum_\lambda \left(g_\lambda a_\lambda\,\mathrm{e}^{-\mathrm{i}\omega_\lambda t} + g_\lambda a_\lambda^\dagger\,\mathrm{e}^{\mathrm{i}\omega_\lambda t}\right) \tag{2.8}$$

The second equality in both lines of (2.8) is valid because H_R (H_A) does not act on the degrees of freedom of $\mathcal{A}$ ($\mathcal{R}$). The quantity which will play a central role in what follows is the *equilibrium autocorrelation function* $g(t')$ of $R(t)$:

$$g(t') = \langle R(t)R(t - t')\rangle = \langle R(t')R(0)\rangle \tag{2.9}$$

where the average $\langle\bullet\rangle$ is taken with respect to the *equilibrium* statistical operator (2.2) of the reservoir. From time-translation invariance at equilibrium, g depends only on t' and not on t and t' separately (hence the second expression in (2.9)), while from the Hermiticity of R we have $g(t') = g^*(-t')$. As discussed in § 1.3.4, the autocorrelation function $g(t')$ plays a fundamental role in quantum linear response theory, where it is customary to write its real and imaginary parts $C(t')$ and $-\chi(t')/2$ separately:

$$C(t') = \frac{1}{2}\langle\{R(t'), R(0)\}\rangle \tag{2.10}$$

$$\chi(t') = \frac{\mathrm{i}}{\hbar}\langle[R(t'), R(0)]\rangle\theta(t') \tag{2.11}$$

where $\{A, B\} = AB + BA$ is the anticommutator of two operators; $\chi(t')$ is the dynamical susceptibility of the reservoir, which contains a step function $\theta(t')$ to enforce causality. As we have seen, in linear response theory, one shows that if the reservoir is submitted to a perturbation $-f(t)R$ (in the Schrödinger picture), where $f(t)$ is a *classical* function, then, to first order in f, the *nonequilibrium average* $\overline{\delta R}(t)$ is

$$\overline{\delta R}(t) = \int \mathrm{d}t'\,\chi(t')f(t - t') \tag{2.12}$$

Using (2.3) and (2.4), it is easy to derive explicit expressions for $g(t')$, $C(t')$, and $\chi(t')$

$$g(t') = \sum_\lambda |g_\lambda|^2\left[n_\lambda\mathrm{e}^{\mathrm{i}\omega_\lambda t'} + (n_\lambda + 1)\mathrm{e}^{-\mathrm{i}\omega_\lambda t'}\right] \tag{2.13}$$

$$C(t') = \sum_\lambda |g_\lambda|^2(2n_\lambda + 1)\cos\omega_\lambda t' \tag{2.14}$$

$$\chi(t') = \frac{2\theta(t')}{\hbar}\sum_\lambda |g_\lambda|^2\sin\omega_\lambda t' \tag{2.15}$$

We observe that the dynamical susceptibility does not depend on the state of the reservoir: it is independent of n_λ. Because the reservoir is large and because the frequencies ω_λ are closely spaced in a frequency interval $\sim 1/\tau_c$, we expect the correlation function to decay with a characteristic time τ_c as in § 1.4.1

$$|g(t')| \sim \mathrm{e}^{-|t'|/\tau_c} \tag{2.16}$$

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[1]I have suppressed the tilde to simplify the notations, as the time dependence avoids any confusion with the Schrödinger picture. I hope that no confusion will arise from using the tilde both for Fourier transforms and for the interaction picture!

because $g(t')$ is a superposition of a large number of complex exponentials oscillating at different frequencies which interfere destructively once $|t'| \gtrsim \tau_c$.

Having examined the properties of the autocorrelation function, we may now revert to the evolution equation (2.7), which can be written in integral form as

$$\tilde{\rho}_{AR}(t) = \rho_{AR}(0) - \frac{i}{\hbar} \int_0^t dt' \left[V(t'), \tilde{\rho}_{AR}(t') \right]$$

We iterate this expression once

$$\begin{aligned}
\tilde{\rho}_{AR}(t) &= \rho_{AR}(0) - \frac{i}{\hbar} \int_0^t dt' \left[V(t'), \rho_{AR}(0) \right] \\
&\quad - \frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' \left[V(t'), \left[V(t''), \tilde{\rho}_{AR}(t'') \right] \right]
\end{aligned}$$

and differentiate with respect to t to obtain

$$\frac{d\tilde{\rho}_{AR}}{dt} = -\frac{i}{\hbar} \left[V(t), \rho_{AR}(0) \right] - \frac{1}{\hbar^2} \int_0^t dt' \left[V(t), \left[V(t'), \tilde{\rho}_{AR}(t') \right] \right] \tag{2.17}$$

We assume the following initial conditions: the system has been put in contact with the reservoir at time $t = 0$, so that the statistical operator ρ_{AR} takes a factorized form at $t = 0$

$$\rho_{AR}(t=0) = \rho(t=0) \otimes \rho_R(t=0) \tag{2.18}$$

This allows us to take the partial trace over the reservoir degrees of freedom. Then the first term in (2.17) vanishes (Exercise 2.1)

$$\text{Tr}_{\mathcal{R}} \left[V(t), \rho_{AR}(0) \right] = \left[A(t), \rho_A(0) \right] \text{Tr}_{\mathcal{R}} \left(R(t) \rho_R \right) = 0$$

where we have made use of (2.3). Under the factorization assumption (2.18), we finally obtain an *exact* equation for the state operator $\tilde{\rho}_A(t) = \tilde{\rho}(t)$ of system $\mathcal{A}$:

$$\frac{d\tilde{\rho}}{dt} = -\frac{1}{\hbar^2} \int_0^t dt' \, \text{Tr}_{\mathcal{R}} \left(\left[V(t), \left[V(t'), \tilde{\rho}_{AR}(t') \right] \right] \right). \tag{2.19}$$

2.1.2 The Markovian approximation

From dimensional analysis, the characteristic evolution time of $\tilde{\rho}_{AR}$ is *a priori* $\sim \hbar/|\mathcal{V}|$, where $\mathcal{V}$ is a typical matrix element of V. We cannot be satisfied with perturbation theory, which is valid only for times t such that $\lesssim \mathcal{V}|t|/\hbar \ll 1$, while we are looking for a theory valid for long times. Two points need to be underlined.

1. We can hope for an approximate factorization at time t, *and not only* at $t = 0$

$$\tilde{\rho}_{AR}(t) = \tilde{\rho}_A(t) \otimes \tilde{\rho}_R(t) + \delta\tilde{\rho}_{AR}(t)$$

$$\tilde{\rho}_A(t) = \text{Tr}_{\mathcal{R}}[\tilde{\rho}_{AR}(t)] \qquad \tilde{\rho}_R(t) = \text{Tr}_{\mathcal{A}}[\tilde{\rho}_{AR}(t)]$$

Indeed, as $\mathcal{R} \gg \mathcal{A}$ (the reservoir is much bigger than the system), we expect that

$$|\delta\tilde{\rho}_{AR}(t)| / |\tilde{\rho}_{AR}(t)| \ll 1$$

This amounts to ignoring the reaction of the system on the reservoir, and leads to irreversible equations for the system.

2. Over times $t \sim \tau_c$, a typical phase Φ between $\mathcal{A}$ and $\mathcal{R}$ evolves according to $\sim |\mathcal{V}|\tau_c/\hbar$. Since there is a loss of memory for $t \gtrsim \tau_c$, Φ undergoes a random walk, and during a time $t \gg \tau_c$, it performs a number of steps $\sim t/\tau_c$; its variance is then

$$\Delta\Phi^2(t \gg \tau_c) \simeq \left(\frac{|\mathcal{V}|\tau_c}{\hbar}\right)^2 \times \frac{t}{\tau_c} = \frac{t}{\tau}$$

When $|\mathcal{V}|\tau_c/\hbar \ll 1$, we thus find the two very different times scales, a microscopic one τ_c and a macroscopic one τ which we were looking for

$$\tau = \left(\frac{\hbar}{|\mathcal{V}|\tau_c}\right)^2 \tau_c \tag{2.20}$$

with $\tau \gg \tau_c$. We may then perform a coarse graining of $\tilde{\rho}$ over time intervals Δt such that $\tau_c \ll \Delta t \ll \tau$

$$\tilde{\rho}(t) \rightarrow \frac{1}{\Delta t} \int_t^{t+\Delta t} \tilde{\rho}(t')\mathrm{d}t' \tag{2.21}$$

Let us emphasize once more that the fundamental condition for the validity of our procedure is the inequality

$$\boxed{\frac{|\mathcal{V}|\tau_c}{\hbar} \ll 1} \tag{2.22}$$

and if it satisfied, one can show rigorously that[2]

1.

$$|\delta\tilde{\rho}_{AR}(t)| = O\left(\frac{|\mathcal{V}|\tau_c}{\hbar}\right)^2 = O\left(\frac{\tau_c}{\tau}\right) \tag{2.23}$$

2.

$$\tilde{\rho}_R(t) = \rho_R(t=0) + O\left(\frac{|\mathcal{V}|\tau_c}{\hbar}\right)^2 = \rho_R(0) + O\left(\frac{\tau_c}{\tau}\right) \tag{2.24}$$

To summarize, the existence of two widely separated time scales, τ et τ_c, with $\tau \gg \tau_c$

$$\tau_c \ll \frac{\hbar}{|\mathcal{V}|} \ll \tau = \frac{\hbar^2}{|\mathcal{V}|^2\tau_c} \tag{2.25}$$

is the crucial condition for the validity of a master equation for the coarse grained[3] $\tilde{\rho}$. The "natural" characteristic time scale $\hbar/|\mathcal{V}|$ is very small compared to τ : the effective coupling is reduced owing to the fact that $\mathcal{A}$ is coupled to a large number of independent modes, a phenomenon called *motion narrowing*. From (2.23) et (2.24), the approximate equation for $\tilde{\rho}$ is

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = -\frac{1}{\hbar^2} \int_0^t \mathrm{d}t' \, \mathrm{Tr}_{\mathcal{R}}\left(\left[V(t), [V(t'), \tilde{\rho}_A(t') \otimes \rho_R(0)]\right]\right) \tag{2.26}$$

Plugging now (2.9) into (2.26), we obtain an equation of motion for $\tilde{\rho} \equiv \tilde{\rho}_A$ which depends only on A and g (Exercise 2.1); because of the double commutator, there are four terms in this equation

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = \frac{1}{\hbar^2} \int_0^t \mathrm{d}t' \, g(t')\Big[A(t-t')\tilde{\rho}(t-t')A(t) - A(t)A(t-t')\tilde{\rho}(t-t') + \Big] + \mathrm{H.c.} \tag{2.27}$$

where H.c.= Hermitian conjugate and we have made the change of variable $t' \rightarrow t - t'$.

Equation (2.27) is still an integro-differential equation containing memory effects, and not a master equation. To obtain a master equation, we note from (2.16) that the times t' which contribute significantly

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[2]Cohen-Tannoudji *et al.* [1992], Chapter IV.
[3]Thus the time derivative must not be understood as $\lim_{\Delta t \to 0} \Delta\tilde{\rho}/\Delta t$, because coarse graining smoothes off the variations of $\tilde{\rho}$ on time scales $\sim \tau_c$.

to the integral are bounded by τ_c, $t' \lesssim \tau_c$. Owing to the fact that the characteristic evolution time of $\tilde{\rho}$ is τ, the difference $|\tilde{\rho}(t - t') - \tilde{\rho}(t)|$ is bounded

$$|\tilde{\rho}(t - t') - \tilde{\rho}(t)| \lesssim \mathcal{O}\left(\frac{|\mathcal{V}|\tau_c}{\hbar}\right)^2 = O\left(\frac{\tau_c}{\tau}\right)$$

and we can replace $\tilde{\rho}(t' - t)$ by $\tilde{\rho}(t)$ in a manner which is consistent with the preceding approximation: the error is of higher order in the small parameter τ_c/τ. In this way, we have justified a Markovian approximation, and $\tilde{\rho}$ is given by a first-order differential equation. Taking $t \gg \tau_c$, we can send the upper limit in the integral to infinity and write

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = \frac{1}{\hbar^2} \int_0^\infty \mathrm{d}t' \, g(t') \Big[A(t - t')\tilde{\rho}(t)A(t) - A(t)A(t - t')\tilde{\rho}(t) + \Big] + \text{H.c.} \tag{2.28}$$

In this form, all reference to the initial conditions has disappeared. It is often convenient (but by no means necessary) to revert to the Schrödinger picture and to write the master equation as

$$\boxed{\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[H_A, \rho] + \frac{1}{\hbar^2}\left(W\rho A + A\rho W^\dagger - AW\rho - \rho W^\dagger A\right)} \tag{2.29}$$

where the operator W is given by

$$\boxed{W = \int_0^\infty g(t')A(-t')\mathrm{d}t'} \tag{2.30}$$

2.2 The quantum optics case

2.2.1 Evolution of the statistical operator

The prototype of the quantum optics case is a two-level sytem interacting with a reservoir. The free system Hamiltonian H_A is

$$H_A = -\frac{1}{2}\hbar\omega\sigma_z \tag{2.31}$$

and the system-reservoir interaction is chosen as

$$V = \hbar\sigma_x R = \hbar\sigma_x \sum_\lambda \left(g_\lambda a_\lambda + g_\lambda^* a_\lambda^\dagger\right) \tag{2.32}$$

so that $A = \sigma_x = \sigma_+ + \sigma_-$, where we have defined $\sigma_\pm = (\sigma_x + \mathrm{i}\sigma_y)/2$. Note that V induces transitions between the two levels. The introduction of $\hbar$ allows us to get rid of the $1/\hbar^2$ factors in (2.28) or (2.29). From the commutation relation

$$[\sigma_z, \sigma_\pm] = \pm 2\sigma_\pm \tag{2.33}$$

we see that

$$[H_A, \sigma_\pm] = \mp\hbar\omega\sigma_\pm \tag{2.34}$$

The operators $\sigma_\pm$ are a kind of "eigenoperators" of H_A: σ_+ (resp. σ_-) decreases (resp. increases) the energy by $\hbar\omega$. Let us generalize this two-level case by writing

$$H_A = \sum_\varepsilon \varepsilon\,\mathcal{P}(\varepsilon) \tag{2.35}$$

where the εs are (discrete) eigenvalues of H_A, that is, unperturbed energies of the system, and $\mathcal{P}(\varepsilon)$ is the projector on the subspace of the eigenvalue ε. The system-reservoir interaction is taken of the following form

$$V = \hbar AR = \hbar A \sum_\lambda \left(g_\lambda a_\lambda + g_\lambda^* a_\lambda^\dagger\right) \tag{2.36}$$

This could be generalized to

$$V = \hbar \sum_\alpha A_\alpha R_\alpha$$

but the summation over indices α serve only to complicate the equations, without bringing any insight into the physics. We define the operator $A(\omega)$ by

$$A(\omega) = \sum_{\varepsilon' - \varepsilon = \hbar\omega} \mathcal{P}(\varepsilon)\, A\, \mathcal{P}(\varepsilon') \tag{2.37}$$

Using $H_A \mathcal{P}(\varepsilon) = \varepsilon \mathcal{P}(\varepsilon)$, we compute the commutator of $A(\omega)$ with H_A which generalizes (2.34)

$$[H_A, A(\omega)] = -\hbar\omega A(\omega) \tag{2.38}$$

Thus $A(\omega)$ decreases the energy by $\hbar\omega$, as was clear from the definition (2.37)

$$H_A[A(\omega)|\varepsilon\rangle] = (\varepsilon - \hbar\omega)[A(\omega)|\varepsilon\rangle]$$

The commutator (2.38) allows us to go to the interaction picture

$$A(\omega, t) = e^{iH_A t/\hbar}\, A(\omega)\, e^{-iH_A t/\hbar} = A(\omega)\, e^{-i\omega t} \tag{2.39}$$

The following relations will be useful

$$A^\dagger(\omega) = A(-\omega)$$
$$[H_A, A^\dagger(\omega)A(\omega)] = 0 \tag{2.40}$$
$$\sum_\omega A(\omega) = \sum_{\varepsilon, \varepsilon'} \mathcal{P}(\varepsilon)\, A\, \mathcal{P}(\varepsilon') = A$$

We now write V in the interaction picture, using the last line of (2.40)

$$V(t) = \hbar \sum_\omega A(\omega) R(t)\, e^{-i\omega t} \tag{2.41}$$

so that the operator W in (2.30) becomes

$$W = \sum_\omega A(\omega) \int_0^\infty dt'\, g(t')\, e^{i\omega t'} \tag{2.42}$$

We define the Fourier-Laplace transform of $g(t)$ as

$$G_\pm(\omega) = G_\mp(-\omega) = \int_0^\infty dt\, g(t)\, e^{\pm i\omega t} \tag{2.43}$$

and get

$$W = \sum_\omega A(\omega) G_+(\omega) = \sum_\omega A^\dagger(\omega) G_-(\omega) \tag{2.44}$$

2.2.2   The secular approximation

We shall use (2.29) for Brownian motion, but in the present case, in order to introduce the secular approximation, it is more convenient to revert to the interaction picture. Let us rewrite the first term in the RHS of (2.28), using the last line of (2.40)

$$
\begin{aligned}
\int_0^\infty dt'\, g(t') A(t - t') \tilde{\rho}(t) A(t) &= \sum_{\omega, \omega'} \int_0^\infty dt'\, g(t') A(\omega)\, e^{-i\omega(t - t')}\, \tilde{\rho}(t)\, A(\omega')\, e^{-i\omega' t} \\
&= \sum_{\omega, \omega'} G_+(\omega) A(\omega) \tilde{\rho}(t) A(\omega')\, e^{-i(\omega + \omega')t} \tag{2.45}
\end{aligned}
$$

The characteristic time scale of $\tilde{\rho}(t)$ is τ, and if $|\omega + \omega'| \gg \tau^{-1}$, the exponential in(2.45) will oscillate very rapidly over a period of time where $\tilde{\rho}$ is approximately constant, and we may expect that its contribution to the evolution of $\tilde{\rho}$ will average to zero: this is called the *secular approximation*. Thus, in the quantum optics case, we need that the relaxation time τ be much bigger that the inverse Bohr frequencies Ω^{-1} of the system, which are determined by H_A: $\tau \gg \Omega^{-1}$. This condition is very well realized in quantum optics, where typically $\tau \sim 10^{-8}$ s and $\Omega^{-1} \sim 10^{-15}$ s. In atomic physics, $\Gamma = 1/\tau$ is the width of excited states, so that the preceding condition also reads $\Gamma \,(\sim 10^8 \,\mathrm{rad.s}^{-1}) \ll \Omega \,(\sim 10^{15} \,\mathrm{rad.s}^{-1})$. Within this approximation, we may neglect in (2.45) all the terms but those with $\omega + \omega' = 0$. Taking into account the four terms in (2.28), we obtain the following evolution equation for $\tilde{\rho}$

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = \sum_\omega \left\{ (G_+(\omega) + G_+^*(\omega))A(\omega)\,\tilde{\rho}\,A(-\omega) - G_+(\omega)A(-\omega)\,A(\omega)\,\tilde{\rho} - G_+^*(\omega)\tilde{\rho}\,A(-\omega)\,A(\omega) \right\} \quad (2.46)$$

The RHS of (2.46) is Hermitian, as it should. It is an interesting observation that this equation can be written in a Lindblad form in the Schrödinger picture

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\,[H_A, \rho] + \mathcal{L}\rho = -\frac{\mathrm{i}}{\hbar}\,[H_A, \rho] + \sum_\mu L_\mu\,\rho\,L_\mu^\dagger - \frac{1}{2}\{K, \rho\}$$

$$K = \frac{1}{2}\sum_\mu L_\mu^\dagger\,L_\mu \quad\quad\quad (2.47)$$

where we recall that $\{A, B\} = AB + BA$ is the anti-commutator of A and B. The L_μs are *quantum jump operators*. They describe the manner in which A is modified when a measurement with result μ is performed on the environment. The Lindblad form is the most general master equation leading to a semi-group dynamics[4], provided the *Liouvillian* $\mathcal{L}$ is a bounded superoperator. In order to cast (2.46) into the Lindblad form, we decompose $G_\pm(\omega)$ in its real and imaginary parts

$$G_\pm(\omega) = \frac{1}{2}\,\Gamma_\pm(\omega) - \mathrm{i}\Delta_\pm(\omega)$$

and define the Lamb shift Hamiltonian

$$H_{\mathrm{LS}} = \sum_\omega \Delta_\pm(\omega)A(-\omega)\,A(\omega)$$

Note that only the second term in the RHS of 2.46 contributes to H_{LS}. From the second line of (2.40), we see that H_{LS} commutes with H_A, so that H_{LS} can be interpreted as a renormalization of the "bare" Hamiltonian H_A. Indeed, since H_A and H_{LS} can be simultaneously diagonalized, there exists a choice (in general non unique) of the projectors $\mathcal{P}(\varepsilon)$s such that

$$\sum_\varepsilon \mathcal{P}(\varepsilon) = I \quad\quad H_A = \sum_\varepsilon \varepsilon\mathcal{P}(\varepsilon) \quad\quad H_{\mathrm{LS}} = \sum_\varepsilon \Delta_\varepsilon\mathcal{P}(\varepsilon)$$

The Δ_εs are energy shifts which can also be computed in second order perturbation theory. The Linblad form of (2.46) is then

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\,[H_A + H_{\mathrm{LS}}, \rho] + \sum_\omega \Gamma_+(\omega)\left[A(\omega)\,\rho\,A(-\omega) - \frac{1}{2}\{A(-\omega)\,A(\omega), \rho\}\right] \quad (2.48)$$

Let us illustrate this result on two important cases.

(i) Two-level system, where $|0\rangle$ and $|1\rangle$ are eigenstates of H_A in (2.31), with eigenvalues $\mp\hbar\omega/2$ respectively

$$\begin{aligned} A(\omega) &= \sigma_+ & A(-\omega) &= \sigma_- \\ \sigma_+|0\rangle &= |1\rangle & \sigma_-|1\rangle &= |0\rangle \end{aligned}$$

---

[4]A semi-group dynamics holds if one can write $\rho(t) = W(t)\rho(0)$, where the superoperator W obeys

$$W(t_1 + t_2) = W(t_2)W(t_1)$$

A superporator acts in a vector space of operators, so the Liouvillian is also a superoperator. In general, W has no inverse, hence the terminology semi-group.

We get $\mathrm{d}\rho/\mathrm{d}t$ in the Lindblad form

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\mathrm{i}}{2}\left[(\omega+\Delta)\sigma_z,\rho\right] + \Gamma_+\left(\sigma_+\rho\,\sigma_- - \frac{1}{2}\left\{\sigma_-\sigma_+,\rho\right\}\right) + \Gamma_-\left(\sigma_-\rho\,\sigma_+ - \frac{1}{2}\left\{\sigma_+\sigma_-,\rho\right\}\right) \tag{2.49}$$

where $\Delta = \Delta_+ - \Delta_-$ while Γ_+ and Γ_- are the transition rates $|0\rangle \leftrightarrow |1\rangle$ (figure 2.1)

$$\Gamma_+ \,:\, |1\rangle \to |0\rangle \qquad \Gamma_- \,:\, |0\rangle \to |1\rangle$$

In the notations of (1.111), $\Gamma_+ = W_{10}$ and $\Gamma_- = W_{01}$, so that detailed balance implies

$$\Gamma_+ = \mathrm{e}^{\hbar\omega/k_{\mathrm{B}}T}\,\Gamma_-$$

These transition rates are given by (Exercise 2.4.2)

$$\begin{aligned}
\Gamma_+ &= 2\pi\sum_\lambda |g_\lambda|^2(n_\lambda+1)\delta(\omega_0-\omega_\lambda)\\
\Gamma_- &= 2\pi\sum_\lambda |g_\lambda|^2 n_\lambda\delta(\omega_0-\omega_\lambda)
\end{aligned} \tag{2.50}$$

which obey detailed balance. $\Gamma = \Gamma_+ + \Gamma_-$ is the relaxation rate of populations and $\Gamma/2$ that of coherences (Exercise??). In the NMR language, we have $T_2 = 2T_1$. As we have seen, the energy levels of H_A are modified by the Lamb shift Δ: $\omega \to \omega + \Delta$

$$\Delta = \sum_\lambda |g_\lambda|^2(2n_\lambda+1)\left(\frac{\mathbb{P}}{\omega_0-\omega_\lambda} + \frac{\mathbb{P}}{\omega_0+\omega_\lambda}\right) \tag{2.51}$$
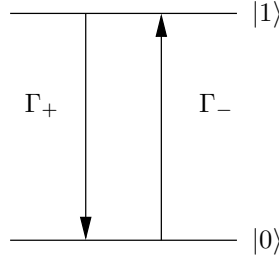
where $\mathbb{P}$ is a Cauchy principal value.

Figure 2.1: Transition rates Γ_+ and Γ_-.

(ii) Harmonic oscillator in equilibrium with a thermalized quantized field. The master equation in the interaction picture may be obtained from (2.49) thanks to the substitution $\sigma_+ \to a$, $\sigma_- \to a^\dagger$, $H_A = \hbar\omega a^\dagger a$

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\left[H_A + H_{\mathrm{LS}},\rho\right] + \Gamma_+\left[a\rho a^\dagger - \frac{1}{2}\{a^\dagger a,\rho\}\right] + \Gamma_-\left[a^\dagger\rho a - \frac{1}{2}\{aa^\dagger,\rho\}\right] \tag{2.52}$$

Detailed derivations of the preceding equation can be found in textbooks on quantum optics (see 'Further reading').

To conclude this section, let us derive a master equation for populations. We shall need one further assumption: the energy levels ε_i of H_A are non degenerate. As $A(\omega)$ decrease the energy by $\hbar\omega$, the matrix elements $\langle\varepsilon_n|A(\omega)|\varepsilon_m\rangle$ are non zero only if $\varepsilon_n = \varepsilon_m - \hbar\omega$. In order to derive an equation for the populations, we must take the nn matrix element of (2.48). Let us define the population of level n

$$P(\varepsilon_n,t) = \langle\varepsilon_n|\rho(t)|\varepsilon_n\rangle \tag{2.53}$$

Then we have to compute the nn matrix element of the RHS of (2.46). Let us look at the first term

$$\Gamma_+(\omega)\langle\varepsilon_n|A(\omega)\rho(t)A(-\omega)|\varepsilon_n\rangle = \Gamma_+(\omega)\langle\varepsilon_n|A(\omega)|\varepsilon_n+\hbar\omega|\rangle\langle\varepsilon_n+\hbar\omega|\rho(t)|\varepsilon_n+\hbar\omega\rangle\langle\varepsilon_n+\hbar\omega|A(-\omega)|\varepsilon_n\rangle$$

$$= \Gamma_+(\omega)|\langle\varepsilon_n|A(\omega)|\varepsilon_n+\hbar\omega\rangle|^2 P(\varepsilon_n+\hbar\omega,t) = W(\varepsilon_n|\varepsilon_n+\hbar\omega)P(\varepsilon_n+\hbar\omega,t)$$

This leads us to the Pauli master equation

$$\frac{\mathrm{d}P(\varepsilon_n,t)}{\mathrm{d}t} = \sum_\omega \left\{ W(\varepsilon_n|\varepsilon_n+\hbar\omega)P(\varepsilon_n+\hbar\omega,t) - W(\varepsilon_n+\hbar\omega|\varepsilon_n)P(\varepsilon_n,t) \right\} \tag{2.54}$$

2.3 Quantum Brownian motion

2.3.1 The master equations

Our last example will be that of a heavy free particle with mass M coupled to a thermal bath of harmonic oscillators with masses m_λ and frequencies ω_λ. As we have seen in § 1.4.1, this is a typical model for Brownian particle motion. A heavy particle interacts with a thermal bath of light particles (molecules), and we recall that one may identify two widely separated time scales: the time scale τ_c for the bath and the time scale τ for the motion of the heavy particle, with $\tau_c \ll \tau$. The full Hamiltonian H_{AR} is assumed to have a translation-invariant form

$$H_{AR} = \frac{P^2}{2M} + \sum_\lambda \frac{P_\lambda^2}{2m_\lambda} + \frac{1}{2}\sum_\lambda m_\lambda\omega_\lambda^2(X-X_\lambda)^2 = H_A + H_R + V \tag{2.55}$$

where (P, P_λ) and (X, X_λ) are momentum and position operators for the particle and the oscillators. The decomposition (2.55) of H_{AR} reads

$$H_A \;=\; \frac{P^2}{2M} \tag{2.56}$$

$$H_R \;=\; \sum_\lambda \left(\frac{P_\lambda^2}{2m_\lambda} + \frac{1}{2}\omega_\lambda^2 X_\lambda^2 \right) = \sum_\lambda \hbar\omega_\lambda a_\lambda^\dagger a_\lambda \tag{2.57}$$

$$V \;=\; \frac{1}{2}\kappa X^2 - XR = H_{\mathrm{CT}} - X\left[\sum_\lambda g_\lambda\left(a_\lambda + a_\lambda^\dagger\right)\right] \tag{2.58}$$

with $g_\lambda = \sqrt{\hbar m_\lambda\omega_\lambda^3/2}$, $\kappa = \sum_\lambda m_\lambda\omega_\lambda^2$, and CT standing for "counter-term" for reasons to be explained below. The operator A is therefore to be identified with the position operator of the Brownian particle, and we have neglected the zero-point energy of the oscillators. It may appear that translation invariance has been broken in (2.56), but this is of course an artefact of the decomposition: as we shall see later on, the contribution of the translation-noninvariant counter-term

$$H_{\mathrm{CT}} = \frac{1}{2}\kappa X^2 \tag{2.59}$$

is canceled by another contribution from the interaction: this is the quantum version of the compensation between the first two terms of (1.63). It will be convenient but by no means necessary (see the comments following (2.73)) to work in the high-temperature limit where (2.4) becomes

$$n_\lambda \simeq n_\lambda + 1 \simeq \frac{k_{\mathrm{B}}T}{\hbar\omega_\lambda} \gg 1 \tag{2.60}$$

We recall that the frequencies ω_λ are assumed to be closely spaced in an interval $\sim 1/\tau_c$, so that the sums over λ can be replaced by integrals over ω. As in § 1.4.1, we define the spectral function $J(\omega)$:

$$J(\omega) = \frac{\pi}{\hbar}\sum_\lambda |g_\lambda|^2\delta(\omega-\omega_\lambda) = \frac{\pi}{2}\sum_\lambda m_\lambda\omega_\lambda^3\delta(\omega-\omega_\lambda) \tag{2.61}$$

From (2.13), (2.14), and (2.58) we find the expressions for the real and imaginary parts of the autocorrelation function $g(t')$

$$C(t') = \frac{2k_{\mathrm{B}}T}{\pi} \int_0^\infty \frac{\mathrm{d}\omega}{\omega}\, J(\omega) \cos \omega t'$$

$$\chi(t') = \frac{2\theta(t')}{\pi} \int_0^\infty \mathrm{d}\omega\, J(\omega) \sin \omega t' = -\frac{\theta(t')}{k_{\mathrm{B}}T} \frac{\mathrm{d}C}{\mathrm{d}t'} \tag{2.62}$$

As in § 1.4.1, we choose a specific form for $J(\omega)$

$$J(\omega) = M\gamma\,\omega\, \left(\frac{\omega_c^2}{\omega^2 + \omega_c^2} \right)$$

With this choice $C(t')$ has a simple analytic form

$$C(t') = M\gamma\omega_c\, \mathrm{e}^{-\omega_c|t'|} = 2M\gamma\delta_c(t') \tag{2.63}$$

Here $\delta_c(t)$ is smeared Dirac δ-function: in the limit $\omega_c \to \infty$, $\delta_c(t)$ becomes a δ-function

$$\lim_{\omega_c \to \infty} \left[\frac{1}{2}\, \omega_c\, \mathrm{e}^{-\omega_c|t|} \right] = \delta(t)$$

. With this notation, the autocorrelation function reads

$$g(t') = 2M\gamma k_{\mathrm{B}}T\delta_c(t') + \mathrm{i}\hbar M\gamma\delta_c'(t') = 2D\delta_c(t') + \mathrm{i}\hbar M\gamma\delta_c'(t') \tag{2.64}$$

where we have used Einstein's relation (1.78) linking the momentum diffusion coefficient $D = M^2 A$ to γ and T, $D = M\gamma k_{\mathrm{B}}T$.

After these preliminaries, we are now ready to give an explicit form for the general master equation (2.29), which in the present case becomes

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar} \left[\frac{P^2}{2M}, \rho \right] - \frac{\mathrm{i}}{\hbar} \left[\frac{1}{2}\kappa X^2, \rho \right] - \frac{1}{\hbar^2} \left(W\rho X + X\rho W - XW\rho - \rho W^\dagger X \right) \tag{2.65}$$

with

$$W = \int_0^\infty g(t')\tilde{X}(-t')\mathrm{d}t' \tag{2.66}$$

The operator $\tilde{X}$ in the interaction picture is given by

$$\tilde{X}(t') = \exp\left[\frac{\mathrm{i}P^2 t'}{2M\hbar} \right] X \exp\left[-\frac{\mathrm{i}P^2 t'}{2M\hbar} \right] = X + \frac{Pt}{M} \tag{2.67}$$

a result which is immediately derived from $[P^2, X] = -2\mathrm{i}\hbar P$. If the particle is put in a potential $U(X)$, for example an harmonic potential $M\Omega^2 X^2/2$, then (2.67) is only approximately valid, and in order to use this equation, we need the condition

$$\tau_c \ll \Omega^{-1}$$

This condition is to be contrasted with that used in the quantum optic case, $\Omega^{-1} \ll \tau$. The term proportional to D on the right-hand side of the master equation involves the integral

$$\frac{2D}{\hbar^2} \int_0^\infty \delta_c(t') \left[\left(X - \frac{Pt'}{M} \right) \rho(t)X + X\rho(t)\left(X - \frac{Pt'}{M} \right) - X\left(X - \frac{Pt'}{M} \right) \rho(t) - \rho(t)\left(X - \frac{Pt'}{M} \right) X \right] \mathrm{d}t'.$$

Owing to the narrow width of $\delta_c(t')$, the terms proportional to Pt'/M are negligible and we are left with the double commutator

$$-\frac{D}{\hbar^2} \big[X, \big[X, \rho(t) \big] \big] \tag{2.68}$$

The term proportional to $M\gamma$ is

$$\frac{\mathrm{i}M\gamma}{\hbar} \int_0^\infty \delta_c'(t') \bigg[\left(X - \frac{Pt'}{M} \right) \rho(t)X + X\rho(t) \left(X - \frac{Pt'}{M} \right)$$
$$- X \left(X - \frac{Pt'}{M} \right) \rho(t) - \rho(t) \left(X - \frac{Pt'}{M} \right) X \bigg] \mathrm{d}t' \tag{2.69}$$

The two integrals that we need are

$$\text{(i)} \quad \int_0^\infty \delta_c'(t')t' \, \mathrm{d}t' = -\frac{1}{2},$$
$$\text{(ii)} \quad \int_0^\infty \delta_c'(t')\mathrm{d}t' = \int_0^\infty \mathrm{d}t' \frac{\mathrm{d}}{\mathrm{d}t'} \left(\frac{\omega_c}{2} \, \mathrm{e}^{-\omega_c|t|} \right) = -\frac{\omega_c}{2} \tag{2.70}$$

Equation (2.69) can be written as a sum of two terms. The first one, which depends on (i), is

$$\frac{\gamma}{2\mathrm{i}\hbar} \big[X, \{P, \rho(t)\} \big] \tag{2.71}$$

and the second one depending on (ii) is

$$\frac{\mathrm{i}M\gamma\omega_c}{\pi\hbar} \big[X^2, \rho(t) \big] = \frac{\mathrm{i}}{\hbar} \left[\frac{1}{2}\kappa X^2, \rho(t) \right] \tag{2.72}$$

because in the Caldeira–Leggett model κ is given by

$$\kappa = \sum_\lambda m_\lambda \omega_\lambda^2 = \frac{2}{\pi} \int_0^\infty \frac{\mathrm{d}\omega}{\omega} \, J(\omega) = M\gamma\omega_c$$

Then the term in (2.72) exactly cancels the contribution of H_{CT} to the evolution of the statistical operator. Collecting all the contributions to $\mathrm{d}\rho/\mathrm{d}t$, we finally obtain the master equation describing the quantum evolution of the Brownian particle:

$$\boxed{\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar} \left[\frac{P^2}{2M}, \rho(t) \right] - \frac{\mathrm{i}\gamma}{2\hbar} \big[X, \{P, \rho(t)\} \big] - \frac{D}{\hbar^2} \big[X, [X, \rho(t)] \big]} \tag{2.73}$$

Equation (2.73) is one of the basic results of the theory of open quantum systems. It should be observed that this equation is not of the Lindblad form. However (see Exercise 2.4.5), it is possible to add a term which is small in the high temperature limit and to cast (2.73) in the Lindblad form. The first term gives the unitary evolution of the wave packet, the second one describes friction, and the last one governs decoherence, as we shall see in detail in the next subsection. A Fokker–Planck equation for the probability distribution of p can be derived from (2.73); see Exercise 2.4.3..

Since the model (2.55) is linear (that is, its classical equations of motion are linear), it can be solved exactly without taking the high-temperature limit. This is done in practice using path-integral methods. One can even put the Brownian particle in a harmonic potential well with frequency Ω. The exact solution at time t is

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar} \left[\frac{P^2}{2M} + \frac{1}{2}M\Omega^2(t)X^2, \rho(t) \right] - \frac{\mathrm{i}\gamma(t)}{2\hbar} \big[X, \{P, \rho(t)\} \big] - \frac{D(t)}{\hbar^2} \big[X, [X, \rho(t)] \big] - \frac{f(t)}{\hbar} \big[X, [P, \rho] \big] \tag{2.74}$$

We note the presence of a fourth term, called anomalous diffusion, which is negligible in the long-time limit $t \to \infty$. The functions $\Omega(t)$, $\gamma(t)$, $D(t)$, and $f(t)$ are given by integrals which must, in general, be computed numerically. In the long-time limit which has been taken in (2.73), analytical evaluation of the integrals is sometimes possible.

2.3.2   Decoherence and Schrödinger cats

The preceding results are of the utmost importance, because they exhibit precise mechanisms for *decoherence.* A Brownian particle is a large object by microscopic standards, and by constructing a quantum state of the particle which is a coherent superposition of two nonoverlapping wave packets, we exhibit an example of a Schrödinger cat. To be specific, let us assume that at $t = 0$ we have a coherent superposition of two Gaussian wave packets centered at $x = \pm a$ and having width $\sigma \ll a$, so that the overlap of the two wave packets is negligible. The initial wave function of the Brownian particle then is

$$\varphi(x) \simeq \frac{1}{\sqrt{2}} \left(\frac{1}{\pi\sigma^2} \right)^{1/4} \left(\exp\left[-\frac{(x - a)^2}{2\sigma^2} \right] + \exp\left[-\frac{(x + a)^2}{2\sigma^2} \right] \right). \tag{2.75}$$

The Fourier transform $\tilde{\varphi}(p)$ of (2.75) is readily computed and the momentum probability distribution $|\tilde{\varphi}(p)|^2$ is found to be

$$|\tilde{\varphi}(p)|^2 = \frac{2\sigma}{\hbar\sqrt{\pi}} \exp\left(-\frac{\sigma^2 p^2}{\hbar^2} \right) \cos^2 \frac{pa}{\hbar} \tag{2.76}$$

$|\tilde{\varphi}(p)|^2$ is a Gaussian of width $\sim \hbar/\sigma$ modulated by fast oscillations of period $\pi\hbar/a \ll \hbar/\sigma$. These oscillations originate in the coherence of the two wave packets in (2.75). Before exploiting (2.73), let us give a qualitative physical explanation for decoherence. The Brownian particle undergoes a large number of collisions with the molecules of the thermal bath. Due to these collisions the particle follows a random walk in momentum space[5] with a diffusion coefficient $D = M^2 A$ (1.78), and the momentum dispersion Δp is

$$\Delta p^2 = 2Dt \tag{2.77}$$

Each of the peaks in $|\tilde{\varphi}(p)|^2$ is broadened under the influence of collisions, and the peaks will be completely blurred out after a decoherence time τ_{dec} found from (2.73) as

$$\Delta p^2 \sim \left(\frac{\pi\hbar}{a} \right)^2 = 2D\tau_{\mathrm{dec}},$$

or

$$\tau_{\mathrm{dec}} \sim \frac{\hbar^2}{Da^2} \tag{2.78}$$

Let us derive this result from the master equation (2.73). We limit ourselves to short times, so that the motion of the Brownian particle can be neglected.[6] This is equivalent to taking the limit $M \to \infty$ in the master equation, and in this limit only the last term on the right-hand side survives (see Exercise ?? for a study of the general case). The off-diagonal matrix elements, or coherences, of the statistical operator obey the differential equation

$$\frac{\partial}{\partial t} \langle x|\rho(t)|x' \rangle = -\frac{D}{\hbar^2}(x - x')^2 \langle x|\rho(t)|x' \rangle \tag{2.79}$$

The off-diagonal matrix elements of ρ decay with a relaxation time τ_{dec}:

$$\boxed{\tau_{\mathrm{dec}} \simeq \frac{\hbar^2}{4Da^2}} \tag{2.80}$$

because $|x - x'| \simeq 2a$, in agreement with the preceding heuristic estimate.

Let us give a very rough estimate for a typical decoherence time. Consider a Brownian particle of radius $R \simeq 1\mu$m in air with viscosity $\eta \sim 10^{-5}$. The friction coefficient γ is given by the Stokes law $\gamma = 6\pi\eta R/M$. For $a = 10\mu$m we find $\tau_{\mathrm{dec}} \sim 10^{-27}$ s. 'Large' Schrödinger cats are really quite short-lived! It has been possible to devise experiments in which one is able to build Schrödinger cats small enough that decoherence can be observed and τ_{dec} measured, thus allowing an experimental verification of the decoherence mechanism.

---

[5]Not to be confused with diffusion in position space!

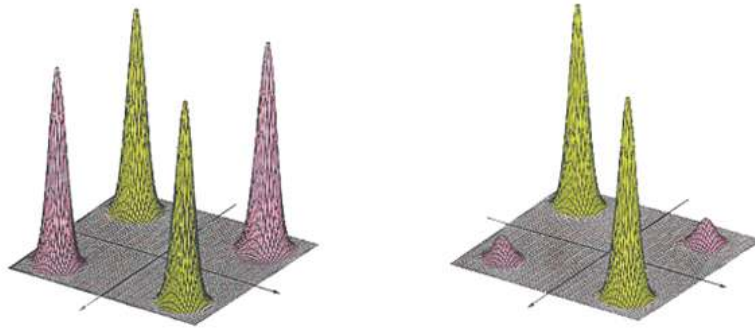[6]This is a general result. In the short-time limit, Brownian motion is dominated by diffusion.

Figure 2.2: Time evolution of the statistical matrix for the superposition (2.75) of two Gaussian wave packets. Figure on the left: $t = 0$. Figure on the right: $t \gg \tau_{\text{dec}}$. After Zurek [1991].

There are other ways of writing the result (2.80). Using $D = M\gamma k_{\text{B}}T$ and introducing the thermal wavelength

$$\lambda_T = \frac{h}{\sqrt{2\pi M k_{\text{B}}T}},$$

that is, the de Broglie wavelength at temperature T, (2.80) becomes

$$\tau_{\text{dec}} \sim \frac{1}{\gamma} \left(\frac{\lambda_T}{a} \right)^2 \tag{2.81}$$

Figure 2.2 shows the evolution of the statistical matrix: at $t = 0$, one observes peaks at $x = \pm a$ and $x' = \pm a'$, but when $\tau \gg \tau_{\text{dec}}$, the peaks at $\{x = a, x' = -a\}$ and at $\{x = -a, x' = a\}$ have disappeared. We are left with an *incoherent* superposition of two wave packets: decoherence has "transformed" a pure state, the coherent superposition (2.75) into an incoherent mixture. The eigenstates of the position operator X do not become entangled with their environment, and they have been called *pointer states*. Interferences with heavy molecules (Figure 2.3) show clearly the decoherence phenomenon. One sees on the upper part of Figure 2.4 that the interference visibility decreases when one increases the pressure of the residual gas. Because of collisions, the coherent superposition of the two wave packets issued from the Young slits is transformed into an incoherent superposition before the molecules hit the screen. Interference is destroyed because which way information is encoded in the environment.
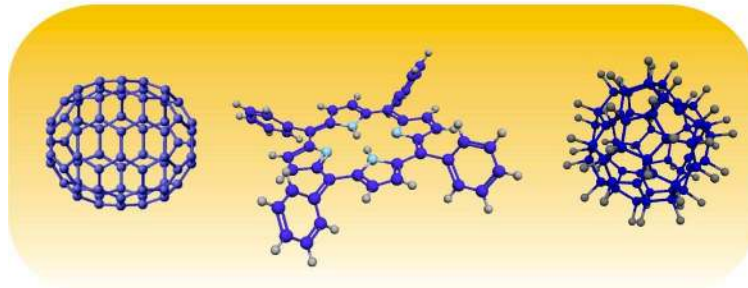

Figure 2.3: Molecules used in interference experiments : (a) C_{70}, (b) $C_{44}H_{30}N_4$, (c) $C_{60}F_{48}$. After Arndt *et. al.* [2005]

The results of the present Chapter are in agreement with the general picture of decoherence. The first general feature is that one finds privileged states in the Hilbert space of states: coherent states in the case
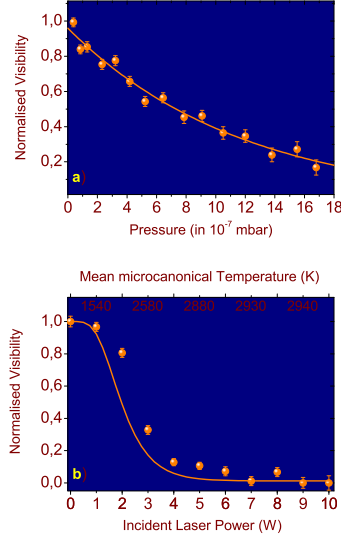
Figure 2.4: Blurring of interferences due to collisions and photon emission. Upper Figure: influence of the pressure. Lower Figure : influence of the temperature. After Arndt *et. al.* [2005].

of Exercise 2.4.4, and position states in that of Brownian motion; these are the pointer states. A generic state of the Hilbert space is not stable when the system is put in contact with an environment but decays into an incoherent superposition of pointer states, which do not become entangled with their environment and are therefore the stable states. The stability of the pointer states can be traced back to the form the system interaction with the environment. For example, the pointer states of the Brownian particle are position states, because the interaction with its environment is proportional to the position operator X, and coherent states are pointer states in the case of Exercise?? because the coupling is proportional to the annihilation operator a. The second general feature is that the decoherence time is inversely proportional to the square of the "distance" between pointer states: this distance is the ordinary one in the case of the position states, and $|z_1 - z_2|$ in the case of the coherent states $|z_1\rangle$ and $|z_2\rangle$ (see Exercise??). The decoherence time is nothing other than the lifetime of Schrödinger cats, and this lifetime is extremely short for macroscopic, and even mesoscopic, objects.

2.4   Exercises

2.4.1   Details of the proof of the master equation

1. Show that if $\rho_{AR}(0) = \rho_A(0) \otimes \rho_R(0)$, then

$$\mathrm{Tr}_{\mathcal{R}}\big[V(t), \rho_{AR}(0\big] = \big[A(t), \rho_A(0)\big]\mathrm{Tr}_{\mathcal{R}}(R(t)\rho_R(0)) = 0.$$

2. Fill in the details of the calculations leading from (2.26) to (2.27) and from (2.28) to (2.29).

2.4.2   Dissipation in a two-level system

1. Starting from (2.49), derive the evolution equation for the matrix elements of the state operator ρ:

$$\begin{aligned}
\frac{\mathrm{d}\rho_{00}}{\mathrm{d}t} &= \big(\Gamma_+\big)\rho_{11} - \big(\Gamma_-\big)\rho_{00}, \\
\frac{\mathrm{d}\rho_{01}}{\mathrm{d}t} &= \mathrm{i}\omega\rho_{01} - \frac{\Gamma}{2}\,\rho_{01}
\end{aligned}$$

Check that the relaxation rate is $\Gamma = \Gamma_+ + \Gamma_-$ for the populations and $\Gamma/2$ for the coherences.

2. Compute the transition rates Γ_+ and Γ_- (2.50) starting from (2.43).

3. From the expressions for Γ_+ and Γ_-, show that at equilibrium the relative populations of the levels $|0\rangle$ and $|1\rangle$ are

$$\mathsf{p}_0 = \frac{\Gamma_-}{\Gamma}, \qquad \mathsf{p}_1 = \frac{\Gamma_+}{\Gamma},$$

and that their ratio is given by Boltzmann's law

$$\frac{\mathsf{p}_1}{\mathsf{p}_0} = \exp\left(-\frac{\hbar\omega_0}{k_\mathrm{B}T}\right).$$

2.4.3 The Fokker–Planck–Kramers equation for a Brownian particle

1. Let $\rho(t)$ be the statistical operator of the Brownian particle of § 2.3.1. Let us define the *Wigner function* $w(x,p;t)$ by

$$w(x,p;t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}py/\hbar} \langle x + \frac{y}{2}|\rho(t)|x - \frac{y}{2}\rangle \mathrm{d}y$$

Show that another expression for $w(x,p;t)$ is

$$w(x,p;t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}xz/\hbar} \langle p + \frac{z}{2}|\rho(t)|x - \frac{z}{2}\rangle \mathrm{d}z$$

Show that integrating the Wigner function over x [p] gives the probability density $w_x(x;t)$ [$w_p(p;t)$].

2. Unlike $w_x(x;t)$ and $w_p(p;t)$, the Wigner function, although real, is not necessarily positive and cannot be interpreted in a straightforward way as a probability distribution in phase space. First, compute the Wigner function for a Gaussian wave packet and check that it is positive in this particular case. Then compute the Wigner function of the superposition (2.75) of two wave packets and check that it is not positive everywhere.

3. Derive from (2.73) the following partial differential equation for $w(x,p;t)$

$$\frac{\partial w}{\partial t} + \frac{p}{M}\frac{\partial w}{\partial x} = \gamma\frac{\partial}{\partial p}[pw] + D\frac{\partial^2 w}{\partial p^2}$$

4. Integrate over x to obtain a Fokker–Planck equation for the probability density $w_p(p;t)$

$$\frac{\partial w_p}{\partial t} = \gamma\frac{\partial}{\partial p}[pw_p] + D\frac{\partial^2 w_p}{\partial p^2}$$

Show that the long-time limit of w_p is a Maxwell distribution and recover the Einstein relation (1.78) between γ and $k_\mathrm{B}T$.

2.4.4 Superposition of coherent states

We wish to study the decoherence of a superposition of two coherent states for a damped quantum oscillator at zero temperature. This is a model for a mode in a cavity coupled to the quantized electromagnetic field. Show from (2.52) that the time evolution of the statistical operator is given at $T = 0$ by

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[H_A, \rho] + \Gamma\left[a\rho a^\dagger - \frac{1}{2}\{a^\dagger a, \rho\}\right]$$

It is instructive to keep the H_A part of the evolution, $H_A = \hbar\omega_0 a^\dagger a$, where ω_0 takes the Lamb shift into account.

1. Let us consider eigenstates $|n\rangle$ of the free Hamiltonian $H_0 = \omega_0 a^\dagger a$, and let ρ_{nm} be the matrix element $\langle n|\rho|m\rangle$ of ρ. Show that the diagonal matrix element ρ_{nn} obeys

$$\frac{d\rho_{nn}}{dt} = -n\Gamma\rho_{nn} + (n+1)\Gamma\rho_{n+1,n+1}$$

Can you give a physical interpretation for the two terms of this equation? Argue that Γ is the rate for spontaneous emission of a photon (or a phonon). What is the evolution equation for the coherence $\rho_{n+1,n}$?

2. Let us introduce the function $C(\lambda, \lambda^*; t)$ by

$$C(\lambda, \lambda^*; t) = \text{Tr}\left(\rho\, e^{\lambda a^\dagger} e^{-\lambda^* a}\right).$$

Show that partial derivatives with respect to λ have the following effect in the trace

$$\frac{\partial}{\partial\lambda} \to \rho\, a^\dagger, \qquad \left(\frac{\partial}{\partial\lambda} - \lambda^*\right) \to a^\dagger\rho$$

Hint: use a standard the identity to commute $\exp(\lambda a^\dagger)$ and $\exp(-\lambda^* a)$. What are the corresponding identities for $\partial/\partial\lambda^*$?

3. Show that $C(\lambda, \lambda^*; t)$ obeys the partial differential equation

$$\left[\frac{\partial}{\partial t} + \left(\frac{\Gamma}{2} - i\omega_0\right)\frac{\partial}{\partial\ln\lambda} + \left(\frac{\Gamma}{2} + i\omega_0\right)\frac{\partial}{\partial\ln\lambda^*}\right] C(\lambda, \lambda^*; t) = 0$$

This equation is solved by the method of characteristics. The solution is (derive it or check it!)

$$C(\lambda, \lambda^*; t) = C_0\left(\lambda \exp[-(\Gamma/2 - i\omega_0)t], \lambda^* \exp[-(\Gamma/2 + i\omega_0)t]\right)$$

with

$$C(\lambda, \lambda^*; t = 0) = C_0(\lambda, \lambda^*).$$

4. Assume that the initial state $t = 0$ is a coherent state $|z\rangle$:

$$|z\rangle = e^{-|z|^2/2} e^{za^\dagger} |0\rangle .$$

Show that in this case

$$C_0 = \exp(\lambda z^* - \lambda^* z),$$

and that the state at time t is the coherent state $|z(t)\rangle$ with

$$z(t) = z\, e^{-i\omega_0 t} e^{-\Gamma t/2}.$$

Therefore, a coherent state remains a coherent state when $\Gamma \neq 0$, but $|z(t)| \to 0$ for $t \gg 1/\Gamma$. In the complex plane, $z(t)$ spirals to the origin. As $\Gamma \ll \omega_0$, one observes many turns around the origin.

5. Let us now consider a superposition of two coherent states at $t = 0$:

$$|\Phi\rangle = c_1|z_1\rangle + c_2|z_2\rangle$$

Show that at $t = 0$

$$C_{12}(t = 0) = \text{Tr}\left(|z_1\rangle\langle z_2| e^{\lambda a^\dagger} e^{-\lambda^* a}\right) = \langle z_2|z_1\rangle e^{\lambda z_2^*} e^{-\lambda^* z_1}$$

What is the interpretation of $C_{12}(t)$? Let us define

$$\eta(t) = \frac{\langle z_2|z_1\rangle}{\langle z_2(t)|z_1(t)\rangle}$$

and write $C_{12}(t)$ in the form

$$C_{12}(t) = \eta(t)\langle z_2(t)|z_1(t)\rangle \, e^{\lambda z_2^*(t)} \, e^{-\lambda^* z_1(t)}$$

Show that

$$|\eta(t)| = \exp\left[-\frac{1}{2}|z_1 - z_2|^2 \left(1 - e^{-\gamma t}\right)\right] \simeq \exp\left[-\frac{\Gamma}{2}|z_1 - z_2|^2\right]$$

where the last expression holds for $\Gamma t \ll 1$. The decoherence time is therefore

$$\tau_{\text{dec}} = \frac{2}{\Gamma |z_1 - z_2|^2}$$

6. Let us choose $z_1 = 0$ (ground state of the oscillator) and $z_2 = z$. From question **1**, the average time for the emission of *one* photon is $\sim (\Gamma |z_2|^2)^{-1}$. Argue that taking the trace over the environment (here the radiation field) shows that the coherence between the components $z_1 = 0$ and z of $|\Psi\rangle$ will be lost after the spontaneous emission of a single photon.

2.5 Further reading

Further information on quantum master equations may be found in Preskill [1999], Cohen-Tannoudji *et al.* [1992], Chapter IV, Dalibard [2003] (in French), Breuer and Petruccione [2002], chapters 3 and 4, Zwanzig [2001], chapter 6, or Le Bellac [2006], chapter 15. The model studied in Section 2.3 was made popular in the article Caldeira-Leggett [1983]. For references on this model at finite temperature, see Zurek [2003].

Chapter 3

The Gallavotti-Cohen fluctuation theorem

As we have seen in Chapter 1, microscopic reversibility implies in a system at equilibrium the fundamental property of detailed balance: any process and its time reversed occur equally frequently. This gives rise to important relations for irreversible processes, for example the symmetry of the Onsager coefficients. Over the past decade, remarkable equalities have been obtained for systems arbitrarily far from equilibrium between direct and time reversed processes, and these equalities have allowed us to extend the relation between fluctuation and dissipation beyond the linear regime. The generalized fluctuation-dissipation theorem follows from the Gallavotti-Cohen fluctuation theorem, which I shall establish in Section 2. In this Chapter, only classical dynamics will be considered, because, to the best of my knowledge, the extension to quantum mechanics is still unclear.

3.1 Crooks and Jarzynski equalities

3.1.1 Derivation of the equalities

Consider a *thermally isolated* system at $t = 0$ in microcanonical equilibrium. The Hamiltonian depends on dynamical variables $x(t')$ and on a control parameter $\lambda(t')$, which varies in a time interval $0 \leq t' \leq t$. The dynamical variables obey a deterministic law between their initial $x_i = x(t' = 0)$ and final values $x_f = x(t' = t)$

$$\lambda(t') \; : \; x_i \to x_f \tag{3.1}$$

During this evolution, the system receives a work W from the outside (there is no heat exchange since the system is assumed to be thermally isolated)

$$H_f(x_f) - H_i(x_i) = W \tag{3.2}$$

The work W is a random variable, because we sample over the initial value x_i by taking the microcanonical average with energy shell E in the initial state. Among the x_is, we keep only those which obey (3.2), so that the probability $P_E(W)$ of observing W is

$$P_E(W) = \frac{\int \mathrm{d}x_i \, \delta(H_i(x_i) - E) \, \delta(W - H_f(x_f) + H_i(x_i))}{\Omega_i(E)} \tag{3.3}$$

where $\Omega_i(E)$ is the initial phase space volume

$$\Omega_i(E) = \int \mathrm{d}x_i \, \delta(H_i(x_i) - E) \tag{3.4}$$

so that $P(W)$ is properly normalized

$$\int_{-\infty}^{+\infty} \mathrm{d}W \, P_E(W) = 1$$

Consider now the time reversed process. An initial point $\overline{x}_f$ will evolve into a final point $\overline{x}_i$, and the average is now on the energy shell

$$H_f(\overline{x}_f) = E + W$$

The probability distribution $\overline{P}_{E+W}(-W)$ is

$$\overline{P}_{E+W}(-W) = \frac{\int \mathrm{d}\overline{x}_f \, \delta(H_f(\overline{x}_f) - E - W) \, \delta(H_f(\overline{x}_f) - H_i(\overline{x}_i) - W)}{\Omega_f(E+W)} \tag{3.5}$$

Since the evolution is Hamiltonian, Liouville's theorem tells us that $\mathrm{d}\overline{x}_f = \mathrm{d}x_i$, so that

$$\boxed{\frac{P_E(W)}{\overline{P}_{E+W}(-W)} = \frac{\Omega_f(E+W)}{\Omega_i(E)} = \mathrm{e}^{[S_f(E+W) - S_i(E)]/k_B}} \tag{3.6}$$

where S is the microcanonical entropy. Equation (3.6) is the fundamental relation of the present Section, from which other identities follow by taking the thermodynamic limit $E \to \infty$, $W/E \to 0$. In this limit, the probabilities converge to functions $P(W)$ and $\overline{P}(-W)$ which are independent of E, while the initial and final microcanonical temperatures $\partial E/\partial S$ are the same. Since $\Delta E = W$, the change in free energy F is

$$\Delta F = W - T[S_f(E+W) - S_i(E)]$$

so that

$$T[S_f(E+W) - S_i(E)] = W - \Delta F$$

There is another way of writing the entropy difference

$$T[S_f(E+W) - S_i(E)] = T[S_f(E) - S_i(E)] + W = -W_{\mathrm{rev}} = -\text{``}\Delta F\text{''}$$

where W_{rev} is the reversible work when going from $i \to f$ at constant energy, and in the last equality, we use the maximum work theorem. We thus get Crooks relation

$$\frac{P(W)}{\overline{P}(-W)} = \mathrm{e}^{\Delta S/k_B} = \mathrm{e}^{\beta(W - \Delta F)} \tag{3.7}$$

where $\Delta F = W - T\Delta S$ is the free energy. Taking an average over W gives the Jarzynski equality

$$\left\langle \mathrm{e}^{-\beta W} \right\rangle = \mathrm{e}^{-\beta \Delta F} \tag{3.8}$$

Finally, if the process lasts a long time, we can write $\Delta S = t\sigma$, where σ is the entropy production rate in a stationary non equilibrium regime, while $W = \Delta F + T\Delta S = Tt\sigma$. Then we get a particular case of the fluctuation theorem (see (3.40))

$$\frac{P(\sigma)}{\overline{P}(-\sigma)} = \mathrm{e}^{t\sigma/k_B} \tag{3.9}$$

3.1.2   An example

Let illustrate these considerations on an example. We us assume that we drag at a fixed speed V a convex two-dimensional object with total circumference $\mathcal{S}$ in a two-dimensional fluid, under the hypothesis that the mean free path of the object is much larger than its dimensions. The object is characterized by a form factor $F(\theta)$, where θ is the inclination of the impact point: $\mathcal{S}F(\theta)\mathrm{d}\theta$ is the length of the surface with inclination θ with respect to the x axis. When a molecule of the fluid hits the object, the energy which is transferred to it is

$$\Delta W = -2mV \sin^2 \theta (v_x - V - v_y \cot \theta)$$

ΔW is a random variable through its dependence on the velocity of the incident molecule and the inclination θ of the impact point. By averaging over the Maxwell distribution of the velocity of the molecules and by integrating over θ, it is possible to compute the probability distribution $P(W)$. The
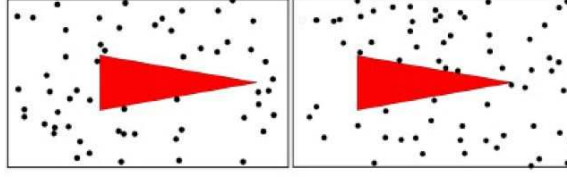
Figure 3.1: Dragging a triangle in a two-dimensional gas. After Cleuren *et al.* [2006].

calculation is tedious, but there are no difficulties of principle: all that is used is energy and momentum conservation. Defining the dimensionless quantities

$$w = \frac{W}{k_{\mathrm{B}}T} \qquad v = V\left(\frac{m}{2k_{\mathrm{B}}T}\right)^{1/2} \qquad \tau = \frac{\mathcal{S}\rho t}{(2m/k_{\mathrm{B}}T)^{1/2}} \tag{3.10}$$

where $\mathcal{S}$ is the circumference of the object and ρ the fluid density, one computes the generating function $G(q)$ of the cumulants of $P(w,\tau)$

$$
\begin{aligned}
G(q,\tau) = \ln\left[\int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}qw}\, P(w,\tau)\mathrm{d}w\right] = \tau \int_0^{2\pi} \mathrm{d}\theta\, F(\theta)v\sin\theta\Big\{\left(\mathrm{erf}[(1-2\mathrm{i}q)v\sin\theta]+1\right) \\
\times\, (1-2\mathrm{i}q)\mathrm{e}^{-4q(\mathrm{i}+q)v^2\sin^2\theta} - 1 - \mathrm{erf}(v\sin\theta)\Big\}
\end{aligned}
\tag{3.11}
$$

Because the reversible work in this problem is clearly zero, the Crooks relation in reduced units reads $P(w) = \exp(\beta w)\overline{p}(-w)$, which follows from

$$\overline{G}(-q-\mathrm{i}) = G(q) \tag{3.12}$$

Indeed we have

$$\overline{G}(-q-\mathrm{i}) - G(q) = -2\tau v \int_0^{2\pi} F(\theta)\sin\theta\mathrm{d}\theta = 0$$

The work distribution is invariant for symmetric objects, because, under velocity inversion, $V \to -V$,

$$F(\theta) = F(2\pi - \theta)$$

Numerical calculations have been performed with a non symmetrical object, a triangle which is dragged in the fluid (Figure 3.1). In this context where $\Delta F = 0$, we have $P(w) = \exp(w)\overline{P}(-w)$, a relation which is very well verified in numerical simulations (Figure 3.2).

3.2 The fluctuation theorem

3.2.1 Markovian dynamics

In order to prove the fluctuation theorem, we start from the master equation (1.106) for $P_t(C)$ or its matrix form (1.109), written for configurations C of the system

$$
\begin{aligned}
\frac{\mathrm{d}P_t(C)}{\mathrm{d}t} &= \sum_{C'}\left[W(C,C')P_t(C') - W(C',C)P_t(C)\right] & (3.13)\\
&= \sum_{C'}\mathcal{W}(C,C')P_t(C') & (3.14)
\end{aligned}
$$

We recall the property of detailed balance, which will play a decisive role in what follows

$$W(C_i,C_j)P_{\mathrm{eq}}(C_j) = W(C_j,C_i)P_{\mathrm{eq}}(C_i) \tag{3.15}$$
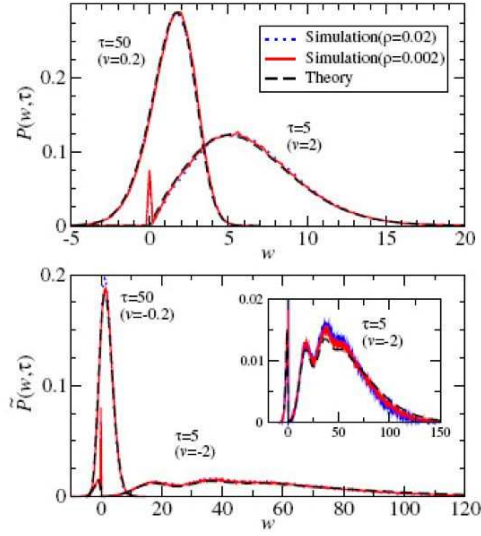
Figure 3.2: The functions $P(w, \tau)$ and $\overline{P}(-w, \tau)$. After Cleuren *et al.* [2006].

then the probability of a trajectory and that of that of its time reversed are identical (Exercise 3.4.1)

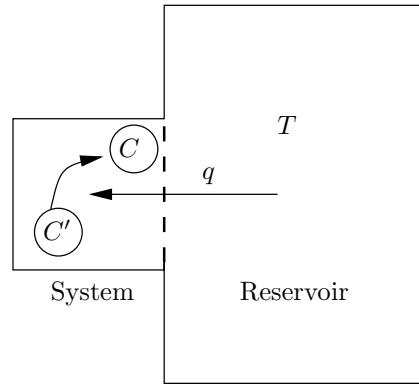$$P(C_k, \cdots, C_1; t_k, \cdots, t_1) = \overline{P}(C_1, \cdots, C_k; t_1, \cdots, t_k) \tag{3.16}$$

Figure 3.3: A system in contact with a heat bath at temperature T.

Let us put our system into contact with a heat bath at temperature T (Figure 3.3), and let $W_q(C, C')$ be the probability per unit time for the transition $C' \to C$, when this transition is accompanied by a heat transfer $q = E(C) - E(C')$ to the system. In other words, the heat bath *delivers* an amount of heat q, where q can be positive or negative. Let $P_t(C, Q)$ be the probability of finding the system at time t in configuration C, given that a total amount of heat Q has been transferred from the heat bath to the system during the time interval $[0, t]$. The heat transfer per unit of time is thus Q/t. W_q and $P_t(C, Q)$ obey the constraints

$$W(C, C') = \sum_q W_q(C, C') \qquad \sum_Q P_t(C, Q) = P_t(C) \tag{3.17}$$

We may write a master equation for $P_t(C, Q)$, which gives a more detailed description of the dynamics

than (3.13)

$$\frac{\mathrm{d}P_t(C,Q)}{\mathrm{d}t} = \sum_q \sum_{C'} \left[W_q(C,C')P_t(C',Q-q) + \delta_{CC'}\mathcal{W}_q(C,C)P_t(C',Q) \right] \qquad (3.18)$$

where

$$\mathcal{W}_q(C,C) = -\sum_{C'} W_q(C',C)$$

and by convention $W_q(C,C) = 0$. It is easily checked (exercise 3.2) that summing over Q gives back the original equation (3.13). Let us now introduce the generating function

$$F_t(C,\lambda) = \sum_Q \mathrm{e}^{\lambda Q}\, P_t(C,Q) \qquad (3.19)$$

and note that, with $Q' = Q - q$

$$\sum_{q,Q} \mathrm{e}^{\lambda Q}\, P_t(C',Q-q) = \sum_q \mathrm{e}^{\lambda q} \sum_{Q'} \mathrm{e}^{\lambda Q'}\, P_t(C',Q') = \sum_q \mathrm{e}^{\lambda q}\, F_t(C',\lambda)$$

It follows that $F_t(C,\lambda)$ obeys a differential equation

$$\frac{\mathrm{d}F_t(C,\lambda)}{\mathrm{d}t} = \sum_q \left[\sum_{C'} \mathrm{e}^{\lambda q} W_q(C,C') + \delta_{CC'}\mathcal{W}_q(C,C) \right] F_t(C',\lambda) \qquad (3.20)$$

Once more, it is convenient to rewrite this equation in matrix form

$$\frac{\mathrm{d}F_t(C,\lambda)}{\mathrm{d}t} \;=\; \sum_{C'} \mathcal{W}_\lambda(C,C')F_t(C',\lambda) \qquad (3.21)$$

$$\mathcal{W}_\lambda(C,C') \;=\; \sum_q \left[\sum_{C'} \mathrm{e}^{\lambda q}\, W_q(C,C') + \delta_{CC'}\mathcal{W}_q(C,C) \right] \qquad (3.22)$$

Note that

$$\left\langle \mathrm{e}^{\lambda Q} \right\rangle = \sum_{C,Q} P_t(C,Q)\mathrm{e}^{\lambda Q} = \sum_C F_t(C,\lambda)$$

Let $v(C,\lambda)$ be a right eigenvector of $\mathcal{W}_\lambda$ with eigenvalue $f(\lambda)$

$$\sum_{C'} \mathcal{W}_\lambda(C,C')v(C',\lambda) = f(\lambda)v(C,\lambda) \qquad (3.23)$$

then, for long times, the asymptotic behavior of $\langle\exp(\lambda Q)\rangle$ will be controlled by the largest eigenvalue $f(\lambda)$ which we denote by $g(\lambda)$

$$\boxed{ t \to \infty \;:\; \left\langle \mathrm{e}^{\lambda Q} \right\rangle \simeq \mathrm{e}^{tg(\lambda)} } \qquad (3.24)$$

Then we observe that $\ln\langle\exp(\lambda Q)\rangle$ is nothing other than the generating function of the cumulants of Q

$$\frac{1}{t}\langle Q \rangle \;=\; \left.\frac{\mathrm{d}g}{\mathrm{d}\lambda}\right|_{\lambda=0} \qquad (3.25)$$

$$\frac{1}{t}\langle Q^2 \rangle_c \;=\; \frac{1}{t}\left(\langle Q^2 \rangle - \langle Q \rangle^2 \right) = \left.\frac{\mathrm{d}^2 g}{\mathrm{d}\lambda^2}\right|_{\lambda=0} \qquad (3.26)$$

and so on. Of course, we expect that $\langle Q \rangle/t = 0$, because for long times the system is in equilibrium with the heat bath. However, we also expect fluctuations, $\langle Q^2 \rangle_c \neq 0$. Finally we note that $g(0) = 0$, because $F_t(C,\lambda = 0) = P_t(C)$ and $P_{\mathrm{eq}}(C)$ is a right eigenvector of $\mathcal{W}_{\lambda=0}$ with eigenvalue zero.

3.2.2   The fluctuation theorem

Let us first remark that we can generalize the detailed balance relation (3.15) as follows

$$W_q(C, C')P_{\text{eq}}(C') = W_{-q}(C', C)P_{\text{eq}}(C) \tag{3.27}$$

Indeed, under time reversal, a heat exchange $+q$ between the heat bath and the system is changed into a heat exchange $-q$, and (3.27) ensures that the probability of a trajectory is the same as that of its time reversed one (Exercise ??)

$$P(C_1, \cdots, C_k; t_1, \cdots, t_k; q_1, \cdots, q_{k-1}) = \overline{P}(C_k, \cdots, C_1; t_k, \cdots, t_1; -q_{k-1}, \cdots, -q_1)$$

Equation (3.27) in the form

$$W_q(C, C') = W_{-q}(C', C)\frac{P_{\text{eq}}(C)}{P_{\text{eq}}(C')} \tag{3.28}$$

allows us to rewrite the eigenvalue equation (3.23) as

$$g(\lambda)v(C, \lambda) = \sum_q \sum_{C'} \left[e^{\lambda q}W_{-q}(C', C)\frac{P_{\text{eq}}(C)}{P_{\text{eq}}(C')} + \delta_{CC'}\mathcal{W}_q(C, C) \right] v(C', \lambda) \tag{3.29}$$

Changing q into $-q$ in the summation allows us to see that $v(C, \lambda)/P_{\text{eq}}(C)$ is a left eigenvector of $\mathcal{W}_{-\lambda}$ with eigenvalue $g(\lambda)$, which is thus an eigenvalue of both $\mathcal{W}_\lambda$ and $\mathcal{W}_{-\lambda}$. This implies

$$\boxed{g(\lambda) = g(-\lambda)} \tag{3.30}$$

In other words, g is an *even* function of λ, and $g(0) = g'(0) = 0$. The physical interpretation of $g'(0) = 0$ is clear: in equilibrium, the probability of a heat transfer Q between the system and the heat bath is the same as that of a heat transfer $-Q$, and we have $\langle Q \rangle = 0$.
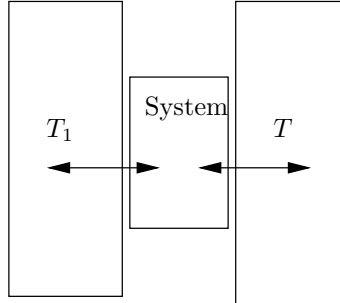

Figure 3.4: A system in contact with two heat baths at temperatures T and T_1.

The coupling to a single heat bath does not teach us a lot, but the situation becomes much more interesting when we couple the system to two heat baths at different temperatures T and T_1, with, for example, $T_1 > T$, so that there is heat transfer between the two baths (Figure 3.4): this leads to a stationary non equilibrium situation, in which $\langle Q \rangle / t \neq 0$. Note that in this case $q \neq E(C) - E(C')$, because a change in internal energy can be due to energy exchange with any of the two heat baths, but (3.27), and thus (3.30), do not depend on this assumption. In order to study this situation, we need a further generalization of detailed balance

$$\exp\left[\frac{q}{k_{\text{B}}T_1} - \frac{q}{k_{\text{B}}T}\right] W_q(C, C')P_{\text{eq}}(C') = W_{-q}(C', C)P_{\text{eq}}(C) \tag{3.31}$$

where $P_{\text{eq}}(C)$

$$P_{\text{eq}}(C) = \frac{1}{Z}\, e^{-E(C)/k_{\text{B}}T} \qquad Z = \sum_C e^{-E(C)/k_{\text{B}}T}$$

is the equilibrium distribution at temperature T, so that (3.31) reduces to (3.27) if $T_1 = T$. To justify (3.31), let us assume that the thermal contact between the system and the heat bath at temperature T has been switched off. Then, taking into account that we may now identify $q = E(C) - E(C')$, we get

$$\mathrm{e}^{[E(C) - E(C')][1/k_\mathrm{B}T_1 - 1/k_\mathrm{B}T]} W_q(C, C') \, \mathrm{e}^{-E(C')/k_\mathrm{B}T} = W_{-q}(C', C) \, \mathrm{e}^{-E(C)/k_\mathrm{B}T}$$

and this equation is nothing other than detailed balance at T_1

$$W_q(C, C') \, \mathrm{e}^{-E(C')/k_\mathrm{B}T_1} = W_{-q}(C', C) \, \mathrm{e}^{-E(C)/k_\mathrm{B}T_1}$$

We may then write the eigenvalue equation as

$$g(\lambda)v(C, \lambda) = \sum_q \sum_{C'} \left\{ \exp\left[\lambda q + \frac{q}{k_\mathrm{B}T} - \frac{q}{k_\mathrm{B}T_1}\right] W_{-q}(C', C) \frac{P_\mathrm{eq}(C)}{P_\mathrm{eq}(C')} + \delta_{CC'} \mathcal{W}_q(C, C) \right\} v(C', \lambda) \quad (3.32)$$

Changing q into $-q$ in the first term of the curly bracket, we see that $v(C, \lambda)/P_\mathrm{eq}(C)$ is a left eigenvector of the matrix

$$\mathcal{W}_{\left[\frac{1}{k_\mathrm{B}T_1} - \frac{1}{k_\mathrm{B}T} - \lambda\right]}$$

so that we obtain the symmetry relation first proved by Gallavotti and Cohen using chaotic dynamical systems, which is called the *Gallavotti-Cohen fluctuation theorem*

$$\boxed{g(\lambda) = g\left(\frac{1}{k_\mathrm{B}T_1} - \frac{1}{k_\mathrm{B}T} - \lambda\right)} \quad (3.33)$$

Let us recall the assumptions we have used to derive this theorem.

1. The dynamics is described by a master equation.

2. Detailed balance holds for transition probabilities.

3.2.3 The function of large deviations

In a stationary regime, $\langle Q \rangle / t = \overline{q}$ and the entropy variation per unit of time is given by standard thermodynamics

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \overline{q}\left(\frac{1}{T} - \frac{1}{T_1}\right) \quad (3.34)$$

We may now ask the following question: what is the probability of observing over a long period of time a heat transfer $q \neq \overline{q}$? This probability is given by the *function of large deviations* $F(q)$ defined by

$$P\left(\frac{Q}{t} = q\right) \simeq \mathrm{e}^{tF(q)} \quad (3.35)$$

where $F(q)$ can be computed from $g(\lambda)$. Indeed, we may write

$$\mathrm{e}^{tg(\lambda)} \simeq \langle \mathrm{e}^{\lambda Q} \rangle = \int \mathrm{d}q \, \mathrm{e}^{\lambda q t} \, P\left(\frac{Q}{t} = q\right) \simeq \mathrm{e}^{t \, \mathrm{Max}|_q [F(q)] + \lambda q]} \quad (3.36)$$

where we have evaluated the integral with a saddle point method. Then the relation between $g(\lambda)$ and $F(q)$ is

$$g(\lambda) = \mathrm{Max}|_q [F(q) + \lambda q] \implies F'(q) = -\lambda \quad (3.37)$$

In other words, $g(\lambda)$ is the Legendre transform of $F(q)$, which means that $F(q)$ is also the Legendre transform of $g(\lambda)$, with $q = g'(\lambda)$

$$F(q) = \mathrm{Max}|_\lambda [g(\lambda) - \lambda q] \implies g'(\lambda) = q \quad (3.38)$$

that is

$$F(q) = [g(\lambda) - \lambda q]\Big|_{q=g'(\lambda)}$$

As a check of the calculation, let us retrieve (3.37)

$$F'(q) = g'(\lambda)\frac{\mathrm{d}\lambda}{\mathrm{d}q} - q\frac{\mathrm{d}\lambda}{\mathrm{d}q} - \lambda = -\lambda$$

Let us write the fluctuation theorem (3.33) as $g(\lambda) = g(a-\lambda)$, $a = [1/k_\mathrm{B}T_1 - 1/k_\mathrm{B}T]$. To a heat transfer q corresponds a value λ_1 of λ, $q = g'(\lambda_1)$, but given that $g'(\lambda) = -g'(a-\lambda)$, we have

$$q = g'(\lambda_1) \qquad -q = g'(a - \lambda_1)$$

This relation and (3.38) allows us to compute $[F(q) - F(-q)]$

$$F(q) - F(-q) = [g(\lambda_1) - \lambda_1 q] - [g(a - \lambda_1) + (a - \lambda_1)q] = -aq$$

Thus the difference $[F(q) - F(-q)]$ is *linear* in q

$$\boxed{F(q) - F(-q) = q\left[\frac{1}{k_\mathrm{B}T} - \frac{1}{k_\mathrm{B}T_1}\right]} \tag{3.39}$$

a result far from obvious as $F(q)$ is *a priori* a complicated function of q. Coming back to (3.34) and (3.35) and using (3.39), we see that

$$\frac{P\left(\frac{Q}{t} = -\overline{q}\right)}{P\left(\frac{Q}{t} = \overline{q}\right)} \simeq \exp\left[-Q\left(\frac{1}{k_\mathrm{B}T} - \frac{1}{k_\mathrm{B}T_1}\right)\right] = \exp\left[-\frac{\Delta S}{k_\mathrm{B}}\right] \tag{3.40}$$

which is exponentially small when $t \to \infty$. It can be said that (3.40) measures the violations of the second law. However, it is not easy to check experimentally, because it is difficult to observe heat exchanges in the "wrong" direction over large time intervals.

It is possible to check analytically (3.40) on a simple example, that of a Brownian particle with mass $M = 1$ coupled to two heat baths at different temperatures. The generalization of (1.73) is then

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -(\gamma + \gamma_1)V + f(t) + f_1(t) \tag{3.41}$$

with

$$\overline{f(t)f(t')} = 2\gamma k_\mathrm{B}T\delta(t - t') = 2A\delta(t - t')$$
$$\overline{f_1(t)f_1(t')} = 2\gamma_1 k_\mathrm{B}T_1\delta(t - t') = 2A_1\delta(t - t') \tag{3.42}$$

while $f(t)$ and $f_1(t)$ are uncorrelated: $\overline{f(t)f_1(t')} = 0$. Since the force due to the heat bath at temperature T is $f(t) - \gamma V$, the energy which is transferred form this bath to the particle is

$$Q = \int_0^t \mathrm{d}t'\, V(t')[-\gamma V(t') + f(t')]$$

and a similar expression for the bath at temperature T_1. The function $g(\lambda)$ can be explicitly computed (Exercise 3.4.2)

$$g(\lambda) = \frac{1}{2}\left[\gamma + \gamma_1 - (\gamma^2 + \gamma_1^2 + 2\gamma\gamma_1(1 - 2\lambda k_\mathrm{B}T + 2\lambda k_\mathrm{B}T_1 - 2\lambda^2 k_\mathrm{B}^2 TT_1)^{1/2}\right] \tag{3.43}$$

which obeys (3.33). If $T = T_1$, $g(\lambda) = g(-\lambda)$, as it should. The heat transfer from the heat bath at T_1 to that at T is

$$\frac{\langle Q \rangle}{t} = \frac{\gamma\gamma_1 k_\mathrm{B}(T_1 - T)}{\gamma + \gamma_1} \tag{3.44}$$

while, if $T = T_1$, the fluctuation of Q is

$$\frac{\langle Q^2 \rangle_c}{t} = \frac{2k_\mathrm{B}T^2\gamma\gamma_1}{\gamma + \gamma_1} \tag{3.45}$$

3.3 Applications of the fluctuation theorem

3.3.1 The fluctuation-dissipation theorem

Using $g(0) = g'(0) = 0$, we may write a Taylor expansion of $g(\lambda)$ in powers of λ and of the small parameter $\theta = (T_1 - T)$

$$g(\lambda) \simeq A(T)\lambda\theta + B(T)\lambda^2 \tag{3.46}$$

There is one further condition on $g(\lambda)$, that is, it must obey (3.33); since θ is small

$$\frac{1}{k_B T_1} - \frac{1}{k_B T} = \frac{T - T_1}{k_B T T_1} \simeq -\frac{\theta}{k_B T^2} = -c\theta$$

We then have

$$A(-c\theta - \lambda)\theta + B(c\theta + \lambda)^2 = A\lambda\theta + B\lambda^2$$

which is verified provided $A = cB$, or

$$\boxed{B(T) = k_B T^2 A(T)} \tag{3.47}$$

This a fluctuation-dissipation theorem, because $A(T)$ is a thermal conductivity

$$\frac{\langle Q \rangle}{t} = \left.\frac{dg}{d\lambda}\right|_{\lambda=0} = A(T)(T_1 - T) + O(T_1 - T)^2 \tag{3.48}$$

while $B(T)$ is an equilibrium fluctuation at $T = T_1$

$$\frac{\langle Q^2 \rangle_c}{t} = \left.\frac{d^2 g}{d\lambda^2}\right|_{\lambda=0} = 2B(T) \tag{3.49}$$

By using (3.46), we have limited ourselves to a linear approximation. However, the theory goes clearly beyond this approximation, but whether the non linear terms are useful in practice is another question!

3.3.2 Onsager's symmetry relations

Everything that has been done with heat reservoirs can be repeated with particle reservoirs. Let us assume that there are two reservoirs of particles $\mathcal{R}$ and $\mathcal{R}_1$ with chemical potentials μ and μ_1. By analogy with (3.33) we get

$$g(\lambda) = g\left(\frac{\mu - \mu_1}{k_B T} - \lambda\right) \tag{3.50}$$

Let us consider a change of configuration $C \to C'$, accompanied by a transfer of n_1 particles from $\mathcal{R}_1$ and n_2 particles from $\mathcal{R}_2$. Detailed balance implies

$$e^{n_1(\mu - \mu_1)/k_B T} e^{n_2(\mu - \mu_2)/k_B T} W_{n_1,n_2}(C, C') P_{eq}(C') = W_{-n_1,-n_2}(C', C) P_{eq}(C) \tag{3.51}$$

The generalization of (3.24) is

$$\left\langle e^{\lambda_1 N_1 + \lambda_2 N_2} \right\rangle \simeq e^{tg(\lambda_1, \lambda_2)} \tag{3.52}$$

where, from (3.33)

$$g(\lambda_1, \lambda_2) = g\left(\frac{\mu - \mu_1}{k_B T} - \lambda_1, \frac{\mu - \mu_2}{k_B T} - \lambda_2\right) \tag{3.53}$$

The second order Taylor expansion of $g(\lambda_1, \lambda_2)$ which obeys (3.53) is (Exercise 3.4.3)

$$g(\lambda_1, \lambda_2) = a_1(\mu - \mu_1)\lambda_1 + b_1[(\mu - \mu_1)\lambda_2 + (\mu - \mu_2)\lambda_1] + c_1(\mu - \mu_2)\lambda_2 - a_1\lambda_1^2 - c_1\lambda_2^2 - 2b\lambda_1\lambda_2 \tag{3.54}$$

and the particle fluxes are given by

$$\frac{\langle N_1 \rangle}{t} = \left.\frac{\partial g}{\partial \lambda_1}\right|_{\lambda_1=\lambda_2=0} = a_1(\mu - \mu_1) + b_1(\mu - \mu_2) = M_{11}(\mu - \mu_1) + M_{12}(\mu - \mu_2)$$

$$\frac{\langle N_2 \rangle}{t} = \left.\frac{\partial g}{\partial \lambda_2}\right|_{\lambda_1=\lambda_2=0} = b_1(\mu - \mu_1) + c_1(\mu - \mu_2) = M_{21}(\mu - \mu_1) + M_{22}(\mu - \mu_2) \tag{3.55}$$

Onsager's symmetry relation in this case is $M_{12} = M_{21} = b_1$. It would also be easy to prove symmetry relations in the case of coupled heat and particle fluxes.

Once more, it is clear that the Onsager relations can be extended beyond linear regime, and once more, whether this extension is useful in practice is still an open question.

3.4 Exercises

3.4.1 Trajectories and time reversed trajectories

3. Use (3.27) to prove detailed balance when $C \to C'$ is accompanied by a heat transfer q from one of the heat baths.

3.4.2 Langevin equation with two heat baths

1. Using the notations of § 3.2.3, define

$$
\begin{aligned}
F(t) &= \frac{1}{\varepsilon} \int_t^{t+\varepsilon} f(t')\mathrm{d}t' \\
F_1(t) &= \frac{1}{\varepsilon} \int_t^{t+\varepsilon} f_1(t')\mathrm{d}t'
\end{aligned}
$$

What are the variances

$$
\langle F^2 \rangle \qquad \langle F_1^2 \rangle \qquad \langle FF_1 \rangle?
$$

2. Derive the following expressions for the variation of the velocity $(V \to v)$

$$
v(t+\varepsilon) - v(t) = (F + F_1)\varepsilon - (\gamma + \gamma_1)v(t)\varepsilon
$$

and for the heat transfer from the bath at temperature T_1

$$
Q(t+\varepsilon) - Q(t) = F_1 v(t)\varepsilon - \gamma_1 v^2(t)\varepsilon + \frac{1}{2}\left(FF_1 + F_1^2\right)\varepsilon^2
$$

Why must one keep terms of order ε^2?

3. Introduce the generating function

$$
G_t(\alpha, \lambda) = \left\langle e^{\alpha v^2(t) + \lambda Q(t)} \right\rangle
$$

Compute $G_{t+\varepsilon}(\alpha, \lambda)$, taking care carefully of terms of order ε^2. Averaging over the random forces (beware that one should average the exponential, not the exponent!), show that

$$
G_{t+\varepsilon}(\alpha, \lambda) = G_t(\alpha, \lambda)\left[1 + \varepsilon(2\alpha(A + A_1) + \lambda A_1) + v^2\varepsilon(-2\alpha(\gamma + \gamma_1) - \lambda\gamma_1 + 4\alpha^2(A + A_1) + \lambda^2 A_1 + 4\lambda\alpha A_1)\right]
$$

This function depends on v^2. Show that if the coefficient of v^2 vanishes

$$
G_{t+\varepsilon}(\alpha, \lambda) = G_t(\alpha, \lambda)(1 + \varepsilon(2\alpha(A + A_1) + \lambda A_1))
$$

Then α is solution of the second order equation

$$
4\alpha^2(A + A_1) + 2\alpha[2\lambda A_1 - 2(\gamma + \gamma_1)] + \lambda^2 A_1 - \lambda\gamma_1 = 0
$$

4. For $t \to \infty$

$$
G_t(\alpha, \lambda) \simeq \left\langle e^{\lambda Q(t)} \right\rangle = e^{tg(\lambda)}
$$

Derive (3.43) from this expression and explain why one of the two solutions of the second order equation for α must be rejected. Hint: observe that the moments of v are finite, but that those of Q are proportional to t. Compute $\langle Q \rangle/t$ and $\langle Q^2 \rangle/t$ and check that you recover (3.45) when $T = T_1$.

3.4.3   Proof of Onsager's symmetry relations

Write the first terms of the Taylor expansion of $g(\lambda_1, \lambda_2)$ in the following form

$$
\begin{aligned}
g(\lambda_1, \lambda_2) \quad = \quad & a_1(\mu - \mu_1)\lambda_1 + a_1'(\mu - \mu_1)\lambda_2 + b_1(\mu - \mu_2)\lambda_1 \\
+ \quad & b_1'(\mu - \mu_2)\lambda_2 + c_1\lambda_1^2 + c_2\lambda_2^2 + c_3\lambda_1\lambda_2
\end{aligned}
$$

and use (3.53) to obtain (3.54).

3.5   Further reading

The derivation of the fluctuation theorem from stochastic dynamics was first proposed by Kurchan, followed by Lebowitz and Spohn. The presentation given here follows closely Derrida and Brunet [2005]; see also Crisanti and Ritort [2003]. The first section is based on Cleuren *et al.* [2006]. For proofs of the fluctuation theorem based on dynamical systems, see Gallavotti and Cohen [1995], Gallavotti [1999], chapter??, or Dorfman [1999], chapter 13.

Chapter 4

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