Six out of equilibrium lectures

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Preface

The purpose of these notes is to introduce a group of subjects in out of equilibrium statistical mechanics that have received considerable attention in the last fifteen years or so. They are mostly connected with time-reversibility and its relation to entropy, are expressed in terms of large deviations, and involve at some level the notion of timescale-separation.

We shall consider systems that contain, in their dynamic rules, an element of noise. There are good reasons for this: On the practical side, a driven system needs to dissipate heat if it is to reach a stationary regime rather than heating up indefinitely. Stochastic systems, where energy is provided by the bath through time-dependent, random forces, are well-studied physical models of heat reservoirs. A second, equally important reason is that very often, dynamical systems in the presence of noise are much easier to study than purely deterministic ones, because then very subtle ergodicity considerations become trivial. If the aim of ergodic theory is to understand how randomness arises from deterministic constituents, once stochasticity is added ‘by hand’ the question is artificially bypassed. One may then concentrate on the issues that are specific to non-equilibrium systems with many degrees of freedom, just as one postpones ergodicity questions in the day to day practice of equilibrium statistical mechanics. One last consideration is that even purely deterministic systems are sometimes more clearly understood as a small-noise limit: This stochastic stability approach is very natural and appealing, not only from the physical, but also from the mathematical point of view (see e.g. Cowieson et al 2005).

Out of equilibrium statistical mechanics is a domain shared between theoretical physicists, mathematical physicists and probabilists, a fact reflected by a severely fragmented literature. Workers in each one of these fields have in mind a different network of relations between subjects and techniques. Two ideas that look similar to a physicist may seem very distant to a probabilist, and vice-versa. The physicist’s point of view – the one I adopt – stresses the relations between dynamics and the statistical mechanics in space-time, between stochastic evolution and quantum mechanics, and is on the alert for hidden symmetries and for scaling.

The first lecture introduces stochastic dynamics in a formalism that uses as much as possible the analogy with quantum mechanics, on the assumption that the reader is already familiar with Shrödinger’s equation. Next, we discuss the consequences of

1 I have followed, as general references, the following: the books by Risken (Risken 1984), Gardiner (Gardiner 1983) and Van Kampen (Van Kampen 1981) for the general stochastic context. Parisi’s book (Parisi 1988) in several places, in particular the relation between stochastic and quantum mechanics. Zinn-Justin’s book (Zinn-Justin 1996) for technical background on path integrals and a more field-theoretic point of view. I have also found very illuminating the Lecture notes of H. Hilhorst (Hilhorst) (in French) and of J. Cardy (Cardy 1999), where the reader may bridge the main gap of these lectures: renormalisation. The review of Hanggi et al (Hanggi et al 1990) has a very comprehensive view of activation processes.
time-reversibility (in particular detailed balance), and how this is intimately related to thermodynamic equilibrium. Crucial for these notes is the fact that the term responsible for the breaking of a time-reversal symmetry in an out of equilibrium system is directly related to entropy production. In lecture three we discuss timescale separation and metastability. In particular, we present through an example a general formalism for metastability (Gaveau et al. 1998; Bovier et al. 2000) based on the spectral decomposition of the dynamical operator. It is quite elementary and intuitive, and is unjustifiably little known. We also describe very briefly the hydrodynamic limit, mainly to present an example where fluctuations become weak through coarse-graining, rather than through low temperatures. This allows us to carry over the ‘low noise’ results, that we introduce for simplicity in the case of low temperatures, for smooth, large-scale fluctuations: this is the Macroscopic Fluctuation Theory (Bertini et al. 2001). In lecture five we present two forms of large-deviations: i) Low-Noise: we stress as much as possible the complete analogy between the ‘Freidlin-Wentzell’ (Freidlin et al. 1984; Kitahara 1975) theory and the standard WKB semiclassical approach of quantum mechanics. ii) Deviations of long-time averages: In the context of glasses this is referred to as Space-time Thermodynamics (Jack et al., 2006), because the long-time large deviation functions are in complete analogy with \((d+1)\)-dimensional thermodynamics. We shall show that the phase transitions encountered in systems with slow dynamics within this formalism are closely related to the spectral manifestations of metastability discussed in lecture three. With all these elements in hand, and playing with the time-reversal symmetry and its breaking, we obtain the Fluctuation Theorem and Jarzynski’s equality, the subject of the last lecture.

The main aim of this short course is to stimulate curiosity. If it feels incomplete I will judge it successful.
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Trajectories, distributions and path integrals.

In this section we introduce equations of motion containing a deterministic part, and a stochastic thermal bath. Next, we make the passage from a description in terms of trajectories to one in terms of distributions. The evolution of 'probability clouds' in space is formally very close to (imaginary time) quantum mechanics. We do our best to exploit this analogy as much as possible because it opens the way for the application of all the methods in quantum mechanics and field theory.

1.1 From trajectories to distributions

1.1.1 Trajectories

Let us start by considering a system satisfying Hamilton’s equations. In addition, we shall allow for the possibility of external forces that do not derive from a potential acting on the system, throughout this work we shall denote them \( f(q) \). Nonconservative forces do work, and tend to heat the system up. If we wish that the system eventually become stationary we need a thermal bath to absorb energy, both theoretically and in practice. The simplest thermostat is the Langevin bath, consisting of friction term proportional to the velocity and white noise. The equations of motion read:

\[
\begin{align*}
\dot{q}_i &= \frac{\partial H}{\partial p_i} = \ldots \text{ unless otherwise stated here } \ldots = \frac{p_i}{m} = v_i \\
\dot{p}_i &= -\frac{\partial H}{\partial q_i} - f_i(q) + \eta_i(t) - \gamma p_i \\
\end{align*}
\]

Forcing Thermal Bath

(1.1)

we shall use throughout \( v_i = p_i/m \). If the thermal bath is itself in equilibrium, noise intensity and friction coefficient are related by:

\[
\langle \eta_i(t)\eta_j(t') \rangle = 2\gamma T \delta_{ij} \delta(t-t')
\]

(1.2)

which, as we shall see, allows the system to equilibrate at temperature \( T \) in the absence of forcing. The parameter \( \gamma \) measures the intensity of coupling to the bath. In an unforced system it does not affect the stationary distribution – the Gibbs-Boltzmann distribution \( \sim e^{-\beta H} \) – but it does control the dynamics: compare for example a system of particles interacting with a potential \( V \) in equilibrium with a medium at temperature \( T \), when the medium is made of air or of honey (small and large \( \gamma \), respectively).
Equation (1.1) can be justified in a number of ways. In section 2.2.1 we shall see how this can be done.

Let us now consider the overdamped case of large $\gamma$. We can formally (and somewhat dangerously) neglect the acceleration term as follows:

$$m \ddot{q}_i + \gamma \dot{q}_i + \frac{\partial V}{\partial q_i} + f_i = \eta_i(t)$$

$$\Downarrow$$

$$\gamma \frac{dq_i}{dt} + \frac{\partial V}{\partial q_i} + f_i = \eta_i(t)$$

$$\Downarrow$$

$$\frac{dq_i}{d\tau} + \frac{\partial V}{\partial q_i} + f_i = \eta_i(\tau)$$

(1.3)

In the last step we have rescaled time as $\gamma \tau = t$, which yields $\langle \eta_i(\tau) \eta_j(\tau') \rangle = 2T \delta_{ij} \delta(\tau - \tau')$. A few things to note in the passage to the overdamped equation (1.3) are:

- We now have half the dynamic variables.
- The velocity $\dot{q}_i$ is now discontinuous in time, as is the noise itself. We have to be careful what we mean by (1.3), for example if we are going to programme it in a computer. We adopt the *Ito convention*, which means, for example in one dimension:

$$q(t + \delta t) - q(t) + \delta t (V' + f)(q(t)) = (\delta t)^{1/2} \eta(t)$$

(1.4)

The simplicity comes from the fact that the force is evaluated in the old time $t$, and does not anticipate the result at the new time $(t + \delta t)$ (Van Kampen 1981; Gardiner 1983; Risken 1984; Hilhorst).

- As we shall see, these ambiguities disappear when we consider the evolution of distribution functions instead of the trajectories.
- Because the velocity is discontinuous, so is the quantity $\sum_i f_i \dot{q}_i$: neglecting inertia makes power become a subtle business. Indeed, some derivations, in particular involving work, become more transparent keeping inertia, which makes velocities a smooth function of time.

### 1.1.2 Distributions

Let us now change point of view, and consider the system rather than from the point of view of individual trajectories with particular noise realisations, as a ‘probability cloud’ evolving in space. The passage from the former to the latter description can be done in several ways, and it is instructive to see their relations.

Consider the Langevin equation (1.3). We wish to obtain the equation of motion of the probability $P(q, t)$. Let us first do it separately for a process in the absence of forces, and for a process of advection in the absence of noise. We obtain respectively:

\[ \text{Which are the analogue of factor-ordering ambiguities in quantum mechanics} \]
From trajectories to distributions

\[ \dot{q}_i = \eta_i \quad \rightarrow \quad \frac{dP}{dt} = T \nabla^2 P \]

\[ \dot{q}_i = -\left( \frac{\partial V}{\partial q_i} + f_i \right) \quad \rightarrow \quad \frac{dP}{dt} = \sum_i \frac{\partial}{\partial q_i} \left[ \frac{\partial V}{\partial q_i} + f_i \right] P \]

The first equation is just diffusion. The second uses the familiar fact that if a distribution is carried by a flow \( \dot{q}_i = g_i(q) \), its evolution is given by the advective derivative \( \dot{P} = \sum_i \frac{\partial (g_i P)}{\partial q_i} \).

A useful remark: A trick one implicitly uses often in computer simulations is that whenever two processes act simultaneously and their effect in a small time-interval is small, one gets the same result by alternating short intervals with each acting alone. If the separate evolutions are \( \frac{dP}{dt} = -H_1 P \) and \( \frac{dP}{dt} = -H_2 P \), we can with the same argument recompose this as \( \frac{dP}{dt} = (H_1 + H_2)P \). Applied to the previous situation, this means that the evolution of the probability for the full Langevin equation (1.3) is:

\[ \dot{P}(q, t) = -H_{FP} P(q, t) \quad (1.5) \]

where we have defined the generator:

\[ H_{FP} = -\sum_i \frac{\partial}{\partial q_i} \left[ T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} + f_i \right] \quad (1.6) \]

Writing (1.5) as a continuity equation, we identify the current:

\[ \dot{P} = -\text{div} \mathbf{J} \text{ with the definition } J_i(q) = \left[ T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} + f_i \right] P \quad (1.7) \]

Exactly the same procedure can be used to derive the evolution of the probability for the case with inertia (1.1). In order to split the system in a diffusion and an advection term, we need to work in phase space. The result is the Kramers equation:

\[ \dot{P}(q, p, t) = -H_K P(q, p, t) \quad (1.8) \]

with

\[ H_K = \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} - \gamma \frac{\partial}{\partial p_i} \left( T \frac{\partial}{\partial p_i} + \frac{p_i}{m} \right) - \frac{\partial}{\partial p_i} f_i(q) \quad (1.9) \]

(summation convention), where we recognise the Poisson bracket associated with Hamilton’s equations, plus a bath, and (eventually) a forcing term.

Again, writing the Kramers equation as a continuity equation:

\[ \frac{\partial P(q, p, t)}{\partial t} = -H_K P(q, p, t) = -\text{div} \mathbf{J} = -\sum_i \left( \frac{\partial J_i}{\partial q_i} + \frac{\partial J_i}{\partial p_i} \right) \quad (1.10) \]
we identify a current:

\[ J_{q_i} = \frac{\partial H}{\partial p_i} P(q, p, t) \quad J_{p_i} = -\left( \gamma T \frac{\partial}{\partial p_i} + \gamma \frac{\partial H}{\partial p_i} + \frac{\partial H}{\partial q_i} + f_i \right) P(q, p, t). \quad (1.11) \]

A surprise is that, even in an unforced, \( f = 0 \) equilibrium stationary state the phase-space current is nonzero. This suggests that we define an alternative quantity, the reduced phase-space current as \cite{Tailleur et al. 2004}:

\[ J_{q_i}^{\text{red}} = J_{q_i} + T \frac{\partial P(q, p)}{\partial p_i} \quad J_{p_i}^{\text{red}} = J_{p_i} - T \frac{\partial P(q, p)}{\partial q_i}. \quad (1.12) \]

The currents \( (1.11) \) and \( (1.12) \) differ by a term without divergence, and hence their fluxes over closed surfaces coincide. The interesting property of \( (1.12) \) is that it is zero for the canonical distribution, as one can easily check. Furthermore, in a case with metastable states it is small everywhere, and it is concentrated along reaction paths.
Gaussian thermostat

In some situations one wishes to study a system with thermostat that preserves the energy. This can be done with a deterministic (noiseless) ‘Gaussian’ (Hoover 1986) thermostat, extensively used in the context of entropy production and the Gallavotti-Cohen theorem. As we shall see later, it is in some cases convenient to have in addition a small amount of energy-preserving noise. We thus consider:

\[
\begin{align*}
\dot{q}_i &= \frac{p_i}{m} \\
\dot{p}_i &= -\frac{\partial H}{\partial q_i} - g_{ij}(\eta_j - f_j(q)) = -\frac{\partial H}{\partial q_i} + g_{ij} \eta_j - f_i(q) + \gamma(t)p_i
\end{align*}
\]

(1.13)

- \(\eta_j\) are white, independent noises of variance \(\epsilon\), unrelated to temperature, since the energy is fixed.
- \(g_{ij} = \delta_{ij} - \frac{p_ip_j}{p^2}\) is the projector onto the space tangential to the energy surface.
- Multiplying the first of (1.13) by \(\frac{\partial V(q)}{\partial q_i}\), the second by \(\frac{p_i}{m}\) and adding, one concludes that energy is conserved provided \(\gamma(t) = \frac{\gamma_0 p^2}{p^2}\).

The product \(g_{ij}(p)\eta_j\) is rather ill-defined because both \(g_{ij}\) and \(\eta_j\) are discontinuous functions of time. The ambiguity is raised by discretising time (Risken 1984), or by specifying the evolution of probability, as we now do.

Repeating the steps leading to the Fokker-Planck and Kramers equation, we find that the probability evolves through:

\[
P'(q,p) = -H_GP(q,p)
\]

(1.14)

where \(H\) is the operator:

\[
H_G = \frac{p_i}{m} \frac{\partial}{\partial q_i} - \frac{\partial V(q)}{\partial q_i} \frac{\partial}{\partial p_i} + \frac{\partial}{\partial q_i} \left[ \gamma p_i \right] - \frac{\partial}{\partial p_i} f_i - \epsilon \frac{\partial}{\partial p_j} g_{ij} g_{il} \frac{\partial}{\partial p_l}
\]

(1.15)

The precise factor ordering in the last term is important, and specifies the meaning of Eq. (1.13). In the absence of driving \(\Gamma = 0\) it is easy to check that \(H\) annihilates any function that depends on the phase-space coordinates only through the energy \(\mathcal{H} = \frac{p^2}{2m} + V\). Hence, the noise respects the microcanonical measure, in that case.

1.1.3 Other spaces. Doi-Peliti variables

The Hilbert spaces associated with probability distributions of the Fokker-Planck and Kramers equations are different, as the former consists of functions of \(N\)-dimensional space \(P(q)\) and the latter of \(2N\)-dimensional space \(P(q,p)\). In fact, other spaces appear naturally (Doi 1976; Hilhorst) when the dynamic variables are not continuous. This
does not bring in any new conceptual feature, but it allows to write other stochastic problems in a familiar ‘quantum’ notation. Let us give two examples:

**Bosons**

We consider particles on a lattice, with no exclusion. Denoting \( n_i \) number of particles in site \( i \), the complete set of configurations is spanned by the space:

\[
|n⟩ = |n_1, \ldots, n_N⟩ = \otimes_{i=1}^{N} |n_i⟩ ,
\]

so that a probability distribution is written as:

\[
P = \sum_{n_1, \ldots, n_N} c_{n_1, \ldots, n_N} |n_1, \ldots, n_N⟩.
\]

We can write any evolution operator in this space introducing the generators

\[
a_i |n_i⟩ = n_i |n_i - 1⟩
\]

\[
a_i^\dagger |n_i⟩ = |n_i + 1⟩
\]

\[
a_i |0⟩ = 0
\]

Note that \( a_i^\dagger \) and \( a_i \) are not mutually Hermitian conjugates. For example, for simple diffusion on a one-dimensional lattice reads \( \dot{P} = -HP \) with

\[
H = -\sum_i (a_{i+1}^\dagger + a_{i-1}^\dagger - 2a_i^\dagger) a_i
\]

**Spins: the Simple Symmetric Exclusion Process**

Boson variables do not lend themselves easily to processes where occupation of sites is limited, because particles exclude one another. In those cases, Fermions and Spins, which have a finite Hilbert space, appear naturally. To be more definite consider the ‘Simple Symmetric Exclusion Process’ on a one-dimensional lattice. This corresponds to the stochastic process on the lattice \( \{1, \ldots, N\} \) where particles jump to neighbouring sites, but with the limitation that each site can accommodate at most one particle. Configurations \( n \in \{0, 1\}^N \) are then identified with ket states

\[
|n⟩ = |n_1, \ldots, n_N⟩ = \otimes_{i=1}^{N} |n_i⟩ ,
\]

which specify the occupation number of each site, namely \( n_i \in \{0, 1\} \). The bulk evolution is given by the transition rates

\[
w(n^{i+1,i}, n) = -(n_i^{i+1} |H_B⟩ |n⟩ = (1 - n_i)n_{i+1}
\]

\[
w(n^{i+1,i}, n) = -(n_i^{i+1} |H_B⟩ |n⟩ = n_i(1 - n_{i+1})
\]

where \( n^{i,j} \) is the configuration which is obtained from the configuration \( n \) by removing a particle in \( i \) and adding it in \( j \).

We introduce the operators \( S_i \), which act as

\[
S_i^+ |n_i⟩ = (1 - n_i) |n_i + 1⟩
\]
Hilbert Space

$$S_i^- |n_i\rangle = n_i |n_i - 1\rangle$$
$$S_i^0 |n_i\rangle = \left(n_i - \frac{1}{2}\right) |n_i\rangle.$$ (1.22)

and satisfy the SU(2) algebra

$$[S_i^0, S_i^\pm] = \pm S_i^\pm$$
$$[S_i^-, S_i^+] = -2 S_i^0.$$ (1.23)

Note again that, in this representation, $S^\pm$ are not mutually Hermitian conjugates.

In terms of these, the evolution of the SSEP is generated by a spin one-half ferromagnet (Schütz et al. 1994)

$$-H_B = \sum_{i=1}^{N-1} \left( S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+ + 2 S_i^0 S_{i+1}^0 - \frac{1}{2} \right),$$ (1.24)

1.2 Hilbert Space

We shall throughout these lectures use the bracket notation, following Kadanoff and Swift (Kadanoff et al. 1986) Doing this, we uncover the similarities and differences between stochastic and quantum dynamics, and allows us to import many techniques developed in quantum many-body and field theory. Here we do everything for the Fokker-Planck case, the generalisation to other dynamics is straightforward. We define, as usual, the $q$ representation:

$$P(q) = \langle q | \psi \rangle$$ (1.25)

The evolution equation becomes:

$$\frac{d}{dt} |\psi\rangle = -H_{FP} |\psi\rangle$$ (1.26)

whose solution is

$$|\psi(t)\rangle = e^{-t H_{FP}} |\psi_o\rangle \rightarrow P(q, t) = \langle q | e^{-t H_{FP}} |\psi_o\rangle.$$ (1.27)

The transition probability is given by the matrix element:

$$P(q, t : q_o, t_o) = \langle q | e^{-(t-t_o) H_{FP}} |q_o\rangle.$$ (1.28)

As in quantum mechanics, it is useful to consider the spectrum of $H_{FP}$. Because $H_{FP}$ is not self-adjoint, we have to distinguish right and left eigenvectors:

$$H_{FP} |\psi^R_a\rangle = \lambda_a |\psi^R_a\rangle ; \quad \langle \psi^L_a | H_{FP} = \lambda_a |\psi^L_a\rangle.$$ (1.29)

The resolution of the identity is:

$$\langle \psi^L_a | |\psi^R_b\rangle = \delta_{ab} ; \quad 1 = \sum_a |\psi^R_a\rangle \langle \psi^L_a|.$$ (1.30)
Defining the (in general, unnormalisable) ‘flat’ state $\langle - |$ as a constant over all configurations:

$$\langle - | q \rangle = 1$$

(1.31)

and using the fact that conservation of probability implies that, at all times

$$1 = \sum_{\text{all configurations}} \langle q | \psi(t) \rangle \rightarrow \frac{d}{dt} \langle - | \psi(t) \rangle = -\langle - | H_{FP} | \psi(t) \rangle = 0 \quad \forall \psi(t)$$

(1.32)

and the fact that a stationary state satisfies

$$\frac{d}{dt} |_{\text{stat}} = -H_{FP} |_{\text{stat}} = 0$$

(1.33)

we have that ‘flat’ and stationary states are the left and right zero-eigenvalue eigenvectors

$$\langle - | H_{FP} = 0 ; \quad H_{FP} |_{\text{stat}} = 0$$

(1.34)

Finally, writing

$$| \psi_o \rangle = \sum_a c_a | \psi_R^a \rangle$$

(1.35)

we have

$$P(q, t) = \langle q | \psi(t) \rangle = \sum_a c_a \langle q | \psi_R^a \rangle e^{-t \lambda_a}$$

(1.36)

Equation (1.36) already shows us that $\lambda_a$ cannot be negative, and that the long-time properties of the probabilities are encoded in the eigenvectors with small eigenvalues. In particular, if all eigenvalues have real parts larger than zero, there is no stationary state’; this happens typically if the system is unbounded.

In the Kramers case, all of what we have said applies, provided one considers functions:

$$P(q, p) = \langle q, p | \psi \rangle$$

(1.37)

**Perron-Frobenius theorem:** $P$ is a probability distribution, so it has to be positive everywhere at all times. If one $\lambda_a$ has a negative real part, it dominates the sum (1.36) for large times, its coefficient going to infinity. Because $\langle - | \psi_o \rangle = 0$, necessarily $\langle q | \psi_o \rangle$ takes positive and negative values, and this will make $P(t)$ at large times not everywhere positive, contrary to the assumption.

1.2.1 Correlations and responses

Correlation functions are averages over many realizations of the process, with different realisations of the random noise each time. They can be expressed in this notation as:

$$C_{AB}(t,t') = \langle A(t)B(t') \rangle_{\text{realisation}} = \langle - | A e^{-(t-t')H} B e^{-t'H} | \text{init} \rangle$$

(1.38)

here $H$ may be the Fokker-Planck, Kramers, or in general any Doi-Peliti operator. Similarly for the response functions.
Hilbert Space

\[ R_{AB}(t, t') = \frac{\delta(A(t))}{\delta h_B(t')} = \langle -A e^{-(t-t')H} \frac{dH}{dh_B} e^{-t'H} | \text{init} \rangle \] (1.39)

where the average \( \langle A \rangle \) is over noise realisations. Eigenvalues with small real parts have something to say about the decay of long-time correlations:

\[ C(t, t') = \langle A(t)A(t') \rangle = \langle -|A| e^{-(t-t')H} A|\text{init} \rangle = \sum \langle -|A|_a R \langle \psi^L_a | A|\text{init} \rangle e^{-\lambda_a t} \]

\[ \sim \langle -|A|_{\text{stat}} \rangle \langle |A|_{\text{init}} \rangle + \langle -|A|_1 R \langle \psi^L_1 | A|\text{init} \rangle e^{-\lambda_1 t} \] (1.40)

which decays to the asymptotic value as an exponential of Re\( \lambda_1 \), the first eigenvector with non-zero real part. The existence of gap between lowest and first eigenvalue leads to exponential decays of correlations.

1.2.2 Conserved quantities

Consider a probability distribution that is concentrated on an energy shell, for example in phase space \( E(q, p) = E_0 \). This can be expressed as an eigenvalue equation:

\[ E(q, p)P(q, p, t) = E_0 P(q, p, t) \] (1.41)

Consider further an evolution that conserves energy, generated by some \( H \). By assumption, there are no transitions between shells of different energies, so the matrix of \( H \) is of block form, each one corresponding to a value of \( E_0 \). This in turn implies that \( E \) commutes with the operator \( H \):

\[ [E, H] = 0. \] (1.42)

Clearly, what we have said applies to any conserved quantity.

The fact that the stochastic process can be now broken into subspaces of fixed energy entails the existence for each \( E_0 \) of a different stationary state \( |\text{stat}_{E_0} \rangle \), and the corresponding flat measure \( \langle -E_0 \rangle \).

1.2.3 Analogy with quantum mechanics

Making the identification:

\[ \hat{q}_i^{op} \longrightarrow T \frac{\partial}{\partial q_i} \] (1.43)

we may write

\[ \tilde{H} \equiv TH_{FP} = - \left( T \frac{\partial}{\partial q_i} \right) \left[ \left( T \frac{\partial}{\partial q_i} \right) + \frac{\partial V}{\partial q_i} + f_i \right] \] (1.44)

and the evolution is
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\[ \dot{P} = -\frac{1}{T} \dot{H} P \tag{1.45} \]

The situation is analogous to quantum mechanics, with \( T \) playing the role of \( \hbar \) and the \( \hat{q}_i^{op} \) the role of ‘momentum operators’. The quantum-like Hamiltonian comes from a ‘classical’ Hamiltonian

\[ \hat{H} = -\dot{q}_i \left[ \dot{q}_i + \frac{\partial V}{\partial q_i} + f_i \right] \tag{1.46} \]

in a phase space with twice the number of variables. This ‘classical’ problem with double number of degrees of freedom will play a key role in the next sections.

1.3 Functional approach

Let us first consider a general and extremely powerful trick to convert an algebraic problem of finding the roots of a system of equations \( Q_a(x) = 0 \) into a statistical problem of calculating a partition function. We compute the sum over roots of a function \( A \):

\[ \langle A(x) \rangle = \sum_{\text{roots of } Q_a} A(x) \]

This can be written

\[ \langle A(x) \rangle = \int dx \ A(x) \ d\delta(Q_a(x)) \ det \left| \frac{\partial Q_a}{\partial x_b}(x) \right| e^{\sum a \dot{x}_a Q_a(x)} \]

The determinant is there to insure that we count each root with a unit weight. We have thus obtained an expression that has the form of a partition function.

The Martin-Siggia-Rose/DeDominicis-Janssen (Martin et al. 1973) approach consists of applying this technique to differential, rather than ordinary equations, in this case the Langevin equation. To make this properly, one should discretise time and write a delta function imposing the equation (1.4) at each time. One obtains a sum over paths:

\[ P(q, t) = \int D[q] \ D[\eta] \ \delta \left[ \dot{q} + \frac{\partial V}{\partial q} + \eta \right] e^{-\int dt \ \eta^2/4T} \] \tag{1.49} \]

Where for the moment we stay in one dimension, and omit the forcing term, the generalisation to several dimensions and \( f \neq 0 \) is straightforward. The determinant is unity in the Ito convention [13], because the matrix of second derivatives (containing the derivative of the equation of motion at time \( t_i \) with respect to \( q(t_j) \)) is upper triangular with ones in the diagonal.
Introducing the integral representation of the delta with a ‘hat’ variable (one per time):

\[ P(q,t) = \int D[q] D[\eta] \int_{-i\infty}^{+i\infty} D[\hat{q}] \ e^{i\int dt [\dot{q} (\dot{q} + \frac{\partial V}{\partial q}) - \eta^2 / 4T]} \] (1.50)

The boundaries are free for \( \hat{q} \). Integrating the Gaussian noise away, we obtain:

\[ P(q,t) = \int D[q] D[\hat{q}] \exp \int dt \left[ \hat{q} \dot{q} - \left\{ -\hat{q} \left( T \dot{q} + \frac{\partial V}{\partial q} \right) \right\} \right] = \int D[q, \hat{q}] \ e^{\pm \int dt [\hat{q} \dot{q} - H]} \]

Making the change of variables \( \hat{q} \to \frac{\hat{q}}{T} \) the evolution equation becomes, for many degrees of freedom:

\[ P(q,t) = \int D[q, \hat{q}] \exp \frac{1}{T} \int dt \left[ \hat{q} \dot{q} - \left\{ -\hat{q} \left( \frac{\partial V}{\partial q} \right) \right\} \right] \]

(summation convention). The exponent is multiplied by \( 1/T \), which thus plays the role of \( 1/\hbar \). From what we know of the path-integral representation of quantum mechanics, we recognise the action associated with the evolution equation (1.45). The analogy with (imaginary time) quantum mechanics can be carried further in the absence of forcing, by making the transformation:

\[ H_{\hbar} = e^{\beta V/2} H_{FP} e^{-\beta V/2} = \frac{2}{T} \sum_i \left[ -\frac{T^2}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{8} \left( \frac{\partial V}{\partial q_i} \right)^2 - \frac{T}{4} \frac{\partial^2 V}{\partial q_i^2} \right] \] (1.53)

We now have an \( H_{\hbar} \) which is truly of the Shrödinger form, albeit with a new potential \( V_{eff} = \frac{1}{8} \left( \frac{\partial V}{\partial q_i} \right)^2 - \frac{T}{4} \frac{\partial^2 V}{\partial q_i^2} \).

All in all, the situation is as in Fig. [1.3] we can go from the Langevin equation to the Fokker-Planck equation for the distribution directly, and then construct a path integral representation of the evolution using the analogy between Fokker-Planck and Shrödinger equations. Alternatively, we can go straight from the Langevin equation to the path integral, through the Martin-Siggia-Rose/deDominicis-Janssen construction. The latter procedure is much more flexible, and is thus extensively used in the physics literature.

### 1.3.1 Lagrangian (Onsager-Machlup) form

As in all phase-space problems where the momenta appear quadratically (in this case the ‘hat’ variables \( \hat{q}_i \)), we have the possibility of integrating them away, thus going to
Fig. 1.1 With the MSR/dDJ one can go straight from stochastic equation to the path-integral. Otherwise, given the equation of motion for the probability distribution one can express it as a path integral as in quantum mechanics textbooks.

the Lagrangian representation (Onsager et al. 1953). Alternatively, we can go straight to this representation by integrating (1.49) over the noise before introducing the ‘hat’ variables. The result is:

\[
P(q,t) = \int D[q] \exp \left[ -\frac{1}{4T} \int dt \left( \frac{\partial V}{\partial q_i} + f_i \right)^2 \right]
\]

Note that we have inherited the Itô convention from (1.4), which means a definite prescription on how to discretise the time integral. This sum takes the form of a partition function at temperature \( T \). This means we can in principle compute it using well-established Monte Carlo methods: a nonequilibrium problem for the configurations becomes an ‘equilibrium’ problem in trajectory-space.

In the absence of forcing \( f = 0 \) we can develop the square in the exponent, and recognising that the double product is a total derivative, we have:

\[
P(q,t) = \int D[q] \exp \left\{ -\frac{1}{4T} \int dt \left[ \frac{\partial^2 V}{\partial q_i} \right]^2 - 2T \frac{\partial V}{\partial q_i} \right\} e^{-\frac{1}{4} \left[ \frac{\partial V}{\partial q_i} \right]^2}
\]

The second derivative in the exponent comes from the correct discretisation (see box). We recognise the action of a polymer – the monomer index being the time – at temperature \( T \) in a potential \( \propto |\nabla V|^2 \). This analogy can be exploited fruitfully (Chandler et al. 1981).
Conventions:
Suppose we had started from (1.53) and constructed the Lagrangian path integral as in quantum mechanics textbooks. We would have obtained (1.55), the exponentials of the potential at the ends of the trajectory being just the change of basis leading to (1.53). The extra term \( \frac{1}{2} \int dt \frac{\partial^2 V}{\partial q^2_i} \) in the exponent appears naturally. In our case, it appeared as part of the integral \( \int dt \dot{q}_i \left( \frac{\partial V}{\partial q_i} \right) \), once we specify what this means in terms of a discrete sum.

The question of discretisation conventions must be treated with care, as they may lead to errors in the results. However, one should not exaggerate the physical importance of the whole problem, as it disappears as soon as the system is regularised by including inertia.

1.3.2 Kramers equation
All the steps above can be performed for a system with inertia. A somewhat confusing fact is that our extended space consists of 4N coordinates, including the 2N original coordinates \((q, p)\) playing the role of coordinates of the extended space, and the 2N ‘hat’ variables \((\hat{q}, \hat{p})\), playing the role of momenta in the extended space, associated now with the operators:

\[
\hat{q}_i^{qp} \rightarrow T \frac{\partial}{\partial q_i} \quad ; \quad \hat{p}_i^{qp} \rightarrow T \frac{\partial}{\partial p_i}
\] (1.56)
2
Time-reversal and Equilibrium

As we have seen in the previous section, stochastic dynamics lead to an evolution that is quite close to a generic quantum problem, often with a non-Hermitian Hamiltonian. Such generality is in a way bad news, since one can hardly expect to find a method to solve a problem that is so general. A special and important class of that of systems that evolve in contact with an equilibrium thermal bath, and are under the action of conservative forces. There is then a symmetry that can be interpreted as time-reversal, which has important consequences. We shall also see that if this symmetry is broken by forces that do work, the symmetry-breaking term can be interpreted as an entropy production rate: this will be the basis of the Nonequilibrium Theorems of section 6.

2.1 Detailed Balance

The detailed balance property is a relation between the probabilities of going from a configuration $a$ to a configuration $b$ and vice-versa:

$$e^{-\beta V(a)} P_{a \rightarrow b} = e^{-\beta V(b)} P_{b \rightarrow a}$$  \hspace{1cm} (2.1)

The name ‘detailed’ comes from the fact that if we only ask for the Gibbs-Boltzmann distribution to be stationary, we need only that (2.1) holds added over configurations, and not term by term. We can telescope (2.1) to obtain for a chain of configurations:

$$P_{a_1 \rightarrow a_2 P_{a_2 \rightarrow a_3} \ldots P_{a_{m-1} \rightarrow a_m} = e^{-\beta [V(a_m) - V(a_1)]} P_{a_m \rightarrow a_{m-1}} \ldots P_{a_3 \rightarrow a_2 P_{a_2 \rightarrow a_1} (2.2)$$

which means that

$$\text{Probability [path]} = e^{-\beta [V(\text{final}) - V(\text{initial})]} \quad \text{Probability [reversed path]}$$

And, in particular, for all closed circuits:

$$\text{Probability [circuit]} = \text{Probability [reversed circuit]}$$

In other words, we have the Onsager-Machlup reversibility:

- The probability of any path going from $a$ to $b$ is equal to the probability the time-reversed path, times a constant that only depends on the endpoints $a, b$.
- Hence, if for some reason there is essentially one type of path that takes from $a$ to $b$, then there is also essentially one path that takes from $b$ to $a$, and it is its time-reversed.

These properties are directly observable experimentally, see \cite{Andrieux et al. 2007}.
2.1.1 Fokker-Planck

Detailed balance holds for the Fokker-Planck evolution without forcing $f_i = 0$. Let us see the implication this has:

\[
\langle q' | e^{-tH_{FP}} | q \rangle e^{-\beta V(q)} = \langle q | e^{-tH_{FP}} | q' \rangle e^{-\beta V(q')}
\]

\[
\langle q' | e^{-tH_{FP}} e^{-\beta V} | q \rangle = \langle q | e^{-tH_{FP}} e^{-\beta V} | q' \rangle = \langle q' | e^{-\beta V} e^{-tH_{FP}^\dagger} | q \rangle
\]

Since this is true $\forall (q, q')$, we have:

\[
e^{\beta V} e^{-tH_{FP}} e^{-\beta V} = e^{-tH_{FP}^\dagger} \forall t \rightarrow e^{\beta V} H_{FP} e^{-\beta V} = H_{FP}^\dagger (2.4)
\]

which in turn means that:

\[
H_b = e^{\beta V/2} H_{FP} e^{-\beta V/2}
\]

is Hermitian, a fact that we have already checked (cfr (2.5)). Equation (2.4) gives also a direct relation between right and left eigenvectors:

\[
|\psi^L_\alpha^\lambda \rangle = e^{\beta V} |\psi^R_\alpha^\lambda \rangle
\]

We now understand why an Hermitian form cannot be obtained when there is forcing: detailed balance is then lost.

2.1.2 Kramers

Let us now see how this generalises to a process with inertia, having an energy $H = \frac{p^2}{2m} + V(q)$. In this case, something like detailed balance holds, but on the condition that we reverse the velocities:

\[
e^{-\beta H(a)} P_{a \rightarrow b} = e^{-\beta H(\bar{b})} P_{b \rightarrow \bar{a}}
\]

where $\bar{a}, \bar{b}$ are the configurations $a, b$ with the velocities reversed. Also in the Kramers case we can telescope (2.7) to obtain relations for trajectories, and for closed circuits, as we did above for the Fokker-Planck evolution.

In operator notation, Eq. (2.7) reads:

\[
\langle q', p' | e^{-tH_K} | q, p \rangle e^{-\beta H(q, p)} = \langle q, -p | e^{-tH_K} | q', -p' \rangle e^{-\beta H(q')}
\]

which leads to:

\[
\Pi e^{\beta H} H_K e^{-\beta H} \Pi^{-1} = H_K^\dagger
\]

where we have introduced the operator that reverses velocities $\Pi p \Pi^{-1} = -p$, and similarly with derivatives. $H_K$ cannot, in general, be taken to an Hermitian form. Applying to (2.9) steps analogous to those leading from (2.4) to (2.5) one finds that Hermiticity is broken because $\Pi^{1/2}$ is not real.
Another form of time reversal: the adjoint

A driven overdamped system admits a form of time-reversal (Bertini et al. 2001; Chetrite et al. 2008) that is not, however, a symmetry. Consider the Fokker-Planck operator with nonconservative forces, and assume we know its stationary distribution:

$$H|\text{stat}\rangle = -\frac{\partial}{\partial q_i} \left( T \frac{\partial}{\partial q_i} + f_i \right) |\text{stat}\rangle = 0 \quad (2.10)$$

Put $$\langle q |\text{stat}\rangle \equiv \phi(q)$$ and compute:

$$\phi^{-1}H \phi = -\left[ T \frac{\partial}{\partial q_i} + \left( 2T \frac{\partial \ln \phi}{\partial q_i} + f_i \right) \right] \frac{\partial}{\partial q_i} = H^\dagger_{\text{adj}} \quad (2.11)$$

Where we have defined the adjoint

$$H_{\text{adj}} = -\frac{\partial}{\partial q_i} \left[ T \frac{\partial}{\partial q_i} - \left( 2T \frac{\partial \ln \phi}{\partial q_i} + f_i \right) \right] \quad (2.12)$$

This describes another diffusion problem at temperature $$T$$ in a new force field:

$$f_i^{\text{rev}} = -\left( 2T \frac{\partial \ln \phi}{\partial q_i} + f_i \right) \quad (2.13)$$

which only coincides with the original one when $$f$$ derives from a potential. This formula is the basis of the Hatano-Sasa formula (Hatano et al. 2001).

A similar but stronger form of time-reversibility arises if we accept that some variables change signs, as velocities do. We refer the reader to Ref. (Graham 1980). Note that in all these cases, we need to know the stationary distribution a priori, so the formulas are moderately useful in practice.

2.2 Equilibrium theorems: Reciprocity and Fluctuation-Dissipation

Detailed balance is a form of time reversal symmetry in the trajectories. It cannot come as a surprise that in equilibrium it implies time-reversal symmetry in the correlation functions. Let us do it for the Kramers equation. Denoting $$|GB\rangle$$ the Gibbs-Boltzmann distribution:

$$C_{AB}(t-t') = \langle -|A e^{-(t-t')H_k} B|GB\rangle = \langle GB|B e^{-(t-t')H_k^\dagger} A|-\rangle$$

$$= \langle -|e^{-\beta H} B e^{-(t-t')H_k^\dagger} A e^{\beta H} |GB\rangle$$

$$= \langle -| P e^{-\beta H} B e^{\beta H} \Pi^{-1} e^{-(t-t')H_k} P e^{-\beta H} A e^{\beta H} \Pi^{-1} |GB\rangle$$

$$= C_{BA}(t-t') \quad (2.14)$$

where we have used (2.9) and we have defined $$\tilde{A}(q, p) = A(q, -p)$$. The same derivation can be done for the Fokker-Planck case for observables dependent on coordinates only.

Another important equilibrium property is the Fluctuation-Dissipation theorem. It relates the response of the expectation of an observable $$A$$ produced by a kick given by
field conjugate to an observable $B$ to the corresponding two-time correlation. Putting $\mathcal{H}_{h} = \mathcal{H} - h_{B}B$, we compute:

$$R_{AB}(t - t') = \frac{\delta(A(t))}{\delta h_{B}(t')} = \langle - | A e^{-(t-t')H} \frac{d\mathcal{H}}{dh_{B}}|_{h_{B}=0} | GB \rangle$$

(2.15)

Because the equilibrium distribution in the presence of a field $| GB \rangle$ satisfies for all $h_{B}$ that $H_{h_{B}}| GB \rangle = 0$ we have:

$$\left( \frac{d\mathcal{H}}{dh_{B}} \right)_{| h_{B}=0} = -H \left( \frac{d}{dh_{B}} | GB \rangle \right)_{| h_{B}=0} = \beta H B | GB \rangle_{h_{B}=0}$$

(2.16)

and substituting in (2.15):

$$R_{AB}(t - t') = \beta \langle - | A e^{-(t-t')H} H B | GB \rangle = \beta \frac{\partial}{\partial t'} C_{AB}(t - t')$$

(2.17)

2.2.1 FDT of the first and second kind. A derivation of the Langevin equation.

At the outset we started with a bath that contained friction proportional to $\gamma$ and noise whose variance is $\gamma T$. This very precise relation between noise and friction is often referred to as ‘Fluctuation Dissipation of the first kind’, because it relates the dissipation and fluctuations of the bath, rather than of the system. If the bath satisfies this relation, a system in contact with it will eventually equilibrate (this might take long) and will then verify the fluctuation dissipation theorem (2.17) – of the ‘second kind’ – for its observables.

Next, assume there is a large number $\alpha = 1, ..., M$ of independent copies of such systems, with coordinates $q^{\alpha}, p^{\alpha}$, all in equilibrium with a bath. We intend to use them in turn as baths for a further system of coordinates $q', p'$ and energy $\mathcal{H}'(q', p')$. To do this we couple them, for example through a term:

$$\mathcal{H} = \sum_{\alpha} \mathcal{H}_{bath} + \mathcal{H}_{system} - M^{-\frac{1}{2}} \sum_{\alpha} q^{\alpha} q'$$

(2.18)

We may ask what is the condition for the coupling term to constitute a legitimate thermal bath for the primed system. The equations of motion of the primed variables are:

$$\dot{q}' = -\frac{\partial \mathcal{H}'}{\partial q'} - h(t)$$

(2.19)

Where the field $h$ is $h = M^{-\frac{1}{2}} \sum_{\alpha} q_{\alpha}$. The large $M$ limit allows us to treat each $M^{-\frac{1}{2}} q^{\alpha} q'$ as a small perturbation to the system $\mathcal{H}_{\alpha}$, and to invoke the central limit theorem to say that $M^{-\frac{1}{2}} q^{\alpha}$ is a Gaussian. Assuming the expectation values of $\langle q_{\alpha} \rangle = 0$
in the absence of coupling, the field $h$ has two contributions for large $M$: i) a random Gaussian noise $\eta(t)$ with correlation $C_{\alpha\alpha}(t, t') = \langle \eta(t)\eta(t') \rangle = \langle q_\alpha(t)q_\alpha(t') \rangle$ and ii) a drift due to the back effect of the $q'$ which acts as a field on the $q_\alpha$. Again, because $M$ is large, the average response of the ensemble $\alpha$ is:

$$M^{-\frac{1}{2}}(q^\alpha) = \int_0^t dt' R_{\alpha\alpha}(t, t')q'(t')$$  \hspace{1cm} (2.20)

The equation of motion of the primed variable becomes:

$$\ddot{q}' = -\frac{\partial H'}{\partial q'} + \eta(t) + \int_0^t dt' R_{\alpha\alpha}(t, t')q'(t')$$ \hspace{1cm} (2.21)

This is in fact the generalised Langevin equation, describing the primed system in contact with a thermal bath with coloured noise and friction with memory. The condition that the bath is a good equilibrium one is precisely:

$$TR_{\alpha\alpha}(t, t') = \frac{\partial}{\partial t'} C_{\alpha\alpha}(t, t')$$  \hspace{1cm} (2.22)

The primed system will, under the action of this dynamics, equilibrate to the Gibbs-Boltzmann distribution.

- Fluctuation dissipation of the second kind for the $q_\alpha$ has become a fluctuation dissipation of the first kind when they are considered as a bath for the primed variable $q'$.
- Friction is the back reaction of the bath to the perturbation exerted by the system, while noise is given by the incoherent addition of motions of the bath’s constituents.
- The fluctuation-dissipation relation regulates the balance between these two effects in such a way as to guarantee that equilibrium is ‘passed on’ to a coupled system.

2.3 Time-reversal violations and Entropy production

In the previous section we have seen that there is a symmetry related to time-reversal in systems that are in contact with an equilibrium thermal bath, and have only conservative forces. Once forcing is allowed, this symmetry is broken: in an interesting manner. As we shall now see, the symmetry-breaking term turns out to be proportional to the power injected by the nonconservative forces, divided by a temperature: it can be interpreted as an entropy production.

$^1$The white noise limit is obtained when $C_{\alpha\alpha}(t - t') \propto \delta(t - t')$.

$^2$With an energy that includes a contribution $\langle [q^\alpha]^2 \rangle$ coming from the interaction term (The factor $\langle [q^\alpha]^2 \rangle$ is the equilibrium expectation for a single isolated $H_\alpha$). This term can compensated by an opposite one in $H'$

$^3$Subtle questions about when can one call this entropy are extensively addressed in the literature (Maes 2003), here we shall not get into these matters.
For simplicity, we shall do this calculation in two cases with inertia, in order to avoid unnecessary complications brought about by the fact mentioned above that the power in an overdamped case is a discontinuous function of time.

**Kramers equation**

Let us attempt to obtain a relation like (2.9) in the presence of forcing. Referring to (1.9) \( H_K = H_{Liouville} + H_b + H_f \) we compute \( \Pi e^{\beta H} H_K e^{-\beta E} \Pi^{-1} \) in detail. First, we make the similarity transformation:

\[
e^{\beta H} H_{Liouville} e^{-\beta H} = H_{Liouville}
\]

\[
e^{\beta H} H_b e^{-\beta H} = \gamma \left( T \frac{\partial}{\partial p_i} - \frac{p_i}{m} \right) \frac{\partial}{\partial p_i}
\]

\[
e^{\beta H} H_f e^{-\beta H} = -f_i \left( \frac{\partial}{\partial p_i} - \beta \frac{p_i}{m} \right)
\]

(2.23)

Next, Hermitian conjugation changes signs of derivatives, and reverses the order of factors. Finally, velocity reversal transforms \( (p_i \rightarrow -p_i) \) and \( \frac{\partial}{\partial p_i} \rightarrow -\frac{\partial}{\partial p_i} \). All in all we get:

\[
\left[ \Pi e^{\beta H} H_K e^{-\beta H} \Pi^{-1} \right] = H_K^{\dagger} - \beta \sum_i f_i v_i
\]

(2.24)

(here again, \( v_i = p_i/m \) is the velocity). As announced, we find that relation (2.9) has now an extra term corresponding to power divided by temperature, an entropy production rate.

**Gaussian Thermostat**

We may repeat the calculation for the Gaussian thermostat (1.15). Only velocity reversal is necessary, and we obtain:

\[
\left[ \Pi H_G \Pi^{-1} \right]^{\dagger} = H_G + [\gamma p_i] \frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_i} [\gamma p_i]
\]

\[
= H_G - (N - 1) \frac{f \cdot p}{p^2}
\]

(2.25)

(summation convention) where \( 2N \) is the dimension of phase-space. Again, this has the interpretation of a power divided by a kinetic temperature \( (\sim p^2) \).

### 2.4 What does a stationary out of equilibrium distribution look like?

A driven system, if coupled to a thermostat will reach a stationary distribution. The problem with out of equilibrium statistical mechanics is that there is no simple, general expression for this distribution. If the thermostat keeps the energy constant, as the Gaussian one we defined above, even if the probability is then restricted to an energy shell, it does not cover it in a uniform, microcanonical way. In fact, if the thermostat is deterministic, the distribution will be a fractal. If, on the other hand, the thermostat...
involves noise, the fractal will be blurred, but the distribution is still non-uniform on the energy shell. Can we get some intuition on this? The purpose of this section is to see, in a relatively simple example (Bonetto et al. 1997a, Kurchan 2007), what happens when a system is forced.

We shall consider a Lorentz gas, or, equivalently, a particle in a billiard as in Figure 2.1 under the effect of a constant field, with periodic boundary conditions. We assume that there is a Gaussian thermostat, which fixes the velocity modulus to be constant, that we can take as unity. The trajectories between bounces are given by:

![Diagram of trajectories](image)

**Fig. 2.1** Left: a trajectory at zero field. Right: trajectory under a very strong field, pointing in the downward direction: the particle follows, through short bounces, the surface of the obstacle, and escapes when the field becomes tangent to it.
What does a stationary out of equilibrium distribution look like?

\[ \dot{p}_x = E - \frac{E}{p^2}p_x \]
\[ \dot{p}_y = -\frac{E}{p^2}p_y \]
\[ p\dot{\theta} = -E \sin \theta = -\frac{d}{d\theta}[-E \cos \theta] \]

(2.26)

where we have defined the angle \((p_x, p_y) = p(\sin \theta, \cos \theta)\) (Figure 2.2). If there were no obstacles, there would be two stationary situations: when the velocity is parallel to the field (stable) and when it is antiparallel (unstable). Such trajectories constitute the attractor and the repellor respectively.

Consider now the effect of obstacles. When the field is off, in the presence of obstacles the system is known (Sinai 1963) to be ergodic. Phase-space points on the energy shell – the Cartesian product of the allowed configurations times the velocity sphere, are visited uniformly. On the other extreme, if the field is very strong, the trajectories stay bouncing close to the surface of the obstacles until they escape along a tangent direction parallel to the field, only to hit a new obstacle – see the right panel of Figure 2.2. If we consider a stationary situation, these ‘trickling down’ trajectories involve only a very restricted part of configuration space. Adding energy-conserving noise to (2.26) does not change dramatically the situation. In conclusion, the stronger the forcing field \(E\), the more focussed the attractor reached at long times is on a subset of the energy shell. As we shall see later, the Gallavotti-Cohen fluctuation relation is, in a certain sense, a measure of this focussing.

**Fig. 2.2** Free trajectory under a field. Attractor \(A\) and repellor \(\bar{A}\) are parallel and antiparallel to the field.
2.5 Spectra of Fokker-Planck, Kramers and Liouville operators

As we have seen above, the detailed balance property implies that the Fokker-Planck operator can be taken to an Hermitian form $H_h$ via the similarity transformation (2.5). This implies that its eigenvalues are real. If, on the other hand, detailed balance is violated, then there is no such transformation, and some eigenvalues come in complex conjugate pairs. In any case, the Perron-Frobenius theorem mentioned above implies that the real parts of eigenvalues are non-negative.

On the other extreme, the Liouville operator corresponding to pure Hamiltonian dynamics

$$H_{Liouville} = \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \quad (2.27)$$

(summation convention) would seem to be, at least superficially, anti-Hermitian, since it has only first derivatives. Its spectrum would be pure imaginary, except that we have to be careful when we define the space of wavefunctions on which it acts. Clearly, the Kramers operator, which in a sense interpolates between both, is neither Hermitian nor anti-Hermitian, and has pairs of complex eigenvalues even in the conservative case, as we have mentioned already.

Consider a strongly chaotic, ‘mixing’ Hamiltonian system. If we start from an initial configuration distributed in a small probability cloud, the probability distribution mixes completely in phase-space – like a drop of ink in a stirred liquid, hence the name. Another way of obtaining the same result is to start from a single configuration, but subject the dynamics to a small noise. The fast mixing of the probability implies a concomitant fast decay of correlation functions to their stationary value. As discussed above (see Eq. (1.40)), this would imply that there is a gap in the real part of the spectrum. Hence, if the deterministic system is sufficiently chaotic, we expect that, in the presence of a small amount of noise, its spectrum will have a gap in the real part of the lowest eigenvalues. When the noise is strictly zero the situation is more subtle, as there are many unstable periodic orbits, on which the correlations are of course periodic in time.

A very interesting question is then what happens when we start from a Hamiltonian system with stochastic noise, and gradually decrease the noise’s intensity. This can be done with the Kramers equation without forcing, or, better, with the energy-conserving thermostat (1.15), letting $\epsilon \to 0$. The remarkable result, consistent with the discussion above, is that, if the system is sufficiently chaotic, as we let $\epsilon \to 0$ some eigenvalues do not become imaginary: they retain a positive real part. These eigenvalues, and the corresponding eigenvectors, are the Ruelle-Pollicott resonances [Ruelle 1986]: the ones that have smaller real part are responsible for the long time relaxation to equilibrium. A simple example of this phenomenon is discussed in the box below.
An instructive example is the particle in a harmonic potential with noise. The diagonalisation of the corresponding Kramers operator is simple, and can be found in Risken’s book [Risken 1984], Chapter 10: The spectrum is as follows. The eigenvalues are labelled by $n_1, n_2 = 0, 1, 2, ...$

- **Stable case** $V = \frac{1}{2} \omega^2 q^2$:
  
  Eigenvalues $\lambda_{n_1, n_2} = \frac{1}{2} \gamma (n_1 + n_2) + \frac{i}{2} \sqrt{4\omega^2 - \gamma^2} (n_1 - n_2)$ The spectrum becomes imaginary in the $\gamma \to 0$ limit of zero coupling to the bath, when the system becomes an undamped harmonic oscillator. This is compatible with the existence of many stable, periodic orbits.

- **Unstable case** $V = -\frac{1}{2} \omega^2 q^2$:
  
  Eigenvalues $\lambda_{n_1, n_2} = \frac{1}{2} \sqrt{\gamma^2 + 4\omega^2} (n_1 + n_2 + 1) + \frac{1}{2} \gamma (n_1 - n_2 - 1)$ All eigenvalues are real and larger than zero. The latter is to be expected, given that there is no stationary state. The fact that even in the limit $\gamma \to 0$ the spectrum stays real may come as a surprise: it underlines the fact that although the Liouville operator seems superficially anti-Hermitian (and would thus lead us to expect pure imaginary eigenvalues), in fact the Hilbert space in which it acts makes it not be so. Again, we find that the spectrum retains a real part as $\gamma \to 0$ when it is has unstable orbits ($q(t) = 0, p(t) = 0$, in this case) that are destroyed by the any amount of noise (see also Refs. [Gaspard et al. 1995; Gaspard 2003]).
Separation of timescales

Many systems have processes happening in very different timescales. Often, what is interesting is what takes long to happen, while the rapid fluctuations are relatively featureless. Consider the following examples:

- **Metastability:** Chemical reactions have often metastable states. Consider a mixture of Oxygen and Hydrogen. It takes a very short time for this gas to become ‘equilibrated’ into a mixture $O_2 + 2H_2$, staying in a stationary state until the reaction $O_2 + 2H_2 \rightarrow 2H_2O$ starts somewhere – an extremely unlikely event – and then rapidly propagates throughout. The true equilibrium state, water vapour, is then reached.

Similarly, diamond eventually decays into graphite, but this process is fortunately slow.

- **Hydrodynamic limit:** Systems with soft modes have slow evolution along these modes, while the ‘hard’ ones relax much faster. The typical example is a liquid, whose macroscopic motion is visible and slow, while the density fluctuations at the molecular scale evolve fast. As we shall see below, in some cases one can make a ‘hydrodynamic’ description, with the fast fluctuations acting as a noise whose intensity goes to zero with the coarse-graining scale.

- **Coarsening and glasses:** Suppose one quenches a ferromagnet to a low, but non-zero temperature. Domains of positive and negative magnetisation start growing. Inside each domain, the system resembles a pure ferromagnetic state with fast magnetisation fluctuations. The domain walls, however, evolve slowly, the slower the larger the domains. A more subtle case is the one of glasses, which have a fast evolution (‘cage motion’) and slow, collective rearrangements (‘aging’).

In all these cases, our ambition is to concentrate as much as possible in what is slow and interesting. In some cases, when we know *a priori* which are the slow coordinates, we may attempt to eliminate the fast fluctuations by allowing them to thermalise, at fixed value of the slow coordinates which we then treat adiabatically. One thus obtains a ‘free-energy landscape’ for the slow variables (see e.g. (E et al. 2002)).

What happens when we do not know exactly who is fast and who is slow? In the next sections we introduce a general approach to metastability, first in detail in a simple warming-up context, and then mention briefly how it works in general. In the last section, we describe the hydrodynamic limit of a transport problem, and how it takes us to a low-noise (quasi-deterministic) situation.
3.1 Metastability

3.1.1 The simple case of weak noise

Consider an overdamped Langevin system. We wish to analyse the spectrum of its Fokker-Planck evolution operator in the weak-noise limit. Because we know that $T$ plays a role analogous to $\hbar$, we shall use what we know from semiclassical Quantum Mechanics. Let us first transform $H_{FP}$ to its Hermitian basis:

$$H_h = e^{\beta V/2} H_{FP} e^{-\beta V/2} = \frac{2}{T} \sum_i \left[-\frac{T^2}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{8} \left(\frac{\partial V}{\partial q_i}\right)^2 - \frac{T}{4} \frac{\partial^2 V}{\partial q_i^2} \right]_{V_{eff}}$$  \hspace{1cm} (3.1)

Consider first a one-dimensional harmonic potential:

$$V = \frac{1}{2} a q^2 ; \quad H_{FP} = -\frac{d}{dq} \left[ T \frac{d}{dq} + a q \right]$$  \hspace{1cm} (3.2)

We have

$$H_h = e^{\beta V/2} H_{FP} e^{-\beta V/2} = \frac{2}{T} \left[-\frac{T^2}{2} \frac{d^2}{dq^2} + \frac{1}{2} \left(\frac{a}{2}\right)^2 q^2 - \frac{T}{4} a \right]$$  \hspace{1cm} (3.3)

Apart from the global factor $\frac{2}{T}$ we recognise the Hamiltonian of a Quantum oscillator with $\omega = |a|/2$, $\hbar = T$ and $\hbar \omega = Ta/2$. The eigenvalues are then $\hbar \omega (n + \frac{1}{2})$, that is:

$$\lambda = \frac{2}{T} \left[ \left(n + \frac{1}{2}\right) \frac{T |a|}{2} - \frac{T a}{4} \right] = \begin{cases} 0, & |a|, 2|a|, \ldots \text{ if } a > 0 \\ |a|, 2|a|, \ldots \text{ if } a < 0 \end{cases}$$  \hspace{1cm} (3.4)

As expected, the lowest eigenvalue is zero in the stable, and positive in the unstable case. The gap between eigenvalues is proportional to the curvature of the potential.

We can extend this result to the stationary point of any potential, using the fact that at low temperature only the neighborhood of the saddle points contribute. Developing $V_{eff}$ around a minimum, which we assume is in $q = 0$, and putting $\sqrt{T} \rightarrow x$ we have

$$V_{eff} = V_{eff}(0) \frac{q^2}{2} + V_{eff}(0) \frac{q^3}{6} + ...$$

$$= V_{eff}(0) \frac{x^2}{2} + V_{eff}(0) \sqrt{T} \frac{x^3}{6} + ...$$  \hspace{1cm} (3.5)

So that

$$H_h = 2 \left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \left(\frac{V''(0)}{2}\right)^2 x^2 - \frac{1}{4} V''(0) + \text{ subdominant} \right]$$  \hspace{1cm} (3.6)

The eigenvalues are given by with $V''(0)$ playing the role of $a$. 
Separation of timescales

The generalisation to many dimensions is straightforward. Since one has to develop the potential only to second order around a saddle, one can then go to the basis where the second derivative matrix is diagonal, and treat each mode as an independent oscillator. Every saddle point yields to this order an independent spectrum in the Fokker-Planck operator, but only local minima have zero eigenvalues. There is then exactly one zero-eigenvalue per minimum. If the calculation is done exactly, one finds that the degeneracy is lifted by a small amount inversely proportional to the passage times between states, in this case exponentially small in the inverse temperature. If there are \( p \) local minima, there are then \( p \) ‘almost zero’ eigenvalues \( \lambda_1, \ldots, \lambda_p \) with the associated escape times \( \lambda_1^{-1}, \ldots, \lambda_p^{-1} \) bounded by the smallest escape time \( t_{\text{pass}} = \min\{\lambda_1^{-1}, \ldots, \lambda_p^{-1}\} \).

Let us now turn to the eigenvectors corresponding to the ‘almost zero’ eigenvalues. The construction we have done above for eigenvalues can be completed to obtain (approximate) right and left eigenvectors. Close to a minimum, we expect the right eigenvector to correspond to a Gibbs distribution peaked around it. Similarly, we expect the left eigenvector to be essentially a constant. This is in fact the case, but the result is stronger, as it holds throughout the basin of attraction of each minimum. The situation is depicted in Fig. 3.1. For small temperatures, it is as if an infinitely high, thin wall would enclose each basin, within which the eigenvectors and eigenvalues are those of the isolated region. Eventually, the finite-temperature corrections which split the degeneracy of ‘almost zero’ eigenvalues, also mix the approximate eigenvectors localised in each basin.

3.1.2 General approach to metastability. Spectra, states and committor functions

It turns out that the low-temperature situation is just an instance of a very general scenario. Indeed, one can turn things around and use the existence of a gap in the spectrum to give a general and useful definition of metastability (Gaveau et al 1998; Bovier et al 2000) (see Biroli et al (2001), for an application to metastability in glasses). Consider an evolution operator having the lowest \( p \) eigenvalues \( \lambda_1, \ldots, \lambda_p \) whose real part is separated by a gap from the others \( \lambda_{p+1}, \lambda_{p+2}, \ldots \), (see Fig 3.2). There are two characteristic times \( t_{\text{pass}} = \min\{\lambda_1^{-1}, \ldots, \lambda_p^{-1}\} \) and \( t^* = \max\{\lambda_{p+1}^{-1}, \lambda_{p+2}^{-1}, \ldots\} \); they will be interpreted as the minimal time needed to escape a metastable state, and to equilibrate within a state, respectively. In the previous section \( t^* \) is of order one and \( t_{\text{pass}} \) is exponentially large in \( T \). At times of order \( t \gg t^* \), the dynamics projects completely to the space below the gap, but if \( t \ll t_{\text{pass}} \) there is still no time for discerning between different eigenvectors below the gap. Clearly, the operator \( \exp[-tH] \) for \( t^* \ll t \ll t_{\text{pass}} \) is essentially a projector onto the space ‘below the gap’ (up to terms of order \( \exp[-t\lambda_a] \), with \( a > p \)).

Within the same accuracy, it turns out that one can then find a basis of \( p \) right eigenvectors \( |P_a\rangle \) which are:

- positive: \( \langle q | P_a \rangle = \langle q | P_a \rangle \geq 0 \);
- almost stationary: \( H | P_a \rangle \sim 0 \quad \forall \ a = 1, \ldots, p \);
- normalised and not zero in non-overlapping regions of space.
Fig. 3.1 Low-temperature spectrum for a multi-valleyed potential $V$ (top), and the associated effective potential $V_{\text{eff}}$ (below). Only the minima of $V$ contribute with near-zero eigenvalues. The near-zero (in this case three-dimensional) subspace is spanned by right eigenfunctions that are essentially the equilibrium distribution in each basin, and left eigenfunctions (the committors) that are essentially constant within each basin. The places where committors take the value one half are the transition states.
As a consequence the $|P_a⟩$ vectors have all the good properties of metastable states: they are positive normalised distributions, non zero only on different regions of the configuration space and are stationary on time scales less than $t_{pass}$. The last property is related to the fact that one can also find a basis of $p$ almost-stationary ($⟨Q_a|H ∼ 0$) left eigenvectors $⟨Q_a|$. They satisfy the approximate orthogonality and normalisation conditions:

$$⟨Q_a|P_b⟩ ∼ δ_{ab}$$ (3.7)

One can also write approximately:

$$e^{-tH} ∼ ∑_a |P_a⟩⟨Q_a|$$ (3.8)

Note that neither $⟨Q_a|$ nor $|P_b⟩$ are exact eigenvectors ‘below the gap’, but linear combinations of them.

The $Q_a(q)$ are the committor functions [Bollhuis et al.; Du et al.] of the states, giving the probability that starting on a certain point $q$ the dynamics (again, in times $t^∗ ≪ t ≪ t_{pass}$) goes to the state $a$. This can be easily seen as follows: the probability of ending in a point $q'$ starting from a point $q$ is, at times of order $t^∗ ≪ t ≪ t_{pass}$

$$Probability ∼ ⟨q'|e^{-tH}|q⟩ ∼ ∑_i ⟨q'|P_a⟩⟨Q_a|q⟩$$ (3.9)

If the point $q'$ is well within the state ‘$a$’, then $P_a(q')$ is large and the other $P_b$ ($b ≠ a$) are small. There is only one non-zero term in this sum, and we conclude that the probability to fall in the state ‘$a$’ is proportional to $Q_a(q)$. Each $Q_a(q) = ⟨Q_a|q⟩$ is essentially one within the basin of attraction of the state $a$, and almost zero everywhere else. The places where the $Q_a(q) ∼ 1$ are called the transition states.

Given any observable $A$, we can calculate its average within the state ‘$a$’ as:

$$⟨A⟩_a = ⟨Q_a|A|P_a⟩$$ (3.10)

Again, the situation described above can be summarised by saying that for times $t^∗ ≪ t ≪ t_{pass}$ everything happens as if there is an infinite wall enclosing each basin of attraction. In the proof, as in the simple example of the previous subsection, the definition is unavoidably linked to the timescales ($t^*, t_{pass}$): if one considers really infinite times, before any other limit, then the distinction between states vanishes. In real life, this separation of timescales might be controlled by a parameter, or it might be just a more or less valid approximation. As an example of the former, consider an Ising ferromagnet of size $L$: the longest relaxation within a state is the time for a domain to grow to the size of the system $t^* ∼ L^2$. The longest overall time is the one needed to flip global magnetisation, which requires jumping the highest energy barrier $t_{pass} ∼ e^{cL^{d−1}}$. For large $L$, there is an ample regime $t^* ≪ t ≪ t_{pass}$ where there are two well-defined states. Many examples for which in fact this construction is the most interesting have no parameter that controls the separation of $t_{pass}$ and $t^*$: the time for relaxation within a metastable state, and the time for escaping it, are different but not infinitely so.
3.2 Transition currents

Given a state metastable state $|P⟩$ constructed as above, we can find the probability current ‘leaking’ from it directly. For example, in a Fokker-Planck case putting $P(q) = ⟨q|P⟩$:

$$J_i(q) \propto \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} + f_i \right) P(q)$$

(3.11)

Because every metastable state $P$ is a linear combinations of the exact eigenvectors $\psi_R^\alpha(q) = ⟨\psi_R^\alpha|q⟩$ with eigenvalue below the gap:

$$P(q) = \sum_{\alpha=1}^{p} c_\alpha \psi^R_\alpha(q)$$

(3.12)

the associated escape currents are (see Fig 3.3) linear combinations of currents obtained by acting on each of them

$$J^\alpha_i \equiv \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} + f_i \right) \psi^R_\alpha(q)$$

(3.13)
Separation of timescales

\[ T \frac{\partial}{\partial t} + \frac{\partial V}{\partial q} \]

\[ J_{AB}(q) \]
\[ J_{BC}(q) \]
\[ J_{CA}(q) \]

Fig. 3.3 Spectrum and escape currents. Acting with \( T \frac{\partial}{\partial t} + \frac{\partial V}{\partial q} \) on the eigenvectors 'below the gap', one obtains a basis for all the interstate currents.

If the stationary state has no current, then there are only \( p - 1 \) independent currents, rather than \( p \) of them.

In many physical situations, we have some idea of the reaction path followed by the current, but we do not know the intensity of such a current or the reaction rate. Let us derive a formula for the rate in terms of an unnormalised current distribution \( J(q) \). The only assumption we make is that the reaction time is slower then any other relaxation [Tailleur et al. 2004]. Suppose one has the current \( J \) escaping a metastable state in an overdamped Langevin problem \( P(q) \) with only conservative forces:

\[ J_i(q) \propto \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} \right) P(q) \quad \text{with} \quad P(q) = \sum_{\alpha=1}^{p} c_\alpha \psi^R_\alpha(q) \]  

(3.14)

and

\[ \int d^N q \psi^L_\alpha(q) \psi^R_\beta(q) = \delta_{\alpha \beta} = \int d^N q \, e^{\beta V} \psi^R_\alpha(q) \psi^R_\beta(q) \]  

(3.15)

The last equality in equation (3.15) is deduced from the relation between right and left eigenvectors (2.6). We first compute:

\[ \int d^N q \, e^{\beta V} \mathbf{J}^2 = \int d^N q \left\{ \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} \right) P \right\} e^{\beta V} \left\{ \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} \right) P \right\} \]

\[ = T \int d^N q \left\{ \left( T \frac{\partial}{\partial q_i} + \frac{\partial V}{\partial q_i} \right) P \right\} \frac{\partial}{\partial q_i} \left( e^{\beta V} P \right) \]

\[ = T \int d^N q \, P \, e^{\beta V} \left( H_F P \right) = \sum_{\alpha=1}^{p} \lambda_\alpha \psi^2_\alpha \]  

(3.16)

and similarly:
\[ \int d^N \eta \ e^{\beta V} \left( \text{div } J \right)^2 = \int d^N \eta (H_{FP} P) \ e^{\beta V} \ (H_{FP} P) = \sum_{\alpha=1} \lambda^2 \ e^{\beta \epsilon_\alpha}, \quad (3.17) \]

where we have used the eigenvalue equation and the normalisation \( \lambda_c^2 \). Let us now assume for simplicity there is only one metastable state, so that there are \( p = 2 \) eigenvalues ‘below the gap’. At large times \( t^* \ll t \ll t_{\text{pass}} \sim \lambda^{-1}_m \), only the first non-zero eigenvalue \( \lambda_m \) contributes to the sums, and we get:

\[ t_{\text{activ}} = \lambda^{-1}_m = \frac{\sum \lambda^2_c \ e^{\beta \epsilon_\alpha}}{\sum \lambda^2_c} = \frac{\int d^N \eta \ e^{\beta V} \ J^2}{T \int d^N \eta \ e^{\beta V} \ (\text{div } J)^2}. \quad (3.18) \]

Note that the normalisation of the current is irrelevant. This formula is valid on the assumption of separation of timescales, irrespective of its cause.

For the Kramers equation, a similar expression can be obtained in the same way, in terms of the reduced current \[1.12\]. A tedious but straightforward calculation yields (Tailleur et al. 2004):

\[ t_{\text{activ}} = \text{Re} \lambda^{-1}_m = \frac{\gamma \int d^N \eta d^N \rho \ e^{\beta E} \left[ \sum \ J_{\text{red}}^q (q, p) J_{\text{red}}^q (q', -p) \right]}{T \int d^N \eta d^N \rho \ e^{\beta E} \left[ \text{div}_{q, p} \left( J_{\text{red}}^q (q, p) \right) \text{div}_{q, p} \left( J_{\text{red}}^q (q', -p) \right) \right]} \quad (3.19) \]

note the sum in the numerator runs on coordinates and not on momenta. This formulas are useful because they do not depend on a global normalisation of the current.

### 3.2.1 Arrhenius formula

The Arrhenius expression for the activated passage at low temperatures case can be easily derived from the formula \(3.18\), using the fact that the numerator is dominated the neighbourhood of the barrier top, and the numerator by the neighbourhood of the bottom of the starting well. Let us show how this works for a one dimensional double well as in Fig. \[3.4\]. The current starts in the metastable state, is approximately constant, and falls in the stable state.

The divergence of the current \( J(q) \) of a state \( \psi^R(q) \) satisfies

\[ \text{div } J = H_{FP} \psi(q) = \lambda_m \psi(q) \quad (3.20) \]

where \( \lambda_m \) is the first non-zero eigenvalue. Now, we have seen that if \( \psi(q) \) is a metastable equilibrium distribution in the departure state, it is proportional there to the Gibbs-Boltzmann distribution in that basin, so that:

\[ \text{div } J \propto \psi(q) \propto e^{-\beta V} \quad (3.21) \]

up to a normalisation. The current in a point \( q \) within the metastable basin is then:

\[ J(q) = \int_{-\infty}^q dq' \text{div} J(q') = \int_{-\infty}^q dq' e^{-\beta V} \sim e^{-\beta V_{\text{min}}} \int_{-\infty}^q dq' e^{-\beta V_{\text{min}}} q'^{2/2} \quad (3.22) \]

where we have used a Gaussian approximation. Around the barrier, we get:

\[ J_{\text{barrier}} \sim \left( \frac{2\pi}{\beta V_{\text{min}}} \right)^{1/2} e^{-\beta V_{\text{min}}} \quad (3.23) \]
The denominator of (3.18) is dominated by the neighbourhood of the minimum:

$$\int_{\text{basin}} dq \, e^{\beta V} (\text{div} \, J)^2 \sim \int dq \, e^{-\beta V} \sim e^{-\beta V_{\text{min}}} \left( \frac{2\pi}{\beta V''_{\text{min}}} \right)^{1/2}$$  \hspace{1cm} (3.24)

The numerator in (3.18) becomes, using the fact that $J$ is essentially constant around the maximum

$$\int_{\text{barrier}} dq \, e^{\beta V} J^2 \sim J^2_{\text{barrier}} \int_{\text{barrier}} dq \, e^{\beta V} \sim e^{\beta V_{\text{Max}}} \left( \frac{2\pi}{\beta V''_{\text{Max}}} \right)^{1/2} J^2_{\text{barrier}}$$  \hspace{1cm} (3.25)

Putting numerator and denominator together, we get:

$$t_{\text{active}} = \lambda^{-1}_{\text{max}} = \frac{\int dq \, e^{\beta V} J^2}{T \int dq \, e^{\beta V} (\text{div} \, J)^2} \sim 2\pi \frac{e^{\beta (V_{\text{Max}} - V_{\text{min}})}}{\sqrt{|V''_{\text{Max}}V''_{\text{min}}|}}$$  \hspace{1cm} (3.26)

which is Arrhenius formula \cite{hanggi1990}, with the good prefactor. Note how simple the argument is, once we have (3.18).

### 3.3 Hydrodynamic Limit and Macroscopic Fluctuations

The Simple Symmetric Exclusion Process of Equations (1.24) and Figure 3.5 has a separation of timescales, this time brought about by a local conservation law (of particle number) rather than by barriers. Consider an $L$-site long, isolated chain, with average occupation one half. Suppose now that we make a vacancy of twenty contiguous unoccupied sites. For this to happen spontaneously is an extremely rare event ($\sim 2^{-20}$), and left on its own, the vacancy will be covered rapidly, in a time of order
one. On the other extreme, consider a slowly varying average density profile, say as a sinusoidal oscillation of length $L$. Such a fluctuation will take a time of order $L^2$ to die out.

This separation of timescales manifests itself in the stochastic evolution operator, which has eigenvalues of order 1 for the most steep and $L^{-2}$ for the smoothest spatial fluctuations, respectively.

We may now choose to study only the smooth fluctuations, corresponding to the lowest eigenvalues, see Spohn (1983), Bertini et al. (2001). To do this we introduce a parametrisation of space $x_k = \frac{k}{L}$ and rescale the time as $t \rightarrow L^2 t$. In the rescaled time, steep fluctuations disappear immediately. At the macroscopic level, the density profiles we consider are smooth functions and discrete gradients can be replaced by continuous ones:

$$\rho_{k+1} - \rho_k \rightarrow \nabla \rho(x_k), \quad \hat{\rho}_{k+1} - \hat{\rho}_k \rightarrow \nabla \hat{\rho}(x_k), \quad \frac{1}{L} \sum_{k=1}^{L-1} \rightarrow \int_0^1 dx \quad (3.27)$$

It can be shown that in terms of these variables, the evolution of the smooth density fluctuations is given by the stochastic equation, Spohn (1983)

$$\dot{\rho} = \frac{1}{2} \nabla^2 \rho + \nabla [\sqrt{\rho(1 - \rho)} \eta]; \quad \rho(0) = \rho_0; \quad \rho(1) = \rho_1 \quad (3.28)$$

where $\eta$ is a white noise of variance $1/(2L)$. This is the formula for the fluctuating hydrodynamics of the exclusion process, Spohn (1983).

Footnote 1: Note that $x$ here is an index labelling the field $\rho(x)$. Comparing with the examples in the first sections, we should make the correspondence $(q_i, i) \rightarrow (\rho(x), x)$.
We can now construct the action with the Martin-Siggia-Rose [Martin et al. 1973] formalism. Performing the usual steps as in section 1.3, introducing conjugate fields $\dot{\rho}(x,t)$, we get:

$$P(\rho^f, t_f; \rho^i, 0) = \int D[\rho] D[\dot{\rho}] e^{-2L \left\{ \int_0^{t_f} \int_0^1 dx dt (\dot{\rho} \dot{\rho} - \dot{\rho} - H) \right\}}$$

(3.29)

This time, $L^{-1}$ plays the role of temperature – or of $\hbar$, and we have the ‘classical’ Hamiltonian density:

$$\hat{H} = \frac{1}{2} \int dx \left[ \rho (1 - \rho) (\nabla \dot{\rho})^2 - \nabla \dot{\rho} \nabla \rho \right]$$

(3.30)

The paths are constrained to be $\rho_i(x)$ and $\rho_f(x)$ at initial and final times, respectively. The values of $\dot{\rho}$ are unconstrained, which is in agreement with the fact that this is a Hamiltonian problem with two sets of boundary conditions.

The message of this section is that we may transfer all the ‘semiclassical’ low-noise (small $T$) techniques to the coarse-grained limit to obtain a ‘Macroscopic Fluctuation Theory’ [Bertini et al. 2001; Jordan et al. 2004].
4
Large Deviations

In equilibrium statistical mechanics we are given the probability of being in any particular configuration. For a dynamical system, we may wish to ask similar questions concerning histories, rather than configurations: what is the probability that the system visits a sequence of configurations at given times, or that during a time-interval its average energy has a given value, and so on. Often these events are rare, their probability is small. In spite of this they may be important: for example, what is interesting in chemistry are reactions that are slow compared to thermal vibrations. In this section we shall study two types of large deviations: those that are rare because they are induced by (weak) noise, and those that are rare because they are sustained for a long time. Technically, this provides us with two small parameters: noise intensity and inverse time-span, respectively.

4.1 Climbing to unusual heights

We now study the probability of finding the system in unusual configurations. The formalism is essentially the WKB theory for semiclassical quantum mechanics, mathematicians know it as the Freidlin-Wentzell (Freidlin et al. 1984) formalism. For simplicity, the discussion in this section will be for the overdamped case, but one can do the same for any other stochastic equation.

In the small-noise limit, whichever its origin (low temperature, hydrodynamic limit), the equations of motion are essentially deterministic. If we ask for the probability $P(q_0, t_0 \rightarrow q, t)$ of the system meeting an appointment at time $t$ in $q_i$ given that it started in $q_0$ at time $t_0$ we may get two sorts of answers:

i) Essentially one if a deterministic path precisely passes by the given points at the given times.

ii) Exponentially small $\sim e^{-\mathcal{F}(q,t)}$ otherwise: only thanks to the noise the system can get out of its deterministic schedule in order meet the appointment (this includes being in the right place at the wrong time). In order to calculate probabilities, we go back to the path-integral expression

$$P(q_0, t_0 \rightarrow q, t) = \int D[q, \dot{q}] e^{\frac{1}{\hbar} \int dt \left( \sum_i \dot{q}_i \frac{\partial V}{\partial q_i} + f_i \right)}$$

As we mentioned in section 1, this is an imaginary-time path-integral with the 'classical' Hamiltonian

$$\hat{H} = - \sum_i \dot{q}_i \left( \dot{q}_i + \frac{\partial V}{\partial q_i} + f_i \right)$$

The path integral is dominated by the extremal trajectories, which satisfy Hamilton's equations:
Large Deviations

\[
\begin{aligned}
\dot{q}_i &= \frac{\partial H}{\partial \dot{q}_i} = - \left( \dot{q}_i + \frac{\partial V}{\partial q_i} + f_i \right) - \dot{q}_i \\
\dot{\hat{q}}_i &= -\frac{\partial H}{\partial q_i} = \sum_j \left( \frac{\partial^2 V}{\partial q_j \partial q_i} \right) \dot{\hat{q}}_j + \frac{\partial f_j}{\partial q_i} \dot{\hat{q}}_j
\end{aligned}
\]  
(4.3)

The probability now takes the large deviation form:

\[
\ln \{ P(q_o, t_o \to q, t) \} = - \frac{1}{T} F_i = - \frac{1}{T} \text{Action} \tag{4.4}
\]

which defines the large deviation function \( F_i(q) \). The action is the integral

\[
\text{Action} = - \int dt \left[ \sum_i \dot{\hat{q}}_i \dot{q}_i - \hat{H}(q, \dot{q}) \right] \tag{4.5}
\]

with \((q, \dot{q})\) solution of (4.3).

Noiseless solution.

A family of solutions of (4.3) can be easily found:

\[
\dot{q}_i = 0 \quad ; \quad \dot{\hat{q}}_i = - \frac{\partial V}{\partial q_i} - f_i \tag{4.6}
\]

The dynamics of the original (hat-less) variables is just the noiseless equation of motion (1.3). The action is zero, as can be easily checked: this means that the large deviation function will be also zero – in fact, its smallest value.

Other solutions.

Other solutions of (4.3) can be found with \( \hat{q}_i \neq 0 \). They do not correspond to motion in the original force field (1.3), signalling the fact that noise is playing an important role. The action is positive, a fact that can be best appreciated in the Lagrangian formalism (1.54). The large deviation function is now positive, and the probability is exponentially suppressed in \( 1/T \), again an indication that noise is playing a role.

Large times

In most cases, we are interested in the long time limit \( F_i \) at large times:

\[
e^{-\Phi F(q)} = \lim_{t \to \infty} P(q_o, t_o \to q, t) \tag{4.7}
\]

or, otherwise stated, in the probability of finding a stationary system in a configuration \( q \). The corresponding large-time deviation function (which we shall denote simply as \( \Phi \)) becomes independent of the initial condition. How can this be?

Consider first a quadratic potential \( V = \frac{1}{2} q^2 \) in one dimension, as in Fig. 4.1. The Hamiltonian is \( \hat{H} = -\dot{q}(\dot{q} + q) \). The ‘classical’ trajectories are given by:

\[
\begin{aligned}
\dot{q} &= -2\ddot{q} + q \\
\dot{\ddot{q}} &= \dot{q}
\end{aligned}
\]  
(4.8)

The solution with \( \dot{q}(t) = 0 \) corresponds to the relaxation to the minimum. If we now start at time \( t_o \) at, say, \( q = 1 \) and ask that at time \( t > t_o \) we be at \( q = -1 \), we have...
Climbing to unusual heights

Fig. 4.1 The \((q, \dot{q})\) space for a Langevin process in a one-dimensional quadratic potential. The incoming straight lines indicate the noiseless ‘downhill’ trajectories, the outgoing straight lines the ‘uphill’ trajectories. Curved trajectories missing the origin are relevant for finite-time large deviations.

\[
V = \frac{1}{2}q^2, \quad \dot{H} = -\dot{\dot{q}}(\dot{q} + q)
\]

to take one of the trajectories with \(\dot{q} > 0\); the one that arrives in \(q = -1\) at the right time. If we now consider very large times \(t\), the solution will be one that passes close to the (hyperbolic) point \((q = 0, \dot{q} = 0)\), in the vicinity of which it will spend a long time. In the limit \(t \to \infty\), the trajectory is the succession of a gradient descent into the origin, and an ‘uphill’ trajectory emerging from the origin. Similarly, the trajectory that starts in \(q = 1\) and ends at large times at \(q = +2\) is composed of a gradient descent towards the left, followed by an uphill motion to the right – the limit of a \(\dot{q} < 0\) ‘bounce’.

In conclusion, in order to calculate the stationary large-deviation function we have to consider the ‘downhill’ trajectory (the anti-instanton) with \(\dot{q} = 0\) from the initial to the stationary point, followed by an ‘uphill’ (instanton) trajectory from the stationary point to the final point. The large deviation function is the sum of the downhill and the uphill actions. As mentioned above, the former is zero: When calculating the probability of reaching a configuration at large times, we may consider that we started from a stationary point - a physically intuitive result since in a short time at the
Fig. 4.2 Trajectories in \((q, \dot{q})\) space for a double-well potential.

beginning the system goes from initial to stationary configuration.

We need the ‘uphill’, instanton trajectories to calculate, via their action, the probability of a rare configuration. For generic dynamics this is hard problem to solve analytically, and even numerically.

4.1.1 Detailed balance and Onsager-Machlup symmetry

As we saw in section 2, if there is detailed balance, and given that one trajectory dominates for the downhill process, we should expect the time-reversed trajectory to dominate for the uphill process. Let us check this explicitly for a multidimensional system with a potential \(V\) and no forcing \(f_i = 0\). We propose, as partial solution of (4.3)

\[
\dot{q}_i = + \frac{\partial V}{\partial q_i}
\]  

(4.9)

Inserting in the first of (4.3), this implies \(\dot{q}_i = - \frac{\partial V}{\partial q_i}\) which, when replaced in the second of (4.3) gives:

\[
\dot{\dot{q}}_i = \sum_j \frac{\partial^2 V}{\partial q_j \partial q_i} \dot{q}_j
\]  

(4.10)
Replacing \( \dot{q}_i = -\frac{\partial V}{\partial q_i} \) in this equation, and using

\[
\frac{d}{dt} \left( -\frac{\partial V}{\partial q_i} \right) = -\sum_j \frac{\partial^2 V}{\partial q_i \partial q_j} \dot{q}_j
\]

we obtain an identity. We conclude that the time-reversed dependence \([4.9]\) is indeed a solution. We may compute the action of the uphill trajectory, which turns out to depend exclusively on the initial and final potentials:

\[
\text{action} = \int dt \sum_i \dot{q}_i \dot{q}_i - \frac{\dot{q}_i}{\partial q_i} + \int dt \sum_i \dot{q}_i \left( \dot{q}_i + \frac{\partial V}{\partial q_i} \right)_{=0} = \int dt \frac{dV}{dt} = V(q) - V(q_{\text{min}})
\]

in accordance with the general situation with detailed balance discussed in Section 2.1. Up to a multiplicative constant, this implies via \([4.4]\) that the stationary probability is the Gibbs-Boltzmann weight, as expected.

On the other hand, repeating the calculation in the case in which there is a generic force term \( f_i \), we get that the second of \([4.3]\) is satisfied by the time-reversed trajectory if:

\[
\sum_j \left( \frac{\partial f_i}{\partial q_j} - \frac{\partial f_j}{\partial q_i} \right) f_j = 0,
\]

which is in general not true. Hence, we reach the important conclusion that in the presence of forces that do not derive from a potential, relaxations into and excursions out of the stationary state are not the time-reversed of one another. Furthermore, we have to calculate the action on the basis of the explicit solution, and this it is no longer miraculously given exclusively in terms of the initial and final configurations.

### 4.1.2 The Arrhenius Law again

In the preceding paragraphs we have assumed that in order to reach the final configuration, only one downhill and one uphill trajectory suffice. This is clearly the case when there is only one stable state. In the presence of metastability, the trajectory may be a sequence of downhill and uphill segments.

For example, in the case of a double-well potential, the passage probability (the Arrhenius law) can be obtained as the probability of falling onto a stable point, then climbing up to an unstable point, and then descending to the next saddle, as in figure 4.2. The probability of descents being of order unity, we are only left with the uphill path. Again, if the system derives from a potential, the probability of climbing depends only on the difference in height between valley and saddle, and we recover the Arrhenius law calculated in previous sections \([3.26]\). In the presence of non-conservative forces, then the path joining stable and unstable saddles has to be computed, and from its action we get the probability.

1 Note that time reversal applies to the \( q \), and not the \( \dot{q} \) variables
In many dimensional energy landscapes, one may wonder if the most probable path still goes through saddles with only one unstable direction. A moment’s thought shows this to be the case, as discussed by Murrel and Laidler (Murrel et al. 1968).

4.1.3 Low noise in phase-space: Kramers and thermostatted.

Let us mention briefly how one proceeds in the case of phase-space dynamics with noise. One obtains by following the same steps as in the previous paragraph, ‘classical’ equations in an extended space \((q_i, p_i, \dot{q}_i, \dot{p}_i)\). There are solutions of these equations that have \(\dot{q}_i = \dot{p}_i = 0\): they correspond to the original noiseless equations in the original space and have zero action. The rest of the solutions have non-zero \((\dot{q}_i, \dot{p}_i)\) and positive action.

In some cases, one may go to a ‘Lagrangian’² description involving only \((q_i, p_i)\), but then the equations obtained contain second time-derivatives, a relic of the noise in the original phase-space.

²Note that \((q, p)\) are the ‘coordinates’, and \((\dot{q}, \dot{p})\) the ‘momenta’ in the 4N-dimensional phase-space.
Climbing to unusual heights

Periodic orbits, complexities and traces

Classical Mechanics

What follows is very sketchy, its only purpose is to stimulate the curiosity of the reader, who will find an excellent reference on the subject (Cvitanovic). As we have seen in the previous sections, the spectrum of an evolution operator contains all the information on the ergodic properties of the system. One way to study the spectrum of any operator $H$ is to compute the trace $\text{Tr} e^{-tH}$, and then obtain the resolvent, which has poles in the eigenvalues $\lambda$ of $H$, through

$$
\sum_i \frac{1}{\lambda - \lambda_i} = \text{Tr}[\lambda - H]^{-1} = \int_0^\infty dt \ \text{Tr} e^{-t(\lambda - H)} \tag{4.13}
$$

The trace on the right hand side is a sum over paths just as seen in the previous sections, the only difference is that we are to consider closed trajectories in which initial and final configurations coincide. For an evolution taking place in phase-space $(q, p)$, it is an integral of probabilities of return after time $t$

$$
\text{Tr} e^{-tH} \sim \int dq \ dp \ P(q, p, t; q, p, t = 0).
$$

As mentioned in section 2, one can study the chaoticity properties of Hamiltonian dynamics by studying the spectrum of its evolution operator in the presence of noise, and then letting the noise level go to zero: one thus uncovers Ruelle-Pollicott resonances. This poses the problem that noise will make energy nonconserved, and generate a slow diffusion in energy. To avoid this, we may use the energy-conserving noise of the Gaussian thermostat in section 1, leading to $H_G$:

$$
H_G = \sum_i \left[ \frac{p_i}{m} \frac{\partial}{\partial q_i} - \frac{\partial V(q)}{\partial q_i} \frac{\partial}{\partial p_i} \right] - \epsilon \sum_{ji} \left[ \frac{\partial}{\partial p_j} g_{ji} \frac{\partial}{\partial p_i} \right] \tag{4.14}
$$

cfr. Eq. (1.15) with $f = 0$.

A trace in the path integral becomes then a sum of periodic orbits on the energy shell. In the small-noise limit those that dominate are the ones having zero action, and these are just the periodic orbits of the original Hamilton’s equations. One thus expresses $\text{Tr} e^{-tH_G}$ as a sum over orbits of period $t$.

The final product is that Equation (4.13) becomes a relation between the resolvent, containing the information on eigenvalues, and a sum of periodic orbits of all periods. The interested reader will find this properly done in (Cvitanovic).

Complexity in Statistical Mechanics

A different application of the same idea (Biroli et al. (2001)) is to count the number of metastable states. With the assumptions of section 3.1, picking a time $t$ intermediate between the time needed to equilibrate within a state $t^*$ , and the time needed to escape it $t_{pass}$, the number of states is given by

$$
N_{\text{states}} \equiv \text{Tr} e^{-tH} \text{ with } t^* \ll t \ll t_{pass}. \tag{4.13}
$$

This becomes a sum over all periodic trajectories of period $t$. 

Climbing to unusual heights
Large Deviations

Sampling transition paths in practice

A problem of great interest in physics and chemistry is the one of computing in practice the escape route (and rate) from a metastable state, for example the decay rate of a metastable molecule. In many cases we have a separation of timescales between molecular vibration and the time needed for the actual decay to occur. In order to compute the probability $P(a, t; b, t_o)$ of starting at $t_o$ in a configuration $a$ belonging to the metastable state and reaching a configuration $b$ belonging to the stable state at time $t$, we may sum over paths going from $a$ to $b$, with their appropriate weight given by the action.

Depending on the dynamics, different approaches are more practical. In the case of a system that is strongly coupled to a thermal bath, and follows a Langevin equation, one can follow the Lagrangian ‘polymer’ analogy, and use any Monte Carlo simulation method for a system in equilibrium at temperature $T$ to sample the paths.

For a system that is closer to being deterministic, a well-developed technique (TPS: ‘Transition Path Sampling’) uses an algorithm that samples trajectories by modifying them slightly at the barrier. This kind of change allows to obtain a new path that still has good chances of being a transition (going from state $a$ to state $b$), at least if the system is not too chaotic.

There is a large body of literature on the subject (see e.g. [Bolhuis et al. 2002; Micheletti et al. 2004]) since the potential applications in chemistry, biochemistry and physics are huge.

4.2 Unusual time averages

In this section we study a different type of large deviation. Instead of asking for the probability of the system reaching an unusual place, we ask for the probability that it sustains an unusual time-average for an observable during a long interval:

$$\frac{1}{t} \int_0^t dt' A(t') = \overline{A}$$  \hspace{1cm} (4.15)

The most celebrated example is the average power, which can be interpreted in some cases as entropy production:

$$\sigma_t = -\frac{1}{t} \int_0^t dt' \frac{\mathbf{f} \cdot \mathbf{v}}{T}$$  \hspace{1cm} (4.16)

where $\mathbf{v} = \dot{q}$ Another example is the average potential energy

$$\mathbf{V} = \frac{1}{t} \int_0^t dt' V(t')$$  \hspace{1cm} (4.17)

Expressing the probability in terms of trajectories:

$$P(A) = \sum_{\text{Trajec.}} \left( \text{Prob. Trajectory} \right) \delta \left( t\overline{A} - \int_0^t dt' A(t') \right)$$  \hspace{1cm} (4.18)
unusual time averages

writing the delta function as an exponential

\[ \delta \left( tA - \int_o^t dt' A(t') \right) = \int_{-i\infty}^{+i\infty} d\mu e^{\mu \left( tA - \int_o^t dt' A(t') \right)} \]  

we get:

\[ P(A) = \int_{-i\infty}^{+i\infty} d\mu e^{\mu tA} \left( \text{Prob. Trajectory} \right) e^{-\mu \int_o^t dt' A(t')} \]

\[ = \int_{-i\infty}^{+i\infty} d\mu e^{\mu tA} e^{-tG(\mu)} \]

which defines the large-deviation function \( G(\mu) \). For example, in the Fokker-Planck case, it reads:

\[ e^{-tG(\mu)} = \int D[q, \hat{q}] e^{\frac{1}{t} \int dt' \left[ \sum_i \dot{q}_i \dot{\hat{q}}_i - H_{FP} + \mu \int_o^t dt' A(t') \right]} \]

What we have done is nothing but the analogue of a passage from a microcanonical calculation of ‘entropy’ = \( \ln A \), to a canonical calculation of ‘free energy’ \( G(\mu)/\mu \) at ‘inverse temperature’ \( \mu \). The ‘space’ in our problem is in fact the time, and ‘extensive quantities’ are those that are proportional to time: we extracted a time in the definition of \( G(\mu) \) in order to make it ‘intensive’. For large \( t \), in analogy with the thermodynamic limit, assuming that \( G(\mu) \) has a good limit, we may evaluate the integral over \( \mu \) by saddle point, to obtain:

\[ \ln P(A) \sim t[\mu^* A - G(\mu^*)] \]

with

\[ A(\mu^*) = \frac{dG}{d\mu} \bigg|_{\mu^*} \]

This is the Legendre transform taking from canonical to microcanonical. Note that \( A(\mu^*) \) plays the role of \( E(\beta) \) in ordinary thermodynamic systems. Now, by simple comparison, equation (4.21) can be brought back to operator language:

\[ e^{-tG(\mu)} = \langle \text{final} | e^{-t(H_{FP} + \mu A(q))} | \text{init} \rangle \]

A similar expression holds for Kramers equation \( H_K \). In the language of the analogy with one-dimensional models, this is just the transfer matrix formalism \( \text{Huang 1987} \), along the time-dimension. If we now introduce the right and left eigenvectors of \( H + \mu A \):

\[ [H + \mu A(q)] \{ \psi^R_i(\mu) \} = \lambda_i(\mu) \{ \psi^R_i(\mu) \} \quad ; \quad \langle \{ \psi^L_i(\mu) \} [H + \mu A(q)] = \lambda_i(\mu) \langle \{ \psi^L_i(\mu) \} \]

we obtain:

\[ e^{-tG(\mu)} = \sum_a \langle \text{final} | \psi^R_a(\mu) \rangle \langle \psi^L_a(\mu) | \text{init} \rangle e^{-t\lambda_a(\mu)} \]

and, as \( t \to \infty \):

\[ G(\mu) = \lambda_{\min}(\mu) \]

where \( \lambda_{\min}(\mu) \) is the eigenvalue with the smallest real part. Again, this is in complete analogy with the expression of free-energy densities in terms of the transfer-matrix lowest eigenvalue.
Note the fundamental difference between this large-deviation functions and those of section 4.1: in that case by ‘large’ deviations we meant that they are exponentially small in the temperature (or the coarse-graining size) while here we mean that they are sustained for long times, and the only large parameter is precisely the time $t$.

4.3 Simulating large deviations (and Quantum Mechanics)

Large deviations can be measured by evolving the system with its real dynamics, and then making a histogram of the deviations obtained. However, equation (4.24) suggests that we try to simulate directly a system that evolves through $H_{FP} + \mu A$ (Giardina et al 2006; Aldous 1994):

$$\dot{P} = -[H_{FP} + \mu A]P \rightarrow P(q, t) = e^{-t[H_{FP} + \mu A]}$$ (4.28)

Clearly, as $t \rightarrow \infty$ the distribution $P$ tends to the eigenvalue with the lowest real part.

We are dealing with a dynamics without probability conservation. In fact, we can reproduce it by using a large number of non-interacting walkers, each performing the original (Langevin) dynamics with independent noises, occasionally giving birth to another walker starting in the same place, or dying. A negative (positive) value of $\mu A(q)$ gives a probability $|\mu A(q)|dt$ of making a clone or of dying, respectively, in a time-interval $dt$. At each time, the global number of clones $M(t)$ changes, in such a way that for long times $M(t)/M(t = 0) \sim e^{-\lambda_{\text{min}}(\mu)t}$. In practice, one can normalise the total number periodically by cloning or decimating all walkers with a random factor. The factor needed to keep the population constant is, again, the exponential of the lowest eigenvalue.

Notice that imaginary-time Shrödinger equation is precisely of the form (4.28), with no drift in the Langevin process and $\mu A$ the quantum potential. Indeed, the method described above was developed for precisely this case, and is called ‘Diffusion Monte Carlo’ (DMC) (Grimm et al).
5

Metastability and dynamical phase transitions

In several places above we have pointed out that the stochastic dynamics can be seen as a kind of ‘thermodynamics in space-time’. Trajectories contribute with a weight given by the (Onsager-Machlup) action, much as energy determines the Gibbs-Boltzmann weight in thermodynamics. Large deviation theory just consists of biasing the measure with an extra weight added to the dynamic action and computing the new sum, which then loses the meaning of a transition probability and becomes a large-deviation function.

Systems with non-trivial dynamical properties sometimes show very little in their static (time-independent) structure. The typical example is that of glasses, which are virtually indistinguishable from liquids from the point of view of organisation of the molecules, until one looks at their dynamics, which is dramatically slower. This situation has motivated some researchers (Jack et al. 2006) to look into space-time thermodynamics - the statistical properties of trajectories - for the missing structure. One considers the large deviation theory of systems that are dynamically non-trivial, and indeed it turns out that one often finds (Garrahan 2007) that there is a rich structure of ‘dynamic’ phase transitions in the large-deviation functions.

In this section we shall see that space-time transitions are closely related to the approach to metastability of section 3, to which they provide useful insights.

5.1 A simple example

Let us start by a simple example of a particle in a potential $V$ performing overdamped Langevin motion at low temperature $T$ (see Fig. 5.1). We shall consider the large deviation function of energy $G(\mu)$, associated with the probability of observing an average energy $\bar{V}$ (4.17) over long time-intervals. As we saw in the previous section, $G(\mu)$ is obtained from the lowest eigenvalue of $H_{FP} - \mu V$.

$$H_{FP} + \mu V = \frac{2}{T} \left[ -T \frac{d^2}{dx^2} + \frac{V'^2}{8} - \frac{T}{4} V'' + \frac{\mu}{2} TV \right]$$

(see Benzi et al. 1985 for a similar application). The lowest eigenvalue at low temperatures is given by the same developments as in section 3.1.1, only that now we have to add the extra term proportional to $\mu$ in (5.1). At small $T$ each minimum in the effective potential
Fig. 5.1 Left: the potential $V$ and the related effective potential $V_{eff}$. Right: energy (horizontal lines) and the associated large-deviation function $G(\mu)$. The system has two first order transitions at $\mu = 0$ and at $\mu = -(V_s - V_r)/|V_s''|$

\[
V_{eff}(\mu) = \frac{V''^2}{8} - \frac{T}{4}V'' + \frac{\mu}{2}TV
\]  

(5.2)

contributes separately, just as in section 3.1.1. To leading order in $T$ the contribution of saddles point of $V(q^*)$ at $q^*$ is $\lambda \sim \mu V(q^*)$ if it is a minimum, and $\lambda \sim |V''(q^*)| + \mu V(q^*)$ if it is a maximum. The lowest amongst all eigenvalues dominates:

\[
G(\mu) = \lambda_{\text{min}} = \min \begin{cases} 
\lambda_L = \mu V_L \\
\lambda_R = \mu V_R \\
\lambda_S = |V_S''| + \mu V_S 
\end{cases}
\]  

(5.3)

The values of $\tilde{V}$ are given by the Legendre transform $V(\mu^*) = \frac{dG}{d\mu}$, and read:

\[
V(\mu^*) = \begin{cases} 
V_L & \mu^* > 0 \\
V_R & \mu^* < 0 \text{ and } \mu^* > -|V_s''|/(V_s - V_r) \\
V_S & \mu^* < -|V_s''|/(V_s - V_r) 
\end{cases}
\]  

(5.4)

there are two first order phase-transitions, see Fig. 5.1

Let us pause and analyse this physically. The scenario is typical first order, with three homogeneous 'phases' in time, corresponding to the three values of Equation 5.4. When we condition a long trajectory to having a time-averaged energy $V_o$, this is realised by the system by making a 'phase coexistence' of periods $t_L, t_S, t_R$ spent in each of the three stationary points, such that $t = t_L + t_S + t_R$ and $V_o t = $
V_L t_L + V_S t_S + V_R t_R. This is strictly analogous to the ice/water coexistence when the total energy is fixed. An important lesson is that if the system is conditioned to having a value of an observable intermediate between that which it takes in two metastable phases, it prefers to achieve this by spending some time in each state, rather than all the time in an intermediate situation.

5.2 Spectral properties and phase transitions

One can in fact show that the situation we have seen above is very general. In particular, it is quite normal that we should have a first order transition at \( \mu = 0 \). To see this, let us use the formalism of section 3. Consider the operator \( H \). If there are \( p \) independent long-lived states, with eigenvalues \( \lambda_a < t_{\text{pass}}^{-1} \sim 0 \), and a time \( t^* \) to thermalise inside a state, we can construct a basis of \( p \) right and left eigenvectors \( P_a, Q_a \), with \( \langle Q_a | P_b \rangle \sim \delta_{ab} \) having essentially zero eigenvalue.

Let us now calculate the eigenvalues of \( H + \mu A \), for small \( \mu \), but still \( \mu \gg t_{\text{pass}}^{-1} \). We may use (non-Hermitian) first order perturbation theory, to get:

\[
\lambda_a \sim \lambda_a(\mu = 0) + \mu \langle Q_a | A | P_a \rangle \sim \mu \langle A \rangle_{\text{in state } a}
\]

(5.5)

In other words, the quasidegenerate eigenvalues split proportionally to the expectation value of the observable \( A \) in each state, and the phase that dominates is

\[
G_\mu = \min_{\text{states } a} \{ \langle A \rangle_a \}
\]

(5.6)

Remarkably, the distribution function has in fact pinned down a ‘pure state’ \( P_a, Q_a \), using the observable \( A \). When the sign of \( \mu \) is reversed, the ‘minimum’ in equation (5.6) is transformed into a ‘maximum’ and the selected state is changes. There is hence always a first order phase transition. Playing with a different observable, we may make a different transition that selects any state. Hence, we conclude that the dynamic phase transition approach is in fact equivalent to the metastability one of that of section 3, but it gives us new tools and a practical perspectives.
6
Fluctuation Theorems and Jarzynski equality

Nonequilibrium work relations, the Fluctuation Theorem [Evans et al. 1993, Evans et al. 1994, Gallavotti et al. 1995], and Jarzynski’s [Jarzynski 1997] equality, are very general results valid for strongly out of equilibrium systems. They concern the large deviations of work. As such they are closely related to – and enrich our perspective of – the second Law of thermodynamics. The two subjects are quite similar, and in fact may in some cases be encompassed into a single, more general result: Crooks’s equality [Crooks 1998], which we shall not review here. These results are very recent – surprisingly so, given their technical simplicity, and have received in the last fifteen years enormous attention. They are both based on the relation (section 2.3) between time-reversal symmetry breaking on one side, and work and entropy on the other.

6.1 The fluctuation theorem(s)

We shall consider here only Langevin processes with inertia, and the Kramers equation. This makes the discussion simpler, because of the fact mentioned in previous sections that power, being a product of force times a velocity, is only a continuous function of time when there is inertia.

We have seen in section 2.3 that the ‘time-reversal’ symmetry becomes, in the presence of forcing:

\[
\Pi e^{\beta H} H_K e^{-\beta H} \Pi^{-1} = H_K^1 + \frac{d(t_{\sigma_1})}{dt} \int_0^t (t') f \cdot v.
\]

Equation (6.1) is the basis for the results we shall discuss. In fact, there are several variants of time reversal, and each gives different identities [Chetrite et al. 2008].
The fluctuation theorem(s)

**General: the implications of an explicitly broken symmetry in statistical mechanics.**

The fluctuation theorem makes use of the explicit breaking of a discrete symmetry, the detailed balance relation. In fact, whenever we have a system composed of a part that is symmetric under a transformation, plus an anti-symmetric perturbation, we can derive a relation for the large deviation of the perturbations. Consider for example the statistical mechanics of a system with variables $s_1,...,s_N$ and energy $E_o$, having the discrete symmetry $E_o(s) = E_o(-s)$. This symmetry implies the vanishing of all odd correlation spin functions. Now, let us perturb the energy with a field $E(s) = E_o(s) - \frac{h}{2} M(s)$, conjugate to a term $M(s) = \sum_i s_i$ with $M(-s) = -M(s)$, so that now

$$E(-s) = E(s) + hM(s) \quad (6.3)$$

Can we conclude something in the presence of $h \neq 0$, when the symmetry is explicitly broken? Indeed, we can: consider the distribution of the symmetry-breaking term

$$P[M(s) = -M] = \int ds \, \delta[M(s) + M] \, e^{-\beta(E_o - \frac{h}{2} M)} \quad (6.4)$$

Changing variables $s \rightarrow -s$, and using the symmetry of $E_o$:

$$P[M(s) = -M] = \int ds \, \delta[-M(s) + M] \, e^{-\beta(E_o + \frac{h}{2} M)} = e^{-\beta h M} P[M(s) = M] \quad (6.5)$$

or

$$\frac{P[M(s) = M]}{P[M(s) = -M]} = e^{\beta h M} \quad (6.6)$$

One wonders if this elementary property has ever been used in other fields of physics before the fluctuation theorem. On the other hand, a derivation of the Fluctuation theorem that makes close contact with this thermodynamic property has been given by Narayan and Dhar (Narayan *et al.* 2004).

The fluctuation theorem is a statement about the distribution $P(\sigma_t)$ of the average quantity $\langle 6.2 \rangle$, when the experimental protocol is repeated many times. It reads:

$$\frac{P(\sigma_t)}{P(-\sigma_t)} \sim e^{t\sigma_t} \quad (6.7)$$

A relation like this was first proposed by Evans, Cohen and Morriss (Evans *et al.* 1993).

The second Law of Thermodynamics states that the work done on a system over long times must be positive. Equation (6.7) is then a statement about the ‘violations’ of the Second Law, when the average work has the opposite sign. The factor $t$ in

---

$^1$The quotation marks are just to remember that since the Second Law applies to the limit of long times $tN \rightarrow \infty$ for a single-instance experiment, these are no true violations.
the exponent to a certain extent quantifies the supression of the probability of such processes when the time is large, thus giving a better perspective of the Second Law.

Equation (6.7) can be reexpressed multiplying by $e^{-\mu \sigma_t}$ and integrating over $\sigma_t$ as a property of the large-deviation function $G(\mu) = \frac{1}{\tau} \int d\sigma_t P(\sigma_t)e^{-\mu \sigma_t}$:

$$G(\mu) = G(1 - \mu) \quad (6.8)$$

The result (6.7)-(6.8) is extremely general (Evans et al. 1993; Gallavotti et al. 1995; Kurchan 1998; Lebowitz et al. 1999), independent on the model’s parameters, and valid for several types of dynamics. Two different settings have to be distinguished:

- **Transient:** Each measurement of $\sigma_t$ is made starting from a thermalised system at temperature $T$, a configuration chosen with the Gibbs-Boltzmann distribution. At time $t = 0$, non-conservative forces are switched on, $\sigma_t$ is proportional to the work they make during a time $t$, which need not be long. The system may be isolated or connected to a thermostat, which then has to be at the same temperature $T$.

- **Stationary:** Here, the sampling is of a system that by assumption has achieved stationarity in the presence of forcing. For this to be possible it needs a thermostat to absorb heat. The system is not in equilibrium, and the fluctuation relation is valid only in the limit of long sampling periods $t \to \infty$.

Another distinction we can make is whether the dynamics is stochastic (e.g. Langevin) or deterministic (the Gaussian thermostat without energy-conserving noise). The only hard case is the stationary and deterministic one, the Gallavotti-Cohen (Gallavotti et al. 1995) theorem. It is not only technically more subtle, but it relies on a real physical condition that the system has to meet, as we shall see.

### 6.1.1 Transient, with or without bath

Equation (2.24) can be rewritten, for all $\mu$ (for the moment an arbitrary number):

$$\left[ H_K - \frac{f \cdot v}{T} \right] = \langle \Pi e^{\beta H} \rangle \left[ H_K - \left( 1 - \mu \right) \frac{f \cdot v}{T} \right] (e^{-\beta N} \Pi^{-1}) \quad (6.9)$$

Using the expression (4.24) for the large deviation function, starting from the Gibbs-Boltzmann distribution $|GB\rangle$, we compute:

$$e^{-t G(\mu)} = \langle - | e^{-t [H_K - \frac{f \cdot v}{T}]} | GB \rangle = \langle GB | e^{-t [H_K - \frac{f \cdot v}{T}]} | - \rangle$$

$$= \langle - | e^{-\beta N} e^{-t [H_K - \frac{f \cdot v}{T}]} e^{\beta H} | GB \rangle$$

$$= \langle - | \Pi e^{-t \left[ H_K + \frac{(1 - \mu) f \cdot p}{\tau} \right] \Pi^{-1} | GB \rangle$$

$$= \langle - | e^{-t \left[ H_K - \frac{(1 - \mu) f \cdot p}{\tau} \right] | GB \rangle = e^{-t G(1 - \mu)} \quad (6.10)$$

i.e. (6.8). Note that we did not have to use any assumptions either on times or on the dynamics.
6.1.2 Stationary with bath

To compute the large-deviation function for long times, we proceed as in the previous section, and introduce eigenvectors and eigenvalues as in (4.25):

\[
[H_K - \frac{\mu}{T} \mathbf{f} \cdot \mathbf{v}] |\psi_i^R\rangle = \lambda_i |\psi_i^R\rangle ; \quad \langle \psi_i^L | [H_K - \frac{\mu}{T} \mathbf{f} \cdot \mathbf{v}] = \lambda_i \langle \psi_i^L |
\]

(6.11)
to get:

\[
e^{-tG(\mu)} = \langle -|e^{-t[H_K - \frac{\mu}{T} \mathbf{f} \cdot \mathbf{v}] \text{init}} = \sum_a \langle -|\psi_a^R \rangle \langle \psi_a^L \rangle \text{init} e^{-t\lambda_a(\mu)}
\]

(6.12)

If the spectrum has a gap, the eigenvalue with the lowest real part dominates, and we have that

\[
G(\mu) = \lambda_{\text{min}}(\mu) \text{ as } t \to \infty.
\]

Now, because \([H_K - \frac{\mu}{T} \mathbf{f} \cdot \mathbf{v}] \text{ and } [H_K - \frac{1}{\epsilon} \mathbf{f} \cdot \mathbf{v}]^\dagger \text{ are related by a similarity transformation (6.9), their spectra are the same. Hence, we have that, to the extent that to leading order in the time } G(\mu) \text{ depends only on eigenvalues and not on eigenvectors:}

\[
G(\mu) = G(1 - \mu)
\]

(6.13)

In this case, (6.13) is valid only at large times. Where can this fail? The problem in the large-time evaluation of (6.12) arises if \(\langle \psi^L(\lambda_{\text{min}}) \rangle \text{init} \sim 0\). At zero noise intensity this may well happen, because eigenvectors may in that case be completely localised.

6.1.3 Gallavotti-Cohen theorem

We shall not derive here the Gallavotti-Cohen theorem, but just say a few words. The Gallavotti Cohen Theorem is the stationary fluctuation theorem for a system in contact with a deterministic Gaussian thermostat, like the one we introduced in (1.13) but with exactly zero noise. It turns out that unlike the stochastic and the transient case, which are essentially always valid, the Gallavotti-Cohen result breaks down in some systems, and in most cases when the forcing is very strong. This is not a defect of the proof, but a reflection of a physical fact: the Fluctuation Relation in the deterministic case holds only if the system has certain ‘ergodic’ properties.

To have a perspective on this, one can consider approaching the deterministic case as a limit of the noisy thermostatted case (1.13). One can reproduce the derivation above for this case (Kurchan 2007), and easily conclude that for every level of noise \(\epsilon\) the theorem is valid, in the limit of large time windows \(t \gg t_{\text{min}}(\epsilon)\), for some time \(t_{\text{min}}(\epsilon)\). The trouble comes from the fact that as \(\epsilon \to 0\) it may happen that \(t_{\text{min}}(\epsilon)\) diverges: in other words, the time \(t_{\text{min}}(\epsilon)\) needed for the correct sampling of fluctuations may become infinite in the deterministic limit. The result of Gallavotti and Cohen proves that this is not the case for a class of very chaotic systems. For this class their theorem implies that \(\lim_{\epsilon \to 0} t_{\text{min}}(\epsilon) < \infty\).

The timescale \(t_{\text{min}}(\epsilon)\) has a clear physical meaning, which we just hint at here. A driven, deterministic, system has an attractor on the energy surface (see sect 2.4). Winding back in time the dynamics defines a repellor which is stationary but unstable. In chaotic Hamiltonian (undriven) systems, attractor and repellor are intertwined, they occupy the same region in phase-space. As the drive is turned on, the attractor
distribution focuses on a region the energy shell, as described in Sect. 2.4. So does the repellor, in a region that may be non-overlapping.

In the presence of weak noise, even if attractor and repellor are in principle separate, the system may occasionally switch from attractor to repellor and back: this is exactly analogous to the ‘coexistence’ we found in lecture 5. The typical time to do this ([Kurchan 2007], see also [Bonetto et al. 1997a]) is precisely $t_{\text{min}}(\epsilon)$ for an otherwise ergodic system. The condition for $t_{\text{min}}(\epsilon)$ to remain finite as the noise goes to zero is then that attractor and repellor overlap sufficiently in phase-space that it needs no noise to jump from one to the other. This is an extra condition the system must satisfy in order that the Gallavotti-Cohen fluctuation theorem to holds. In a word, the applicability of the Gallavotti-Cohen fluctuation theorem is, for a chaotic deterministic system, a symptom that attractor and repellor have not divorced under the effect of forcing.

6.2 Jarzynski’s equality

Jarzynski’s equality is a remarkable generalisation of the second principle. Consider a system with an energy dependent upon a parameter (volume, magnetic field, ...) which we denote $\alpha$. We start from a Gibbs-Boltzmann equilibrium corresponding to parameter $\alpha_{\text{initial}}$ and then evolve while changing $\alpha(t)$ at arbitrary speed up to a time $t$ with $\alpha_{\text{final}} = \alpha(t)$. The equality is then:

$$e^{-\beta[F(\alpha_{\text{final}}) - F(\alpha_{\text{initial}})]} = \langle e^{-\beta \text{work}} \rangle_{\alpha_{\text{initial}} \to \alpha_{\text{final}}}$$

(6.14)

The average is over trajectories starting from equilibrium at $t = 0$, but otherwise arbitrary. Note the surprising appearance of $F(\alpha_{\text{final}})$, an equilibrium quantity, despite the fact that the system is not in equilibrium at time $t$. We shall prove this result for a Langevin system with inertia. It is valid independently of the friction coefficient $\gamma$, indeed even if $\gamma = 0$ and the system is isolated.

From (6.14) we can go to the second principle, taking logarithms on both sides and using Jensen’s inequality $\langle e^A \rangle \geq e^{\langle A \rangle}$

$$F(\alpha_{\text{final}}) - F(\alpha_{\text{initial}}) \leq \text{work}$$

(6.15)

The time-dependent energy is:

$$H_\alpha = H(q, p, \alpha) = \sum_i \frac{p_i^2}{2m} + V(q, \alpha)$$

(6.16)

If the parameter $\alpha$ depends on time, it does work:

$$\int dt \sum_i \dot{q}_i \frac{\partial V}{\partial q_i} = \int dt \left( \frac{dH_\alpha}{dt} - \frac{\partial H_\alpha}{\partial \alpha} \cdot \dot{\alpha} \right) = H_\alpha^{\text{final}} - H_\alpha^{\text{initial}} - \int dt \left( \frac{\partial H_\alpha}{\partial t} \right)$$

We assume we start from the equilibrium configuration $\langle GB(\alpha_1) \rangle$ corresponding to a given value $\alpha_1$. The total evolution over a time $t$ can be written by breaking the time in short intervals as in Fig. 6.1.
Because $\langle - | H_\alpha = \langle - |$, we have

$$1 = \langle e^{-\delta t H_{\alpha M}} ... e^{-\delta t H_{\alpha 2} e^{-\delta t H_{\alpha 1}} | GB (\alpha_1)} \rangle = \langle GB (\alpha_1) \rangle e^{-\delta t H_{\alpha 1}} e^{-\delta t H_{\alpha 2} ... e^{-\delta t H_{\alpha M}} | -} \rangle$$

$$= \frac{Z_{\alpha_{M}}}{Z_{\alpha_1}} \langle e^{-\delta t H_{\alpha 1}^1} e^{-\delta t H_{\alpha 2}^1} ... e^{-\delta t H_{\alpha M}^1} e^{\beta H_{\alpha M}} | GB (\alpha_M) \rangle$$

(6.18)

As in all these theorems, we wish to introduce time-reversal. We proceed as follows:

insert factors between every two exponentials

$$e^{-\delta t H_{\alpha 1}^1} e^{-\delta t H_{\alpha 2}^1} \uparrow\downarrow e^{-\delta t H_{\alpha 2}^1} e^{-\delta t H_{\alpha M}^1} e^{\beta H_{\alpha M}}$$

and use in each factor:

$$e^{-\beta H_{\alpha r} e^{-\delta t H_{\alpha r}} e^{\beta H_{\alpha r}} \Pi e^{-\delta t H_{\alpha r}} \Pi^{-1} \quad (6.20)$$

Putting everything in (6.18), using that the $\Pi^2 = 1$ and that $e^{-\delta t H_{\alpha M}} | GB (\alpha_M) \rangle = | GB (\alpha_M) \rangle$ we get:

$$1 = \frac{Z_{\alpha_{M}}}{Z_{\alpha_1}} \langle e^{-\delta t H_{\alpha 1} e^{-\beta (H_{\alpha 1} - H_{\alpha 2})} e^{-\delta t H_{\alpha 2} e^{-\beta (H_{\alpha 2} - H_{\alpha 3})} ... e^{-\delta t H_{\alpha M}}} | GB (\alpha_M) \rangle \rangle$$

(6.21)

Because $\mathcal{H}_{\alpha r} \sim \mathcal{H}_{\alpha (r+1)} \propto \delta \alpha$, and using, as usual, that $e^{\delta A} e^{\delta B} \sim e^{\delta (A+B) + O((\delta t)^2)}$

for small $\delta t$:

$$1 = \frac{Z_{\alpha_{M}}}{Z_{\alpha_1}} \langle e^{-\delta t H_{\alpha 1} e^{-\beta (H_{\alpha 1} - H_{\alpha 2})} e^{-\delta t H_{\alpha 2} e^{-\beta (H_{\alpha 2} - H_{\alpha 3})} ... e^{-\delta t H_{\alpha M}}} | GB (\alpha_M) \rangle \rangle$$

(6.22)

which, by simple comparison means that

$$1 = e^{\beta (F_{\alpha M} - F_{\alpha 1})} \langle e^{-\beta \int dt \frac{d\mathcal{H}}{H}} \rangle$$

(6.23)

where the average is over trajectories starting from initial points chosen with the equilibrium distribution at $(\alpha_M)$ and ending anywhere where evolution and noise takes them.

We finally get

$$e^{-\beta (F_{\text{final}} - F_{\text{initial}})} = \langle e^{-\beta \int dt \frac{d\mathcal{H}}{H}} \rangle_{\text{initial} \to \text{any}}$$

(6.24)

The average is over trajectories starting from equilibrium at $\alpha_{\text{initial}}$ and ending anywhere that the dynamics takes them. The interpretation of $\text{work} = \int dt \frac{d\mathcal{H}}{H}$ has generated controversy [Peliti 2008], it is the work done by the system on the external sources (e.g. pistons, etc) of the ‘fields’ $\alpha$. Here again, subtly different equalities can be obtained depending on the precise expression used for work, see [Jarzynski 2007].
6.3 A paradox

The Jarzynski equality has been criticised (Crooks et al. 2007) on the basis that it is supposed to fail for a process of free expansion. This paradox was completely resolved by Crooks and Jarzynski. The resolution is in itself instructive, because it highlights the role of rare fluctuations. The argument goes as follows: if we open the tap of a bottle with gas, letting it freely expand into an empty room, there is no work done, and yet there is a change in the free energies before and after: Jarzynski’s equality must be violated.

Let us first distinguish two ways of making a free expansion: with a sliding wall (Fig. 6.2) or with a rapidly receding piston (Fig. 6.3). In the case of the sliding wall
initial condition, but this requires that the right-hand compartment in Fig. 6.2 be also full. If such is the case, when we slide the wall open there is neither work done nor free-energy change.

This seems like a cheat, because we could have a solid piston receding infinitely fast as in Fig. 6.3 and in that case no need of an equilibrated right hand compartment. Following Crooks and Jarzynski, suppose then that the piston is pulled backwards a huge velocity \( v \). If \( v \gg (kT)^{1/2} \), it is highly unlikely that any gas particle will hit the piston as it recedes, so in almost any run of the experiment no work is done. There are, however, very rare realisations of the experiment in which an unusually energetic particle catches up with the piston, bounces, and loses most of its velocity in the process. This can be best seen if one considers the time-reversed process (Fig. 6.3) in which a rapidly incoming piston hits a slow moving particle. It turns out (Crooks et al. 2007) that the rare realizations in which this strong ‘particle cooling’ happens suffice to account for the exponential of the free energy difference.

This example beautifully illustrates the role of rare fluctuations in Jarzynski’s equality, and the extent to which what dominates the equation can be an extremely atypical process that violates our intuition, which is designed to apply to probable events.

### 6.4 Experimental work

A serious account of both the Fluctuation theorem and Jarzynski’s equality should discuss the, by now quite considerable, experimental work. We shall not do this here, but just refer the interested reader to the References (Ritort 2007).

Let us make however a few remarks, from a theoretician’s perspective. The fluctuation theorem is, as its name suggests, a theorem. As such it need not be tested experimentally. The question is, of course, to what extent a specific physical system satisfies the hypotheses. Clearly, no real system has a Gaussian thermostat. Even a Langevin thermostat is an idealisation – a question that has been brought up in the context of Jarzynski’s equality, (see below). The usual way out is to say that the
thermostat is ‘far away’ and then its nature becomes irrelevant. This would normally sound extremely reasonable, but bear in mind that, as the previous section shows, intuition may be misleading when applied to large deviations. At any rate, if the nature of the thermostat is indeed not important, then we might as well suppose it is a stochastic one, so that the fluctuation theorem holds without any assumption related to ergodicity.

Consider for example the Lyon experiment (Ciliberto et al. 1998) where a liquid is enclosed between two horizontal plates, the lower at higher temperature than the upper one $T_d > T_u$. Heat is transmitted by (Rayleigh-Benard) convection. The fluctuation theorem establishes a relation between having a heat flux $J$ in one sense and in the other, $P(J)/P(-J) \sim e^{-(\beta_u - \beta_d)Jt}$ (Eckmann et al.). Surely, one argues, the top and bottom plates can be considered to be in contact with a good Langevinian bath, the nature of Rayleigh-Benard convection cannot depend on that. If this assumption is correct, then the validity of the fluctuation theorem is not in doubt, as no ergodicity properties are required of the system when there is a Langevin bath. But in fact, the experiment does not find a fluctuation relation with the true top and bottom temperatures (and indeed, with such temperatures the violations of the second law would be unobservable). Why is that? It would seem – but this needs further elucidation – that what the experiment is in fact testing is a pre-asymptotic result, because the time-window is not long enough. One can of course ask if at this pre-asymptotic level there is for some other reason another fluctuation relation, with a higher effective temperature, but this requires a different theory (Bonetto et al. 1997a).

Let us now turn very briefly to the Jarzynski equality. In this case, experimental work (Ritort 2007) has been made not so much to test the equality, as in the case of the fluctuation theorem, but to use it to evaluate free-energy differences with fast, out of equilibrium, measurements. For example, two RNA strands are unzipped by pulling with optical tweezers, and the work that this costs is measured (Ritort 2006). The experiment is repeated many times, and from the work distribution the equilibrium free-energy difference is measured. If we move too fast, it is the rarer and rarer runs that dominate, so the experiment has to be repeated many times. Here again, the example of the piston in the previous section is very illuminating: if the piston recedes very fast, only in very rare repetitions of the experiment will a fast particle catch up with it and be stopped: but this event dominates the average in Jarzynski’s equality!

Let us say a final word concerning Jarzynski’s equality in the presence of a (water) bath. It has been argued (Cohen et al. 2004) that the water can not be considered as a Langevinian – or in fact as any other equilibrium – bath, while the system is evolving fast. This is indeed so, but the problem is solved (Jarzynski 1997) by ‘moving the bath away’, i.e. by including the surrounding water as part of the system.
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