Advanced Statistical Mechanics

M2 ICFP 2024-2025

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Theoretical Physics track F. van Wijland

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Introduction and goals

Equilibrium statistical mechanics tells us that there is no need, under certain conditions, to know the specific microscopic evolution rules of a physical system to predict the probability, at large times, to find it in a given microstate. Quite remarkably, for an isolated system with ergodic dynamics, all microstates are postulated to be equally likely to be observed, and the postulate shows no sign of questioning. It follows that if a system is in contact with a huge energy reservoir with inverse temperature β, and again under some conditions on the nature of interactions between the system and the thermostat, the probability to observe a given microstate is proportional to the Boltzmann factor $\mathrm{e}^{-\beta H}$, where H is the energy of the microstate. This is the basis of equilibrium statistical mechanics. From there, the goal of statistical mechanics is to infer macroscopic phase behaviors given an explicit expression for the energy H of a microstate. Knowing the behavior of two interacting water molecules falls short of letting us know whether our system is an ice cube, a glass of water or just steam. One of the great successes of statistical mechanics is the understanding of phase transitions. And by understanding we refer to a qualitative understanding, but also to a quantitative one, downto such remarkable features as the emergence of universality at a second order critical point. In what follows, we assume some familiarity with the theory of phase transitions, mean-field, renormalization group ideas and universality, coarse-graining and Landau theory, *etc.*.

But what we want achieve in this course somewhat departs from what you have learned by practicing equilibrium statistical mechanics. Instead, we want to re-establish the arrow of time and we wish to construct a statistical mechanical approach to dynamical evolution. This will complement our toolbox for the description of equilibrium systems, but it will also be a route to the description of systems evolving far from equilibrium, when no generic theory is available.

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Chapter 1

Statistical Dynamics and Markov Processes

A master equation is a linear, first order in time, evolution equation for the probability to observe a set of degrees of freedom in some prescribed configuration. In this first chapter, one of the goals is to show that a master equation is actually quite a general manner to describe the dynamics of a physical system, then to explore the properties of a master equation, and finally to connect the master equation to first-passage probabilities.

At the end of this chapter, you should be able to

- know the basic properties of a master equation;
- understand how to fully characterize the time realization of a process described by a master equation;
- know how to write and manipulate (for averages) a master equation, once a model is defined;
- know how to connect the mean first passage time to the adjoint master equation.

1.1 The physics behind a master equation

1.1.1 Phase space and Liouville equation

A physical system is, at a microscopic level, characterized by its coordinates in phase space, $\Gamma = \{q, p\}$ and its time evolution is entirely contained in the explicit form of its Hamiltonian $\mathscr{H}(\Gamma)$. Given an initial set of positions and velocities, integrating the equations of motion

$$\dot{p} = -\frac{\partial \mathscr{H}}{\partial q}, \quad \dot{q} = \frac{\partial \mathscr{H}}{\partial p} \tag{1.1}$$

The phase space density $\rho(\Gamma, t)$ evolves according to the Liouville equation. Due to he conservation of probability, we have that

$$\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma} \rho) = 0 \tag{1.2}$$

and thus we must have that

$$\begin{aligned}\frac{\mathrm{d}\rho}{\mathrm{d}t} =& \partial_t \rho + \{\rho, \mathscr{H}\} \\ =& -\rho \partial_\Gamma \cdot \left(\dot{\Gamma}\right) \\ =& 0\end{aligned} \tag{1.3}$$

where $\{f, g\} = \partial_q f \partial_p g - \partial_p f \partial_q g$. The incompressibility of phase space

$$\partial_\Gamma \cdot \dot{\Gamma} = \partial_{q_i} \dot{q}_i + \partial_{p_i} \dot{p}_i = 0 \tag{1.4}$$

relects the symplectic nature of the Hamiltonian dynamics. Liouville's equation is thus a linear first-order in time evolution equation

$$\partial_t \rho = \{\mathscr{H}, \rho\} = -i\mathscr{L}\rho \tag{1.5}$$

where the Liouvillian $\mathscr{L}$ is by convention defined with a $-i$ prefactor. Of course we know that under some conditions (closed isolated system with a fixed volume), in the long time limit the equilibrium solution is uniform over phase space. We know this is true, but it's in general impossible to prove, and the reasons behind this property are rather subtle (they are to be found in the chaotic and mixing properties of the dynamics). However, in general, ρ is hard to get, and in general, we are simply not interest in ρ. It is only a subset of the degrees of freedom of the system that is of interest to us.

1.1.2 Projection operator at the level of probabilities

There are various ways to implement the Mori-Zwanzig idea of projecting onto relevant degrees of freedom (we refer to [207] for a pedagogical introduction). One of these aproaches, proposed by Nakajima and Zwanzig [140, 205, 119], operates directly at the level of probability densities, which we find very convenient, mostly for discussion purposes, at this stage of the lectures. We imagine that the probability of a set of degrees of freedom denoted by c (we shall use discrete summations, but c may as refer to a set of canonically conjugate phase space variables, and then $\mathbf{w}$ becomes a first order differential operator) evolves according to a linear, first order in time, differential equation (such as the Liouville equation):

$$\partial_t p(c,t) = \sum_{c'} \mathbf{w}_{cc'} p(c',t) \tag{1.6}$$

where $\mathbf{w}$ is some operator (in Hamiltonian dynamics, $\mathbf{w} = -i\mathscr{L}$ is called the Liouvillean). But it turns out that we are only interested in a subset of the degrees of freedom, namely those for which the physical observable $C(c)$ takes the value $\mathscr{C}$. Our goal is really to study

$$P(\mathscr{C}, t) = \mathrm{Prob}\{C(c(t)) = \mathscr{C}\} = \sum_c \delta_{\mathscr{C}, C(c)} p(c,t) \tag{1.7}$$

Of course, the choice of the observable C depends on context and

- C can refer to the position of a tagged particle;

- C can refer to a collective density mode;
- C can refer to a composite observable such as the kinetic energy of the system.

To proceed, one introduces $\Omega_{\mathscr{C}} = \sum_c \delta_{\mathscr{C},C(c)}$ which counts how many microstates c have the same value $\mathscr{C}$ of $C(c)$. We also introduce an operator $\mathscr{P}$ that applies to any function $f(c)$ of the microstates c:

$$\mathscr{P}f(c) = \frac{1}{\Omega(C(c))}\sum_{c'}\delta_{C(c'),C(c)}f(c') \tag{1.8}$$

One can verify that $\mathscr{P}^2 = \mathscr{P}$, which means that $\mathscr{P}$ is a projector. It is then used to define both $\bar{p}(c,t) = \mathscr{P}p(c,t)$ and $q = p - \bar{p} = \mathscr{Q}p$. By construction $\bar{p}(c,t) = P(C(c),t)/\Omega_{C(c)}$ but the probabillity P we are after can *a posteriori* be reconstructed from the knowledge of $\bar{p}$:

$$P(\mathscr{C},t) = \sum_c \delta_{\mathscr{C},C(c)}\bar{p}(c,t) \tag{1.9}$$

The evolution equation for p, $\partial_t p = \mathbf{w}p$ splits into two coupled evolution equations for $\bar{p}$ and for q,

$$\partial_t \bar{p} = \mathscr{P}\mathbf{w}\bar{p} + \mathscr{P}\mathbf{w}q,\ \partial_t q = \mathscr{Q}\mathbf{w}\bar{p} + \mathscr{Q}\mathbf{w}q \tag{1.10}$$

hence $q(t) = \int_0^t \mathrm{d}t' \mathrm{e}^{\mathscr{Q}\mathbf{w}(t-t')}\mathscr{Q}\mathbf{w}\bar{p}(t')$. We have chosen an initial condition such that $q(c,0) = 0$, namely one in which the value of $C(c)$ is the same. The expression for q can then be substituted into the evolution equation for $\bar{p}$, thus leading to a linear equation for $\bar{p}$ alone:

$$\partial_t \bar{p} = \mathscr{P}\mathbf{w}\bar{p} + \int_0^t \mathrm{d}t' \mathscr{P}\mathbf{w}\mathrm{e}^{\mathscr{Q}\mathbf{w}(t-t')}\mathscr{Q}\mathbf{w}\bar{p}(t') \tag{1.11}$$

But we are after $P(C,t)$, not after $\bar{p}(c,t)$, so that one final step is required. We multiply Eq. (1.11) with $\delta_{\mathscr{C},C(c)}$ and we sum over c:

$$\partial_t P(C,t) = \sum_{c,c'}\delta_{\mathscr{C},C(c)}(\mathscr{P}\mathbf{w})_{cc'}\bar{p}(c',t) + \int_0^t \mathrm{d}t' \sum_{c,c'}\delta_{\mathscr{C},C(c)}(\mathscr{P}\mathbf{w}\mathrm{e}^{\mathscr{Q}\mathbf{w}(t-t')}\mathscr{Q}\mathbf{w})_{cc'}\bar{p}(c',t') \tag{1.12}$$

Then we use the trick that

$$\sum_{c'}\ldots = \sum_{C'}\sum_{c'}\delta_{\mathscr{C}(c'),C'} \tag{1.13}$$

to finally arrive at

$$\partial_t P(C,t) = \sum_{C'}\left[\sum_{c,c'}\delta_{\mathscr{C},C(c)}(\mathscr{P}\mathbf{w})_{cc'}\right]P(C',t) + \int_0^t \mathrm{d}t' \sum_{C'}\left[\sum_{c,c'}\sum_{c,c'}\delta_{\mathscr{C},C(c)}(\mathscr{P}\mathbf{w}\mathrm{e}^{\mathscr{Q}\mathbf{w}(t-t')}\mathscr{Q}\mathbf{w})_{cc'}\right]P(C',t') \tag{1.14}$$

The general for of the evolution equation for P is thus

$$\partial_t P(C,t) = \sum_{C'} M^{(1)}_{CC'}P(C',t) + \int_0^t \mathrm{d}t' \sum_{C'} M^{(2)}_{CC'}(t-t')P(C',t') \tag{1.15}$$

If the choice of the slow degrees of freedom is appropriate, and in general, then $M^{(2)}$ will exhibit a rapid exponential decay over a typical time scale τ which will justify to replace $M^{(2)}(t-t')$ by an effective $M^{(2)}(0)\tau\delta(t-t')$ operator, and the resulting equation for P reads

$$\partial_t P = \mathbb{W}P,\ \mathbb{W} \simeq M^{(1)} + \tau M^{(2)}(0) \tag{1.16}$$

This so-called Markov approximation applies when there is a decoupling of the fast and irrelevant degrees of freedom from the physically relevant degrees of freedom whose physics develops over time scales large with respect to that of the fast degrees of freedom. Of course, lots of relevant physical cases do not exhibit a clear-cut decoupling between the slow and the fast degrees of freedom and it may also be that $M^{(2)}(t-t')$ slowly decays as a power law (as for instance in visco-elastic materials where the memory kernel goes by the name of the creep function). All in all, in what follows, we shall always assume that there is a level of description at which an equation of the form $\partial_t\rho = \mathbb{W}\rho$ can be our starting point. In general, except at the microscopic level, $\mathbb{W}$ is a complicated operator (that is certainly not of order one in terms of differentiation with respect to space and momentum). We shall now take such an operator $\mathbb{W}$ for granted.

Note that if the existence of $\mathbb{W}$ is assumed, the conservation of probability at all times forces and the requirement that P remains non-negative force $\mathbb{W}$ to be a master equation matrix.

1.1.3 Projection operator at the level of observables

The Mori-Zwanzig projection technique can be implemented by other means, but beyond the specifics, the method draws on the same idea. Our starting assumption is that a given observable $A(\Gamma(t))$ of interest, depending on phase space coordinates Γ, evolves according to a first-order in time differential equation of the form

$$\frac{\mathrm{d}A}{\mathrm{d}t} = i\mathscr{L}A \tag{1.17}$$

where $\mathscr{L}$ is the Liouvillean, $-i\mathscr{L} = \{\mathscr{H}, \ldots\}$ that also evolves the phase space density, $\partial_t\rho = -i\mathscr{L}\rho$. Formally, and as long as $\mathscr{H}$ does not explicitly depend on time, we have that

$$A(t) = \mathrm{e}^{i\mathscr{L}t}A(0) \tag{1.18}$$

In the space of all possible observables, we can choose to introduce a projection operator along A, defined by

$$\mathscr{P}X(\Gamma) = \frac{(A,X)}{(A,A)}A \tag{1.19}$$

where (A,B) denotes a scalar product yet to be specified. One possible choice involves the stationary distribution ρ_{ss} of the Liouville equation, $(A,B) = \int \mathrm{d}\Gamma\rho_{\mathrm{ss}}(\Gamma)A(\Gamma)B(\Gamma) = \langle AB\rangle_{\mathrm{ss}}$ and it corresponds to an equal time correlation in the steady-state. At this stage, we invoke the Dyson identity

$$\mathrm{e}^{i\mathscr{L}t} = \mathrm{e}^{i\mathscr{Q}\mathscr{L}t} + \int_0^t \mathrm{d}t'\mathrm{e}^{i\mathscr{L}(t-t')}\mathscr{P}\mathscr{L}\mathrm{e}^{i\mathscr{Q}\mathscr{L}t'} \tag{1.20}$$

which can be established by differentiating and then integrating the quantity $\mathrm{e}^{-i\mathscr{L}t}\mathrm{e}^{i\mathscr{Q}t}$ with respect to time. This identity is applied to $i\mathscr{Q}\mathscr{L}A$ and the resulting equation for A reads

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \Omega A + \int_0^t \mathrm{d}t' K(t-t')A(t') + F(t) \tag{1.21}$$

where Ω, K and F are given by:

$$\Omega = \frac{(i\mathscr{L}A, A)}{(A, A)},\ F(t) = \mathrm{e}^{it\mathscr{Q}\mathscr{L}}\mathscr{Q}i\mathscr{L}A,\ K(\tau) = \frac{(i\mathscr{L}F(t), A)}{(A, A)} \tag{1.22}$$

The physical interpretation of F as a random force comes from the fact that $\mathscr{P}F = 0$: F involves degrees of freedom orthogonal to A that we do not wish to describe. Note that the same approach can be repeated with a set of several observables A, but then a few adaptations are needed. Further adjustments are needed when $\mathscr{H}$ explicitly depends on time.

1.2 Master Equation

1.2.1 Rates

To begin with, we use the notation $\mathscr{C}$ to refer to the possible microscopic configurations that a system can be found in: it may well be the set of positions and momenta of all the particles in the system, or the spin configuration of a magnet, *etc.*. We use a discrete notation, with discrete summations, but it is understood that the $\mathscr{C}$'s could also refer to continuous variables (unless specified otherwise). Let $W(\mathscr{C} \to \mathscr{C}')\mathrm{d}t$ be the probability that, between t and $t + \mathrm{d}t$, the system hops from configuration $\mathscr{C}$ to configuration $\mathscr{C}' \neq \mathscr{C}$ (by convention, $W(\mathscr{C} \to \mathscr{C}) = 0$). This defines the rate $W(\mathscr{C} \to \mathscr{C}')$ of hopping from $\mathscr{C}$ to $\mathscr{C}'$. The rate at which the system leaves configuration $\mathscr{C}$ is the so-called escape rate,

$$r(\mathscr{C}) = \sum_{\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}') \tag{1.23}$$

and it tells us that the probability that, between t and $t + \mathrm{d}t$, the systems leaves state $\mathscr{C}$, is $r(\mathscr{C})\mathrm{d}t$. If we are interested in the probability $P(\mathscr{C}, t)$ to find the system in state $\mathscr{C}$ at time t, we can always write that

$$\begin{aligned} P(\mathscr{C}, t + \mathrm{d}t) = &\sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})\mathrm{d}t \times P(\mathscr{C}', t) \\ &+ (1 - r(\mathscr{C})\mathrm{d}t)P(\mathscr{C}, t) \end{aligned} \tag{1.24}$$

where the first line in the rhs is the probability to be in state $\mathscr{C}'$ and to hop to state $\mathscr{C}$ between t and $t+\mathrm{d}t$ (summed over all possible $\mathscr{C}'$ configurations), while the second line in the rhs is the probability to already be in state $\mathscr{C}$ and not to move between t and $t + \mathrm{d}t$. In the continuous limit, this leads to

$$\partial_t P(\mathscr{C}, t) = \sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P(\mathscr{C}', t) - r(\mathscr{C})P(\mathscr{C}, t) \tag{1.25}$$

which is a standard balance equation, with a gain term $\sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C}) P(\mathscr{C}', t)$ and a loss term $r(\mathscr{C})P(\mathscr{C}, t)$. Such an equation is called a master equation, and the dynamics is a continuous-time random walk on a weighted directed graph with vertices $\mathscr{C}$ (the oriented $\mathscr{C} \to \mathscr{C}'$ edge has weight $W(\mathscr{C} \to \mathscr{C}')$).

In matrix form, using the notation $P(t)$ to refer to a column vector with entries $P(\mathscr{C}, t)$ index by $\mathscr{C}$, the master equation reads

$$\partial_t P = \mathbb{W} P \tag{1.26}$$

where

$$\mathbb{W}_{\mathscr{C},\mathscr{C}'} = W(\mathscr{C}' \to \mathscr{C}) - r(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'} \tag{1.27}$$

are the matrix elements of the evolution operator $\mathbb{W}$. Conservation of probability follows from the property that

$$\forall \mathscr{C}', \ \sum_{\mathscr{C}} \mathbb{W}_{\mathscr{C},\mathscr{C}'} = \sum_{\mathscr{C}} W(\mathscr{C}' \to \mathscr{C}) - r(\mathscr{C}') = 0 \tag{1.28}$$

because indeed

$$\sum_{\mathscr{C}} \partial_t P(\mathscr{C}, t) = \frac{\mathrm{d}}{\mathrm{d}t} \sum_{\mathscr{C}} P(\mathscr{C}, t) = \sum_{\mathscr{C},\mathscr{C}'} \mathbb{W}_{\mathscr{C},\mathscr{C}'} P(\mathscr{C}', t) = 0 \tag{1.29}$$

which means that $\sum_{\mathscr{C}} P(\mathscr{C}, t) = \sum_{\mathscr{C}} P(\mathscr{C}, 0) = 1$. This also tells us that the conservation of probability is expressed through the existence of a left eigenvector $p_{\mathscr{C}} = 1$ with eigenvalue 0 (Eq. (1.28) is exactly $p\mathbb{W} = 0$ when written in terms of the components). The uniform vector $p_{\mathscr{C}}$ sometimes goes by the name of projection state. Since 0 is an eigenvalue of $\mathbb{W}$ there must also exist (at least one) eigenvector P_{ss} such that $\mathbb{W}P_{\mathrm{ss}} = 0$. This is a steady-state (or a stationary-state).

When looking at the (weighted directed) graph of configurations, several things can happen. The graph may not be connected. This means that the corresponding subsets of configurations have independent evolutions (and $\mathbb{W}$ can be cast in a block diagonal form). Within a given connected component, either the graph is strongly connected (and that is what we shall assume afterwards), or it is not. In the latter case, the probability will be drained out of a set of configurations (to eventually reach zero in the infinite time limit), and the remaining set of states form an absorbing set of states, because if the system would initially start from within this subset of states, the system would never visit those other drained out states. Within such a subset, $\mathbb{W}$ is upper triangular by blocks (it is reducible). When the set of states is strongly connected the term irreducible is used. For those curious of the vocabulary correspondence with networks, see [69].

This being said, we know there is at least one steady-state P_{ss}. Let's establish that in the case of a strongly connected graph, the steady-state is unique. One way to do that is to invoke the Perron-Frobenius theorem for the matrix $M = \mathbf{1} + \mathbb{W}\mathrm{d}t$ such that

$$P(t + \mathrm{d}t) = MP(t) \tag{1.30}$$

as one does for Markov chains. The theorem states that for a matrix M with positive entries $M_{\mathscr{C},\mathscr{C}'} > 0$ (which is achieved for small enough $\mathrm{d}t$, and which applies equally well to M^T) there exists a positive real number r that is an eigenvalue of M (or of M^T) and any other eigenvalue (possibly complex) has a smaller modulus than r. In addition, r is nondegenerate and the components of the corresponding eigenvector are of the same sign. In addition, when the theorem is applied to M^T, r satisfies the inequality

$$\min_{\mathscr{C}} \sum_{\mathscr{C}'} M^T_{\mathscr{C},\mathscr{C}'} \leq r \leq \max_{\mathscr{C}} \sum_{\mathscr{C}'} M^T_{\mathscr{C},\mathscr{C}'} \tag{1.31}$$

where both bounds are equal to one for stochastic matrices ($M^T_{\mathscr{C},\mathscr{C}'} = \delta_{\mathscr{C},\mathscr{C}'} + \mathrm{d}t[W(\mathscr{C} \to \mathscr{C}') - r(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'}]$), hence $r = 1$.

Alternatively, one can follow Van Kampen [195] and introduce a positive convex function f (for instance $f(x) = x\ln x - x + 1$) along with the linear combination

$$H(t) = \sum_{\mathscr{C}} P_{\rm ss}(\mathscr{C}) f\left(\frac{P(\mathscr{C},t)}{P_{\rm ss}(\mathscr{C})}\right) \tag{1.32}$$

Then the idea is to differentiate with respect to time, and to use the master equation:

$$\begin{aligned}
\frac{\mathrm{d}H}{\mathrm{d}t} &= \sum_{\mathscr{C},\mathscr{C}'} (W(\mathscr{C}' \to \mathscr{C})P(\mathscr{C}',t) - W(\mathscr{C} \to \mathscr{C}')P(\mathscr{C},t)) f'\left(\frac{P(\mathscr{C},t)}{P_{\rm ss}(\mathscr{C})}\right) \\
&= \sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P_{\rm ss}(\mathscr{C}')\left[\frac{P(\mathscr{C}',t)}{P_{\rm ss}(\mathscr{C}')} f'\left(\frac{P(\mathscr{C},t)}{P_{\rm ss}(\mathscr{C})}\right) - \frac{P(\mathscr{C}',t)}{P_{\rm ss}(\mathscr{C}')} f'\left(\frac{P(\mathscr{C}',t)}{P_{\rm ss}(\mathscr{C}')}\right)\right] \\
&= \sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P_{\rm ss}(\mathscr{C}')\left[x_{\mathscr{C}'} f'(x_{\mathscr{C}}) - x_{\mathscr{C}'} f'(x_{\mathscr{C}'})\right]
\end{aligned} \tag{1.33}$$

where $x_{\mathscr{C}} = \frac{P(\mathscr{C},t)}{P_{\rm ss}(\mathscr{C})}$. Now we use a little trick, namely that for any set $y_{\mathscr{C}}$, we have that

$$\sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P_{\rm ss}(\mathscr{C}')(y_{\mathscr{C}} - y_{\mathscr{C}'}) = 0 \tag{1.34}$$

That's because we can always use the fact that

$$\begin{aligned}
\sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P_{\rm ss}(\mathscr{C}')(y_{\mathscr{C}} - y_{\mathscr{C}'}) &= \sum_{\mathscr{C}} y_{\mathscr{C}} \left[\sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})P_{\rm ss}(\mathscr{C}')\right] \\
&\quad - \sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}')P_{\rm ss}(\mathscr{C}) y_{\mathscr{C}} \\
&= \sum_{\mathscr{C}} y_{\mathscr{C}} \left[\sum_{\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}')P_{\rm ss}(\mathscr{C})\right] \\
&\quad - \sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}')P_{\rm ss}(\mathscr{C}) y_{\mathscr{C}} \\
&= 0
\end{aligned} \tag{1.35}$$

By choosing $y_{\mathscr{C}} = f(x_{\mathscr{C}}) - x_{\mathscr{C}} f'(x_{\mathscr{C}})$ and by adding Eq. (1.34) to Eq. (1.33), we arrive at

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \sum_{\mathscr{C},\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C}) P_{\mathrm{ss}}(\mathscr{C}') \left[(x_{\mathscr{C}'} - x_{\mathscr{C}}) f'(x_{\mathscr{C}}) - (f(x_{\mathscr{C}'}) - f(x_{\mathscr{C}})) \right] \tag{1.36}$$

where the right-hand side is negative by convexity of f, unless $x_{\mathscr{C}} = x_{\mathscr{C}'}$. The function H thus decreases monotonously while being positive, so it must reach a limit. In the long time limit we have that $\frac{\mathrm{d}H}{\mathrm{d}t} = 0$ hence $x_{\mathscr{C}} = x'_{\mathscr{C}}$ for all pairs of states. This is possible iff $\lim_{t\to+\infty} P(\mathscr{C}, t) = P_{\mathrm{ss}}(\mathscr{C})$, hence the uniqueness of the solution of the master equation.

Needless to say, the uniqueness property, derived for a strongly connected graph of configurations, neither applies in the infinite number of configurations limit (whether countable or continuous). This is great news as this means that there is room for interesting behavior in the large system size limit.

We have covered the steady-state, which tells us about the long time limit of the probability of occurrence of a configuration, but we'd now like to understand how trajectories in configuration space behave.

1.2.2 Averages

In this subsection we explain how, in practice, we can use the master equation to determine the average of a physical quantity $B(\mathscr{C})$ at time t. The master equation $\partial_t P = \mathbb{W}P$ has $P(t) = \mathrm{e}^{\mathbb{W}t} P(0)$ as its solution, where $P(t)$ is a vector with entries $P(\mathscr{C}, t)$. If we are interested in the average of a physical quantity B we know that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle B\rangle = \sum_{\mathscr{C}} B(\mathscr{C}) \partial_t P(\mathscr{C}, t) = \sum_{\mathscr{C}} B(\mathscr{C}) (\mathbb{W}P(t))(\mathscr{C}) \tag{1.37}$$

It is sometimes convenient to introduce the vector p with entries $p_{\mathscr{C}} = 1$ then we see that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle B\rangle = \sum_{\mathscr{C}} p_{\mathscr{C}} B(\mathscr{C}) (\mathbb{W}P(t))(\mathscr{C}) = p^T B \mathbb{W} P = p^T([B, \mathbb{W}])P \tag{1.38}$$

where we have used that p^T is left eigenvector of $\mathbb{W}$ with eigenvalue 0, and B refers to the diagonal matrix with entries $B(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'}$. The solution of Eq. (1.37) reads $\langle B\rangle(t) = \sum_{\mathscr{C}} B(\mathscr{C}) \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}'} P(\mathscr{C}', 0)$.

Now we would like to make sense of a two-point average of the form $\langle B(t)A(0)\rangle$. For this we use $\langle B\rangle(t) = \sum_{\mathscr{C}} B(\mathscr{C}) \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}'} P(\mathscr{C}', 0)$ for an initial state fixed at $\mathscr{C}_0$. We thus have that

$$\langle B\rangle(t)|_{\text{at fixed initial state } \mathscr{C}_0} = \sum_{\mathscr{C}} B(\mathscr{C}) \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}_0} \tag{1.39}$$

Of course, if in state $\mathscr{C}_0$ the observable A has the value $A(\mathscr{C}_0)$, this tells us that

$$\langle B(t)A(0)\rangle|_{\text{at fixed initial state } \mathscr{C}_0} = \sum_{\mathscr{C}} B(\mathscr{C}) \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}_0} A(\mathscr{C}_0) \tag{1.40}$$

In addition, if $\mathscr{C}_0$ itself is sampled according to the stationary distribution, the whole expression of Eq. (1.40) must be averaged, and this leads to

$$\langle B(t)A(0)\rangle = \sum_{\mathscr{C},\mathscr{C}_0} B(\mathscr{C}) \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}_0} A(\mathscr{C}_0)P_{\rm ss}(\mathscr{C}_0) \tag{1.41}$$

1.2.3 Trajectories and histories

Let's go back to what the existence of rates actually means. Unlike Markov chains, a system described by a master equation evolves in continuous time by means of discontinuous jumps from one configuration to another and the time τ the system stays in a given state $\mathscr{C}$ is itself a random variable. If $\pi(\tau,\mathscr{C})\mathrm{d}\tau$ denotes the probability to stay in state $\mathscr{C}$ for a duration τ and to hop to some other state between τ and $\tau+\mathrm{d}\tau$, we see that

$$\pi(\mathscr{C},\tau)\mathrm{d}\tau = f(\mathscr{C},\tau)\times r(\mathscr{C})\mathrm{d}\tau \tag{1.42}$$

where $f(\mathscr{C},\tau)$ is the probability to stay in state $\mathscr{C}$ for a duration τ and $r(\mathscr{C})\mathrm{d}\tau$ is the probability to exit configuration $\mathscr{C}$ between τ and $\tau+\mathrm{d}\tau$. Then we must have that

$$f(\mathscr{C},\tau+\mathrm{d}\tau) = f(\mathscr{C},\tau)\times \text{ the probability not to hop between } \tau \text{ and } \tau+\mathrm{d}\tau = f(\mathscr{C},\tau)(1-r(\mathscr{C})\mathrm{d}\tau) \tag{1.43}$$

hence $\frac{\mathrm{d}f}{\mathrm{d}\tau} = -r(\mathscr{C})f$ and since $f(\mathscr{C},0)=1$ we have $f(\mathscr{C},\tau)=\mathrm{e}^{-r(\mathscr{C})\tau}$ and finally $\pi(\mathscr{C},\tau) = r(\mathscr{C})\mathrm{d}\tau\mathrm{e}^{-r(\mathscr{C})\tau}$. With this in mind, we see that a trajectory is not only a sequence of visited states, but also a sequence of occupation times. When working over a given time window $[0,t_{\rm obs}]$, a time-realization of the process (otherwise called a trajectory) visits K (not necessarily distinct) states (and K itself is a random variable). Schematically, a trajectory can be represented by

$$\mathscr{C}_0 \xrightarrow{\tau_0} \mathscr{C}_1 \xrightarrow{\tau_1} \ldots \xrightarrow{\tau_{K-1}} \mathscr{C}_K \xrightarrow{\tau_K} \mathscr{C}_K \tag{1.44}$$

where however τ_K is constrained by the fact that $t_{\rm obs} = \sum_{j=0}^{K}\tau_j$. Hence the probability of a trajectory is given by

$$\begin{aligned}\mathscr{P}[\text{traj}] = &\underbrace{P_{\rm init}(\mathscr{C}_0)}_{\text{sampling of the initial state}} \times \underbrace{\pi(\mathscr{C}_0,\tau_0)\mathrm{d}\tau_0}_{\text{time spent in state } \mathscr{C}_0} \times \underbrace{\frac{W(\mathscr{C}_0\to\mathscr{C}_1)}{r(\mathscr{C}_0)}}_{\text{prob of hopping from } \mathscr{C}_0 \text{ to } \mathscr{C}_1} \\ &\times \pi(\mathscr{C}_1,\tau_1)\mathrm{d}\tau_1\frac{W(\mathscr{C}_1\to\mathscr{C}_2)}{r(\mathscr{C}_1)} \times \ldots \times \pi(\mathscr{C}_{K-1},\tau_{K-1})\mathrm{d}\tau_{K-1}\frac{W(\mathscr{C}_{K-1}\to\mathscr{C}_K)}{r(\mathscr{C}_{K-1})} \\ &\times \underbrace{\mathrm{e}^{-r(\mathscr{C}_K)\tau_K}}_{\text{prob to remain a duration } \tau_K \text{ in state } \mathscr{C}_K} \times \underbrace{\delta(t_{\rm obs}-\tau_0-\ldots-\tau_K)}_{\text{constraint fixing } \tau_K}\end{aligned} \tag{1.45}$$

The time reversed trajectory, which we will be needing shortly, has a probability

$$\begin{aligned}\mathscr{P}[\text{traj}^{\rm R}] =& P_{\rm fin}(\mathscr{C}_K)\times\pi(\mathscr{C}_K,\tau_K)\mathrm{d}\tau_K\frac{W(\mathscr{C}_K\to\mathscr{C}_{K-1})}{r(\mathscr{C}_K)}\ldots\pi(\mathscr{C}_1,\tau_1)\mathrm{d}\tau_1\frac{W(\mathscr{C}_1\to\mathscr{C}_0)}{r(\mathscr{C}_0)} \\ &\times \mathrm{e}^{-r(\mathscr{C}_0)\tau_0}\delta(t_{\rm obs}-\tau_0-\ldots-\tau_K)\end{aligned} \tag{1.46}$$

This allows us to define the trajectory dependent quantity $\bar{Q}[\text{traj}] = \ln \frac{\mathscr{P}[\text{traj}]}{\mathscr{P}[\text{traj}^{\text{R}}]}$. We defer the analysis of the physical content of $\bar{Q}$ to a bit later. We first establish an interesting property of the distribution of $\bar{Q}$, denoted by

$$P(\bar{Q}, t) = \text{Prob}\{\bar{Q}[\text{traj}] = \bar{Q}\} \tag{1.47}$$

with the standard notational sloppiness that mixes up a random variable and the value that it can be found in. By definition we have that

$$\begin{aligned} P(\bar{Q}, t) =& \sum_{\text{traj}} \delta(\bar{Q} - \bar{Q}[\text{traj}])\mathscr{P}[\text{traj}] \\ =& \sum_{\text{traj}} \delta(\bar{Q} - \bar{Q}[\text{traj}])\mathscr{P}[\text{traj}^{\text{R}}]\text{e}^{\bar{Q}[\text{traj}]} \\ =& \text{e}^{\bar{Q}} \sum_{\text{traj}} \delta(\bar{Q} + \bar{Q}[\text{traj}^{\text{R}}])\mathscr{P}[\text{traj}^{\text{R}}] \\ =& \text{e}^{\bar{Q}} \sum_{\text{traj}^{\text{R}}} \delta(\bar{Q} + \bar{Q}[\text{traj}^{\text{R}}])\mathscr{P}[\text{traj}^{\text{R}}] \\ =& \text{e}^{\bar{Q}} P(-\bar{Q}, t) \end{aligned} \tag{1.48}$$

This result is known as the Evans-Searles fluctuation theorem [64],

$$\frac{P(\bar{Q}, t)}{P(-\bar{Q}, t)} = \text{e}^{\bar{Q}}, \ \langle \text{e}^{-\bar{Q}} \rangle = 1 \tag{1.49}$$

At this stage, it can be viewed as a sophisticated way of rephrasing the conservation of probability. The reasons why it is more than that are to be found in the physical meaning of $\bar{Q}$ itself (and on the idea to consider time-reversal as an interesting transformation).

When making $\bar{Q}[\text{traj}]$ explicit, one sees that there are two contributions:

$$\bar{Q}[\text{traj}] = \ln \frac{P_{\text{init}}(\mathscr{C}_0)}{P_{\text{fin}}(\mathscr{C}_K)} + \sum_{j=0}^{K-1} \ln \frac{W(\mathscr{C}_j \to \mathscr{C}_{j+1})}{W(\mathscr{C}_{j+1} \to \mathscr{C}_j)} \tag{1.50}$$

and that the information about the times spent in each of the microstates has disappeared. The notation Q_S is used [123] for the second bit,

$$Q_S = \sum_{j=0}^{K-1} \ln \frac{W(\mathscr{C}_j \to \mathscr{C}_{j+1})}{W(\mathscr{C}_{j+1} \to \mathscr{C}_j)} \tag{1.51}$$

It depends only on the history of the process, understood as been the sequence of visited states. One of our tasks is now to understand the extent to which these rather formal quantities have any physical meaning, and any use at all. Before we do that, we simply note that

$$\langle \bar{Q} \rangle = -\sum_{\text{traj}} \mathscr{P}[\text{traj}] \ln \frac{\mathscr{P}[\text{traj}^{\text{R}}]}{\mathscr{P}[\text{traj}]} \tag{1.52}$$

and this has clear information-theoretic content: this is the Kullback-Leibler relative entropy measuring the "distance" of the time-reversed process to the original, forward-in-time, process.

Note on the KL divergence.– For any two probability distributions over some events indexed by i, say p_i and q_i, the quantity $D(p \parallel q) = \sum_i p_i \ln \frac{p_i}{q_i}$ verifies

$$D(p \parallel q) \geq 0 \text{ with equality iff } \forall i,\ p_i = q_i \tag{1.53}$$

Indeed, if the t_i's are in $[0,1]$ such that $\sum_j t_j = 1$, then the concavity of the logarithm tells us that

$$\ln(\sum_j t_j x_j) \geq \sum_j t_j \ln x_j \tag{1.54}$$

and choosing $t_j = p_j$, $x_i = \frac{q_j}{p_j}$, tells us that

$$\ln(\sum_j p_j \frac{q_j}{p_j}) \geq \sum_j p_j \ln \frac{q_j}{p_j} \tag{1.55}$$

and the left hand side vanishes, hence $D(p \parallel q) \geq 0$. The quantity $D(p \parallel q)$ is the Kullback–Leibler divergence (or the relative entropy). It somehow tells us how similar the two distributions p_i and q_i are. It is tempting to see it as the distance from q to p, though $D(p \parallel q)$ is obviously not a distance in any mathematical sense (it's not even symmetric in p and q).

1.2.4 Evolution of the Shannon entropy

Let S be the Shannon entropy over configurations,

$$S(t) = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \ln P(\mathscr{C}, t) \tag{1.56}$$

then, using the master equation, and after a few manipulations one arrives at

$$\begin{aligned} \frac{\mathrm{d}S}{\mathrm{d}t} =& \frac{1}{2} \sum_{\mathscr{C},\mathscr{C}'} \left[P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}') - P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C}) \right] \ln \frac{P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}')}{P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C})} \\ & - \sum_{\mathscr{C},\mathscr{C}'} P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}') \ln \frac{W(\mathscr{C} \to \mathscr{C}')}{W(\mathscr{C}' \to \mathscr{C})} \end{aligned} \tag{1.57}$$

which features two contributions that balance each other in the steady-state. The first one is

$$\sigma_{\mathrm{irr}} = \frac{1}{2} \sum_{\mathscr{C},\mathscr{C}'} \left[P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}') - P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C}) \right] \ln \frac{P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}')}{P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C})} \geq 0 \tag{1.58}$$

and it vanishes iff the detailed balance condition,

$$P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}') = P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C}) \tag{1.59}$$

is fulfilled. The second one reads

$$J_S = \sum_{\mathscr{C},\mathscr{C}'} P(\mathscr{C},t)\,W(\mathscr{C}\to\mathscr{C}')\ln\frac{W(\mathscr{C}\to\mathscr{C}')}{W(\mathscr{C}'\to\mathscr{C})} = \langle\sum_{\mathscr{C}'} W(\mathscr{C}\to\mathscr{C}')\ln\frac{W(\mathscr{C}\to\mathscr{C}')}{W(\mathscr{C}'\to\mathscr{C})}\rangle = \langle\frac{\mathrm{d}Q_S}{\mathrm{d}t}\rangle \tag{1.60}$$

The reason why $J_S = \langle\frac{\mathrm{d}Q_S}{\mathrm{d}t}\rangle$ takes a bit of experience to realize at first sight. This is because whenever the system hops from one configuration $\mathscr{C}$ to some other configuration $\mathscr{C}'$, Q_S varies by $\ln\frac{W(\mathscr{C}\to\mathscr{C}')}{W(\mathscr{C}'\to\mathscr{C})}$, which occurs at a rate $W(\mathscr{C}\to\mathscr{C}')$. This can (and will) be seen more mathematically later. In the stationary state, we must have $\frac{\mathrm{d}S}{\mathrm{d}t}=0$ and thus we expect

$$J_S = \sigma_{\mathrm{irr}} \geq 0 \tag{1.61}$$

with equality iff the detailed balance condition is fulfilled in the steady-state. This hints at a physical meaning of J_S as being an entropy production rate. The second example in what follows will confirm our intuition.

1.2.5 Of birth and death

A simple example of a process described by a master equation is a death process in which independent particles disappear with a rate γ. The probability $P(n,t)$ to find n particles in the system at time t evolves according to

$$\partial_t P(n,t) = \gamma(n+1)P(n+1,t) - \gamma n P(n,t) \tag{1.62}$$

and from there (though this is sort of obvious) one can derive the evolution of the mean particle number:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle n\rangle &= \sum_n n\left[\gamma(n+1)P(n+1,t) - \gamma n P(n,t)\right]\\ &= \sum_n \left[(n-1)\gamma n P(n,t) - n\gamma n P(n,t)\right]\\ &= -\gamma\sum_n nP(n,t)\\ &= -\gamma\langle n\rangle\end{aligned} \tag{1.63}$$

so that $\langle n\rangle(t) = \langle n\rangle(0)\mathrm{e}^{-\gamma t}$ which we could have written from the outset. If the initial distribution $P(n,0) = \mathrm{e}^{-\lambda}\frac{\lambda^n}{n!}$ is a Poisson distribution, then $P(n,t)$ is as well (with a parameter $\lambda\mathrm{e}^{-\gamma t}$) throughout time. This can be seen by injecting $P(n,t) = \mathrm{e}^{-z(t)}\frac{z(t)^n}{n!}$ into Eq. (1.62), which leads to

$$\forall n,\ -\dot{z} + n\frac{\dot{z}}{z} = \gamma(z-n) \tag{1.64}$$

which in turn imposes $\dot{z} = -\gamma z$, that is $z(t) = \mathrm{e}^{-\gamma t}\lambda$.

1.2.6 One dimensional random walkers on a lattice

Consider N random walkers on a one-dimensional lattice with L sites with periodic boundary conditions. Each particle can hop left or right with a rate p or q, provided the target site is empty, as configurations with more than one particle per site are forbidden. This is an asymmetric simple exclusion process (ASEP). The occupation numbers n_i for each lattice site $i = 1, \dots, L$ can only be 0 and 1. The master equation governing the evolution of a configuration $\mathscr{C} = \{n_1, \dots, n_L\}$ reads

$$\begin{aligned}\partial_t P(n_1,\dots,n_L,t) =& p\sum_{i=1}^{L}(1-n_{i+1})n_i P(n_1,\dots,1-n_i,1-n_{i+1},\dots,n_L,t)\\ &+ q\sum_{i=1}^{L}(1-n_i)n_{i+1}P(n_1,\dots,1-n_i,1-n_{i+1},\dots,n_L,t)\\ &- p\sum_{i=1}^{L} n_{i+1}(1-n_i)P(n_1,\dots,n_i,n_{i+1},\dots,n_L,t)\\ &- q\sum_{i=1}^{L} n_i(1-n_{i+1})P(n_1,\dots,n_i,n_{i+1},\dots,n_L,t)\end{aligned} \tag{1.65}$$

The prefactor $(1-n_{i+1})n_i$ in the rhs of the first line ensures that a particle is actually present in $i+1$ (so that this contributes only if $1-n_{i+1}=1$, and once the hop has occurred the final configuration indeed has $n_{i+1}=0$). The n_i factor ensures that $1-n_i$, namely the particle number at site i before the jump, is indeed null, so that before the jump i is empty. One can verify that the steady-state is uniform,

$$P_{\rm ss}(\{n_i\}) = \frac{1}{\binom{L}{N}} \tag{1.66}$$

Let's see what the formal quantity Q_S becomes in this example. Whenever a particle hops right (resp. left), Q_S picks up a contribution $\ln\frac{q}{p}$ (resp.$\ln\frac{p}{q}$), so that

$$Q_S = (\text{total number of hops to the right} - \text{total number of hops to the left})\ln\frac{q}{p} = Q\ln\frac{q}{p} \tag{1.67}$$

where Q is the total integrated particle current (in time and space) over the time interval $[0, t_{\rm obs}]$. Of course, $J = \langle\frac{{\rm d}Q}{{\rm d}t}\rangle$ stands for the average particle current flowing through the ring, and thus, in this particular example,

$$J_S = \underbrace{\ln\frac{q}{p}}_{\text{an external applied field}} \times \underbrace{J}_{\text{a current as a response to the applied field}} \tag{1.68}$$

which is a structure that is ubiquitous in driven systems. The field times the current is in general the power injected by the driving force into the system (and it is made altogether dimensionless by dividing by a temperature), so that J_S is the injected power divided by temperature. That is exactly what would expect from an entropy production rate on the basis of phenomenological thermodynamics. More examples will be investigated afterwards.

1.3 The adjoint Master Equation and first passage problems

For this section, a comprehensive reference with many applications is the book by Redner [163]. Specific applications to finance can be found here [62].

1.3.1 Backward master equation

Consider the probability $P(\mathscr{C}, t|\mathscr{C}', t')$ that, starting from configuration $\mathscr{C}'$ at time t', the system is in state $\mathscr{C}$ at time t. Then P is a solution of the forward master equation,

$$\partial_t P(\mathscr{C}, t|\mathscr{C}', t') = \mathbb{W}_{\mathscr{C},\mathscr{C}''} P(\mathscr{C}'', t|\mathscr{C}', t') \tag{1.69}$$

which can be solved into

$$P(\mathscr{C}, t|\mathscr{C}', t') = \left[\mathrm{e}^{\mathbb{W}(t-t')}\right]_{\mathscr{C},\mathscr{C}''} \underbrace{P(\mathscr{C}'', t'|\mathscr{C}', t')}_{\delta_{\mathscr{C}'',\mathscr{C}'}} = \left[\mathrm{e}^{\mathbb{W}(t-t')}\right]_{\mathscr{C},\mathscr{C}'} \tag{1.70}$$

This can be used to establish that

$$-\partial_{t'} P(\mathscr{C}, t|\mathscr{C}', t') = P(\mathscr{C}, t|\mathscr{C}'', t')\mathbb{W}_{\mathscr{C}'',\mathscr{C}'} \tag{1.71}$$

A probabilistic interpretation is easy to come by:

$$\begin{aligned} P(\mathscr{C}, t|\mathscr{C}', t' - \mathrm{d}t') =& P(\mathscr{C}, t|\mathscr{C}'', t') \times \underbrace{W(\mathscr{C}' \to \mathscr{C})\mathrm{d}t}_{\substack{\text{prob that between } t \text{ and } t+\mathrm{d}t \text{ a jump from } \mathscr{C}' \text{ to } \mathscr{C}'' \text{ has taken place}}} \\ &+ P(\mathscr{C}, t|\mathscr{C}', t') \times \underbrace{1 - r(\mathscr{C}')\mathrm{d}t'}_{\substack{\text{prob that no jump has taken place between } t' \text{ and } t'+\mathrm{d}t'}} \end{aligned} \tag{1.72}$$

Equation (1.71), which is known as the backward master equation, can also be cast in the form

$$\partial_{t'} P(\mathscr{C}, t|\mathscr{C}', t') = -(\mathbb{W}^T)_{\mathscr{C}',\mathscr{C}''} P(\mathscr{C}, t|\mathscr{C}'', t') \tag{1.73}$$

which again leads to

$$\begin{aligned} P(\mathscr{C}, t|\mathscr{C}', t') &= \left[\mathrm{e}^{-\mathbb{W}^T(t'-t)}\right]_{\mathscr{C}',\mathscr{C}''} P(\mathscr{C}, t|\mathscr{C}'', t) \\ &= \left[\mathrm{e}^{\mathbb{W}^T(t-t')}\right]_{\mathscr{C}',\mathscr{C}} \\ &= \left[\mathrm{e}^{\mathbb{W}(t-t')}\right]_{\mathscr{C},\mathscr{C}'} \end{aligned} \tag{1.74}$$

which is of course consistent. In the field of mathematics, a master equation is often written in its backward form rather than in its forward form.

1.3.2 First passage probability and mean first-passage time

Let $\mathscr{A}$ be a fixed set of absorbing configurations. We ask about the (survival) probability $S(\mathscr{C},t)$ that, starting from $\mathscr{C}\notin\mathscr{A}$, the system has never visited any member of $\mathscr{A}$ up until time t:

$$S(\mathscr{C},t)=\sum_{\mathscr{C}''\notin\mathscr{A}}P(\mathscr{C}'',t|\mathscr{C},0) \tag{1.75}$$

The boundary conditions on S are

$$\forall t,\,\forall\mathscr{C}\in\mathscr{A},\;S(\mathscr{C},t)=0 \text{ and } \forall\mathscr{C}\notin\mathscr{A},\;S(\mathscr{C},0)=1 \tag{1.76}$$

By linearity of the backward master equation, we can find an evolution equation for S:

$$\begin{aligned}\partial_t S(\mathscr{C},t)&=\sum_{\mathscr{C}''\notin\mathscr{A}}\partial_t P(\mathscr{C}'',t|\mathscr{C},0)\\&=\sum_{\mathscr{C}''\notin\mathscr{A}}\partial_t P(\mathscr{C}'',0|\mathscr{C},-t)\\&=\sum_{\mathscr{C}''\notin\mathscr{A}}(\mathbb{W}^T)_{\mathscr{C},\mathscr{C}'''}P(\mathscr{C}'',t|\mathscr{C}''',t')\\&=\sum_{\mathscr{C}''}S(\mathscr{C}'',t)\,W(\mathscr{C}\to\mathscr{C}'')-r(\mathscr{C})S(\mathscr{C},t)\\&=\mathbb{W}_{\mathscr{C}'',\mathscr{C}}S(\mathscr{C}'',t)\end{aligned} \tag{1.77}$$

or $\partial_t S=\mathbb{W}^T S$. The probability to hit an element of $\mathscr{A}$ for the first time at time t, starting from $\mathscr{C}$, is

$$S(\mathscr{C},t)=1-\int_0^t F_{\mathscr{A}}(\mathscr{C},t)\mathrm{d}t,\;F_{\mathscr{A}}=-\frac{\mathrm{d}S}{\mathrm{d}t} \tag{1.78}$$

The mean first-passage time to set $\mathscr{A}$ starting from $\mathscr{C}$ is given by

$$T_{\mathscr{A}}(\mathscr{C})=\int_0^{+\infty}\mathrm{d}t\;t\,F_{\mathscr{A}}(\mathscr{C},t) \tag{1.79}$$

Using that $F_{\mathscr{A}}(\mathscr{C},t)=-\partial_t S$ and an integration by parts, we see that

$$T_{\mathscr{A}}(\mathscr{C})=\int_0^{+\infty}\mathrm{d}t\,S(\mathscr{C},t) \tag{1.80}$$

where $S(\mathscr{C},0)=1$ and $\lim_{t\to+\infty}tS(\mathscr{C},t)=0$ were used. We thus immediately find that

$$\mathbb{W}^T T_{\mathscr{A}}=-1,\;\text{ or }(\mathbb{W}^T)_{\mathscr{C},\mathscr{C}'}T_{\mathscr{A}}(\mathscr{C}')=-1 \tag{1.81}$$

This equation will prove particularly useful in the chapter on rare events.

Another wording that does not invoke absorbing states is as follows (Van Kampen refers to this as being the renewal approach in chapter XII [195]). Let $F(\mathscr{C}_1,\mathscr{C}_2,t)$ be the probability

to visit configuration $\mathscr{C}_1$ for the first time at time t, given the process started at $\mathscr{C}_2$ at $t = 0$. We can write the propagator as follows:

$$t > 0,\ \mathscr{C} \neq \mathscr{C}',\ \ P(\mathscr{C}, t|\mathscr{C}', 0) = \int_0^t \mathrm{d}\tau F(\mathscr{C}, \mathscr{C}', \tau) P(\mathscr{C}, t|\mathscr{C}, \tau) \tag{1.82}$$

and then we can obtain $F_{\mathscr{A}}(\mathscr{C}, t) = \sum_{\mathscr{C}' \in \mathscr{A}} F(\mathscr{C}', \mathscr{C}, t)$. When the rates do not depend on time, $P(\mathscr{C}, t|\mathscr{C}, \tau) = P(\mathscr{C}, t - \tau|\mathscr{C}, 0)$ and Eq. (1.82) is a convolution that can be Laplace transformed with respect to t:

$$\hat{F}(\mathscr{C}, \mathscr{C}', z) = \frac{\hat{P}(\mathscr{C}, z|\mathscr{C}', 0)}{\hat{P}(\mathscr{C}, z|\mathscr{C}, 0)} \tag{1.83}$$

with $\hat{P}(\mathscr{C}, z|\mathscr{C}', 0) = \int_0^{+\infty} \mathrm{d}t \mathrm{e}^{-zt} \left[\mathrm{e}^{\mathbb{W}t}\right]_{\mathscr{C},\mathscr{C}'}$. Equivalently, we thus have that

$$\hat{F}(\mathscr{C}, \mathscr{C}', z) = \frac{\left[(z\mathbf{1} - \mathbb{W})^{-1}\right]_{\mathscr{C},\mathscr{C}'}}{\left[(z\mathbf{1} - \mathbb{W})^{-1}\right]_{\mathscr{C},\mathscr{C}}} \tag{1.84}$$

This shows that, at least formally, once P is known, one has access to F. As a boundary condition, we have that $F(\mathscr{C}, \mathscr{C}', 0) = \delta_{\mathscr{C},\mathscr{C}'}$. Then one can again introduce $S(\mathscr{C}, t) = 1 - \int_0^t F_{\mathscr{A}}(\mathscr{C}, t')\mathrm{d}t'$ which is the probability that, starting from $\mathscr{C}$, the first visit to any configuration of set $\mathscr{A}$ occurs after time t. Of course, for any set $\mathscr{C}$ in $\mathscr{A}$, $S(\mathscr{C}, t) = 0$ or, equivalently, $F(\mathscr{C}, \mathscr{C}, t') = \delta(t')$. And for any $\mathscr{C} \notin \mathscr{A}$ we have again $S(\mathscr{C}, 0) = 1$ as it is certain that the first visit to $\mathscr{A}$ will occur after $t = 0$.

The equation

$$\hat{F}(\mathscr{C}, \mathscr{C}'', z) = \frac{\hat{P}(\mathscr{C}, z|\mathscr{C}'', 0)}{\hat{P}(\mathscr{C}, z|\mathscr{C}, 0)} \tag{1.85}$$

can be multiplied with $\mathbb{W}_{\mathscr{C}'',\mathscr{C}'}$ and summed over $\mathscr{C}''$,

$$\sum_{\mathscr{C}''} \mathbb{W}^T_{\mathscr{C}',\mathscr{C}''} \hat{F}(\mathscr{C}, \mathscr{C}'', z) = \frac{\sum_{\mathscr{C}''} \mathbb{W}^T_{\mathscr{C}',\mathscr{C}''} \hat{P}(\mathscr{C}, z|\mathscr{C}'', 0)}{\hat{P}(\mathscr{C}, z|\mathscr{C}, 0)} \tag{1.86}$$

where, using Eq. (1.73),

$$\sum_{\mathscr{C}''} \mathbb{W}^T_{\mathscr{C}',\mathscr{C}''} \hat{P}(\mathscr{C}, z|\mathscr{C}'', 0) = \int_0^{+\infty} \mathrm{d}t \mathrm{e}^{-zt} \partial_t P(\mathscr{C}, t|\mathscr{C}', 0) = z\hat{P}(\mathscr{C}, z|\mathscr{C}', 0) - \delta_{\mathscr{C},\mathscr{C}'} \tag{1.87}$$

and thus

$$\sum_{\mathscr{C}''} \mathbb{W}^T_{\mathscr{C}',\mathscr{C}''} \hat{F}(\mathscr{C}, \mathscr{C}'', z) = \frac{z\hat{P}(\mathscr{C}, z|\mathscr{C}', 0) - \delta_{\mathscr{C},\mathscr{C}'}}{\hat{P}(\mathscr{C}, z|\mathscr{C}, 0)} \tag{1.88}$$

so that for $\mathscr{C} \neq \mathscr{C}'$, we have

$$\sum_{\mathscr{C}''} \mathbb{W}^T_{\mathscr{C}',\mathscr{C}''} \hat{F}(\mathscr{C}, \mathscr{C}'', z) = \frac{z\hat{P}(\mathscr{C}, z|\mathscr{C}', 0)}{\hat{P}(\mathscr{C}, z|\mathscr{C}, 0)} \tag{1.89}$$

and the average first passage time $\tau(\mathscr{C},\mathscr{C}'') = -\left.\frac{\mathrm{d}\hat{F}}{\mathrm{d}z}\right|_{z=0}$ thus verifies

$$\sum_{\mathscr{C}''} \mathbb{W}^{T}_{\mathscr{C}',\mathscr{C}''}\tau(\mathscr{C},\mathscr{C}'') = -\lim_{z\to 0}\frac{\hat{P}(\mathscr{C},z|\mathscr{C}',0)}{\hat{P}(\mathscr{C},z|\mathscr{C},0)} = -1 \tag{1.90}$$

It is possible to verify by brute force that the right-hand side in Eq. (1.90) is indeed –1. This is because, as $t\to+\infty$, $P(\mathscr{C},t|\mathscr{C}')\to P_{\rm ss}(\mathscr{C})$ and thus $\hat{P}(\mathscr{C},z|\mathscr{C}')\sim\frac{1}{z}P_{\rm ss}(\mathscr{C})\sim\hat{P}(\mathscr{C},z|\mathscr{C})$ (the memory of the initial state is forgotten).

M2 ICFP 2024-2025

Advanced Statistical Mechanics

Theoretical Physics track F. van Wijland

Chapter 2

Stochastic Dynamics

2.1 What is the question?

In order to set the goal of this chapter straight, it's a good idea to have a clear physical picture in mind. Consider a colloidal particle (micron sized) in a bath of water molecules (3.4 Å in size). The whole system is assumed to be in equilibrium. Of course, one is absolutely not

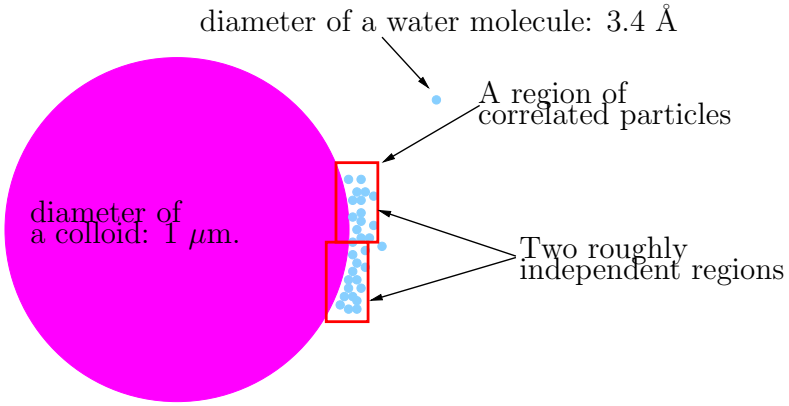

Figure 2.1: The regions of correlated particles are large enough so that they exceed in size the water molecules correlation length (also a few Å), but small enough so that there is a large number of these independent regions. For this to be possible, the separation of length scales between the bath particles and the colloid must be sufficient. Here we have four orders of magnitude.

interested in the properties of the bath of water molecules. What we are after are the statics and dynamics of the colloidal particle. The latter can in addition be subjected to gravity or to some optical laser-induced trapping, or to some electric field (if the colloid is charged). The Hamiltonian of the system has several contributions:

$$\mathscr{H} = \underbrace{\mathscr{H}_0(\mathbf{R},\mathbf{P})}_{\text{colloid, mass } M} + \underbrace{\mathscr{H}_b\left(\{\mathbf{r}_i,\mathbf{p}_i\}\right)}_{\text{water molecules}} + \underbrace{\sum_i V_i(\mathbf{R}-\mathbf{r}_i)}_{\text{interaction of the bath with the colloid}} \tag{2.1}$$

and the corresponding equations of motion read

$$m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\mathbf{F}_i - \partial_{\mathbf{r}_i}\mathscr{H}_b, \;\; M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -\partial_{\mathbf{R}}\mathscr{H}_0 + \sum_i \mathbf{F}_i \tag{2.2}$$

where $\mathbf{F}_i = -\partial_{\mathbf{R}} V_i(\mathbf{R} - \mathbf{r}_i)$ is the force exerted by water molecule i on the colloid. Regarding the statics, we can rely on equilibrium statistical mechanics to assert that one can actually forget about the molecules of the bath. The bath properties enter through a single number, namely its temperature T ($\beta = T^{-1}$), which is actually remarkable, and

$$P(\mathbf{R}, \mathbf{P}) \propto \mathrm{e}^{-\beta\mathscr{H}_0(\mathbf{R},\mathbf{P})} \tag{2.3}$$

Of course, this is true only if certain conditions are fulfilled (short range interactions, the bath is much bigger than the colloid, *etc.*). Regarding the dynamics, we would like to obtain an evolution equation for $\mathbf{R}$ only, forgetting about the bath molecules, or rather, forgetting about individual water molecules, but still retaining some of the relevant properties of the bath they make up. The last contribution is interesting, because if we sample our initial state from the Boltzmann distribution for the water molecules, then $\sum_i \mathbf{F}_i$ is a random variable. This is the sum of a large number of identically distributed random variables. They are correlated, but given the scale separation between the colloid and the water molecules, we expect that we can group $\sum_i \mathbf{F}_i$ into $\sum_{\text{regions}} \sum_{i\in\text{region}} \mathbf{F}_i$, where within a given region the water molecules are indeed correlated, while regions are independent. This is possible if the correlation length of the water molecules is smaller than the size of the colloid, and if it is sufficiently smaller so that there can be a large number of these independent regions, then the central limit theorem applies and we can write something like

$$\sum_i \mathbf{F}_i = \langle \sum_i \mathbf{F}_i \rangle_b + \text{Gaussian fluctuations} \tag{2.4}$$

where in principle $\langle \sum_i \mathbf{F}_i \rangle_b$ functionally depends on $\mathbf{R}$. Of course, we know what to expect for this average contribution. If for some external reason (gravity, electric field, pulling the center of the optical trap) the colloid has a net motion, it will have to push the water molecules away, and this will cause a viscous drag, that is a force proportional to $-\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}$. This viscous drag $-\gamma\dot{\mathbf{R}}$ involves a friction coefficient γ that can, for large enough colloids, be computed using hydrodynamics (for a colloid of radius a, $\gamma = 6\pi\eta a$ where η is the viscosity of water). Perhaps memory effects will come into play and the drag force could be a little more complicated, but if the repeated collisions of the water molecules occur at a high enough frequency (10^{13} Hz roughly [154] to be compared with the typical time at which velocity equilibrates, 10^{-9} s), memory effects can be considered irrelevant. Note that our arguments are explaining why we should expect that $\sum_i \mathbf{F}_i$ is a Gaussian random *variable*. But a little more discussion would be needed to ensure that this is a Gaussian *process* (this would involve a coarse-graining in time on top of the spatial coarse-graining we have just described by splitting space into regions small enough so that there is a large number of them, but big enough for possible correlations between these regions to be negligible).

The lesson we draw from this discussion is the following: if there is a separation of time and spatial scales, then things simplify considerably. The chapter begins with a formal hypothesis on

the existence of scale separation in a (continuous) master equation. This brings us to discussing what a Langevin equation is from a rather mathematical standpoint. Then we return to this introductory section in the quantum case to give a flavor of what a quantum Langevin equation is. And finally, we present an important tool to describe stochastic processes, path integrals.

2.2 Master equation, again

2.2.1 For one and several continuous variables

In a continuum notation, with x denoting a vector in a possible large dimensional space (though we'll stick to a one-dimensional derivation to begin with), with probability density $p(x,t)$, the master equation reads

$$\partial_t p(x,t) = \int \mathrm{d}x' w(x' \to x) p(x',t) - \int \mathrm{d}x' w(x \to x') p(x,t) \tag{2.5}$$

Writing $w(x \to x')$ as a function of the step size $x'-x$ and of the local position x, $w(x \to x') = \omega(x, x'-x)$, we can rewrite Eq. (2.5) as

$$\begin{aligned}
\partial_t p(x,t) &= \int \mathrm{d}x' w(x' \to x) p(x',t) - \int \mathrm{d}x' w(x \to x') p(x,t) \\
&= \int \mathrm{d}x' \omega(x', x-x') p(x',t) - \int \mathrm{d}x' \omega(x, x'-x) p(x,t) \\
&= \int \mathrm{d}r \omega(x-r, r) p(x-r,t) - \int \mathrm{d}r \omega(x,r) p(x,t) \\
&= \sum_{n\geq 1} \frac{(-1)^n}{n!} \partial_x^n \left[\left(\int \mathrm{d}r r^n \omega(x,r) \right) p(x,t) \right]
\end{aligned} \tag{2.6}$$

where the last line is written without any loss of generality as long as the whole series expansion is used. As expected, the master equation respects conservation of probability,

$$\partial_t p(x,t) = -\partial_x \cdot J \tag{2.7}$$

where J is the probability current. In one space dimension we have that

$$J(x,t) = -\sum_{n\geq 1} \frac{(-1)^n}{n!} \partial_x^{n-1} [a_n(x) p(x,t)] \tag{2.8}$$

where $a_n(x) = \int \mathrm{d}r r^n \omega(x,r)$. When we restore space indices $\mu = 1, \ldots, d$, things become a little heavier,

$$\begin{aligned}
\partial_t p(x,t) &= \int \mathrm{d}x' w(x' \to x) p(x',t) - \int \mathrm{d}x' w(x \to x') p(x,t) \\
&= \int \mathrm{d}x' \omega(x', x-x') p(x',t) - \int \mathrm{d}x' \omega(x, x'-x) p(x,t) \\
&= \int \mathrm{d}r \omega(x-r, r) p(x-r,t) - \int \mathrm{d}r \omega(x,r) p(x,t) \\
&= \sum_{n\geq 1} \frac{(-1)^n}{n!} \sum_{\mu_1,\ldots,\mu_n=1}^{d} \partial_{x^{\mu_1}} \ldots \partial_{x^{\mu_n}} \left[a_n^{\mu_1 \cdots \mu_n}(x) p(x,t) \right]
\end{aligned} \tag{2.9}$$

with

$$a_n^{\mu_1\cdots\mu_n}(x) = \int \mathrm{d}^d r r^{\mu_1}\dots r^{\mu_n}\omega(x,r) \tag{2.10}$$

Note that the probability current is always defined up to a curl (or its d-dimensional generalization), since

$$J'^{\mu} = J^{\mu} + \varepsilon^{\mu\nu\alpha_1\cdots\alpha_{d-2}}\partial_\nu H^{\alpha_1\cdots\alpha_{d-2}} \tag{2.11}$$

where H is an arbitrary $d-2$ dimensional tensor, verifies $\partial_\mu J'^{\mu} = \partial_\mu J^{\mu}$. While the above formula Eq. (2.10) appears to be a simple extension of the $d=1$ equation barely worthy of being mentioned, it will later prove important to understand how one can write a functional Fokker-Planck equation for a stochastic field $\phi(\mathbf{x},t)$ with continuous values, living in continuous space $\mathbf{x}\in\mathbb{R}^d$, where the discrete index $\mu = 1,\dots,d$ is now replaced by $\mathbf{x}$ living in the continuum and thus taking an noncountable infinite set of values. At the very least, if one has to deal with a stochastic field instead of a stochastic variable, it will prove convenient, for formal manipulations, to think of $\mathbf{x}$ has living in some discrete space $\mathbb{Z}^d$, to replace the uncountable infinite of indices by a countable one.

The so-called Kramers-Moyal coefficient $a_n(x) = \int \mathrm{d}r r^n \omega(x,r)$ that appears in the expansion has an simple physical meaning as we shall now see.

2.2.2 Infinitesimal jumps, and their moments

Start from position x_0 at time t_0 and study the random process over an infinitesimally small time window of duration Δt, between t_0 and $t_0+\Delta t$. Then the position evolves from x_0 to $x_0+\Delta x$ where Δx is random. The n-th moment of Δx is obtained as

$$\langle \Delta x^n\rangle = \int \mathrm{d}u u^n p(x_0+u, t_0+\Delta t|x_0,t_0) \tag{2.12}$$

where $p(x_0+u,t|x_0,t_0)$ is the solution to the partial differential equation at the end of Eq. (2.6) with initial condition $p(x_0+u,t_0|x_0,t_0)=\delta(u)$. Expanding

$$\begin{aligned} p(x_0+u,t_+\Delta t|x_0,t_0) =& \delta(u) + \Delta t\partial_t p + O(\Delta t^2) \\ =& \delta(u) + \Delta t\sum_{n\geq 1}(-1)^n\partial_u^n(a_n(x_0+u)\delta(u)) + O(\Delta t^2) \end{aligned} \tag{2.13}$$

immediately tells us that

$$\langle \Delta x^n\rangle = a_n(x_0)\Delta t + O(\Delta t^2),\ \lim_{\Delta t\to 0}\frac{\langle \Delta x^n\rangle}{\Delta t} = a_n(x_0) \tag{2.14}$$

The moments of the infinitesimal positional increment are identical to the Kramers-Moyal coefficients a_n (times Δt).

2.2.3 Approximations

If, as in our introductory motivational example, physics dictates that the scale over which r varies is much smaller than the typical scale over which x evolves, then expanding $\omega(x-r,x)$

in powers of r and truncating the resulting series expansion is legitimate. Forgetting about all $n \geq 2$ terms, we get

$$\partial_t p = -\partial_x(a_1 p) \tag{2.15}$$

and the resulting random process is simply deterministic, which is not very random. Forgetting all $n \geq 3$ terms is the celebrated diffusive approximation:

$$\partial_t p = -\partial_x(a_1 p) + \frac{1}{2}\partial_x^2(a_2 p) \tag{2.16}$$

and we shall call this equation a Fokker-Planck equation. Think again of the colloid whose position variations due to the kicks executed by the water molecules are much smaller than the micronic size of the colloid itself. It is remarkable that truncating the series expansion to the $n = 1$ or $n = 2$ orders still allows to interpret the truncated Eq. (2.6) as an equation for a probability distribution which has to remain non-negative. Truncating the series to any arbitrary order $n \geq 3$ may lead to mathematical inconsistencies, and should thus be done with great caution (see a recent work in quantitative finance [158]), as nothing warrants p will remain non-negative.

For completeness, and remaining at the level of the diffusive approximation, if x is a vector with d coordinates, with components x^μ, $\mu = 1, \ldots, d$, then the Kramers-Moyal coefficients become tensors,

$$i = 1, \ldots, n,\ \mu_i = 1, \ldots, d,\ a_n^{\mu_1 \cdots \mu_n}(x) = \lim_{\Delta t \to 0} \frac{\langle \Delta x^{\mu_1} \ldots \Delta x^{\mu_n} \rangle}{\Delta t} \tag{2.17}$$

and the corresponding diffusive Fokker-Planck equation then reads

$$\partial_t p = -\partial_{x^\mu}(a^\mu(x) p) + \frac{1}{2}\partial_{x^\mu}\partial_{x^\nu}(a^{\mu\nu} p) \tag{2.18}$$

Sometimes the notation $\omega^{\mu\nu}$ is used instead of $a^{\mu\nu}$. Its inverse $\omega_{\mu\nu}$ ($\omega_{\mu\alpha}\omega^{\alpha\nu} = \delta_\nu^\mu$) which is symmetric and positive-definite defines a metric tensor which can prove useful to identify as such in a variety of contexts (much in the same way as in quantum mechanics on curved spaces, as discussed in [54] or more recently in section 2.5 of [37]). If $\omega(x)$ denotes the determinant of $\omega_{\mu\nu}$ then $K(x,t) = P(x,t)/\sqrt{\omega(x)}$ evolves according to

$$\partial_t K = -\boldsymbol{\nabla}_\mu(h^\mu K) + \frac{1}{2}\nabla_\mu\nabla_\nu(\omega^{\mu\nu} K) \tag{2.19}$$

where $\nabla_\mu = \partial_\mu$ when acting on a scalar, and $\nabla_\mu A^\nu = \partial_\mu + \Gamma^\rho_{\mu\nu} A^\rho$ when acting on a vector A^ν. The Christoffel symbols are explicitly given by

$$\Gamma^\mu_{\rho\sigma} = \frac{1}{2}\omega^{\mu\nu}(\partial_\rho \omega_{\nu\sigma} + \partial_\sigma \omega_{\nu\rho} - \partial_\nu \omega_{\rho\sigma}) \tag{2.20}$$

and the vector h^μ is given by

$$h^\mu = a^\mu - \frac{1}{2}\Gamma^\rho_{\nu\rho}\omega^{\nu\mu} \tag{2.21}$$

2.3 Langevin equation

In this section the goal is to explore the properties of an abstract stochastic differential equation. The connection with the physical problems of interest will appear towards the end. We'll now define a random process via a recursion relation, the continuum limit of which is a so-called Langevin equation. The process we shall define is Markovian, so that we expect that there exists a master equation that describes its statistics. The question will then be: what is the corresponding master equation?

2.3.1 Gaussian random variables

We consider a set of M Gaussian variables ξ_m distributed according to

$$P(\boldsymbol{\xi}) = Z^{-1} \mathrm{e}^{-\frac{1}{2}\boldsymbol{\xi}\cdot\Gamma\boldsymbol{\xi}} \tag{2.22}$$

where $\Gamma_{mm'}$ is a positive matrix (which we choose to be symmetric without loss of generality). The normalization factor is $Z = (2\pi)^{M/2}/\sqrt{\det\Gamma}$. A known property of the Gaussian distribution is that its generating function has the expression

$$G[\mathbf{h}] = \langle \mathrm{e}^{\mathbf{h}\cdot\boldsymbol{\xi}} \rangle = \mathrm{e}^{\frac{1}{2}\mathbf{h}\cdot\Gamma^{-1}\mathbf{h}} \tag{2.23}$$

By definition, this means that a Gaussian variable has no cumulant of order greater than or equal to three. There are two straightforward consequences of Eq. (2.23). The first one is that, if one introduces

$$G_{ij} = \left.\frac{\partial^2 \ln G}{\partial h_i \partial h_j}\right|_{\mathbf{h}=0} = (\Gamma^{-1})_{ij} \tag{2.24}$$

then we must have

$$\langle \xi_i \xi_j \rangle = G_{ij} \tag{2.25}$$

The second consequence is Wick's theorem, which states that

$$\langle \xi_1 \dots \xi_{2k} \rangle = \sum{}' G_{i_1 i_2} \dots G_{i_{2k-1}, i_{2k}} \tag{2.26}$$

where the symbol $\sum'$ bears on all the $(2k-1)!!$ distinct pairings $\{i_1, \dots, i_{2k}\}$ of $\{1, \dots, 2k\}$.

We may picture the Gaussian variable as a discrete time process in which $m = 1, \dots, M$ is viewed as a time-slice index. We denote by $t_m = m\Delta t$ and we take the $\Delta t \to 0$ limit with the ratio $M = t_{\mathrm{obs}}/\Delta t$ going to infinity as t_{obs} is fixed. In this limit, the Gaussian probability can be rewritten

$$\begin{aligned} P[\boldsymbol{\xi}]\mathrm{d}^M\xi &= Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\sum_{m,m'=1}^{M}\xi_m\Gamma_{m,m'}\xi'_m} \\ &= Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\int \mathrm{d}t\mathrm{d}t'\xi(t)\Gamma(t,t')\xi(t')} \end{aligned} \tag{2.27}$$

where $\sum_m \leftrightarrow \int \mathrm{d}t/\Delta t$, and where

$$\xi(t) = \Delta t^{-1/2}\xi_{t/\Delta t}, \ \Gamma(t,t') = \Delta t^{-1}\Gamma_{t/\Delta t, t'/\Delta t} \tag{2.28}$$

The noise kernel $\Gamma(t,t')$ has the dimension of an inverse time. The inverse kernel $G(t,t')$ which verifies

$$\int \mathrm{d}t_2 \Gamma(t_1,t_2)G(t_2,t_3) = \delta(t_1-t_3) \tag{2.29}$$

can of course be viewed as the continuum analog of $G_{ij}/\Delta t$:

$$\begin{aligned} \sum_{m_2} \Gamma_{m_1,m_2} G_{m_2,m_3} &= \delta_{m_1,m_3} \\ \int \mathrm{d}t_2 \Delta t^{-1} \Delta t \Gamma(t_1,t_2) G_{t_2/\delta,t_3/\delta} &= \Delta t \delta(t_1-t_3) \end{aligned} \tag{2.30}$$

which indeed leads to identifying $G(t_2,t_3) = G_{t_2/\Delta t,t_3/\Delta t}/\Delta t = \langle \xi(t_2)\xi(t_3)\rangle$.

In terms of notation, we use the path-integral notation

$$\begin{aligned} P[\boldsymbol{\xi}]\mathrm{d}^M\xi =& Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\sum_{m,m'=1}^M \xi_m \Gamma_{m,m'}\xi'_m} \\ =& P[\xi(t)]\mathscr{D}\xi,\ P[\xi] = \mathrm{e}^{-\frac{1}{2}\int \mathrm{d}t\mathrm{d}t' \xi(t)\Gamma(t,t')\xi(t')} \end{aligned} \tag{2.31}$$

but this only makes sense as the continuum limit of a discretized version.

In terms of vocabulary, if $\Gamma_{ij} = G_{ij} = \delta_{ij}$ then $\Gamma(t,t') = G(t,t') = \delta(t-t')$ and the resulting limiting process $\xi(t)$ is called a Gaussian white noise. Whenever Γ is not a δ kernel, one refers to ξ as a colored Gaussian process.

At this stage, it is not clear what the process $\xi(t)$ represents, and it is not clear either why, if ξ_m is a perfectly well-behaved Gaussian variable, the $\xi(t) = \xi_m/\sqrt{\Delta t}$ (with $t = m\Delta t$) counterpart would be too. Suppose we want to evaluate, for a given Δt, the quantity

$$x_M = \Delta t^{1/2} \sum_{m=0}^{M} \xi_m \tag{2.32}$$

then it is clear that $\langle x_M\rangle = 0$ and that

$$\langle x_M^2\rangle = \Delta t M = t_{\mathrm{obs}} \tag{2.33}$$

without even taking any $\Delta t \to 0$ limit. This shows that the quantity x_M has a well-defined limit as $\Delta t \to 0$ (M going to infinity, Δt going to zero, while keeping $t_{\mathrm{obs}} = M\Delta t$ fixed). If we had used the continuous notation, we would have written, with $x(t_{\mathrm{obs}}) = x_M$,

$$x(t_{\mathrm{obs}}) = \Delta t^{1/2} \sum_m \xi_m = \int_0^{t_{\mathrm{obs}}} \mathrm{d}s \xi(s) \tag{2.34}$$

and similarly

$$\langle x(t_{\mathrm{obs}})^2\rangle = \int_0^{t_{\mathrm{obs}}} \mathrm{d}s_1 \int_0^{t_{\mathrm{obs}}} \mathrm{d}s_2 \langle \xi(s_1)\xi(s_2)\rangle = \int_0^{t_{\mathrm{obs}}} \mathrm{d}s_1 \int_0^{t_{\mathrm{obs}}} \mathrm{d}s_2 \delta(s_1-s_2) = t_{\mathrm{obs}} \tag{2.35}$$

and we do find the same result. Of course, if the Δt prefactor had, for some reason, been absent from the definition of x_M, we would not have obtained any well defined $\Delta t \to 0$ limit.

2.3.2 Stochastic differential equation

Let x_0 fixed and define x_n via the following recursion relation,

$$x_{m+1} - x_m = f(x_m)\Delta t + g(x_m)\sqrt{\Delta t}\eta_m,\ m = 0, 2, \ldots \tag{2.36}$$

where the η_m's are independent zero-mean Gaussian variables with unit variance,

$$\langle \eta_m \eta_{m'} \rangle = \delta_{mm'} \tag{2.37}$$

For the moment, the functions f and g are arbitrary and $\Delta t > 0$ will eventually be taken as small as possible. With the recursion Eq. (2.36), one constructs a sequence $x_1, x_2 \ldots$ of random variables. It is tempting to define

$$x(t) = x_{t/\Delta t} \tag{2.38}$$

and to write that Eq. (2.36) amounts to

$$\Delta x = x(t + \Delta t) - x(t) = f(x(t))\Delta t + g(x(t))\Delta\eta \tag{2.39}$$

where $\Delta\eta$ is a Gaussian variable with zero mean and variance Δt ($\Delta\eta$ is the continuum version of $\sqrt{\Delta t}\eta_m$ with $m = t/\Delta t$). Let η be a Gaussian process characterized by $G(t, t') = \langle \eta(t)\eta(t') \rangle = \delta(t - t')$, then one can write that $\Delta\eta = \int_t^{t+\Delta t} \mathrm{d}s\eta(s)$, as these quantities have the same statistics. They are both Gaussian and can bee seen to have the same variance:

$$\langle \Delta\eta^2 \rangle = \int_t^{t+\Delta t} \mathrm{d}_1\mathrm{d}t_2 \langle \eta(t_1)\eta(t_2) \rangle = \Delta t \tag{2.40}$$

It is then natural to adopt the following continuum time formulation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = f(x(t)) + g(x(t))\eta(t) \tag{2.41}$$

We immediately see that while it is fine to assume that the sequence can help us build a continuous function $x(t)$, it is certainly not right to assume that x is differentiable, simply because

$$\frac{x_{m+1} - x_m}{\Delta t} = f(x_m) + g(x_m)\frac{\eta_m}{\sqrt{\Delta t}} \tag{2.42}$$

and since η_m is $O(1)$ in Δt, the last term diverges to infinity as $\Delta t^{-1/2}$. It is therefore unlikely that Eq. (2.41) will ever appear as such in the mathematical literature. What is actually written is

$$\mathrm{d}x = f(x(t))\mathrm{d}t + g(x(t))d\eta(t) \tag{2.43}$$

where $\mathrm{d}\eta$ is a Gaussian variable with variance $\mathrm{d}t$ ($\mathrm{d}B$ or $\mathrm{d}\,W$ are often favorite notations among mathematicians, not $\mathrm{d}\eta$). Of course, there are unavoidable problems that we will run into by insisting to work with Eq. (2.41) as if x were a differentiable function. All these problems disappear when a discretized formulation is used.

One such problem is the following. Consider a discretized process

$$\Delta x = x(t + \Delta t) - x(t) = f(x + \alpha\Delta x)\Delta t + g(x + \alpha\Delta x)\Delta\eta \tag{2.44}$$

where $0 \leq \alpha \leq 1$. Quite naïvely, the continuum limit of Eq. (2.44) is exactly the same as that of Eq. (2.36), namely $\dot{x} = f + g\eta$. However, as we see from Eq. (2.44), Δx is $O(\sqrt{\Delta t})$ and thus, when we write $g(x + \alpha\Delta x)\Delta\eta$ instead of $g(x)\Delta\eta$ we neglect terms that are of order $\alpha g'(x)\Delta x\Delta\eta \sim O(\Delta t)$, that is terms of the same order as the deterministic contribution $f\Delta t$. However, whether we write $f(x + \alpha\Delta x)\Delta t$ or $f(x)\Delta t$ shouldn't make any difference in the $\Delta t \to 0$ limit. For now, we shall stick to the discretized process defined by Eq. (2.36) or Eq. (2.39). We will now determine the statistical properties of Δx.

2.3.3 Infinitesimal jumps

Start at time t_0 with $x = x(t_0)$ which is fixed, and consider the random variable $\Delta x = x(t_0 + \Delta t) - x(t_0)$ for small Δt. We know that

$$\Delta x = f(x(t_0))\Delta t + g(x(t_0))\Delta\eta \tag{2.45}$$

so that taking the average leads to $\langle\Delta x\rangle = f(x(t_0))\Delta t$. The second moment reads

$$\begin{aligned}\langle\Delta x^2\rangle =& \langle f(x(t_0))^2\Delta t^2 + g(x(t_0))^2\Delta\eta^2 + 2f(x(t_0))\Delta t g(x(t_0))\Delta\eta\rangle \\ =& g(x(t_0))^2\langle\Delta\eta^2\rangle + O(\Delta t^{3/2}) \\ =& g(x(t_0))^2\Delta t + O(\Delta t^{3/2})\end{aligned} \tag{2.46}$$

The third moment reads

$$\begin{aligned}\langle\Delta x^3\rangle =& \langle f(x(t_0))^3\Delta t^3 + g(x(t_0))^3\Delta\eta^3 + 3f(x(t_0))\Delta t g(x(t_0))^2\Delta\eta^2 + 3f(x(t_0))^2\Delta t^2 g(x(t_0))\Delta\eta\rangle \\ =& O(\Delta t^{3/2})\end{aligned} \tag{2.47}$$

and we therefore realize that

$$\lim_{\Delta t\to 0}\frac{\langle\Delta x\rangle}{\Delta t} = f(x(t_0)),\quad \lim_{\Delta t\to 0}\frac{\langle\Delta x^2\rangle}{\Delta t} = g(x(t_0))^2,\quad \lim_{\Delta t\to 0}\frac{\langle\Delta x^k\rangle}{\Delta t} = 0 \text{ for } k \geq 3 \tag{2.48}$$

This means that the process $x(t)$ is entirely defined by the first two moments of Δx and that it must have exactly the same properties as a process described by a Fokker-Planck equation with exactly the same first two moments of Δx. In other words, the Langevin equation Eq. (2.39) for x must contain the same physics as the Fokker-Planck equation Eq. (2.16) with

$$a_1 = f,\ \ a_2 = g^2 \tag{2.49}$$

or

$$\dot{x} = f + g\eta \iff \Delta x = x(t + \Delta t) - x(t) = f(x)\Delta t + g(x)\Delta\eta \iff \partial_t p = -\partial_x(fp) + \frac{1}{2}\partial_x^2(g^2 p) \tag{2.50}$$

where $0 \leq \alpha \leq 1$. Quite naïvely, the continuum limit of Eq. (2.44) is exactly the same as that of Eq. (2.36), namely $\dot{x} = f + g\eta$. However, as we see from Eq. (2.44), Δx is $O(\sqrt{\Delta t})$ and thus, when we write $g(x + \alpha\Delta x)\Delta\eta$ instead of $g(x)\Delta\eta$ we neglect terms that are of order $\alpha g'(x)\Delta x\Delta\eta \sim O(\Delta t)$, that is terms of the same order as the deterministic contribution $f\Delta t$. However, whether we write $f(x + \alpha\Delta x)\Delta t$ or $f(x)\Delta t$ shouldn't make any difference in the $\Delta t \to 0$ limit. For now, we shall stick to the discretized process defined by Eq. (2.36) or Eq. (2.39). We will now determine the statistical properties of Δx.

2.3.3 Infinitesimal jumps

Start at time t_0 with $x = x(t_0)$ which is fixed, and consider the random variable $\Delta x = x(t_0 + \Delta t) - x(t_0)$ for small Δt. We know that

$$\Delta x = f(x(t_0))\Delta t + g(x(t_0))\Delta\eta \tag{2.45}$$

so that taking the average leads to $\langle\Delta x\rangle = f(x(t_0))\Delta t$. The second moment reads

$$\begin{aligned}\langle\Delta x^2\rangle =& \langle f(x(t_0))^2\Delta t^2 + g(x(t_0))^2\Delta\eta^2 + 2f(x(t_0))\Delta t g(x(t_0))\Delta\eta\rangle \\ =& g(x(t_0))^2\langle\Delta\eta^2\rangle + O(\Delta t^{3/2}) \\ =& g(x(t_0))^2\Delta t + O(\Delta t^{3/2})\end{aligned} \tag{2.46}$$

The third moment reads

$$\begin{aligned}\langle\Delta x^3\rangle =& \langle f(x(t_0))^3\Delta t^3 + g(x(t_0))^3\Delta\eta^3 + 3f(x(t_0))\Delta t g(x(t_0))^2\Delta\eta^2 + 3f(x(t_0))^2\Delta t^2 g(x(t_0))\Delta\eta\rangle \\ =& O(\Delta t^{3/2})\end{aligned} \tag{2.47}$$

and we therefore realize that

$$\lim_{\Delta t\to 0}\frac{\langle\Delta x\rangle}{\Delta t} = f(x(t_0)),\quad \lim_{\Delta t\to 0}\frac{\langle\Delta x^2\rangle}{\Delta t} = g(x(t_0))^2,\quad \lim_{\Delta t\to 0}\frac{\langle\Delta x^k\rangle}{\Delta t} = 0 \text{ for } k \geq 3 \tag{2.48}$$

This means that the process $x(t)$ is entirely defined by the first two moments of Δx and that it must have exactly the same properties as a process described by a Fokker-Planck equation with exactly the same first two moments of Δx. In other words, the Langevin equation Eq. (2.39) for x must contain the same physics as the Fokker-Planck equation Eq. (2.16) with

$$a_1 = f,\ \ a_2 = g^2 \tag{2.49}$$

or

$$\dot{x} = f + g\eta \iff \Delta x = x(t + \Delta t) - x(t) = f(x)\Delta t + g(x)\Delta\eta \iff \partial_t p = -\partial_x(fp) + \frac{1}{2}\partial_x^2(g^2 p) \tag{2.50}$$

2.3.4 Stochastic calculus: differentiation

Let's get back to the issue that we brushed upon higher up. Since there is a variety of discretized processes that naively lead to the same visual stochastic differential equation, it may be worth exploring these various discretized equations. Take $0 \leq \alpha \leq 1$ and consider Eq (2.44) which we repeat here:

$$\Delta x = x(t+\Delta t) - x(t) = f(x+\alpha\Delta x)\Delta t + g(x+\alpha\Delta x)\Delta\eta \tag{2.51}$$

For $\alpha = 0$ this is the case considered before and the Langevin equation $\dot{x} = f + g\eta$ understood in this very discretization scheme is called an Itō-discretized Langevin equation. For $\alpha = 1/2$ this is the Stratonovich discretization, and for $\alpha = 1$ this is the Hänggi-Klimontovich discretization. Before we argue about why these discretization schemes are of any interest, we want to point that for $\alpha = 0$, the discretized Langevin equation is rather easy to implement numerically, as x_{m+1} is explicitly given in terms of x_m and of the noise η_m : $x_{m+1} = x_m + \Delta t f(x_m) + \sqrt{\Delta t} g(x_m)\eta_m$. Whenever $\alpha \neq 0$ this becomes an implicit equation for x_m and this is obviously less convenient, at least numerically. There are however connections between $\alpha = 0$ and $\alpha \neq 0$. To make this connection explicit, we evaluate the moments of $\Delta x = x_{m+1} - x_m = x(t+\Delta t) - x(t)$ to leading order in the $\Delta t \to 0$ limit. The first one is the trickiest one:

$$\begin{aligned}\langle \Delta x \rangle =& \langle \Delta t f(x(t)+\alpha\Delta x) + g(x(t)+\alpha\Delta x)\Delta\eta \rangle \\ =& \Delta t f(x(t)) + O(\Delta t^{3/2}) + \langle \left[g(x(t)) + \alpha g'(x(t))\Delta x \right] \Delta\eta \rangle \\ =& \Delta t f(x(t)) + O(\Delta t^{3/2}) + \alpha g'(x(t)) \langle \Delta x \Delta\eta \rangle\end{aligned} \tag{2.52}$$

and again

$$\begin{aligned}\langle \Delta x \Delta\eta \rangle =& \langle \Delta\eta \left[\Delta t f(x(t)+\alpha\Delta x) + g(x(t)+\alpha\Delta x)\Delta\eta \right] \rangle \\ =& \langle \Delta\eta g(x(t))\Delta\eta \rangle + O(\Delta t^{3/2}) \\ =& g(x(t))\Delta t + O(\Delta t^{3/2})\end{aligned} \tag{2.53}$$

so that eventually

$$\langle \Delta x \rangle = \Delta t \left[f(x(t)) + \alpha g'(x(t)) g(x(t)) \right] + O(\Delta t^{3/2}) \tag{2.54}$$

By a similar method, one sees that

$$\lim_{\Delta t \to 0} \frac{\langle \Delta x^2 \rangle}{\Delta t} = g(x)^2, \quad \lim_{\Delta t \to 0} \frac{\langle \Delta x^k \rangle}{\Delta t} = 0 \text{ for } k \geq 3 \tag{2.55}$$

so that we now have a proof that whether $\dot{x} = f + g\eta$ is understood with $\alpha = 0$ or $\alpha \neq 0$, this corresponds to different physical processes described by different Fokker-Planck equations:

$$\begin{aligned}\dot{x} \overset{0}{=} f + g\eta \iff & \Delta x = x(t+\Delta t) - x(t) = f(x)\Delta t + g(x)\Delta\eta \\ \iff & \partial_t p = -\partial_x(fp) + \frac{1}{2}\partial_x^2(g^2 p) \\ \dot{x} \overset{\alpha}{=} f + g\eta \iff & \Delta x = x(t+\Delta t) - x(t) = f(x+\alpha\Delta x)\Delta t + g(x+\alpha\Delta x)\Delta\eta \\ \iff & \partial_t p = -\partial_x((f + \alpha g' g)p) + \frac{1}{2}\partial_x^2(g^2 p)\end{aligned} \tag{2.56}$$

because the process of Eq. (2.44) has $a_1 = f + \alpha g' g$ and $a_2 = g^2$. That also means that it is always possible to go back and forth between two processes that are discretized differently:

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{x} \overset{0}{=} f + \alpha g' g + g\eta \tag{2.57}$$

or, even more generally,

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{x} \overset{\alpha'}{=} f + (\alpha - \alpha') g' g + g\eta \tag{2.58}$$

where the same Fokker-Planck equation $\partial_t p = -\partial_x[(f + \alpha g' g)p] + \frac{1}{2}\partial_x(g^2 p)$ applies to either formulation. Henceforth, whenever a stochastic differential equation is written, and when g is not a constant, we'll specify its underlying discretization rule by dressing the equal sign with a superscript α. It would be tempting to conclude that these difficulties only occur when g is not a constant (because if g is a constant, $g' = 0$ and all the trouble disappears), and since Langevin equations with a nontrivial g are probably an exception, there is no point in spending time on these mathematical details. None of these two reasons is true: first, if x evolves according to an additive Langevin equation (that is with a constant g) then any $u(t) = U(x(t))$ won't, and second, there are plenty of situations where a multiplicative noise (g a nontrivial function of x) shows up.

Consider now an auxilary random process $u(t) = U(x(t))$ built directly from x (where U is some smooth enough function). Let's see how u evolves in time:

$$\begin{aligned}
\Delta u =& u(t + \Delta t) - u(t) = U(x + \Delta x) - U(x) \\
=& \Delta x U' + \frac{1}{2}\Delta x^2 U''(x) + O(\Delta t^{3/2}) \\
=& (f(x)\Delta t + g(x + \alpha \Delta x)\Delta\eta) U'(x) + \frac{1}{2}\Delta x^2 U''(x) + O(\Delta t^{3/2}) \\
=& (f(x)\Delta t + \alpha g'(x)\Delta x \Delta\eta) U'(x) + \frac{1}{2}\Delta x^2 U''(x) + U'(x) g(x)\Delta\eta + O(\Delta t^{3/2}) \\
=& (f(x)\Delta t + \alpha g'(x) g(x)\Delta\eta^2) U'(x) + \frac{1}{2}\Delta x^2 U''(x) + U'(x) g(x)\Delta\eta + O(\Delta t^{3/2})
\end{aligned} \tag{2.59}$$

so that

$$\lim_{\Delta t \to 0} \frac{\langle \Delta u \rangle}{\Delta t} = (f + \alpha g' g) U' + \frac{1}{2} g^2 U'' \tag{2.60}$$

However, the second moment of Δu is much simpler to derive,

$$\lim_{\Delta t \to 0} \frac{\langle \Delta u^2 \rangle}{\Delta t} = g^2 U'^2 \tag{2.61}$$

and as expected $\lim_{\Delta t \to 0} \frac{\langle \Delta u^k \rangle}{\Delta t} = 0$ for $k \geq 3$. This means that u too evolves according to a Langevin equation.

In the particular case $\alpha = 0$, because we have

$$\text{for } \alpha = 0, \lim_{\Delta t \to 0} \frac{\langle \Delta u \rangle}{\Delta t} = f U' + \frac{1}{2} g^2 U'', \lim_{\Delta t \to 0} \frac{\langle \Delta u^2 \rangle}{\Delta t} = g^2 U'^2 \tag{2.62}$$

we see that the process must evolve according to the following Itō-discretized Langevin equation

$$\dot{u} \overset{0}{=} fU' + \frac{1}{2} g^2 U'' + U' g\eta \tag{2.63}$$

This Eq. (2.63) is the celebrated Itō's lemma, where the piece that corrects the standard chain rule of differential calculus has been highlighted in red.

Note also that for α arbitrary, we have that

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{0}{=} fU' + \alpha g' g U' + \frac{1}{2} g^2 U'' + U' g\eta \tag{2.64}$$

and thus, using the correspondence in Eq. (2.58)

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{\alpha}{=} fU' + \alpha g' g U' - \alpha \left[\frac{\mathrm{d}}{\mathrm{d}u} \left(gU' \right) \right] gU' + \frac{1}{2} g^2 U'' + U' g\eta \tag{2.65}$$

or, equivalently, using that $\left[\frac{\mathrm{d}}{\mathrm{d}u} \left(gU' \right) \right] gU' = g' g U' + g^2 U''$

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{\alpha}{=} fU' + \left(\frac{1}{2} - \alpha \right) g^2 U'' + U' g\eta \tag{2.66}$$

This means in particular that for the Stratonovich discretization with $\alpha = 1/2$ we have

$$\dot{x} \overset{1/2}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{1/2}{=} fU' + U' g\eta, \; u(t) = U(x(t)) \tag{2.67}$$

That is really remarkable! This means that even though neither x nor u are differentiable, when resorting to the Stratonovich discretization, we can manipulate these functions as if they were actually differentiable since the chain rule of derivation applies. This is not the only advantage of the Stratonovich discretization. It is also, quite simply, the only natural discretization scheme that follows from the elimination of the fast degrees of freedom (this will be seen during the tutorials).

All of the above formulas have been derived for scalar functions and they become somewhat more complex in higher space dimension. For instance, the α-discretized process

$$\dot{x}^\mu \overset{\alpha}{=} f^\mu + g^{\mu i} \eta_i \tag{2.68}$$

with $\mu = 1, \ldots, d$ and i running between 1 and an integer less than d, has

$$a_1^\mu = f^\mu + \alpha \partial_\nu g^{\mu i} g^{\nu i}, \; a_2^{\mu\nu} = g^{\mu i} g^{\nu i} = \omega^{\mu\nu} \tag{2.69}$$

and Itō's lemma becomes

$$\dot{u}^\mu = \partial_\nu U^\mu f^\nu + \frac{1}{2} \partial_\nu \partial_\rho U^\mu \omega^{\nu\rho} + \partial_\nu U^\mu g^{\nu i} \eta_i \tag{2.70}$$

2.3.5 Stochastic calculus: integration

We want to understand how integrating a function of a Langevin process can be done, and whether there are any pitfalls. We consider a random process $x(t)$ which evolves according to the Langevin equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} \overset{\alpha}{=} f(x) + g(x)\eta\,, \tag{2.71}$$

understood as α-discretized. First, we focus on observables of the form

$$\mathcal{O}_0 = \int_0^{t_{\rm obs}} \mathrm{d}t\, h(x(t))\,, \tag{2.72}$$

where h is a (smooth enough) arbitrary function, which, when expressed in terms of the discrete-time companion process, reads

$$\mathcal{O}_0 = \lim_{\Delta t\to 0} \sum_{k=0}^{M} \Delta t\, h(x_k) \tag{2.73}$$

with $M = t_{\rm obs}/\Delta t$. In the $\Delta t \to 0$ limit, one could have also written

$$\mathcal{O}_0 = \lim_{\Delta t\to 0} \sum_{k=0}^{M} \Delta t\, h(x_k + \alpha'\Delta x_k)\,, \tag{2.74}$$

for any $\alpha' \in [0,1]$ with $\Delta x_k = x_{k+1} - x_k$. In other words, in the continuous-time limit, the specific discretization scheme of the integral in Eq. (2.72) is irrelevant, and no special care is in order.

Other interesting observables that, for example, often arise in the field of stochastic thermodynamics [176, 177] are of the form

$$\mathcal{O}_1 \overset{\alpha'}{=} \int_0^{t_{\rm obs}} \mathrm{d}t\, \dot{x}(t)\, h(x(t))\,, \tag{2.75}$$

which in terms of the discrete-time companion process reads

$$\mathcal{O}_1 = \lim_{\Delta t\to 0} \sum_{k=0}^{M-1} \Delta t\, \frac{\Delta x_k}{\Delta t}\, h(x_k + \alpha'\Delta x_k)\,. \tag{2.76}$$

The discretization scheme has been made explicit above the equality sign by the α' label appearing in Eq. (2.75). Due to the scaling $\Delta x_k = O(\sqrt{\Delta t})$, the discretization of the integral, namely the point at which the function h is evaluated, is relevant even in the $\Delta t \to 0$ limit. This statement is very similar to the fact that one needs to specify the discretization of g in the discrete-time companion process of Eq. (2.71). Note that α and α' are not necessarily related: α determines the evolution of the process x while α' enters the definition of the observable

$\mathcal{O}_1$. Integrals of the form Eq. (2.75) with $\alpha' = 0$ (respectively $\alpha' = 1/2$) are referred to as Itō integrals (respectively, Stratonovich integrals).

The observable $\mathcal{O}_2$, defined by its discrete expression as

$$\mathcal{O}_2 = \lim_{\Delta t \to 0} \sum_{k=0}^{M-1} \Delta t \, \frac{\Delta x_k^2}{\Delta t} \, h(x_k) \, , \tag{2.77}$$

shows that it is finite in the $\Delta t \to 0$ limit. The discretization of h is irrelevant to define the continuous-time limit of $\mathcal{O}_2$.

2.3.6 Stochastic calculus with a white yet non-Gaussian noise

It is possible to extend the rules of stochastic calculus to non-Gaussian yet white noises [55, 67, 113]. This has application in engineering, but also to finance [160]. Consider the following differential equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} \overset{0}{=} f(x) + g(x)\eta \tag{2.78}$$

where $\eta(t)$ is a white noise with zero average. A white noise is a random process with connected correlations

$$\langle \eta(t_1) \dots \eta(t_n) \rangle_c = \kappa_n \delta(t_1 - t_2) \dots \delta(t_{n-1} - t_n) \tag{2.79}$$

such that the moments of $\Delta\eta = \int_{t_0}^{t_0+\Delta t} \eta(s)\mathrm{d}s$ are given by $\langle \Delta\eta^n \rangle = \kappa_n \Delta t$. Over a time interval $[0, t_{\rm obs}]$ a number of points n is drawn from a Poisson distribution with density ν (average $\nu t_{\rm obs}$), and to each of these points a uniform random variable $t_i \in [0, t_{\rm obs}]$ is introduced along with a random number ℓ_i drawn from some distribution $\pi(\ell)$ (for $i = 1, \dots, n$, the t_i's and the ℓ_i's are independent). Then $\eta(t) = \sum_i \ell_i \delta(t - t_i)$ is a Poisson point process, with generating functional $Z[h] = \langle \mathrm{e}^{-\int h\eta} \rangle = \mathrm{e}^{\int \mathrm{d}t \left(\langle \mathrm{e}^{-\ell h(t)} \rangle_\pi - 1 \right)}$. With these notations, one readily sees that $\kappa_n = \nu \langle \ell^n \rangle_\pi$. The scaling limit in which $\nu \to +\infty$ while keeping $\nu \langle \ell^2 \rangle$ fixed leads to a Gaussian noise. It is possible to perform stochastic calculus with such a white yet non Gaussian noise, but this is beyond the scope of this presentation.

Note that to leading order in Δt, the n-th moment is also the n-th cumulant of $\Delta\eta$. This immediately tells us that Eq. (2.78) must indeed be endowed with a discretized meaning. If we integrate it between t_0 and $t_0 + \Delta t$ we arrive at the Itō-discretized form

$$\Delta x = x(t_0 + \Delta t) - x(t_0) = f(x_0)\Delta t + g(x_0)\Delta\eta \tag{2.80}$$

and thus $\lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} \to +\infty$ (at the slowest, this ratio diverges as $1/\sqrt{\Delta t}$ when $\kappa_{n \geq 3} = 0$). Thus, just as before, a differential equation Eq. (2.78) acquires its full meaning when accompanied with its discretized counterpart Eq. (2.80). It is possible to determine the n-th moment of the infinitesimal increment Δx,

$$\lim_{\Delta t \to 0} \frac{\langle \Delta x^n \rangle}{\Delta t} = \begin{cases} f(x_0) \text{ if } n = 1 \\ g(x_0)^n \kappa_n \text{ if } n \geq 2 \end{cases} \tag{2.81}$$

This shows us that the random process defined by Eq. (2.80) is strictly equivalent to the process whose master equation is Eq. (2.7) on condition that we identify $a_n(x_0) = \kappa_n g(x_0)^n$. These are

simply two ways to describe the same physical process. When the noise has Gaussian statistics, namely when $\kappa_n = 0$ for all $n \geq 3$, the corresponding differential equation is called a Langevin equation.

Performing differential calculus with a process evolving under the action of a white but non-Gaussian noise is significantly harder that in the standard Langevin case. We refer to [55, 67, 113] for further details.

2.3.7 Connection between stochastic calculus and physics

It's time that we connect the abstract Langevin equation $\dot{x} = f + g\eta$ to some actual physical processes. We want to identify the degrees of freedom x that evolves according to a stochastic differential equation (x will be shown to be either the velocity or the position). We want to identify what the deterministic contribution f is in relevant physical situations. And finally, we have seen that working with a nontrivial function g (that is not a constant) leads to a host of mathematical difficulties. Was it really worth the pain if no physical situations with a nontrivial g can be encountered? We'll see that unfortunately, such nontrivial functions g appear everywhere.

Back to the colloid in a bath of water molecules

If we get back to the physical picture of section 2.1, where a colloidal particle is embedded in a bath of water molecules, on the basis of general statistical arguments, we see that the position $\mathbf{R}$ and the momentum $\mathbf{P}$ of the colloid must evolve according to

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = \mathbf{F}_0 + \mathbf{F}_b \tag{2.82}$$

where $\mathbf{P} = M\dot{\mathbf{R}}$. The force $\mathbf{F}_0$ is the result of interactions not caused by the bath particles (say gravity, optical trapping, or possibly some interactions with other colloidal particles). And the idea is that, statistically speaking, the forces exerted by the water molecules can be encapsulated into a fluctuating force $\mathbf{F}_b = \sum_i \mathbf{F}_i$. When averaged over the configurations of the bath, the quantity $\langle \mathbf{F}_b \rangle_b$ depends functionnally on the trajectory $\mathbf{R}$. It is actually difficult to write the most general term that can be found, but this average being a vector, it must be a linear combination of vectors ($\mathbf{R}$, $\dot{\mathbf{R}}$, $\ddot{\mathbf{R}}$, *etc.*) weighted with scalar coefficients that could possibly be trajectory dependent as well. For instance, when there is no $\mathbf{R}$ dependence in the coefficients, we have

$$\langle \mathbf{F}_b \rangle_b = -\sum_{n\geq 0} b_n \frac{\mathrm{d}^{n+1}\mathbf{R}}{\mathrm{d}t^{n+1}} \tag{2.83}$$

This is exactly equivalent to introducing a memory kernel M_R such that

$$\langle \mathbf{F}_b \rangle_b = -\int_0^t \mathrm{d}t' M_R(t-t')\dot{\mathbf{R}}(t') \tag{2.84}$$

where $b_n = \frac{1}{n!}(-1)^n \int \mathrm{d}s s^n M_R(s)$. In principle, the memory kernel can also functionnally depend on a scalar combination of the components of the trajectory $\mathbf{R}$. We will see examples of

that shortly. But for now, let us assume that the general form of the equation for the evolution of $\mathbf{R}$ is

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = \mathbf{F}_0 - \int_0^t M_R(t-t')\dot{\mathbf{R}}(t) + \boldsymbol{\xi} \tag{2.85}$$

where $\boldsymbol{\xi}$ is, on general grounds, a Gaussian noise. We denote by

$$\langle \xi^\mu(t)\xi^\nu(t')\rangle = TM_C^{\mu\nu}(t-t') \tag{2.86}$$

its correlations. We have factored out the temperature T of the bath, because if T vanishes, there will be no fluctuations. Else, and without further reasoning or hypothesis, M_C is an arbitrary kernel. Of course, it cannot be completly arbitrary. We know that in equilibrium, whatever energy lost to the bath by the particle via viscous friction, can at some point be returned to the colloid in the form of random kicks exerted by the water molecules. There must therefore exist a strong connection, in equilibrium, between M_R and M_C. These two kernels are also expected to decay over similar time scales, because they have the same physical origin.

In general, and this requires to be examined on a case-by-case basis, lots of simplifications can be made. For instance, when the time-scale over which M_R or M_C decays is much shorter than any time scale relevant to the motion of the colloidal particule itself, one can write that

$$M_R(t) \simeq \gamma\delta(t) \tag{2.87}$$

and similarly that $M_C(t) \simeq T\gamma'\delta(t)$. The coefficient γ has a simple interpretation: this is the viscous drag and in cases where the separation of scale renders a hydrodynamic approach legitimate, we know, *e.g.* for a sphere of radius a, that $\gamma = 6\pi\eta_{\text{water}}a$, where η_{water} is the viscosity of water. This is the so-called Markov approximation. As will soon become clear 3, γ' and γ are actually related.

We have just discussed what happens when the time scale intrinsic to the bath is short, but the inertial time scale $\tau_{\text{inertia}} = M/\gamma$ may itself be very short. Think of a bead falling under gravity in a vertical column of water. Then the bead very rapidly reaches its limit velocity. The equation of motion for $\mathbf{R}$ can be written with $\mathbf{V} = \dot{\mathbf{R}}$ as

$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}t} = -\frac{1}{\tau_{\text{inertia}}}\left[\mathbf{V} - \frac{1}{\gamma}\boldsymbol{\xi} - \frac{1}{\gamma}\mathbf{F}_0\right] \tag{2.88}$$

and when τ_{inertia} is short, the balance of the viscous drag with the external forces is almost instantaneous. In that limit, the Langevin equation simplifies into

$$\mathbf{0} = -\gamma\mathbf{V} + \mathbf{F}_0 + \boldsymbol{\xi} \tag{2.89}$$

or

$$\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} = \mu\mathbf{F}_0 + \mu\boldsymbol{\xi} \tag{2.90}$$

where $\mu = 1/\gamma$ is known as the mobility. This is exactly the form of stochastic Langevin equation that we have considered throughout this chapter. It is also known as the overdamped limit

TABLE I. Overview of the characteristic times and frequencies for a Brownian particle in a harmonic potential. τ_p and τ_f are related to the Brownian particle through the properties of the particle with density ρ_p and radius a and of the fluid with density ρ_f and viscosity η. τ_k is connected to the property of the harmonic potential, its spring constant k, also referred to as the trap stiffness. The values are calculated for a polystyrene sphere (a=0.5 μm) in water (ρ_p/ρ_f=1.05, η=0.001 Pa s). The equivalent values in the frequency domain are ϕ_p, ϕ_f, and ϕ_k. ϕ_k corresponds to the corner frequency of the power spectrum.

Time constant (μs)	Frequency constant (MHz)	Determining factor
$\tau_p=m/(6\pi\eta a)=0.06$	$\phi_p=1/(2\pi\tau_p)=2.65$	Inertia of the particle
$\tau_f=a^2\rho_f/\eta=0.25$	$\phi_f=1/(2\pi\tau_f)=0.68$	Inertia of the surrounding displaced fluid
$\tau_k=6\pi\eta a/k=147$	$\phi_k=1/(2\pi\tau_k)=0.001$	Harmonic potential (optical trap) for k_1=64 μN/m

Figure 2.2: The notations τ_p and τ_k refer, respectively, to τ_{inertia} and τ_{relax}.

of Eq. (2.88).

It is instructive to have a look at real experimental data, shown in Fig. 2.2, extracted from [126], to get a grasp of the actual numbers at stake. The overdamped limit is valid in the small mass and/or high-friction limit. Given that the friction is proportional to the viscosity of the surrounding fluid, the overdamped limit is valid whenever the Reynolds number (evaluated at the scale of the particle) is actually very low. We refer to the pegagogical article Life at low Reynolds number [162] for a very pragmatic discussion.

Starting with an additive noise

Start with the example of the colloid in water, without any external forces

$$m\dot{v} = -\gamma v + \sqrt{2\gamma' T}\eta \tag{2.91}$$

in which the discretization is irrelevant. If interested in the evolution of the kinetic energy $K = mv^2/2$ of the particle (in one space dimension, for simplicity) we can write

$$\dot{K} = -\gamma\frac{2}{m}K + \sqrt{2\gamma' T}\sqrt{\frac{2K}{m}}\eta \tag{2.92}$$

but the resulting equation does feature a multiplicative noise. Since the discretization is irrelevant, let's assume in the first place that it was Stratonovich discretized, because then we know that we can manipulate $v(t)$ as if it were a differentiable function, and thus the resulting equation for K is also Stratonovich-discretized, and we should write

$$\dot{K} \overset{1/2}{=} -\gamma\frac{2}{m}K + 2\sqrt{\frac{\gamma' TK}{m}}\eta \tag{2.93}$$

which is equivalent to

$$\begin{aligned}\dot{K} &\overset{0}{=} -\gamma\frac{2}{m}K + \frac{1}{2}\left[2\sqrt{\frac{\gamma' TK}{m}}\right]\frac{\mathrm{d}}{\mathrm{d}K}\left[2\sqrt{\frac{\gamma' TK}{m}}\right] + 2\sqrt{\frac{\gamma' TK}{m}}\eta \\ &\overset{0}{=} -\gamma\frac{2}{m}K + \frac{\gamma' T}{m} + 2\sqrt{\frac{\gamma' TK}{m}}\eta\end{aligned} \tag{2.94}$$

and thus $\langle \dot{K} \rangle = \gamma \frac{2}{m} \left(\langle K \rangle - \frac{\gamma'}{\gamma} T/2 \right)$, which confirms that in equilibrium equipartition is achieved on condition that $\gamma' = \gamma$. Hence, the dynamics of the colloid is constrained by the fact that at large times it is in thermal equilibrium. This imposes $\gamma = \gamma'$. The conclusion is that even if we started off from an additive Langevin equation (g is a constant) the Langevin equation for K has a multiplicative noise (g is not a constant).

Note that if an external force field was acting on the particle we would have

$$m\dot{v} = -\gamma v - V'(x) + \sqrt{2\gamma T}\eta \tag{2.95}$$

If the viscous damping is large, this means that the force $F = -V'$ very rapidly balances out the force exerted by the thermostat, $F_b = -\gamma v + \sqrt{2\gamma T}\eta$, and the inertial term $m\dot{v}$ can be omitted. When this overdamped limit is justified, the Langevin equation takes the form

$$\gamma \dot{x} = -V' + \sqrt{2\gamma T} \text{ or } \dot{x} = -\mu V'(x) + \sqrt{2\mu T}\eta \tag{2.96}$$

where $\mu = \gamma^{-1}$ is the so-called mobility. When in addition $V(x) = \frac{k}{2}x^2$ is a harmonic potential, then the resulting Langevin equation is exactly of the same form as Eq. (2.91), $\dot{x} = -\mu k x + \sqrt{2\mu T}\eta$. A Langevin equation of the form $\dot{y} = -\kappa y + g\eta$, where g is a constant, is an Ornstein-Uhlenbeck process. It is the only stationary Gaussian process (by Doob's theorem). It is extremely important to fully master the details of the properties of an Ornstein-Uhlenbeck process (hence its repeated appearances in the tutorials).

Plain diffusion, confined though

The viscous friction γ is in general a constant coefficient, except when the vicinity of a wall affects the hydrodynamic flow around the particle under consideration. With the upsurge of microfluidic devices, diffusion in confined geometries (micro and nanofluidics, pores, channels, even in quasi 1d settings) demands that hydrodynamic interactions be taken into consideration. Some recent experimental references are [120, 9, 91, 155]. the bottom line is that if z denotes the distance of the particle to the wall, the transverse and longitudinal friction coefficients pick up a dependence on z

$$\gamma_\perp(z) = \gamma \left(1 + \frac{9}{8}\frac{R}{z} \right) \tag{2.97}$$

$$\gamma_\parallel(z) = \gamma \left(1 + \frac{9}{16}\frac{R}{z} \right) \tag{2.98}$$

as derived by Brenner [29]. This means that even when describing the purely diffusive motion of a confined colloid, multiplicative noise will show up.

Black and Scholes

Black and Scholes were two scholars working in on the modeling of financial markets. Back in 1973 [25] they came up with a model for the evolution of the price of a specific type of asset (European-style option). We refer to [61] for an introduction and for financial motivations. The

equation they wrote is a Langevin equation for the share price S of a stock (a risky asset). In Itō discretization, it is postulated that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \mu S + \sigma S \eta \tag{2.99}$$

where η has unit variance and where σ is the volatility of the stock. In the Stratonovitch discretization we have

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \mu S - \frac{1}{2}\sigma^2 S + \sigma S \eta \tag{2.100}$$

so that $S(t) = S_0 \exp\left[(\mu - \sigma^2/2)t + \sigma \int_0^t \mathrm{d}\tau \eta(\tau)\right]$. Of course μ could also depend on S or on time (and then things would have to be changed). One ends up facing the statistics of an exponential functional of Brownian motion. This type of functionals has appeared in mathematical finance [204], but also in the physics of one-dimensional disordered systems [43], or in the nonequilibrium evolution of chemical processes [96]. The Black and Scholes equation is a prototypical example of a Langevin equation with multiplicative noise.

Rotational diffusion

Dielectric relaxation. Let $\mathbf{p}$ be an electric dipole, such that $\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \boldsymbol{\omega} \times \mathbf{p}$ with the equation of motion $I\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t} = -\zeta\boldsymbol{\omega} + \mathbf{p}\times\mathbf{E} + \boldsymbol{\lambda}$. Neglecting inertia, one ends up with $\zeta\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = (\mathbf{p}\times\mathbf{E})\times\mathbf{p} + \boldsymbol{\lambda}\times\mathbf{p}$. Multplicative noise occurs and the Stratonovich rule is to be understood. It is the only one consistent with modulus conservation. If in a simulation the Itô rule is erroneously used, then modulus stops being conserved.

Active Brownian Particle

When one models the motion of an active particle under the action of a self-propulsion force, it turns out that writing

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = v_0 \mathbf{u} \tag{2.101}$$

faithfully reflects the observed properties of an individual particle [36]. In this model, $\mathbf{u}$ is a unit vector the tip of which executes a Brownian motion at the surface of the unit sphere, with a rotational diffusion constant D_r. In two space dimensions, the polar angle ϕ indexing the direction of $\mathbf{u} = (\cos\phi, \sin\phi)$ is undergoing a simple Brownian motion,

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \sqrt{2D_r}\xi \tag{2.102}$$

where ξ is a Gaussian white noise with correlations $\langle \xi(t)\xi(t')\rangle = \delta(t-t')$. But these particles live in three dimensions, and $\mathbf{u}$ is characterized by two angles. The evolution equation for $\mathbf{u}$ reads

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{\alpha}{=} (\mathbf{u}\cdot\boldsymbol{\eta})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta} \tag{2.103}$$

where the components η^μ of $\boldsymbol{\eta}$ are independent Gaussian white noises, $\langle \eta^\mu(t)\eta^\nu(t')\rangle = 2D_r\delta^{\mu\nu}\delta(t-t')$. Dotting Eq. (2.104) with $\mathbf{u}$ shows that $\mathbf{u}^2$ is indeed conserved. But for this calculation to

be legitimate, we must be allowed to manipulate $\mathbf{u}$ as if it were a smooth function, which means that Eq. (2.104) must be understood in a Stratonovich sense ($\alpha = 1/2$). It's Itō counterpart reads

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{0}{=} -(d-1)D_r\mathbf{u} + (\mathbf{u}\cdot\boldsymbol{\eta})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta} \tag{2.104}$$

where d is the number of space dimensions.

Formula Eq. (2.104) can checked using Eq. (2.69), with $g^{\mu i} = \sqrt{2D_r}(u^\mu u^i - \mathbf{u}^2\delta^{\mu i})$ (here $i, \mu = 1, \ldots, d$), we have $\partial_\nu g^{\mu i} = \sqrt{2D_r}(\delta^{\mu\nu}u^i + u^\mu\delta^{\nu i} - 2u^\nu\delta^{\mu i})$, and thus, after an explicit evaluation,

$$\partial_\nu g^{\mu i} g^{\nu i} = -(d-1)2D_r u^\mu \mathbf{u}^2 \tag{2.105}$$

so that $a_1^\mu = \frac{1}{2}\partial_\nu g^{\mu i} g^{\nu i} = -(d-1)D_r u^\mu \mathbf{u}^2$.

2.4 Path integration

This section aims at introducing one more tool in the stochastic processes toolbox, beyond the master equation and stochastic differential equations. We have seen the importance of working with trajectories in chapter 1. This is one motivation. Another motivation comes from the fact that path integrals pervade all areas of theoretical physics (high energy, condensed matter) and whatever tool has been developed in one field can be exported to another field. We follow Janssen [99] and De Dominicis [58] who used the work of Martin, Siggia and Rose [132] to adapt path integral techniques to stochastic processes.

2.4.1 Starting from a Langevin equation

We discretize the α-discretized Langevin equation $\frac{\mathrm{d}x}{\mathrm{d}t} = f(x(t)) + g(x(t))\xi(t)$ in the standard way

$$\Delta x_n = x_{n+1} - x_n = f_n \Delta t + g_n\sqrt{\Delta t}\xi_n \tag{2.106}$$

where ξ_n is a Gaussian variable with unit variance $\langle \xi_n \xi_m \rangle = \delta_{nm}$ and where $f_n = f(x_n + \alpha\Delta x_n)$, $g_n = g(x_n + \alpha\Delta x_n)$. From the discretized form we see that $\Delta x_n = O(\sqrt{\Delta t})$. The initial value x_0 is given, and the noise index runs from $i = 0$ up to $M-1$, where $M = t_{\mathrm{obs}}/\Delta t$ is the number of time slices we have cut the time interval $[0, t_{\mathrm{obs}}]$ into. The trajectory of interest is given by the x_j sequence, $j = 1, \ldots, M$. By averaging a given observable $A(x(t_{\mathrm{obs}}))$ one actually means that

$$\langle A(x_M)\rangle = \int \prod_{i=0}^{M-1} \frac{\mathrm{d}\xi_i}{\sqrt{2\pi}} \mathrm{e}^{-\sum_i \frac{\xi_i^2}{2}} A(x_M[\{\xi_\ell\}]) \tag{2.107}$$

where $x_M[\{\xi_\ell\}]$ is the solution of the Langevin equation for a given sequence of the random numbers ξ_i, $i = 0, \ldots, M-1$. We now change variables from the ξ_i's to the x_j's. Given that

$$\xi_i = \frac{x_{i+1} - x_i - f_i\Delta t}{g_i\sqrt{\Delta t}} \tag{2.108}$$

we easily see that the Jacobian matrix $J = \left(\frac{\partial \xi_i}{x_j}\right)_{i=0,\dots,M-1, j=1,\dots,M}$ is a triangular matrix (whose diagonal and diagonal strip just below contain the only nonzero elements), whose diagonal elements are

$$\frac{\partial \xi_j}{\partial x_{j+1}} = \frac{1 - \alpha f_j' \Delta t - \alpha \frac{g_j'}{g_j}(\Delta x_j - f_j \Delta t)}{g_j \sqrt{\Delta t}} \tag{2.109}$$

For $i > j+1$, we have that $\frac{\partial \xi_i}{\partial x_{j+1}} = 0$, as the position at a given time cannot depend on the later value of the noise. Hence the determinant of the Jacobian matrix is given by the product of the diagonal entries. Hence we have that

$$\langle A(x_M) \rangle = \int \prod_{j=1}^{M} \frac{\mathrm{d}x_i}{\sqrt{2\pi}} \prod_{i=0}^{M-1} \left(\frac{1 - \alpha f_i' \Delta t - \alpha \frac{g_i'}{g_i}(\Delta x_i - f_i \Delta t)}{g_i \sqrt{\Delta t}} \right) \left\{ \mathrm{e}^{-\frac{1}{2} \sum_i \left(\frac{x_{i+1} - x_i - f_i \Delta t}{g_i \sqrt{\Delta t}} \right)^2} \right\} A(x_M) \tag{2.110}$$

It is convenient to rewrite the exponential factor and as

$$\mathrm{e}^{-\frac{1}{2}\left(\frac{x_{i+1} - x_i - f_i \Delta t}{g_i \sqrt{\Delta t}} \right)^2} = \int \mathrm{d}\bar{x}_i \frac{\sqrt{\Delta t} g_i}{\sqrt{2\pi}} \mathrm{e}^{\Delta t \frac{1}{2} g_i^2 \bar{x}_i^2 - \bar{x}_i (\Delta x_i - f_i' \Delta t)} \tag{2.111}$$

which results in

$$\begin{aligned} \langle A(x_M) \rangle = \int \prod_{i=0}^{M-1} \prod_{j=1}^{M} \frac{\mathrm{d}\bar{x}_i \mathrm{d}x_j}{2\pi} \prod_{i=0}^{M-1} \left(1 - \alpha f_i' \Delta t - \alpha \frac{g_i'}{g_i}(\Delta x_i - f_i \Delta t) \right) \\ \times \mathrm{e}^{-\Delta t \sum_{i=0}^{M-1} \left[\bar{x}_i (\Delta x_i / \Delta t - f_i') - \frac{1}{2} g_i^2 \bar{x}_i^2 \right]} A(x_M) \end{aligned} \tag{2.112}$$

The last step is to note that $\Delta x_i - f_i \Delta t = \Delta x_i - f_i \Delta t - g_i^2 \Delta t \bar{x}_i + g_i^2 \Delta t \bar{x}_i$, so that

$$\begin{aligned} \int \mathrm{d}\bar{x}_i \left(1 - \alpha f_i' \Delta t - \alpha \frac{g_i'}{g_i}(\Delta x_i - f_i \Delta t) \right) \mathrm{e}^{-\Delta t \left[\bar{x}_i (\Delta x_i / \Delta t - f_i') - \frac{1}{2} g_i^2 \bar{x}_i^2 \right]} = \\ \int \mathrm{d}\bar{x}_i \left(1 - \alpha f_i' \Delta t - \alpha g_i' g_i \bar{x}_i \Delta t \right) \mathrm{e}^{-\Delta t \left[\bar{x}_i (\Delta x_i / \Delta t - f_i') - \frac{1}{2} g_i^2 \bar{x}_i^2 \right]} \end{aligned} \tag{2.113}$$

where we have used that

$$\frac{\partial}{\partial \bar{x}_i} \mathrm{e}^{-\Delta t \left[\bar{x}_i (\Delta x_i / \Delta t - f_i) - \frac{1}{2} g_i^2 \bar{x}_i^2 \right]} = -(\Delta x_i - f_i \Delta t - g_i^2 \Delta t \bar{x}_i) \tag{2.114}$$

which integrates to zero. The final step is to convert the Jacobian into an exponential:

$$1 - \alpha f_i' \Delta t - \alpha g_i' g_i \bar{x}_i \Delta t \simeq \mathrm{e}^{-\alpha f_i' \Delta t - \alpha g_i' g_i \bar{x}_i \Delta t} \tag{2.115}$$

which eventually allows us to conclude that

$$\langle A(x_M) \rangle = \int \prod_{i=0}^{M-1} \prod_{j=1}^{M} \frac{\mathrm{d}\bar{x}_i \mathrm{d}x_j}{2\pi} \mathrm{e}^{-\Delta t \sum_{i=0}^{M-1} \left[\bar{x}_i (\Delta x_i / \Delta t - f_i) - \frac{1}{2} g_i^2 \bar{x}_i^2 + \alpha f_i' + \alpha \bar{x}_i g_i' g_i \right]} A(x_M) \tag{2.116}$$

2.4.2 Janssen-De Dominicis dynamical action

A continuum version of this discrete expression reads

$$\langle A(x(t_{\rm obs}))\rangle = \int \mathcal{D}\bar{x}\mathcal{D}x \mathrm{e}^{-S} A(x(t_{\rm obs})) \tag{2.117}$$

where

$$S[\bar{x},x] = \int \mathrm{d}t \left[\bar{x}(\dot{x}-f) + \alpha f' - \frac{1}{2}g^2\bar{x}^2 + \alpha g' g\bar{x}\right] \tag{2.118}$$

The expression that can be found in Janssen's lecture notes [99] looks definitely different:

$$S[\bar{x},x] = \int \mathrm{d}t \left[\bar{x}(\dot{x}-f) + \alpha f' - \frac{1}{2}\left(\bar{x} - \alpha\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 g^2\right] \tag{2.119}$$

but the reason is simple: he starts from an Itō discretized equation $\dot{x} \overset{0}{=} f + g\eta$, which, is equivalent to $\dot{x} \overset{\alpha}{=\!=} f - \alpha g' g + g\eta$. Using $f - \alpha g' g$ in Eq. (2.118) instead of f, indeed leads to Eq. (2.119).

In the action Eq. (2.119) the α-discretization is understood, but we could have transformed the original α-discretized Langevin equation into an Itō equation,

$$\alpha = 0, \quad \frac{\mathrm{d}x}{\mathrm{d}t} = f + \alpha g' g + g\xi \tag{2.120}$$

which has the corresponding action,

$$S[\bar{x},x] = \int \mathrm{d}t \left[\bar{x}(\dot{x} - f - \alpha g' g) - \frac{1}{2}\bar{x}^2 g^2\right] \tag{2.121}$$

where Eqs. (2.121) and (2.119) are fully equivalent: they describe the same dynamics for the same system. Janssen explains in [99] how the α-dependent vertices in (2.119) eventually sum up to zero. A basic difference between Eq. (2.121) and Eq. (2.119) is the equal time value of the two point correlation function involving the response field, which, for consistency, has to be taken equal to $\langle \bar{x}(t)x(t)\rangle = \alpha$ when working with Eq. (2.119). Discussing time-reversibility issues requires to work with $\alpha = 1/2$.

In general it is not possible to perform nonlinear changes of fields within a path-integral, or at least with none of the discretizations schemes discussed above. So-called covariant schemes, namely allowing for the use of standard differential calculus within path integrals, are reviewed in [49], which goes well beyond the scope of these notes.

2.4.3 Onsager-Machlup functional

In the particular case of g being a constant function, it is relatively easy to integrate out the response field $\bar{x}$. Integrating it out explicitly leads to

$$\langle A(x(t_{\rm obs}))\rangle = \int \mathcal{D}x \mathrm{e}^{-S} A(x(t_{\rm obs})) \tag{2.122}$$

where now

$$S[\bar{x},x]=\int \mathrm{d}t\left[\frac{1}{2g^2}(\dot{x}-f)^2+\alpha f'\right] \tag{2.123}$$

is known as the Onsager-Machlup [146, 128] dynamical action. It has the clear advantage of involving a single field, which is the field of interest. But it proves less convenient for perturbation expansions and for determining intrinsically dynamical quantities such as response functions.

In the path-integral formulation of quantum mechanics, the matrix elements of the evolution operator $U(x_2,t_2|x_1,t_1)=\langle x_2|\mathrm{e}^{-\frac{i}{\hbar}\hat{H}(t_2-t_1)}|x_1\rangle$ can be expressed [70] as

$$U(x_2,t_2|x_1,t_1)=\int_{x(t_1)=x_1,\,x(t_2)=x_2}\mathscr{D}x\mathrm{e}^{\frac{i}{\hbar}S[x]},\ S[x]=\int \mathrm{d}tL(x,\dot{x})=\int \mathrm{d}t\left[\frac{m}{2}\dot{x}^2-V(x)\right] \tag{2.124}$$

Using the Euclidean time $\tau=it$,

$$U(x_2,t_2|x_1,t_1)=\int_{x(t_1)=x_1,\,x(t_2)=x_2}\mathscr{D}x\mathrm{e}^{-\frac{1}{\hbar}\int \mathrm{d}\tau\left[\frac{m}{2}\left(\frac{\mathrm{d}x}{\mathrm{d}\tau}\right)^2+V(x(\tau))\right]} \tag{2.125}$$

and one could introduce an auxiliary field that we call p, such that

$$\mathrm{e}^{-\frac{1}{\hbar}\int \mathrm{d}\tau\frac{m}{2}\dot{x}^2}=\int \mathscr{D}p\mathrm{e}^{\frac{1}{\hbar}\int \mathrm{d}t\left(\frac{(ip)^2}{2m}-ip\dot{x}\right)} \tag{2.126}$$

and then

$$U(x_2,t_2|x_1,t_1)=\int_{x(t_1)=x_1,\,x(t_2)=x_2}\mathscr{D}x\mathscr{D}p\mathrm{e}^{-\frac{1}{\hbar}\int \mathrm{d}\tau[ip\dot{x}-H(x,p)]},\ H(x,p)=\frac{(ip)^2}{2m}-V(x) \tag{2.127}$$

In this alternative formulation where the momentum field is introduced, it is seen to play a role similar to the response field $\bar{x}$ in the Janssen-De Dominicis formulation. A book devoted to path integrals and their applications is that of Kleinert [117].

2.4.4 Dirty way for Itō

Once clean derivations of these path integral formulations have been derived, and once it has been realized that the Itō-discretization turns the Jacobian into a mere multiplicative constant, it is possible to pretend that things could be done in three lines. Let us sketch this "derivation", which can only be solidly justified for the Itō discretization. Again we start from $\dot{x}\overset{0}{=}f+g\eta$. And we ask about the average of a quantity $A(t)=A(x(t))$. By definition

$$\langle A\rangle=\int \mathscr{D}\eta\mathrm{e}^{-\frac{1}{2}\int \eta^2}A(x[\eta](t)) \tag{2.128}$$

and when we write $x[\eta](t)$ we see x as the solution of the $\dot{x}\overset{0}{=}f+g\eta$ stochastic differential equation in which η is a given function. Hence $x[\eta](t)$ is a functional of η. We introduce a functional δ

$$1=\int \mathscr{D}X\delta(X-x[\eta]) \tag{2.129}$$

and we arrive at

$$\langle A\rangle = \int \mathscr{D}\eta \int \mathscr{D}X \delta(X - x[\eta]) \mathrm{e}^{-\frac{1}{2}\int \eta^2} A(X(t)) \tag{2.130}$$

But surely $\delta(X - x[\eta])$ and $\delta(\dot{X} - f - g\eta)$ must be proportional. If they differ only by a multiplicative constant then

$$\langle A\rangle = \int \mathscr{D}\eta \int \mathscr{D}X \delta(\dot{X} - f(X) - g(X)\eta) \mathrm{e}^{-\frac{1}{2}\int \eta^2} A(X(t)) \tag{2.131}$$

Now we resort to a Fourier representation of the functional δ:

$$\delta(\dot{X} - f(X) - g(X)\eta) = \int \mathscr{D}\bar{X} \mathrm{e}^{-\int \bar{X}(\dot{X} - f(X) - g(X)\eta)} \tag{2.132}$$

and we perform the Gaussian η integration:

$$\int \mathscr{D}\eta \mathrm{e}^{-\frac{1}{2}\int \eta^2} \mathrm{e}^{\int \bar{X} g(X)\eta} = \mathrm{e}^{\frac{1}{2}\int g^2 \bar{X}^2} \tag{2.133}$$

so that, finally,

$$\langle A\rangle = \int \mathscr{D}\bar{X}\mathscr{D}X A(X(t)) \mathrm{e}^{-\int \left[\bar{X}(\dot{X} - f(X)) - \frac{1}{2} g^2 \bar{X}^2\right]} \tag{2.134}$$

This is exactly the same form as that found by the more rigorous derivation based on a discretized process, on condition that $\alpha = 0$ is used throughout. It is indeed only in the Itō discretization that the Jacobian in Eq. (2.109) is a simple multiplicative constant. In the present derivation, this is equivalent to asserting that

$$\begin{aligned} \delta(X - x[\eta]) =& \delta(\dot{X} - f - g\eta) \det \frac{\delta(\dot{X} - f - g\eta)}{\delta X} \\ =& \delta(\dot{X} - f - g\eta) \det \left[\frac{\mathrm{d}}{\mathrm{d}t} - f'(X) - g'(X)\eta\right] \\ =& \mathrm{Cst}\delta(\dot{X} - f - g\eta) \end{aligned} \tag{2.135}$$

where $\det\left[\frac{\mathrm{d}}{\mathrm{d}t} - f'(X) - g'(X)\eta\right]$ is a multiplicative constant independent of X. The take-home message is that these loosely rigorous manipulations of path integrals and functionals are perfectly legitimate, at least when starting from an Itō-discretized process. And we certainly know that for any other discretization scheme this Jacobian becomes nontrivial.

2.5 Quantum Langevin Equation

2.5.1 Another take at a classical Langevin equation

Consider a particle of mass M, position $\mathbf{R}$, momentum $\mathbf{P}$ in an environment composed of a large number N of particles i (with mass m_i and phase space coordinates $\mathbf{r}_i, \mathbf{p}_i$). The Hamiltonian of the whole system reads

$$H(\mathbf{R}, \mathbf{P}, \{\mathbf{r}_i, \mathbf{p}_i\}) = H_0(\mathbf{R}, \mathbf{P}) + \sum_i V_i(\mathbf{R} - \mathbf{r}_i) + H_b(\{\mathbf{r}_i, \mathbf{p}_i\}) \tag{2.136}$$

where the N particles are the bath and V describes the coupling of the bath particles to the system of interest. The equations of motions read

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t} = -\partial_{\mathbf{R}}H_0 + \sum_i \mathbf{F}_i,\ m_i\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\partial_{\mathbf{r}_i}H_b - \mathbf{F}_i \tag{2.137}$$

where $\mathbf{F}_i = \partial_{\mathbf{r_i}}V_i$ is the force exerted by bath particle i on the tracer of interest. We assume that at the initial time $t = 0^-$ the bath is in equilibrium and decoupled from from the tracer, and the tracer particle starts from $\mathbf{R}(0^+) = \mathbf{0}$. Our goal is to establish an evolution equation for $\mathbf{R}$ alone, after integrating out the degrees of freedom of the bath. For instance, we would like to be able to determine

$$\langle\sum_i \mathbf{F}_i\rangle_{\text{only over the bath particles}} = \langle\sum_i \mathbf{F}_i\rangle_b \tag{2.138}$$

as a functional of the trajectory of the tracer. Because the positions of the bath particles are initially sampled from the Boltzmann distribution, $\sum_i \mathbf{F}_i$ is a random variable, and we can split

$$\sum_i \mathbf{F}_i = \langle\sum_i \mathbf{F}_i\rangle_b + \text{zero average noise} \tag{2.139}$$

Of course, under the assumption of short-ranged correlations between the bath particles and the tracer, and between the bath particles themselves, $\sum_i \mathbf{F}_i$ must have Gaussian statistics. Let's focus on $\langle\sum_i \mathbf{F}_i\rangle_b$ first. This average depends on $\mathbf{R}$ and is a vector, so that it necessarily takes the form

$$\langle\sum_i \mathbf{F}_i\rangle_b = \int_0^t \mathrm{d}t' \mathit{\Gamma}(t,t')\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t'}(t') \tag{2.140}$$

where $\mathit{\Gamma}(t,t',[\mathbf{R}])$ is a linear operator acting on the time derivative of $\mathbf{R}$ (that's a convention for $\mathit{\Gamma}$). The noise contribution must respect the detailed balance condition. In general, the coarse-graining of the bath degrees of freedom remains a rather abstract procedure, though progress can be done when there exists a clear-cut separation of time scales [60], including in nonequilibrium settings [95].

A special case is one in which $\mathbf{F}_i = -k_i(\mathbf{R} - \mathbf{r}_i)$ and $H_b = \sum_i \left[\frac{\mathbf{p}_i^2}{2m_i}\right]$, because then

$$m_i\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\mathbf{F}_i \tag{2.141}$$

which, using the Green's function $G(t,t') = \frac{\sin\omega|t-t'|}{\omega}$ of $\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \omega^2$ leads to

$$\mathbf{r}_i(t) = \mathbf{r}_i(0)\cos\omega_i t + \frac{\mathbf{p}_i(0)}{m_i\omega_i}\sin\omega_i t + \omega_i\int_0^t \mathrm{d}t' \sin\omega_i(t-t')\mathbf{R}(t') \tag{2.142}$$

so that

$$\begin{aligned}
\mathbf{r}_i(t) - \mathbf{R}(t) =& \mathbf{r}_i(0)\cos\omega_i t + \frac{\mathbf{p}_i(0)}{m_i\omega_i}\sin\omega_i t + \int_0^t \mathrm{d}t'\omega_i \sin\omega_i(t-t')\mathbf{R}(t') - \mathbf{R}(t)\\
\mathbf{r}_i(t) - \mathbf{R}(t) =& \mathbf{r}_i(0)\cos\omega_i t + \frac{\mathbf{p}_i(0)}{m_i\omega_i}\sin\omega_i t - \int_0^t \mathrm{d}t' \cos\omega_i(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\mathbf{R}(t')
\end{aligned} \tag{2.143}$$

$$\begin{aligned} M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t} &= -\partial_{\mathbf{R}}H_0 - \sum_i k_i(\mathbf{R}-\mathbf{r}_i) \\ &= -\partial_{\mathbf{R}}H_0 + \sum_i k_i\left[\mathbf{r}_i(0)\cos\omega_i t + \frac{\mathbf{p}_i(0)}{m_i\omega_i}\sin\omega_i t - \int_0^t \mathrm{d}t'\cos\omega_i(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\mathbf{R}(t')\right] \\ &= -\partial_{\mathbf{R}}H_0 - \int_0^{+\infty}\mathrm{d}t' M_R(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\mathbf{R}(t') + \boldsymbol{\xi}(t) \end{aligned} \tag{2.144}$$

where

$$M_R(\tau) = \theta(\tau)\sum_i k_i\cos\omega_i\tau \tag{2.145}$$

and

$$\boldsymbol{\xi}(t) = \sum_i k_i\left[\mathbf{r}_i(0)\cos\omega_i t + \frac{\mathbf{p}_i(0)}{m_i\omega_i}\sin\omega_i t\right] \tag{2.146}$$

The function $\boldsymbol{\xi}$ is random because the initial positions and momenta are drawn from a Boltzmann distribution. The random variables are Gaussian because the energy of the bath is quadratic($\langle\frac{k_i\mathbf{r}_i(0)^2}{2}\rangle = dT/2$ and $\langle\frac{\mathbf{p}_i(0)^2}{2m_i}\rangle = d\frac{T}{2}$). Hence $\boldsymbol{\xi}$ is a Gaussian variable with correlations

$$\begin{aligned} \langle\xi^\mu(t)\xi^\nu(t')\rangle &= \delta^{\mu\nu}\sum_i k_i T\left[\cos\omega_i t\cos\omega_i t' + \sin\omega_i t\sin\omega_i t'\right] \\ &= T\delta^{\mu\nu}\sum_i k_i\cos\omega_i(t-t') \\ &= M_C(t-t') \end{aligned} \tag{2.147}$$

Because $M_C(\tau) = T(M_R(\tau) + M_R(-\tau))$ (which is often called Kubo's second fluctuation-dissipation theorem) we know that the dynamics is equilibrium. Of course, any other result would have been suspicious. The present derivation has been discussed by several authors [75, 71, 206, 32] and further discussion can be found in L. Cugliandolo's lecture notes, subsection 2.4.2. There a discussion of the various ingredients ω_i and m_i characterizing the bath is carried out. An important conclusion that we can draw from this calculation is that generically, integrating the bath degrees of freedom out leads to a generalized Langevin equation. Another important conclusion is that this purely dynamical approach, which contrasts with the statistical one of the earlier chapters, shows us how to adapt our approach to the quantum world.

2.5.2 Quantum Langevin equation

What are the relevant questions, and why?

The rest of this chapter heavily relies on [87]. Our goal is to understand how one can design a quantum version of

$$m\ddot{x} = -V'(x) - \gamma\dot{x} + \sqrt{2\gamma T}\eta \tag{2.148}$$

where η is a white Gaussian noise with correlations $\delta(t-t')$. This was done in [75] and we will follow their derivation. There are several reasons for searching for a quantum analog of Eq. (2.148):

- with the advent of nanoelectronics and spintronics [180, 7], the effects of thermal noise start interfering with quantum phenomena. Then of course the Langevin equation of interest reads
$$\frac{q}{C}+Ri+L\frac{\mathrm{d}i}{\mathrm{d}t}=e(t) \text{ or } L\ddot{q}=-R\dot{q}+\frac{q}{C}+e(t) \tag{2.149}$$
where e stands for Johnson–Nyquist noise (the electromagnetic noise generated by the black-body radiation occurs regardless of any applied voltage);
- as temperature is lowered, purely quantum noise will eventually dominate, and it is unclear how this is described;
- the above is connected with the question of how classical physics emerges from quantum physics;
- the emergence of the violation of microscopic time-reversibility is well understood at the classical level, and it is interesting to see how it comes about in the quantum version.

Derivation

We proceed exactly along the lines of section 2.5.1 (in one space dimension for simplicity) and we consider a system with Hamiltonian

$$\hat{H}=\hat{H}_0(\hat{R})+\sum_i V_i(\hat{R}-\hat{r}_i)+\hat{H}_b,\ \hat{H}_b=\sum_i\frac{\hat{p}_i^2}{2m_i} \tag{2.150}$$

where the coupling of the system to the degrees of freedom of the bath is via a harmonic potential

$$V_i(\hat{R}-\hat{r}_i)=\frac{1}{2}k_i(\hat{R}-\hat{r}_i)^2 \tag{2.151}$$

The equations of motion now read

$$\frac{\mathrm{d}\hat{R}}{\mathrm{d}t}=\frac{i}{\hbar}[\hat{H},\hat{R}],\ \frac{\mathrm{d}\hat{P}}{\mathrm{d}t}=\frac{i}{\hbar}[\hat{H},\hat{P}],\ \frac{\mathrm{d}\hat{r}_i}{\mathrm{d}t}=\frac{i}{\hbar}[\hat{H},\hat{r}_i],\ \frac{\mathrm{d}\hat{p}_i}{\mathrm{d}t}=\frac{i}{\hbar}[\hat{H},\hat{p}_i] \tag{2.152}$$

and for the bath degrees of freedom, these equations simplify into

$$\frac{\mathrm{d}\hat{r}_i}{\mathrm{d}t}=\frac{\hat{p}_i}{m_i},\ \frac{\mathrm{d}\hat{p}_i}{\mathrm{d}t}=\frac{i}{\hbar}[\hat{H},\hat{p}_i]=-k_i(\hat{r}_i-\hat{R}) \tag{2.153}$$

where we have used that $[\hat{r}_i,\hat{p}_j]=i\hbar\delta_{ij}$. For the tracer particle of interest, we have

$$\frac{\mathrm{d}\hat{R}}{\mathrm{d}t}=\frac{\hat{P}}{M},\ \frac{\mathrm{d}\hat{P}}{\mathrm{d}t}=-\partial_R H_0(\hat{P},\hat{R})-\sum_i k_i(\hat{R}-\hat{r}_i) \tag{2.154}$$

and again

$$\hat{r}_i(t) - \hat{R}(t) = \hat{r}_i(0)\cos\omega_i t + \frac{\hat{p}_i(0)}{m_i\omega_i}\sin\omega_i t - \int_0^t \mathrm{d}t' \cos\omega_i(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\hat{R}(t') \tag{2.155}$$

so that again

$$\frac{\mathrm{d}\hat{R}}{\mathrm{d}t} = \frac{\hat{P}}{M},\ \frac{\mathrm{d}\hat{P}}{\mathrm{d}t} = -\partial_R H_0(\hat{P},\hat{R}) - \int_0^t \mathrm{d}t' M_R(t-t')\frac{\mathrm{d}\hat{R}}{\mathrm{d}t'} + \hat{\xi} \tag{2.156}$$

where now the operator $\hat{\xi}$ reads

$$\hat{\xi}(t) = \sum_i \left[\hat{r}_i(0)\cos\omega_i t + \frac{\hat{p}_i(0)}{m_i\omega_i}\sin\omega_i t\right] \tag{2.157}$$

while the dissipation kernel M_R has exactly the same expression as in the classical case in Eq. (2.145),

$$M_R(\tau) = \theta(\tau)\sum_i k_i \cos\omega_i\tau \tag{2.158}$$

Averaging over both quantum and thermal fluctuations leads to

$$\langle\{\hat{\xi}(t)\hat{\xi}(t')\}\rangle = \sum_i \left[\cos\omega_i t\cos\omega_i t'\langle[\hat{r}_i(0)]^2\rangle + \frac{1}{m_i^2\omega_i^2}\sin\omega_i t\sin\omega_i t'\langle[\hat{p}_i(0)]^2\rangle\right] \tag{2.159}$$

where $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ refers to the anticommutator of $\hat{A}$ and $\hat{B}$. We introduce the raising and lowering operators

$$a_j^\dagger = \sqrt{\frac{m_j\omega_j}{2\hbar}}\left(\hat{r}_j + \frac{i}{m_j\omega_j}\hat{p}_j\right),\ a_j = \sqrt{\frac{m_j\omega_j}{2\hbar}}\left(\hat{r}_j - \frac{i}{m_j\omega_j}\hat{p}_j\right) \tag{2.160}$$

or $\hat{r}_j = \sqrt{\frac{\hbar}{2m_j\omega_j}}(a_j^\dagger + a_j)$ and $\hat{p}_j = i\sqrt{\frac{\hbar\omega_j m_j}{2}}(a_j^\dagger - a_j)$. Hence, at any given time,

$$\begin{aligned}\langle\hat{r}_j^2\rangle =& \frac{\hbar}{2m_j\omega_j}\langle a_j^{\dagger 2} + a_j^2 + 2a_j^\dagger a_j + 1\rangle \\ =& \frac{\hbar}{2m_j\omega_j}\left[\frac{\mathrm{e}^{\beta\hbar\omega_j}+1}{\mathrm{e}^{\beta\hbar\omega_j}-1}\right] \\ =& \frac{\hbar}{2m_j\omega_j}\coth\frac{\beta\hbar\omega_j}{2}\end{aligned} \tag{2.161}$$

where we have used the equilibrium phonon statistics $\langle a_j^\dagger a_j\rangle = \frac{1}{\mathrm{e}^{\beta\hbar\omega_j}-1}$. Similarly, we have that

$$\begin{aligned}\langle\hat{p}_j^2\rangle =& -\frac{\hbar\omega_j m_j}{2}\langle a_j^{\dagger 2} + a_j^2 - 2a_j^\dagger a_j - 1\rangle \\ =& \frac{\hbar\omega_j m_j}{2}\coth\frac{\beta\hbar\omega_j}{2}\end{aligned} \tag{2.162}$$

and thus

$$\langle\{\hat{\xi}(t)\hat{\xi}(t')\}\rangle = \sum_j \frac{\hbar}{2m_j\omega_j} \coth\frac{\beta\hbar\omega_j}{2} \cos\omega_j(t-t') \tag{2.163}$$

Note that in the classical limit $\beta\hbar\omega_j \ll 1$,

$$\langle\hat{\xi}(t)\hat{\xi}(t')\rangle \simeq \sum_j \frac{\hbar}{2m_j\omega_j}\frac{2}{\beta\hbar\omega_j} \cos\omega_j(t-t') = T\sum_j \frac{1}{m_j\omega_j^2} \cos\omega_i(t-t') \tag{2.164}$$

which coincides with the formula obtained in Eq. (2.147) with $\omega_j^2 = k_j/m_j$.

Equation (2.156) is a quantum Langevin equation. Note that, before any limit is taken, there is no particular issue with differentiability, so that any operator $\hat{A} = A(\hat{R},\hat{P})$ evolves according to

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{i}{\hbar}[\hat{H},\hat{A}] \tag{2.165}$$

and the commutator must be determined explicitly before the $\hat{r}_j$'s are substituted for the $\hat{\xi}_j$'s.

If the properties of the bath are such that the distribution of k_j's and of the m_j's can be approximated by $\sum_j k_j \ldots \to 2\gamma\int_0^{+\infty}\frac{1}{\pi}\mathrm{d}\omega\ldots$ (with $\omega_j^2 = k_j/m_j$) then

$$2M_C(\tau) = \langle\{\hat{\xi}(t)\hat{\xi}(t')\}\rangle \simeq \frac{2\gamma\hbar}{\pi}\int_0^{+\infty}\mathrm{d}\omega\omega\coth(\beta\hbar\omega/2)\cos\omega\tau \tag{2.166}$$

At high frequency, $\omega\coth(\beta\hbar\omega/2)\sim\omega$ which means that at very low temperatures

$$2M_C(\tau) = \langle\{\hat{\xi}(t)\hat{\xi}(t')\}\rangle \simeq 2i\hbar\gamma\frac{\mathrm{d}}{\mathrm{d}\tau}\delta(\tau) \tag{2.167}$$

while in the high temperature regime, where $\omega\coth(\beta\hbar\omega/2) \sim \frac{2}{\beta\hbar}$ we recover the classical behavior

$$M_C(\tau) = \langle\{\hat{\xi}(t)\hat{\xi}(t')\}\rangle \simeq 2\gamma T\delta(\tau) \tag{2.168}$$

A more careful study shows that

$$\begin{aligned} M_C(t) =& \frac{\gamma\hbar}{\pi}\int_0^{+\infty}\mathrm{d}\omega\ \cos\omega t\,\omega\,(\coth\beta\hbar\omega - 1) \\ &+ \gamma\hbar\int_{-\infty}^{+\infty}\frac{\mathrm{d}\omega}{2\pi}|\omega|\mathrm{e}^{i\omega t} \\ =& -\frac{\gamma\pi}{\beta^2\hbar}\frac{1}{\sinh^2\pi t/(\beta\hbar)} \end{aligned} \tag{2.169}$$

where the minus sign expresses anticorrelations. The thermal correlation time is directly read off the exponential decay of $\sinh^2$ at large argument,

$$\tau_{\text{correl}} = \frac{\beta\hbar}{2\pi} \tag{2.170}$$

as is dictated by dimensional analysis (1 ps at 1 K, that's pretty short). This time diverges at zero temperature, and at $T = 0$ we have

$$M_C(t) = -\frac{\gamma\hbar}{\pi}\frac{1}{t^2} \tag{2.171}$$

2.5.3 Quantum Brownian motion

Let's further explore the properties of a quantum Langevin equation in the absence of an external potential. We want to determine the evolution of the particle's (kinetic) energy along with its mean-square displacement. The equations of motion are somewhat simpler

$$\dot{\hat{R}} = \hat{P}/m,\ \dot{P} = -\gamma\hat{P}/m + \hat{\xi} \tag{2.172}$$

and they can directly be integrated into

$$\hat{P}(t) = \mathrm{e}^{-\gamma t/m}\hat{P}(0) + \int_0^t \mathrm{d}t' \mathrm{e}^{-\gamma(t-t')/m}\hat{\xi}(t') \tag{2.173}$$

so that the kinetic energy reads

$$\begin{aligned} K =& \frac{1}{2m}\hat{P}(t)^2 \\ =& \frac{1}{2m}\Big[\mathrm{e}^{-2\gamma t/m}\hat{P}(0)^2 + 2\mathrm{e}^{-\gamma t/m}\hat{P}(0)\int_0^t \mathrm{d}t' \mathrm{e}^{-\gamma(t-t')/m}\hat{\xi}(t') \\ &+ \int_0^t \mathrm{d}t'\mathrm{d}t'' \mathrm{e}^{-\gamma(t-t')/m-\gamma(t-t'')/m}\hat{\xi}(t')\hat{\xi}(t'')\Big] \end{aligned} \tag{2.174}$$

and hence

$$\begin{aligned} \langle K\rangle =& \frac{1}{2m}\mathrm{e}^{-2\gamma t/m}\hat{P}(0)^2 \\ &+ \frac{\gamma\hbar}{m\pi}\int_0^{+\infty}\mathrm{d}\omega\omega\coth(\beta\hbar\omega/2)\int_0^t \mathrm{d}t'\mathrm{d}t''\mathrm{e}^{-\gamma(t'-t'')/m-\gamma(t-t'')/m}\cos\omega(t'-t'') \end{aligned} \tag{2.175}$$

and in the $t \to +\infty$ limit, using that,

$$\int_0^t \mathrm{d}t'\mathrm{d}t''\mathrm{e}^{-\gamma(t'-t'')/m-\gamma(t-t'')/m}\cos\omega(t'-t'') = \frac{1}{\omega^2+(\gamma/m)^2}(1+\mathrm{e}^{-2t\gamma/m}-2\mathrm{e}^{-t\gamma/m}\cos\omega t) \tag{2.176}$$

we arrive at

$$\langle K\rangle = \frac{\gamma\hbar}{m\pi}\int_0^{+\infty}\mathrm{d}\omega\omega\coth(\beta\hbar\omega/2)\frac{1}{\omega^2+(\gamma/m)^2} \tag{2.177}$$

where we realize that the $\omega \to +\infty$ part of the integral diverges. When rewriting $\langle K\rangle$ as

$$\begin{aligned} \langle K\rangle =& \frac{\gamma\hbar}{m\pi}\int_0^{+\infty}\mathrm{d}\omega\omega(\coth(\beta\hbar\omega/2)-1)\frac{1}{\omega^2+(\gamma/m)^2} \\ &+ \frac{\gamma\hbar}{m\pi}\int_0^{+\infty}\mathrm{d}\omega\frac{\omega}{\omega^2+(\gamma/m)^2} \end{aligned} \tag{2.178}$$

we see that the first bit is well-defined while the second contribution diverges. In the first contribution, when $\gamma \to 0$, we can use that

$$\frac{\gamma}{\pi m}\int_0^{+\infty}\mathrm{d}\omega\frac{1}{\omega^2+(\gamma/m)^2}\ldots \simeq \int_0^{+\infty}\mathrm{d}\omega\delta(\omega)\ldots \tag{2.179}$$

to evaluate the integral,

$$\langle K\rangle \simeq \frac{T}{2} + \frac{\gamma\hbar}{\pi}\int_0^{+\infty} \mathrm{d}\omega \frac{\omega}{\omega^2 + (\gamma/m)^2} \tag{2.180}$$

There is no way round the infinite influence of the zero point fluctuations of the heat bath. The second infinite integral is of course unphysical as is, and the continuum formulation can be fixed by introducing an upper frequency cut-off Ω that allows to evaluate

$$\frac{\gamma}{\pi m}\int_0^{+\infty} \mathrm{d}\omega \frac{\omega}{\omega^2 + (\gamma/m)^2} \simeq \frac{\gamma\hbar}{4m\pi}\ln(1 + (\Omega m/\gamma)^2) \tag{2.181}$$

This term does not depend on temperature, and even though the energy of a particle cannot be observed, its energy variations can (as they are independent of this contribution). A discussion of the relevant orders of magnitude is provided in [87].

The mean-square displacement is obtained by integrating and then squaring the velocity $\hat{P}/m$:

$$\hat{R}(t) - \hat{R}(0) = \hat{P}(0)\frac{1 - \mathrm{e}^{-\gamma t/m}}{\gamma} + \frac{1}{m}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \mathrm{e}^{-\gamma(t_1 - t_2)/m}\hat{\xi}(t_2) \tag{2.182}$$

A somewhat tedious calculation leads to

$$\begin{aligned}\langle(\hat{R}(t) - \hat{R}(t_0))^2\rangle =& \langle \hat{P}(t_0)^2/m^2\rangle \left(\frac{\mathrm{e}^{-\gamma t/m} - \mathrm{e}^{-\gamma t_0/m}}{\gamma/m}\right)^2 \\ &+ \frac{\gamma\hbar}{m^2}\int_{-\infty}^{+\infty} \mathrm{d}\omega \frac{\omega\coth(\beta\hbar\omega/2)}{\omega^2 + (\gamma/m)^2}\left|\frac{\mathrm{e}^{i\omega t} - \mathrm{e}^{i\omega t_0}}{i\omega} + \frac{\mathrm{e}^{-\gamma t/m} - \mathrm{e}^{-\gamma t_0/m}}{\gamma/m}\right|^2\end{aligned} \tag{2.183}$$

And again the ω integral requires an upper cut-off to remain convergent. However, the cut-off is only necessary for the contribution that is not time-translation invariant. If one introduces a cut-off and then send the initial condition to $-\infty$, one easily sees that

$$\langle(\hat{R}(t) - \hat{R}(t_0))^2\rangle = \frac{\gamma\hbar}{m^2}\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi}\frac{\omega\coth(\beta\hbar\omega/2)}{\omega^2 + (\gamma/m)^2}\frac{4\sin^2(\omega(t - t_0)/2)}{\omega^2} \tag{2.184}$$

where the integral is convergent without the need of a cut-off. If the ω domain of the integral that dominates is such that the approximation

$$\frac{4\sin^2(\omega(t - t_0)/2)}{\omega^2} \simeq 2\pi|t - t_0|\delta(\omega) \tag{2.185}$$

is valid (namely when $\beta\hbar\omega \ll 1$, that is at high temperatures), then

$$\langle(\hat{R}(t) - \hat{R}(t_0))^2\rangle = \frac{2T}{\gamma}|t - t_0| \tag{2.186}$$

which is the expected classical result. In the opposite low temperature regime where $\omega\coth(\beta\hbar\omega/2) \simeq |\omega|$ we have

$$\langle(\hat{R}(t) - \hat{R}(t_0))^2\rangle = \frac{4\gamma\hbar}{\pi m^2}\int_0^{+\infty} \mathrm{d}\omega \frac{1}{\omega^2 + (\gamma/m)^2}\frac{\sinh^2(\omega(t - t_0)/2)}{\omega} \tag{2.187}$$

By working in the dimensionless variable $x = \omega m/\gamma$, the integral reads

$$\begin{aligned}\langle(\hat{R}(t) - \hat{R}(t_0))^2\rangle =& \frac{4\hbar}{\pi\gamma}\int_0^{+\infty} \mathrm{d}x \frac{1}{x^2+1}\frac{\sin^2(x(\gamma/m)(t-t_0)/2)}{x} \\ \simeq& \frac{\hbar}{\pi\gamma}\ln\left[\frac{\gamma}{m}(t-t_0)\right]\end{aligned} \tag{2.188}$$

for $\frac{\gamma}{m}(t - t_0) \gg 1$. This mean-square displacement is entirely driven by quantum fluctuations, those of the zero point energy of the bath of oscillators. It is strongly subdiffusive and washed out downto very low temperatures by thermal fluctuations. The crossover time is $\tau_\times \sim \beta\hbar \ln \frac{\beta\hbar}{m/\gamma}$.

Chapter 3

Time reversal and its consequences

This chapter is all about the arrow of time.

3.1 Defining equilibrium

3.1.1 Statistical mechanics with trajectories and the definition of equilibrium

A trajectory of a physical system evolving according to a master equation over a time window $[0, t_{\rm obs}]$ such as

$$\partial_t P(\mathscr{C}, t) = \sum_{\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}') P(\mathscr{C}', t) - r(\mathscr{C}) P(\mathscr{C}, t),\ r(\mathscr{C}) = \sum_{\mathscr{C}''} W(\mathscr{C} \to \mathscr{C}'') \tag{3.1}$$

with an evolution operator $\mathbb{W}$,

$$\mathbb{W}_{\mathscr{C},\mathscr{C}'} = W(\mathscr{C} \to C') - r(\mathscr{C}) \delta_{\mathscr{C},\mathscr{C}'} \tag{3.2}$$

is a sequence of occupied states $\mathscr{C}_0, \ldots, \mathscr{C}_K$ and of holding times $\tau_0, \ldots, \tau_K$ such that $\tau_0 + \ldots + \tau_K = t_{\rm obs}$. The probability of a trajectory with K jumps is

$$\mathscr{P}[\text{traj}] = P_i(\mathscr{C}_0) \left[\prod_{j=0}^{K-1} \mathrm{d}\tau_j r(\mathscr{C}_j) \mathrm{e}^{-r(\mathscr{C}_j)\tau_j} \right] \mathrm{e}^{-r(\mathscr{C}_K)\tau_K} \delta(\tau_0 + \ldots + \tau_K - t_{\rm obs}) \mathrm{d}\tau_K \prod_{j=0}^{K-1} \frac{W(\mathscr{C}_j \to \mathscr{C}_{j+1})}{r(\mathscr{C}_j)} \tag{3.3}$$

because the probability to hold over a duration τ in some state $\mathscr{C}$ is $\mathrm{e}^{-r(\mathscr{C})\tau}$ and the probability to jump to some other state between τ and $\tau + \mathrm{d}\tau$ is $r(\mathscr{C})\mathrm{d}\tau$.

The time-reversed trajectory $\text{traj}^{\rm R}$ has a probability

$$\mathscr{P}[\text{traj}^{\rm R}] = P_f(\mathscr{C}_K) \left[\prod_{j=K}^{1} \mathrm{d}\tau_j r(\mathscr{C}_j) \mathrm{e}^{-r(\mathscr{C}_j)\tau_j} \right] \mathrm{e}^{-r(\mathscr{C}_0)\tau_0} \delta(\tau_0 + \ldots + \tau_K - t_{\rm obs}) \mathrm{d}\tau_0 \prod_{j=K}^{1} \frac{W(\mathscr{C}_j \to \mathscr{C}_{j-1})}{r(\mathscr{C}_j)} \tag{3.4}$$

and thus

$$\frac{\mathscr{P}[\text{traj}]}{\mathscr{P}[\text{traj}^{\text{R}}]} = \frac{P_i(\mathscr{C}_0)}{P_f(\mathscr{C}_K)} \prod_{j=0}^{K-1} \frac{W(\mathscr{C}_j \to \mathscr{C}_{j+1})}{W(\mathscr{C}_{j+1} \to \mathscr{C}_j)} \tag{3.5}$$

We have already defined two trajectory-dependent observables,

$$\overline{Q}[\text{traj}] = \ln \frac{\mathscr{P}[\text{traj}]}{\mathscr{P}[\text{traj}^{\text{R}}]},\ Q_S[\text{traj}] = \overline{Q}[\text{traj}] - \ln \frac{P_i(\mathscr{C}_0)}{P_f(\mathscr{C}_K)} \tag{3.6}$$

which, in addition to exhibiting interesting mathematical properties, turn out to be endowed with a rich physical meaning.

Consider a system that has reached its stationary state and consider the system over an arbitrary time window. The stationary state is an equilibrium one iff $\langle Q_S \rangle = \langle \bar{Q} \rangle = 0$. Because the variation rate of the Shannon entropy $S = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \ln P(\mathscr{C}, t)$ vanishes in the stationary state, this imposes in particular that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sigma_{\text{irr}} - J_S = 0 \text{ with } J_S = \langle \dot{Q}_S \rangle = 0 \tag{3.7}$$

The steady-state ditribution P_{ss} can then be promoted to the status of an equilibrium distribution, which we generically denote by P_{eq}. In turn, because of the explicit expression of σ_{irr} in Eq. (1.58), namely

$$\sigma_{\text{irr}} = \frac{1}{2} \sum_{\mathscr{C},\mathscr{C}'} \left[P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}') - P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C}) \right] \ln \frac{P(\mathscr{C}, t)\, W(\mathscr{C} \to \mathscr{C}')}{P(\mathscr{C}', t)\, W(\mathscr{C}' \to \mathscr{C})} \geq 0 \tag{3.8}$$

which verifies $\sigma_{\text{irr}} \geq 0$ with equality iff the detailed-balance condition is fulfilled:

$$P_{\text{eq}}(\mathscr{C})\, W(\mathscr{C} \to \mathscr{C}') = P_{\text{eq}}(\mathscr{C}')\, W(\mathscr{C}' \to \mathscr{C}) \tag{3.9}$$

The detailed balance condition is not always easy to verify explicitly, and sometimes actually determining $\bar{Q}$ for a given trajectory proves much simpler. In turn, one realizes that if the detailed balance condition is fulfilled, then in the stationary/equilibrium state we have that $\bar{Q}[\text{traj}] = 0$ without the need for averaging. This can be viewed as an alternative definition of equilibrium.

3.1.2 The words and world of stochastic energetics

In the last 25 years, there have been many efforts devoted to somehow extending concepts inherited from good old thermodynamics to scales and systems that are *a priori* well beyond the range of application of thermodynamics. The latter basically applies to macroscopic systems undergoing transformations between equilibrium states. In what follows we will see the extent to which many features of thermodynamics survive even when considering small and fluctuating systems.

Let us begin by introducing $\hat{S}(t) = -\ln P(\mathscr{C}(t), t)$ where $P(\mathscr{C}, t)$ is the probability distribution over states at time t, and where $\mathscr{C}(t)$ is the state the system is in at time t. Upon averaging, we have that

$$S(t) = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \ln P(\mathscr{C}, t) \tag{3.10}$$

which is the Shannon entropy that we have already introduced. Note, however, that unlike S, $\hat{S}$ is a fluctuating random variable. Consider now a small time interval $[t, t + \Delta t]$, then

$$\hat{S}(t + \Delta t) - \hat{S}(t) = -\ln \frac{P(\mathscr{C}(t + \Delta t), t}{P(\mathscr{C}, t)} - \Delta t \left. \frac{\partial_t P(\mathscr{C}, t)}{P(\mathscr{C}, t)} \right|_{\mathscr{C}=\mathscr{C}(t)} \tag{3.11}$$

Hence, if we average, we arrive at

$$\begin{aligned} \frac{S(t + \Delta t) - S(t)}{\Delta t} = & \frac{\mathrm{d}S}{\mathrm{d}t} = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \sum_{\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}') \ln \frac{P(\mathscr{C}', t)}{P(\mathscr{C}, t)} \\ = & \sigma_{\mathrm{irr}} - J_S \end{aligned} \tag{3.12}$$

which is quite reassuring. Over a large time interval $[0, t_{\mathrm{obs}}]$, we have that

$$\hat{S}(t_{\mathrm{obs}}) - \hat{S}(0) = -\ln \frac{P(\mathscr{C}_K, t_{\mathrm{obs}})}{P(\mathscr{C}_0, 0)} = \bar{Q} - Q_S \tag{3.13}$$

or that $\bar{Q} = \Delta\hat{S} + Q_S$ (with, on average, $\Delta S = \langle \Delta\hat{S} \rangle = \Delta S_{\mathrm{system}}$ that is the entropy variation of the system). If one views $\bar{Q}$ as the fluctuating counterpart of the global entropy variation (say that $\langle \bar{Q} \rangle = \Delta S_{\mathrm{global}}$) and Q_S as the fluctuating counterpart to entropy exchanged with the external medium, $\Delta S_{\mathrm{ext}} = \langle Q_S \rangle$, then we see that

$$\bar{Q} = \Delta\hat{S} + Q_S \text{ implies } \Delta S_{\mathrm{global}} = \Delta S_{\text{of the system}} + \Delta S_{\mathrm{ext}} \tag{3.14}$$

and the second principle of thermodynamics appears to be a property of the averages: we know that $\Delta S_{\mathrm{global}} = \langle \bar{Q} \rangle \geq 0$ is a Kullback-Leibler divergence and that it is thus positive (we also know that $\frac{\mathrm{d}}{\mathrm{d}t} \langle \bar{Q} \rangle = \sigma_{\mathrm{irr}} \geq 0$), so that we have proved that

$$\Delta S_{\mathrm{global}} = \Delta S_{\text{of the system}} + \Delta S_{\mathrm{ext}} \geq 0 \tag{3.15}$$

Of course, this an average property, and nothing guarantees that the individual terms in the left-hand side of Eq. (3.14) have definite signs. One also understands *a posteriori* why the second principle holds in thermodynamics. Because thermodynamics applies to macroscopic systems, and because $\hat{S}$ is an extensive quantity, it self averages to its average S in the large system size limit, and there is basically no difference between $\hat{S}$ and S due to the law of large numbers. However, the second principle holds irrespective of the system being large or small. The smaller the system, the more important deviations from the average are.

It would be great if we could find a more physical interpretation of Q_S ($\langle Q_S \rangle = \Delta S_{\mathrm{ext}}$) in terms of the heat given out to the thermostat (divided by temperature). This is done for instance in the review by Seifert [176] (at the level of Langevin dynamics where the thermostat appears more clearly) and in the book by the founder of stochastic thermodynamics, Sekimoto [177]. This is the topic of the next subsection.

Let us begin by introducing $\hat{S}(t) = -\ln P(\mathscr{C}(t), t)$ where $P(\mathscr{C}, t)$ is the probability distribution over states at time t, and where $\mathscr{C}(t)$ is the state the system is in at time t. Upon averaging, we have that

$$S(t) = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \ln P(\mathscr{C}, t) \tag{3.10}$$

which is the Shannon entropy that we have already introduced. Note, however, that unlike S, $\hat{S}$ is a fluctuating random variable. Consider now a small time interval $[t, t + \Delta t]$, then

$$\hat{S}(t + \Delta t) - \hat{S}(t) = -\ln \frac{P(\mathscr{C}(t + \Delta t), t}{P(\mathscr{C}, t)} - \Delta t \left. \frac{\partial_t P(\mathscr{C}, t)}{P(\mathscr{C}, t)} \right|_{\mathscr{C}=\mathscr{C}(t)} \tag{3.11}$$

Hence, if we average, we arrive at

$$\begin{aligned} \frac{S(t + \Delta t) - S(t)}{\Delta t} = & \frac{\mathrm{d}S}{\mathrm{d}t} = -\sum_{\mathscr{C}} P(\mathscr{C}, t) \sum_{\mathscr{C}'} W(\mathscr{C} \to \mathscr{C}') \ln \frac{P(\mathscr{C}', t)}{P(\mathscr{C}, t)} \\ = & \sigma_{\mathrm{irr}} - J_S \end{aligned} \tag{3.12}$$

which is quite reassuring. Over a large time interval $[0, t_{\mathrm{obs}}]$, we have that

$$\hat{S}(t_{\mathrm{obs}}) - \hat{S}(0) = -\ln \frac{P(\mathscr{C}_K, t_{\mathrm{obs}})}{P(\mathscr{C}_0, 0)} = \bar{Q} - Q_S \tag{3.13}$$

or that $\bar{Q} = \Delta\hat{S} + Q_S$ (with, on average, $\Delta S = \langle \Delta\hat{S} \rangle = \Delta S_{\mathrm{system}}$ that is the entropy variation of the system). If one views $\bar{Q}$ as the fluctuating counterpart of the global entropy variation (say that $\langle \bar{Q} \rangle = \Delta S_{\mathrm{global}}$) and Q_S as the fluctuating counterpart to entropy exchanged with the external medium, $\Delta S_{\mathrm{ext}} = \langle Q_S \rangle$, then we see that

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It would be great if we could find a more physical interpretation of Q_S ($\langle Q_S \rangle = \Delta S_{\mathrm{ext}}$) in terms of the heat given out to the thermostat (divided by temperature). This is done for instance in the review by Seifert [176] (at the level of Langevin dynamics where the thermostat appears more clearly) and in the book by the founder of stochastic thermodynamics, Sekimoto [177]. This is the topic of the next subsection.

3.1.3 Application to Langevin dynamics

Let's work out an example taken from the previous chapter. Consider a Langevin equation for a particle with position $\mathbf{r}$,

$$m\ddot{\mathbf{r}} = -\int \mathrm{d}t' M_R(t-t')\dot{\mathbf{r}} + \mathbf{F} + \boldsymbol{\eta},\ \langle \eta^\mu(t)\eta^\nu(t')\rangle = TM_C(t-t')\delta^{\mu\nu} \tag{3.16}$$

where T is the temperature of the bath the particle is in contact with and where $\mathbf{F}$ is some external force. For simplicity, we work in the low inertia and Markov approximations, which allows us to neglect the $m\ddot{\mathbf{r}}$ contribution, and to write $M_R = \gamma\delta(t)$, $M_C = 2\gamma'\delta(t)$, where γ and γ' are *a priori* different. The Langevin equation simplifies into

$$\gamma\dot{\mathbf{r}} = \mathbf{F} + \sqrt{2\gamma' T}\boldsymbol{\eta},\ \langle \eta^\mu(t)\eta^\nu(t')\rangle = \delta^{\mu\nu}\delta(t-t') \tag{3.17}$$

We readily see that the probabillity of a trajectory is, using the Onsager-Machlup formulation,

$$\mathscr{P}[\mathbf{r}] \propto P_{\mathrm{init}}(\mathbf{r}(0)) \exp\left[-\frac{1}{4\gamma' T}\int_0^{t_{\mathrm{obs}}} \mathrm{d}t(\gamma\dot{\mathbf{r}} - \mathbf{F})^2 - \frac{1}{2\gamma}\int_0^{t_{\mathrm{obs}}} \mathrm{d}t\partial_{\mathbf{r}}\cdot\mathbf{F}\right] \tag{3.18}$$

We have chosen to work with the Stratonovich-discretized path integral formulation (hence the extra bit involving the divergence of the force field $\mathbf{F}$) because we are about to perform a time-reversal operation, and the Stratonovich discretization is consistent with time-reversal (for an arbitrary α, the time-reversed process turns out to be discretized with an $(1-\alpha)$ discretization). For the time-reversed process we have

$$\mathscr{P}[\mathbf{r}^{\mathrm{R}}] \propto P_{\mathrm{fin}}(\mathbf{r}^{\mathrm{R}}(0)) \exp\left[-\frac{1}{4\gamma' T}\int_0^{t_{\mathrm{obs}}} \mathrm{d}t(\gamma\dot{\mathbf{r}} + \mathbf{F})^2 - \frac{1}{2\gamma}\int_0^{t_{\mathrm{obs}}} \mathrm{d}t\partial_{\mathbf{r}}\cdot\mathbf{F}_0\right] \tag{3.19}$$

where we have used that $\mathbf{r}^{\mathrm{R}}(t) = \mathbf{r}(t_{\mathrm{obs}} - t)$. This leads to

$$\begin{aligned}\bar{Q}[\mathbf{r}] = &\ln\frac{P_{\mathrm{init}}(\mathbf{r}(0))}{P_{\mathrm{fin}}(\mathbf{r}(t_{\mathrm{obs}}))} \\ &+ \frac{\gamma}{\gamma' T}\int_0^{t_{\mathrm{obs}}} \mathrm{d}t\dot{\mathbf{r}}\cdot\mathbf{F}\end{aligned} \tag{3.20}$$

In the particular case in which we start from equilibrium, and the force field $\mathbf{F} = -\partial_{\mathbf{r}} V$ is conservative, we remain in equilibrium and we know that

$$\frac{P_{\mathrm{init}}(\mathbf{r}(0))}{P_{\mathrm{fin}}(\mathbf{r}(t_{\mathrm{obs}}))} = \frac{P_{\mathrm{eq}}(\mathbf{r}(0))}{P_{\mathrm{eq}}(\mathbf{r}(t_{\mathrm{obs}}))} = \mathrm{e}^{-\beta V(\mathbf{r}(0)) + \beta V(\mathbf{r}(t_{\mathrm{obs}}))} \tag{3.21}$$

while $\int_0^{t_{\mathrm{obs}}} \mathrm{d}t\partial_{\mathbf{r}}\cdot\mathbf{F} = -[V]_0^{t_{\mathrm{obs}}}$ so that

$$\bar{Q}[\mathbf{r}] = -\beta\Delta V + \frac{\gamma}{\gamma' T}\Delta V \tag{3.22}$$

This quantity strictly vanishes when $\gamma' = \gamma$ which expresses that equilibrium is achieved only if the noise amplitude is adjusted so that $\gamma' = \gamma$, which is a property of the bath that must

hold independently of the system. Henceforth we will work with $\gamma' = \gamma$.

This strong connection between the amplitude of the dissipation kernel M_R (γ) and the correlation kernel M_C (γ) is of course not limited to the Markov approximation (nor to the overdamped limit), and it can be verified to lead to the equality of M_R and M_C by exactly the same sort of manipulations (up to the extra care due to the fact that one is dealing with non-trivial memory kernels). From now on, when writing a Langevin equation, the terms describing the force $\mathbf{F}_b = -\gamma\dot{\mathbf{r}} + \sqrt{2\gamma T}\boldsymbol{\eta}$ exerted by the bath on the particle will always incorporate that constraint (that Kubo has called the second fluctuation-dissipation theorem). In equilibrium we see that $\bar{Q}$ is not extensive in time because it only involves boundary terms (and its average obviously vanishes).

Let's see what $\bar{Q}$ for an arbitrary force $\mathbf{F}$. Then we see that

$$\bar{Q}[\mathbf{r}] = \ln \frac{P_{\text{init}}(\mathbf{r}(0))}{P_{\text{fin}}(\mathbf{r}(t_{\text{obs}}))} + \frac{1}{T}\int_0^{t_{\text{obs}}} \mathrm{d}t\dot{\mathbf{r}}\cdot\mathbf{F} \tag{3.23}$$

The first contribution are boundary terms at $t = 0$ and $t = t_{\text{obs}}$, representing $\Delta\hat{S}$, but the last one has a straightforward physical interpretation:

$$Q_S = \beta\int_0^{t_{\text{obs}}} \mathrm{d}t\dot{\mathbf{r}}\cdot\mathbf{F} \tag{3.24}$$

is the work injected by the force into the system. Since we are working in the overdamped limit, we have $\mathbf{F} + \mathbf{F}_b = \mathbf{0}$, where $\mathbf{F}_b = -\gamma\dot{\mathbf{r}} + \sqrt{2\gamma T}\boldsymbol{\eta}$ is the force exerted by the bath on the system, so that $\mathbf{F} = -\mathbf{F}_b$ is also the force exerted by the particle on the bath. This helps us define the heat exchanged between the system and the external world: this is the work exerted by the system on the environment and the standard interpretation that $\Delta S_{\text{ext}} = \langle Q_S\rangle = \frac{Q_{\text{ext}}}{T}$ holds very nicely in this particular setting.

Hence, on average and in the stationary state, we have that

$$\langle\bar{Q}\rangle = \frac{1}{T}\langle\int_0^{t_{\text{obs}}} \mathrm{d}t\dot{\mathbf{r}}\cdot\mathbf{F}\rangle \tag{3.25}$$

and the entropy production rate J_S then reads

$$J_S = \frac{1}{T}\langle\dot{\mathbf{r}}\cdot\mathbf{F}\rangle \geq 0 \tag{3.26}$$

It is remarkable that this inequality, which could have been written on the basis of the second principle of thermodynamics, actually applies to a small and fluctuating system, in terms of averages. What is truly remarkable is that this is a proof of the second principle.

The possibililty to study small and fluctuating systems with ideas commonly valid at the macroscopic level and for equilibrium states had led to the creation of a subfield of statistical mechanics known as stochastic energetics or stochastic thermodynamics. Two important references are the book by Sekimoto [177] who started this field back in 1998, and the review by Seifert [176]. More recent books include [152] and [167].

3.1.4 Consequences of equilibrium for the evolution operator

Consider an equilibrium dynamics whose evolution operator is written in a new basis. We introduce the matrix P with entries $P_{\mathscr{C},\mathscr{C}'} = P_{\rm eq}(\mathscr{C})^{-1/2}\delta_{\mathscr{C},\mathscr{C}'}$ and define

$$\mathbb{W}_s = P\mathbb{W}P^{-1},\ \mathbb{W}_{s,\mathscr{C},\mathscr{C}'} = P_{\rm eq}(\mathscr{C})^{-1/2}\,W(\mathscr{C}'\to\mathscr{C})P_{\rm eq}(\mathscr{C}')^{+1/2} - r(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'} \tag{3.27}$$

but because of the detailed balance condition,

$$\sqrt{\frac{P_{\rm eq}(\mathscr{C}')}{P_{\rm eq}(\mathscr{C})}} = \sqrt{\frac{W(\mathscr{C}\to\mathscr{C}')}{W(\mathscr{C}'\to\mathscr{C})}} \tag{3.28}$$

so that

$$\begin{aligned}\mathbb{W}_{s,\mathscr{C},\mathscr{C}'} =& = W(\mathscr{C}'\to\mathscr{C})\sqrt{\frac{W(\mathscr{C}\to\mathscr{C}')}{W(\mathscr{C}'\to\mathscr{C})}} - r(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'}\\ =&\sqrt{W(\mathscr{C}'\to\mathscr{C})\,W(\mathscr{C}\to\mathscr{C}')} - r(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'}\end{aligned} \tag{3.29}$$

and thus $\mathbb{W}_s^T = \mathbb{W}_s$. In this new basis, $\mathbb{W}_s$ is symmetric, and since it is real, it is also Hermitian. The ground state of $-\mathbb{W}_s$ is the vector with $\sqrt{P_{\rm eq}(\mathscr{C})}$ entries (and the corresponding eigenvalue is 0). It is then tempting to view the classical dynamics problem in terms of a quantum mechanics problem with Hamiltonian $\mathbb{H} = -\mathbb{W}_s$. One has to be aware of this analogy, but cautious: quantum mechanics has an i while stochastic dynamics doesn't, $\mathbb{H}$ is Hermitian only for equilibrium dynamics. This is a connection we will come back to later.

It is instructive to study the particular case of $\dot{\mathbf{x}} = -\partial_{\mathbf{x}}V + \sqrt{2T}\boldsymbol{\eta}$ for which the Fokker-Planck equation reads

$$\partial_t p = \partial_{\mathbf{x}}\cdot((\partial_{\mathbf{x}}V)p) + T\partial_{\mathbf{x}}^2 p \tag{3.30}$$

and thus

$$\mathbb{W}\bullet = T\partial_{\mathbf{x}}^2\bullet + \partial_{\mathbf{x}}\cdot((\partial_{\mathbf{x}}V)\bullet),\ \mathbb{H} = -T\partial_{\mathbf{x}}^2 + \frac{1}{4T}(\partial_{\mathbf{x}}V)^2 - \frac{1}{2}\partial_{\mathbf{x}}^2 V \tag{3.31}$$

and we are left with a Schrödinger operator for a particle with mass $m = \frac{\hbar^2}{2T}$ in some external potential $U(\mathbf{x}) = \frac{1}{4T}(\partial_{\mathbf{x}}V)^2 - \frac{1}{2}\partial_{\mathbf{x}}^2 V$. Later we will exploit the analogy between the semi-classical $\hbar\to 0$ limit and the low-temperature/low-noise limit $T\to 0$. There is some physical meaning to the quantity $U(\mathbf{x})$. One of them is

$$\frac{{\rm d}V}{{\rm d}t} \overset{0}{=} -(\partial_{\mathbf{x}}V)^2 + T\partial_{\mathbf{x}}^2 V + \sqrt{2T}\partial_{\mathbf{x}}V\cdot\boldsymbol{\eta} \tag{3.32}$$

so that it is almost the average rate of variation of the energy V. Up to a constant coming from the diagonal elements of the Laplacian, the diagonal term in $\mathbb{H}$ can also be interpreted as the escape rate (the escape rate is given by the diagonal elements of the evolution operator). Hence $r(\mathscr{C}) = r(\mathbf{x}) = {\rm Cst} + U(\mathbf{x})$ is the rate at which the particle escapes from location $\mathbf{x}$ [13].

The formal connection between stochastic dynamics and quantum mechanics has been exploited by Nelson [142, 110] and is briefly sketched in chapter 19 of [149]. Given a quantum mechanical problem with Hamiltonian $\hat{H}$ whose ground-state wave function ψ_0 is known, and real, we can define $\beta V = -2\ln\psi_0$ and consider $\mathbb{W} = \psi_0\hat{H}\psi_0^{-1}$. This is the evolution operator for an overdamped Langevin particle in a potential V.

3.1.5 Equilibrium is a degree-of-freedom-dependent notion

The discussion that follows is taken almost *verbatim* from [147] and we have kept the heavy referencing which does proper justice to the existing literature (way better than anything else in the present notes).

For equilibrium systems, time-reversal symmetry (TRS) is ensured irrespectively of the degree of coarse graining and holds both for microscopic and coarse-grained mesoscopic descriptions. For systems out of equilibrium, on the contrary, this question is more subtle and the possible existence of TRS depends on the degrees of freedom which are being considered. This makes its characterization—in particular using an entropy production rate—a somewhat ambiguous task, which has attracted a lot of interest both theoretically [84, 98, 74, 141, 130, 33, 166, 179, 48, 184, 47, 27, 131] and experimentally [136, 198, 165, 72, 73, 93, 20, 94].

To illustrate this, consider a zero-Reynolds swimmer at position $\mathbf{r}(t)$ moving through a fluid thanks to the displacement of some degrees of freedom $\mathbf{x}_i(t)$. (Think about the motion of a flagellum.) The solution of Stokes equation will lead to a flow $\mathbf{u}(t)$ and a self-propulsion speed $\mathbf{v}_p(t)$, which results from a propulsion force $\mathbf{f}(t)$ exerted on the fluid. (By Newton third law, $\mathbf{f}$ is equal and opposite to $\mathbf{f}_p$ in the equation of motion $m\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + \mathbf{f}_p + \sqrt{2\gamma T}\boldsymbol{\eta}$) A recording of $\mathbf{r}(t)$ and $\mathbf{x}_i(t)$ of duration $t_{\rm obs}$ played backward is also a solution of Stokes equation. It would involve a force $-\mathbf{f}(t_{\rm obs}-t)$, a speed $-\mathbf{v}_p(t_{\rm obs}-t)$ and a flow $-\mathbf{u}(t_{\rm obs}-t)$. It is, however, distinguishable from the forward trajectory: our swimmer will swim backward, a 'pusher' would become a 'puller'. In probabilistic terms, the trajectory $\mathbf{r}(t)$ given the displacements $\mathbf{x}_i(t)$ is equally likely to occur as $\mathbf{r}(t_{\rm obs}-t)$ given $\mathbf{x}_i(t_{\rm obs}-t)$, even though they can be distinguished by the flow they generate.

The situation is reminiscent of the equilibrium Langevin dynamics of a passive charged particle at $\mathbf{r}(t)$ in a magnetic field $\mathbf{B}(t)$ created by electrons at positions $\mathbf{x}_i(t)$, moving deterministically in a coil:

$$m\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + q\dot{\mathbf{r}}\times\mathbf{B}(t) + \sqrt{2\gamma kT}\boldsymbol{\eta}\ , \tag{3.33}$$

with q the charge of the particle, γ its damping coefficient, m its mass, and $k_{\rm B}T$ the temperature. The reverse trajectories $\mathbf{x}_i(t_f-t)$ lead to a magnetic field $-\mathbf{B}(t_{\rm obs}-t)$ so that $\mathbf{r}(t_f-t)$ is equally likely to occur as $\mathbf{r}(t)$ was in the presence of $\mathbf{B}(t)$. Mathematically, the conditional probabilities of observing $\mathbf{r}(t)$ given $\mathbf{x}_i(t)$ and $\mathbf{r}(t_{\rm obs}-t)$ given $\mathbf{x}_i(t_{\rm obs}-t)$ are thus equal and the corresponding entropy production rate vanishes $J_S = \lim_{t\to\infty}\frac{1}{t}\log\frac{P[\{\mathbf{r}(t)\}|\{\mathbf{x}_i(t)\}]}{P[\{\mathbf{r}(t_{\rm obs}-t)\}|\{\mathbf{x}_i(t_{\rm obs}-t)\}]} = 0$, consistently with thermodynamics. In a given experiment, however, it is not the conditional probability which is measured, but the joint probability of observing $\mathbf{r}(t)$ and $\mathbf{x}_i(t)$. When the electrons are driven by a fixed potential difference, for instance, they will not generate $\mathbf{x}_i(t)$ and $\mathbf{x}_i(t_{\rm obs}-t)$ with equal probability. The observation of $\mathbf{r}(t)$ and $\mathbf{r}(t_{\rm obs}-t)$ will thus not be equally likely: they do not inherit the underlying TRS dynamics Eq. (3.33) would have if the dynamics of $\mathbf{x}_i(t)$ were time reversible. This *induced* irreversibility can be measured by comparing the occurrence frequency of $\mathbf{r}(t)$ and $\mathbf{r}(t_{\rm obs}-t)$ for the same field $\mathbf{B}(t)=\mathbf{B}_0$. The corresponding 'Shannon' entropy production rate is now finite, given by $\sigma = 2q^2|B_0|^2/(\gamma m)$. Note that this 'entropy-production rate' solely measures the irreversibility of the trajectories $\mathbf{r}(t)$ in an experiment with a fixed magnetic field. In particular, it is not a measure of the creation of thermodynamic entropy in our magnetic system since the magnetic field has to be flipped under time-reversal. Equation (3.33) has also be used to describe the hair bundle of sensory cells [56]. There, the

term analogous to $\mathbf{B}(t)$ has a different origin and does not flip under time reversal and thus leads to a non-vanishing thermodynamic entropy production rate. Whether a given definition of J_S can be connected to the thermodynamic entropy production rate or not depends on the physics of the system under study; it can always be connected to a measure of irreversibility in the sense described above.

In living (or active) matter, the internal processes leading to $\mathbf{x}_i(t)$ are often strongly irreversible. In living systems, they rely on an imbalance between the concentrations of ATP and ADP+P [3, 111] in the cells. For Janus self-diffusiophoretic colloids, it is the irreversible transmutation of hydrogen peroxyde into oxygen and water [104, 148] which powers self-propulsion. The observation of $\mathbf{r}(t)$ and $\mathbf{r}(t_{\rm obs}-t)$ thus need not occur with equal probabilities. (An interesting exception is when self-propulsion emerges from spontaneous symmetry breaking as in Quincke rollers [30].) Let us stress that the most irreversible process in active system is, generically, the one generating $\mathbf{x}_i(t)$, and not the dynamics of $\mathbf{r}(t)$. When trying to measure the energy dissipated in an active system, say using calorimetry, one would expect that this process strongly dominates all other sources of irreversibility. A large part of the irreversibility is thus lost if the irreversible process leading to the active force is not modelled [156, 48]. This is, in particular, the case of the equation of motion $m\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + \mathbf{f}_p + \sqrt{2\gamma T}\boldsymbol{\eta}$ in which the active force is an input of the problem whose origin is unspecified. The 'dissipation' measured through $w_p = \langle \mathbf{f}_p \cdot \dot{\mathbf{r}} \rangle$ thus cannot capture the full irreversibility of the system. It is nevertheless an interesting object of study since it quantifies the violation of TRS encapsulated in the degrees of freedom $\mathbf{r}(t)$ and $\underline{\mathrm{f}}_p(t)$.

Let us first show that, even at the level of dynamics $m\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + \mathbf{f}_p + \sqrt{2\gamma T}\boldsymbol{\eta}$, the existence of TRS remains ambiguous and depends on which degrees of freedom are under study. We start by considering the situation depicted in Fig. 3.1, which compares the trajectory of a model run-and-tumble bacteria in two space dimensions with its time-reversed counterpart. The underlying stochastic dynamics is given by

$$\dot{\mathbf{r}}(t) = v_0\mathbf{u}(\theta(t)) + \sqrt{2D}\boldsymbol{\eta}(t),\ D = T/\gamma,\ v_0 = f_p/\gamma \tag{3.34}$$

where v_0 is a fixed self-propulsion speed and $\theta(t)$ is fully randomized at rate α. The trajectory presented in Fig. 3.1a records the time evolution of both the particle position $\mathbf{r}(t)$ and its orientation $\theta(t)$.

Note that $\mathbf{r}(t)$ and $\theta(t)$ uniquely characterize the realization of the noise through $\sqrt{2D}\boldsymbol{\eta}(t) = \dot{\mathbf{r}}(t) - v_0\mathbf{u}(\theta(t))$. One can show that for the reversed trajectory $\mathbf{r}^{\rm R}(t) = \mathbf{r}(t_{\rm obs}-t)$, $\theta^{\rm R}(t) = \theta(t_{\rm obs}-t)$ to be observed, the surrounding fluid molecules have to produce a different noise $\boldsymbol{\eta}^{\rm R}(t)$ such that $\sqrt{2D}\boldsymbol{\eta}^{\rm R}(t) = -\sqrt{2D}\boldsymbol{\eta}(t_{\rm obs}-t) - 2v_0\mathbf{u}(\theta(t_{\rm obs}-t))$. This shows that time-reversed trajectories are obtained by making the noise $\boldsymbol{\eta}^{\rm R}$ work against the active force to make the active particle retrace its steps. Using the Gaussian weights of these two noise realizations, their relative probability to occur can be computed, leading to a path-wise entropy production:

$$\bar{Q}[\{\mathbf{r}(t),\theta(t)\}] = \frac{\mu}{D}\int_0^{t_{\rm obs}} {\rm d}t\dot{\mathbf{r}}\cdot\mathbf{f}_p + \ln\frac{P_0(\mathbf{r}_0,\theta_0)}{P_f(\mathbf{r}_f,\theta_f)}, \tag{3.35}$$

where $P_f(\mathbf{r}_f,\theta_f)$ is the probability of being at $\mathbf{r}_f \equiv \mathbf{r}(t_{\rm obs})$ and $\theta_f \equiv \theta(t_{\rm obs})$ given that the initial condition was sampled according to P_0. The right-hand side of Eq. (3.35) measures both

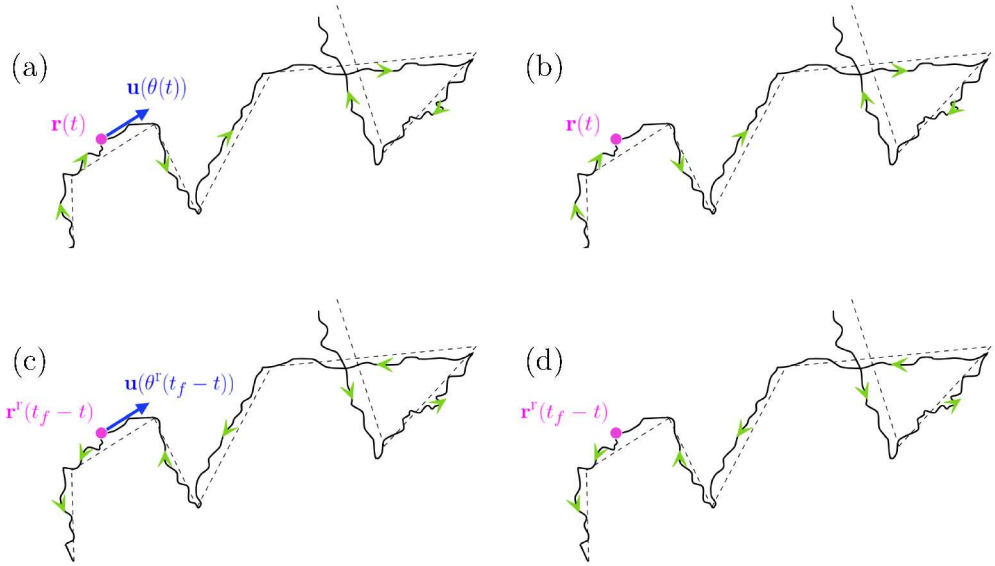

Figure 3.1: Trajectories of a run-and-tumble particle experiencing translational noise. The noise-less trajectory is drawn as a dashed line and the direction of time is indicated by green arrows. One may record the position and orientation of the particle (a) or solely its position (b). The time-reversed trajectories of (a) and (b) are shown in (c) and (d). Their likeliness are clearly different since the noise has to fight self-propulsion in (c), but not necessarily in (d).

the heat transferred to the bath, $-\hat{Q} \equiv \int_0^{t_{\rm obs}} \dot{\mathbf{r}} \cdot \mathbf{f}_p \, dt$, and the change in the 'stochastic' Shannon entropy $\Delta\hat{S} = \ln \frac{P_0(\mathbf{r}_0,\theta_0)}{P_f(\mathbf{r}_f,\theta_f)}$ between P_0 and P_f associated to the trajectory $\{\mathbf{r}(t),\theta(t)\}$ [175]. Taking the average over the forward path probability, and using the positivity of the Kullback-Leibler divergence, leads to a generalized second law $\langle \Delta\hat{S}\rangle > \frac{\mu}{D}\langle\hat{Q}\rangle$. Alternatively, taking the limit $t_{\rm obs} \to \infty$, leads to the steady-state entropy production *rate*

$$J_S = \lim_{t_{\rm obs}\to\infty} \frac{1}{t_{\rm obs}} \bar{Q} = \frac{\mu\langle \dot{\mathbf{r}} \cdot \mathbf{f}_p\rangle}{D} = \frac{\mu w_p}{D} \, , \tag{3.36}$$

where we have used the ergodicity of the dynamics. Equation (3.36) relates the entropy production rate to the average dissipation of the active force w_p . The dissipation, thus, measures the irreversibility of the active dynamics [31, 143] in Eq. (3.34), which stems from the alignment of the velocity with the self-propulsion force. An atypically strong noise is indeed needed to generate the time-reversed trajectories. Physically, the entropy production rate J_S measures the (inverse) timescale over which the self-propulsion makes the trajectory irreversible: at short timescales, the translational diffusion arising from Brownian motion dominates self-propulsion, hence, hiding the irreversible character of the dynamics; on longer timescales, translational diffusion plays a lesser role in transport than self-propulsion, which makes the irreversibility stemming from the latter more apparent. Note that J_S diverges as D goes to zero, so that the dynamics becomes strongly irreversible in this limit.

The situation is completely different if one tries to characterize the TRS breaking for the trajectory shown in Figs. 3.1b&d. There, only the position of the particle is measured and its original and final orientations are unknown. If the system is endowed with periodic boundary conditions, the steady state distribution is an isotropic, uniform distribution so that it is equally likely to find trajectories with $\theta(t)$ or the flipped orientation $\tilde{\theta}(t) = \pi - \theta(t)$. The entropy production thus vanishes since the time reversed of any trajectory with $\theta(t)$ can be realized with the same probability by a trajectory starting from the final position $\mathbf{r}(t_{\rm obs})$ with a flipped orientation $\tilde{\theta}(t_{\rm obs})$. Note that this symmetry resembles that of underdamped Langevin equations in which the time-reversal symmetry in configuration space emerges from a symmetry in phase-space upon flipping the velocities under time reversal. This parallel between active particles and underdamped passive ones has been exploited to reveal a similar symmetry of the evolution operator of AOUPs [74, 130, 33]. Note that this TRS in position space is independent of the value of D and holds even for $D = 0$.

Finally, we comment on the fact that whether or not one observes TRS in active systems depends on what can be measured. Consider for example Quincke colloidal particles [30]. These particles acquire self-propulsion through the spontaneous breaking of a symmetry: their polarity stems from an asymmetric charge distribution on their surface. For an isolated particle, measuring this asymmetry or the flow of the surrounding fluid are required to distinguish a forward trajectory from a time-reversed one. In sum, in a dilute, uniform active system, the observation of a breakdown of TRS depend on the degrees of freedom which are considered. Describing the energy source [156, 48], or considering the inertia of these typically overdamped systems [179], will lead to different characterization of the irreversibility of the dynamics. This strongly differs from equilibrium dynamics, in which TRS holds irrespective of the degree of coarse-graining.

3.2 Consequences of time reversibility

3.2.1 The fluctuation-dissipation theorem (FDT) at the level of a master equation

Consider a system whose dynamics is governed by a Master Equation with an evolution operator $\mathbb{W}_0$. Let $P_{\rm ss}$ be the steady-state of the master equation, and let the elements of the evolution operator be denoted by

$$\mathbb{W}_{0\mathscr{C},\mathscr{C}'} = W_0(\mathscr{C}' \to \mathscr{C}) - r_0(\mathscr{C})\delta_{\mathscr{C},\mathscr{C}'} \tag{3.37}$$

where $W_0(\mathscr{C} \to \mathscr{C}')$ is the rate at which the system hops from state $\mathscr{C}$ to state $\mathscr{C}'$, and where $r_0(\mathscr{C}) = \sum_{\mathscr{C}'} W_0(\mathscr{C} \to \mathscr{C}')$ is the rate at which the system escapes from state $\mathscr{C}$. We now perturb the dynamics by coupling an infinitesimal force $h(t)$ to an observable $A(\mathscr{C})$ in the following way. The transition rate is changed into

$$W(\mathscr{C} \to \mathscr{C}') = W_0(\mathscr{C} \to \mathscr{C}')\mathrm{e}^{\frac{\beta}{2}h(t)(A(\mathscr{C}')-A(\mathscr{C}))} \simeq W_0(\mathscr{C} \to \mathscr{C}')\left[1 + \frac{\beta h}{2}(A(\mathscr{C}') - A(\mathscr{C}))\right] \tag{3.38}$$

and the rate of escape from configuration $\mathscr{C}$ is changed into $r + \delta r$ with

$$\delta r(\mathscr{C}) = \frac{\beta h}{2}\sum_{\mathscr{C}'} W_0(\mathscr{C} \to \mathscr{C}')(A(\mathscr{C}') - A(\mathscr{C})) \tag{3.39}$$

If we were dealing with an equilibrium dynamics, a possibility for the rates $W(\mathscr{C} \to \mathscr{C}')$ would be $W_0(\mathscr{C} \to \mathscr{C}') = \gamma \mathrm{e}^{-\frac{\beta}{2}(\mathscr{H}_0(\mathscr{C}')-\mathscr{H}_0(\mathscr{C}))}$ because this would guarantee, owing to the detailed balance condition, that $P_{\rm eq}(\mathscr{C}) \sim \mathrm{e}^{-\beta\mathscr{H}_0(\mathscr{C})}$. And then the choice of perturbation in Eq. (3.38) amounts to changing $\mathscr{H}_0(\mathscr{C})$ into $\mathscr{H}_0(\mathscr{C}) - h(t)A(\mathscr{C})$.

The deviation $\delta P(\mathscr{C}, t)$ of the probability to find the system in state $\mathscr{C}$ at time t with respect to $P_{\rm ss}(\mathscr{C})$ evolves according to

$$\partial_t \delta P(t) = \mathbb{W}_0 \delta P + \delta\mathbb{W} P_{\rm ss} \tag{3.40}$$

so that

$$\delta P(t) = \int_0^t \mathrm{d}\tau \mathrm{e}^{\mathbb{W}_0(t-\tau)}\delta\mathbb{W}P_{\rm ss} \tag{3.41}$$

which we rewrite

$$\delta P(\mathscr{C}, t) = \sum_{\mathscr{C}',\mathscr{C}''}\int_0^t \mathrm{d}\tau \left[\mathrm{e}^{\mathbb{W}_0(t-\tau)}\right]_{\mathscr{C},\mathscr{C}'} \delta\mathbb{W}_{\mathscr{C}',\mathscr{C}''}P_{\rm ss}(\mathscr{C}'') \tag{3.42}$$

The matrix elements of $\delta\mathbb{W}$ read

$$\begin{aligned}\delta\mathbb{W}_{\mathscr{C}',\mathscr{C}''} =& -\frac{\beta h}{2}\mathbb{W}_{0\mathscr{C}',\mathscr{C}''}A(\mathscr{C}'') + \frac{\beta h}{2}W_0(\mathscr{C}'' \to \mathscr{C}')A(\mathscr{C}') \\ & -\frac{\beta h}{2}\delta_{\mathscr{C}',\mathscr{C}''}\sum_{\mathscr{C}'''} W_0(\mathscr{C}' \to \mathscr{C}''')A(\mathscr{C}''')\end{aligned} \tag{3.43}$$

hence we find that

$$\sum_{\mathscr{C}''} \delta\mathbb{W}_{\mathscr{C}',\mathscr{C}''} P_{\rm ss}(\mathscr{C}'') = -\frac{\beta h}{2}(\mathbb{W}_0 A P_{\rm ss})(\mathscr{C}') - \delta r(\mathscr{C}') P_{\rm ss}(\mathscr{C}') \tag{3.44}$$

where the last two terms in the rhs of Eq. (3.43) build up the second contribution in the rhs of Eq. (3.44), as can be seen from

$$\begin{aligned} &\sum_{\mathscr{C}''} \left[\frac{\beta h}{2} W_0(\mathscr{C}'' \to \mathscr{C}') A(\mathscr{C}') - \frac{\beta h}{2} \delta_{\mathscr{C}',\mathscr{C}''} \sum_{\mathscr{C}'''} W_0(\mathscr{C}' \to \mathscr{C}''') A(\mathscr{C}''') \right] P_{\rm ss}(\mathscr{C}'') \\ &= \frac{\beta h}{2} \sum_{\mathscr{C}''} W_0(\mathscr{C}' \to \mathscr{C}'') A(\mathscr{C}') P_{\rm ss}(\mathscr{C}') - \frac{\beta h}{2} \delta_{\mathscr{C}',\mathscr{C}''} \sum_{\mathscr{C}'''} W_0(\mathscr{C}' \to \mathscr{C}''') A(\mathscr{C}''') P_{\rm ss}(\mathscr{C}'') \\ &= -\delta r(\mathscr{C}') P_{\rm ss}(\mathscr{C}') \end{aligned} \tag{3.45}$$

A physical observable $B(\mathscr{C})$ responds at time t to a variation of h at an earlier time ($t' < t$, else there is no response) by varying by an amount $\delta\langle B(t)\rangle$ such that

$$\begin{aligned} \delta\langle B(t)\rangle &= \sum_{\mathscr{C}} B(\mathscr{C}) \delta P(\mathscr{C}, t) \\ &= -\frac{\beta}{2} \sum_{\mathscr{C},\mathscr{C}',\mathscr{C}''} \int_0^t {\rm d}\tau h(\tau) B(\mathscr{C}) \left[{\rm e}^{\mathbb{W}_0(t-\tau)} \right]_{\mathscr{C},\mathscr{C}'} \mathbb{W}_{0\mathscr{C}',\mathscr{C}''} A(\mathscr{C}'') P_{\rm ss}(\mathscr{C}'') \\ &\quad -\frac{\beta}{2} \sum_{\mathscr{C},\mathscr{C}',\mathscr{C}''} \int_0^t {\rm d}\tau B(\mathscr{C}) \left[{\rm e}^{\mathbb{W}_0(t-\tau)} \right]_{\mathscr{C},\mathscr{C}'} \delta r(\mathscr{C}', \tau) P_{\rm sst}(\mathscr{C}') \\ &= -\frac{\beta}{2} \frac{\rm d}{{\rm d}t} \sum_{\mathscr{C},\mathscr{C}',\mathscr{C}''} \int_0^t {\rm d}\tau h(\tau) B(\mathscr{C}) \left[{\rm e}^{\mathbb{W}_0(t-\tau)} \right]_{\mathscr{C},\mathscr{C}''} A(\mathscr{C}'') P_{\rm ss}(\mathscr{C}'') \\ &\quad -\frac{\beta}{2} \sum_{\mathscr{C},\mathscr{C}',\mathscr{C}''} \int_0^t {\rm d}\tau B(\mathscr{C}) \left[{\rm e}^{\mathbb{W}_0(t-\tau)} \right]_{\mathscr{C},\mathscr{C}'} \delta r(\mathscr{C}', \tau) P_{\rm ss}(\mathscr{C}') \end{aligned} \tag{3.46}$$

from which we deduce that

$$\frac{\delta\langle B(t)\rangle}{\delta h(t')} = -\frac{\beta}{2} \frac{\rm d}{{\rm d}t} \langle B(t) A(t')\rangle - \langle B(t) \frac{\partial \delta r}{\partial h(t')}\rangle \tag{3.47}$$

This Eq. (3.47) has sometimes been dubbed a generalized FDT (FDT is for fluctuation-dissipation theorem), because the equation connects the response $R(t,t') = \frac{\delta\langle B(t)\rangle}{\delta h(t')}$ of the system observed through the quantity B, to its stationary state correlations. More can be learned about the generalized FDT in [16, 17, 14, 15].

In the event of dynamic rules satisfying the detailed balance property with respect to some distribution $P_{\rm ss}(\mathscr{C}) = P_{\rm eq}(\mathscr{C})$, it is easy to see that the contribution $-\langle B(t) \frac{\partial \delta r}{\partial h(t')}\rangle$ simplifies

into the exact first bit appearing in the right hand side of Eq. (3.47). We return to the identity

$$\begin{aligned}\delta r(\mathscr{C}')P_{\rm eq}(\mathscr{C}') =& -\frac{\beta h}{2}\sum_{\mathscr{C}''} W_0(\mathscr{C}'\to\mathscr{C}'')A(\mathscr{C}')P_{\rm eq}(\mathscr{C}') + \frac{\beta h}{2}\delta_{\mathscr{C}',\mathscr{C}''}\sum_{\mathscr{C}'''} W_0(\mathscr{C}'\to\mathscr{C}''')A(\mathscr{C}''')P_{\rm eq}(\mathscr{C}')\\ =&\frac{\beta h}{2}\sum_{\mathscr{C}''}\left[W_0(\mathscr{C}'\to\mathscr{C}'')A(\mathscr{C}'')P_{\rm eq}(\mathscr{C}') - W_0(\mathscr{C}'\to\mathscr{C}'')A(\mathscr{C}')P_{\rm eq}(\mathscr{C}')\right]\\ =&\frac{\beta h}{2}\sum_{\mathscr{C}''}\left[W_0(\mathscr{C}'\to\mathscr{C}'')A(\mathscr{C}'')P(\mathscr{C}') - W_0(\mathscr{C}''\to\mathscr{C}')A(\mathscr{C}')P(\mathscr{C}'')\right]\\ =&-\frac{\beta h}{2}\sum_{\mathscr{C}'\mathscr{C}''}\mathbb{W}_{0\mathscr{C}'\mathscr{C}''}A(\mathscr{C}'')P_{\rm eq}(\mathscr{C}'')\end{aligned} \tag{3.48}$$

where, in the last line, we used that $W_0(\mathscr{C}'\to\mathscr{C}'')P_{\rm eq}(\mathscr{C}') = W_0(\mathscr{C}''\to\mathscr{C}')P_{\rm eq}(\mathscr{C}'')$. Finally, getting back to the correlation of interest, we have that

$$\begin{aligned}\langle B(t)\frac{\delta r}{\delta h(t')}\rangle &= \sum_{\mathscr{C},\mathscr{C}'} B(\mathscr{C})[{\rm e}^{\mathbb{W}_0(t-t')}]_{\mathscr{C},\mathscr{C}'}\delta r(\mathscr{C}',t')P_{\rm eq}(\mathscr{C}')\\ &= \frac{\beta}{2}\sum_{\mathscr{C},\mathscr{C}',\mathscr{C}''} B(\mathscr{C})[{\rm e}^{\mathbb{W}_0(t-t')}]_{\mathscr{C},\mathscr{C}'}\mathbb{W}_{0\mathscr{C}',\mathscr{C}''}A(\mathscr{C}'')P_{\rm eq}(\mathscr{C}'')\\ &= \frac{\beta}{2}\frac{\rm d}{{\rm d}t}\langle B(t)A(t')\rangle\end{aligned} \tag{3.49}$$

Hence, altogether we have that $R(t,t') = \frac{\delta\langle B(t)\rangle}{\delta h(t')}$ is given by

$$R(t,t') = -\beta\frac{\rm d}{{\rm d}t}\langle B(t)A(t')\rangle \tag{3.50}$$

Using that there is time-translation invariance in the stationary (equilibrium) state, we can write $R(t,t') = R(t-t')$ and $C(t,t') = \langle B(t)A(t')\rangle = C(t-t')$. But we further have that $C(t,t') = C(-t,-t') = C(t'-t)$, or $C(t) = C(-t)$ while $R(t)\propto\theta(t)$. Altogther the fluctuation-dissipation theorem can be written as

$$R(t) - R(-t) = -\beta\frac{{\rm d}C}{{\rm d}t} \tag{3.51}$$

There are several remarkable features that call for comments:

- the connection between R and C is fully independent of the quantities that are being observed or perturbed. The FDT is true regardless of A and B.
- the ratio $-\dot{C}/R = T$ is a universal number. That's the only place where the thermostat appears. This means that whatever thermometer one uses, the outcome of the measurement will always be the same.

- a translation of the mathematical statement of the FDT is that the response of the system to some nonequilbrium perturbation is identical to the spontaneous rate of relaxation of fluctuations in the unperturbed equilibrium state (up to the temperature as a prefactor).

The FDT generalizes in a much less compact form to nonlinear response. This is beyond the scope of these notes.

Interestingly, while R and C are observable-dependent, in equilibrium $T = -\dot{C}/R$ is not. But it may happen that in some nonequilibrium settings (in particular for mean-field systems where some simplifications occur), the $-\dot{C}/R$ ratio actually becomes observable-independent and the extent to which it can be interpreted as an effective temperature is a nontrivial question. A review on this challenging issue is that of Cugliandolo [45], but more recent references can be found with applications to active matter [46].

3.2.2 The FDT at the level of a Langevin equation and the Harada-Sasa equality

Consider an overdamped equilibrium dynamics for a particle with position x in some external potential $V(x)$ (we work in $d = 1$ to make notations lighter), that has reached equilibrium for a long time, whose evolution is

$$\dot{x} = -V' + f + \sqrt{2T}\eta \tag{3.52}$$

where f is an infinitesimal small perturbing force that acts as of time $t' > 0$. And we ask about how a quantity $B(x(t)) = B(t)$ responds,

$$R(t,t') = \left.\frac{\delta\langle B(t)\rangle}{\delta f(t')}\right|_{f=0} \tag{3.53}$$

with

$$\langle B\rangle = \int \mathscr{D}x B(x(t)) \mathrm{e}^{-\frac{1}{4T}\int \mathrm{d}s(\dot{x}+V'-f)^2} \tag{3.54}$$

so that

$$R(t,t') = \frac{1}{2T}\langle B(x(t))(\dot{x}+V')(t')\rangle \tag{3.55}$$

and in a similar fashion

$$R(-t,-t') = \frac{1}{2T}\langle B(x(-t))(\dot{x}+V')(-t')\rangle \tag{3.56}$$

so that

$$\begin{aligned} R(t,t') - R(-t,-t') =& \frac{1}{2T}\left[\langle B(x(t))\dot{x}(t') - B(x(-t))\dot{x}(-t')\rangle\right] \\ &+ \frac{1}{2T}\langle B(x(t))\,V'(x(t')) - B(x(-t))\,V'(x(-t'))\rangle \end{aligned} \tag{3.57}$$

At this stage we use that in equilibrium the dynamics is time-reversible so that $\langle B(x(t))\,V'(x(t')) - B(x(-t))\,V'(x(-t'))\rangle = 0$ while

$$\langle B(x(t))\dot{x}(t') - B(x(-t))\dot{x}(-t')\rangle = 2\frac{\mathrm{d}}{\mathrm{d}t'}\langle B(x(t))\dot{x}(t')\rangle \tag{3.58}$$

which again leads to $R(\tau) - R(-\tau) = -\frac{1}{T}\frac{\mathrm{d}}{\mathrm{d}\tau}\langle B(\tau)x(0)\rangle$.

The entropy production rate in the presence of an external force f that drives the system out of equilibrium is given by

$$J_S = \frac{1}{T}\langle \dot{x} f\rangle = \lim_{t\to 0}\frac{\mathrm{d}}{\mathrm{d}t}\Big[TR(t) + \dot{C}(t)\Big] \tag{3.59}$$

which is the Harada-Sasa equality (the proof that can be found here [100, 101] is a bit tricky). Here R and C are the position response and the position auto-correlation function.

3.2.3 As a discrete symmetry of a dynamical action

We will illustrate the Fluctuation-Dissipation theorem in the case of a system whose evolution is governed by a Langevin equation of the form

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \beta\mathbf{F} + \boldsymbol{\xi} \tag{3.60}$$

where $\mathbf{F} = -\partial_{\mathbf{r}} V$ is a conservative force. We assume the system is in equilibrium, and that at time $t = 0$, it is perturbed by an additional, time-dependent, contribution to its potential energy, in the form $\delta V = -h(t)A(\mathbf{r}(t))$. The quantity A is a physical observable. We would like to know how an observable $B(\mathbf{r}(t))$ reacts to the perturbation, so that we introduce the response function

$$R(t', t) = \frac{\delta\langle B(t')\rangle}{\delta h(t)} \tag{3.61}$$

We use the Janssen-De Dominicis action with $\alpha = 1/2$, and we see that

$$R(t', t) = \langle B(\mathbf{r}(t'))[\tilde{\mathbf{r}}\cdot\boldsymbol{\nabla} A](t)\rangle \tag{3.62}$$

The action being invariant, up to a boundary term, with respect to the change of fields

$$t \to t_{\mathrm{obs}} - t,\ \mathbf{r}^{\mathrm{R}}[t] = \mathbf{r}[t_{\mathrm{obs}} - t], \tilde{\mathbf{r}}^{\mathrm{R}}[t] = -\tilde{\mathbf{r}}[t_{\mathrm{obs}} - t] + \beta\boldsymbol{\nabla} V(\mathbf{r}(t_{\mathrm{obs}} - t)) \tag{3.63}$$

we write that

$$\begin{aligned} R(t_{\mathrm{obs}} - t', t_{\mathrm{obs}} - t) =& \langle B(\mathbf{r}(t'))[(-\tilde{\mathbf{r}} + \beta\partial_{\mathbf{r}} V)\cdot\boldsymbol{\nabla} A](t)\rangle \\ =& R(t', t) + \langle B(\mathbf{r}(t'))[\beta\boldsymbol{\nabla} V\cdot\partial_{\mathbf{r}} A](t)\rangle \end{aligned} \tag{3.64}$$

We use that, when inserted into a correlation function, the Euler-Lagrange equation

$$\frac{\delta S}{\delta\tilde{\mathbf{r}}(t)} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} + \beta\partial_{\mathbf{r}} V - 2\tilde{\mathbf{r}} = 0 \tag{3.65}$$

remains identically zero. This implies, after multiplying Eq. (3.65) by $B(\mathbf{r}(t'))\boldsymbol{\nabla} A(\mathbf{r}(t))$, that

$$\langle B(t')\frac{\mathrm{d}A(t)}{\mathrm{d}t}\rangle + \langle B(t')\beta\boldsymbol{\nabla} V(t)\rangle - 2\langle B(t')\tilde{\mathbf{r}}(t)\rangle = 0 \tag{3.66}$$

and hence

$$R(t_{\rm obs}-t',t_{\rm obs}-t)=R(t',t)-\beta\frac{\mathrm{d}}{\mathrm{d}t}\langle B(\mathbf{r}(t'))A(\mathbf{r}(t))\rangle \tag{3.67}$$

In equilibrium, when time translation invariance is recovered, and by setting $\tau=t'-t$, we thus find that

$$-\beta\partial_\tau\langle A(0)B(\tau)\rangle=R(\tau)-R(-\tau) \tag{3.68}$$

Note that the discrete and nonlinear symmetry of Eq. (3.63) can already be observed at the level of a Langevin equation $\dot{\mathbf{r}}=-\partial_{\mathbf{r}}V+\sqrt{2T}\boldsymbol{\eta}$, where $\mathbf{r}^{\rm R}$ is seen to evolve with the same equation as $\mathbf{r}$ under the noise $\boldsymbol{\eta}^{\rm R}=-\boldsymbol{\eta}+\sqrt{\frac{2}{T}}\partial_{\mathbf{r}}V$.

3.2.4 Connection of time-reversal to supersymmetry

We begin with a one-dimensional process $x(t)$ whose dynamics is governed by the following Langevin equation

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\beta F(x)+\eta \tag{3.69}$$

where $F(x)=-V'(x)$ and $\langle\eta(t)\eta(t')\rangle=2\delta(t-t')$. The Janssen-De Dominicis dynamic partition function for this process is obtained by setting α to 0 in the α-discretized path integral obtained by Janssen:

$$Z_\alpha=\int\mathscr{D}\bar{x}\mathscr{D}x\mathrm{e}^{-\int\mathrm{d}t\left(\bar{x}\frac{\mathrm{d}x}{\mathrm{d}t}-\left(\bar{x}-\alpha\frac{\mathrm{d}}{\mathrm{d}x}\right)\beta F(x)-\left(\bar{x}-\alpha\frac{\mathrm{d}}{\mathrm{d}x}\right)^2\right)} \tag{3.70}$$

The parameter α fine-tunes the time at which coupling of $\bar{x}$ to the Langevin equation for $x(t)$ is performed (which is coded in the value of $\Theta(0)=\alpha$). In the sequel, we shall adopt the Stratonovitch convention for which $\alpha=1/2$, by analogy to what is usually done when dealing the multplicative noise in a Langevin equation. One way to represent the additional interaction terms due to $\alpha=1/2$ rather than $\alpha=0$ is by means of a path integral over a pair of fermion field $\bar{c}$, c,

$$Z_{1/2}=\int\mathscr{D}\bar{x}\mathscr{D}x\mathscr{D}\bar{c}\mathscr{D}c\mathrm{e}^{-\int\mathrm{d}t\left(\bar{x}\frac{\mathrm{d}x}{\mathrm{d}t}-\bar{x}\beta F(x))-\bar{x}^2+\bar{c}\frac{\mathrm{d}c}{\mathrm{d}t}-\bar{c}\beta\frac{\mathrm{d}F}{\mathrm{d}x}c\right)} \tag{3.71}$$

It is convenient to introduce a pair of conjugate Grassmann variables $\bar{\theta}$ and θ and to construct a superfield $\phi(z)$, with $z=(t,\bar{\theta},\theta)$):

$$\phi(z)=x+\bar{\theta}c+\bar{c}\theta+\theta\bar{\theta}\bar{x} \tag{3.72}$$

In the following, we shall use the notation $\mathrm{d}z=\mathrm{d}t\mathrm{d}\bar{\theta}\mathrm{d}\theta$. It is not hard to see that

$$Z_{1/2}=\int\mathscr{D}\phi\mathrm{e}^{-S[\phi]} \tag{3.73}$$

where the action reads

$$S[\phi]=\int\mathrm{d}z\left[\frac{1}{2}\phi D^{(2)}\phi+\beta V(\phi)\right] \tag{3.74}$$

and the operator $D^{(2)}$ has the expression

$$D^{(2)}=-2\frac{\partial^2}{\partial\bar{\theta}\partial\theta}-2\theta\frac{\partial^2}{\partial\theta\partial t}+\frac{\partial}{\partial t} \tag{3.75}$$

The superscript (2) will now be omitted, $D^{(2)} = D$. This is the supersymmetric formulation of the stochastic dynamics. Let's find out where the terminology comes from.

We define the following infinitesimal transformation from z to $z' = z + \delta z$,

$$\delta t = \varepsilon\bar{\theta},\ \delta\bar{\theta} = -\bar{\varepsilon},\ \delta\theta = -\varepsilon \tag{3.76}$$

where ε and $\bar{\varepsilon}$ are infinitesimal Grassmann variables. The primed field ϕ' is defined by $\phi'(z) = \phi(z')$, which leads to $\phi'(z) = \phi(z) + \delta\phi(z)$

$$\delta x = \varepsilon\bar{c} - \bar{\varepsilon}c,\ \ \delta\bar{x} = \varepsilon\dot{\bar{c}},\ \ \delta\bar{c} = \bar{\varepsilon}\bar{x},\ \ \delta c = \varepsilon(\bar{x} - \dot{x}) \tag{3.77}$$

It is not hard to verify that $D' = D$, which requires using that $\frac{\partial}{\partial\bar{\theta}} = \frac{\partial}{\partial\bar{\theta}'} - \varepsilon\frac{\partial}{\partial t'}$; the partial derivatives with respect to θ and t remain invariant by going to their primed counterparts.

A convenient way to exploit this property is to introduce a source field $J = h + \bar{\theta}j + \bar{j}\theta + \theta\bar{\theta}\bar{h}$ such that

$$\int \mathrm{d}z J\phi = \int \mathrm{d}t\left[\bar{h}x + \bar{x}h + \bar{j}c + \bar{c}j\right] \tag{3.78}$$

and hence, given that $S[\phi'] = S[\phi]$, we must have that

$$\langle \int \delta\phi J\rangle = 0 \tag{3.79}$$

where the brackets denote an average with respect to the source dependent partition function $Z[J]$ defined by

$$Z[J] = \int \mathscr{D}\phi \mathrm{e}^{-S[\phi] + \int J\phi} \tag{3.80}$$

We have that

$$J\delta\phi = \varepsilon\left[\bar{h}\bar{c} + h\dot{\bar{c}} + \bar{j}(\dot{x} - \bar{x})\right] + \bar{\varepsilon}\left[-\bar{h}c + \bar{x}j\right] = 0 \tag{3.81}$$

and identifying to 0 the prefactor of ε in $\langle J\delta\phi\rangle$ leads to

$$\int \langle \bar{h}\bar{c} + h\dot{\bar{c}} + \bar{j}(\dot{x} - \bar{x})\rangle = 0 \tag{3.82}$$

or, alternatively

$$\int \left[-\bar{h}\frac{\delta Z}{\delta j} - h\frac{\mathrm{d}}{\mathrm{d}t}\frac{\delta Z}{\delta j} + \bar{j}\left(\frac{\mathrm{d}}{\mathrm{d}t}\frac{\delta Z}{\delta\bar{h}} - \frac{\delta Z}{\delta h}\right)\right] = 0 \tag{3.83}$$

and doing the same with $\bar{\varepsilon}$ one obtains

$$\int \left[-\bar{h}c + \bar{x}j\right] = 0 \tag{3.84}$$

which we also rewrite in the form

$$\int \left[-\bar{h}\frac{\delta Z}{\delta\bar{j}} + j\frac{\delta Z}{\delta h}\right] = 0 \tag{3.85}$$

If one applies $\frac{\delta^2}{\delta\bar{h}(t')\delta\bar{j}(t)}$ to (3.83) one arrives at

$$\langle c(t)\bar{c}(t')\rangle + \frac{\mathrm{d}}{\mathrm{d}t}\langle x(t)x(t')\rangle - \langle x(t')\bar{x}(t)\rangle = 0 \tag{3.86}$$

Similarly we apply $\frac{\delta^2}{\delta\bar{h}(t)\delta j(t')}$ to (3.85) one obtains

$$-\langle c(t)\bar{c}(t')\rangle + \langle x(t)\bar{x}(t')\rangle = 0 \tag{3.87}$$

We now add (3.86) and (3.87)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x(t')x(t)\rangle = \langle x(t')\bar{x}(t)\rangle - \langle x(t)\bar{x}(t')\rangle \tag{3.88}$$

This is the fluctuation-dissipation theorem.

3.3 Fluctuations theorems

3.3.1 Gallavotti-Cohen theorem

Our presentations rests on [123] but the original ideas are from [63, 82]. By now we have a pretty clear idea of what the entropy production stands for physically. In a Langevin process where the force exerted by the thermostat $-\dot{\mathbf{x}} + \sqrt{2T}\boldsymbol{\eta}$ balances out the other forces $-\partial_{\mathbf{x}} V + \mathbf{f}$ (where $\mathbf{f}$ is non-conservative), we know that the entropy production is the work of the non-conservative force on the particle (up to $1/T$). It turns out that Q_S has interesting symmetry properties. First, for a process described by a master equation, we recall that

$$Q_S(t_{\rm obs}) = \sum_{j=0}^{K-1} \ln \frac{W(\mathscr{C}_j \to \mathscr{C}_{j+1})}{W(\mathscr{C}_{j+1} \to \mathscr{C}_j)} \tag{3.89}$$

where $\mathscr{C}_0, \ldots, \mathscr{C}_k$ is the sequence of configurations visited over some time interval $[0, t_{\rm obs}]$. The quantity Q_S is obviously time extensive (because it involves K terms and $\langle K\rangle = t t_{\rm obs}\langle r(\mathscr{C})\rangle$ is time extensive), so that we expect that its probability distribution to decay exponentially with time (this will be proved later). This suggests that the correct quantity to explore, just as in thermodynamics, is the so-called large deviation function of Q_S:

$$\pi(q) = \lim_{t\to+\infty} \frac{1}{t} \ln P(Q_S, t),\ q = Q_S/t \tag{3.90}$$

which focuses on the intensive counterpart of Q_S. Our goal is to derive a property of $\pi(q)$.

To do so, we write a master equation for the probability $P(\mathscr{C}, Q_S, t)$ to observe configuration $\mathscr{C}$ at time t and that the system has accumulated Q_S up until that time. It reads

$$\partial_t P(\mathscr{C}, Q_S, t) = \sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C}) P(\mathscr{C}', Q_S - \ln \frac{W(\mathscr{C}' \to \mathscr{C})}{W(\mathscr{C} \to \mathscr{C}')}, t) - r(\mathscr{C}) P(\mathscr{C}, Q_S, t) \tag{3.91}$$

If one applies $\frac{\delta^2}{\delta\bar{h}(t')\delta\bar{j}(t)}$ to (3.83) one arrives at

$$\langle c(t)\bar{c}(t')\rangle + \frac{\mathrm{d}}{\mathrm{d}t}\langle x(t)x(t')\rangle - \langle x(t')\bar{x}(t)\rangle = 0 \tag{3.86}$$

Similarly we apply $\frac{\delta^2}{\delta\bar{h}(t)\delta j(t')}$ to (3.85) one obtains

$$-\langle c(t)\bar{c}(t')\rangle + \langle x(t)\bar{x}(t')\rangle = 0 \tag{3.87}$$

We now add (3.86) and (3.87)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x(t')x(t)\rangle = \langle x(t')\bar{x}(t)\rangle - \langle x(t)\bar{x}(t')\rangle \tag{3.88}$$

This is the fluctuation-dissipation theorem.

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To do so, we write a master equation for the probability $P(\mathscr{C}, Q_S, t)$ to observe configuration $\mathscr{C}$ at time t and that the system has accumulated Q_S up until that time. It reads

$$\partial_t P(\mathscr{C}, Q_S, t) = \sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C}) P(\mathscr{C}', Q_S - \ln \frac{W(\mathscr{C}' \to \mathscr{C})}{W(\mathscr{C} \to \mathscr{C}')}, t) - r(\mathscr{C}) P(\mathscr{C}, Q_S, t) \tag{3.91}$$

The trick is to go to the generating function $\hat{P}(\mathscr{C}, s, t) = \sum_{Q_S} \mathrm{e}^{-sQ_S} P(\mathscr{C}, Q_S, t)$ and to find that $\hat{P}$ evolves according to

$$\partial_t \hat{P}(\mathscr{C}, s, t) = \sum_{\mathscr{C}'} W(\mathscr{C}' \to \mathscr{C})^{1-s} W(\mathscr{C} \to \mathscr{C}')^s \hat{P}(\mathscr{C}', s, t) - r(\mathscr{C}) \hat{P}(\mathscr{C}, s, t) \tag{3.92}$$

and we see that $\hat{P}$ is evolved through an operator $\mathbb{W}(s)$ with elements

$$[\mathbb{W}(s)]_{\mathscr{C},\mathscr{C}'} = W(\mathscr{C}' \to \mathscr{C})^{1-s} W(\mathscr{C} \to \mathscr{C}')^s - r(\mathscr{C}) \delta_{\mathscr{C},\mathscr{C}'} \tag{3.93}$$

and it is now visible that $(\mathbb{W}(s))^T = \mathbb{W}(1-s)$. The largest eigenvalue $\psi(s)$ of $\mathbb{W}(s)$ then also verifies $\psi(s) = \psi(1-s)$. This allows us to write that at large times

$$\hat{P}(\mathscr{C}, s, t) = \sum_{\mathscr{C}'} \left[\mathrm{e}^{\mathbb{W}(s)t}\right]_{\mathscr{C},\mathscr{C}'} \hat{P}(\mathscr{C}', s, 0) \simeq \mathrm{e}^{\psi(s)t} \tilde{P}(\mathscr{C}, s) \tag{3.94}$$

where $\tilde{P}(\mathscr{C}, s)$ is related to the projection of the eigenvector related to ψ onto the initial state. We arrive at the large time behavior of $P(Q_S, t)$ by writing that

$$P(Q_S, t) = \int \frac{\mathrm{d}s}{2\pi i} \mathrm{e}^{sQ_S} \sum_{\mathscr{C}} \hat{P}(\mathscr{C}, s, t) \propto \int \frac{\mathrm{d}s}{2\pi i} \mathrm{e}^{sQ_S} \mathrm{e}^{t\psi(s)} \tag{3.95}$$

and this directly tells us that $\pi(q) = \max_s\{sq + \psi(s)\}$. But since $\psi(s) = \psi(1-s)$ we find the Gallavotti-Cohen theorem:

$$\pi(q) - \pi(-q) = q \tag{3.96}$$

The quantity $\psi(s)$ has a meaning of its own. This is the generating function of the cumulants of Q_S,

$$\psi(s) = \lim_{t+\infty} \frac{\ln\langle \mathrm{e}^{-sQ_S}\rangle}{t}, \quad \frac{\langle Q_S^k\rangle_c}{t} \simeq (-1)^k \left.\frac{\mathrm{d}^k \psi}{\mathrm{d}s^k}\right|_{s=0} \tag{3.97}$$

The Gallavotti-Cohen theorem is, in terms of our theoretical understanding of the second law, an extremely valuable result. It tells us that the possibility of observing rare fluctuations that go against the second law of thermodynamics decays exponentially fast in the observation time (regardless of the size of the system). And if for some reason Q_S is also extensive in the system size, the probability becomes exponentially small in the system size as well.

As we could see in the example of subsection where particles are hopping right or left under the action of an external field E that biases their diffusion, when the external drive couples to a conserved quantity,

$$J_S = E \times J \tag{3.98}$$

where J was the particle current. It may then be more physical to focus on the large deviation of the total particle current Q, whose probability $P(Q, t)$ inherits the symmetry property of π. And similarly, the cumulant generating function $\phi(\lambda, E) = \lim_{t\to+\infty} \frac{\langle \mathrm{e}^{-\lambda Q}\rangle}{t}$ inherits the symmetry property of ψ, namely $\phi(\lambda, E) = \phi(E - \lambda, E)$.

It is in fact a very generic situation that when some driving force is applied the quantity Q_S can be written as

$$Q_S = \sum_A E_A Q_A \tag{3.99}$$

where E_A is the external field leading to a flow $J_A = \langle \dot{Q}_A \rangle$ of the quantity A (A can be the number of particles, and then J_A is the particle current, but it can also be the energy or the momentum, and then the corresponding currents are the heat flux or the stress tensor). And in that case, the Gallavotti-Cohen theorem extends to the generating function of the set of currents. The generating function defined by

$$\phi(\{\lambda_A, E_A\}) = \lim_{t\to+\infty} \frac{\ln\langle \mathrm{e}^{-\sum_A \lambda_A Q_A}\rangle}{t} \tag{3.100}$$

verifies

$$\phi(\{\lambda_A, E_A\}) = \phi(\{E_A - \lambda_A, E_A\}) \tag{3.101}$$

We'll now draw consequences of this mathematical symmetry, which were derived much earlier than the Gallavotti-Cohen theorem by other methods.

3.3.2 More consequences for equilibrium dynamics: Green-Kubo relations and Onsager reciprocal relations

It is instructive to derive classical results of the so-called linear response theory as simple consequences of the Gallavotti-Cohen theorem. To do this we borrow from [11, 88].

Affinities and fluxes

We now consider a generic system in a nonequilibrium steady-state that can be described by a set of fluxes Q_A ($J_A = \langle \dot{Q}_A \rangle$) and conjugate forces or affinities E_A. Here the index A refers to a locally conserved quantity. What we have in mind for the J_A's are the particle, energy, momentum, magnetic, electric, *etc.* fluxes, while the conjugate affinities E_A are the chemical potential difference (divided by $k_{\mathrm{B}}T$), the thermal gradient, the shear rate, the magnetic or electric field, *etc.*. With these notations, we may write that

$$Q_S = \sum_A E_A Q_A, \;\; J_S = \sum_A E_A J_A \tag{3.102}$$

and we now that the generating function defined by

$$\phi(\{\lambda_A, E_A\}) = \lim_{t\to+\infty} \frac{\ln\langle \mathrm{e}^{-\sum_A \lambda_A Q_A}\rangle}{t} \tag{3.103}$$

verifies

$$\phi(\{\lambda_A, E_A\}) = \phi(\{E_A - \lambda_A, E_A\}) \tag{3.104}$$

For instance, with this definition, we have $J_A = \frac{\langle Q_A\rangle}{t} = -\left.\frac{\partial\phi}{\partial\lambda_A}\right|_{\lambda=0}$. And the integrated currents Q_A have correlations $\langle Q_A Q_B\rangle_c/t = \left.\frac{\partial^2\phi}{\partial\lambda_A\partial\lambda_B}\right|_{\lambda=0}$.

Onsager reciprocal relations

Assume now that for small imposed forces, we carry out a series expansion of the average fluxes in powers of the affinities:

$$J_A = \sum_B L_{AB} E_B + \sum_{B,C} M_{ABC} E_B E_C + \dots \tag{3.105}$$

The L_{AB} are Onsager's linear response coefficients. These thus appear as

$$L_{AB} = \left.\frac{\partial J_A}{\partial E_B}\right|_{E=0} = -\left.\frac{\partial^2 \phi}{\partial E_B \partial \lambda_A}\right|_{\ell=0,E=0} \tag{3.106}$$

We now differentiate (3.104) with respect to λ_A and E_B:

$$\left.\frac{\partial^2 \phi}{\partial E_B \partial \ell_A}\right|_{\ell=0,E=0} = -\left.\frac{\partial^2 \phi}{\partial \ell_A \partial \ell_B}\right|_{\ell=0,E=0} - \left.\frac{\partial^2 \phi}{\partial \ell_A \partial E_B}\right|_{\ell=0,E=0} \tag{3.107}$$

and we see what remains after setting $E = 0$ and $\lambda = 0$:

$$2\left.\frac{\partial^2 \phi}{\partial \lambda_A \partial E_B}\right|_{\lambda=0,E=0} = -\left.\frac{\partial^2 \phi}{\partial \lambda_A \partial \lambda_B}\right|_{\lambda=0,E=0} = -2L_{AB} \tag{3.108}$$

Hence the equality

$$L_{AB} = \frac{1}{2}\left.\frac{\partial^2 \phi}{\partial \lambda_A \partial \lambda_B}\right|_{\lambda=0,E=0} \tag{3.109}$$

ensures that $L_{AB} = L_{BA}$. This is Onsager's reciprocal relation. If we spell out that relationship in terms of the local currents, we arrive at

$$L_{AB} = \frac{1}{2t}\langle Q_A Q_B \rangle = \frac{1}{2}\int \mathrm{d}\tau \langle j_A(\tau) j_B(0) \rangle \tag{3.110}$$

which appears under the name of Yamamoto-Zwanzig relation (the notation j_A refers to a space integrated current).

Green-Kubo relations

Specializing the above to $A = B$ leads to

$$L_{AA} = \frac{1}{2}\left.\frac{\partial^2 \phi}{\partial \lambda_A \partial \lambda_B}\right|_{\lambda=0,E=0} = \frac{1}{2}\frac{\langle Q_A^2 \rangle}{t} = \frac{1}{2}\int \mathrm{d}\tau \langle j_A(0) j_A(\tau) \rangle \tag{3.111}$$

This is the Green-Kubo relation.

M2 ICFP 2024-2025

Advanced Statistical Mechanics

Theoretical Physics track F. van Wijland

Chapter 4

Metastability and rare events

The notion of metastability, while ubiquitous, is rather fuzzy in the existing literaure, due to the variety of field-dependent definitions. The definition of a metastable state that we shall use here is the following. This is an excited state of the dynamics whose relaxation rate is very close to 0, which corresponds to a very long life-time. This definition applies in or out of equilibrium, but what we shall cover below deals mostly with equilibrium dynamics.

4.1 Thermally activated events

4.1.1 Motivations

We follow [39] for the this short introduction. In a host of many-body systems, such a simple fluids, proteins, polymers, *etc.*, rare but important, thermally activated events, actually control the dynamics, while being responsible for very slow relaxational processes. An activated event is one in which a potential barrier is crossed over by means of a rare, atypical, realization of the thermal noise felt by the system. One immediately realizes that this sentence is problematic in itself, as it makes unequivocal sense in one space dimension only. Else, in higher dimension, what could a potential barrier stand for: an isolated bump, a ridge separating two gutters (just to mention three-dimensional situations). Hence, beyond the content of this chapter, the real physical difficulty often is to find the proper one-dimensional variable (that surely depends on many degrees of freedom) in terms of discussing the dynamics by means of a one-dimensional landscape makes some sense. Such a one-dimensional combination of the degrees of freedom is termed a reaction coordinate. It's a central concept in physics and chemical physics (see [157, 196] for two very recent discussions). There is a least one family of examples in which the reaction coordinate is intuitively easy to guess: take an Ising model below its critical temperature, an energy barrier separates the up phase from the down phase, and the global magnetization plays the role of a collective coordinate. Once the one-dimensional coordinate is found, how to estimate the time-scale it takes the system to cross over the potential barrier is yet another problem. This is the one we focus on in this chapter. In practice, as Chandler [39] puts it, *"Rare events" are dynamical processes that occur so infrequently it is impractical to obtain quantitative information about them through straightforward trajectory calculations* (here Chandler refers to the numerical integration, or sampling, of the microscopic equations of mo-

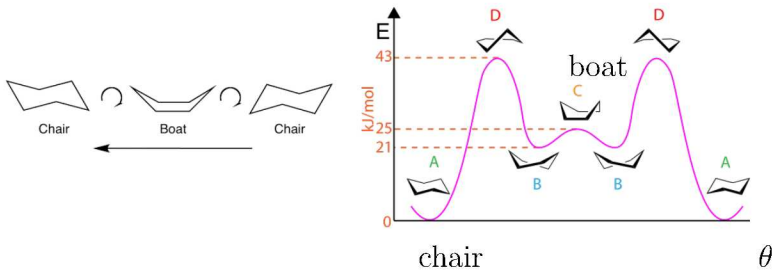

Figure 4.1: It takes 10^{-11} s for a molecule to diffuse over a length of the order of its own diameter, and the motion is persistent over 10^{-12} s (that's the momentum decorrelation time). The isomerization time, by contrast, is 10^{-1} s. We refer to [201] for an explicit construction of the collective coordinate θ.

tion).

A simple molecular example is that of cyclohexane isomerization, between the boat (metastable) and the chair (stable) configurations: Given the orders of magnitude in Fig. 4.1, there is no question that the isomerization is a rare event. In the limit where the energy (or free-energy) barrier is much larger than $k_{\mathrm{B}}T$, progress can be made to estimate the barrier-crossing time.

4.1.2 First-passage time based approach

Our starting point is an overdamped Langevin equation for some d-dimensional degree of freedom $\mathbf{r}(t)$ evolving in some external potential $V(\mathbf{r})$:

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = -\boldsymbol{\nabla} V(\mathbf{r}) + \sqrt{2T}\boldsymbol{\eta} \tag{4.1}$$

where the mobility has been set to unity. We assume the potential landscape displays two wells located at $\mathbf{x}_1$ (where the particle starts from with zero velocity) and at $\mathbf{x}_2$ separated by a saddle at $\mathbf{x}_\star$ (in a well, the Hessian of the potential is positive definite). In the following, the Hessian at the saddle has one negative eigenvalue $\lambda_\star < 0$ and $d-1$ positive ones. The energy barrier is $\Delta V = V(\mathbf{x}_\star) - V(\mathbf{x}_1)$. In the $\beta\Delta V \gg 1$ regime, we will show that it takes a time

$$\tau_{\mathrm{Kramers}} \simeq \frac{2\pi}{-\lambda_\star}\sqrt{\frac{|\det \mathrm{Hess}\, V(\mathbf{x}_\star)|}{\det \mathrm{Hess}\, V(\mathbf{x}_1)}}\mathrm{e}^{\beta\Delta V} \tag{4.2}$$

This is known as the Eyring-Kramers formula [65, 118]. Before we look at the mathematics behind this formula, a simple explanation for its leading behavior is in order. The particle has

a probability $P(\mathbf{x}_1) \sim \mathrm{e}^{-\beta V(\mathbf{x}_1)}$ to be sitting at $\mathbf{x}_1$ and a hopping rate $\tau^{-1}_{\text{Kramers}}$. At the top of the hill (in $d = 1$) it has a probability $P(\mathbf{x}_\star) \sim \mathrm{e}^{-\beta V(\mathbf{x}_\star)}$ to be found and a constant undressed mobility, so that the detailed balance condition forces

$$\tau^{-1}_{\text{Kramers}} P(\mathbf{x}_1) \simeq P(\mathbf{x}_\star) \tag{4.3}$$

which is indeed giving us the leading behavior in $\beta \Delta V \gg 1$ of Eq. (4.2). This leading behavior is actually valid not only for a broad range of equilibrium dynamics (such as the underdamped Langevin one) but also, to some extent, in specific out of equilibrium settings [28].

Let's now have a look at the proof. Our interest goes to the mean first passage time $\tau(\mathbf{y}, \mathbf{x})$ to location $\mathbf{y}$ starting from location $\mathbf{x}$. This average time is the solution of the following PDE:

$$-\boldsymbol{\nabla} V(\mathbf{x}_1) \cdot \partial_{\mathbf{x}_1} \tau + T \partial^2_{\mathbf{x}_1} \tau = -1, \ \tau(\mathbf{x}_1, \mathbf{x}_1) = 0 \tag{4.4}$$

This equation is equivalent to

$$\partial_{\mathbf{x}} \cdot \left[\mathrm{e}^{-\beta V(\mathbf{x})} \partial_{\mathbf{x}} \tau \right] = -\frac{1}{T} \mathrm{e}^{-\beta V}, \ \tau(\mathbf{x}, \mathbf{x}) = 0 \tag{4.5}$$

It is instructive to begin with the one-dimensional case with $x_1 < x_\star < x_2$. Then we readily see that

$$\partial_x \tau = \frac{1}{T} \mathrm{e}^{\beta V(x)} \left(\int_x^{x_1} \mathrm{d}x' \mathrm{e}^{-\beta V(x')} + a \right) \tag{4.6}$$

where the integration constant a vanishes because we impose $\partial_x \tau(y, x)|_{x=x_1} = 0$. Hence we must have that

$$\tau(x_\star, x_1) = \frac{1}{T} \int_{x_\star}^{x_1} \mathrm{d}x'' \mathrm{e}^{\beta V(x'')} \int_{x''}^{x_1} \mathrm{d}x \mathrm{e}^{-\beta V(x)} = \frac{1}{T} \int_{x_1}^{x_\star} \mathrm{d}x'' \mathrm{e}^{\beta V(x'')} \int_{x_1}^{x''} \mathrm{d}x \mathrm{e}^{-\beta V(x)} \tag{4.7}$$

Using that in the low temperature regime one has

$$\int_{x_1}^{x''} \mathrm{d}x \mathrm{e}^{-\beta V(x)} \simeq \mathrm{e}^{-\beta V(x_1)} \sqrt{\frac{2\pi T}{V''(x_1)}} \tag{4.8}$$

along with

$$\int_{x_1}^{x_\star} \mathrm{d}x'' \mathrm{e}^{\beta V(x'')} \simeq \mathrm{e}^{\beta V(x_\star)} \sqrt{\frac{2\pi T}{-V''(x_\star)}} \tag{4.9}$$

we eventually arrive at

$$\tau(x_\star, x_1) \simeq \frac{1}{T} \sqrt{\frac{2\pi T}{-V''(x_\star)}} \mathrm{e}^{-\beta V(x_1)} \sqrt{\frac{2\pi T}{V''(x_1)}} \simeq \frac{2\pi}{\sqrt{-V''(x_\star) V''(x_1)}} \mathrm{e}^{\beta \Delta V} = \frac{2\pi}{-V''(x_\star)} \sqrt{\frac{|V''(x_\star)|}{V''(x_1)}} \mathrm{e}^{\beta \Delta V} \tag{4.10}$$

which is the one-dimensional version of Eq. (4.2). This result is also known as the Arrhenius law. In space dimension higher than one, the reasoning is almost unchanged, up to the fact that fluctuations in the direction transverse to the line of steepest descent will affect the prefactor.

With the conditions on V that we have imposed, the line of steepest decsent exists and it is unique. Starting again from

$$\partial_{\mathbf{x}_1} \cdot \left[\mathrm{e}^{-\beta V(\mathbf{x}_1)} \partial_{\mathbf{x}_1} \tau \right] = -\frac{1}{T} \mathrm{e}^{-\beta V} \tag{4.11}$$

we integrate over a volume $\mathcal{D}$ such that $\mathbf{x}_1 \in \mathcal{D}$ and whose boundary includes $\mathbf{x}_\star \in \partial\mathcal{D}$:

$$\int_{\partial\mathcal{D}} \left[\mathrm{e}^{-\beta V(\mathbf{y})} \partial_{\mathbf{y}} \tau \right] \cdot \mathrm{d}^{d-1}\mathbf{S}_{\mathbf{y}} = -\frac{1}{T} \int_{\mathcal{D}} \mathrm{e}^{-\beta V(\mathbf{y})} \mathrm{d}^d y \tag{4.12}$$

So far the domain $\mathcal{D}$ is arbitrary. We choose it to be a small tube joining $\mathbf{x}_1$ to $\mathbf{x}_\star$ along the direction of steepest ascent (that is, arriving at $\mathbf{x}_\star$ along the nondegenerate eigenvector $\mathbf{n}$ of $\mathrm{Hess}\, V(\mathbf{x}_\star)$ with the negative eigenvalue $\lambda_\star$). The integral over $\mathcal{D}$ simplifies into

$$\int_{\mathcal{D}} \mathrm{e}^{-\beta V(\mathbf{y})} \mathrm{d}^d y \simeq \frac{(2\pi T)^{d/2}}{\sqrt{\mathrm{Hess}\, V(\mathbf{x}_1)}} \mathrm{e}^{-\beta V(\mathbf{x}_1)} \tag{4.13}$$

The surface integral is trickier to evaluate. The vicinity of the saddle will dominate the integral, so that we can write

$$V(\mathbf{y}) = -\frac{\lambda_\star}{2}(y - x_\star)^2 + \frac{1}{2}(\mathbf{y} - \mathbf{x}_\star)_\perp . \cdot \mathrm{Hess}_\perp V(\mathbf{x}_\star)(\mathbf{y} - \mathbf{x}_\star)_\perp \tag{4.14}$$

where $(\mathbf{y} - \mathbf{x}_\star)_\perp = \mathbf{y} - \mathbf{x}_\star - [(\mathbf{y} - \mathbf{x}_\star) \cdot \mathbf{n}]\mathbf{n}$ and $y - x_\star = (\mathbf{y} - \mathbf{x}_\star) \cdot \mathbf{n}$. This brings us back to the one-dimensional problem,

$$\int_{\partial\mathcal{D}} \left[\mathrm{e}^{-\beta V(\mathbf{y})} \partial_{\mathbf{y}} \tau \right] \cdot \mathrm{d}^{d-1}\mathbf{S}_{\mathbf{y}} \simeq \frac{(2\pi T)^{(d-1)/2}}{\sqrt{\det \mathrm{Hess}_\perp V}} \partial_y \tau \mathrm{e}^{\beta \frac{\lambda_\star}{2}(y - x_\star)^2} \tag{4.15}$$

so that

$$\partial_y \tau = -\frac{1}{T} \mathrm{e}^{-\beta \frac{\lambda_\star}{2}(y - x_\star)^2} \frac{\sqrt{\det \mathrm{Hess}_\perp V}}{(2\pi T)^{(d-1)/2}} \frac{(2\pi T)^{d/2}}{\sqrt{\mathrm{Hess}\, V(\mathbf{x}_1)}} \mathrm{e}^{-\beta V(\mathbf{x}_1)} \tag{4.16}$$

and one more integration leads to

$$\tau(\mathbf{x}_\star, \mathbf{x}_1) = \frac{1}{T} \frac{\sqrt{2\pi}}{\sqrt{-\lambda_\star}} \frac{\sqrt{\det \mathrm{Hess}_\perp V}}{(2\pi T)^{(d-1)/2}} \frac{(2\pi T)^{d/2}}{\sqrt{\mathrm{Hess}\, V(\mathbf{x}_1)}} \mathrm{e}^{-\beta V(\mathbf{x}_1)} \tag{4.17}$$

Finally, using that $\det \mathrm{Hess}_\perp V = \lambda_\star \det \mathrm{Hess}\, V(\mathbf{x}_\star)$ we arrive at the desired result Eq. (4.2).

There are several limitations to this method:

- for equilibrium dynamics, it fails to work in the presence of memory kernels;
- it fails to work for out-of-equilibrium dynamics, quite notably when non-Gaussian statistics are involved [21].

This suggests that alternative approaches may, in some cases, prove more convenient.

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4.1.3 Fokker-Planck based approach

The overall wording is a bit different from that of the previous section, but the mathematics are identical. In the Fokker-Planck based approach, the idea is the following. Consider again a one-dimensional potential landscape and assume that j particles per time unit are injected at x_1 while they are absorbed at x_2. In the one-dimensional setting, j is also the particle current,

$$j = -T\partial_x P_{\rm ss} - V' P_{\rm ss} \tag{4.19}$$

where $P_{\rm ss}$ is the steady-state distribution harboring a particle flow. This equation, at fixed j, can be solved:

$$P_{\rm ss}(x) = C\mathrm{e}^{-\beta V(x)} - \frac{j}{T}\int_{x_2}^{x} \mathrm{d}y \mathrm{e}^{-\beta(V(x)-V(y))}\mathrm{d}y \tag{4.20}$$

and C vanishes because of the absorbing boundary at x_2 such that $P_{\rm ss}(x_2) = 0$. The time of interest is given by

$$\tau_K^{-1} = \frac{j}{\int_{x_1}^{x_2} \mathrm{d}y' P_{\rm ss}(y')} \tag{4.21}$$

and the expected behavior is recovered. This method can be adapted to higher dimensions.

4.1.4 Path-integral approach

The fraction of trajectories going uphill, and hence the typical time it takes to realize such a trajectory, is proportional to

$$\tau_K^{-1} = \int_{x(0)=x_m,\, x(t_{\rm obs})=x_M} \mathscr{D}x \mathrm{e}^{-S[x]} \tag{4.22}$$

where the Onsager-Machlup action is given by

$$S[x] = \int_0^{t_{\rm obs}} \mathrm{d}t \left[\frac{\dot{x}^2}{4T} + \frac{1}{2T}\dot{x}\, V' + \frac{1}{4T} V'^2 - \frac{1}{2} V''\right] \tag{4.23}$$

In the low temperature limit, the last term can be discarded, and we are left with

$$S[x] = \frac{1}{T}\int_0^{t_{\rm obs}} \mathrm{d}t \left[\frac{\dot{x}^2 + 2\dot{x}\, V' + V'^2}{4}\right] \tag{4.24}$$

The connection to the semi-classical WKB approach is now clear, up to $\frac{i}{\hbar} \leftrightarrow \frac{-1}{T}$. We are thus dealing with a quantum mechanical problem with Lagrangian $L = \frac{\dot{x}^2+2\dot{x}\,V'+V'^2}{4}$, that is with a Hamiltonian $\mathcal{H}(x,p) = p\dot{x} - L$ (with $p = \frac{\partial L}{\partial \dot{x}} = (\dot{x} + V')/2$). The Hamiltonian reads

$$\mathcal{H} = p^2 - pV' \tag{4.25}$$

Note that at the initial starting point we have $\mathcal{H} = 0$ (no initial velocity, $V'(x_1) = 0$, hence $p(0) = 0$), and since at the classical level this is a constant of motion, we must have $\mathcal{H} = 0$ throughout the classical trajectory connecting x_1 to $x_\star$. This means that the trajectory we are after verifies $p = V'$ and thus

$$\dot{x} = +V' \tag{4.26}$$

Note that this is the steepest ascent trajectory obtained by time-reversing the steepest descent one. The Lagrangian at the classical trajectory is $L = \dot{x}\,V'$ which means that $S[x] = \frac{1}{T}\Delta V$. This leads, again, to $\tau_K \sim \mathrm{e}^{\beta \Delta V}$.

We could have used the Janssen-De Dominicis action,

$$S[x] = \frac{1}{T}\int_0^{t_{\rm obs}} \mathrm{d}t \left[\bar{x}(\dot{x} + V') - \bar{x}^2\right] \tag{4.27}$$

where the Itō discretization has been used (the correction is $O(T)$ for a Stratonovich discretized action). The Euler-Lagrange equations read

$$\frac{\delta S}{\delta \bar{x}} = \dot{x} + V' - 2\bar{x} = 0, \; \frac{\delta S}{\delta x} = -\dot{\bar{x}} + \bar{x}\,V'' = 0 \tag{4.28}$$

These equations are strictly equivalent to

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial \bar{x}}, \; \dot{\bar{x}} = -\frac{\partial \mathcal{H}}{\partial x} \tag{4.29}$$

where $\mathcal{H}(x,\bar{x}) = \bar{x}^2 - \bar{x}\,V'$. These equations are solved by $\dot{x} = \bar{x} = V'$ and this takes us back to the Kramers formula.

Note, however, that obtaining the curvature-dependent prefactor by a path-integral method (which requires integrating out the Gaussian fluctuations around the classical trajectory) is a rather complicated task [34].

4.2 Stochastic resonance

4.2.1 The phenomenon: handwaving

In his 1981 paper [146], Nicolis suggests that solar variability (a source of noise) may have some influence on climate, and on glaciation cycles in particular. In these years, climate was viewed as a dynamical system with a phase diagram exhibiting the possibility of bifurcations between stable states. He also says that glaciation cycles fail to be easily explained, because transitions between states are not easily accounted for, or, when they are, too small time scales are involved. We will come back to a more precise connection to climate change (as suggested in [23]), but for now, we investigate the possible effect arising from coupling a noisy bistable system to a random source of noise. We build on the first theory [24] (an exhaustive review, including many more applications, can be found here [84]). Let's consider a particle in a double well potential in contact with a thermostat. Such a system is modeled by a Langevin equation of the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -V'(x) + \sqrt{2T}\eta(t),\ V(x) = -a\frac{x^2}{2} + \frac{x^4}{4} \tag{4.30}$$

where, for the case of interest to us, $a > 0$, so that in equilibrium the particle spends equal time in the two symmetric potential wells at $\pm\sqrt{a}$ (and the top of the barrier is located at $x = 0$). We shall denote by $\tau^{(\pm)}(y)$ the time it takes to first visit location $x = 0$ starting from $y > 0$ or $y < 0$. These times are random variables, and the moments $M_n^{(\pm)}(y) = \langle[\tau^{(\pm)}(y)]^n\rangle$ can be found from the adjoint Fokker-Planck equation:

$$T\partial_y^2 M^{(\pm)} - V'(y)\partial_y M^{(\pm)} = -nM_{n-1}^{(\pm)},\ n \geq 1 \tag{4.31}$$

with the boundary condition $M_n^{(\pm)}(0) = 0$ for $n \geq 1$. In the low temperature limit, as we have seen in 4.1.2,

$$M_1^{(\pm)}(y = 0) \simeq M_1^{(\pm)}(\pm\sqrt{a}) \simeq \frac{\pi}{a\sqrt{2}}\mathrm{e}^{\frac{a^2}{4T}} \tag{4.32}$$

and a similar analysis leads to

$$M_2^{(\pm)}(y = 0) \simeq 2M_1^{(\pm)}(\pm\sqrt{a})^2 \simeq \frac{\pi^2}{a^2}\mathrm{e}^{\frac{a^2}{2T}} \tag{4.33}$$

and that tells us that $\mathrm{var}(\tau^{(\pm)}(y)) \sim \langle\tau^{(\pm)}(y))\rangle^2$ so that no typical time scale emerges, and plotting the power spectrum of x, $\langle|x(\omega)|^2\rangle$ would show no structure (this is the Fourier transform of $\langle x(t)x(0)\rangle$.

We now subject the particle to an additional forcing $f = A\cos\Omega t$ with the force scale much smaller than $a^{3/2}$, which is the scale of the largest conservative force along the potential landscape. As a caricature, we split the equation of motion for x into two equations that express what is happening at $t = 0$ and at $t = \pi/\Omega$, when the amplitude of the force is $+A$ and $-A$, respectively. The effective equations then read $\dot{x} = ax - x^3 \pm A + \sqrt{2T}\eta$ and the two stable minimal now lie at $x_+ = \sqrt{a} + a^{3/2}A/2$ and $x_- = -\sqrt{a} + a^{3/2}A/2$, which are not symmetric

anymore. This leads to first passage times to the origin $\tau^{(\pm)}$ that are also different depending on the starting position,

$$M_1^{(\pm)}(0) \simeq \frac{\pi}{a\sqrt{2}} \mathrm{e}^{\frac{a^2-4A\sqrt{a}}{4T}} \tag{4.34}$$

after evaluating $V(x_\pm) - V(0)$ for $V(x) = ax^2/2 - x^4/4 - Ax$. This is useful for a qualitative understanding of the forced equation. Starting from $x = x_+ = \sqrt{a}$ at time $t = 0$ we see that as time passes the escape time increases as well to the point that it reaches its maximal value at $t = \pi/\Omega$. We expect that the time it takes to escape the basin lies in between the two extremes $M_1^{(\pm)}(0)$. And if $M_1^{(+)} \gtrsim \pi/\Omega$ and $M_1^{(-)} \ll \pi/\Omega$ then we expect that the escape time is of the order of π/Ω with a variance of the order $M_1^{(-)}$. Then this means that starting from x_+ the particle will jump to x_- at time π/Ω where it will send again a time of the order of π/Ω before jumping to x_+ at time $2\pi/\Omega$. The picture is that the particle jumps from one basin to the other at the same period as that of the forcing. But for this to happen, the $M_1^{(+)} \gtrsim \pi/\Omega$ and $M_1^{(-)} \ll \pi/\Omega$ inequalities must be satisfied, which imposes a given temperature range

$$T_- = \frac{a^2}{2} \frac{2 - 4Aa^{-3/2}}{2\ln(2\sqrt{2}a/\Omega)}, \; T_+ = \frac{a^2}{2} \frac{2 + 4Aa^{-3/2}}{2\ln(2\sqrt{2}a/\Omega)} \tag{4.35}$$

such that at T_- we have $M_1^{(-)} \simeq \frac{\pi}{\Omega}$ and at T_+ we have $M_1^{(+)} \simeq \frac{\pi}{\Omega}$. Hence, by working at a temperature $T_- \leq T \leq T_+$ the power spectrum of x will display a peak at $\omega = \Omega$ when $Aa^{-3/2} \ll 1$. This is the phenomenon of stochastic resonance. The full derivation of the adiabatic approximation can be found in [114]. A simpler approach can be found in [135]: the idea is to view the bistable system as a two state system (the two states correspond to the two minima). If $p_\pm$ is the equilibrium distribution in either well in the absence of forcing and $\delta p_\pm$ is the perturbation induced by the forcing, then we have

$$\delta p(x_\pm, t) = B\cos(\Omega t + \phi) \tag{4.36}$$

with $\tan\phi = -\frac{\Omega}{2}\tau_\pm$ and, for the amplitude

$$B = A\frac{a}{2T}\frac{1}{\sqrt{1 + (\Omega\tau_\pm)^2/4}}, \; \tau_\pm = \frac{\sqrt{2}\pi}{a}\mathrm{e}^{\beta a^2/4} \tag{4.37}$$

as shown in Fig. 2 of [84]. Of course we expected somehow the synchronization to the period of the forcing, but the response of the probability to occupy each basin is negligible unless the period of the forcing approaches the Kramers' time. At the corresponding temperature, however weak the forcing is, it is hugely amplified.

Recent applications of stochastic resonance include the sorting of molecules [5], and the study of climate.

4.2.2 Application to climate science

Very early on, the phenomenon of stochastic resonance was invoked in climate science [23, 86, 8]. Of course, in the example above, the position x should be thought of as a global temperature

(or perhaps a global ice volume when studying quaternary glaciations). The bistable potential driving the internal dynamics of x is subjected to a random force that accounts for the internal variability of the phenomena.

Cyclic phenomena are aplenty. For instance, glacial cycle have a 100 000 year period which prompted the authors in [23] to come up with an interpretation in terms of stochastic resonance). We cite their abstract *verbatim*,

> An amplification of random perturbations by the interaction of non-linearities internal to the climatic system with external, orbital forcing is found. This stochastic resonance is investigated in a highly simplified, zero-dimensional climate model. It is conceivable that this new type of resonance might play a role in explaining the 10^5 year peak in the power spectra of paleoclimatic records.

The connection to the model above deserves much more than a few words, but the idea is that there are two stable possible climates (just as the potential in subsection 4.2.1 has two minima, and the role of the external forcing is played by the changes in the ellipticity of the earth's orbit (at a period of the order of 10^5 years but with a relative amplitude of $10^{-1}\%$). The question is then to understand how the periodic forcing couples to temperature to yield a 10 K cycle. The authors of [23] suggest a zero-dimensional model (no space, temperature plays the role of x in subsection 4.2.1). The naive explanations (based on a purely determinstc dynamical system) lead to oscillation of the order of 1 K, and adding a white noise (with no intrinsic time-scale), by the mechanism of stochastic resonance, is able to lead to the correct order of magnitude. Of course, the crudeness of the model left many other explanations open, and it is unclear, according to the literature, that stochastic resonance plays any role in glacial cycles. However, the idea that a weak perturbation could lead to noise amplification proved very fruitful. More recently, the authors of [86] suggested that, during glacial times, variability over a 10^3 year period (abrupt warmings, also known as Dansgaard-Oeschger events), could actually be attributed to stochastic resonance. The idea is that a circulation mode of the Atlantic ocean is a nonlinear dynamical system with two minima. The excitation is the variability of the salinity balance of the northern North Atlantic, which causes a transient jump of the climate from the stable cold mode to the unstable warm mode.

4.3 Metastability: dynamics versus statics

Metastability is a purely dynamical phenomenon and it is characterized by the existence of eigenmodes of the evolution operator with eigenvalues very close to 0, markedly away from the rest of the fast-relaxing modes. Understanding the gemetry and the topology of the dynamical pathways related to these slow modes is of course essential, and this is what we sketch first in subsection 4.3.1. However, as has appeared in the calculation of the Kramers escape time, it also seems that lots of information are contained in the energy landscape itself, and it is tempting to adopt a viewpoint in which all of the relevant structures for the slow dynamics assocuated to metastability can be read off the energy landscape. This is what we very briefly present in subsection 4.3.2.

4.3.1 Dynamics: Barriers and reaction paths

This following discussion is based on [190, 189]. As in the example of the cyclohexane molecule, there are many physical situations where the dynamics of a system can be split into relatively fast relaxation processes (at a scale τ_{fast}, within a given local basin) and slower and rarer activation events ocurring between (metastable) states (local minima of the energy landscape) over time scales τ_K. The existence of these two time scales can be a consequence of low temperature effectively increasing energy barriers, as in the Kramers calculation before, or it can result from the existence of a collective effects (leading, as in an Ising ferromagnet, to an effective free energy barrier of order L^{d-1} (where L is the linear system size). It is of course highly desirable to understand how physical paths transit through canyons and saddles. One reason is that if a barrier is known, it may be possible to resort to specific simulation methods to actually observe an activated even which would otherwise not be accessible within a reasonable amount of computer time. This is what the method known as Transition Path Sampling (TPS) [26] does, for instance. We would now like to superficially describe a procedure able to determine reaction paths and barriers. We shall take the example of an overdamped Langevin dynamics (though extensions to the underdamped case can be achieved [188]), with unit mobility, at temperature T, namely $\dot{\mathbf{r}} = -\partial_{\mathbf{r}} V + \sqrt{2T}\boldsymbol{\eta}$. The key idea is to realize that the relevant information is encapsulated in the local probability current $\mathbf{J} = -\partial_{\mathbf{r}} VP - T\partial_{\mathbf{r}} P$ (here $\partial_t P = \mathbb{W}P = \partial_{\mathbf{r}} \cdot ((\partial_{\mathbf{r}} V)P) + T\partial_{\mathbf{r}} P) = -\partial_{\mathbf{r}} \cdot \mathbf{J}$). In equilibrium, the current components eventually relax to zero because $\lim_{t\to\infty} P(\mathbf{r}, t) = Z^{-1}\mathrm{e}^{-\beta V(\mathbf{r})}$. For systems with the sort of separation of time scales mentioned earlier, there is a first stage of the dynamics during which $P(\mathbf{r}, t)$ relaxes into a combination of contributions centered on the metastable states. Then the rare activated transitions between metastable states achieve the relaxation of $P(\mathbf{r}, t)$ to its equilibrium expression. These two time scales can also be identified for the dynamics of the probability current. While the probability density rapidly relaxes into the metastable states, the probability current converges on the same time scale to the most probable transition paths between the metastable states. Then, the late time relaxation towards equilibrium corresponds to a progressive vanishing of the current, when the net flux between each metastable state vanishes. This demands to be supported by some mathematical reasoning, but at least this is a very credible scenario. Note that the same line of reasoning holds for nonequilibrium systems though the probability current never vanishes and instead converges to its steady-state value. If one were able to simulate the evolution of the probability current, one would thus have all the knowledge relevant for the transitions between metastable states, while only having to simulate the system for relatively short time-scales (similar to the equilibration time within a metastable state). Simulating directly the transition current is thus, in itself, a desirable goal.

It is then possible to show that each component J_μ of the current evolves according to

$$\partial_t J_\mu = \mathbb{W} J_\mu - (\partial_\mu \partial_\nu V) J_\nu \tag{4.38}$$

This can be verified after a slightly tedious explicit calculation. This is an equation that does not involve P, in which the only requirement is to start from an initial current deriving from some initial distribution. The current evolving through Eq. (4.38) converges to the stationary distribution of currents between metastable states on the same time scale as the usual Langevin equation converges to metastable states (again, this is asserted without proof, but this can be

established). It is thus not necessary to wait for rare events to identify the transition path between the metastable states. If there are several metastable states and transitions with different rates, the current distribution at longer times concentrates on the paths between regions that have not yet mutually equilibrated, and vanishes in transitions between states that have had the time to mutually equilibrate.

If indeed there is a separation of timescales $\tau_{\rm fast} \ll \tau_K$ this means that $\mathbb{W}$ has a gap, namely a set of k eigenvalues close to zero (of the order of $-\tau_{K,k}^{-1}$ each) markedly separated from the rest of the eigenvalues $-\tau_{\rm fast}^{-1}$ much lower down. The distribution at intermediate times $\tau_{\rm fast} \ll t \ll \tau_K$ is a linear combination of Gaussians centered around in of the k minima. They are all the narrower as temperature is closer to zero.

For the purpose of discussion, we enlarge the space in which $\mathbb{W}$ acts by introducing d fermionic operators c_μ ($\{c_\mu, c_\nu^\dagger\} = \delta_{\mu\nu}$),

$$\mathbb{W}_e = \mathbb{W} - \partial_\mu \partial_\nu V c_\mu^\dagger c_\nu \tag{4.39}$$

This operators acts in the tensor space of functions with fermionic states. The total number of fermions in a given state is given by the action $\hat{N} = \sum_\mu c_\mu^\dagger c_\mu$ on that state. It turns out that $[\mathbb{W}_e, \hat{N}] = 0$, because indeed

$$\begin{aligned} [\mathbb{W}_e, \hat{N}] =& - [\partial_\alpha \partial_\beta V c_\alpha^\dagger c_\beta, c_\mu^\dagger c_\mu] \\ =& - \partial_\alpha \partial_\beta V [c_\alpha^\dagger c_\beta, c_\mu^\dagger c_\mu] \\ =& 0 \end{aligned} \tag{4.40}$$

so that it is possible to classify the eigenstates of $\mathbb{W}_e$ according to their number of fermions. At zero fermion, we are back onto the traditional Fokker-Planck equation and $|\Phi^{(0)}\rangle = P \otimes |0\rangle$ and P quickly converges towards local minima. Consider now a one-fermion vector, written as a linear combination of one-fermion states $|\Phi^{(1)}\rangle = \sum_\mu J_\mu(\mathbf{r}, t) \otimes c_\mu^\dagger |0\rangle$, then $\Phi^{(1)}$ converges to reaction paths joining two minima passing through sadlles with a single unstable direction. The coefficients J_μ appearing in this expansion evolve according to Eq. (4.38). It would then be interesting to simulate a process exactly described by Eq. (4.38). One simply remarks that $\mathbf{J} = \langle \mathbf{u} \rangle$, where $\mathbf{u}$ is a set of degrees of freedom evolving through $\dot{u}_\mu = -\partial_\mu \partial_\nu V u_\nu$. If $P(\mathbf{r}, \mathbf{u}, t)$ is the pdf of the joint variable $(\mathbf{r}, \mathbf{u})$ then indeed

$$\partial_t P = \mathbb{W} P + \partial_{u_\mu} (\partial_\mu \partial_\nu V u_\nu P) \tag{4.41}$$

and we see that Eq. (4.38) is recovered for $\mathbf{J} = \langle \mathbf{u} \rangle$. We refer interested readers to [189], and especially to the double-well case which is fully worked out in that article.

To put it in a nutshell, if we focus on the one-dimensional setting, and denoting by r_λ and ℓ_λ the right and left eigenvectors of the Fokker-Planck evolution operator with eigenvalue $-\lambda \geq 0$, then we know that

$$p(x, t) = \sum_\lambda a_\lambda \mathrm{e}^{-\lambda t} r_\lambda(x) \tag{4.42}$$

where $a_\lambda = \int \mathrm{d}y \ell_\lambda(y) p(y,0)$ contains the information on the initial state. We shall assume that λ_1 is almost degenerate with $\lambda_0 = 0$ and that all excited states lie sufficiently far away from λ_1. At large times, using $a_0 = a_{\lambda_0}$ and $a_1 = a_{\lambda_1}$, $p(x,t) \simeq a_0 r_0(x) + a_1 \mathrm{e}^{-\lambda_1 t} r_1(x)$ and thus the current reads

$$\partial_x j = -\partial_t p = a_1 \lambda_1 \mathrm{e}^{-\lambda_1 t} r_1(x), \; j(x,t) = a_1 \lambda_1 \mathrm{e}^{-\lambda_1 t} \int_{-\infty}^{x} \mathrm{d}y r_1(y) \tag{4.43}$$

and the probability current flowing through the two wells is roughly a constant. The ground state in the one-fermion sector $\int_{-\infty}^{x} \mathrm{d}y r_1(y)$ thus describes the steady-current between the two wells.

4.3.2 Statics: Reading metastability on the energy landscape

For a particle in a bistable potential evolving via Langevin dynamics, it is rather obvious that if the energy barrier between the energy minima is large enough, the particle may remain confined within one of the wells for a very long period of time. In a similar fashion, for an Ising model it is known that below the Curie temperature, the phase space splits into two regions that become disconnected in the thermodynamic limit, but that, in finite size, rare transitions from an spin-up ordered phase to a spin-down ordered phase are allowed. This is because in the Ising model, our knowledge of the phase diagram is shaped by almost a century of investigation, and we know that the physics can be projected onto that of magnetization (which plays the role of an order parameter, or that of a reaction coordinate), thus effectively reducing the complexity of the problem to that of a particle in a bistable potential in one dimension. The ergodicity breaking at work in the Ising model, in the large system size limit, leads to a splitting of the partition function

$$Z = \sum_{\mathscr{C}} \mathrm{e}^{-\beta H[\mathscr{C}]} = \mathrm{e}^{-\beta N f_-} + \mathrm{e}^{-\beta N f_+} \tag{4.44}$$

where $f_\pm$ are the free energies in the presence of a magnetic field, with $f_+ < f_-$ if the field is positive. There are physical systems that display a much greater complexity, and for which identifying what order is, or what the correct order paramater looks like, is highly non trivial. Take a simple fluid made of molecules, then it is known that at high temperature the liquid state is stable, while at low temperatures the system should be found in an ordered crystalline state. And yet, this is not what is always observed. Take silica (SiO_2) for instance, and cool it down, then an amorphous solid is obtained, instead of a crystal made of periodic tetrahedra. And the accompanying time scales (as measured for instance by viscosity) become overwhelmingly large as seen in Fig. 4.2 as they vary by ten orders of magnitude when temperature varies by a factor two. And yet, silica is amorphous, it doesn't display any obvious sort of order. If some sort of phase transition is at work, a bit as in an Ising model scenario, then perhaps the system gets trapped into some long-lived metastable state, and stays there for all practical purposes. Without any further insight the question becomes how we can find such states. In the Ising model, we know that adding a small magnetic field h coupled to magnetization helps bypass ergodocity breaking. There is a very powerful technique that somehow helps polarize the system into one of his (possibly many) metastable states without prior knowledge of its physical properties. This is what we describe now very sketchily.

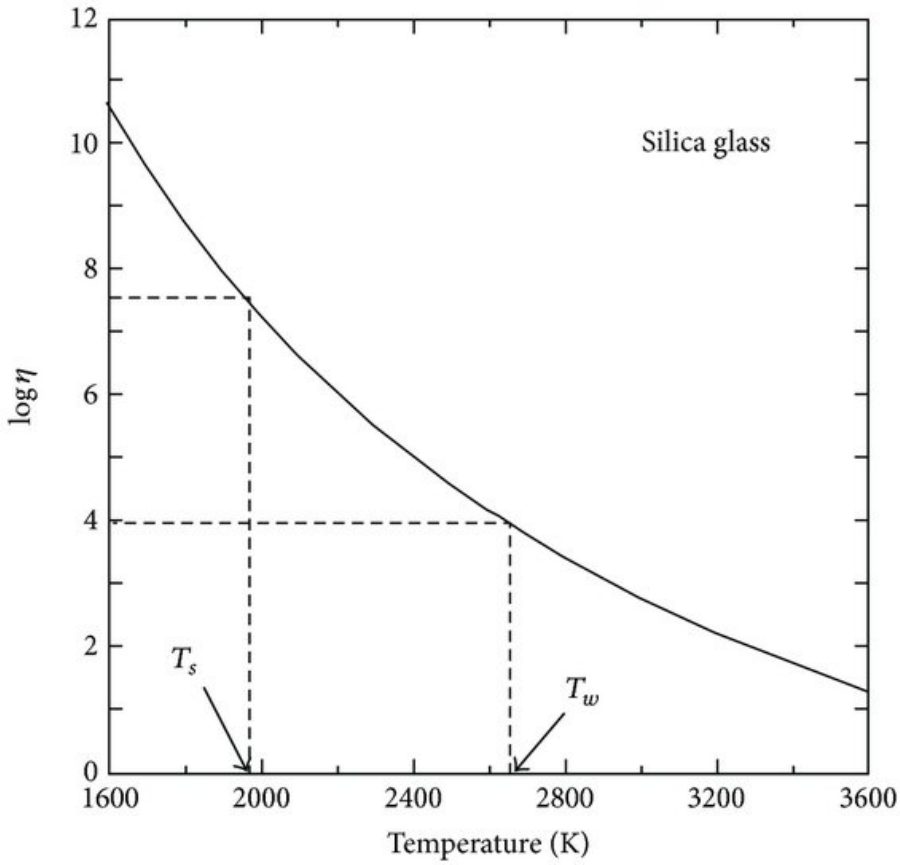

Figure 4.2: Viscosity of silica glass as a function of temperature.

Consider a system, described by some field $\phi(\mathbf{x})$ living in a d-dimensional space (and possibly possessing several components), that has a Hamiltonian $H[\phi]$ that makes the identification of its minima challenging. This can be either because H depends on parameters that display some sort of frozen randomness, or more simply because H is consistent with some sort of amorphous order as in the glass example given above. The presentation closely rests on [139] (and to some extent [136, 137]). The canonical partition function is $\int \mathscr{D}\phi \mathrm{e}^{-\beta H[\phi]}$ but we may choose to bias the statistics in a direction $\sigma(\mathbf{x})$ that plays a role similar to the magnetic field in the Ising model, up to the fact that for now σ is unspecified. One way to do this is to introduce a small attractive coupling g ($g \to 0^+$ at the end of the calculation), and to compute the free energy at a given σ

$$F_\phi[\sigma](\beta, g) = -\frac{1}{\beta} \ln \left[\int \mathscr{D}\phi \mathrm{e}^{-\beta H[\phi] - \frac{g}{2}\int (\phi - \sigma)^2} \right] \tag{4.45}$$

Of course if σ is poorly chosen then this free energy is going to yield a large number, but the closer σ is to stable configurations, the smaller that free energy will be. We now assume that σ is in contact with a thermostat at inverse temperature β' with energy $F_\phi[\sigma](\beta, g)$. Then the free energy of σ is

$$F_\sigma(\beta') = -\frac{1}{\beta'} \ln \left[\int \mathscr{D}\sigma \left(\int \mathscr{D}\phi \mathrm{e}^{-\beta H[\phi] - \frac{g}{2}\int (\phi - \sigma)^2} \right)^{\beta'/\beta} \right] \tag{4.46}$$

which seems a little complicated to evaluate. But in the particular case in which $\frac{\beta'}{\beta} = m$ is an integer, which we temporarily assume, and we can write that

$$\begin{aligned} F_\sigma(\beta m) &= -\frac{1}{\beta m} \ln \left[\int \mathscr{D}\sigma \left(\int \mathscr{D}\phi \mathrm{e}^{-\beta H[\phi] - \frac{g}{2}\int (\phi - \sigma)^2} \right)^m \right] \\ &= -\frac{1}{\beta m} \ln \left[\int \mathscr{D}\sigma \prod_{a=1}^m \mathscr{D}\phi_a \mathrm{e}^{-\beta \sum_{a=1}^m H[\phi_a] - \frac{g}{2}\sum_{a=1}^m \int (\phi_a - \sigma)^2} \right] \\ &= -\frac{1}{\beta m} \ln \left[\int \mathscr{D}\sigma \prod_{a=1}^m \mathscr{D}\phi_a \mathrm{e}^{-\beta \sum_{a=1}^m H[\phi_a] - \frac{gm}{2}\sigma^2 - \frac{g}{2}\sum_{a=1}^m \phi_a^2 - \sigma g \sum_a \phi_a} \right] \\ &\quad -\frac{1}{\beta m} \ln \left[\prod_{a=1}^m \mathscr{D}\phi_a \mathrm{e}^{-\beta \sum_{a=1}^m H[\phi_a] - \frac{g}{2m}\sum_{a<b} (\phi_a - \phi_b)^2} \right] \end{aligned} \tag{4.47}$$

Determining this free energy amounts to studying m copies of the system that are weakly coupled to each other by means of an attractive interaction with strength $g \to 0^+$. The idea is that by being weakly coupled, the various systems will fall into the same minimum of the energy landscape. Yet the original energy landscape is recovered only when $\beta' = \beta$, which ultimately sends $m \to 1$: $F_\phi(\beta) = F_\sigma(\beta)$. This may seem an unreasonable mathematical procedure, but a theorem of complex analysis tells us that if an analytic function is known on the set of integers, then it is known on the full complex plane, and thus the continuation to values $m \to 1$ makes sens. Of course, it is hard to prove that the hypotheses behind this theorem (Carlson's theorem [103]) are fulfilled in realistic physical conditions. So that we should not be shocked that eventually the $m \to 1$ limit is taken. All it takes is to be able to continue m to

the real axis. If a nonzero correlation $\langle \phi_a \phi_b \rangle_c$ survives the $g \to 0$ limit (to be taken after the $N \to +\infty$ limit) then this means that there exists a thermodynamic phenomenon occurring akin to a phase transition. It is possible to show that for some dynamical evolutions, there is a one-to-one correspondence between this statics-based definition of metastability, and a genuine dynamical definition [45].

There are interesting information that can be inferred by exploring the m dependence. As explained in [139], we can split the quantity $F_\sigma(\beta')$ into

$$S_{\rm hs} = \beta'^2 \frac{\partial F_\sigma}{\partial \beta'}\bigg|_{\beta'=\beta} = \beta \left.\frac{\partial F_\sigma}{\partial m}\right|_{m=1} \tag{4.48}$$

and

$$U_{\rm hs} = \left.\frac{\partial \beta' F_\sigma}{\partial \beta'}\right|_{\beta'=\beta} = \left.\frac{\partial m F_\sigma}{\partial m}\right|_{m=1} \tag{4.49}$$

such that $F_\sigma(\beta) = F_\phi(\beta) = U_{\rm hs} - \frac{1}{\beta} S_{\rm hs}$. The quantities $S_{\rm hs}$ and $U_{\rm hs}$ are respectively the entropy and the internal energy of the field σ with the index "hs" referring to hidden states. Such ideas have been instrumental in understanding the emergence of glassy behavior [153].

Chapter 5

The mean-field approximation

It is actually remarkable that one of the most celebrated contributions of Giorgio Parisi, one of the 2021 Nobel laureates, is the solution of a mean-field disordered Ising model, but also of systems without disorder [153]. And he should certainly be praised for having shown the beauties of a mean-field analysis for unusually complex systems. Mean-field ideas pervade the whole theoretical physics literature. In field theories, the $(\boldsymbol{\phi}^2)^2$ theory with $O(N)$ symmetry is often studied in the $N \gg 1$ limit [201, 141], much in the same way as $SU(N)$ invariant gauge theories [187], with the idea that $\boldsymbol{\phi}^2 = \sum_{\alpha=1}^{N} \phi_\alpha^2$ is the sum of a large number of components and this can therefore be, by the law of large numbers, split into a deterministic part extensive in N and a fluctuating part of order $O(\sqrt{N})$. For the corresponding field theories to remain well-defined as $N \gg 1$, the coupling constants must be scaled with $1/N$. In the study by t'Hooft, the corresponding Feynman diagrams considerably simplify (planar diagrams survive). In the $O(N)$ theory, only one loop diagrams survive.

5.1 The Ising model

5.1.1 Questioning what mean-field really is

The Ising model is a good starting point for our discussion (and the reader is referred to [153] for an inspired introduction). A collection of $N = L^d$ spins $\sigma_{\mathbf{x}} = \pm 1$ sitting on the vertices $\mathbf{x}$ of a d-dimensional hypercubic lattice with a Hamiltonian

$$H[\{\sigma_{\mathbf{x}}\}] = -J \sum_{\langle \mathbf{x},\mathbf{y} \rangle} \sigma_{\mathbf{x}} \sigma_{\mathbf{y}} - h \sum_{\mathbf{x}} \sigma_{\mathbf{x}} \tag{5.1}$$

is in contact with a thermal bath at inverse temperature β. The notation $\sum_{\langle \mathbf{x},\mathbf{y} \rangle}$ refers to a summation over distinct pairs of nearest neighbors on the hypercubic lattice. One can easily see that in equilibrium

$$\langle \sigma_{\mathbf{x}} \rangle = \langle \tanh \left[\beta J \sum_{\mathbf{y} \text{ nn of } \mathbf{x}} \sigma_{\mathbf{y}} + \beta h \right] \rangle \tag{5.2}$$

The quantity $h_{\mathbf{x}} = h + J \sum_{\mathbf{y} \text{ nn of } \mathbf{x}} \sigma_{\mathbf{y}}$ in the tanh has a simple interpretation: this is the local fluctuating field felt by spin $\sigma_{\mathbf{x}}$ caused by the external field h but also by the $2d$ nearest

neihboring spins $\sigma_{\mathbf{y}}$. On average, $\langle h_{\mathbf{x}} \rangle = 2dJm + h$, where $m = \langle \sigma_{\mathbf{z}} \rangle$ is the (uniform) average magnetization in equilibrium. If $h_{\mathbf{x}}$ has negligible fluctuations then we can write that

$$m = \tanh(2d\beta Jm + \beta h) \tag{5.3}$$

and we are back onto the well-known mean-field approximations. However, there is no *a priori* reason for $h_{\mathbf{x}}$ to have a very peaked distribution, unless the summation over the nearest neighbors $\sum_{\mathbf{y}\text{ nn of }\mathbf{x}} \sigma_{\mathbf{y}}$ is over a very large number of neighbors. Then the law of large numbers tells us that

$$\sum_{\mathbf{y}\text{ nn of }\mathbf{x}} \sigma_{\mathbf{y}} = 2dm + O(\sqrt{d}) \tag{5.4}$$

where the $O(\sqrt{d})$ random variable exists as long as the correlation length between spins remains finite. We immediately realize that a few adjustments in the definition of the model may be necessary. If we really insist on taking $d \gg 1$ then, for the transition temperature to remain finite, we want to work at finite $\hat{J} = dJ$ when $d \to +\infty$. Very often, instead of resorting to mean-field as an approximation, the Ising model is from the start defined on a complete graph [108] with N vertices carrying a spin $\sigma_i = \pm 1$,

$$\beta H[\{\sigma_i\}] = -\frac{K}{2N} \sum_{i,j} \sigma_i \sigma_j - h \sum_i \sigma_i,\ K = \beta J \tag{5.5}$$

And it sometimes known as the Husimi-Temperley model.

5.1.2 Statics

As is apparent, the energy of a microscopic configuration of the spins can be cast in the form

$$\beta H[\{\sigma_i\}] = -\frac{K}{2N} S^2 - hS \tag{5.6}$$

where $S = \sum_i \sigma_i$ is the total (fluctuating) magnetization. Since the energy depends on S only, we simply use the fact that there are $\Omega_N(S) = \binom{N}{\frac{N+S}{2}}$ microscopic configurations with the value $\sum_i \sigma_i = S$, and therefore the canonical partition function reads

$$Z = \sum_{\{\sigma_i\}} \mathrm{e}^{-\beta H[\{\sigma_i\}]} = \sum_{S=-N,-N+2,\ldots,N} \Omega_N(S) \mathrm{e}^{\frac{K}{2N} S^2 + hS} \tag{5.7}$$

which we write in the form

$$Z = \sum_{S=-N,-N+2,\ldots,N} \mathrm{e}^{-N\beta f(S,N)} \tag{5.8}$$

where $\beta f(S,N) = \frac{1+s}{2} \ln \frac{1+s}{2} + \frac{1-s}{2} \ln \frac{1-s}{2} - Ks^2/2 - hs$ depends on $s = S/N$ only, as expected, up to negligible $O(\ln N/N)$ corrections when $N \gg 1$. After replacing $\sum_S \to N \int_{-1}^{+1} \mathrm{d}s$, one usually implements a saddle point approximation to determine the phase diagram,

$$m = \langle s \rangle = \mathrm{argmin}\{f\} \tag{5.9}$$

with

$$\frac{\partial f}{\partial s} = \frac{1}{2}\ln\frac{1+s}{1-s} - Ks - h = 0 \tag{5.10}$$

that leads to $m = \tanh(Km + h)$. We are back onto the same equation as is obtained by other formulations of the mean-field approximation. The function f exhibits a double-well structure below T_c (symmetric when $h = 0$) and is a single well above T_c. As $s \to 0$, we have

$$\beta f(s) = \frac{1}{2}(1-K)s^2 + \frac{1}{12}s^4 - hs \tag{5.11}$$

The standard mean field critical exponents are easily recovered:

$$m \propto |K-1|^{\beta},\ \beta = 1/2,\ K \to 1^{+} \tag{5.12}$$

The susceptibility is obtained as $\chi = \left.\frac{\partial m}{\partial h}\right|_{h=0}$, so that after differentiating $m = \tanh(Km + h)$ we get

$$\chi = (K\chi + 1)(1-m^2),\ \chi = \frac{1-m^2}{1-K(1-m^2)} \tag{5.13}$$

and the susceptibility behaves as

$$\chi \propto A_{\pm}|K-1|^{-\gamma},\ \gamma = 1,\ K \to \pm 1,\ \frac{A_+}{A_-} = 2 \tag{5.14}$$

but it is of course more difficult to come up with a definition of the correlation length. However, if we define $\xi \sim |K-1|^{-\nu}$, with $\nu = 1/2$, we recover known hyperscaling relations at $d = 4$.

The mean-field approach can also be used to understand the role of finite-size scaling, including at a first order transition point (see section 4 in [163]). Sit for instance below the critical temperature and work at nonzero external field h. Then the magnetization undergoes a discontinuous jump at $h = 0$ from m_0 to $-m_0$ as h is decreased across 0. There are two solutions to $\frac{\partial f}{\partial s} = 0$, but as long as $h \neq 0$, even if the partition function is the sum of two contributions, only one of them dominates. Right at $h = 0^{+}$, the magnetization becomes

$$\begin{aligned} m =& \frac{s_+ \mathrm{e}^{-N\beta f(s_+)} + s_- \mathrm{e}^{-N\beta f(s_-)}}{\mathrm{e}^{-N\beta f(s_+)} + \mathrm{e}^{-N\beta f(s_-)}} \\ \overset{h\to 0}{\simeq}& m_+(T < T_c)\frac{\mathrm{e}^{-N\beta f(s_+)} - \mathrm{e}^{-N\beta f(s_-)}}{\mathrm{e}^{-N\beta f(s_+)} - \mathrm{e}^{-N\beta f(s_-)}} \\ \simeq& m_+(T < T_c)\tanh N\beta(f_+ - f_-)/2 \\ \simeq& m_+(T < T_c)\tanh(N\beta h m_+) \end{aligned} \tag{5.15}$$

and thus as $N \to +\infty$ we recover the expected magnetization jump.

The mean-field approximation can in principle be improved [91] in a systematic fashion, which can be turned into a useful procedure, for instance in inference problems [180].

Just as a side remark, the mean-field model also allows to explicitly probe such finer quantities as the Yang-Lee zeroes of the partition function $Z(K,h)$ (see [1] and section 9 of [117], or [173]), which all lie on the imaginary axis of h. Indeed, if $\rho(z)$ is the density of zeroes of Z in the complex plane of $z = \mathrm{e}^h$ at fixed K, then Z is a polynomial of order N in Z and it can be written in the form $Z = \prod_{i=1}^{N}(z - z_i)$, where the z_i's are the zeroes of Z, and thus $\frac{1}{N}\ln Z = \frac{1}{N}\sum_i \ln(z - z_i) = \int \mathrm{d}^2 r' \rho(z') \ln(z - z')$ which leads to

$$\int \mathrm{d}^2 r' \rho(z') \ln(z - z') = -\beta f(m(h,K),h), \;\; z = \mathrm{e}^h \tag{5.16}$$

This is an integral equation that is not easily solved as such, but clearly taking the Laplacian leads to

$$\rho(z) = -\pi\beta 4 \frac{\partial}{\partial z}\frac{\partial}{\partial z^*} f(m(h,K),h) \tag{5.17}$$

hence ρ is the Hilbert transform of the right-hand side of Eq. (5.17). It is now time we turn to the dynamics of the Ising model.

5.1.3 Glauber dynamics

At the level of the dynamics (for $h = 0$), Glauber-like transition rates for individual spins

$$w(\sigma_i \to -\sigma_i) = \gamma \mathrm{e}^{-\beta(H[\sigma_1,\ldots,-\sigma_i,\ldots,\sigma_N]-H[\sigma_1,\ldots,\sigma_i,\ldots,\sigma_N])} = \gamma \mathrm{e}^{-K\sigma_i S/N + K/N} \tag{5.18}$$

where γ sets the time scale, convert into a transition rate for S of the form

$$W(S \to S \pm 2) = \gamma \frac{N \mp S}{2} \mathrm{e}^{\pm KS/N} \tag{5.19}$$

and thus

$$\frac{\mathrm{d}\langle S\rangle}{\mathrm{d}t} = +2\langle W(S \to S+2) - W(S \to S-2)\rangle \tag{5.20}$$

hence

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 2\langle \frac{1-s}{2}\mathrm{e}^{Ks} - \frac{1+s}{2}\mathrm{e}^{-Ks}\rangle \tag{5.21}$$

Note that the rate in Eq. (5.18) is consistent with detailed balance for $P_{\mathrm{eq}}[\sigma_1,\ldots,\sigma_N] = \mathrm{e}^{-\beta H[\sigma_1,\ldots,\sigma_N]}/Z$, just as much as the rate in Eq. (5.19) is consistent with detailed balance with respect to $P_{\mathrm{eq}}(S) = \binom{N}{\frac{N+S}{2}}\mathrm{e}^{-\beta H}/Z$.

If we accept that $P(S,t) = \mathrm{e}^{-Nw(s,t)}$ takes a large deviation form at all times, then s can be replaced with m into an average and

$$\frac{\mathrm{d}m}{\mathrm{d}t} = (1-m)\mathrm{e}^{Km} - (1+m)\mathrm{e}^{-Km} = 2\sinh Km - 2m\cosh Km \tag{5.22}$$

Not surprisingly, in the long time limit, $m = \tanh Km$. Of course, from this evolution equation, one can infer the relaxation rate of the magnetization, but we have no information on the relaxation of correlations, as we basically know nothing about the hierarchy of relaxations rates at work in this system. These relaxation rates are (up to a sign) the eigenvalues of the evolution operators, and it is desirable to elaborate methods to find these rates.

5.1.4 From the master equation to a quantum problem

A convenient procedure is to rewrite the evolution operator in a spin basis. The space of the 2^N configurations is indexed by vectors $|\sigma_1,\dots,\sigma_N\rangle$ and the linear combination $|\psi(t)\rangle = \sum_{\sigma_1,\dots,\sigma_N} P(\sigma_1,\dots,\sigma_N,t)|\psi\rangle$ is seen to evolves as $\frac{\mathrm{d}|\psi\rangle}{\mathrm{d}t} = \mathbb{W}|\psi(t)\rangle$. The master equation for P reads

$$\begin{aligned}\partial_t P(\sigma_1,\dots,\sigma_N,t) = &\sum_j w(-\sigma_j\to\sigma_j)P(\sigma_1,\dots,-\sigma_j,\dots,\sigma_N)\\ &-\sum_j w(\sigma_j\to-\sigma_j)P(\sigma_1,\dots,\sigma_j,\dots,\sigma_N)\end{aligned} \tag{5.23}$$

Then we multiply to the right by $|\sigma_1,\dots,\sigma_N\rangle$, then sum over $\sum_{\sigma_1,\dots,\sigma_N}$ and finally arrive at

$$\begin{aligned}\frac{\mathrm{d}|\psi\rangle}{\mathrm{d}t} = &\sum_i w(\sigma_i\to-\sigma_i)P(\sigma_1,\dots,\sigma_i,\dots,\sigma_N,t)\\ \times&\left[|\sigma_1,\dots,-\sigma_i,\dots,\sigma_N\rangle - |\sigma_1,\dots,\sigma_i,\dots,\sigma_N\rangle\right]\end{aligned} \tag{5.24}$$

As a final step, introducing the operators σ_j^z and σ_j^x such that

$$\sigma_j^z|\sigma_1,\dots,\sigma_N\rangle = \sigma_j|\sigma_1,\dots,\sigma_N\rangle \tag{5.25}$$

and

$$\sigma_j^x|\sigma_1,\dots,\sigma_j,\dots,\sigma_N\rangle = |\sigma_1,\dots,-\sigma_j,\dots,\sigma_N\rangle \tag{5.26}$$

we see that

$$\mathbb{W} = \sum_i (\sigma_i^x - 1)\,\omega(\sigma_i^z) \tag{5.27}$$

with

$$\omega(\sigma_i) = w(\sigma_i\to-\sigma_i) = \gamma \mathrm{e}^{-K\sigma_i S/N} \tag{5.28}$$

At last, because $\sigma_j^x\sigma_j^z = -i\sigma_j^y$ we see that

$$\begin{aligned}\mathbb{W} =&\sum_i(\sigma_i^x-1)\gamma \mathrm{e}^{-K\sigma_i^z S^z/N + K/N}\\ =&\gamma\sum_i(\sigma_i^x-1)\left[\cosh(KS^z/N) - \sigma_i^z\sinh(KS^z/N)\right]\\ =&\gamma\left[(S^x-N)\cosh(KS^z/N) + (iS^y+S^z)\sinh(KS^z/N)\right]\end{aligned} \tag{5.29}$$

and we are now studying a quantum mechanical problem involving a $\frac{N}{2}$ spin (beware, the spin is $\mathbf{S}/2$). This is in general a difficult problem, unless one is interested in the low-lying states, namely in the states with the longest lifetimes, which are anyhow the most interesting ones. One way to proceed has been put forward by Ruijgrok and Tjon [172]. It consists in noting that if a and $a^\dagger$ are a pair of conjugate bosonic annihilation and creation operators, $[a, a^\dagger]$,

then the spin algebra is verified by

$$\begin{aligned} S^z &= 2a^\dagger a - N \\ S^x &= \sqrt{N}\left[a^\dagger\left(1-\frac{a^\dagger a}{N}\right)^{1/2} + \left(1-\frac{a^\dagger a}{N}\right)^{1/2} a\right] \\ S^y &= -i\sqrt{N}\left[a^\dagger\left(1-\frac{a^\dagger a}{N}\right)^{1/2} - \left(1-\frac{a^\dagger a}{N}\right)^{1/2} a\right] \end{aligned} \tag{5.30}$$

as first found by Holstein and Primakoff. We could (as done in [172]) rewrite $\mathbb{W}$ in terms of a and $a^\dagger$, and then, for instance in the paramagnetic phase where $a^\dagger a \ll N$, we resort to a small a, $a^\dagger$ expansion.

In hindsight, we realize that the question we asked about the relaxation rates is a nontrivial one: it amounts to studying a many-body strongly correlated quantum system, and finding its whole energy spectrum. In some favorable cases (mean-field is one of these) this can be done, but in most cases one must resort to approximation methods. These are often easier to implement when one uses a path-integral formulation as a starting point (simply because this is a language common to other areas of theoretical physics).

5.1.5 An exact field-theoretic representation of the master equation

In Eq. (5.40) we asked whether it was possible to write a stochastic differential equation for s in the form

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \text{deterministic part} + \text{noise} \tag{5.31}$$

If this is possible, the deterministic part can only be the same as that of Eq. (5.40), but finding the correct noise is an open question. In what follows, we will show that a path-integral formulation allows to bypass the noise issue.

The goal is to obtain a formulation of the dynamical properties in an integral form without resorting to any approximation. We follow the approach of [10]. Let us start from a fixed magnetization $S(0)$ and focus on the $[0, \Delta t]$ interval. Suppose we are interested in the average of some magnetization dependent observable $A(S)$ at time Δt, then

$$\langle A\rangle(\Delta t) = \langle A(S(0)+\Delta S)\rangle \tag{5.32}$$

where $\Delta S = S(\Delta t) - S(0)$ can take the values ± 2 or 0. We now use two identities,

$$\int \mathrm{d}M(0)\delta(M(0)-S(0)) = 1, \quad \int \mathrm{d}M(\Delta t)\int \frac{\mathrm{d}\hat{M}(0)}{2\pi i}\mathrm{e}^{-\hat{M}(0)(\Delta M-\Delta S)} = 1 \tag{5.33}$$

where $\Delta M = M(\Delta t) - M(0)$. Thus we can write that

$$\langle A\rangle(\Delta t) = \int \mathrm{d}M(0)\int \mathrm{d}M(\Delta t)\int \frac{\mathrm{d}\hat{M}(0)}{2\pi i}\mathrm{e}^{-\hat{M}(0)\Delta M}A(M(\Delta t))\langle \mathrm{e}^{\hat{M}(0)\Delta S}\rangle\delta(M(0)-S(0)) \tag{5.34}$$

where $\langle \mathrm{e}^{\hat{M}(0)\Delta S}\rangle$ is an average over the possible values of ΔS:

$$\begin{aligned}\langle \mathrm{e}^{\hat{M}(0)\Delta S}\rangle =& \mathrm{e}^{2\hat{M}}\, W(S(0)\to S(0)+2)\Delta t + \mathrm{e}^{-2\hat{M}}\, W(S(0)\to S(0)-2)\Delta t \\ &+ (1-\Delta t\,[W(S(0)\to S(0)+2)+W(S(0)\to S(0)-2)]) \\ =& 1+\Delta t\left(\mathrm{e}^{2\hat{M}}-1\right) W(S(0)\to S(0)+2)+\Delta t\left(\mathrm{e}^{-2\hat{M}}-1\right) W(S(0)\to S(0)-2) \\ \simeq& \mathrm{e}^{\Delta t\left(\mathrm{e}^{2\hat{M}}-1\right) W(S(0)\to S(0)+2)+\Delta t\left(\mathrm{e}^{-2\hat{M}}-1\right) W(S(0)\to S(0)-2)}\end{aligned} \tag{5.35}$$

Altogether we thus arrive at

$$\begin{aligned}\langle A\rangle(\Delta t) = & \int \mathrm{d}M(0)\mathrm{d}M(\Delta t)\int \frac{\mathrm{d}\hat{M}(0)}{2\pi i} A(M(\Delta t)) \\ & \times \mathrm{e}^{-\Delta t\left[\hat{M}(0)\frac{\Delta M}{\Delta t}+\frac{N-M(0)}{2} W(M(0)\to M(0)+2)(1-\mathrm{e}^{2\hat{M}(0)})+\frac{N+M(0)}{2} W(M(0)\to M(0)-2)(1-\mathrm{e}^{-2\hat{M}(0)})\right]} \\ & \times \delta(M(0)-S(0))\end{aligned} \tag{5.36}$$

and we prefer writing this otherwise:

$$\langle A\rangle(\Delta t) = \int \mathscr{D}M\mathscr{D}\hat{M}\, A(M(t_{\mathrm{obs}}))\mathrm{e}^{-S[\hat{M},M]} \tag{5.37}$$

with the dynamical action given by

$$S[\hat{M},M] = \int_0^{+\infty}\left[\hat{M}\partial_t M + \frac{N-M}{2} W(M\to M+2)(1-\mathrm{e}^{2\hat{M}}) + \frac{N+M}{2} W(M\to M-2)(1-\mathrm{e}^{-2\hat{M}})\right] \tag{5.38}$$

up to a contribution involving the initial state. It is remarkable that we can write a path-integral formulation of the discrete process without approximations (beyond those inherent to writing path integrals). Of course, from the method presented here one sees that restoring space dependence is straightforward. Note that we have extended the upper bound of the time integral in the action to infinity, simply because whatever occurs after t_{obs} is of no relevance and does not contribute to the average of $A(t_{\mathrm{obs}})$.

5.1.6 More on relaxation times

The many pedagogical appendices of [140] have been used for this subsection and for subsection 5.1.8. We start from the fact that $s = m + \delta s/\sqrt{N}$, where the variance of the random variable δs is $O(1)$. This means that we can write

$$\frac{\mathrm{d}s}{\mathrm{d}t} = 2\sinh Ks - 2s\cosh Ks + \text{noise} \tag{5.39}$$

where the noise term is such that the probability to observe a given value s is peaked as $N \gg 1$. We also expect that when s is close to m, these will differ by $O\left(\frac{1}{\sqrt{N}}\right)$ fluctuations and in that