Out-of-equilibrium Statistical Physics

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Introduction: Stochastic processes in statistical physics

In these notes, we give a brief introduction to statistical physics from the point of view of stochastic processes. There are questions that equilibrium statistical physics cannot address, for instance, what is the correlation between an observable measured at time t and the same observable measured at time $t + \tau$? To answer this question, it is not enough to provide the energy of each configuration of the system, one should also define the dynamics of the system, that is, how the system evolves from one configuration to another; this is different from quantum systems, the dynamics of which is given by the Hamiltonian. Since the system can explore states that are not minimum energy ones, this dynamics should contain a random component: it should be *stochastic*. This dynamics should also be compatible with equilibrium: the probability distribution should converge, at long time, towards the Boltzmann distribution. We will see that providing the system with a dynamics also allows to give a precise meaning to concepts as ergodicity or even... equilibrium.

Defining systems with their dynamics also allows one to study systems that are out of equilibrium. One can identify several classes of non-equilibrium systems. The first consists of systems that evolve too slowly to reach equilibrium in a reasonable time; such slow dynamics can be found in disordered systems, such as glasses, or systems evolving close to a critical point. The second class is composed of driven systems, for instance systems submitted to a temperature or a density gradient, or systems submitted to a time varying control parameter, such as thermal engines. The third class is made of systems which are driven at the local scale, such as crowds of sheeps or flocks of birds, or tissues; these systems are called *active*.

In Chap. 1, we define discrete processes, that is, processes that evolve on a finite set of states. We define both the random dynamics on the set of states and the corresponding dynamics for the probability distribution. We determine the properties that these dynamics need to satisfy for the system to be at equilibrium. In Chap. 2, we define processes in continuous space, such as the Langevin equation, and the corresponding deterministic partial differential equation for the probability distribution. In Chap. 3, we focus on simple driven systems: we show how their fluctuations are related to their response to a force and then introduce stochastic thermodynamics, that define the quantities and laws of thermodynamics to stochastic processes. In Chap. 4, we define the stochastic dynamics of fields, determine when they are compatible with equilibrium, and treat questions specific to fields.

Chapter 1

Discrete processes

1.1 Random walk

1.1.1 Stochastic process

We introduce the simplest model that we can think of to model, for instance, the dynamics of a speck of dust in the air. At time $t = 0$, the particle is located at the origin: $x_0 = 0$. The particle moves at discrete times on a lattice: its position at time $t \in \mathbb{N}$ is given by $x_t \in \mathbb{Z}$. At each time, the particle makes a unit jump to the "left" or to the "right":

$$x_{t+1} = x_t + s_t, \tag{1.1}$$

where $s_t = -1$ with probability $1/2$ and $s_t = 1$ with probability $1/2$. The jumps are independent.

We can write

$$x_t = \sum_{t'=0}^{t-1} s_{t'}, \tag{1.2}$$

which allows to compute the average and the variance of the random variable x_t:

$$\langle x_t \rangle = \sum_{t'=0}^{t-1} \langle s_{t'} \rangle = 0, \tag{1.3}$$

$$\langle x_t^2 \rangle = \left\langle \left(\sum_{t'=0}^{t-1} s_{t'} \right)^2 \right\rangle = \sum_{t',t''=0}^{t-1} \langle s_{t'} s_{t''} \rangle = \sum_{t',t''=0}^{t-1} \delta_{t',t''} = t. \tag{1.4}$$

We have used that $\langle s_t^2 \rangle = 1$ and $\langle s_{t'} s_{t''} \rangle = 0$ if $t' \neq t''$.

1.1.2 Probability density

Exact solution, convergence

We now consider the probability $p_{x,t}$ for the particle to be at position x at time t; it is given by the binomial coefficient

$$p_{x,t} = \begin{cases} 2^{-t} \binom{t}{\frac{x+t}{2}} & \text{if } x + t \text{ is even,} \\ 0 & \text{if } x + t \text{ is odd.} \end{cases} \tag{1.5}$$

The condition comes from the fact that the particle cannot be at en even position after an odd number of jumps and vice-versa.

From the central limit theorem, the normalized position $y_t = x_t / \sqrt{t}$ converges in law towards the normalized centered normal law: its density satisfies

$$f_{y_t}(u) \underset{t \to \infty}{\longrightarrow} \frac{1}{\sqrt{2\pi}} e^{-u^2/2}. \tag{1.6}$$

This is often written under the non-rigorous form

$$p_{x,t} \underset{t \to \infty}{\approx} \frac{1}{\sqrt{2\pi t}} e^{-x^2/(2t)}. \tag{1.7}$$

Evolution

We will actually be more interested in the *evolution* of the probability density. To be at x at time $t + 1$, the particle should have been at $x - 1$ or at $x + 1$ at time t, and the jump to x has a probability $1/2$, thus

$$p_{x,t+1} = \frac{1}{2} \left(p_{x-1,t} + p_{x+1,t} \right). \tag{1.8}$$

This is the first and simplest evolution equation that we will see. We first make simple comments on this equation, which hold in the general case. We can rewrite the evolution equation for the difference between the density at time $t + 1$ and the density at time t:

$$p_{x,t+1} - p_{x,t} = \frac{1}{2}p_{x-1,t} - p_{x,t} + \frac{1}{2}p_{x+1,t} = \sum_{y \in \mathbb{Z}} M_{xy} p_{y,t}. \tag{1.9}$$

This equation is the *master equation* of the problem; it is a linear equation for the density $p_{x,t}$. In our case, the "matrix" M is given by

$$M_{xy} = \frac{1}{2}\delta_{x-1,y} - \delta_{x,y} + \frac{1}{2}\delta_{x+1,y}. \tag{1.10}$$

The probability is conserved: $\sum_x p_{x,t} = 1$ at all times; this implies

$$\sum_x M_{xy} = 0. \tag{1.11}$$

With this matrix formulation, we can write the probability density at any times as

$$p_{x,t} = \sum_y (\mathbf{1} + M)^t_{xy} p_{y,0}, \tag{1.12}$$

where $\mathbf{1}$ is the identity matrix.

Stationary solution

The condition for p_x^* to be a stationary density is

$$(Mp^*)_x = \sum_y M_{xy} p_y^* = 0. \tag{1.13}$$

Here, it leads to $p_x^* = a \in \mathbb{R}$, which cannot be normalized: this stochastic process admits a stationary measure, but not a stationary density.

We note that the conservation of the probability (1.11) can be written as $M^T U = 0$, where U is a vector with all its components equal to one. This means that 0 is an eigenvalue of M^T; thus it is also an eigenvalue of M, which always admits a stationary measure.

1.2 Continuous time random walks

1.2.1 Examples

Random walk on $\mathbb{Z}$

We will see that it is easier to work with continuous time processes, where the master equation (1.9) becomes a differential equation.

We consider again the random walk on $\mathbb{Z}$ but, here, during a time interval δt, the particle can jump to the left or to the right with a probability $\delta t/2$ in each direction. The master equation then reads

$$p_x(t + \delta t) = (1 - \delta t)p_x(t) + \frac{\delta t}{2}p_{x-1}(t) + \frac{\delta t}{2}p_{x+1}(t), \tag{1.14}$$

from which we can write the master equation

$$\dot{p}_x(t + \delta t) = \frac{1}{2}p_{x-1}(t) - p_x(t) + \frac{1}{2}p_{x+1}(t) \tag{1.15}$$

$$= \sum_y M_{xy} p_y(t), \tag{1.16}$$

where the matrix M is still given by Eq. (1.10).

Considering the density as a vector, we can write

$$p(t) = e^{tM} p(0). \tag{1.17}$$

Random walk on a circle

We consider now a model that admits a stationary density. For that purpose, we consider N sites placed on a circle, meaning that the site N is identified with the site 0; this can be seen as a random walk on $\mathbb{Z}/N\mathbb{Z}$.

For $N = 6$, the matrix M reads

$$M = \begin{pmatrix} -1 & 1/2 & 0 & 0 & 0 & 1/2 \\ 1/2 & -1 & 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & -1 & 1/2 & 0 & 0 \\ 0 & 0 & 1/2 & -1 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 & -1 & 1/2 \\ 1/2 & 0 & 0 & 0 & 1/2 & -1 \end{pmatrix}. \tag{1.18}$$

We can check that the sum of the coefficients over each column is zero.

It is easy to verify that the uniform distribution $p_x = 1/N$ is a stationary solution of the master equation. The uniform distribution corresponds to the equilibrium Boltzmann distribution when the energy is the same on all sites.

Oriented random walk on a circle

We introduce a model that is close to the previous one but that will be useful to discuss the concept of equilibrium. The particle moves on the same circle with N sites, but now it can jump to the right only, with a probability δt in a time δt. For $N = 6$, the matrix M now reads

$$M = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{pmatrix}. \tag{1.19}$$

The uniform distribution is still a stationary distribution but, as we shall see, its status is not the same as before.

1.2.2 Probability current, stationary and equilibrium states

We here consider the general case where a system can take a state $i \in \{1, \ldots, N\}$. During a time δt, the system can jump from the state i to the state j with probability $k_{ji}\delta t$, where k_{ji} is the *transition rate*. The master equation still takes the form (1.16), with

$$M_{ij} = k_{ij}. \tag{1.20}$$

To satisfy the probability conservation, we set

$$k_{ii} = -\sum_{j \neq i} k_{ji}. \tag{1.21}$$

For a given probability distribution p_i, we define the *probability current* between the sites i and j as

$$j_{ji} = k_{ji} p_i - k_{ij} p_j. \tag{1.22}$$

We can rewrite the master equation with the currents:

$$\dot{p}_i = \sum_{j} k_{ij} p_j = \sum_{j \neq i} k_{ij} p_j + k_{ii} p_i \tag{1.23}$$

$$= \sum_{j \neq i} k_{ij} p_j - \sum_{j \neq i} k_{ji} p_i \tag{1.24}$$

$$= \sum_{j \neq i} j_{ij}. \tag{1.25}$$

The right hand side can be seen as a discrete divergence.

In particular, for the stationary distribution, $\sum_{j \neq i} j_{ij} = 0$: the total probability current towards the state i vanishes. We now compute the probability current for the stationary distribution, $p_i = 1/N$, for the symmetric and oriented random walks on the circle. For the symmetric random walk, we find that all the currents vanish. On the contrary, for the oriented random walk, we find that $j_{i+1,i} = 1/N$. We thus see that the nature of the stationary state depends on the process.

We say that the system is at *equilibrium* if it is in a stationary state and the currents vanish. A stationary state with finite currents is a *non-equilibrium stationary state*, sometimes abbreviated NESS.

1.2.3   Random walk in an energy landscape, detailed balance

Until now, we have only considered dynamics where the stationary state is uniform. We now attribute an energy E_i to each state i and determine the necessary conditions for (i) the system to admit an equilibrium stationary distribution and (ii) this distribution to match the equilibrium canonical Boltzmann distribution at temperature T:

$$p_i^{\text{eq}} = \frac{1}{Z} \exp\left(-\frac{E_i}{T} \right), \tag{1.26}$$

where the Boltzmann constant has been set to one and $Z = \sum_i \exp(-E_i/T)$.

Looking for equilibrium distributions is easier than looking for stationary ones, because the condition is stronger, and local, in the first case. A distribution p_i^* is an equilibrium distribution if

$$j_{ij} = k_{ij} p_j^* - k_{ji} p_i^* = 0, \tag{1.27}$$

for all pairs (i, j). Inserting the Boltzmann distribution (1.26) in the vanishing current condition (1.27), we obtain:

$$k_{ij} e^{-E_j/T} = k_{ji} e^{-E_i/T}. \tag{1.28}$$

This is the *detailed balance* condition. It is a necessary and sufficient condition for the system to admit the Boltzmann distribution as an equilibrium distribution.

There are an infinity of choices that satisfy the detailed balance condition. In order to define such a dynamics, we usually first define the graph of states g_{ij}: $g_{ij} = 1$ if the system can jump directly from state i to state j and $g_{ij} = 0$ otherwise. Then usual choices are

- The Glauber dynamics:

$$k_{ij} = g_{ij} e^{-E_i/T}. \tag{1.29}$$

- The Metropolis dynamics:

$$k_{ij} = \begin{cases} g_{ij} & \text{if } E_i \leq E_j \\ g_{ij} e^{(E_j - E_i)/T} & \text{if } E_i > E_j \end{cases}. \tag{1.30}$$

These dynamics are usually used to

- Search the minimum of a function without being trapped in local minima, which is used in simulated annealing, where the temperature is slowly reduced.

- Sample a complex phase space to compute averages; this is notably used for the Ising model.

1.2.4   Convergence towards the stationary distribution, ergodicity

As noted for the random walks, a master equation always admit a stationary distribution p^*. We can wonder if, starting from a distribution p_0, the master equation will drive the system towards the stationary distribution.

To answer this question, we first need to define a distance between a distribution p and the stationary distribution p^*. We use the *relative entropy*, or Kullback-Leibler divergence, defined by

$$D(p, p') = \sum_i p_i \ln\left(\frac{p_i}{p_i'} \right). \tag{1.31}$$

Clearly, $D(p, p) = 0$ and, since $\ln(x) \leq x - 1$,

$$D(p, p') = -\sum_i p_i \ln\left(\frac{p_i'}{p_i} \right) \geq -\sum_i p_i \left(\frac{p_i'}{p_i} - 1 \right) = 0. \tag{1.32}$$

Although the relative entropy quantifies a "distance" between two distributions, it is not a metric since it is not symmetric.

We now compute the evolution of the relative entropy with respect to the stationary solution:

$$\frac{d}{dt} D(p(t), p^*) = \sum_i \dot{p}_i \ln\left(\frac{p_i}{p_i^*}\right) \tag{1.33}$$

$$= \sum_{i,j} M_{ij} p_j \ln\left(\frac{p_i p_j^*}{p_i^* p_j}\right) \tag{1.34}$$

$$\leq \sum_{i,j} M_{ij} p_j \frac{p_i p_j^*}{p_i^* p_j} \tag{1.35}$$

$$= 0. \tag{1.36}$$

We have used twice the normalization condition $\sum_i \dot{p}_i = 0$ or $\sum_i M_{ij} = 0$ and the inequality $\ln(x) \leq x - 1$.

We have thus showed that the relative entropy is a Lyapunov function of the master equation. The equality is reached when, for any pair of states $\langle ij \rangle$, either $p_i p_j^* = p_i^* p_j$ or $M_{ij} = 0$. The first case means that the distribution over the pair $\langle ij \rangle$ is proportional to the stationary distribution. As a consequence, if the dynamics is *ergodic*, meaning that there is a path with nonzero transition rates linking any pair of states, then the distribution converges towards the stationary distribution.

If the dynamics is not ergodic, the dimension of the space of stationary distributions is given by the number of connected components of states, and the distribution converges to a stationary distribution on each connected component.

1.2.5 Free energy

The result of the previous section does not require the transition rates to satisfy detailed balance. If they do, the stationary solution is the equilibrium distribution p^{eq} (Eq. (1.26)):

$$p_i^{\mathrm{eq}} = \exp\left(\frac{F^{\mathrm{eq}} - E_i}{T}\right), \tag{1.37}$$

where $F^{\mathrm{eq}} = -T \ln(Z)$, with $Z = \sum_i \exp(-E_i/T)$. The relative entropy between a distribution p and the equilibrium distribution reads

$$D(p, p^{\mathrm{eq}}) = \sum_i p_i \ln\left(\frac{p_i}{p_i^{\mathrm{eq}}}\right) \tag{1.38}$$

$$= \sum_i \left[p_i \ln(p_i) + p_i \left(\frac{E_i - F^{\mathrm{eq}}}{T}\right) \right] \tag{1.39}$$

$$= \frac{F - F^{\mathrm{eq}}}{T}, \tag{1.40}$$

where we have introduced the free energy, the average energy, and the entropy of the distribution p:

$$F = U - TS, \tag{1.41}$$

$$U = \sum_i p_i E_i, \tag{1.42}$$

$$S = -\sum_i p_i \ln(p_i). \tag{1.43}$$

The Lyapunov function of a dynamics that satisfies detailed balance is thus the free energy. The distribution converges towards the equilibrium distribution and the free energy decays towards the free energy of the equilibrium distribution, which is the distribution with the lowest free energy.

Chapter 2

Continuous processes

2.1 Langevin and Fokker-Planck equations

The construction of the Langevin equation from physical ground, and of the Fokker-Planck equation from the Langevin equation is a standard topic of advanced statistical mechanics. We follow more or less the presentation of Ref. [1] chap. 10, or Ref. [2] chap. 9, with some ideas borrowed from Refs. [3, 4].

2.1.1 Particle in an external potential

Let us consider a particle of mass m in an external potential $U(\mathbf{r})$, and in contact with a thermal bath at temperature T. A typical example of potential is the harmonic trap, $U(\mathbf{r}) = \frac{1}{2}\kappa\mathbf{r}^2$. Let us denote $\mathbf{r}$ and $\mathbf{v} = \frac{d\mathbf{r}}{dt}$ the position and velocity of the particle. At equilibrium, the joint probability density of $\mathbf{v}$ and $\mathbf{r}$ is given by the Boltzmann distribution

$$P_{\text{eq}}(\mathbf{v}, \mathbf{r}) \propto e^{-\frac{1}{k_B T}\left(\frac{m\mathbf{v}^2}{2} + U(\mathbf{r})\right)}, \tag{2.1}$$

where k_B is the Boltzmann constant, and the proportionality coefficient is the partition function. We are usually interested in the statistics of the position only:

$$p_{\text{eq}}(\mathbf{r}) = \int d\mathbf{v} P_{\text{eq}}(\mathbf{v}, \mathbf{r}) \propto e^{-\frac{U(\mathbf{r})}{k_B T}}. \tag{2.2}$$

The canonical ensemble framework gives us the equilibrium statistics, but not information of the dynamics. What does a typical trajectory $\mathbf{r}(t)$ of the particle look like? What are the expressions of the time correlations $\langle\mathbf{r}(t_1)\mathbf{r}(t_2)\rangle$? To obtain such information, we need to specify a dynamical model. In doing so, we should be careful to recover Eqs. (2.1)-(2.2) for the (large time) equilibrium probability distribution. As we have seen in the previous section for the Ising model, the dynamical model leading to a given statistics is not unique. We therefore need a physically motivated dynamical description.

2.1.2 Langevin equation

We assume that our particle is immersed in a fluid medium, and that it is much larger than the fluid molecules. The fluid has two effects on the particle.

- It induces a friction force proportional to the velocity: $\mathbf{F}_{\text{friction}} = -\lambda\mathbf{v}$.

- The collisions between the fluid molecules and the particle give rise to random force $\mathbf{f}(t)$ acting on the particle. We assume that this force is isotropic, gaussian distributed (as a result of the central limit theorem for the collisions), and uncorrelated at the observation timescales (the microscopic timescale is very small).

Since $\mathbf{f}$ is Gaussian, it is enough to specify its average and its correlations:

$$\langle f_\alpha(t)\rangle = 0, \qquad\qquad \langle f_\alpha(t) f_\beta(t')\rangle = \Lambda\delta_{\alpha\beta}\delta(t-t'), \tag{2.3}$$

with $\alpha, \beta = x, y, z$ (in dimension $d = 3$), $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$ and 0 otherwise. $\delta(t)$ is the Dirac delta function, it should be understood physically as a function of unit integral ($\int_{-\infty}^{\infty}\delta(t) = 1$) that is concentrated on a vanishingly small interval around 0. For the moment, Λ is an arbitrary parameter.

We can now write Newton's equation of motion for the particle:

$$\boxed{m\frac{d\mathbf{v}}{dt} = -\lambda\mathbf{v} - \nabla U(\mathbf{r}) + \mathbf{f}(t)} \tag{2.4}$$

where $-\nabla U$ is the force exterted by the external potential on the particle. This stochastic differential equation is known as the Langevin equation. For the moment, we do not attempt to give a precise mathematical meaning.

2.1.3   Side remark: increments scaling as $\sqrt{\Delta t}$

Before continuing, let us make a brief aside and define the time integral of $f(t)$ in dimension 1,

$$\frac{dW}{dt} = f(t) \qquad \Leftrightarrow \qquad W(t) = \int_0^t f(s)ds. \tag{2.5}$$

It is interesting to look at the increment ΔW of W over a short time Δt,

$$\Delta W = W(t + \Delta t) - W(t) = \int_t^{t+\Delta t} f(s)ds. \tag{2.6}$$

ΔW is a Gaussian random variable (as a linear combination of Gaussian random variables). It has a vanishing average $\langle \Delta W \rangle = 0$ and a variance

$$\langle (\Delta W)^2 \rangle = \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \langle f(s)f(s') \rangle = \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \delta(s - s') = \Lambda\Delta t. \tag{2.7}$$

That means that ΔW scales as $O(\sqrt{\Delta t})$, instead of $O(\Delta t)$ for a regular function. Most of the difficulties associated with stochastic differential equations (such as the Langevin equation) come from this observation.

For completeness, the probability distribution of ΔW is

$$P(\Delta W) = \frac{1}{\sqrt{2\pi\Lambda\Delta t}}e^{-\frac{(\Delta W)^2}{2\Lambda\Delta t}}. \tag{2.8}$$

2.1.4   Velocity correlations and important relations

Fluctuation-dissipation relation

We now manipulate Eq. (2.4) in the absence of external potential ($U = 0$). In the process, we will obtain several important relations. When $U = 0$, Eq. (2.4) is an inhomogeneous first order differential equation for $\mathbf{v}$. Setting the initial condition at time t_0, the general solution is

$$\mathbf{v}(t) = \mathbf{v}(t_0)e^{-\zeta(t-t_0)} + \frac{1}{m}\int_{t_0}^t ds\, e^{-\zeta(t-s)}\mathbf{f}(s), \tag{2.9}$$

with $\zeta = \lambda/m$ the relaxation rate of the system. Equilibrium is reached when the system has had an infinite time to equilibrate, that is to say when $t_0 \to -\infty$. The initial condition is forgotten, leading to

$$\mathbf{v}(t) = \frac{1}{m}\int_{-\infty}^t ds\, e^{-\zeta(t-s)}\mathbf{f}(s). \tag{2.10}$$

Since $\langle f(t) \rangle = 0$, the average value of the velocity vanishes: $\langle \mathbf{v}(t) \rangle = 0$. Using Eq. (2.3), we can compute the correlation at equal time,

$$\langle \mathbf{v}(t)^2 \rangle = \frac{1}{m^2}\int_{-\infty}^t ds \int_{-\infty}^t ds' e^{-\zeta(2t-s-s')}\langle \mathbf{f}(s)\cdot\mathbf{f}(s') \rangle = \frac{d\Lambda}{m^2}\int_{-\infty}^t ds\, e^{-2\zeta(t-s)} = \frac{d\Lambda}{2\zeta m^2}, \tag{2.11}$$

where d is the dimension of the system. At equilibrium, the equipartition of energy should hold:

$$\frac{1}{2}m\langle \mathbf{v}(t)^2 \rangle = d\frac{k_B T}{2}. \tag{2.12}$$

This fixes the noise strength Λ in terms of the friction coefficient λ and the temperature T:

$$\boxed{\Lambda = 2\lambda k_B T} \tag{2.13}$$

This relation is known as a *fluctuation-dissipation relation*: it indeed relates the fluctuations Λ of the random force to the dissipation λ in the fluid.

Diffusion constant

An interesting quantity to consider is the diffusion coefficient D. Let us define the displacement $\Delta\mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(0)$. Anticipating on the result, we may expect that the displacement has a Brownian motion scaling, that is to say that the variance is proportional to time: $\langle(\Delta\mathbf{r})^2\rangle \underset{t\to\infty}{\sim} 2dDt$ at equilibrium. In other words, D is defined as

$$D = \frac{1}{2d}\lim_{t\to\infty}\frac{d\langle\Delta\mathbf{r}^2\rangle}{dt} = \frac{1}{2}\lim_{t\to\infty}\frac{d\langle\Delta x^2\rangle}{dt}. \tag{2.14}$$

Here Δx denotes any of the components of $\Delta\mathbf{r}$; they are all equivalent by isotropy, and mutually independent (this will be shown below).

Green-Kubo relation

By definition, $\Delta\mathbf{r} = \int_0^t ds\, \mathbf{v}(s)$. This leads to

$$\frac{d}{dt}\langle\Delta\mathbf{r}^2\rangle = \frac{d}{dt}\int_0^t ds \int_0^t ds'\langle\mathbf{v}(s)\cdot\mathbf{v}(s')\rangle = 2\int_0^t ds\langle\mathbf{v}(t)\cdot\mathbf{v}(s)\rangle = 2\int_0^t ds'\langle\mathbf{v}(s')\cdot\mathbf{v}(0)\rangle. \tag{2.15}$$

The key ingredient behind the last equality is the time translation invariance that holds at equilibrium: $\langle\mathbf{v}(t+\tau)\cdot\mathbf{v}(t)\rangle = \langle\mathbf{v}(\tau)\cdot\mathbf{v}(0)\rangle$ (this will be shown below). Using Eqs. (2.14)-(2.15), the diffusion constant is expressed as:

$$\boxed{D = \frac{1}{d}\int_0^\infty dt\, \langle\mathbf{v}(t)\cdot\mathbf{v}(0)\rangle} \tag{2.16}$$

This relation connects a kinetic coefficient (D) to a dynamic correlation function. It is known as a *Green-Kubo relation.*

Einstein relation

Let us now compute explicitely the velocity correlations $\langle v_\alpha(t+\tau)v_\beta(t)\rangle$ $(\tau > 0)$ from Eq. (2.10), where α and β are spatial components.

$$\langle v_\alpha(t+\tau)v_\beta(t)\rangle = \frac{1}{m^2}\int_{-\infty}^{t+\tau} ds \int_{-\infty}^t ds'e^{-\zeta(2t+\tau-s-s')}\langle f_\alpha(s)f_\beta(s')\rangle \tag{2.17}$$

$$= \delta_{\alpha\beta}\frac{\Lambda}{m^2}\int_{-\infty}^t dse^{-\zeta(2t+\tau-2s)} \tag{2.18}$$

$$= \delta_{\alpha\beta}\frac{\Lambda}{2m^2\zeta}e^{-\zeta\tau} \tag{2.19}$$

This shows, as expected, both the independence of the spatial component, and the time translation invariance. We can now inject the expression of the velocity correlation in the Green-Kubo relation (2.16), and use the fluctuation-dissipation relation (2.13) to obtain

$$\boxed{D = \frac{k_BT}{\lambda}} \tag{2.20}$$

This relation between the diffusion constant and the friction coefficient is known as the *Einstein relation.*

2.1.5   The Fokker-Planck equation in dimension 1

Let us start from the Langevin equation (2.4) without external potential, and for simplicity in 1D:

$$m\frac{dv}{dt} = -\lambda v + f(t), \tag{2.21}$$

with $\langle f(t)\rangle = 0$ and $\langle f(t)f(t')\rangle = \Lambda\delta(t-t')$. Our final goal is to obtain a (deterministic) differential equation for the time evolution of the probability $P(v,t)$ that the particle has velocity v at time t.

Statistics of the velocity increments

It is first useful to compute to the statistics of a velocity increment $w = v(t + \Delta t) - v(t)$. We note that the process is Markovian, that is to say that the evolution of v is given only by its value at the time considered (and not its value in the past): w depends only on Δt and $v(t)$. The formal expression of w is

$$w = -\zeta \int_t^{t+\Delta t} v(t')dt' + \frac{1}{m} \int_t^{t+\Delta t} f(t')dt'. \tag{2.22}$$

We can now compute the moments of w at order Δt. First the average,

$$\langle w \rangle = -\zeta v \Delta t + O(\Delta t^2), \tag{2.23}$$

with $v = v(t)$. And then the variance,

$$\langle w^2 \rangle = \zeta^2 \iint_t^{t+\Delta t} dt'dt'' \langle v(t')v(t'') \rangle - \frac{2\zeta}{m} \iint_t^{t+\Delta t} dt'dt'' \langle f(t')v(t'') \rangle + \frac{1}{m^2} \iint_t^{t+\Delta t} dt'dt'' \langle f(t')f(t'') \rangle. \tag{2.24}$$

Let us investigate the three terms of this expression:

- Since $\langle v(t')v(t'') \rangle \approx v(t)^2$ when Δt is small, the first term is of order $(\Delta t)^2$.

- The second term is the most complicated to deal with. We need to compute the correlations between the velocity and the random force: $g(t, t_0) = \langle v(t)f(t_0) \rangle$. By causality, the velocity at a given time is not affected by the noise in the future: $g(t, t_0) = 0$ if $t < t_0$. Then, by multiplying Eq. (2.21) by $f(t_0)$ and averaging, one finds

$$\partial_t g(t, t_0) = -\zeta g(t, t_0) + \frac{\Lambda}{m} \delta(t - t_0). \tag{2.25}$$

  For $t > t_0$, this gives $g(t, t_0) = Ae^{-\zeta(t - t_0)}$. And integrating between t_0^- and t_0^+, one obtains $g(t_0^+, t_0) - g(t_0^-, t_0) = \frac{\Lambda}{m}$. This leads to $A = g(t_0^+, t_0) = \Lambda/m$. Finally,

$$\langle v(t)f(t_0) \rangle = \begin{cases} \frac{\Lambda}{m} e^{-\zeta(t - t_0)} & \text{if } t > t_0 \\ 0 & \text{if } t < t_0 \end{cases}. \tag{2.26}$$

  One checks that the double integral in Eq. (2.24) is of order $(\Delta t)^2$: $\iint_t^{t+\Delta t} dt'dt'' \langle f(t')v(t'') \rangle = O(\Delta t^2)$.

- The third term of Eq. (2.24) is easy to compute from the correlations of the random force: $\iint_t^{t+\Delta t} dt'dt'' \langle f(t')f(t'') \rangle = \Lambda \Delta t$.

At the end of the day, Eq. (2.24) reduces to

$$\langle w^2 \rangle = \frac{\Lambda}{m^2} \Delta t + o(\Delta t) = 2\zeta^2 D \Delta t + o(\Delta t), \tag{2.27}$$

where we used the fluctuation dissipation relation (2.13) and the Einstein relation (2.20). D is the diffusion coefficient of the particle.

More generally, the moments of the velocity increments can be written as

$$\boxed{\langle w^n \rangle = M_n(v)\Delta t + o(\Delta t).} \tag{2.28}$$

We already computed $M_1 = -\zeta v$ and $M_2 = 2\zeta^2 D$.

An important remark, that we state here without proof, is that the statistics of w is actually Gaussian. This comes from the fact that v derives from a linear equation with Gaussian noise. The Gaussianity of w implies that moments for $n \geq 3$ are expressed as powers of $\langle w \rangle$ and $\langle w^2 \rangle$. As such, $\langle w^n \rangle = O(\Delta t^2)$ for $n \geq 3$, that is to say $M_n = 0$ for $n \geq 3$.

Kramers-Moyal expansion

We now focus of the probability $P(v,t)$ of observing a velocity v at time t. We denote $\pi(w,v,\Delta t)$ the probability of having a velocity increment v between t and $t + \Delta t$ that we studied previously. Since the process is Markovian, we can write the probability of v at time $t + \Delta$ as an integral over the increments:

$$P(v, t + \Delta t) = \int_{-\infty}^{\infty} dw P(v - w, t)\pi(w, v - w, \Delta t). \tag{2.29}$$

For small Δt, w is small. We can expand $P(v - w, t)$ around v, refactor the expression, and use the definition of the moments of w:

$$P(v, t + \Delta t) = \int_{-\infty}^{\infty} dw \sum_{n=0}^{\infty} \frac{(-w)^n}{n!} \frac{\partial^n}{\partial v^n} \left[P(v, t)\pi(w, v, \Delta t) \right], \tag{2.30}$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial v^n} \left[P(v, t) \int_{-\infty}^{\infty} dw \, w^n \pi(w, v, \Delta t) \right], \tag{2.31}$$

$$= P(v, t) + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial v^n} [P(v, t)\langle w^n \rangle]. \tag{2.32}$$

Finally, since the moments scale linearly with time, Eq. (2.28), we obtain the Kramers-Moyal expansion:

$$\boxed{\frac{\partial P(v, t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial v^n}(M_n P)} \tag{2.33}$$

This equation holds for an arbitrary statistics of the increments w, beyond the specifics of Eq. (2.21).

Fokker-Planck equation

The Kramers-Moyal expansion is almost always truncated at order $n = 2$, either because this truncation is exact (as in our Gaussian case $M_n = 0, n \geq 3$) or as an approximation. This leads to the *Fokker-Planck equation*:

$$\boxed{\frac{\partial P(v, t)}{\partial t} = -\frac{\partial}{\partial v}(M_1 P) + \frac{1}{2} \frac{\partial^2}{\partial v^2}(M_2 P)} \tag{2.34}$$

For our specific Langevin equation (2.21), the associated Fokker-Planck equation is

$$\boxed{\frac{\partial P(v, t)}{\partial t} = -\frac{\partial}{\partial v}(\zeta v P) + \frac{\partial^2}{\partial v^2}(\zeta^2 D P)} \tag{2.35}$$

Note that this is often written as a continuity equation with a current $J(v, t)$,

$$\frac{\partial P(v, t)}{\partial t} = -\frac{\partial J(v, t)}{\partial x}, \tag{2.36}$$

$$J(v, t) = \zeta v P - \frac{\partial}{\partial v}(\zeta^2 D P). \tag{2.37}$$

Stationary solution

The Fokker-Planck equation (2.35) can be actually solved starting from an initial probability distribution $P(v, 0) = \delta(v - v_0)$, and therefore from an arbitrary intial probability law. We shall not do this here. Instead, we restrict ourselves to the stationary solution satifying $\partial_t P_{\text{stat}} = 0$. We look for a solution with no flux: $J_{\text{stat}}(v, t) = 0$:

$$\zeta^2 D \frac{\partial P_{\text{stat}}(v)}{\partial v} - \zeta v P_{\text{stat}}(v) = 0. \tag{2.38}$$

We solve this equation and obtain

$$P_{\text{stat}}(v) = C e^{-\frac{1}{2\zeta D}v^2} = C e^{-\frac{1}{k_B T}\frac{1}{2}mv^2}, \tag{2.39}$$

where we used the Einstein relation (2.20). After all this work, we do obtain, as expected, the equilibrium probability distribution of the canonical ensemble!

Backward Kolmogorov equation

As a side remark, it is instructive to know that there is a "backwards" equivalent to the Fokker-Planck equation. One considers the probability $P(v_f, t_f; v_i, t_i)$ that the particle has a velocity v_f at time t_f knowing that it had a velocity v_i at time $t_i < t_f$. The goal is to study the dependence of the process at fixed final state (v_f, t_f) when the initial condition is varied. The resulting equation is known as the *backward Kolmogorov equation*. We state it both generally and in our specific case:

$$\frac{\partial P(v_f, t_f; v_i, t_i)}{\partial t_i} = -M_1(v_i)\frac{\partial P}{\partial v_i} - M_2(v_i)\frac{1}{2}\frac{\partial^2 P}{\partial v_i^2} \tag{2.40}$$

$$= -\zeta v_i \frac{\partial P}{\partial v_i} - \zeta^2 D \frac{\partial^2 P}{\partial v_i^2}. \tag{2.41}$$

Formally, the backward and the forward (Fokker-Planck) equations can be written as

$$\frac{\partial P(v_f, t_f; v_i, t_i)}{\partial t_i} = -\mathcal{L}_i P(v_f, t_f | v_i, t_i), \tag{2.42}$$

$$\frac{\partial P(v_f, t_f; v_i, t_i)}{\partial t_f} = \mathcal{L}_f^\dagger P(v_f, tf | v_i, t_i), \tag{2.43}$$

where $\mathcal{L}_i$ acts on v_i and $\mathcal{L}_f$ on v_f. The operators are

$$\mathcal{L}\bullet = M_1(v)\frac{\partial}{\partial v}\bullet + \frac{1}{2}M_2(v)\frac{\partial^2}{\partial v^2}\bullet, \tag{2.44}$$

$$\mathcal{L}^\dagger\bullet = -\frac{\partial}{\partial v}[M_1(v)\bullet] + \frac{1}{2}\frac{\partial^2}{\partial v^2}[M_2(v)\bullet]. \tag{2.45}$$

$\mathcal{L}^\dagger$ is the adjoint of $\mathcal{L}$ in the sense that $\int dv [\mathcal{L}f](v)g(v) = \int dv f(v)[\mathcal{L}^\dagger g](v)$ for all functions $f(v), g(v)$.

2.1.6   The general Fokker-Planck equation

Fokker-Planck equation for a multidimensional process

Let us consider an arbitrary (Markovian) stochastic process in dimension m, $\mathbf{X}(t) = (X_1(t), \ldots, X_m(t))$. We denote its increments $\mathbf{Y} = \mathbf{X}(t + \Delta t) - \mathbf{X}(t)$ and assume that the lowest moments read

$$\langle Y_i \rangle = M_i^{(1)}(\mathbf{X})\,\Delta t + o(\Delta t), \tag{2.46}$$

$$\langle Y_i Y_j \rangle = M_{ij}^{(2)}(\mathbf{X})\,\Delta t + o(\Delta t), \tag{2.47}$$

where i, j are components of the vector. $M^{(1)}$ is called the drift vector, and $M^{(2)}$ is (twice) the diffusion matrix. The higher order correlations are either zero (Gaussian process) or neglected for the analysis. The framework that we developed in the 1D case can be extended and we obtain the following Fokker-Planck equation for the probability $P(\mathbf{X}, t)$:

$$\boxed{\frac{\partial P(\mathbf{X}, t)}{\partial t} = -\sum_{i=1}^m \frac{\partial}{\partial X_i}\left[M_i^{(1)}(\mathbf{X})P(\mathbf{X}, t)\right] + \frac{1}{2}\sum_{i,j=1}^m \frac{\partial}{\partial X_i \partial X_j}\left[M_{ij}^{(2)}(\mathbf{X})P(\mathbf{X}, t)\right]} \tag{2.48}$$

Multidimensional Langevin equation

The stochastic process is often given by a m-dimensional Langevin equation (with additive diagonal noise),

$$\frac{dX_i}{dt} = g_i(\mathbf{X}) + \sqrt{2D_i}\eta_i(t), \tag{2.49}$$

where g_i is the deterministic drift part and η_i are Gaussian white noises satisfying $\langle \eta_i(t) \rangle = 0, \langle \eta_i(t)\eta_j(t') \rangle = \delta_{ij}\delta(t - t')$. We will come back to this type of equation in the next section.

From Eq. (2.49) one can prove that $M^{(1)}$ and $M^{(2)}$ are given by

$$M_i^{(1)}(\mathbf{X}) = g_i(\mathbf{X}) \qquad\qquad\qquad M_{ij}^{(2)} = 2D_i\delta_{ij}. \tag{2.50}$$

Note that we restricted ourselves to additive noise: D_i is assumed to be independent of $\mathbf{X}$. We will treat multiplicative noise later. The generalization of Eq. (2.50) to $D_i(\mathbf{X})$ will be true only in the Ito formalism.

Kramers equation

It is now time to come back to the Langevin equation with potential (2.4). We write it as a system of first order equations,

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}, \tag{2.51}$$

$$\frac{d\mathbf{v}}{dt} = -\zeta\mathbf{v} - \frac{1}{m}\nabla U(\mathbf{r}) + \frac{1}{m}\mathbf{f}(t). \tag{2.52}$$

The state of the system is $\mathbf{X} = (r_1, \ldots, r_d, v_1, \ldots, v_d)$. From Eq. (2.49) and (2.50), we deduce that the evolution of the probability $P(\mathbf{r}, \mathbf{v}, t)$ is given by

$$\boxed{\frac{\partial P(\mathbf{r}, \mathbf{v}, t)}{\partial t} = -\nabla_r \cdot [\mathbf{v}P] + \nabla_v \cdot \left[\left(\zeta\mathbf{v} + \frac{1}{m}\nabla U(\mathbf{r})\right)P\right] + D\nabla_v^2 P} \tag{2.53}$$

where ∇_r and ∇_v denote respectively the gradients with respect to $\mathbf{r}$ and $\mathbf{v}$. This equation is known as *Kramers equation*.

The equilibrium probability distribution (2.1),

$$P_{\text{eq}}(\mathbf{v}, \mathbf{r}) = \frac{1}{Z}e^{-\frac{1}{k_B T}\left(\frac{m\mathbf{v}^2}{2} + U(\mathbf{r})\right)}, \tag{2.54}$$

is a stationary solution of the Kramers equation. One indeed checks that

$$\nabla_r \cdot [\mathbf{v}P_{\text{eq}}] = \nabla_v \cdot \left[\frac{1}{m}\nabla U(\mathbf{r})P_{\text{eq}}\right] \tag{2.55}$$

and that

$$\zeta\mathbf{v}P_{\text{eq}} + D\nabla P_{\text{eq}} = 0 \tag{2.56}$$

given the fluctuation-dissipation relation (2.13) and Einstein relation (2.20). We have acheived our goal of building a dynamical theory consistent with thermal equilibrium.

2.1.7 The overdamped regime

Overdamped Langevin equation

In a lot of situations, we can neglect the inertial term $(m\partial_t v)$ in the Langevin equation (2.4). This is the case when the dynamics is strongly overdamped (strong viscous friction) and we are not interested in the short time scales (of order ζ^{-1}). The motion of the particle is assumed to be described by the *overdamped Langevin equation*,

$$\lambda\frac{d\mathbf{r}}{dt} = -\nabla U(\mathbf{r}) + \mathbf{f}(t). \tag{2.57}$$

The velocity degrees of freedom (which are assumed to relax fast) have disappeared from the problem and we are left with the position $\mathbf{r}$ only.

Smoluchovski equation

The Fokker-Planck equation (2.48) for the probability distribution $p(\mathbf{r}, t)$ associated with the overdamped Langevin equation is known as the *Smoluchovski equation*. It reads

$$\boxed{\frac{\partial p(\mathbf{r}, t)}{\partial t} = \frac{1}{\lambda}\nabla \cdot [\nabla U(\mathbf{r})p(\mathbf{r}, t)] + \frac{k_B T}{\lambda}\nabla^2 p(\mathbf{r}, t)} \tag{2.58}$$

where we used the fluctuation-dissipation relation (2.13). Note that the Smoluchovski equation can be derived as the large friction limit of the Kramers equation (2.53) (but it is not trivial to do it properly).

It is customary to write the Smoluchovski equation as a continuity equation

$$\frac{\partial p(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \tag{2.59}$$

$$\mathbf{j}(\mathbf{r}, t) = -\frac{1}{\lambda}\left[\nabla U(\mathbf{r})p(\mathbf{r}, t) + k_B T\nabla p(\mathbf{r}, t)\right]. \tag{2.60}$$

The solution with no flux $\mathbf{j} = 0$ is the equilibrium probability $p_{\text{eq}}(\mathbf{r})$.

$$\frac{\nabla p_{\text{eq}}(\mathbf{r})}{p_{\text{eq}}(\mathbf{r})} = \nabla \ln p_{\text{eq}}(\mathbf{r}) = -\frac{\nabla U(\mathbf{r})}{k_B T} \tag{2.61}$$

$$\ln p_{\text{eq}}(\mathbf{r}) = -\frac{U(\mathbf{r})}{k_B T} + c \tag{2.62}$$

$$p_{\text{eq}}(\mathbf{r}) \propto e^{-\frac{U(\mathbf{r})}{k_B T}} \tag{2.63}$$

As expected, we obtain the Boltzmann distribution.

Non-equilibrium free energy

As for discrete random variables, we can define a non-equilibrium free energy and show that it is a Lyapunov function (its time derivative is always negative). Given a probability distribution $p(\mathbf{r}, t)$, we can define an internal energy $E(t)$ and an entropy $S(t)$ by

$$E(t) = \int d\mathbf{r}\, p(\mathbf{r}, t) U(\mathbf{r}), \qquad\qquad S(t) = -k_B \int d\mathbf{r}\, p(\mathbf{r}, t) \ln p(\mathbf{r}, t). \tag{2.64}$$

From this, we define a (non equilibrium) free energy $F(t)$ and a free energy density $f(\mathbf{r}, t)$,

$$F(t) = E(t) - TS(t) = \int d\mathbf{r}\, p(\mathbf{r}, t) \left[U(\mathbf{r}) + k_B T \ln p(\mathbf{r}, t) \right] = \int d\mathbf{r}\, p(\mathbf{r}, t) f(\mathbf{r}, t), \tag{2.65}$$

$$f(\mathbf{r}, t) = U(\mathbf{r}) + k_B T \ln p(\mathbf{r}, t). \tag{2.66}$$

The time evolution of this free energy is given by

$$\frac{dF}{dt} = \int d\mathbf{r}\, \frac{\partial p(\mathbf{r}, t)}{\partial t} \left\{ U(\mathbf{r}) + k_B T [\ln p(\mathbf{r}, t) + 1] \right\} \tag{2.67}$$

$$= \int d\mathbf{r}\, \frac{\partial p(\mathbf{r}, t)}{\partial t} f(\mathbf{r}, t). \tag{2.68}$$

We used the conservation of the total probability: $\frac{\partial}{\partial t} \int d\mathbf{r}\, p(\mathbf{r}, t) = 0$. We now inject the Smoluchovski equation (2.58) and perform an integration by parts.

$$\frac{dF}{dt} = \frac{1}{\lambda} \int d\mathbf{r}\, \nabla \cdot \left[\nabla U(\mathbf{r}) p(\mathbf{r}, t) + k_B T \nabla p(\mathbf{r}, t) \right] f(\mathbf{r}, t) \tag{2.69}$$

$$= -\frac{1}{\lambda} \int d\mathbf{r}\, \left[\nabla U(\mathbf{r}) p(\mathbf{r}, t) + k_B T \nabla p(\mathbf{r}, t) \right] \cdot \nabla f(\mathbf{r}, t) \tag{2.70}$$

$$= -\frac{1}{\lambda} \int d\mathbf{r}\, p(\mathbf{r}, t) \left[\nabla U(\mathbf{r}) + k_B T \nabla \ln p(\mathbf{r}, t) \right] \cdot \nabla f(\mathbf{r}, t) \tag{2.71}$$

$$= -\frac{1}{\lambda} \int d\mathbf{r}\, p(\mathbf{r}, t) \| \nabla f(\mathbf{r}, t) \|^2. \tag{2.72}$$

This implies that $\frac{dF}{dt} \leq 0$. It is a Lyapunov function of the system. It becomes zero when $\nabla f = 0$ that is to say when the system is at equilibrium, with the Boltzmann probability law $p_{\text{eq}}(\mathbf{r}) \propto e^{-\frac{U(\mathbf{r})}{k_B T}}$.

2.2   Several models in and out-of-equilibrium

2.2.1   Particles in a 1D ratchet potential

Overdamped particle in a ratchet potential

As a first example, let us consider a Brownian particle in a periodic potential. We define

$$U(x) = U_0 \left[\sin\left(\frac{2\pi x}{L} \right) + \alpha \sin\left(\frac{4\pi x}{L} \right) \right], \tag{2.73}$$

with $x \in [0, L]$ is the coordinate on a circle of length L. The case $\alpha = 0$ corresponds to a symmetric sine potential, while $\alpha \neq 0$ leads to a left/right asymmetry, see Fig. 2.1. This asymmetry is reminiscent of the
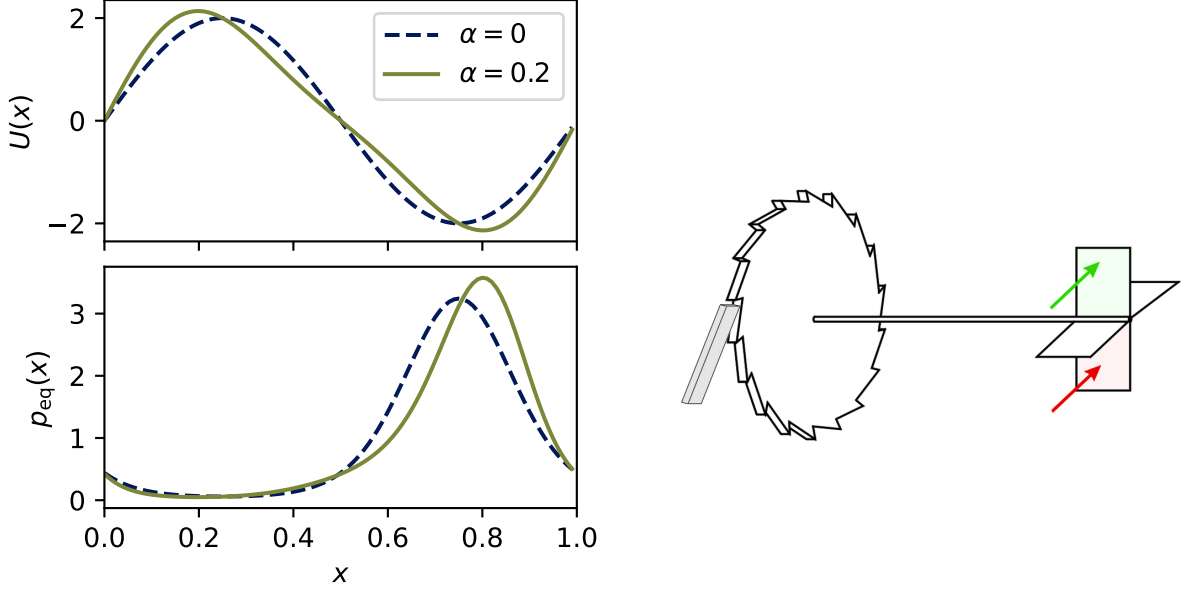
Figure 2.1: Periodic potential $U(x)$ according to Eq. (2.73) for $\alpha = 0$ and 0.2 ($U_0 = 2, L = 1$). Equilibrium probability laws at temperature $k_B T = 1$, Eq. (2.78). The asymmetric potential ($\alpha = 0.2$) mimics the Feynman ratchet thought experiment (aegon, CC BY-SA 3.0, via Wikimedia Commons).

Feynman ratchet thought experiment, see Fig. 2.1. Imagine a wheel blocked by a ratchet that allows a single direction of rotation. Can we use thermal energy to make the wheel turn in this direction? If so, we are able to extract work from a single-temperature system and therefore to break the second law of thermodynamics!

The equations of motion of the particle were derived in the previous section. The overdamped Langevin equation for the position is

$$\lambda \frac{dx}{dt} = -\partial_x U(x) + f(t), \tag{2.74}$$

$$\tag{2.75}$$

and the associated Fokker-Planck (or Smoluchovski) equation is

$$\frac{\partial p(x,t)}{\partial t} = -\partial_x J(x,t), \tag{2.76}$$

$$J(x,t) = -\frac{1}{\lambda}[\partial_x U(x)p(x,t) - k_B T \partial_x p(x,t)]. \tag{2.77}$$

The equilibrium probability law is the Boltzmann probability law

$$p_{\text{eq}}(x) = \frac{1}{Z} e^{-\frac{U(x)}{k_B T}}, \tag{2.78}$$

see Fig. 2.1. It corresponds to an absence of net flux: $J_{\text{eq}} = 0$. The answer to the Feynman paradox is that the ratchet needs to be connected to a spring. The thermal fluctuations leading to an 'opening' of ratchet and a wheel turning in the 'wrong' direction are as likely as fluctuations leading to a 'correct' rotation. The wheel does not turn on average.

We now examine two out-of-equilibrium situations: when the particle is forced, and when its noise is correlated in time.

Driven overdamped Brownian particle

Let us add an external constant force F on the particle. The Langevin equation becomes

$$\lambda \frac{dx}{dt} = F - \partial_x U(x) + f(t). \tag{2.79}$$

In the Fokker-Planck equation, the external force is simply added to the one coming from the potential:

$$\frac{\partial p(x,t)}{\partial t} = -\partial_x J(x,t), \tag{2.80}$$

$$J(x,t) = -\frac{1}{\lambda}[(\partial_x U(x) - F)p(x,t) - k_B T \partial_x p(x,t)]. \tag{2.81}$$

We shall see that there is no (normalizable) stationary solution to this solution with zero flux. Instead, the stationary solution, $\partial_t p(x,t) = 0$, leads to the more general relation $\partial_x J(x,t) = 0$ that is to say to a constant homogeneous flux $J(x) = J_{\text{stat}}$. The stationary flux and the stationary probability $p_{\text{stat}}(x)$ are linked by

$$k_B T \partial_x p_{\text{stat}}(x) + \partial_x W(x) p_{\text{stat}}(x) = -\lambda J_{\text{stat}}, \tag{2.82}$$

with $W(x) = U(x) - Fx$. The solution of this first-order differential equation is

$$p_{\text{stat}}(x) = e^{-\beta W(x)} \left[A - \lambda \beta J_{\text{stat}} \int_0^x dx' e^{\beta W(x')} \right]. \tag{2.83}$$

We end up with two unknown constants J_{stat} and A. Their values are set by (i) imposing the periodic of the solution $p_{\text{stat}}(L) = p_{\text{stat}}(0)$, and (ii) using the normalization of the probability law $\int_0^L p_{\text{stat}}(x)dx$. This leads to the two equations

$$A\left(1 - e^{-\beta FL}\right) - \lambda \beta J_{\text{stat}} \int_0^L dx e^{\beta W(x)} = 0, \tag{2.84}$$

$$A \int_0^L dx e^{-\beta W(x)} - \lambda \beta J_{\text{stat}} \int_0^L dx e^{-\beta W(x)} \int_0^x dx' e^{\beta W(x')} = 1. \tag{2.85}$$

After some manipulations, we obtain the stationary flux

$$J_{\text{stat}} = \frac{k_B T}{\lambda} \frac{1 - e^{-\beta FL}}{\int_0^L dx e^{\beta W(x)} \int_0^L dx e^{-\beta W(x)} - (1 - e^{-\beta FL}) \int_0^L dx e^{-\beta W(x)} \int_0^x dx' e^{\beta W(x')}}. \tag{2.86}$$

This expression is a bit tedious, but takes a simple form at small force $F \ll k_B T$ that is to say in the linear response regime:

$$J_{\text{stat}} \sim \frac{FL}{\lambda} \frac{1}{\int_0^L dx e^{\beta U(x)} \int_0^L dx e^{-\beta U(x)}}, \tag{2.87}$$

where $U(x)$ is the potential in which the particle is dragged. In general, the integrals cannot be computed explicitly. An exception is the sine potential, Eq. (2.73) with $\alpha = 0$, $U(x) = U_0 \sin(2\pi x/L)$. In this case,

$$J_{\text{stat}} \sim \frac{F}{\lambda L} \left[I_0 \left(\frac{U_0}{k_B T} \right) \right]^{-2}, \tag{2.88}$$

where I_0 is a modified Bessel function. One can show that the average velocity of the particle is $\langle v \rangle = L J_{\text{stat}}$. Eq. (2.88) therefore gives the linear response relation,

$$\frac{\lambda \langle v \rangle}{F} = \left[I_0 \left(\frac{U_0}{k_B T} \right) \right]^{-2}. \tag{2.89}$$

Fig. 2.2 shows the stationary flux as a function of the force for both the symmetric and asymmetric potential. For the asymmetric potential ($\alpha = 0.2$), we remark that the response to $+F$ is different from the response to $-F$. If one uses a slow oscilatory forcing (for instance $+F$ for $t \in [0, T/2]$ and $-F$ for $t \in [T/2, T]$, etc.), the particle would move on average to the left!

Active Ornstein-Uhlenbeck particle

We saw that for a particle at thermal equilibrium, there is no net flux, even in an asymmetric potential? But what about an out-of-equilibrium particle that has a noise $\xi(t)$ that is correlated in time. We introduce the model of the active Ornstein-Uhlenbeck particle (AOUP) in which $\xi(t)$ is an Ornstein-Uhlenbeck process. The Langevin equations are

$$\frac{dx}{dt} = -\frac{1}{\lambda}\partial_x U(x) + \xi(t), \tag{2.90}$$

$$\tau \frac{d\xi}{dt} = -\xi + \sqrt{2D}\eta(t), \tag{2.91}$$
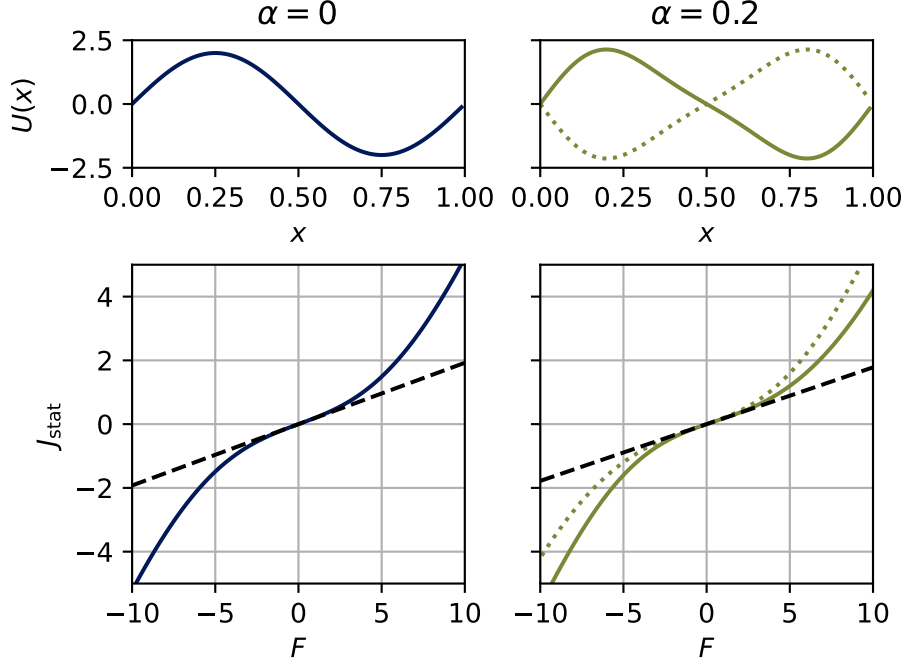
Figure 2.2: Stationary flux J_{stat} as a function of the force F on a particle in a periodic potential, Eq. (2.73). The solid lines correspond to Eq. (2.86) and the dashed black lines are the linear response from Eq. (2.87). When the potential is asymmetric ($\alpha = 0.2$), the (non-linear) response to a force is also asymmetric: a forcing to the left leads to a greater velocity than a forcing to the right. This is shown graphically with the dotted lines that correspond to the opposite potential $-U(x)$.
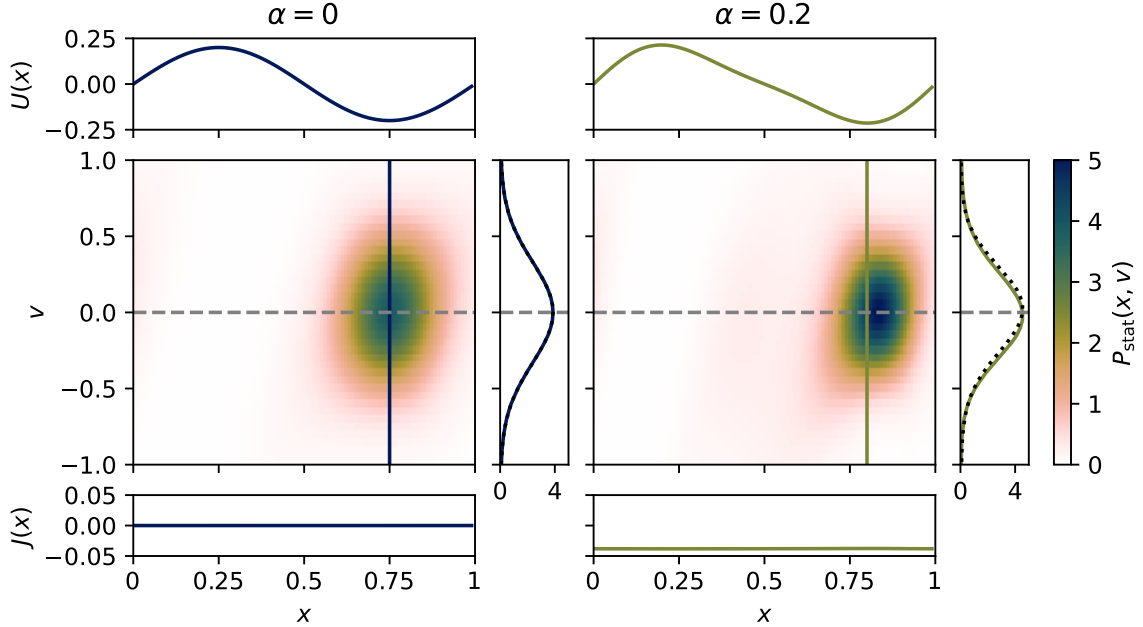
Figure 2.3: Numerical solution of the stationary solution of the Fokker-Planck equation for an AOUP in an external potential, Eq. (2.94) with $U(x)$ given by Eq. (2.73) (parameters: $U_0 = 0.2, \lambda = D = \tau = 1$). When the potential is symmetric ($\alpha = 0$) there is no net motion of the particle $J(x) = \int dv P(x, v) = 0$. But when the potential is asymmetric ($\alpha = 0.2$), there is a net flux to the right ($J \approx -0.04$). This is seen from the slight asymmetry of the cut $P(x_{\min}, v)$ where $x_{\min}$ is the minimum of the potential: the reversed curve ($v \mapsto -v$) is shown with black dots.

with $\eta(t)$ a Gaussian white noise with average $\langle \eta(t) \rangle = 0$ and unit covariance $\langle \eta(t)\eta(t') \rangle = \delta(t - t')$. When $\tau = 0$, we recover the equilibrium Langevin equation ($\xi(t) = \sqrt{2D}\eta(t)$). Eq. (2.91) is an Ornstein-Uhlenbeck process: the statistics of ξ is obtained as we did in the previous section. In particular, the stationary convariance is $\langle \xi(t)\xi(t') \rangle = \frac{D}{\tau}e^{-|t-t'|/\tau}$. We note that τ is the correlation time of the noise.

The equations (2.90)-(2.91) can be recast in term of the variables (x, v) where $v = \partial_t x$ is the velocity of the particle. The rearrangement leads to

$$\frac{dx}{dt} = v, \tag{2.92}$$

$$\tau \frac{dv}{dt} = -v - \frac{1}{\lambda}\left(\partial_x U + \tau v \partial_{xx} U\right) + \sqrt{2D}\eta(t). \tag{2.93}$$

Again, the case $\tau = 0$ gives back the equilibrium Langevin equation. We can finally obtain a Fokker-Planck equation for the probability $P(x, v, t)$ that the particle is at x with a velocity v at time t. Following the methods of the previous section, we have

$$\frac{\partial P}{\partial t}(x, v, t) = -\frac{\partial J_x}{\partial x} - \frac{\partial J_v}{\partial v}, \tag{2.94}$$

$$J_x(x, v, t) = vP(x, v, t), \tag{2.95}$$

$$J_v(x, v, t) = -\left[v + \frac{1}{\lambda}\left(\partial_x U + \tau v \partial_{xx} U\right)\right]P(x, v, t) - \frac{D}{\tau^2}\frac{\partial P}{\partial v}(x, v, t). \tag{2.96}$$

If we focus only on the probablity $p(x, t) = \int dv P(x, v, t)$, we can write

$$\frac{\partial p}{\partial t}(x, t) = -\frac{\partial J}{\partial x} \tag{2.97}$$

$$J(x, t) = \int dv J_x(x, v, t) = \int dv\, vP(x, v, t). \tag{2.98}$$

Eq. (2.94) is hard to handle analytically, but we can solve it numerically. The stationary probability $P_{\text{stat}}(x, v)$ is plotted in Fig. 2.3. For a symmetric potential ($\alpha = 0$), the stationary flux $J_{\text{stat}} = J(x, t) = 0$ vanishes. On the other hand, for an asymmetric potential, we have a net flux $J_{\text{stat}} < 0$. Introducing a time-correlated noise make the particle move on average to the left! This is an example of a *non-equilibrium stationary state* (NESS). We also notice that as soon as a system is out-of-equilibrium, there is a possibility to extract work from it, something we cannot do at equilibrium.

2.2.2 Active Brownian particle in 2D

Let us now introduce an example of self-propelled particle in 2D. Such a self-propulsion implies that the particle has access to an external energy source and is therefore out of equilibrium. There are several possible models: active Brownian particle (ABP), run-and-tumble particle, active Ornstein-Uhlenbeck particle (cf previous subsection). Let us describe an ABP. It moves at a velocity U in some direction θ in the plane. And this orientation is diffusing in time with a coefficient D_r. The equations of motion are

$$\frac{d\mathbf{r}}{dt} = U\hat{\mathbf{e}}(\theta(t)), \tag{2.99}$$

$$\frac{d\theta}{dt} = \sqrt{2D_r}\nu(t) \tag{2.100}$$

with $\hat{\mathbf{e}}(\theta) = \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$ and $\nu(t)$ a Gaussian white noise of unit variance ($\langle \nu(t)\nu(t') \rangle = \delta(t - t')$). For simplicity we did not add a noise term in the equation for $\mathbf{r}$. The particle reorient itself of a timescale D_r^{-1}, which corresponds to a persistence length $\ell_p = U/D_r$ (typical distance over which the trajectory is straight).

One can write a Fokker-Planck equation for the probability $P(\mathbf{r}, \theta, t)$ that the particle is at a position $\mathbf{r}$ with orientation θ at time t:

$$\frac{\partial P}{\partial t}(\mathbf{r}, \theta, t) = -\nabla \cdot [U\hat{\mathbf{e}}(\theta)P(\mathbf{r}, \theta, t)] + D_r\frac{\partial P}{\partial \theta^2}(\mathbf{r}, \theta, t). \tag{2.101}$$

We shall not work directly with the Fokker-Planck equation. Instead, we compute the mean square displacement (MSD)

$$\Delta^2(t) = \left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle \tag{2.102}$$
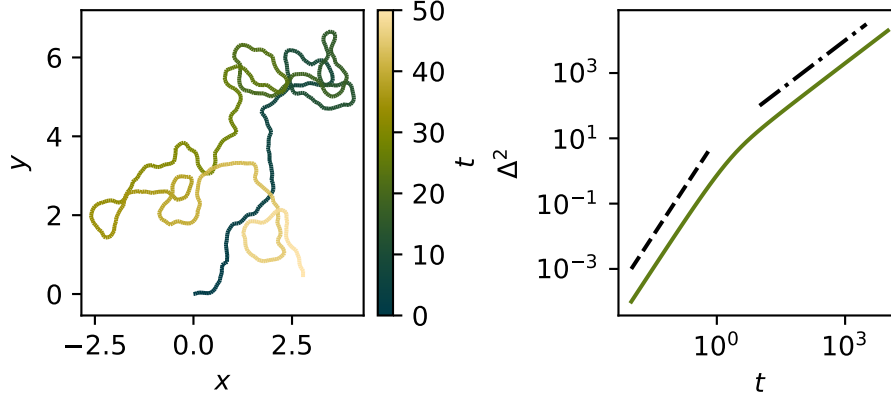
Figure 2.4: Left: typical trajectory of an active Brownian particle ($U = D_r = 1$). Right, mean square displacement Δ^2 from Eq. (2.107). The two black lines show the slopes 2 and 1 corresponding to the limits of short and large times.

directly from the Langevin equations (2.99)-(2.100). We remind the reader that for a diffusive particle $\Delta^2 \sim t$ while for a ballistic particle (propagating in a straight line) $\Delta^2(t) \sim t^2$. Injecting Eq. (2.99) into Eq. (2.102), we obtain

$$\Delta^2(t) = U^2 \left\langle \int_0^t dt_1 \hat{\mathbf{e}}(\theta(t_1)) \cdot \int_0^t dt_2 \hat{\mathbf{e}}(\theta(t_2)) \right\rangle = U^2 \int_0^t dt_1 \int_0^t dt_2 \langle \cos\left[\theta(t_1) - \theta(t_2)\right]\rangle. \tag{2.103}$$

Since Eq. (2.100) is invariant by a time translation, it is enough to compute (for $t > 0$)

$$\langle \cos\left[\theta(T + t) - \theta(t)\right]\rangle = \mathrm{Re}\langle e^{i\phi(t)}\rangle, \tag{2.104}$$

with

$$\phi(t) = \theta(t) - \theta(0) = \sqrt{2D_r} \int_0^t dt' \nu(t'). \tag{2.105}$$

One checks that ϕ is a Gaussian random variable with average $\langle\phi(t)\rangle = 0$ and variance $\langle\phi(t)^2\rangle = 2D_r t$. In Eq. (2.104), we recognize the characteristic function of ϕ[1]:

$$\langle \cos\left[\theta(T + t) - \theta(t)\right]\rangle = \mathrm{Re}\ e^{i\langle\phi(t)\rangle - \frac{1}{2}\langle\phi(t)^2\rangle} = e^{-D_r t}. \tag{2.106}$$

We can finally inject this expression in Eq (2.103) and obtain

$$\Delta^2(t) = \frac{2U^2}{D_r} \left(t - \frac{1 - e^{-D_r t}}{D_r} \right). \tag{2.107}$$

It is useful to investigate the limits of short time and large time:

$$\Delta^2(t) \sim \begin{cases} (Ut)^2 & \text{if } t \ll D_r^{-1} \\ 2\frac{U^2}{D_r}t & \text{if } t \gg D_r^{-1} \end{cases}. \tag{2.108}$$

The particle is ballistic at short time (with a velocity U) and diffusive at large time (with an effective diffusion constant U^2/D_r).

As a side remark, an assembly of interacting ABPs (that repel one another at short distance) can have a highly non-trivial behavior at high density: the particles can separate in two phases: a dense one ("liquid") and a dilute one ("gas"'). This phenomenon is known as motility-induced phase separation (MIPS).

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[1] Consider a Gaussian random variable x of average μ and standard deviation σ. Its probability law is $p(x) = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-x^2/(2\sigma^2)}$. The characteristic function is the Fourier transform of the probability law: $G(k) = \langle e^{ikx}\rangle$. Its expression is $G(k) = e^{ik\mu - \frac{1}{2}\sigma^2 k^2}$.

2.3 Multiplicative noise

When modeling a (1D) stochastic process $x(t)$, we are tempted to write a general Langevin equation as

$$\frac{dx}{dt} = a(x) + b(x)\eta(t), \qquad (2.109)$$

with $\eta(t)$ a Gaussian white noise of unit variance $\langle \eta(t)\eta(t')\rangle = \delta(t-t')^2$. In the previous sections, we always had $b(x) = b$ independent of x. In this case, called *additive noise*, Eq. (2.109) is well defined. But when b depends explicitly on x, the noise is *multiplicative*, and we will see that Eq. (2.109) is ambiguous. We will need to specify an *interpretation* of the stochastic differential equation.

The basic and advanced concepts of stochastic differential equations, in particular the discussion of the Ito-Stratonovich dilemma, can be found in Refs. [5, 6], or in Ref. [7] for a more mathematical treatement.

2.3.1 Examples

Let us give some physically motivated examples of stochastic differential equations with multiplicative noise.

- It may happen that a physical parameter of a system is subjected to thermal noise. For instance, the frequency of an oscillator may be noisy. In this case, we talk about *external noise*. A simple equation for a complex oscillator $z(t)$ is

$$\frac{dz}{dt} = iz(t)[\omega + \sqrt{2\gamma}\eta(t)], \qquad (2.110)$$

where ω is the average frequency of the oscillator and γ encodes the fluctuations of the frequency.

- Imagine a collection of $n(t)$ radioactive particles decaying with average rate α. The fluctuations of the decay rate are of the order of the fluctuations of the number of particles, that is to say $\sqrt{n}$. We may write a stochastic equation of the form

$$\frac{dn}{dt} = -\alpha n(t) + \sqrt{2\Gamma n(t)}\eta(t), \qquad (2.111)$$

where Γ set the scale of the fluctuations. Since the multiplicative nature of the noise comes from the system itself, we talk about *internal noise*. (Note that this kind of problem is usually better dealt at the discrete level with a master equation [5].)

- In mathematical finance, and in particular in the Black and Scholes model, the price of an asset $S(t)$ may be modeled by the following stochastic differential equation with multiplicative noise,

$$\frac{dS}{dt} = \mu S(t) + \sigma S(t)\eta(t), \qquad (2.112)$$

where σ is the volatility of the asset. This equation is also called geometric Brownian motion is a more general context.

2.3.2 Interpreting the multiplicative noise

Let us try to give a meaning to Eq. (2.109). The main question is what is the value of $\Delta x_t = x(t+\Delta t) - x(t)$ for a small time increment Δt?

We first consider the Brownian motion (or Wiener process) $W(t) = \int_0^t dt\,\eta(t)$ and write $\Delta W_t = W(t + \Delta t) - W(t) = \int_t^{t+\Delta t} \eta(t)dt$. It is easy to see that ΔW_t is a Gaussian variable with standard deviation $\sqrt{\Delta t}$. ΔW_t is therefore of the order $O(\sqrt{\Delta t})$, which is much larger that Δt. From Eq. (2.109), we expect the same for Δx_t: it is also of order $\sqrt{\Delta t}$. This creates a problem when discretizing Eq. (2.109) at order Δt: we may write

$$x(t + \Delta t) - x(t) = a(x^*)\Delta t + b(x^*)\Delta W_t. \qquad (2.113)$$

Clearly x^* should be between $x(t)$ and $x(t + \Delta t)$. But these two values differ by an order $\sqrt{\Delta t}$. And we can see that changing x^* by $O(\sqrt{\Delta t})$ changes Eq. (2.113) by a factor $O(\Delta t)$ that we cannot neglect!

We therefore need to prescribe the value of x^*. Two popular conventions are

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[2]For simplicity, we do not include an explicit time dependence of a and b.

- Ito interpretation: $x^* = x(t)$,

- Stratonovich interpretation: $x^* = \frac{1}{2}[x(t) + x(t + \Delta t)]$.

We now describe the consequences of each interpretation, without providing all the proofs that can be found in the litterature [5, 6].

2.3.3 Ito interpretation and Ito formula

The Ito interpretation corresponds to $x^* = x(t)$ in Eq. (2.113). Eq. (2.109) becomes

$$x(t + \Delta t) - x(t) \overset{I}{=} a(x(t))\Delta t + b(x(t))\Delta W_t. \tag{2.114}$$

We use the notation $\overset{I}{=}$ to denote the Ito convention. Let us list a few properties of the Ito interpretation.

- It is natural from a mathematical perspective since the solution of the equation is a Markov process: the time evolution of $x(t)$ for $t > t_0$ depends only on the value $x(t_0)$ and the realization of the noise $\eta(t)$ for $t > t_0$. In particular the values of the process $x(t)$ and of the noise $\eta(t)$ at the same time are independent: for an arbitrary function f we have $\langle f(x(t))\eta(t)\rangle = 0$.

- However, one peculiarity is that the chain rule cannot be applied naively. Let us consider a function $f(x)$, and its increment $\Delta f_t = f(x(t+\Delta t)) - f(x(t))$. Then $\Delta f_t \neq f'(x(t))\Delta x$. Instead, the correct differentiation rule is

$$\Delta f_t \overset{I}{=} \left[a(x(t))f'(x(t)) + \frac{1}{2}b(x(t))^2 f''(x(t)) \right] \Delta t + b(x(t))f'(x(t))\Delta W_t, \tag{2.115}$$

which may be written as

$$\boxed{\frac{df}{dt} \overset{I}{=} a(x(t))f'(x(t)) + \frac{1}{2}b(x(t))^2 f''(x(t)) + b(x(t))f'(x(t))\eta(t),} \tag{2.116}$$

with $\langle \eta(t)\eta(t')\rangle = \delta(t - t')$. Note the additional term $b(x)f'(x)/2$ compared with the naive expectation. This important result is known as the Ito formula.

- The Fokker-Planck equation associated with the Ito stochastic differential equation is:

$$\frac{\partial p}{\partial t}(x, t) = -\frac{\partial}{\partial x}\left[a(x)p(x, t) \right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[b(x)^2 p(x, t) \right]. \tag{2.117}$$

Note that the Fokker-Planck equation defines uniquely the stochastic process. It is not subjected to problems of interpretation.

Sketch of the derivation of the Ito formula, Eq. (2.116).

$$f(x(t + \Delta t)) = f(x(t) + a(x(t))\Delta t + b(x(t))\Delta W) \tag{2.118}$$

$$= f(x(t)) + f'(x(t))\{a(x(t))\Delta t + b(x(t))\Delta W\} + \frac{1}{2}f''(x(t))\{a(x(t))\Delta t + b(x(t))\Delta W\}^2 \tag{2.119}$$

$$= f(x(t)) + f'(x(t))\{a(x(t))\Delta t + b(x(t))\Delta W\} + \frac{1}{2}b(x(t))^2 f''(x(t))(\Delta W)^2 \tag{2.120}$$

$$= f(x(t)) + \left\{ f'(x(t))a(x(t)) + \frac{1}{2}b(x(t))^2 f''(x(t)) \right\}\Delta t + f'(x(t))b(x(t))\Delta W \tag{2.121}$$

We restricted ourselves to order Δt and use that $(\Delta W)^2 = \Delta t$. This last equality is actually rigourous from a mathematical standpoint, but we shall not prove it here, see for instance [6, 7].

Derivation of the Fokker-Planck equation, Eq. (2.117).   Let us consider an arbitrary function $f(x)$ and consider the time evolution of its average $\langle f(x)\rangle(t)$. From the Ito formula (2.116),

$$\frac{d\langle f(x)\rangle}{dt} = \left\langle a(x(t))f'(x(t)) + \frac{1}{2}b(x(t))^2 f''(x(t)) \right\rangle \tag{2.122}$$

$$= \int dx\, p(x,t)\left[a(x)f'(x) + \frac{1}{2}b(x)^2 f''(x)\right] \tag{2.123}$$

$$= \int dx\, f(x)\left[-\partial_x(a(x)p(x,t)) + \frac{1}{2}\partial_{xx}[b(x)^2 p(x,t)]\right]. \tag{2.124}$$

We introduced the probability distribution $p(x,t)$ and performed integrations by parts. We notice that we can also write $\langle f(x)\rangle(t) = \int dx f(x)p(x,t)$, and therefore

$$\frac{d\langle f(x)\rangle}{dt} = \int dx\, f(x)\partial_t p(x,t). \tag{2.125}$$

Using that f is an arbitrary function, Eqs. (2.124)-(2.125) give the Fokker-Planck equation (2.117).

2.3.4 Stratonovich interpretation

The Stratonovich interpretation corresponds to $x^* = x(t+\Delta t/2)$ in Eq. (2.113) (midpoint discretization). Let us compare it to the Ito interpretation.

- It is unnatural at first sight since $x(t)$ becomes an anticipating function.

- But one big advantage is that the chain rule holds:

$$\Delta f(x(t)) \overset{S}{=} f'(x(t))\left[a(x(t))\Delta t + b(x(t))\Delta W_t\right]. \tag{2.126}$$

- The Fokker-Planck equation in the Stratonovich convention reads:

$$\frac{\partial p}{\partial t}(x,t) = -\frac{\partial}{\partial x}\left[a(x)p(x,t)\right] + \frac{1}{2}\frac{\partial}{\partial x}\left[b(x)\frac{\partial}{\partial x}\left(b(x)p(x,t)\right)\right]. \tag{2.127}$$

- By comparing the Fokker-Planck equations (2.117) and (2.127). One notices that one can go from one interpretation to another by changing the drift term:

$$\frac{dx}{dt} \overset{S}{=} a(x) + b(x)\eta(t) \qquad \Leftrightarrow \qquad \frac{dx}{dt} \overset{I}{=} \left[a(x) + \frac{1}{2}b(x)\partial_x b(x)\right] + b(x)\eta(t). \tag{2.128}$$

  The Ito or Stratonovich convention is merely a matter of choice: the same system can be described in one interpretation or the other. Note that the change of drift term Eq. (2.128) is consistent with the differentiation rules Eqs (2.116) and (2.126).

Equivalence between Ito and Stratonovich conventions.   We prove our claims backward: we prove Eq. (2.128), then Eq. (2.127) follows from the Ito Fokker-Planck equation, and Eq. (2.126) is an application of the Ito formula.

Starting from Eq. (2.109) in the Stratonovich convention, we write[3]

$$x(t) = x(0) + \int_0^t dt'\, a(x(t')) + S\int_0^t b(x(t'))\eta(t')dt' \tag{2.129}$$

where $S\int$ denotes the integral in the Stratonovich convention. We discretize the path into N intervals of size Δt and write $t_n = n\Delta t$, $x_n = x(t_n)$, $\Delta x_n = x_{n+1} - x_n$, $\Delta W_n = \int_{t_n}^{t_{n+1}} \eta(t')dt'$. By definition the Stratonovich integral is

$$S\int_0^t b(x(t'))\eta(t')dt' = \lim_{\Delta t\to 0}\sum_{n=0}^{N-1} b\left(\frac{x_n + x_{n+1}}{2}\right)\Delta W_n. \tag{2.130}$$

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[3]The following lines are a bit sketchy, see Ref. [6], section 4.3.6. for more details.

We expand b, use the Stratonovich value of Δx_n and only keep the terms up to order $O(\Delta t)$.

$$S \int_0^t b(x(t'))\eta(t')dt' = \lim_{\Delta t \to 0} \sum_{n=0}^{N-1} \left[b(x_n) + \frac{1}{2} b'(x_n)\Delta x_n + o((\Delta t)^{1/2}) \right] \Delta W_n \tag{2.131}$$

$$= \lim_{\Delta t \to 0} \sum_{n=0}^{N-1} \left[b(x_n) + \frac{1}{2} b'(x_n) \left(a(x_n^*)\Delta t + b(x_n^*)\Delta W_n \right) + o((\Delta t)^{1/2}) \right] \Delta W_n \tag{2.132}$$

$$= \lim_{\Delta t \to 0} \sum_{n=0}^{N-1} b(x_n)\Delta W_n + \frac{1}{2} b'(x_n)b(x_n)(\Delta W_n)^2 + o(\Delta t) \tag{2.133}$$

$$= \lim_{\Delta t \to 0} \sum_{n=0}^{N-1} b(x_n)\Delta W_n + \frac{1}{2} b'(x_n)b(x_n)\Delta t + o(\Delta t) \tag{2.134}$$

$$= I \int_0^t b(x(t'))\eta(t')dt' + \int_0^t \frac{1}{2} b'(x(t'))b(x(t'))dt' \tag{2.135}$$

The Ito integral is defined as

$$I \int_0^t b(x(t'))\eta(t')dt' = \lim_{\Delta t \to 0} \sum_{n=0}^{N-1} b(x_n)\Delta W_n. \tag{2.136}$$

Injecting into Eq. (2.129), we obtain

$$x(t) = x(0) + \int_0^t dt' \left[a(x(t')) + \frac{1}{2} b'(x(t'))b(x(t')) \right] + I \int_0^t b(x(t'))\eta(t')dt'. \tag{2.137}$$

This provides the equivalent Ito equation, given by Eq. (2.128).

2.3.5 Which one to use for a given physical system?

Although one can choose freely the interpretation, the question of which one is the most natural for a given system remains. In particular, it is natural to see $a(x)$ as a force acting on the particle, that would remain unchanged in the absence of noise.

Stratonovich for physical systems with external noise

In actual physical systems, the external noise has a finite correlation time τ. The delta-correlated noise

$$\langle \eta(t)\eta(t') \rangle = \delta(t - t') \tag{2.138}$$

is an idealization of something like

$$\langle \eta_\tau(t)\eta_\tau(t') \rangle = \frac{1}{2\tau} e^{-\frac{|t-t'|}{\tau}} \tag{2.139}$$

where we chose an exponential decay for simplicity. The equation

$$\frac{dx}{dt} = a(x) + b(x)\eta_\tau(t) \tag{2.140}$$

is well-defined (not subjected to a choice of interpretation), and it is natural to wonder what is the correct limit of vanishing correlation time $\tau \to 0$. Wong and Zakai showed [8] that it is the Stratonovich equation

$$\frac{dx}{dt} \stackrel{S}{=} a(x) + b(x)\eta(t). \tag{2.141}$$

This provides a basis to use the Stratonovich interpretation for physical systems with external noise, see Ref. [5] for a detailed discussion.

For instance, the noisy complex oscillator, Eq. (2.110) should be interpreted as (see Ref. [6])

$$\frac{dz}{dt} \stackrel{S}{=} iz(t)[\omega + \sqrt{2\gamma}\eta(t)] \qquad \Leftrightarrow \qquad \frac{dz}{dt} \stackrel{I}{=} z(t)[(i\omega - \gamma) + i\sqrt{2\gamma}\eta(t)] \tag{2.142}$$

One checks that the average value and the correlation are

$$\langle z(t) \rangle = z(0)e^{(i\omega-\gamma)t}, \tag{2.143}$$

$$\langle z(t)z(t')^* \rangle = |z(0)|^2 e^{i\omega(t-t')-\gamma|t-t'|}. \tag{2.144}$$

The noise induces a damping term: the initial condition is lost, and a dephasing is produced.

Ito when explicitly assumed, and for internal noise

The Ito convention mostly occurs in situations where it is assumed from the start. As we said before it is the most natural convention to start with from a mathematical perspective. The Ito convention is also often the correct one for systems with internal noise: when the noise comes from the fluctuations of the variable itself (such as a number of particles), it is reasonable to evaluate its variable at the beginning of a time interval Δt. We give a few examples with Ito convention below.

- The stochastic equation for radioactive decay, Eq. (2.111), is best interpreted in the Ito convention. The Fokker-Planck equation is

$$\frac{\partial p(n,t)}{\partial t} = \alpha \frac{\partial}{\partial n} \left[np(n,t) \right] + \Gamma \frac{\partial^2}{\partial n^2} \left[np(n,t) \right]. \tag{2.145}$$

  This gives the expected equation for the decay of the average value,

$$\frac{d\langle n \rangle}{dt} = -\alpha \langle n \rangle. \tag{2.146}$$

  One checks that a different equation would have been obtained in the Stratonovich convention. See Ref. [5] for more details.

- The geometric Brownian motion in the Black-Scholes model, Eq. (2.112), is to be understood in the Ito sense,

$$\frac{dS}{dt} \stackrel{I}{=} \mu S(t) + \sigma S(t)\eta(t). \tag{2.147}$$

  Applying the Ito formula, one obtains

$$\frac{d}{dt} \log S = \mu - \frac{1}{2}\sigma^2 + \sigma\eta(t), \tag{2.148}$$

  that is to say

$$S(t) = \exp \left[\left(\mu - \frac{1}{2}\sigma^2 \right) t + \sigma \int_0^t dt' \eta(t') \right]. \tag{2.149}$$

  The main question of option pricing is the following one. Assume that you are offered an option that guarantees you to be paid an amount $K(S(T))$ at time T (for instance $K(S(T)) = \max(S(T) - K_0, 0)$ with fixed K_0). What is the correct price of such an option at time $t = 0$? See Ref. [7] for more details.

- In a latter chapter, we will introduce the stochastic partial differential equation for a density field $\rho(x,t)$, known as the Dean-Kawasaki equation [9]. The multiplicative noise will take the form $\sqrt{\rho(x,t)}\eta(x,t)$ with η a Gaussian white noise. The Ito convention will be assumed from the start to perform the derivation from the microscopic equations for the particles.

2.3.6   Change of variables

Even for a stochastic differential equation with additive noise, a choice of convention may be needed. The most obvious case is if one needs to consider averages of the type $\langle f(x(t))\eta(t) \rangle$ where $x(t)$ is the stochastic process, $\eta(t)$ is the noise and f is an arbitrary function.

In practice the problem often arises when one performs a change of variable $\tilde{x}(t) = \phi(x(t))$ where ϕ is a non-linear function. Even if the noise in the equation for $x(t)$ is additive, the noise for $\tilde{x}(t)$ will be multiplicative. Care must be taken when performing the change of variable. See Ref. [10] for a detailed discussion.

A simple example is the kinetic energy of a particle. We start with the Langevin equation for the velocity of the particle,

$$\frac{dv}{dt} = -\zeta v + \sqrt{\frac{2\zeta k_B T}{m}}\eta(t), \tag{2.150}$$

and define the kinetic energy $K(v) = \frac{1}{2}mv^2$. If we choose Stratonovich, we can perform the change of variable as usual:

$$\frac{dK}{dt} \stackrel{S}{=} K'(v)\frac{dv}{dt} \stackrel{S}{=} -2\zeta K(v) + \sqrt{4\zeta k_B T K(v)}\eta(t). \tag{2.151}$$

On the contrary, in the Ito interpretation, one needs to use the Ito formula (or the correspondance between Ito and Stratonovich equation) to obtain

$$\frac{dK}{dt} \overset{I}{=} -2\zeta K(v) + \zeta k_B T + \sqrt{4\zeta k_B T K(v)}\eta(t). \tag{2.152}$$

This last equation gives the evolution of the average kinetic energy as $\frac{d\langle K\rangle}{dt} = -2\zeta \left(\langle K\rangle - \frac{k_B T}{2}\right)$, and therefore the averge kinetic energy at equilibrium: $\langle K\rangle = \frac{k_B T}{2}$ which satisfies the equipartition of energy.

2.4 Path integral approach to Langevin equation

Let us start with the following Langevin equation with additive noise,

$$\frac{dx}{dt} = a(x(t)) + \sqrt{2D}\eta(t), \tag{2.153}$$

where η is a Gaussian white noise of unit variance. Our goal is to determine the probability of a given path $\{x(t)\}$ between times $t = 0$ and $t = t_f$, knowing the initial position x_0: $P\left[\{x(t)\}_{t=0}^{t_f}|x_0\right]$.

Probability of a discretized path

In order to acheive our goal, we discretize Eq. (2.153) into $N \gg 1$ time intervals of duration $\Delta t \ll 1$, with $t_f = N\Delta t$. Even for additive noise, path integrals require a precise discretization scheme [11]: we choose the Stratonovich convention. We denote $x_n = x(n\Delta t)$ and obtain

$$x_{n+1} - x_n = a_n\Delta t + \sqrt{2D\Delta t}\gamma_n, \tag{2.154}$$

with γ_n independent Gaussian numbers of unit variance. Within the Stratonovich discretization,

$$a_n \overset{S}{=} a\left(\frac{x_n + x_{n+1}}{2}\right) \approx a(x_n) + \frac{1}{2}a'(x_n)(x_{n+1} - x_n). \tag{2.155}$$

The probability of a discrete path $x_1, \ldots, x_N$ starting from x_0 can be written as

$$P_N(x_1, \ldots, x_N|x_0) = \prod_{n=0}^{N-1} p(x_{n+1}|x_n). \tag{2.156}$$

We used the Markovian nature of the discrete process, and $p(x_{n+1}|x_n)$ denotes the probability of observing x_{n+1} knowning x_n. Using Eqs. (2.154)-(2.155), we notice that γ_n and x_{n+1} are linked by an affine change of variables,

$$\gamma_n = \frac{1}{\sqrt{2D\Delta t}}\left[\left(1 - \frac{1}{2}a'(x_n)\Delta t\right)(x_{n+1} - x_n) - a(x_n)\Delta t\right]. \tag{2.157}$$

The probability law of γ_n is $p(\gamma_n) = \frac{1}{\sqrt{2\pi}}e^{-\frac{\gamma_n^2}{2}}$. The change of variable, Eq. (2.157), leads to

$$p(x_{n+1}|x_n) = \frac{1 - \frac{1}{2}a'(x_n)\Delta t}{\sqrt{4\pi D\Delta t}}e^{-\frac{1}{4D\Delta t}\left[1 - \frac{1}{2}a'(x_n)\Delta t\right]^2(x_{n+1} - x_n - a(x_n)\Delta t)^2}. \tag{2.158}$$

For small Δt, we can write the term inside the exponential at order Δt as

$$p(x_{n+1}|x_n) \approx \frac{1}{\sqrt{4\pi D\Delta t}}e^{-\Delta t\frac{1}{2}a'(x_n)}e^{-\Delta t\frac{1}{4D}\left(\frac{x_{n+1} - x_n}{\Delta t} - a(x_n)\right)^2}. \tag{2.159}$$

The probability of a discrete path, Eq. (2.156), is

$$P_N(x_1, \ldots, x_N|x_0) = \frac{1}{(2\pi D\Delta t)^{N/2}}e^{-\Delta t\sum_{n=0}^{N-1}\left[\frac{1}{4D}\left(\frac{x_{n+1} - x_n}{\Delta t} - a(x_n)\right)^2 + \frac{1}{2}a'(x_n)\right]}. \tag{2.160}$$

Onsager-Machlup action

It is customary to write the continuous limit of Eq. (2.160) as

$$P\left[\{x(t)\}_{t=0}^{t_f}|x_0\right] = \mathcal{N}e^{-S[\{x(t)\}]} \tag{2.161}$$

with the action

$$\boxed{S[\{x(t)\}] \overset{S}{=} \int_0^{t_f} dt\left(\frac{1}{4D}\left[\dot{x}(t) - a(x(t))\right]^2 + \frac{1}{2}a'(x(t))\right)} \tag{2.162}$$

and a diverging normalization factor $\mathcal{N}$ that we usually forget; note however that it is independent of the initial condition and the force field. Eq. (2.162) is known as the Onsager-Machlup action.

The same computation can be done in the Ito formalism, and one obtains

$$S[\{x(t)\}] \overset{I}{=} \frac{1}{4D}\int_0^{t_f} dt\left[\dot{x}(t) - a(x(t))\right]^2. \tag{2.163}$$

Comment on the Ito and Stratonovich integrals

We stress that $S[\{x(t)\}]$ is *the same* in Eqs. (2.162) and (2.163). The convention enters in the definition of the integral from a discretized path. To emphasize this point, let us consider the following observable

$$\mathcal{W}_\alpha \overset{\alpha}{=} \int_0^{t_f} \dot{x}(t)f(x(t))dt, \tag{2.164}$$

where $\alpha = I$ or S. If f is a (position-dependent) force, $\mathcal{W}_\alpha$ is interpreted as the work (see the next chapter on stochastic thermodynamics). The integrals $\mathcal{W}_I$ and $\mathcal{W}_S$ are *defined* as

$$\mathcal{W}_I = \lim_{\Delta t \to 0} \Delta t \sum_{n=0}^{N-1} \frac{x_{n+1} - x_n}{\Delta t} f(x_n), \tag{2.165}$$

$$\mathcal{W}_S = \lim_{\Delta t \to 0} \Delta t \sum_{n=0}^{N-1} \frac{x_{n+1} - x_n}{\Delta t} f\left(\frac{x_n + x_{n+1}}{2}\right), \tag{2.166}$$

with $x_n = x(n\Delta t)$. Since $x_{n+1} - x_n = O(\sqrt{\Delta t})$, the two definitions are not equivalent. In fact, assuming Eq. (2.153), it can be shown that

$$\mathcal{W}_S = \mathcal{W}_I + D\int_0^{t_f} f'(x(t))dt, \tag{2.167}$$

where the last integral is shown to be independent of the convention. One can prove that $\int dt\,\dot{x}^2(t)$ and $\int dt\,a(x(t))^2$ are also convention-independent. Therefore, Eq. (2.167) gives the equality between Eqs. (2.162) and (2.163). In stochastic thermodynamics, the work will be assumed to be given by the Stratonovich convention, Eq. (2.166) which is why we will stick to this convention. See Ref. [11] for more details on these subtle issues.

Meaning of the Onsager-Machlup action

Let us finally point out that the meaning of Eqs. (2.161)-(2.162) is not clear from a mathematical perspective: (i) a typical path $\{x(t)\}$ is typically non differentiable, so $\dot{x}(t)$ is ill-defined, and (ii) the normalization $\mathcal{N}$ is diverging. Both problems can be solved by considering two differentiable paths $X_1(t)$ and $X_2(t)$ and writing the ratio of the probability that a realization $x(t)$ of the stochastic differential equation is close to one of the paths. The precise meaning of Eqs. (2.161)-(2.162) is

$$\lim_{\epsilon \to 0} \frac{\text{Prob}\left(|x(t) - X_1(t)| < \epsilon \quad \forall t \in [0, t_f]\right)}{\text{Prob}\left(|x(t) - X_2(t)| < \epsilon \quad \forall t \in [0, t_f]\right)} = e^{-S[\{X_1(t)\}] + S[\{X_2(t)\}]}. \tag{2.168}$$

2.5   The Feynman-Kac formula

This section is mostly based on Chaps. 7 and 8 of Ref. [7]. We shall state the results without any proof.

Let us start with the generic Ito stochastic differential equation

$$\frac{dx}{dt} \overset{I}{=} a(x(t)) + b(x(t))\eta(t), \tag{2.169}$$

with $\langle \eta(t)\eta(t') \rangle = \delta(t - t')$. We consider the probability $P(x_f, t_f; x_i, t_i)$ that the particle is at x_f at time t_f knowing that it was at x_i at time t_i. The boundary condition (initial or final depending on the context) is

$$P(x_f, t; x_i, t) = \delta(x_f - x_i). \tag{2.170}$$

We already saw the Fokker-Planck equation, also known as the forward Kolmogorov equation,

$$\frac{\partial P(x_f, t_f; x_i, t_i)}{\partial t_f} = \mathcal{L}_f^\dagger P(x_f, t_f; x_i, t_i), \tag{2.171}$$

with Eq. (2.170) as initial condition. But there is a backward equivalent, the backward Kolmogorov equation

$$\frac{\partial P(x_f, t_f; x_i, t_i)}{\partial t_i} = -\mathcal{L}_i P(x_f, t_f; x_i, t_i), \tag{2.172}$$

with Eq. (2.170) as final condition. $\mathcal{L}_i$ acts on x_i while $\mathcal{L}_f^\dagger$ acts on x_f. The operator $\mathcal{L}$ is the generator of the process[4] and $\mathcal{L}^\dagger$ is its adjoint. In the case of Eq. (2.169), there are given by

$$\mathcal{L}f(x) = a(x)\partial_x f(x) + \frac{1}{2}b(x)^2 \partial_{xx} f(x), \tag{2.173}$$

$$\mathcal{L}^\dagger f(x) = -\partial_x[a(x)f(x)] + \frac{1}{2}\partial_{xx}[b(x)^2 f(x)]. \tag{2.174}$$

A slight generalization of the backward Kolmogorov equation is that if a function $u(x, t)$ satifies the system

$$\begin{cases} \frac{\partial u(x,t)}{\partial t} = -\mathcal{L}u(x,t) & \text{for } t < t_f \\ u(x, t_f) = \Phi(x) \end{cases} \tag{2.175}$$

for an arbitrary final condition Φ at time t_f, then u can be expressed as

$$u(x_i, t_i) = \mathbb{E}\left[\Phi(x(t_f))|x(t_i) = x_i\right], \tag{2.176}$$

where $x(t)$ follows the stochastic differential equation (2.169), $\mathbb{E}$ denotes a conditional expectation (average given an initial condition), and $t_i \leq t_f$. Eqs. (2.175)-(2.175) are actually equivalent. The backward Kolmogorov equation (2.174) corresponds to the case $\Phi(x) = \delta(x - x_f)$.

We can go further and add a space-dependent decay $q(x)$. It may be interpreted as a probability that at each small time interval the "particle" can disappear from the system, and then give no contribution at the final time. We consider the partial differential equation

$$\begin{cases} \frac{\partial v(x,t)}{\partial t} = -\mathcal{L}v(x,t) - q(x)v(x,t) & \text{for } t < t_f \\ v(x, t_f) = \Phi(x) \end{cases}. \tag{2.177}$$

It is equivalent to

$$v(x_i, t_i) = \mathbb{E}\left[\exp\left(-\int_{t_i}^{t_f} dt\, q(x(t))\right)\Phi(x(t_f))\middle| x(t_i) = x_i\right], \tag{2.178}$$

with $x(t)$ following Eq. (2.169). This equivalence is known as the Feynman-Kac formula. The Feynman-Kac formula enters into problem of mathematical finance (where $\Phi(x(t_f))$ is intepreted as a cost in the future) for instance in the Black-Scholes formula [7]. It is also useful in some quantum mechanics problems, in particular in connection with path integrals.

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[4]Its formal definition is $\lim_{\epsilon \to 0^+} \frac{1}{\epsilon}\left(\mathbb{E}[f(x(\epsilon))|x(0) = x_0] - f(x_0)\right) = \mathcal{L}f(x_0)$ for an arbitrary function f [7].

Chapter 3

Driven systems

3.1 Correlation, linear response, and fluctuation-dissipation theorem

3.1.1 Statement of the fluctuation-dissipation theorem

We consider a system evolving with a stochastic dynamics compatible with equilibrium: master equation with detailed balance, Langevin equation with the Einstein relation, etc. We define the different quantities using the notations for a discrete system, but their definitions are similar for a continuous system.

A configuration of the system is defined by the probability p_i to occupy the state i with energy E_i. For an observable A taking the value A_i on the site i, we define its average value at time t as

$$\langle A(t) \rangle = \sum_i A_i p_i(t). \tag{3.1}$$

We can also define the two-time correlation of two observables:

$$\langle A(t)B(t') \rangle = \sum_{i,j} A_i B_j p_i(t) p_j(t'). \tag{3.2}$$

When the system is at equilibrium, the correlation function is a function of the time difference only:

$$\langle A(t)B(t') \rangle = C_{AB}(t - t'). \tag{3.3}$$

We will compare this correlation to the linear response to an energy variation $E_i \rightarrow E_i - f(t)B_i$, where $f(t)$ is the small force conjugated to the observable B. This force affects the average value of the observable A: $\langle A(t) \rangle \rightarrow \langle A(t) \rangle + \delta\langle A(t) \rangle$. In the linear response regime close to equilibrium, the variation can be written as

$$\delta\langle A(t) \rangle = \int_{-\infty}^{t} R_{AB}(t - t')f(t')dt', \tag{3.4}$$

which defines the response function $R_{AB}(t)$. Causality implies that $R_{AB}(t) = 0$ for $t < 0$.

The fluctuation-dissipation theorem relates the response to the correlation: for $t \geq 0$,

$$R_{AB}(t) = -\frac{1}{T}\dot{C}_{AB}(t), \tag{3.5}$$

where T is the temperature of the system.

3.1.2 Proof for a discrete system

Here, we assume that the probability distribution $p(t) = (p_i(t))$ follows the master equation

$$\dot{p}(t) = Mp(t), \tag{3.6}$$

where the components of M, the transition rates M_{ij}, satisfy the detailed balance condition,

$$M_{ij}e^{-E_j/T} = M_{ji}e^{-E_i/T}. \tag{3.7}$$

First, we compute the correlation at equilibrium, $C_{AB}(t) = \langle A(t)B(0) \rangle$. At time 0, the system is at equilibrium and the probability to observe the state j is $p_j^{\text{eq}} = e^{-E_j/T}/Z$, where the observable B takes the value B_j. Being in the state j at time $t = 0$, the system as then the probability $(e^{tM})_{ij}$ to be in the state i at time t, where the observable A takes the value A_i. The correlation is thus

$$C_{AB}(t) = \sum_{i,j} A_i \left(e^{tM} \right)_{ij} B_j p_j^{\text{eq}}. \tag{3.8}$$

Second, we compute the response to an energy change $\delta E_i = -f(t)B_i$. This energy change induces a change $\delta M(t)$ in the transition rates, which have to satisfy detailed balance:

$$[M_{ij} + \delta M_{ij}(t)] \exp\left(-\frac{E_j - f(t)B_j}{T} \right) = [M_{ji} + \delta M_{ji}(t)] \exp\left(-\frac{E_i - f(t)B_i}{T} \right). \tag{3.9}$$

At first order in $f(t)$, writing $\delta M(t) = f(t)M'$, we find

$$\left(M_{ij} \frac{B_j}{T} + M'_{ij} \right) p_j^{\text{eq}} = \left(M_{ji} \frac{B_i}{T} + M'_{ji} \right) p_i^{\text{eq}}. \tag{3.10}$$

The variation of the transition rates induce a variation of the probability distribution, $p_i = p_i^{\text{eq}} + \delta p_i$, which follows,

$$\delta \dot{p}(t) = M \delta p(t) + f(t)M' p^{\text{eq}}. \tag{3.11}$$

The solution is thus

$$\delta p(t) = \int_{-\infty}^{t} e^{(t-t')M} M' p^{\text{eq}} f(t') dt'. \tag{3.12}$$

From this, we deduce the variation of the average of the observable A:

$$\delta \langle A(t) \rangle = \sum_i A_i \delta p_i(t) = \int_{-\infty}^{t} \sum_{i,j} A_i \left(e^{(t-t')M} M' \right)_{ij} p_j^{\text{eq}} f(t') dt', \tag{3.13}$$

which is of the form (3.4), with the response function

$$R_{AB}(t) = \sum_{i,j} A_i \left(e^{tM} M' \right)_{ij} p_j^{\text{eq}}. \tag{3.14}$$

We now use the detailed balance condition on the transition rates M'_{ij} to express $M' p^{\text{eq}}$. Summing over j in Eq. (3.10), the right hand side vanishes because of probability conservation, $\sum_j M_{ji} = \sum_j M'_{ji} = 0$, and we obtain

$$\sum_j M'_{ij} p_j^{\text{eq}} = -M_{ij} \frac{B_j}{T} p_j^{\text{eq}}. \tag{3.15}$$

Using this relation in the response (3.14) and the fact that $\partial_t(e^{tM}) = e^{tM}M$, we get

$$R_{AB}(t) = -\frac{1}{T} \sum_{i,j} A_i \left(e^{tM} M \right)_{ij} B_j p_j^{\text{eq}} = -\frac{1}{T} \dot{C}_{AB}(t). \tag{3.16}$$

3.1.3   Proof for a system obeying the Fokker-Planck equation

We can see how this demonstration translates for a continuous system, which we take one-dimensional here, where the probability distribution $p(x,t)$ obeys the Fokker-Planck equation associated to an overdamped Langevin equation in a potential $V(x)$:

$$\dot{p}(x,t) = \partial_x \left[D \partial_x p(x,t) + \lambda^{-1} p(x,t) \partial_x V(x) \right]. \tag{3.17}$$

Defining the Fokker-Planck operator $\mathcal{L}g(x) = \partial_x \left[D \partial_x g(x) + \lambda^{-1} g(x) \partial_x V(x) \right]$, we can write the correlation between the observables A and B as

$$C_{AB}(t) = \langle A(t)B(0) \rangle = \int A(x) \left[e^{t\mathcal{L}} \left(B p^{\text{eq}} \right) \right](x) dx. \tag{3.18}$$

We now turn to the response to the energy variation $\delta V(x,t) = -f(t)B(x)$. This energy variation induces a change in the differential operator, $\delta\mathcal{L} = f(t)\mathcal{L}'$, with $\mathcal{L}'g(x) = -\lambda^{-1}\partial_x[g(x)\partial_x B(x)]$. The subsequent variation of the distribution, $\delta p(x,t)$, follows

$$\delta\dot{p}(x,t) = \mathcal{L}\delta p(x,t) + \mathcal{L}'p^{\text{eq}}(x), \tag{3.19}$$

and it is thus given by

$$\delta p(x,t) = \int_{-\infty}^{t} e^{(t-t')\mathcal{L}}\mathcal{L}'p^{\text{eq}}(x)f(t')dt'. \tag{3.20}$$

The response function giving the variation of the average of the observable A is

$$R_{AB}(t) = \frac{\delta\langle A(t)\rangle}{\delta f(0)} = \int A(x)e^{t\mathcal{L}}\mathcal{L}'p^{\text{eq}}(x)dx. \tag{3.21}$$

In order to express $\mathcal{L}'p^{\text{eq}}$ as a function of $\mathcal{L}$, we compute

$$\mathcal{L}\left(Bp^{\text{eq}}\right)(x) = \partial_x\left(D\partial_x[B(x)p^{\text{eq}}(x)] + \lambda^{-1}B(x)p^{\text{eq}}(x)\partial_x V(x)\right) = D\partial_x[p^{\text{eq}}(x)\partial_x B(r)] = -T\mathcal{L}'p^{\text{eq}}(x). \tag{3.22}$$

Hence

$$R_{AB}(t) = -\frac{1}{T}\int A(x)e^{t\mathcal{L}}\mathcal{L}(Bp^{\text{eq}})(x)dx = -\frac{1}{T}\dot{C}_{AB}(t). \tag{3.23}$$

3.1.4 Applications

If the system under study is a particle moving in a d-dimensional space, with coordinates X_α, we can take $A = X_\alpha$ and $B = X_\beta$. In this case, the correlation is

$$C_{\alpha\beta}(t) = \langle X_\alpha(t)X_\beta(0)\rangle \tag{3.24}$$

and the force conjugated to B is a physical uniform force in the direction β, F_β, so that the response is

$$R_{\alpha\beta}(t) = \frac{\delta\langle X_\alpha(t)\rangle}{\delta F_\beta(0)}. \tag{3.25}$$

The fluctuation-dissipation theorem states that

$$\frac{\delta\langle X_\alpha(t)\rangle}{\delta F_\beta(0)} = -\frac{1}{T}\partial_t\langle X_\alpha(t)X_\beta(0)\rangle. \tag{3.26}$$

3.1.5 Reversibility

At equilibrium, the correlations functions are even in time:

$$C_{AB}(t) = \langle A(t)B(0)\rangle = C_{AB}(-t) = \langle A(0)B(t)\rangle, \tag{3.27}$$

a property which is called *reversibility*.

We prove this relation within the master equation framework. Equation (3.8) gives, for $t > 0$,

$$C_{AB}(t) = \sum_{i,j} A_i\left(e^{tM}\right)_{ij} B_j p_j^{\text{eq}} = A^T e^{tM}PB, \tag{3.28}$$

where we have defined the diagonal matrix P,

$$P_{ij} = \delta_{ij}p_j^{\text{eq}}. \tag{3.29}$$

Conversely,

$$C_{AB}(-t) = B^T e^{tM}PA. \tag{3.30}$$

We now need to use detailed balance, $M_{ij}p_j^{\text{eq}} = M_{ji}p_i^{\text{eq}}$, which reads in matrix notation $MP = PM^T$ or

$$M^T = P^{-1}MP. \tag{3.31}$$

Exponentiating, we find

$$e^{tM^T} = P^{-1}e^{tM}P. \tag{3.32}$$

Taking the transpose of Eq. (3.30), we thus find

$$C_{AB}(-t) = A^T P e^{tM^T}B = A^T PP^{-1}e^{tM}PB = A^T e^{tM}PB = C_{AB}(t). \tag{3.33}$$

3.2   Introduction to stochastic thermodynamics

In this section, we introduce stochastic thermodynamics, which aims at defining the thermodynamic quantities, such as energy, entropy, heat, and work at the single trajectory scale, and to study the statistical properties of these quantities. This presentation mainly follows Ref. [12].

3.2.1   Work and heat for an overdamped Langevin equation

The simplest system that can be used to introduce the basic quantities of stochastic thermodynamics is the one-dimensional overdamped Langevin equation (Eq. (2.57)), which we write

$$\dot{x}(t) = \mu F(x(t), \lambda(t)) + \xi(t), \tag{3.34}$$

where μ is the mobility, the inverse of the friction coefficient, $\lambda(t)$ a control parameter and $\xi(t)$ is the Gaussian white noise with correlation

$$\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t') \tag{3.35}$$

with $D = \mu T$. We can split the force F as

$$F(x, \lambda) = -\partial_x V(x, \lambda) + f(x, \lambda), \tag{3.36}$$

where f represents a nonconservative drive, which may be present even in a one-dimensional system if it is defined on a circle.

Stochastic thermodynamics gives a thermodynamic interpretation of the Langevin equation by associating to it the quantities entering the first law of thermodynamics, namely the energy, the heat, and the work. The first law of thermodynamics reads

$$dE = \delta w + \delta q, \tag{3.37}$$

where dE is the energy variation, δw is the work received by the system and δq is the heat received by the system from its environment. The small quantities are written with d if they are variations of well defined quantities, and with δ otherwise. The convention on the sign of the work and the heat may differ from one book or article to the other.

The energy variation can be written as

$$dE = \partial_x V dx + \partial_\lambda V d\lambda. \tag{3.38}$$

The work received by the system has two contributions: one comes from the variation of the control parameter $\lambda(t)$, the other from the non-conservative force:

$$\delta w = \partial_\lambda V d\lambda + f dx. \tag{3.39}$$

Combining Eqs. (3.37, 3.38, 3.39), we obtain the heat received by the system

$$\delta q = (\partial_x V - f)dx = -F dx. \tag{3.40}$$

This means that the work of the total force, $F dx$, is fully dissipated, which is to be expected in an overdamped system.

3.2.2   Entropy and second law

In order to discuss the second law of thermodynamics, we need to define the entropy at the level of a single trajectory.

From the definition of the entropy of a distribution (Eq. (1.43) in the discrete case, Eq. (2.64) in the continuous case), it is "natural" to attribute the entropy

$$s = -\ln p(x) \tag{3.41}$$

to a location x. Together with the position x, this quantity involves the distribution $p(x,t)$, which is the solution of the Smoluchovski equation (Eq. (2.58)):

$$\partial_t p = -\partial_x j = -\mu \partial_x (Fp - T\partial_x p). \tag{3.42}$$

We now compute the temporal evolution of the entropy:

$$\dot{s} = -\frac{\partial_t p(x,t)}{p(x,t)} - \frac{\partial_x p(x,t)}{p(x,t)}\dot{x} \tag{3.43}$$

$$= -\frac{\partial_t p(x,t)}{p(x,t)} + \frac{j(x,t)}{Dp(x,t)}\dot{x} - \frac{1}{T}F(x,t)\dot{x} \tag{3.44}$$

$$= -\frac{\partial_t p(x,t)}{p(x,t)} + \frac{j(x,t)}{Dp(x,t)}\dot{x} + \frac{\dot{q}}{T}, \tag{3.45}$$

where we have recognized $\dot{q} = \delta q/dt$. By analogy with thermodynamics, we identify $\dot{q}/T$ as the variation of the entropy of the medium, or thermostat,

$$\dot{s}_{\mathrm{m}} = -\frac{\dot{q}}{T}. \tag{3.46}$$

The variation of the total entropy, $s_{\mathrm{tot}} = s + s_{\mathrm{m}}$, is given by

$$\dot{s}_{\mathrm{tot}} = -\frac{\partial_t p(x,t)}{p(x,t)} + \frac{j(x,t)}{Dp(x,t)}\dot{x}. \tag{3.47}$$

We now want to average this quantity with the probability $p(x,t)$. It is straightforward for the first term:

$$\left\langle \frac{\partial_t p(x,t)}{p(x,t)} \right\rangle = \int \frac{\partial_t p(x,t)}{p(x,t)}p(x,t)dx = \int \partial_t p(x,t)dx = 0, \tag{3.48}$$

because of probability conservation. For the second term, we need to compute an average of the form $\langle g(x)\dot{x} \rangle$; this is not trivial and we need to take a step back. We note that, actually, this calculation is required to compute the average received heat, $\langle \dot{q} \rangle = -\langle F(x)\dot{x} \rangle$.

The difficulty lies in the fact that the definition of the quantity $g(x)\dot{x}$ requires to choose a convention, typically Ito or Stratonovitch. In stochastic thermodynamics, the symmetric Stratonovitch convention is preferred, and is the one implicitly chosen for the heat. With this convention, the discretization of $g(x)\dot{x}$ over a small time interval dt and displacement dx, is

$$g(x)\dot{x} = \frac{g(x) + g(x+dx)}{2}\left[\mu F(x) + \frac{d\xi}{dt}\right] \tag{3.49}$$

$$= \left[g(x) + \frac{dx}{2}\partial_x g(x) + \mathcal{O}(dx^2)\right]\left[\mu F(x) + \frac{d\xi}{dt}\right] \tag{3.50}$$

$$= g(x)\mu F(x) + \frac{dxd\xi}{2dt}\partial_x g(x) + g(x)\frac{d\xi}{dt} + \frac{dx}{2}\partial_x g(x)\mu F(x) + \mathcal{O}(dx^2). \tag{3.51}$$

We now want to average this quantity. The first term is straightforward and gives $\langle g(x)\mu F(x) \rangle$. For the second term, we average separately over the position and the noise realization; the latter gives $\langle dxd\xi \rangle = \langle d\xi^2 \rangle = 2Ddt$. The remaining terms do not contribute at leading order in dt. We thus have

$$\langle g(x)\dot{x} \rangle = \langle g(x)\mu F(x) \rangle + D\langle \partial_x g(x) \rangle \tag{3.52}$$

$$= \int p(x)\left[g(x)\mu F(x) + D\partial_x g(x)\right]dx \tag{3.53}$$

$$= \int g(x)\left[\mu F(x)p(x) - D\partial_x p(x)\right]dx \tag{3.54}$$

$$= \int g(x)j(x)dx \tag{3.55}$$

$$= \left\langle g(x)\frac{j(x)}{p(x)} \right\rangle. \tag{3.56}$$

We can finally evaluate the average total entropy variation:

$$\dot{S}_{\mathrm{tot}} = \langle \dot{s}_{\mathrm{tot}} \rangle = \left\langle \frac{j(x)^2}{Dp(x)^2} \right\rangle \geq 0. \tag{3.57}$$

This inequality corresponds to the second law of thermodynamics: it shows that the entropy, which may decay along a particular trajectory, increases on average.

The first and second law of stochastic thermodynamics can be verified, for instance, in a Brownian Carnot Engine [13].

3.2.3   Fluctuation theorems

Probabilities of the path and the reversed path

After having defined and derived the first and second law of stochastic thermodynamics, we now consider the fluctuation of the trajectories and related quantities. At the root of this analysis is the probability to observe a given trajectory $x(t)$, given an initial state x_0 and a driving $\lambda(t)$, which is given by (Sec. 2.4):

$$p[x(t)|x_0] = \mathcal{N}\exp(-\mathcal{A}[x(t), \lambda(t)]), \tag{3.58}$$

where the action reads, with the the Stratonovitch convention,

$$\mathcal{A}[x(t), \lambda(t)] = \int_0^{t_\mathrm{f}} \left(\frac{[\dot{x}(t) - \mu F(x(t), \lambda(t))]^2}{4D} + \frac{\mu}{2}\partial_x F(x(t), \lambda(t)) \right) dt, \tag{3.59}$$

and $\mathcal{N}$ is a normalization constant that does not depend on x_0 and $\lambda(t)$.

It is interesting to compare the probability to observe a path $x(t)$ to the probability to observe the reversed path $x^\dagger(t) = x(t_\mathrm{f} - t)$ when the driving is also reversed, $\lambda^\dagger(t) = \lambda(t_\mathrm{f} - t)$. We denote $p^\dagger$ the probability to observe a path with the driving $\lambda^\dagger$; it is given by the action $\mathcal{A}^\dagger$. From the expression of the action, we have, for initial states x_0 and $x_0^\dagger$,

$$\frac{p[x(t)|x_0]}{p^\dagger[x^\dagger(t)|x_0^\dagger]} = \exp\left(\mathcal{A}^\dagger[x^\dagger(t)] - \mathcal{A}[x(t)]\right) \tag{3.60}$$

$$= \exp\left(\frac{1}{T}\int_0^{t_\mathrm{f}} \dot{x}(t) F(x(t), \lambda(t)) dt\right) \tag{3.61}$$

$$= \exp(\Delta s_\mathrm{m}), \tag{3.62}$$

where $\Delta s_\mathrm{m} = \int_0^{t_\mathrm{f}} \dot{s}_\mathrm{m}(t) dt$ and we have used the fact that $\dot{x}F = -\dot{q} = T\dot{s}_\mathrm{m}$. Only the cross terms $\dot{x}F$ do not cancel because $\dot{x}^\dagger(t) = -\dot{x}(t_\mathrm{f} - t)$.

Introducing initial distributions $p(x_0)$ and $p^\dagger(x_0^\dagger)$, we have

$$\frac{p[x(t)]}{p^\dagger[x^\dagger(t)]} = \frac{p[x(t)|x_0]}{p^\dagger[x^\dagger(t)|x_0^\dagger]}\frac{p(x_0)}{p^\dagger(x_0^\dagger)} = \exp(\Delta s_\mathrm{m})\frac{p(x_0)}{p^\dagger(x_0^\dagger)}. \tag{3.63}$$

We will use different choices for the distributions $p(x_0)$ and $p^\dagger(x_0^\dagger)$.

If the distribution $p^\dagger(x)$ is the solution of the Smoluchowski equation at time t_f with the initial condition $p(x)$ at time $t = 0$, then these probabilities are related to the initial and final entropies, $p(x_0) = \exp(-s(0))$ and $p^\dagger(x_0^\dagger) = \exp(-s(t_\mathrm{f}))$ (Eq. (3.41)). As a consequence,

$$\frac{p[x(t)]}{p^\dagger[x^\dagger(t)]} = \exp(\Delta s_\mathrm{m} - s(0) + s(t_\mathrm{f})) = \exp(\Delta s_\mathrm{tot}). \tag{3.64}$$

Another interesting choice is to take for these distributions the equilibrium distributions at times 0 and t_f, that is, for the values of the control parameter λ_0 and $\lambda(t_\mathrm{f}) = \lambda_\mathrm{f}$. These equilibrium probabilities are given by

$$p_\mathrm{eq}(x, \lambda) = \exp\left(\frac{\mathcal{F}(\lambda) - V(x, \lambda)}{T}\right), \tag{3.65}$$

where we have introduced the free energy

$$\mathcal{F}(\lambda) = \int \exp\left(-\frac{V(x, \lambda)}{T}\right) dx. \tag{3.66}$$

In this case, we have

$$\frac{p[x(t)]}{p^\dagger[x^\dagger(t)]} = \exp\left(\Delta s_\mathrm{m} + \frac{\mathcal{F}(\lambda_0) - \mathcal{F}(\lambda_\mathrm{f}) - V(x_0, \lambda_0) + V(x_0^\dagger, \lambda_\mathrm{f})}{T}\right) \tag{3.67}$$

$$= \exp\left(\frac{\Delta E - q - \Delta\mathcal{F}}{T}\right) \tag{3.68}$$

$$= \exp\left(\frac{w - \Delta\mathcal{F}}{T}\right). \tag{3.69}$$

The quantity $w - \Delta\mathcal{F}$ may be referred to as the dissipated work: this is the work that does not affect the free energy of the system.

Jarzynski equality

In order to obtain useful expressions, we now want to compute averages over the paths. To do so, we rearrange Eq. (3.63) and introduce an arbitrary function $g[x(t)]$:

$$g[x(t)]p[x(t)]\exp(-\Delta s_{\mathrm{m}})\frac{p^\dagger(x_0^\dagger)}{p(x_0)} = g[x(t)]p^\dagger[x^\dagger(t)]. \tag{3.70}$$

Now integrating over the paths, we obtain

$$\left\langle g[x(t)]\exp(-\Delta s_{\mathrm{m}})\frac{p^\dagger(x_0^\dagger)}{p(x_0)}\right\rangle = \left\langle g[x^\dagger(t)]\right\rangle^\dagger, \tag{3.71}$$

where $\langle\cdot\rangle^\dagger$ represents an average for the reverse process.

Taking the equilibrium distributions at the beginning and the end of the process and $g = 1$, we obtain

$$\left\langle \exp\left(\frac{\Delta\mathcal{F} - w}{T}\right)\right\rangle = 1. \tag{3.72}$$

This relation is the Jarzynski equality; it is often written as

$$\left\langle \exp\left(-\frac{w}{T}\right)\right\rangle = \exp\left(-\frac{\Delta\mathcal{F}}{T}\right). \tag{3.73}$$

The Jarzynski equality allows to obtain the free energy difference between two states by driving many times the system from one to the other and measuring the work. The protocol should start at equilibrium; however, there is no need to wait for equilibrium at the end of the process since the part of the trajectory where the control parameter λ is constant does not contribute to the work. It has been derived in 1997 and been in 2002 to measure the folding energy of RNA hairpins [14].

Crooks fluctuation relation

The Jarzynski equality provides the average of a function of the work, but it does not say much about the distribution of the work. Instead of integrating Eq. (3.70) over all the paths, we can select the paths corresponding to a work $\bar{w}$ by using $g[x(t)] = \delta(w[x(t)] - \bar{w})$. We obtain

$$\delta(w[x(t)] - \bar{w})p[x(t)]\exp(-\Delta s_{\mathrm{m}})\frac{p^\dagger(x_0^\dagger)}{p(x_0)} = \delta(w[x(t)] - \bar{w})p^\dagger[x^\dagger(t)], \tag{3.74}$$

Integrating over all the paths, with the initial and final configurations at equilibrium, we find

$$p(\bar{w})\exp\left(\frac{\Delta\mathcal{F} - \bar{w}}{T}\right) = p^\dagger(-\bar{w}). \tag{3.75}$$

The right hand side is not obvious to obtain, the detailed derivation is

$$\int [dx(t)]\delta(w[x(t)] - \bar{w})p^\dagger[x^\dagger(t)] = \int [dx^\dagger(t)]\delta(w[x(t)] - \bar{w})p^\dagger[x^\dagger(t)], \tag{3.76}$$

$$= \int [dx(t)]\delta(w[x^\dagger(t)] - \bar{w})p^\dagger[x(t)], \tag{3.77}$$

$$= \int [dx(t)]\delta(-w[x(t)] - \bar{w})p^\dagger[x(t)], \tag{3.78}$$

$$= p^\dagger(-\bar{w}). \tag{3.79}$$

We have used (i) the fact that the Jacobian of the variable change from $[dx(t)]$ to $[dx^\dagger(t)]$ is 1. (ii) A renaming of the variables $x(t) \leftrightarrow x^\dagger(t)$. (iii) The fact that the work of the reverse trajectory is the opposite of the work of the forward trajectory, $w[x^\dagger(t)] = -w[x(t)]$. Renaming $\bar{w} \to w$, we have

$$\frac{p(w)}{p^\dagger(-w)} = \exp\left(\frac{w - \Delta\mathcal{F}}{T}\right), \tag{3.80}$$

which is the Crooks fluctuation theorem.

Integrating the Crooks theorem written in the form (3.75) allows to recover the Jarzynski equality.

The Crooks theorem allows to determine free energy differences even more reliably than the Jarzinski equality (JE). Using the same protocol as the for the JE and computing the distributions of the forward and reverse works, the Crooks theorem tells that the free energy difference is given by the work where the distributions cross. It has been used to determine RNA folding energies [15].

Entropy production –   The same applies for the total entropy production, which is also antisymmetric:
$\Delta s_{\text{tot}}[x^\dagger(t)] = -\Delta s_{\text{tot}}[x(t)]$. Following the same steps, we obtain

$$\frac{p(\Delta s_{\text{tot}})}{p^\dagger(-\Delta s_{\text{tot}})} = e^{\Delta s_{\text{tot}}}. \tag{3.81}$$

In a NESS, the forward and reverse processes are identical and

$$\frac{p(\Delta s_{\text{tot}})}{p(-\Delta s_{\text{tot}})} = e^{\Delta s_{\text{tot}}}. \tag{3.82}$$

3.2.4   Discrete processes

We have introduced the basic concepts of stochastic thermodynamics for a simple and intuitive system, a one-dimensional and overdamped continuous process; actually, this is the framework within which stochastic thermodynamics has been developped. In order to be applicable beyond this system, it needs to be generalized to more general systems, ideally to a discrete process, which we now address.

Heat, entropy, and second law

The system is defined by the master equation $\dot{p} = Mp$, where the coefficients of M are the transition rates k_{yx} to jump from a state x to a state y. We assume that the transition rates satisfy the detailed balance for a temperature T and an energy landscape $V_x(\lambda)$. If the system is in contact with several reservoirs or if a driving is applied, the transition rates associated to the different reservoirs and drivings can be added.

A trajectory $x(t)$ involves jumps from x_i to y_i at times t_i. For the transition i, we assume that the energy change corresponds to the heat received from the reservoir,

$$q_i = V_{y_i}(t_i) - V_{x_i}(t_i). \tag{3.83}$$

Using detailed balance, this quantity can be written from the transition rates,

$$q_i = -T \ln \left(\frac{k_{y_i x_i}(t_i)}{k_{x_i y_i}(t_i)} \right). \tag{3.84}$$

The associated entropy increase in the medium $\Delta s_{\text{m},i}$ is, as before,

$$\Delta s_{\text{m},i} = -\frac{q_i}{T} = \ln \left(\frac{k_{y_i x_i}(t_i)}{k_{x_i y_i}(t_i)} \right). \tag{3.85}$$

The entropy change in the medium per unit time is thus given by

$$\dot{s}_{\text{m}}(t) = \sum_i \delta(t - t_i) \ln \left(\frac{k_{y_i x_i}(t_i)}{k_{x_i y_i}(t_i)} \right). \tag{3.86}$$

We define the entropy of the system in the state x and with a distribution $p(x)$ as for a continuous system (Eq. (3.41)):

$$s = -\ln p(x). \tag{3.87}$$

Its evolution is

$$\dot{s}(t) = -\frac{\partial_t p_x(t)}{p_x(t)} + \sum_i \delta(t - t_i) \ln \left(\frac{p_{x_i}(t_i)}{p_{y_i}(t_i)} \right). \tag{3.88}$$

Summing this quantity with Eq. (3.86), we obtain the total entropy variation,

$$\dot{s}_{\text{tot}}(t) = -\frac{\partial_t p_x(t)}{p_x(t)} + \sum_i \delta(t - t_i) \ln \left(\frac{k_{y_i x_i}(t_i) p_{x_i}(t_i)}{k_{x_i y_i}(t_i) p_{y_i}(t_i)} \right). \tag{3.89}$$

Based on the continuous case, we may expect this quantity to be positive on average.

To average the total entropy variation, we need to compute averages of terms involving transitions, such as $\langle \sum_i \delta(t - t_i) d_{x_i y_i} \rangle$, where d_{xy} is an arbitrary function over the pairs of states. This average is given by

$$\left\langle \sum_i \delta(t - t_i) d_{y_i x_i} \right\rangle = \sum_{x,y} d_{yx} k_{yx} p_x(t). \tag{3.90}$$

We thus get

$$\dot{S}_{\text{tot}} = \langle \dot{s}_{\text{tot}} \rangle = \sum_{x,y} k_{yx} p_x(t) \ln \left(\frac{k_{yx}(t)p_x(t)}{k_{xy}(t)p_y(t)} \right) \tag{3.91}$$

$$= \sum_{\langle x,y \rangle} [k_{yx} p_x(t) - k_{xy} p_y(t)] \ln \left(\frac{k_{yx}(t)p_x(t)}{k_{xy}(t)p_y(t)} \right) \tag{3.92}$$

$$\geq 0. \tag{3.93}$$

The inequality comes from the fact that the term in the sum is of the form $(a-b)[f(a)-f(b)]$ with $a = k_{yx}p_x(t)$, $b = k_{xy}p_y(t)$ and $f(u) = \ln(u)$, and this combination is positive if f is increasing.

Assuming that the expression (3.85) for entropy increase in the medium can be used even when detailed balance does not hold, Eq. (3.92) gives the mean entropy production in a NESS.

Action and fluctuation theorems

We now turn to the fluctuation theorems. To extend them to the discrete case, we need the probability to observe a trajectory $x(t)$. As for the discrete case, we consider time intervals of small duration Δt and write the probability to observe the sequence $x_1, \ldots, x_N$, starting from x_0:

$$p(x_1, \ldots, x_N | x_0) = \prod_n p(x_{n+1} | x_n) = \prod_n \left(\delta_{x_{n+1} x_n} + \Delta t k_{x_{n+1} x_n} \right). \tag{3.94}$$

In the intervals $[t_i, t_{i+1}]$ between two jumps, the process remains at $y_i = x_{i+1}$ and the term in brackets is $1 - r_{x_{i+1}} \Delta t$, where r_x denotes the exit rate from a state x, $r_x = -k_{xx} = \sum_y k_{xy}$. Taking the product over the small time intervals gives a contribution $\exp(-[t_{i+1} - t_i]r_{x_{i+1}})$. Whenever a small time interval contains a jump, the term in brackets is $\Delta t\, k_{y_i x_i}$. Finally, the probability to observe the trajectory is

$$p[x(t)|x_0] = \exp \left(- \int r_{x(t)} dt \right) \prod_i \Delta t\, k_{y_i x_i}. \tag{3.95}$$

It may seem strange to have a dependence on Δt; it may be understood as follows. Imagine that we want to sum over the trajectories that start at x_0 and end at x_1 after a single jump. In the discretized version, this involves a sum over the small interval where the jump occurs; this sum being multiplied by Δt, it becomes an integral in the limit $\Delta t \to 0$. The associated probability is

$$p[x(t) = (x_0, x_1)] = \int_0^{t_{\text{f}}} \exp \left(-t r_{x_0} - (t_{\text{f}} - t)r_{x_1} \right) k_{x_1 x_0} dt. \tag{3.96}$$

Similarly, if there are n_{j} jumps, the duration Δt will enter as $\Delta t^{n_{\text{j}}}$, which corresponds to the n_j integrals over the transition times. Having this signification of the sum over the trajectories in mind, we omit the Δt factor and write the probability of a trajectory as

$$p[x(t)|x_0] = \exp(-\mathcal{A}[x(t)]), \tag{3.97}$$

where we have introduced the action

$$\mathcal{A}[x(t)] = \int r_{x(t)} dt - \sum_i \ln(k_{y_i x_i}). \tag{3.98}$$

As for the continuous case, we can define the reverse trajectory $x^\dagger(t)$. When considering the reverse trajectory, we also assume that the eventual time dependence of the rates has been reversed. The ratio of the probabilities to observe the trajectory $x(t)$ for the forward process and the trajectory $x^\dagger(t)$ for the reverse process is

$$\frac{p[x(t)|x_0]}{p^\dagger[x^\dagger(t)|x_0^\dagger]} = \exp \left(\mathcal{A}^\dagger[x^\dagger(t)] - \mathcal{A}[x(t)] \right) = \exp \left(\sum_i \ln \left(\frac{k_{y_i x_i}}{k_{x_i y_i}} \right) \right) = \exp(\Delta s_{\text{m}}), \tag{3.99}$$

which is the same result as for the continous case.

To translate the results of Sec. 3.2.3, we need to define the work. This is easily done by coming back to the first law of thermodynamics, $\Delta E = V_{x_{\text{f}}}(t_{\text{f}}) - V_{x_0}(t_0) = w + q$. The energy change along a trajectory

can be split in the energy change during the transitions, which is attributed to the heat received from the reservoir, and the energy change between the transitions, which is attributed to the work exerted to change the energy of the states:

$$\Delta E = \sum_i \left([V_{y_i}(t_i) - V_{x_i}(t_i)] + [V_{x_i}(t_i) - V_{x_i}(t_{i-1})] \right) = \sum_i q_i + \int \dot{V}_{x(t)}(t)dt = q + w, \qquad (3.100)$$

where $\dot{V}_x(t)$ denotes the derivative of the energy of the state x with respect to time. With this definition, all the results of the previous section apply.

3.2.5   Thermodynamic uncertainty relations

Instead of presenting in detail the thermodynamic uncertainty relations, we will restric ourselves to a simple example, the biased random walk, and briefly discuss the general result and how it is obtained.

Cost of precision of a biased random walk

We consider a random walk with jump rates k_- and k_+, the ratio of which provides the dimensionless energy gain, or affinity, A of moving to the right: $A = \ln(k_+/k_-)$. A particle starting from $x = 0$ at time $t = 0$ moves on average due to the bias while its distribution spreads. We are interested in the average and the variance of its position at time t, $\langle x(t) \rangle$ and $\langle [x(t) - \langle x(t) \rangle]^2 \rangle$.

The position of the particle after a time t is given by $x(t) = n_+(t) - n_-(t)$, where $n_\pm(t)$ are the number of jumps to the left and to the right. These number are Poisson processes:

$$p(n_\nu(t) = n) = \frac{(k_\nu t)^n}{n!} e^{-k_\nu t}, \qquad (3.101)$$

for $\nu \in \{-, +\}$. As a consequence, their mean and variance are $\langle n_\nu(t) \rangle = k_\nu t$, $\langle [n_\nu(t) - \langle n_\nu(t) \rangle]^2 \rangle = k_\nu t$. We can thus obtain the mean and variance of $x(t)$, the later being the sum of the variances of the independent variables $n_-(t)$ and $n_+(t)$:

$$\langle x(t) \rangle = (k_+ - k_-)t, \qquad (3.102)$$

$$\langle [x(t) - \langle x(t) \rangle]^2 \rangle = (k_+ + k_-)t. \qquad (3.103)$$

The relative uncertainty on the final position is

$$\epsilon^2 = \frac{\langle [x(t) - \langle x(t) \rangle]^2 \rangle}{\langle x(t) \rangle^2} = \frac{2(k_+ + k_-)}{(k_+ - k_-)^2 t}. \qquad (3.104)$$

As expected, the uncertainty decreases with time.

It is now interesting to compare the uncertainty with the entropy generated during the process.

$$\dot{S}_{\text{tot}} = \langle \dot{s}_{\text{tot}} \rangle = \sum_{\langle x,y \rangle} [k_{yx} p_x(t) - k_{xy} p_y(t)] \ln\left(\frac{k_{yx}(t) p_x(t)}{k_{xy}(t) p_y(t)} \right) \qquad (3.105)$$

$$= \sum_x [k_+ p_x(t) - k_- p_{x+1}(t)] \ln\left(\frac{k_+ p_x(t)}{k_- p_{x+1}(t)} \right) \qquad (3.106)$$

$$= \sum_x [k_+ p_x(t) - k_- p_{x+1}(t)] \ln\left(\frac{k_+}{k_-} \right) + \sum_x [k_+ p_x(t) - k_- p_{x+1}(t)] \ln\left(\frac{p_x(t)}{p_{x+1}(t)} \right) \qquad (3.107)$$

$$= (k_+ - k_-) \ln\left(\frac{k_+}{k_-} \right) - \sum_x p_x(t) \left[k_+ \ln\left(\frac{p_{x+1}(t)}{p_x(t)} \right) + k_- \ln\left(\frac{p_{x-1}(t)}{p_x(t)} \right) \right] \qquad (3.108)$$

$$\geq (k_+ - k_-) \ln\left(\frac{k_+}{k_-} \right), \qquad (3.109)$$

where the last inequality has been obtained from $\ln(u) \leq u - 1$. The remaining contribution is the entropy creation rate due to the irreversibility of the process. The contribution that we have bounded comes from the spreading of the distribution; considering a random walk on a circle, this contribution is zero if the distribution is uniform.

After a time t, the entropy increase is thus $\Delta S_{\text{tot}} = t\dot{S}_{\text{tot}}$ and

$$\epsilon^2 \Delta S_{\text{tot}} \geq \frac{k_+ + k_-}{k_+ - k_-} \ln\left(\frac{k_+}{k_-}\right) = A \coth\left(\frac{A}{2}\right) \geq 2. \tag{3.110}$$

This is a *thermodynamic uncertainty relation*, which states that precision comes with an entropic cost. The bound is saturated for $A = 0$, that is, at equilibrium.

General current fluctuations and bounds

This relation can be generalized to any current [16] (Secs. 6 and 7). For two states x, y, we define the empirical current $\hat{j}_{yx}$ as the number of times the system jumps from x to y minus the number of times the system jumps from y to x, divided by the time. A generalized current j is the linear combination of the currents associated to a transition. The relative uncertainty of such current is still $\epsilon^2 = \langle(\hat{j} - \langle\hat{j}\rangle)^2\rangle/\langle\hat{j}\rangle^2$.

The first step to obtain a general thermodynamic uncertainty relation is to use the probability of individual paths to obtain the probability of the currents. The second step is to bound the fluctuations and to compare this bound to the entropy creation.

Chapter 4

Fluctuating fields

4.1 Interfaces

4.1.1 Edwards-Wilkinson equation

The Edwards-Wilkinson equation (EW) is one of the simplest stochastic equations for a field. We consider an interface that has a height $h(\mathbf{r}, t)$ at position $\mathbf{r}$ and time t. We assume that this interface evolves diffusively, with a diffusion coefficient ν. The interface is also moved by a noise term with variance $2D$ that we assume to be uncorrelated in both space and time. The EW equation reads

$$\frac{\partial h}{\partial t}(\mathbf{r}, t) = \nu \nabla^2 h(\mathbf{r}, t) + \eta(\mathbf{r}, t), \tag{4.1}$$

with $\eta(\mathbf{r}, t)$ a Gaussian white noise of average $\langle \eta(\mathbf{r}, t) \rangle = 0$ and covariance

$$\langle \eta(\mathbf{r}, t)\eta(\mathbf{r}', t') \rangle = 2D\delta(\mathbf{r} - \mathbf{r}')\delta(t - t'). \tag{4.2}$$

In the following, we consider a flat initial interface $h(\mathbf{r}, 0) = 0$. The EW equation is a diffusion equation with a forcing term $\eta(\mathbf{r}, t)$. Its general solution is

$$h(\mathbf{r}, t) = \int_0^t dt' \int d\mathbf{r}' \eta(\mathbf{r}', t')G(\mathbf{r} - \mathbf{r}', t - t'), \tag{4.3}$$

where $G(\mathbf{r}, t)$ is the Green function of the diffusion equation, that is to say the solution of

$$\left(\frac{\partial}{\partial t} - \nu \nabla^2 \right) G(\mathbf{r}, t) = \delta(\mathbf{r})\delta(t). \tag{4.4}$$

Eq. (4.1) is a linear equation with Gaussian noise: its solution is also a Gaussian process. The statistics of $h(\mathbf{r}, t)$ is entirely characterized by its average value and its covariance. From Eq. (4.3), we immediately obtain

$$\langle h(\mathbf{r}, t) \rangle = 0. \tag{4.5}$$

From the invariance by translation, the covariance is $\langle h(\mathbf{R}, t)h(\mathbf{R}+\mathbf{r}, t+\tau) \rangle \equiv C(\mathbf{r}, t, \tau)$[1]. Using Eq. (4.2) and reorganizing the integrals, we obtain

$$C(\mathbf{r}, t, \tau) = 2D \int_0^t dt' \int d\mathbf{r}' G(\mathbf{r}', t')G(\mathbf{r}' + \mathbf{r}, t' + \tau). \tag{4.6}$$

The Green function of the diffusion equation in dimension d, solution of Eq. (4.4), is the Gaussian kernel

$$G(\mathbf{r}, t) = \frac{1}{(4\pi\nu t)^{d/2}}\Theta(t)e^{-\frac{\mathbf{r}^2}{4\nu t}} \tag{4.7}$$

where $\Theta(t)$ is the Heaviside function (1 when $t \geq 0$, 0 otherwise).

---

[1]For completeness, one should also consider $\langle h(\mathbf{R}, t + \tau)h(\mathbf{R} + \mathbf{r}, t) \rangle$.

Let us focus on the correlations at equal time ($\tau = 0$):

$$C(\mathbf{r}, t, 0) = 2D \int_0^t dt' \frac{1}{(4\pi\nu t')^d} \int d\mathbf{r}' e^{-\frac{1}{4\nu t'}\left[\mathbf{r}'^2 + (\mathbf{r}' + \mathbf{r})^2\right]} \tag{4.8}$$

$$= 2D \int_0^t dt' \frac{1}{(8\pi\nu t')^{d/2}} e^{-\frac{\mathbf{r}^2}{8\nu t'}}. \tag{4.9}$$

In dimension $d = 1$, the integral converges for $\mathbf{r} = 0$. We obtain the following expression for the variance of the height,

$$\langle h(r, t)^2 \rangle = C(0, t, 0) = D\sqrt{\frac{2t}{\pi\nu}} \sim t^{2\beta}. \tag{4.10}$$

$\beta = 1/4$ is called the *growth exponent*.

In dimensions 2 and 3, the covariance $C(\mathbf{r}, t, 0)$ diverges when $\mathbf{r} \to 0$. The usual way around this problem is to introduce a microscopic cutoff distance a. This cutoff is intepreted either a lattice step of a microscopic model for which the EW equation is the continuous limit; or as a correlation distance for the noise $\eta(\mathbf{r}, t)$. The effective variance in dimensions 2 and 3 is [17]

$$\langle h(\mathbf{r}, t) h(\mathbf{r} + a\hat{\mathbf{e}}_x, t) \rangle = \begin{cases} \frac{D}{4\pi\nu} \ln \frac{\nu t}{a^2} & \text{in } d = 2 \\ \frac{D}{4\pi\nu a} & \text{in } d = 3 \end{cases}. \tag{4.11}$$

In dimension 2 the divergence is logarithmic in time, while in dimension 3 the diffusion stabilizes the interface at a constant variance.

Periodic line

It is instructive to study the EW equation on a 1D line of length L with periodic boundary conditions. The computations are a bit tedious and we will not reproduce them in detail. The interested reader will check that the Green function of the problem is

$$G(r, t) = \frac{1}{L} \sum_{n=-\infty}^{\infty} e^{ik_n r - \nu k_n^2 t}, \tag{4.12}$$

with $k_n = 2\pi n/L$. It is the Jacobi theta function, up to scaling factors.

We are interested in the average width $W(t)$ of the interface, defined as

$$W^2(t) = \left\langle \frac{1}{L} \int_0^L dr [h(r, t) - \bar{h}(t)]^2 \right\rangle \tag{4.13}$$

where $\bar{h}(t)$ is the spatial average of h at time t,

$$\bar{h}(t) = \frac{1}{L} \int_0^L dr \, h(r, t). \tag{4.14}$$

One shows that W obeys a so-called *Family-Vicsek scaling*,

$$W = L^\alpha f\left(\frac{t}{L^z}\right). \tag{4.15}$$

The *roughness exponent* is $\alpha = 1/2$ and the *dynamic exponent* is $z = 2$. The function f has the following limit behaviors[2],

$$f(u) \underset{u \to 0}{\sim} u^\beta \qquad\qquad\qquad f(u) \underset{u \to \infty}{\sim} u^0. \tag{4.16}$$

We recover the growth exponent $\beta = \alpha/z = 1/4$, it governs the short-time behavior $t \ll L^2$. At large time, the width is set (in terms of the length) by the roughness exponent.

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[2]The explicit expression of f is $f(u) = \left[4D \sum_{n=1}^{\infty} \frac{1 - e^{-8\pi^2 n^2 u}}{8\pi^2 n^2}\right]^{1/2}$. It is related to theta functions.

4.1.2   Kardar-Parisi-Zhang equation

For some realistic systems, the up-down symmetry $(h \mapsto -h)$ is broken. It happens for instance if the interfaces grows by deposition. A large class of these systems are well described by the Kardar-Parisi-Zhang equation (KPZ),

$$\frac{\partial h}{\partial t}(\mathbf{r}, t) = \nu \nabla^2 h(\mathbf{r}, t) + \frac{\lambda}{2}(\nabla h)^2 + \eta(\mathbf{r}, t), \tag{4.17}$$

with $\eta(\mathbf{r}, t)$ having the same properties as in the previous part (see Eq. (4.2)). The additional term favors the growth (increase of h) in the zone where the interface is not flat (when $\lambda > 0$). Due to its non-linear nature, the KPZ equation is much more difficult to study. It has given rise to a large number of works (and review) even in the 1D case $d = 1$.

It can be shown that the KPZ equation obeys a Family-Vicsek scaling [18], Eqs. (4.15)-(4.16), with exponents

$$\alpha = \frac{1}{2}, \qquad\qquad z = \frac{3}{2}, \qquad\qquad \beta = \frac{1}{3}. \tag{4.18}$$

The growth exponent $\beta = 1/3$ is characteristic of the KPZ universality class.

Finally, let us consider the KPZ equation (4.17) on the infinite line $(L \to \infty)$ with fixed parameters (say $\nu = 1/2, D = 1/2, \lambda = 2$ without loss of generality [18]) and call $h_\infty(x, t)$ its solution. The exponents (4.18) suggest a growth $h \sim t^\beta$ with a spatial extent $\ell \sim t^{1/z}$. This suggests to define the random field

$$\mathfrak{h}(r) = \lim_{t \to \infty} t^{-\beta} h_\infty(t^{/z} r, t). : xa \tag{4.19}$$

This limit is known as the *KPZ fixed point in infinite volume*. If we start from a flat interface $(h_\infty(r, t = 0) = 0)$, the one-point probability distribution of $\mathfrak{h} = \mathfrak{h}(r)$ (independent of r) is given by the celebrated Tracy-Widom distribution $p_{TW}(\mathfrak{h})$ which is highly asymmetric:

$$p_{TW}(\mathfrak{h}) \sim \begin{cases} e^{-\frac{1}{24}|\mathfrak{h}|^3} & \mathfrak{h} \to -\infty \\ e^{-\frac{2}{3}|\mathfrak{h}|^{3/2}} & \mathfrak{h} \to \infty \end{cases}. \tag{4.20}$$

Note that the Tracy-Widom distribution also corresponds to the distribution of the largest eigenvalue of a random matrix distributed according to the Gaussian orthogonal ensemble (in the large size limit). The Gaussian orthogonal ensemble $\text{GOE}(n)$ is an ensemble of $n \times n$ symmetric random matrices with Gaussian weights. Such a matrix can be generated as $H = (G + G^T)/\sqrt{2n}$ with G a $n \times n$ matrix of iid random number from a standard normal distribution. But we often prefer to define the probability measure on symmetric matrices $P(H) \propto \exp(-\frac{n}{4}\text{Tr}(H^2))$. See Ref. [19] for more details on random matrices.

4.2   Fluctuating fields at equilibrium

4.2.1   Energy functional

In this section, we consider a scalar field $\phi(\mathbf{x}, t) \in \mathbb{R}$ with $\mathbf{x} \in \mathbb{R}^d$. Physically, it may represent a density field, magnetization field, concentration field, etc. Most of the framework can be extended to a vector field $\boldsymbol{\phi} \in \mathbb{R}^k$, or to a complex field.

An important distinction is to be made between conserved fields - for instance a density field - which satisfy $\int d\mathbf{x}\, \phi(\mathbf{x}, t) = \text{const}$, and non conserved fields - such as a magnetization field - for which there is no such constraint.

At equilibrium, we have a energy $H[\phi]$ (or free energy depending of the case[3]). The equilibrium probability of observing a given configuration is $P_{\text{eq}}[\phi] \propto e^{-\frac{1}{T}H[\phi]}$. Let us give some basic examples. We provide the expression of the functional derivative $\frac{\delta H}{\delta \phi(\mathbf{x})}$ that will be useful for the dynamics.

- Gaussian field with correlation length ξ.

$$H[\phi] = \int d\mathbf{x} \left[\frac{1}{2}(\nabla \phi(\mathbf{x}))^2 + \frac{1}{2\xi^2}\phi(\mathbf{x})^2 \right] \tag{4.21}$$

$$\frac{\delta H}{\delta \phi(\mathbf{x})} = -\nabla^2 \phi(\mathbf{x}) + \xi^{-2}\phi(\mathbf{x}) \tag{4.22}$$

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[3]For simplicity we keep the notation $H[\phi]$ independently of the fact that it is an energy or a free energy.

- Ginzburg-Landau Hamiltonian. This is used to decribed the (non-conserved) magnetization of the Ising model in a mean-field approximation. t is the distance to the critical temperature and h the magnetic field.

$$H[\phi] = \int d\mathbf{x} \left[\frac{t}{2}\phi(\mathbf{x})^2 + \frac{u}{4}\phi(\mathbf{x})^4 + \frac{1}{2}(\nabla\phi)^2 - h\phi(\mathbf{x}) \right] \tag{4.23}$$

$$\frac{\delta H}{\delta\phi(\mathbf{x})} = t\phi(\mathbf{x}) + u\phi(\mathbf{x})^3 - \nabla^2\phi(\mathbf{x}) - h \tag{4.24}$$

- Cahn-Hilliard free energy. This is used to describe the phase separation for a (conserved) density field. The two stable phases are $\phi(\mathbf{x}) = \pm 1$.

$$H[\phi] = \int d\mathbf{x} \left[\frac{1}{4}(\phi(\mathbf{x})^2 - 1)^2 + \frac{\gamma}{2}(\nabla\phi)^2 \right] \tag{4.25}$$

$$\frac{\delta H}{\delta\phi(\mathbf{x})} = \phi(\mathbf{x})^3 - \phi(\mathbf{x}) - \gamma\nabla^2\phi(\mathbf{x}) \tag{4.26}$$

This is of course very similar to the Ginzburg-Landau Hamiltonian, but is used in a different context.

As for a particle, the equilibrium energy does not provide the dynamics. It is perfectly admissible to describe this dynamics with a deterministic (partial differential) equation for the average value. But we sometimes prefer to use a stochastic description.

4.2.2 Stochastic partial differential equation

We consider a stochastic (partial) differential equation of the form,

$$\partial_t\phi(\mathbf{x}, t) = A_\mathbf{x}[\phi(t)] + \int d\mathbf{y}\, B_\mathbf{xy}\eta(\mathbf{y}, t) \tag{4.27}$$

where η is a spatiotemporal Gaussian noise of vanishing average $\eta(\mathbf{x}, t) = 0$ which is delta-correlated in both space and time,

$$\langle\eta(\mathbf{x}, t)\eta(\mathbf{x}', t')\rangle = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{4.28}$$

For simplicity, we assume that the noise is additive: $B_\mathbf{xy}$ is independent of ϕ.

The Fokker-Planck equation associated with Eq. (4.27) is

$$\partial_t P[\phi] = -\int d\mathbf{x}\frac{\delta}{\delta\phi(\mathbf{x})}\left(A_\mathbf{x}[\phi]P[\phi]\right) + \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\,\Gamma_\mathbf{xy}\frac{\delta^2 P[\phi]}{\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})} \tag{4.29}$$

with $\Gamma_\mathbf{xy} = \int d\mathbf{z}\, B_\mathbf{xz}B_\mathbf{yz}$.

We now return to our problem of prescribing the dynamics of an equilibrium model. We follow the Hohenberg & Halperin classification [20] (models A and B).

4.2.3 Relaxational dynamics (Model A)

The simplest dynamics given a Hamiltonian $H[\phi]$ is to relax following the "gradient":

$$\partial_t\phi(\mathbf{x}, t) = -\mu\frac{\delta H[\phi]}{\delta\phi(\mathbf{x})} + \xi(\mathbf{x}, t), \tag{4.30}$$

where μ is a mobility parameter and the noise ξ has a covariance

$$\langle\xi(\mathbf{x}, t)\xi(\mathbf{x}', t')\rangle = 2\mu T\delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{4.31}$$

It is important to note that we prescribed the strength of the noise to be $2\mu T$ to satisfy the fluctuation-dissipation relation and obtain the equilibrium probability in a few lines.

Eq. (4.30) corresponds to Eq. (4.27) with $A_\mathbf{x}[\phi] = -\mu\frac{\delta F[\phi]}{\delta\phi(\mathbf{x})}$ and $B_\mathbf{xy} = \sqrt{2\mu T}\delta(\mathbf{x} - \mathbf{y})$. The Fokker-Planck equation (4.29) is

$$\partial_t P[\phi] = \mu\int d\mathbf{x}\frac{\delta}{\delta\phi(\mathbf{x})}\left\{ \frac{\delta H[\phi]}{\delta\phi(\mathbf{x})}P[\phi] + T\frac{\delta P[\phi]}{\delta\phi(\mathbf{x})} \right\} \tag{4.32}$$

As expected, the equilibrium probability law $P[\phi] \propto e^{-\frac{1}{T}F[\phi]}$ is a stationary solution of the Fokker-Planck equation.

For concreteness, the model A equation associated with the Ginzburg-Landau Hamiltonian (4.23) is

$$\partial_t\phi(\mathbf{x}, t) = \mu\left[-t\phi(\mathbf{x}) - u\phi^3(\mathbf{x}) + \nabla^2\phi(\mathbf{x}) + h \right] + \sqrt{2\mu T}\eta(x, t). \tag{4.33}$$

4.2.4 Relaxational dynamics for a conserved field (Model B)

The model A does not conserve the total integral of the field. For a conserved field, the equation needs to be a conservation equation of the form $\partial_t \phi + \nabla \cdot \mathbf{J} = 0$, where $\mathbf{J}$ is the flux. A possible choice is the so-called model B. For simplicity, we write it in dimension 1,

$$\partial_t \phi(x,t) = -\partial_x \left\{ -\mu \partial_x \frac{\delta H[\phi]}{\delta \phi(x)} + \xi(x,t) \right\}, \tag{4.34}$$

$$\langle \xi(x,t)\xi(x',t') \rangle = 2\mu T \delta(x-x')\delta(t-t'). \tag{4.35}$$

Once again, we chose to satisfy the fluctuation-dissipation relation between the mobility and the noise strength.

One checks (using integration by parts) that Eq. (4.34) corresponds to Eq. (4.27) with $A_x[\phi] = \mu \partial_{xx} \frac{\delta H[\phi]}{\delta \phi(\mathbf{x})}$ and $B_{xy} = \sqrt{2\mu T}\partial_y \delta(x-y)$. The Fokker-Planck equation (4.29) is

$$\partial_t P[\phi] = \mu \int dx \frac{\delta}{\delta\phi(x)} \left(\partial_{xx}\frac{\delta H[\phi]}{\delta\phi(x)} P[\phi] \right) - \mu T \int dxdy [\partial_{yy}\delta(x-y)] \frac{\delta^2 P[\phi]}{\delta\phi(x)\delta\phi(y)} \tag{4.36}$$

$$= \mu \int dx \partial_x \frac{\delta}{\delta\phi(x)} \left[\partial_x \frac{\delta H[\phi]}{\delta\phi(x)} P[\phi] - T\partial_x \frac{\delta P[\phi]}{\delta\phi(x)} \right]. \tag{4.37}$$

We integrated by parts the second term, and used the fact that derivatives with respect to x and $\phi(x)$ commute. As in model A, the equilibrium probability law $P[\phi] \propto e^{-\frac{1}{T}H[\phi]}$ is a stationary solution of the Fokker-Planck equation.

As an example, let us write the stochastic version of the Cahn-Hilliard equation in arbitrary dimension, for the free-energy given by Eq. (4.25):

$$\partial_t \phi(\mathbf{x}) = \mu\nabla^2 \cdot [\phi(\mathbf{x})^3 - \phi(\mathbf{x}) - \gamma\nabla^2\phi(\mathbf{x})] + \zeta(x,t), \tag{4.38}$$

where ζ is a conserved noise of covariance $\langle \zeta(\mathbf{x},t)\zeta(\mathbf{x}',t') \rangle = 2\mu T\delta(t-t')\nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}'}\delta(\mathbf{x}-\mathbf{x}')$. We often prefer to write ζ as the divergence of a vectorial noise $\boldsymbol{\xi}$,

$$\zeta(\mathbf{x},t) = \nabla \cdot [\sqrt{2\mu T}\boldsymbol{\xi}(\mathbf{x},t)] \tag{4.39}$$

$$\langle \xi_\alpha(\mathbf{x},t)\xi_\beta(\mathbf{x}',t') \rangle = \delta_{\alpha\beta}\delta(\mathbf{x}-\mathbf{x}')\delta(t-t'), \tag{4.40}$$

where α, β denote spatial components.

4.3 Out-of-equilibrium stochastic fields

We now give a few examples of out-of-equilibrium stochastic field theory that have been proposed recently for different systems. They are all based on an equilibrium theory, but incorporate additional terms that violate fluctuation-dissipation relations and allow for net current in the stationary states.

Driven electrolyte. Démery & Dean [21] modeled an electrolytic solution as coupled stochastic equations for two species: positive particles that are driven to the right by an electric field $\mathbf{E} = E\mathbf{e}_x$, and negative particles that are driven to the left. It is assumed that the perturbations around an homogeneous density $\bar{\rho}$ are small. The perturbation to the density of positive particles is denoted $\phi_+(\mathbf{x})$ and the one of the negative particles is $\phi_-(\mathbf{x})$. The derivation of the equations is based on a linearization of the Dean-Kawasaki equation that we will describe below.

In the absence of electric field, the free energy of the system is

$$H[\phi_+,\phi_-] = \frac{1}{2}\int d\mathbf{x}d\mathbf{y} \sum_{\alpha,\beta=\pm 1} \phi_\alpha(\mathbf{x})V_{\alpha\beta}(\mathbf{x}-\mathbf{y})\phi_\beta(\mathbf{y}) + \frac{T}{2\bar{\rho}}\int d\mathbf{x}\left[\phi_+(\mathbf{x})^2 + \phi_-(\mathbf{x})^2\right]. \tag{4.41}$$

The first term accounts for the interaction between particles of species α and β with a potential $V_{\alpha\beta}$. The second term is a linearized entropy.

In presence of an electric field, the coupled stochastic differential equations for $\phi_\pm$ are:

$$\partial_t \phi_+(\mathbf{x}) = -\nabla \cdot \left[-\bar{\rho}\nabla\frac{\partial H}{\partial\phi_+(\mathbf{x})} + \mathbf{E}\phi_+(\mathbf{x}) + \sqrt{2\bar{\rho}T}\boldsymbol{\xi}_+(\mathbf{x}) \right], \tag{4.42}$$

$$\partial_t \phi_-(\mathbf{x}) = -\nabla \cdot \left[-\bar{\rho}\nabla\frac{\partial H}{\partial\phi_-(\mathbf{x})} - \mathbf{E}\phi_-(\mathbf{x}) + \sqrt{2\bar{\rho}T}\boldsymbol{\xi}_-(\mathbf{x}) \right]. \tag{4.43}$$

The mean density $\bar{\rho}$ plays the role of the mobility. $\boldsymbol{\xi}_{\pm}$ are Gaussian white noises of uncorrelated components and unit variance. The non-equilibrium effect of the electric field is visible in the additional fluxes $\pm\mathbf{E}\phi_{\pm}$ that encode the fact that positive particles are driven to the right while negative particles are driven to the left.

Such a Gaussian theory produces an analytical prediction for the conductivity (ratio of electric current over electric field) of the electrolyte [21].

Active models B+.   The phase separation of a passive fluid is often described with the Cahn-Hilliard Hamiltonian, Eq. (4.25),

$$H[\phi] = \int d\mathbf{x} \left[\frac{1}{4}(\phi(\mathbf{x})^2 - 1)^2 + \frac{\gamma}{2}(\nabla\phi)^2 \right]. \tag{4.44}$$

But phase separations may also occur in an out-of-equilibrium context. For instance self-propeled active Brownian particles experience a phase separation at high density and high activity. This separation between a dense (liquid-like) phase and a dilute (gaz-like) phase is known as motility induced phase separation. To describe such a phenomenon with a field theory, additional terms are required. One model that was proposed [22] is the active model B+:

$$\partial_t \phi(\mathbf{r}) = -\nabla \cdot \mathbf{J}(\mathbf{r}) \tag{4.45}$$

with the current

$$\mathbf{J}(\mathbf{r}) = -\mu\nabla\frac{\delta H}{\delta\phi(\mathbf{r})} - \lambda\nabla[(\nabla\phi)^2] + \zeta(\nabla^2\phi)\nabla\phi + \sqrt{2\mu T}\boldsymbol{\xi}(\mathbf{r}). \tag{4.46}$$

The two additional terms λ and ζ allowed by symmetry cannot be derived from a Hamiltonian. These terms have been linked to unsual behaviors of interfaces, and entropy production in the system.

Non-reciprocal Cahn-Hilliard equation.   As a last example, we mention the case of two species, with densities $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ that both undergo phase separations, but interact "non-reciprocally" [23]. By this, we mean that the effect of species 1 on species 2 is not the symmetric of the effect of species 2 on species 1. You may imagine foxes hunting rabbits and rabbits fleeing away from foxes. Starting with a Cahn-Hilliard-like free energy,

$$H[\phi_1, \phi_2] = \int d\mathbf{r} \left\{ \sum_{i=1}^{2} \left[\frac{1}{4}(\phi_i(\mathbf{r})^2 - 1)^2 + \frac{\gamma}{2}(\nabla\phi_i)^2 \right] + \chi\phi_1(\mathbf{r})\phi_2(\mathbf{r}) + \chi'\phi_1(\mathbf{r})^2\phi_2(\mathbf{r})^2 \right\}, \tag{4.47}$$

one incorporates the non-reciprocal effect with a coefficient α, leading to the coupled equations,

$$\partial_t \phi_1(\mathbf{r}) = \nabla \cdot \left[\mu\nabla \left\{ \frac{\partial H}{\partial\phi_1(\mathbf{r})} + \alpha\phi_2(\mathbf{r}) \right\} + \sqrt{2\mu T}\boldsymbol{\xi}_1(\mathbf{r}) \right], \tag{4.48}$$

$$\partial_t \phi_2(\mathbf{r}) = \nabla \cdot \left[\mu\nabla \left\{ \frac{\partial H}{\partial\phi_2(\mathbf{x})} - \alpha\phi_1(\mathbf{r}) \right\} + \sqrt{2\mu T}\boldsymbol{\xi}_2(\mathbf{r}) \right], \tag{4.49}$$

with $\boldsymbol{\xi}_i$ being the usual Gaussian white noises. Such a non-equilibrium model exhibits both pattern formation and traveling density waves [23].

4.4   From microscopics to field theories

Given a microscopic system of interacting particles, a legitimate question is whether we can build a (fluctuating) field theory for the density field of the system. In general, this is a daunting challenge. But we introduce here two problems in which this has been done explicitely. The details are rather technical, and we will stick topresenting the main ideas.

4.4.1   The Dean-Kawasaki equation

We want to describe a system of N overdamped particles interacting via a pairwise potential $V(\mathbf{r})$. The coupled Langevin equations for the positions $\mathbf{R}_i$ of the particles are

$$\partial_t \mathbf{R}_i = -\sum_{i=1}^{N} \nabla_i V(\mathbf{R}_i(t) - \mathbf{R}_j(t)) + \sqrt{2T}\boldsymbol{\eta}_i(t), \tag{4.50}$$

where η_i are Gaussian white noises of covariance $\langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\delta(t - t')$ (we dropped the mobility cofficient for simplicity). We define the local fluctuating density $\rho(\mathbf{r}, t)$ as

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i(t)). \tag{4.51}$$

Using a Ito calculus computation that we will not reproduce here, Dean showed [9] that $\rho(\mathbf{r}, t)$ obeys the following stochastic differential equation:

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \left[-\rho(\mathbf{r}, t)\frac{\partial H[\rho]}{\partial \rho(\mathbf{r})} + \sqrt{2T\rho(\mathbf{r}, t)}\boldsymbol{\eta}(\mathbf{r}, t) \right], \tag{4.52}$$

with the free energy

$$H[\rho] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho(\mathbf{r})V(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') + T \int d\mathbf{r}\rho(\mathbf{r}) \log \rho(\mathbf{r}). \tag{4.53}$$

The first term is the interaction energy between the particles, the second term is the entropy of the system. $\boldsymbol{\eta}(\mathbf{r}, t)$ is a Gaussian white noise of covariance $\langle \eta_\alpha(\mathbf{r}, t)\eta_\beta(\mathbf{r}', t')\rangle = \delta_{\alpha\beta}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$. In Eq. (4.52), Ito convention is assumed.

Eq. (4.52) is known as the Dean-Kawasaki equation [24]. It is an exact equation for ρ given by Eq. (4.51). But it is hard to handle because (i) it is non linear in ρ, and (ii) the noise is multiplicative.

The analog of the Dean-Kawasaki equation for the probability $P[\rho]$ of observing a given density field is the Kawasaki equation [24],

$$\partial_t P[\rho] = -\int d\mathbf{r}\frac{\delta}{\delta\rho(\mathbf{r})}\nabla \cdot \left[\rho(\mathbf{r})\nabla \left(\frac{\delta H}{\delta\rho(\mathbf{r})}P[\rho] + T\frac{\delta P}{\delta\rho(\mathbf{r})} \right) \right]. \tag{4.54}$$

The equilibrium probability $P[\rho] \propto \exp\left(-\frac{1}{T}H[\rho]\right)$ is solution of the Kawasaki equation (4.54).

One big advantage of the Dean-Kawasaki equation (4.52) is that it can be easily extended to out-of-equilibrium situations such as driven or active systems. Progress have been made in several directions, in particular by linearizing the equation around an homogeneous density profile. See Refs. [24, 25, 21] for more details.

4.4.2 Fluctuating hydrodynamics of a lattice model

Starting from a microscopic model, such as the symmetric exclusion principle (SEP, Fig. 4.1), it is tempting to wonder whether there is a continuous limit at large length scales and large times. That is to say if we can describe the system with a "hydrodynamic" equation for a continuous density field $\rho(x, t)$.

Indeed, a diffusive 1D lattice model can be described at large scale by two quantities $D(\rho)$ and $\sigma(\rho)$ [26]. $D(\rho)$ is linked to the average flux in the system when there is a small inbalance of density between the left and the right, while $\sigma(\rho)$ is linked to the variance of the flux for a uniform density. In the general case, $D(\rho)$ and $\sigma(\rho)$ are linked by a fluctuation-dissipation relation: $\sigma(\rho) = \frac{2T}{f''(\rho)}D(\rho)$ where $f(\rho)$ is the microscopic free-energy. In the case of the SEP, $D(\rho) = 1/2, \sigma(\rho) = \rho(1 - \rho)$ and $f(\rho) = T[\rho \log \rho + (1 - \rho)\log(1 - \rho)]$.

Given these definitions, the dynamics of the lattice model at large time, on diffusive length scales is assumed to be given by the following fluctuating hydrodynamics equation:

$$\partial_t \rho(x, t) = \partial_x \left[D(\rho(x, t))\partial_x \rho(x, t) + \sqrt{\sigma(\rho(x, t))}\eta(x, t) \right], \tag{4.55}$$

with $\langle \eta(x, t)\eta(x', t')\rangle = \delta(x - x')\delta(t - t')$. The Ito convention is assumed.

On can go further by writing the path integral description of Eq. (4.55). This approach is known as macroscopic fluctuation theory [27]. Things become technical quickly, and we only sketch the main steps. We consider the probability $P(\rho(x, 0) \to \rho(x, T))$ of having a density profile $\rho(x, T)$ at time T knowing that we started from the initial density profile $\rho(x, 0)$. We write this probability as a path integral over the evolution of the density ρ and the flux j:

$$P(\rho(x, 0) \to \rho(x, T)) \propto \int \mathcal{D}j\mathcal{D}\rho \, P(\{j(x, t), \rho(x, t)\}). \tag{4.56}$$
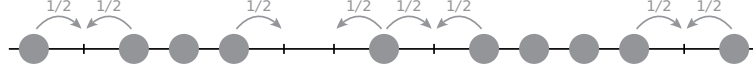
Figure 4.1: In the symmetric exclusion process (SEP), particles are on a discrete line. During a short time interval Δt, a given particle has a probability $\frac{1}{2}\Delta t$ to jump to the right, and the same probability to jumpy to the left. Hard-core exclusion is enforced meaning that a particle cannot jump if its arrival site is occupied. We can define $\eta_i(t) \in \{0,1\}$ the occupation of site i at time t (1 means occupied, 0 empty). At large distance L, the system evolves on a diffusive timescale $\tau \sim L^2$. We may write $\eta_i(t) \simeq \rho\left(\frac{i}{L}, \frac{t}{L^2}\right)$ with $L \gg 1$. ρ is the fluctuating field that we want to describe.

The probability $P(\{j(x,t), \rho(x,t)\})$ of a given path is

$$P(\{j(x,t), \rho(x,t)\}) \propto e^{-I(j,\rho)} \mathbb{I}\left(\partial_t \rho(x,t) + \partial_x j(x,t)\right) \tag{4.57}$$

where $\mathbb{I}$ is a delta function enforcing the relationship between the density and the flux, and $I(j,\rho)$ is the action and reads

$$I(j,\rho) = \int dx \int_0^T dt \frac{[j(x,t) + D(\rho(x,t))\partial_x \rho(x,t)]^2}{2\sigma(\rho(x,t))}. \tag{4.58}$$

One checks that this is analogous to the path integral approach to the usual Langevin equation.

The delta function may be represented with an auxilliary field $H(x,t)$:

$$\mathbb{I}\left(\partial_t \rho(x,t) + \partial_x j(x,t)\right) = \int \mathcal{D}H e^{-\int dx \int_0^T dt H(x,t)[(\partial_t \rho(x,t) + \partial_x j(x,t)]}, \tag{4.59}$$

where it is customary to drop the imaginary number i from the exponential. And after performing a Gaussian integration over the field j, one eventually obtains

$$P(\rho(x,0) \rightarrow \rho(x,T)) \propto \int \mathcal{D}\rho \mathcal{D}H \exp\left[-\int dx \int_0^T dt \left\{ H\partial_t \rho + D(\rho)\partial_x \rho \partial_x H - \frac{\sigma(\rho)}{2}(\partial_x H)^2 \right\}\right]. \tag{4.60}$$

At large times, one wants to approximate the integral by the minimum of the action and perform a saddle point approximation. The optimal path (ρ^*, H^*) (denote (q,p) in the litterature...) satisfies the following coupled differential equations,

$$\partial_t \rho^* = \partial_x[D(\rho^*)\partial_x \rho^*] - \partial_x[\sigma(\rho^*)\partial_x H^*], \tag{4.61}$$

$$\partial_t H^* = -D(\rho^*)\partial_x^2 H^* - \frac{1}{2}(\partial_x \rho^*)^2. \tag{4.62}$$

One notes that in general these equations are non-linear. Furthermore, the devil is in the details, and in this case in the boundary conditions associated with the latest equations. They render any computation very technical.

One recent success of MFT is the computation of the full probability law $X(t)$ of a tagged particle in the SEP from the macroscopic equations [28].

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