Chapter 1

Equilibrium Statistical Mechanics

1.1 Basic postulates

If we quickly review classical statistical mechanics the starting point is quite simply Hamilton's equations of motion for the phase space coordinates $\Gamma = \{q, p\}$, where q refers to the positions of the particles making up the system (and possibly rotational degrees of freedom, or else), and p stand for the conjugate momenta $p = \frac{\partial L}{\partial \dot{q}}$, where L is the Langrangian of the system. The Hamiltonian $H(q,p) = \dot{q}p - L(q,\dot{q})$ ()with $\dot{q}(q,p)$ being the implicit solution of $p = \frac{\partial L}{\partial \dot{q}}$) is then used to write the equations of motion:

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

which are, in simple notations, Newton's equations of motion.

In statistical mechanics, a key concept is that of Gibbs ensemble: this is a collection of $M \gg 1$ systems that are, from a macroscopic point of view, prepared in an identical manner. While from one system to another the positions of the particles may differ, some macroscopic quantities are the same. Some Gibbs ensembles have specific names. For instance, the micro-canonical ensemble refers to a collection of systems sharing in common the same total energy, the same number of particles, and the same volume.

Out of this collection of M identically prepared systems, we call $n(\Gamma, t)\mathrm{d}\Gamma$ the number of systems whose phase space coordinates are between Γ and $\Gamma + \mathrm{d}\Gamma$. Of course, this Γ notation is a short cut for a large dimensional vector

$$\Gamma = \{\mathbf{r}_i, \mathbf{p}_i\}_{i=1,\ldots,N},\ \mathrm{d}\Gamma = \mathrm{d}^d r_1 \ldots \mathrm{d}^d r_N \mathrm{d}^d p_1 \ldots \mathrm{d}^d p_N \tag{1.2}$$

where d is the embedding space dimension ($d = 1$, 2 or 3 depending on the physical context), N is the number of particles, and the $\mathbf{p}_i$'s are the momenta conjugate to the positions $\mathbf{r}_i$ of he particles making up the system.

Very often, one considers $\frac{1}{M} n \mathrm{d}\Gamma$, and this quantity is the probability to find one of the M systems with its phase space coordinates between Γ and $\Gamma + \mathrm{d}\Gamma$, and one works with $\rho = n/M$

as ρ (which then becomes a probability density over the collection of M systems).

Because systems are neither created nor destroyed, the systems can be viewed as the M particles of a locally conserved fluid flowing in phase space, with the continuity equation

$$\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma}\rho) = 0 \tag{1.3}$$

involving the local current $\dot{\Gamma}\rho$ in phase space (and again, $\dot{\Gamma}$ is a short notation for $\{\dot{\mathbf{r}}_i, \dot{\mathbf{p}}_i\}$ while the divergence $\partial_\Gamma \cdot$ is a divergence in phase space with respect to the $2dN$ coordinates $\mathbf{r}_1, \ldots, \mathbf{p}_N$). This conservation equation simply expresses that the M systems are independent.

However, due to Hamilton's equations of motion, the fluid of systems is actually incompressible. Indeed the velocity of the fluid is

$$\dot{\Gamma} = \{\dot{\mathbf{r}}_i, \dot{\mathbf{p}}_i\} \tag{1.4}$$

and it is divergenceless

$$\begin{aligned} \partial_\Gamma \cdot \dot{\Gamma} =& \sum_i \partial_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \sum_i \partial_{\mathbf{p}_i} \dot{\mathbf{p}}_i \\ =& \sum_i \partial_{\mathbf{r}_i} \cdot \left[\frac{\partial H}{\partial \mathbf{p}_i}\right] + \sum_i \partial_{\mathbf{p}_i} \cdot \left[-\frac{\partial H}{\partial \mathbf{r}_i}\right] \\ =& 0 \end{aligned} \tag{1.5}$$

another way of phrasing this property is to look at the evolution of $\rho(t) = \rho(\Gamma(t), t)$ in a Lagrangian way, namely along the motion, by considering the total derivative of ρ:

$$\begin{aligned} \frac{\mathrm{d}\rho}{\mathrm{d}t} =& \partial_t \rho + (\dot{\Gamma} \cdot \partial_\Gamma)\rho \\ =& \underbrace{\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma}\rho)}_{=0 \text{ by the continuity equation}} - \rho \underbrace{\partial_\Gamma \cdot \dot{\Gamma}}_{=0 \text{ due to incompressibility}} \\ =& 0 \end{aligned} \tag{1.6}$$

Hence the phase space density is a constant along the motion. This tells us that

$$\begin{aligned} 0 =& \partial_t \rho + (\dot{\Gamma} \cdot \partial_\Gamma)\rho \\ =& \partial_t \rho + \sum_i \dot{\mathbf{r}}_i \cdot \partial_{\mathbf{r}_i} \rho + \sum_i \dot{\mathbf{p}}_i \cdot \partial_{\mathbf{p}_i} \rho \\ =& \partial_t \rho + \sum_i \left[\frac{\partial H}{\partial \mathbf{p}_i}\right] \cdot \partial_{\mathbf{r}_i} \rho + \sum_i \left[-\frac{\partial H}{\partial \mathbf{r}_i}\right] \cdot \partial_{\mathbf{p}_i} \rho \\ =& \partial_t \rho + \partial_p H \partial_q \rho - \partial_q H \partial_p \rho \\ =& \partial_t \rho - \{H, \rho\} \end{aligned} \tag{1.7}$$

where the Poisson brackets notation is defined as

$$\{F(\Gamma = (q,p)), G(\Gamma)\} = \partial_q F \partial_q G - \partial_q G \partial_p F = \sum_i \left[\partial_{\mathbf{r}i} F \cdot \partial_{\mathbf{p}_i} G - \partial_{\mathbf{r}i} G \cdot \partial_{\mathbf{p}_i} F\right] \tag{1.8}$$

This linear, first order in time, differential equation governing the evolution of $\rho(\Gamma, t)$, namely,

$$\partial_t \rho = \{H, \rho\} = -i\mathscr{L}\rho, \; -i\mathscr{L} = \{H, \; \} \tag{1.9}$$

is also known at the Liouville equation ($\mathscr{L}$ is the Liouvillian). The big question is: can we solve it? And the short answer is: in general, no.

Our goal is indeed to obtain ρ so that we can make averages to determine the properties of the system of interest.

This is where the two postulates of equilibrium statistical mechanics come into play. The first one is that, at large times, when the system has settled in a steady-state, one can equate a time average performed in the course of the evolution of the physical system of interest, with an average over a collection of systems prepared in the same conditions. This is the ergodic hypothesis.

The second postulate is way stronger: if the system is initially closed and isolated, at fixed volume then at large times $\rho(\Gamma, t)$ converges to a constant. This means that in equilibrium, all the microstates Γ that the system can be found in are equally likely to be observed. In the microcanoncal Gibbs ensemble characterized by ρ, we have

$$\begin{aligned} \overline{A(\Gamma)} = \lim_{\tau \to +\infty} \frac{1}{\tau} \int_0^\tau \mathrm{d}t A(\Gamma(t)) &\overset{\text{ergodic}}{=} \int \mathrm{d}\Gamma \rho(\Gamma) A(\Gamma) \\ &\overset{\text{equiprobability}}{=} \frac{\int \mathrm{d}\Gamma A(\Gamma)}{\int \mathrm{d}\Gamma} \end{aligned} \tag{1.10}$$

The denominator $\Omega = \int \mathrm{d}\Gamma$ is finite because one integrates only over space space coordinates that respect the finite volume and finite energy constraints that are prescribed. The normalization constant Ω (which often incorporates prefactors such as $\frac{1}{N!}$ or h^{-dN}, where h is Planck's constant) is known as the microcanonical partition function.

In practice, and depending on the modeling, instead of phase space coordinates Γ one may be interested in a spin configuration, or in the conformation of a polymer, or *etc.*. To make notations somewhat lighter, we'll henceforth use $\mathscr{C}$ as a generic microstate, and use discrete summation $\sum_{\mathscr{C}}$ instead of integrals over phase space, but depending on context, one should use $\sum_{\mathscr{C}}$ or $\int \mathrm{d}\Gamma$ or whatever is appropriate. In this discrete notation, $P(\mathscr{C})$ plays the role of $\rho(\Gamma)$. In the microcanonical ensemble, $\Omega = \sum_{\mathscr{C} \text{ with fixed energy } E} 1$.

It turns out that the Shannon entropy $S = -\sum_{\mathscr{C}} P(\mathscr{C}) \ln P(\mathscr{C})$ is the largest when the random variable is uniform, which is the case of interest. It reduces to $S = \ln \Omega$ for our uniform distribution $P(\mathscr{C}) = \frac{1}{\Omega}$, or, better, introducing physical units, $S = k_{\mathrm{B}} \ln \Omega$ so that direct contact with the thermodynamic entropy is achieved.

1.2 The canonical ensemble, and the concept of a thermostat

Once we have our statistical mechanics postulates, we can apply them to a rather common situation: that of a system $\mathcal{S}$ embedded in some much larger system $\mathcal{R}$ (that we shall call a reservoir), while the reunion $\mathcal{S} \cup \mathcal{R}$ is actually isolated with energy E. This is the cartoon of Fig. 1.1.

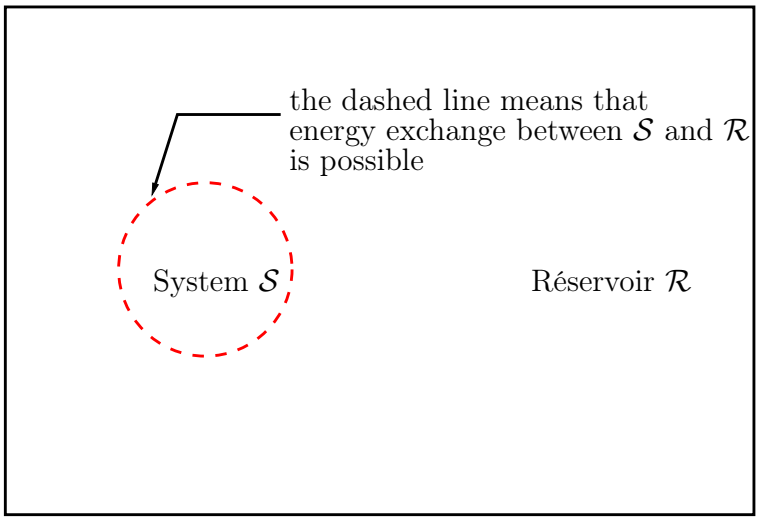

Figure 1.1: The whole system $\mathcal{S} \cup \mathcal{R}$ is isolated and thus the microcanonical postulate applies to it.

Our interest goes only to the system, not to its surrounding environment. Fortunately, it is possible to determine the probability $P(\mathscr{C}_\mathcal{S})$ to find the system in state $\mathscr{C}_\mathcal{S}$ regardless of the microstate of the environment $\mathcal{R}$:

$$\begin{aligned} P(\mathscr{C}_\mathcal{S}) =& \frac{\text{number of configurations of } \mathcal{R} \text{ compatible with state } \mathscr{C}_\mathcal{S}}{\text{total number of configurations}} \\ =& \frac{\Omega_\mathcal{R}(\text{with energy } E - E_\mathcal{S}(\mathscr{C}_\mathcal{S}))}{\Omega_{\mathcal{S}\cup\mathcal{R}}(E)} \end{aligned} \tag{1.11}$$

But since the system is much small than the reservoir, we can make the following approximation,

$$\begin{aligned} P(\mathscr{C}_\mathcal{S}) =& \frac{\Omega_\mathcal{R}(E - E_\mathcal{S}(\mathscr{C}_\mathcal{S}))}{\Omega_{\mathcal{S}\cup\mathcal{R}}(E)} \\ =& \frac{\mathrm{e}^{\frac{1}{k_\mathrm{B}} S_\mathcal{R}(E - E_\mathcal{S}(\mathscr{C}_\mathcal{S}))}}{\Omega_{\mathcal{S}\cup\mathcal{R}}(E)} \\ \simeq& \text{a } \mathscr{C}_\mathcal{S}\text{-independent constant} \times \mathrm{e}^{-\frac{1}{k_\mathrm{B}} \frac{\partial S_\mathcal{R}}{\partial E} E_\mathcal{S}} \\ =& \frac{1}{Z} \mathrm{e}^{-\beta E_\mathcal{S}(\mathscr{C}_\mathcal{S})} \end{aligned} \tag{1.12}$$

where $\beta = \frac{1}{k_B T_{\mathcal{R}}}$ and $T_{\mathcal{R}} = \frac{1}{\partial S_{\mathcal{R}}/\partial E}$ is the temperature of the reservoir. In this formula, Z appears to be a normalization constant,

$$Z = \sum_{\mathscr{C}} \mathrm{e}^{-\beta E_{\mathcal{S}}(\mathscr{C}_{\mathcal{S}})} \tag{1.13}$$

and it is remarkable that, in the expression of he Boltzmann distribution $P(\mathscr{C}_{\mathcal{S}}) = \frac{1}{Z}\mathrm{e}^{-\beta E_{\mathcal{S}}(\mathscr{C}_{\mathcal{S}})}$, the only place where the reservoir appears is through its inverse temperature β. The reservoir is called a thermostat. Note that the system $\mathcal{S}$ does not have to be a macroscopic system.

Of course, there are some hypotheses that we haven't detailed. One of them is that the interactions between the system and the reservoir must be short-ranged. And needless to say, asserting that Z is merely a normalization constant is a gross understatement, as we know that

$$F = -\frac{1}{\beta} \ln Z \tag{1.14}$$

is the free energy of the system, out of which many physical properties can be extracted (by differentiation with respect to β). Such systems $\mathcal{S}$ that are in contact with a thermostat, and whose energy can thus fluctuate, are said to be prepared in canonical conditions (this is Gibbs' canonical ensemble: a collection of systems with fixed volume and fixed particle number, in contact with a thermostat imposing a fixed temperature).

In a mathematical language, Z is the generating function of the energy of the system (which is a random variable). Forgetting about the $\mathcal{S}$ index, when we write

$$Z = \sum_{\mathscr{C}} \mathrm{e}^{-\beta E(\mathscr{C})} \tag{1.15}$$

we see that $\langle E \rangle = -\partial_\beta \ln Z$, $\langle E^2 \rangle - \langle E \rangle^2 = \partial_\beta^2 \ln Z$, and thus the free energy (or rather $\ln Z = -\beta F$) is the generating function of the cumulants of the energy of the system,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = U,\ \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = \beta^{-2} C_v \tag{1.16}$$

where U is the ineternal energy and C_v the heat capacity. The entropy can be retrieved from $S = -\frac{\partial F}{\partial T}$ and it is a simple exercise to verify that, again,

$$S/k_B = -\sum_{\mathscr{C}} P(\mathscr{C}) \ln P(\mathscr{C}) \tag{1.17}$$

where now $P(\mathscr{C}) = \mathrm{e}^{-\beta E(\mathscr{C})}/Z$ is the canonical distribution. Maximizing $S[P] = -\sum_{\mathscr{C}} P(\mathscr{C}) \ln P(\mathscr{C})$ under the constrains that not only $\sum_{\mathscr{C}} P(\mathscr{C}) = 1$ but also that $U = \sum_C E(\mathscr{C}) P(\mathscr{C})$ are fixed leads exactly to the canonical distribution, where the coeffeicient β is an implicit function of U.

All this is the realm of equilibrium statistical mechanics. A particularly dense and to-the-point book is that of Chandler [18] in case refreshing one's memory would be necessary.

The take home message of this section is

- Start from a complex systems whose dynamics can in general not be solved but in in some specific conditions invoke two simplifying postulates;
- Postulate that the probability of observing a given microstate has a the microcanonical form (or canonical one if a thermostat can be defined), then all static, one point quantities can in principle be obtained;
- this is remarkable that no information on a reservoir is needed beyond its temperature;
- but be humble, as it may actually be very hard to extract the physics from a partition function, even when all the equilibrium conditions are gathered;
- and, still in equilibrium, we know nothing about relaxation processes, time-correlations, *etc.*. Time doesn't just disappear as a relevant variable just because a system is in equilibrium;
- and realize that equilibrium conditions are the exception rather than the rule.

1.3 Why does it work?

As mentioned above, the equilibrium machinery does have limitations: the number of systems for which one can actually exactly compute Ω or Z is extremely limited (some one-dimensional systems, including the Ising model with an external magnetic field, a few two-dimensional systems including the Ising model without a field) and the whole point of statistical mechanics is to have the Boltzmann formula spit out what it knows on the macroscopic behavior of the system. Beyond exactly-solvable models that are so rare, a zoo of approximations have been invented, and numerical techniques able to efficiently sample the Boltzmann distribution have been designed over the years.

And yet, it is a legitimate question to understand why the equilibrium machinery works so well (beyond technical difficulties). This is a field of mathematical physics of its own known as ergodic theory and dynamical systems. One of the key ingredients is that the dynamics of the system must display chaotic properties, and more precisely, it must display the ability to mix probabilities appropriately. These mixing properties are measured by quantifying the time it takes for the probability distribution to forget its initial distribution. This time must be short enough, which is of course a sloppy statement unless other reference times are specified. Such discussions are taken up in the book by Dorfman [26]. That book is about understanding why these are difficult questions.

Chapter 2

The Langevin Equation

2.1 What is the question?

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

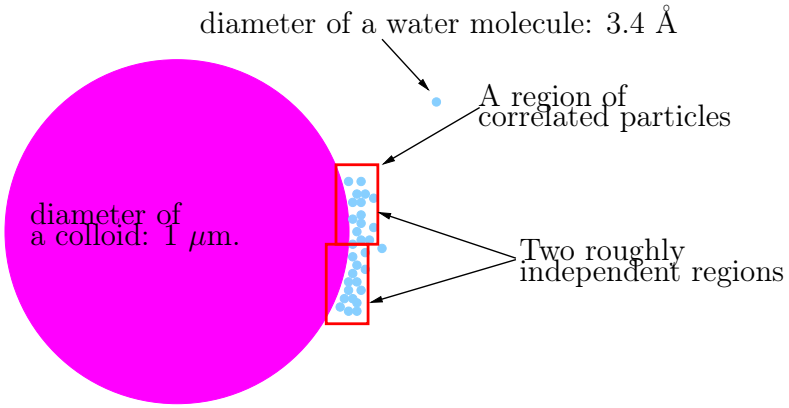

Figure 2.1: The regions of correlated particles are large enough so that they exceed in size the water molecules correlation length (also a few Å), but small enough so that there is a large number of these independent regions. For this to be possible, the separation of length scales between the bath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

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

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

and the corresponding equations of motion read

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

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

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

Of course, this is true only if certain conditions are fulfilled (short range interactions, the bath is much bigger than the colloid, *etc.*). Regarding the dynamics, we would like to obtain an evolution equation for $\mathbf{R}$ only, forgetting about the bath molecules, or rather, forgetting about individual water molecules, but still retaining some of the relevant properties of the bath they make up. The last contribution is interesting, because if we sample our initial state from the Boltzmann distribution for the water molecules, then $\sum_i \mathbf{F}_i$ is a random variable. This is the sum of a large number of identically distributed random variables. They are correlated, but given the scale separation between the colloid and the water molecules, we expect that we can group $\sum_i \mathbf{F}_i$ into $\sum_{\text{regions}} \sum_{i\in\text{region}} \mathbf{F}_i$, where within a given region the water molecules are indeed correlated, while regions are independent (as shown in Fig. 2.1). This is possible if the correlation length of the water molecules is smaller than the size of the colloid, and if it is sufficiently smaller so that there can be a large number of these independent regions, then the central limit theorem applies and we can write something like

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

where in principle $\langle \sum_i \mathbf{F}_i \rangle_b$ functionally depends on $\mathbf{R}$. Of course, we know what to expect for this average contribution. If for some external reason (gravity, electric field, pulling the center of the optical trap) the colloid has a net motion, it will have to push the water molecules away, and this will cause a viscous drag, that is a force proportional to $-\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}$. In a much more general fashion, since $\langle \sum_i \mathbf{F}_i \rangle_b$ is a vector it can only be expressed with the available vectors, namely $\mathbf{R}$, but also $\dot{\mathbf{R}}$, $\ddot{\mathbf{R}}$, and so on and so forth. It is thus possible *a priori* to express it as

$$\langle \sum_i \mathbf{F}_i \rangle_b = \sum_n \lambda_n \frac{\mathrm{d}^n\mathbf{R}}{\mathrm{d}t^n} \tag{2.5}$$

or,

$$\langle \sum_i \mathbf{F}_i \rangle_b = \int \mathrm{d}t' \Gamma(t-t')\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t'} \tag{2.6}$$

where Γ is some memory kernel whose expansion is related to the λ_n coefficients. However, obtaining Γ explicitly is of course beyond our reach. In addition, the λ_n or Γ are scalars, but they could also depend on scalars constructed with the function $\mathbf{R}$.

When we can actually write that $\langle \sum_i \mathbf{F}_i \rangle_b$ is a simple viscous drag $-\gamma \dot{\mathbf{R}}$ that involves a friction coefficient γ, then we can, for large enough colloids, compute γ using hydrodynamics (for a colloid of radius a, $\gamma = 6\pi\eta a$ where η is the viscosity of water). Perhaps memory effects will come into play and the drag force could be a little more complicated, but if the repeated collisions of the water molecules occur at a high enough frequency (10^{13} Hz roughly [86] to be compared with the typical time at which velocity equilibrates, 10^{-9} s), memory effects can be considered irrelevant and $\Gamma(t)$ will be proportional to $\delta(t)$.

The lesson we draw from this discussion is the following: if there is a separation of time and spatial scales, then things seem to simply considerably. But so much more remains to be done:

- Can we actually determine $\langle \sum_i \mathbf{F}_i \rangle_b$ as a functional of $\mathbf{R}$? Can the viscous drag term pop out of a calculation in which this average could be explicitly carried out?
- That there are Gaussian fluctuations remains rather vague. Are they colored or memory–less? How does their amplitude depend on $\mathbf{R}$ (if at all)?
- And is there anything generic that can be stated regarding the viscous drag kernel and force fluctuations?

2.2 The Feynman-Vernon-Caldeira-Leggett-Ford-Kac-Mazur approach

2.2.1 The model

The Hamiltonian of the system at $t > 0$ has several contributions:

$$\mathscr{H} = \underbrace{\mathscr{H}_0(\mathbf{R},\mathbf{P})}_{\text{colloid, mass } M} + \underbrace{\mathscr{H}_b\left(\{\mathbf{r}_i,\mathbf{p}_i\}\right)}_{\text{water molecules}} + \underbrace{\sum_i V_i(\mathbf{R}-\mathbf{r}_i)}_{\text{interaction of the bath with the colloid}} \tag{2.7}$$

and the corresponding equations of motion read

$$m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\mathbf{F}_i - \partial_{\mathbf{r}_i}\mathscr{H}_b, \;\; M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -\partial_{\mathbf{R}}\mathscr{H}_0 + \sum_i \mathbf{F}_i \tag{2.8}$$

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

$$P(\mathbf{R},\mathbf{P}) \propto \mathrm{e}^{-\beta\mathscr{H}_0(\mathbf{R},\mathbf{P})} \tag{2.9}$$

Let us now focus on the following situation. We assume that the bath is for now alone, and that at $t = 0$ it is indeed in thermal equilibrium. We further assume that it is made of an

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$$m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\mathbf{F}_i - \partial_{\mathbf{r}_i}\mathscr{H}_b, \;\; M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -\partial_{\mathbf{R}}\mathscr{H}_0 + \sum_i \mathbf{F}_i \tag{2.8}$$

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

$$P(\mathbf{R},\mathbf{P}) \propto \mathrm{e}^{-\beta\mathscr{H}_0(\mathbf{R},\mathbf{P})} \tag{2.9}$$

Let us now focus on the following situation. We assume that the bath is for now alone, and that at $t = 0$ it is indeed in thermal equilibrium. We further assume that it is made of an

assembly of harmonic osccilators

$$\mathscr{H}_b + \sum_i V(\mathbf{r}_i) = \sum_i \left[\frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} k_i \mathbf{r}_i^2 \right] \tag{2.10}$$

Note that, due to equipartition of energy, at $t \leq 0$ we have

$$\langle r_i^\mu(0) r_j^\nu(0) \rangle = \delta_{ij} \delta^{\mu\nu} \frac{k_\mathrm{B} T}{m_i k_i}, \; \langle p_i^\mu(0) p_j^\nu(0) \rangle = \delta_{ij} \delta^{\mu\nu} m_i k_\mathrm{B} T, \; \langle r_i^\mu(0) p_j^\nu(0) \rangle = 0 \tag{2.11}$$

where the $\mu, \nu = 1, \ldots, d$ indices refer to the d possible space directions. Then the colloidal particle is placed at the initial time $t = 0$ at location $\mathbf{R}(0) = \mathbf{0}$ and now there is an interaction of the particle with the bath, so that

$$\sum_i V_i(\mathbf{r}_i) \to \sum_i V_i(\mathbf{R} - \mathbf{r}_i) \tag{2.12}$$

The force $\mathbf{F}_i$ exerted by the bath on the particle is $\mathbf{F}_i = -k_i(\mathbf{R} - \mathbf{r}_i)$ and the equation of motion of a particle of the bath is

$$m_i \frac{\mathrm{d}^2 \mathbf{r}_i}{\mathrm{d}t^2} = -\mathbf{F}_i \tag{2.13}$$

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

$$\mathbf{r}_i(t) = \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t + \omega_i \int_0^t \mathrm{d}t' \sin \omega_i (t - t') \mathbf{R}(t') \tag{2.14}$$

so that

$$\begin{aligned} \mathbf{r}_i(t) - \mathbf{R}(t) =& \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t + \int_0^t \mathrm{d}t' \omega_i \sin \omega_i (t - t') \mathbf{R}(t') - \mathbf{R}(t) \\ \mathbf{r}_i(t) - \mathbf{R}(t) =& \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t - \int_0^t \mathrm{d}t' \cos \omega_i (t - t') \frac{\mathrm{d}}{\mathrm{d}t'} \mathbf{R}(t') \end{aligned} \tag{2.15}$$

$$\begin{aligned} M \frac{\mathrm{d}^2 \mathbf{R}}{\mathrm{d}t} =& -\partial_{\mathbf{R}} H_0 - \sum_i k_i (\mathbf{R} - \mathbf{r}_i) \\ =& -\partial_{\mathbf{R}} H_0 + \sum_i k_i \left[\mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t - \int_0^t \mathrm{d}t' \cos \omega_i (t - t') \frac{\mathrm{d}}{\mathrm{d}t'} \mathbf{R}(t') \right] \\ =& -\partial_{\mathbf{R}} H_0 - \int_0^t \mathrm{d}t' M_R(t - t') \frac{\mathrm{d}}{\mathrm{d}t'} \mathbf{R}(t') + \boldsymbol{\xi}(t) \end{aligned} \tag{2.16}$$

where

$$M_R(\tau) = \theta(\tau) \sum_i k_i \cos \omega_i \tau \tag{2.17}$$

and

$$\boldsymbol{\xi}(t) = \sum_i k_i \left[\mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t \right] \tag{2.18}$$

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

$$\begin{aligned}\langle \xi^\mu(t)\xi^\nu(t')\rangle =& \delta^{\mu\nu}\sum_i k_i T\left[\cos\omega_i t\cos\omega_i t' + \sin\omega_i t \sin\omega_i t'\right]\\ =& T\delta^{\mu\nu}\sum_i k_i \cos\omega_i(t-t')\\ =& M_C(t-t')\end{aligned} \tag{2.19}$$

The present derivation has been discussed by several authors [34, 113, 13] and further discussion can be found in L. Cugliandolo's lecture notes, subsection 2.4.2. There a discussion of the various ingredients ω_i and m_i characterizing the bath is carried out. An important conclusion that we can draw from this calculation is that generically, integrating the bath degrees of freedom out leads to a generalized Langevin equation. Another important conclusion is that this purely dynamical approach, which contrasts with the statistical one of the earlier chapters, shows us how to adapt our approach to the quantum world.

2.2.2 The resulting generalized Langevin equation and the Markov limit

Let us summarize our findings: it is possible to mimic the effect of the bath by replacing its degrees of freedom by two ingredients, a friction force and a noise term. These ensure that the statics of $\mathbf{R}$ is identical to the one that would be obtained by explicitly considering the individual bath degrees of freedom. The resulting equation reads

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -\partial_{\mathbf{R}}H_0 - \int_0^t \mathrm{d}t' M_R(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\mathbf{R}(t') + \boldsymbol{\xi}(t) \tag{2.20}$$

with the friction kernel given by

$$M_R(t) = \theta(\tau)\sum_i k_i \cos\omega_i t \tag{2.21}$$

and $\boldsymbol{\xi}$ which has Gaussian statistics

$$\langle \xi^\mu(t)\xi^\nu(t')\rangle = \delta^{\mu\nu}M_C(t-t') \tag{2.22}$$

and quite remarkably we notice that $M_C(\tau) = T(M_R(\tau) + M_R(-\tau))$ (which is often called Kubo's second fluctuation-dissipation theorem). This property is rooted in the equilibrium nature of the dynamics, as we will discuss later. This is of course not a coincidence. We know at large time the degree of freedom of the colloid will be equilibrated, but why this is connected to the equality of M_C and M_R is still unclear. However, we do expect that M_R and M_C must be strongly connected, because whatever energy the colloid loses to the bath through viscous

friction will be reinjected by the bath into the colloid by means of random kicks. At this moment in the lectures, we have however no clue on how to bridge Eq. (2.20) directly to the fact that at large times, $\mathbf{R}$ and $\mathbf{P}$ are sampled according to the Boltzmann distribution $\mathrm{e}^{-\beta\mathscr{H}_0(\mathbf{R},\mathbf{P})}$. We will be able to make this technical step in the next chapter. However, we know that this must be true since our starting point is an equilibrium system, each subsystem of which is in equilibrium as well.

What the ω_i's are exactly is difficult to pinpoint if the analysis is restricted to the present model of oscillators. And in general, for a given bath, there will be a distribution of these frequencies. For instance

$$M_R(t) = \theta(\tau) m \sum_i \omega_i^2 \cos\omega_i t \simeq \theta(\tau) m \int \mathrm{d}\omega g(\omega) \cos(\omega t) \tag{2.23}$$

where $g(\omega)\mathrm{d}\omega$ is the number of ω_i's between ω and $\omega + \mathrm{d}\omega$. Depending on the density $g(\omega)$, the memory kernel can display a variety of behaviors, from very short-range to slow power-law decay. For instance, for $g(\omega) \propto \frac{1}{\omega^2+\tau_c^{-2}}$ we see that $M_R(t) \propto \exp(-t/\tau_c)$, where τ_c is a correlation time reflecting the properties of the bath. This means that, for instance

$$M_C(t) = 2T\gamma \frac{1}{2\tau_c} \mathrm{e}^{-|t|/\tau_c} \tag{2.24}$$

which defines the constant γ. And if τ_c is much shorter than any other time scale (resulting from the dynamics of $\mathbf{R}$ itself) then we can make the Markov approximation

$$M_C(t) = 2T\gamma\delta(t) \tag{2.25}$$

which consists in neglecting memory effects. Whether one considers a colloid in water or a microvesicle in an oocyte, the approximation is justified, or not. For instance, in [36], M_R is directly measured by microrheology methods and it is not short ranged, as shown in Fig. 2.2. Within the Markov approximation, we can then write

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -\partial_{\mathbf{R}}\mathscr{H}_0 - \gamma\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} + \boldsymbol{\xi} \tag{2.26}$$

and

$$\langle \xi^\mu(t)\xi^\nu(t')\rangle = 2\gamma T\delta^{\mu\nu}\delta(t-t') \tag{2.27}$$

This is a so-called Gaussian white noise.

2.3 The large damping limit

2.3.1 Underdamped *vs.* Overdamped

In the additional limit where the damping is large, the bath exerting an effective force $\mathbf{F}_b = -\gamma\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} + \boldsymbol{\xi}$ will quickly equilibrate the external forces $\mathbf{F} = -\partial_{\mathbf{R}}\mathscr{H}_0$, and one can then write

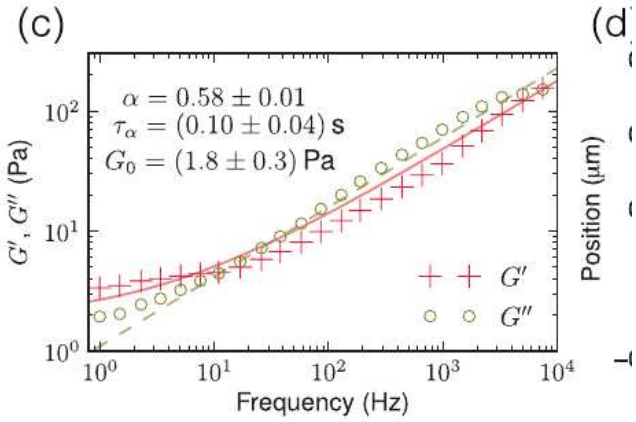


Figure 2.2: Notations wise, the kernel M_R is, basically, and in Fourier transform, $\propto G^{-1}$.

that $\mathbf{F} + \mathbf{F}_b = \mathbf{0}$. To better grasp and quantify the corresponding scaling limit, we introduce make a small detour via a particular case, that of a colloid in a harmonic trap. Then we have $\mathscr{H}_0 = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}m\Omega^2\mathbf{R}^2$, where $\Omega^2 = k/M$ is a characeristic of the trap. The equation of motion

$$M\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} = -M\Omega^2\mathbf{R} - \gamma\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} + \boldsymbol{\xi} \tag{2.28}$$

which one could rewrite as

$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}t} = -\frac{\gamma}{M}\left(\mathbf{V} - \mathbf{V}_{\mathrm{ext}}\right) \tag{2.29}$$

with $\mathbf{V} = \dot{\mathbf{R}}$ and $\mathbf{V}_{\mathrm{ext}} = \frac{1}{\gamma}(\mathbf{F} + \mathbf{F}_b)$. shows that three time scales are competing. These are $\tau_{\mathrm{inertia}} = M/\gamma$, $\tau_0 = \Omega^{-1}$ and $\tau_{\mathrm{relax}} = \frac{\gamma}{M\Omega^2}$. In the regime where $\tau_{\mathrm{inertia}} \ll \tau_0, \tau_{\mathrm{relax}}$ we see that inertia can be forgotten, and the resulting equation reads indeed

$$\mathbf{V} \simeq \mathbf{V}_{\mathrm{ext}}, \; -\partial_{\mathbf{R}}\mathscr{H}_0 - \gamma\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} + \boldsymbol{\xi} = \mathbf{0} \tag{2.30}$$

It is instructive to have a look at real experimental data, shown in Fig. 2.3, extracted from [65]. The overdamped limit is justified by a separation of more than three orders of magnitude.

2.3.2 Ornstein-Uhlenbeck process, or modeling a colloid in an optical trap

The motion of a colloidal particle in an optical trap is consistent with the Markov small inertia limits. Using aone-dimensional notation, the position X of the colloid thus evolves as

$$\dot{X} = -\mu k X + \sqrt{2\mu T}\eta \tag{2.31}$$

where $\mu = 1/\gamma$ is the mobility of the particle, and where η is a Gaussian white noise with correlations $\langle \eta(t)\eta(t')\rangle = \delta(t - t')$. The stiffness of the trap is denoted by k. This is both a pedagogical example, in the sense that this is extremely useful to understand how things work

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

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

Figure 2.3: The notations τ_p and τ_k refer, respectively, to τ_{inertia} and τ_{relax}.

in this simple setting from the begining to the end, but this is also an example that is at the core of active microrheology and it is thus of great of experimental relevance. What is our goal here? Well, starting from some initial position X_0 the particle will equilibrate after some time, at we know that at large time the probability $p(x,t)\mathrm{d}x$ to observe $x \leq X(t) \leq x+\mathrm{d}x$ is given by $p(x, t\to\infty) \sim \mathrm{e}^{-\beta k x^2/2}$. But we are asking about intermediate times and about dynamical quantities, such as the position auto-correlation function.

First, we integrate Eq. (2.31) and we find that

$$X(t) = X_0\mathrm{e}^{-\mu k t} + \sqrt{2\mu T}\int_0^t \mathrm{d}t'\mathrm{e}^{-\mu k(t-t')}\eta(t') \tag{2.32}$$

and thus $\tau_{\text{init}} = (k\mu)^{-1}$ is the time it takes to forget about the initial position X_0. On average, X relaxes to the center of the trap exponentially fast:

$$\langle X(t)\rangle = X_0\mathrm{e}^{-\mu k t} \tag{2.33}$$

because $\langle\eta\rangle = 0$. But by a similar manipulation we can actually determine the auto-correlation $\langle X(t)X(t')\rangle$:

$$\begin{aligned}
\langle X(t)X(t')\rangle =& X_0\mathrm{e}^{-\mu k t}X_0\mathrm{e}^{-\mu k t'} + 2\mu T\int_0^t \mathrm{d}t_1\int_0^{t'}\mathrm{d}t_2\mathrm{e}^{-\mu k(t-t_1)-\mu k(t'-t_2)}\langle\eta(t_1)\eta(t_2)\rangle \\
&+ X_0\mathrm{e}^{-\mu k t}\sqrt{2\mu T}\int_0^{t'}\mathrm{d}t_2\mathrm{e}^{-\mu k(t'-t_2)}\langle\eta(t_2)\rangle + X_0\mathrm{e}^{-\mu k t'}\sqrt{2\mu T}\int_0^{t}\mathrm{d}t_1\mathrm{e}^{-\mu k(t-t_1)}\langle\eta(t_1)\rangle \\
=& X_0\mathrm{e}^{-\mu k t}X_0\mathrm{e}^{-\mu k t'} + 2\mu T\int_0^t \mathrm{d}t_1\int_0^{t'}\mathrm{d}t_2\mathrm{e}^{-\mu k(t-t_1)-\mu k(t'-t_2)}\delta(t_2-t_1) \\
=& X_0\mathrm{e}^{-\mu k t}X_0\mathrm{e}^{-\mu k t'} + 2\mu T\int_0^{\min\{t,t'\}}\mathrm{d}t_1\mathrm{e}^{-\mu k(t-t_1)-\mu k(t'-t_1)} \\
=& X_0\mathrm{e}^{-\mu k t}X_0\mathrm{e}^{-\mu k t'} + \frac{T}{k}\left(\mathrm{e}^{-\mu k|t-t'|} - \mathrm{e}^{-\mu k(t+t')}\right)
\end{aligned} \tag{2.34}$$

In passing, we thus remark that for $t, t' \gg \tau_{\text{init}}$, the process indeed becomes stationary, as its autocorrelation function depends on the time-difference only:

$$\langle X(t)X(t')\rangle = \frac{T}{k}\mathrm{e}^{-\mu k|t-t'|} \tag{2.35}$$

and at equal times, we do recover the expected equipartition result, namely $\langle X(t)^2\rangle = \frac{T}{k}$ for $t \gg \tau_{\text{init}}$.

It is actually possible to obtain $p(x,t)$ without any additional calculation. It is sufficient to note that, according to Eq. (2.32), X is a linear combination of Gaussian variables, and thus X too is a Gaussian variable. A Gaussian is characterized by its mean and its variance, which we both have,

$$\langle X(t)\rangle = X_0\mathrm{e}^{-\mu kt},\ \langle X(t)^2\rangle - \langle X(t)\rangle^2 = \frac{T}{k}\left(1-\mathrm{e}^{-2\mu kt}\right) \tag{2.36}$$

so that we can directly write that

$$p(x,t) = \frac{1}{\sqrt{2\pi\frac{T}{k}(1-\mathrm{e}^{-2\mu kt})}}\mathrm{e}^{-\frac{k}{T}\frac{(x-X_0\mathrm{e}^{-\mu kt})^2}{2(1-\mathrm{e}^{-2\mu kt})}} \tag{2.37}$$

Langevin equations for which exact calculations are available are not plentiful, so that this example often serves as a guide when trying to approximate the evolution of a stochastic process.

Chapter 3

Stochastic calculus

3.1 Mathematical trouble ahead

3.1.1 Gaussian processes

This is a seemingly detached subsection on how to manipulate a vectorial Gaussian variable. We use it to properly define a Gaussian process as a large vectorial Gaussian variable with a number of components going to infinity as a discretization time-scale is sent to 0.

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

$$P(\boldsymbol{\xi}) = Z^{-1} \mathrm{e}^{-\frac{1}{2}\boldsymbol{\xi}\cdot\Gamma\boldsymbol{\xi}} \tag{3.1}$$

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

$$G[\mathbf{h}] = \langle \mathrm{e}^{\mathbf{h}\cdot\boldsymbol{\xi}} \rangle = \mathrm{e}^{\frac{1}{2}\mathbf{h}\cdot\Gamma^{-1}\mathbf{h}} \tag{3.2}$$

By definition, this means that a Gaussian variable has no cumulant of order greater than or equal to three. There are two straightforward consequences of Eq. (3.2). The first one is that, if one introduces

$$G_{ij} = \left.\frac{\partial^2 \ln G}{\partial h_i \partial h_j}\right|_{\mathbf{h}=0} = (\Gamma^{-1})_{ij} \tag{3.3}$$

then we must have

$$\langle \xi_i \xi_j \rangle = G_{ij} \tag{3.4}$$

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

$$\langle \xi_1 \dots \xi_{2k} \rangle = \sum{}' G_{i_1 i_2} \dots G_{i_{2k-1}, i_{2k}} \tag{3.5}$$

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

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

$$\begin{aligned} P[\boldsymbol{\xi}]\mathrm{d}^M\xi =& Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\sum_{m,m'=1}^{M}\xi_m\Gamma_{m,m'}\xi'_m} \\ =& Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\int \mathrm{d}t\mathrm{d}t'\xi(t)\Gamma(t,t')\xi(t')} \end{aligned} \tag{3.6}$$

where $\sum_m \leftrightarrow \int \mathrm{d}t/\Delta t$ (in the spirit of a Riemmann sum, and if this eventually makes sense), and where

$$\xi(t) = \Delta t^{-1/2}\xi_{t/\Delta t},\ \Gamma(t,t') = \Delta t^{-1}\Gamma_{t/\Delta t,t'/\Delta t} \tag{3.7}$$

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

$$\int \mathrm{d}t_2\Gamma(t_1,t_2)G(t_2,t_3) = \delta(t_1-t_3) \tag{3.8}$$

can of course be viewed as the continuum analog of G_{ij}:

$$\begin{aligned} \sum_{m_2}\Gamma_{m_1,m_2}G_{m_2,m_3} &= \delta_{m_1,m_3} \\ \int \mathrm{d}t_2\Delta t^{-1}\Delta t\Gamma(t_1,t_2)G_{t_2/\delta,t_3/\delta} &= \Delta t\delta(t_1-t_3) \end{aligned} \tag{3.9}$$

which leads to identifying $G(t_2,t_3) = \Delta t^{-1}G_{t_2/\Delta t,t_3/\Delta t} = \langle\xi(t_2)\xi(t_3)\rangle$.

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

$$\begin{aligned} P[\boldsymbol{\xi}]\mathrm{d}^M\xi =& Z^{-1}\mathrm{d}^M\xi \mathrm{e}^{-\frac{1}{2}\sum_{m,m'=1}^{M}\xi_m\Gamma_{m,m'}\xi'_m} \\ =& P[\xi(t)]\mathscr{D}\xi,\ P[\xi] = \mathrm{e}^{-\frac{1}{2}\int \mathrm{d}t\mathrm{d}t'\xi(t)\Gamma(t,t')\xi(t')} \end{aligned} \tag{3.10}$$

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

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

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

$$x_M = \Delta t^{1/2}\sum_{m=0}^{M}\xi_m \tag{3.11}$$

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

$$\langle x_M^2\rangle = \Delta t M = t_{\rm obs} \tag{3.12}$$

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

$$x(t_{\rm obs}) = \Delta t^{1/2} \sum m\xi_m = \int_0^{t_{\rm obs}} {\rm d}s\xi(s) \tag{3.13}$$

and similarly

$$\langle x(t_{\rm obs})^2 \rangle = \int_0^{t_{\rm obs}} {\rm d}s_1 \int_0^{t_{\rm obs}} {\rm d}s_2 \langle \xi(s_1)\xi(s_2)\rangle = \int_0^{t_{\rm obs}} {\rm d}s_1 \int_0^{t_{\rm obs}} {\rm d}s_2 \delta(s_1 - s_2) = t_{\rm obs} \tag{3.14}$$

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

3.1.2 Brownian motion, plain and simple

In the whole chapter our interest will go to Langevin equations in which the memory kernels are well approximated by δ functions expressing the very short range nature in time. This encompasses the underdamped Langevin equation

$$m\ddot{\mathbf{r}} = \mathbf{F} - \gamma\dot{\mathbf{r}} + \sqrt{2\gamma T}\boldsymbol{\eta} \tag{3.15}$$

which can also be cast in the form

$$\frac{\rm d}{{\rm d}t}\begin{pmatrix} \mathbf{r} \\ \mathbf{v} \end{pmatrix} = \begin{pmatrix} \mathbf{v} \\ \frac{1}{m}(\mathbf{F} - \gamma\mathbf{v} + \sqrt{2\gamma T}\boldsymbol{\eta}) \end{pmatrix} \tag{3.16}$$

or more simply an underdamped Langevin equation

$$\dot{\mathbf{r}} = \mu\mathbf{F} + \sqrt{2\mu T}\boldsymbol{\eta} \tag{3.17}$$

and these equations are all of the form $\dot{x}^\mu = f^\mu + g^{\mu i}\eta_i$, where μ is a label indexing the components of the process of interest (whether $(\mathbf{r}, \mathbf{v})$ or $\mathbf{r}$ alone), while i is an index labeling the noise components (i runs at most up to the dimension of the variable of interest). In what follows, for simplicity we will always focus on a Langevin process of the form $\dot{x} = f + g\eta$ where f and η are arbitrary. Whathever complication possibly arising from working with vectorial—rather than scalar—variables will be addressed in due time, and none of them will actually prove deep.

Before we actually learn how to manipulate such equations, we want to point some of their intrinsic mathematical issues. To this end we look at a one dimensional Brownian motion

$$\dot{x} = \sqrt{2\mu T}\eta \tag{3.18}$$

where η is a Gaussian white noise with correlations $\langle \eta(t)\eta(t')\rangle = \delta(t - t')$. Then $x(t) - x(0) = \sqrt{2D}\int_0^t {\rm d}t'\eta(t')$ and we see that $x(t) - x(0)$ has variance

$$\langle (x(t) - x(0))^2 \rangle = 2Dt \tag{3.19}$$

or

$$\langle (x(t) - x(t'))^2 \rangle = 2D(t - t'),\ t' \leq t \tag{3.20}$$

and thus $\Delta x = x(t + \Delta t) - x(t)$ has variance $\langle \Delta x^2 \rangle = 2D\Delta t$. This immediately tells us that as $\Delta t \to 0$ the displacement Δx is typically of order $\sqrt{\Delta t}$ and thus that $\frac{\Delta x}{\Delta t}$ is of order $\Delta t^{-1/2}$, which diverges as $\Delta t \to 0$. This is the mathematical translation of the statement that a Brownian motion trajectory, in spite of being continuous everywhere, is nowhere differentiable. There is no such thing as a free lunch. If we insist on writing something like $\dot{x}$ it cannot, strictly speaking, have the usual meaning that

$$\dot{x} = \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} \tag{3.21}$$

because we know this is infinite.

In order to realize the sort of trouble that lies ahead of us, let's consider $y = x^2/2$ and pretend we can manipulate $\dot{x} = \sqrt{2D}\eta$ as we if these were smooth enough functions. Then we multiply $\dot{x} = \sqrt{2D}\eta$ by x and we get

$$\dot{y} = \sqrt{2D}\sqrt{2y}\eta \tag{3.22}$$

and though we know that $\langle y(t) \rangle = Dt$ (for $x(0) = 0$), which means that $\langle \dot{y} \rangle = D$ we hardly see how we can ever average Eq. (3.18) to actually see that result directly. In fact we shouldn't be alarmed. Only a very naive person would manipulate non-differentiable functions as it they were. And we are not naive. Let's see how to sort all this out.

3.2 Discretizing a Langevin equation

3.2.1 Procedure

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

$$x_{m+1} - x_m = f(x_m)\Delta t + g(x_m)\sqrt{\Delta t}\xi_m,\ m = 0, 2, \ldots \tag{3.23}$$

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

$$\langle \xi_m \xi_{m'} \rangle = \delta_{mm'} \tag{3.24}$$

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

$$x(t) = x_{t/\Delta t} \tag{3.25}$$

and to write that Eq. (3.19) amounts to

$$\Delta x = x(t + \Delta t) - x(t) = f(x(t))\Delta t + g(x(t))\Delta\eta \tag{3.26}$$

where $\Delta\eta$ is a Gaussian variable with zero mean and variance Δt. Let η be a Gaussian process characterized by $G(t, t') = \langle \eta(t)\eta(t') \rangle = \delta(t - t')$, then one can write that $\Delta\eta = \int_t^{t+\Delta t} \mathrm{d}s\eta(s)$,

as these quantities have the same statistics. They are both Gaussian and can be seen to have the same variance:

$$\langle \Delta\eta^2 \rangle = \int_t^{t+\Delta t} \mathrm{d}_1 \mathrm{d}t_2 \langle \eta(t_1)\eta(t_2)\rangle = \Delta t \tag{3.27}$$

It is then natural to adopt the following continuum time formulation for Eq. (3.19)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = f(x(t)) + g(x(t))\eta(t) \tag{3.28}$$

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

$$\frac{x_{m+1} - x_m}{\Delta t} = f(x_m) + g(x_m)\frac{\eta_m}{\sqrt{\Delta t}} \tag{3.29}$$

and since η_m is $O(1)$ in Δt, the last term diverges to infinity as $\Delta t^{-1/2}$. It is therefore unlikely that Eq. (3.24) will ever appear as such in the mathematical literature. What is actually written is

$$\mathrm{d}x = f(x(t))\mathrm{d}t + g(x(t))d\eta(t) \tag{3.30}$$

where $\mathrm{d}\eta$ is a Gaussian variable with variance $\mathrm{d}t$ ($\mathrm{d}B$ or $\mathrm{d}\,W$ are often favorite notations among mathematicians, not $\mathrm{d}\eta$). Of course, there are anavoidable problems that we will run into by insisting to work with Eq. (3.24) as if x were a differentiable function. All these problems disappear when a discretized formulation is used.

One such problem is the following. Consider a discretized

$$\Delta x = x(t+\Delta t) - x(t) = f(x + \alpha\Delta x)\Delta t + g(x + \alpha\Delta x)\Delta\eta \tag{3.31}$$

where $0 \leq \alpha \leq 1$ is some arbitrary real number. Quite naïvely, the continuum limit of Eq. (3.27) is exactly the same as that of Eq. (3.19), namely $\dot{x} = f + g\eta$. However, as wee see from Eq. (3.27), Δx is $O(\sqrt{\Delta t})$ and thus, when we write $g(x+\alpha\Delta)\Delta\eta$ instead of $g(x)\Delta\eta$ we neglect terms that are of order $\alpha g'(x)\Delta x\Delta\eta \sim O(\Delta t)$, that is terms of the same order as the deterministic contribution $f\Delta t$. However, whether we write $f(x+\alpha\Delta x)\Delta t$ or $f(x)\Delta t$ shouldn't make any difference in the $\Delta t \to 0$ limit. For now, we shall stick to the discretized process defined by Eq. (3.19) or Eq. (3.22). We will now determine the statistical properties of Δx.

3.2.2 Infinitesimal jumps

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

$$\Delta x = f(x(t_0))\Delta t + g(x(t_0))\Delta\eta \tag{3.32}$$

which is another way of rewriting $x_{m+1} - x_m = f(x_m)\Delta t + g(x_m)\sqrt{\Delta t}\xi_m$,. We now take the average, which leads to $\langle \Delta x\rangle = f(x(t_0))\Delta t$ (remember that x_0 and thus $f(x(t_0))$ are not

random, since x_0 is fixed and we average only over what occurs between t_0 and $t_0 + \Delta t$). The second moment reads

$$\begin{aligned}\langle \Delta x^2 \rangle =& \langle f(x(t_0))^2 \Delta t^2 + g(x(t_0))^2 \Delta\eta^2 + 2f(x(t_0))\Delta t g(x(t_0))\Delta\eta \rangle \\ =& g(x(t_0))^2 \langle \Delta\eta^2 \rangle + O(\Delta t^{3/2}) \\ =& g(x(t_0))^2 \Delta t + O(\Delta t^{3/2})\end{aligned} \tag{3.33}$$

The third moment reads

$$\begin{aligned}\langle \Delta x^3 \rangle =& \langle f(x(t_0))^3 \Delta t^3 + g(x(t_0))^3 \Delta\eta^3 + 3f(x(t_0))\Delta t g(x(t_0))^2 \Delta\eta^2 + 3f(x(t_0))^2 \Delta t^2 g(x(t_0))\Delta\eta \rangle \\ =& O(\Delta t^{3/2})\end{aligned} \tag{3.34}$$

and we therefore realize that

$$\lim_{\Delta t\to 0} \frac{\langle \Delta x \rangle}{\Delta t} = f(x(t_0)), \quad \lim_{\Delta t\to 0} \frac{\langle \Delta x^2 \rangle}{\Delta t} = g(x(t_0))^2, \quad \lim_{\Delta t\to 0} \frac{\langle \Delta x^k \rangle}{\Delta t} = 0 \text{ for } k \geq 3 \tag{3.35}$$

This means that the process $x(t)$ is entirely defined by the first two moments of Δx as $\Delta t \to 0$.

3.2.3 Stochastic calculus: differentiation and Itō's lemma

Let's get back to the issue that we brushed upon higher up. Since there is a variety of discretized processes that naively lead to the same visual stochastic differential equation, it may be worth exploring these various discretized equations. Take $0 \leq \alpha \leq 1$ and consider Eq (3.27) which we repeat here:

$$\Delta x = x(t + \Delta t) - x(t) = f(x + \alpha \Delta x)\Delta t + g(x + \alpha \Delta x)\Delta\eta \tag{3.36}$$

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

$$\begin{aligned}\langle \Delta x \rangle =& \langle \Delta t f(x(t) + \alpha \Delta x) + g(x(t) + \alpha \Delta x)\Delta\eta \rangle \\ =& \Delta t f(x(t)) + O(\Delta t^{3/2}) + \langle \left[g(x(t)) + \alpha g'(x(t))\Delta x \right] \Delta\eta \rangle \\ =& \Delta t f(x(t)) + O(\Delta t^{3/2}) + \alpha g'(x(t)) \langle \Delta x \Delta\eta \rangle\end{aligned} \tag{3.37}$$

and again

$$\begin{aligned}\langle \Delta x \Delta\eta \rangle =& \langle \Delta\eta \left[\Delta t f(x(t) + \alpha \Delta x) + g(x(t) + \alpha \Delta x)\Delta\eta \right] \rangle \\ =& \langle \Delta\eta g(x(t))\Delta\eta \rangle + O(\Delta t^{3/2}) \\ =& g(x(t))\Delta t + O(\Delta t^{3/2})\end{aligned} \tag{3.38}$$

so that eventually

$$\langle \Delta x \rangle = \Delta t \left[f(x(t)) + \alpha g'(x(t)) g(x(t)) \right] + O(\Delta t^{3/2}) \tag{3.39}$$

By a similar method, one sees that

$$\lim_{\Delta t \to 0} \frac{\langle \Delta x^2 \rangle}{\Delta t} = g(x)^2, \quad \lim_{\Delta t \to 0} \frac{\langle \Delta x^k \rangle}{\Delta t} = 0 \text{ for } k \geq 3 \tag{3.40}$$

so that we now have a proof that whether $\dot{x} = f + g\eta$ is understood with $\alpha = 0$ or $\alpha \neq 0$, this corresponds to different physical processes because the process of Eq. (3.27) has $\frac{\langle \Delta x \rangle}{\Delta t} = f + \alpha g' g$ and $\frac{\langle \Delta x^2 \rangle}{\Delta t} = g^2$. From now on, because otherwise we have no idea how to understand the corresponding Langevin equation, instead of writing $\dot{x} = f + g\eta$ we shall write $\dot{x} \overset{\alpha}{=} f + g\eta$ to refer to a Langevin equation that is the $\Delta t \to 0$ limit of Eq. (3.27).

That also means that it is always possible to go back and forth between two processes that are discretized differently:

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{x} \overset{0}{=} f + \alpha g' g + g\eta \tag{3.41}$$

or, even more generally,

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{x} \overset{\alpha'}{=} f + (\alpha - \alpha') g' g + g\eta \tag{3.42}$$

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

In order to find out the limitations of manipulating x as if it were differentiable, we now investigate the fate of the chain rule. Consider now an auxilary random process $u(t) = U(x(t))$ built directly from x (where U is some smooth enough function). Let's see how u evolves in time:

$$\begin{aligned}
\Delta u =& u(t + \Delta t) - u(t) = U(x + \Delta x) - U(x) \\
=& \Delta x U' + \frac{1}{2} \Delta x^2 U''(x) + O(\Delta t^{3/2}) \\
=& (f(x)\Delta t + g(x + \alpha \Delta x)\Delta \eta) U'(x) + \frac{1}{2} \Delta x^2 U''(x) \\
=& (f(x)\Delta t + \alpha g'(x) \Delta x \Delta \eta) U'(x) + \frac{1}{2} \Delta x^2 U''(x) + U'(x) g(x) \Delta \eta \\
=& (f(x)\Delta t + \alpha g'(x) g(x) \Delta \eta^2) U'(x) + \frac{1}{2} \Delta x^2 U''(x) + U'(x) g(x) \Delta \eta
\end{aligned} \tag{3.43}$$

so that

$$\lim_{\Delta t\to 0}\frac{\langle \Delta u\rangle}{\Delta t} = (f+\alpha g' g)\,U' + \frac{1}{2}g^2\,U'' \tag{3.44}$$

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

$$\lim_{\Delta t\to 0}\frac{\langle \Delta u^2\rangle}{\Delta t} = g^2\,U'^2 \tag{3.45}$$

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

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

$$\text{for } \alpha = 0,\ \lim_{\Delta t\to 0}\frac{\langle \Delta u\rangle}{\Delta t} = fU' + \frac{1}{2}g^2\,U'',\ \lim_{\Delta t\to 0}\frac{\langle \Delta u^2\rangle}{\Delta t} = g^2\,U'^2 \tag{3.46}$$

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

$$\dot{u} \overset{0}{=} fU' + \frac{1}{2}g^2\,U'' + U'g\eta \tag{3.47}$$

This Eq. (3.43) is the celebrated Itō's lemma, where the piece that corrects the standard chain rule of differential calculus has been highlighted in red.

Note also that for α arbitrary, we have that

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{0}{=} fU' + \alpha g' g U' + \frac{1}{2}g^2\,U'' + U'g\eta \tag{3.48}$$

and thus, using the correspondence in Eq. (3.38)

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{\alpha}{=} fU' + \alpha g' g U' - \alpha\left[\frac{\mathrm{d}}{\mathrm{d}u}\left(gU'\right)\right] gU' + \frac{1}{2}g^2\,U'' + U'g\eta \tag{3.49}$$

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

$$\dot{x} \overset{\alpha}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{\alpha}{=} fU' + \alpha g' g U' + \left(\frac{1}{2} - \alpha\right) g' g U' + \left(\frac{1}{2} - \alpha\right))g^2\,U'' + U'g\eta \tag{3.50}$$

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

$$\dot{x} \overset{1/2}{=} f + g\eta \Longleftrightarrow \dot{u} \overset{1/2}{=} fU' + U'g\eta,\ u(t) = U(x(t)) \tag{3.51}$$

That is really remarkable! This means that even though neither x nor u are differentiable, when resorting to the Stratonovich discretization, we can manipulate these functions as if they were actually differentiable since the chain rule of differentiation applies. This is not the only advantage of the Stratonovich discretization. It is also, quite simply, the only natural discretization

scheme that follows from the elimination of the fast degrees of freedom.

As a conclusion to this section, we return to our original example of subsection 3.1.2 and Eq. (3.18). There we looked at $\dot{x} = \sqrt{2D}\eta$ and defined $y = x^2/2$ and without really thinking we arrive at $\dot{y} = 2\sqrt{D}\sqrt{y}\eta$. We are now more educated than back then and here is a line of reasoning within which this is correct and justified. Start from $\dot{x} = \sqrt{2D}\eta$, which can be understood in any sense one wishes, because the noise is additive (the corresponding g is a constant). For instance we can think of this equation as $\dot{x} \overset{1/2}{=} \sqrt{2D}\eta$. Then we know that the chain rule applies (this is Stratonovich discretization), and thus what we should really have written is $\dot{y} \overset{1/2}{=} 2\sqrt{D}\sqrt{y}\eta$. Using the correspondence of Eq. (3.38), we see than a strictly equivalent equation is

$$\dot{y} \overset{0}{=} \frac{1}{2} 2\sqrt{D}\sqrt{y} \frac{\mathrm{d}(2D\sqrt{y})}{\mathrm{d}y} + 2\sqrt{D}\sqrt{y}\eta \overset{0}{=} D + 2\sqrt{D}\sqrt{y}\eta \tag{3.52}$$

so that $\langle \dot{y} = D$. An alternative would have been to directly use Itō's lemma to $u(t) = y(t) = x(t)^2/2$,

$$\frac{\mathrm{d}y}{\mathrm{d}t} \overset{0}{=} U'\dot{x} + \frac{1}{2} g^2 U'' + gU'\eta \overset{0}{=} x(\sqrt{2D}\eta) + \frac{1}{2} \times 2D \times 1 + \sqrt{2D}x\eta \overset{0}{=} D + 2\sqrt{Dy}\eta \tag{3.53}$$

which is consistent.

3.3 Why bother, in physics, about multiplicative noise?

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

3.3.1 Starting with an additive noise

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

$$m\dot{v} = -\gamma v + \sqrt{2\gamma' T}\eta \tag{3.54}$$

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

$$\dot{K} = -\gamma \frac{2}{m} K + \sqrt{2\gamma' T}\sqrt{\frac{2K}{m}}\eta \tag{3.55}$$

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

$$\dot{K} \overset{1/2}{=} -\gamma \frac{2}{m} K + 2\sqrt{\frac{\gamma' TK}{m}}\eta \tag{3.56}$$

which is equivalent to

$$\begin{aligned} \dot{K} &\overset{0}{=} -\gamma \frac{2}{m} K + \frac{1}{2}\left[2\sqrt{\frac{\gamma' TK}{m}}\right] \frac{\mathrm{d}}{\mathrm{d}K}\left[2\sqrt{\frac{\gamma' TK}{m}}\right] + 2\sqrt{\frac{\gamma' TK}{m}}\eta \\ &\overset{0}{=} -\gamma \frac{2}{m} K + \frac{\gamma' T}{m} + 2\sqrt{\frac{\gamma' TK}{m}}\eta \end{aligned} \tag{3.57}$$

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

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

$$m\dot{v} = -\gamma v - V'(x) + \sqrt{2\gamma T}\eta \tag{3.58}$$

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

$$\gamma \dot{x} = -V' + \sqrt{2\gamma T} \text{ or } \dot{x} = -\mu V'(x) + \sqrt{2\mu T}\eta \tag{3.59}$$

where $\mu = \gamma^{-1}$ is the so-called mobility. When in addition $V(x) = \frac{k}{2}x^2$ is a harmonic potential, then the resulting Langevin equation is exactly of the same form as Eq. (3.50), $\dot{x} = -\mu k x + \sqrt{2\mu T}\eta$. A Langevin equation of the form $\dot{y} = -\kappa y + g\eta$, where g is a constant, is an Ornstein-Uhlenbeck process. It is the only stationary Gaussian process (by Doob's theorem). It is extremely important to fully master the details of the properties of an Ornstein-Uhlenbeck process (hence its repeated appearances in the tutorials).

3.3.2 Plain diffusion, confined though

The viscous friction γ is in general a constant coefficient, except when the vicinity of a wall affects the hydrodynamic flow around the particle under consideration. With the upsurge of microfluidic devices, diffusion in confined geometries (micro and nanofluidics, pores, channels, even in quasi 1d settings) demands that hydrodynamic interactions be taken into consideration. Some recent experimental references are [62, 1, 42, 87]. the bottom line is that if z denotes the

distance of the particle to the wall, the transverse and longitudinal friction coefficients pick up a dependence on z

$$\gamma_\perp(z) = \gamma\left(1+\frac{9}{8}\frac{R}{z}\right) \tag{3.60}$$

$$\gamma_\parallel(z) = \gamma\left(1+\frac{9}{16}\frac{R}{z}\right) \tag{3.61}$$

as derived by Brenner [12]. This means that even when describing the purely diffusive motion of a confined colloid, multiplicative noise will show up.

3.3.3 Black and Scholes

Black and Scholes were two scholars working in on the modeling of financial markets. Back in 1973 [8] they came up with a model for the evolution of the price of a specific type of asset (European-style option). We refer to [27] for an introduction and for financial motivations. The equation they wrote is a Langevin equation for the shrare price S of a stock (a risky asset). In Itō discretization, it is postulated that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \mu S + \sigma S\eta \tag{3.62}$$

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

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \mu S - \frac{1}{2}\sigma^2 S + \sigma S\eta \tag{3.63}$$

so that $S(t) = S_0 \exp\left[(\mu-\sigma^2/2)t + \sigma\int_0^t \mathrm{d}\tau\eta(\tau)\right]$. Of course μ could also depend on S or on time (and then things would have to be changed). One ends up facing the statistics of an exponential functional of Brownian motion. This type of functionals has appeared in mathematical finance [112], but also in the physics of one-dimensional disordered systems [21], or in the nonequilibrium evolution of chemical processes [45]. The Black and Scholes equation is a prototypical example of a Langevin equation with multiplicative noise.

3.3.4 Rotational diffusion

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

3.3.5 Active Brownian Particle

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

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = v_0\mathbf{u} \tag{3.64}$$

faithfully reflects the observed properties of an individual particle [17]. In this model, $\mathbf{u}$ is a unit vector the tip of which executes a Brownian motion at the surface of the unit sphere, with a rotational diffusion constant D_r. In two space dimensions, the polar angle ϕ indexing the direction of $\mathbf{u} = (\cos\phi, \sin\phi)$ is undergoing a simple Brownian motion,

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \sqrt{2D_r}\xi \tag{3.65}$$

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

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{\alpha}{=} (\mathbf{u}\cdot\boldsymbol{\eta})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta} \tag{3.66}$$

where the components η^μ of $\boldsymbol{\eta}$ are independent Gaussian white noises, $\langle \eta^\mu(t)\eta^\nu(t')\rangle = 2D_r\delta^{\mu\nu}\delta(t-t')$. Dotting Eq. (3.63) with $\mathbf{u}$ shows that $\mathbf{u}^2$ is indeed conserved. But for this calculation to be legitimate, we must be allowed to manipulate $\mathbf{u}$ as if it were a smooth function, which means that Eq. (3.63) must be understood in a Stratonovich sense ($\alpha = 1/2$). It's Itō counterpart reads

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{0}{=} -(d-1)D_r\mathbf{u} + (\mathbf{u}\cdot\boldsymbol{\eta})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta} \tag{3.67}$$

where d is the number of space dimensions.

Formula Eq. (3.63) can checked using Eq. (**??**), with $g^{\mu i} = \sqrt{2D_r}(u^\mu u^i - \mathbf{u}^2\delta^{\mu i})$ (here $i, \mu = 1, \ldots, d$), we have $\partial_\nu g^{\mu i} = \sqrt{2D_r}(\delta^{\mu\nu}u^i + u^\mu\delta^{\nu i} - 2u^\nu\delta^{\mu i})$, and thus, after an explicit evaluation,

$$\partial_\nu g^{\mu i} g^{\nu i} = -(d-1)2D_r u^\mu \mathbf{u}^2 \tag{3.68}$$

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

3.4 Path integral representation of a Langevin process

This section aims at introducing one more tool in the stochastic processes toolbox, beyond the master equation and stochastic differential equations. We have seen the importance of working with trajectories in chapter **??**. This is one motivation. Another motivation comes from the fact that path integrals pervade all areas of theoretical physics (high energy, condensed matter) and whatever tool has been developed in one field can be exported to another field. We follow Janssen [46] and De Dominicis [25] who used the work of Martin, Siggia and Rose [75] to adapt path integral techniques to stochastic processes.

3.4.1 Starting from a Langevin equation

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

$$\Delta x_n = x_{n+1} - x_n = f_n \Delta t + g_n \sqrt{\Delta t}\xi_n \tag{3.69}$$

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

$$\langle A(x_M) \rangle = \int \prod_{i=0}^{M-1} \frac{\mathrm{d}\xi_i}{\sqrt{2\pi}} \mathrm{e}^{-\sum_i \frac{\xi_i^2}{2}} A(x_M[\{\xi_\ell\}]) \tag{3.70}$$

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

$$\xi_i = \frac{x_{i+1} - x_i - f_i \Delta t}{g_i \sqrt{\Delta t}} \tag{3.71}$$

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

$$\frac{\partial \xi_j}{\partial x_{j+1}} = \frac{1 - \alpha f_j' \Delta t - \alpha \frac{g_j'}{g_j}(\Delta x_j - f_j \Delta t)}{g_j \sqrt{\Delta t}} \tag{3.72}$$

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

$$\langle A(x_M) \rangle = \int \prod_{j=1}^{M} \frac{\mathrm{d}x_i}{\sqrt{2\pi}} \prod_{i=0}^{M-1} \left(\frac{1 - \alpha f_i' \Delta t - \alpha \frac{g_i'}{g_i}(\Delta x_i - f_i \Delta t)}{g_i \sqrt{\Delta t}} \right) \mathrm{e}^{-\frac{1}{2}\sum_i \left(\frac{x_{i+1} - x_i - f_i \Delta t}{g_i \sqrt{\Delta t}} \right)^2} A(x_M) \tag{3.73}$$

For the particular case of a constant function g things simplify considerably, and the Jacobian can be rewritten as

$$\prod_j \frac{\partial \xi_j}{\partial x_{j+1}} = \frac{1-\alpha f_j' \Delta t}{g_j \sqrt{\Delta t}} = \text{Cste}^{-\alpha \sum_j f_j' \Delta t} \tag{3.74}$$

so that altogther we can write that

$$\langle A(x_M)\rangle = \int \prod_{j=1}^{M} \frac{\mathrm{d}x_i}{\sqrt{2\pi}} \prod_{i=0}^{M-1} (g\Delta t)^{-M/2} \mathrm{e}^{-\Delta t \sum_i \left[\frac{1}{2g^2}\left(\frac{\Delta x_i}{\Delta t}-f_i\right)^2 + \alpha f_i'\right]} A(x_M) \tag{3.75}$$

Returning to a continuous time notation, it is traditional to write the $M \gg 1$ limit of Eq. (3.71) as

$$\langle A(t_{\text{obs}})\rangle = \int \mathscr{D}x A(x(t_{\text{obs}})) \mathrm{e}^{-S[x]} \tag{3.76}$$

where the dynamical action, also known as the Onsager-Machlup functional [81, 67], has the expression

$$S[x] = \int_0^{t_{\text{obs}}} \mathrm{d}t \left[\frac{1}{2g^2}(\dot{x}-f)^2 + \alpha f'\right] \tag{3.77}$$

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

$$\langle A(x(t_{\text{obs}}))\rangle = \int \mathcal{D}\bar{x}\mathcal{D}x \mathrm{e}^{-S} A(x(t_{\text{obs}})) \tag{3.78}$$

where now

$$S[\bar{x},x] = \int \mathrm{d}t \left[\frac{1}{2g^2}(\dot{x}-f)^2 + \alpha f'\right] \tag{3.79}$$

is known as the Onsager-Machlup [81, 67] dynamical action.

3.4.2 Dirty way for Itō

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

$$\langle A\rangle = \int \mathscr{D}\eta \mathrm{e}^{-\frac{1}{2}\int \eta^2} A(x[\eta](t)) \tag{3.80}$$

and when we write $x[\eta](t)$ we see x as the solution of the $\dot{x} \overset{0}{=} f + g\eta$ stochastic differential equation in which η is a given function. Hence $x[\eta](t)$ is a functional of η. By asserting that $\mathscr{D}\eta$ and $\mathscr{D}x$ differ only by a multiplicative constant (which is the same as asserting thet Jacobian is a constant), we immediately get

$$\langle A\rangle = \int \mathscr{D}x A(x(t_{\text{obs}})) \mathrm{e}^{-\frac{1}{2g^2}\int (\dot{x}-f)^2} \tag{3.81}$$

This is exactly the same form as that found by the more rigorous derivation based on a discretized process, on condition that $\alpha = 0$ is used throughout.

3.4.3 Defining equilibrium

Given a random process $x(t)$ extending over the time window $[0, t_{\rm obs}]$, and given the probability $\mathscr{P}[x]$ to observe a full time realization of this process over $[0, t_{\rm obs}]$ we define

$$\Sigma[x] = \ln \frac{\mathscr{P}[x]}{\mathscr{P}[x^{\rm R}]} \tag{3.82}$$

where the time-reversed trajectory is defined by $x^{\rm R}(t) = x(t_{\rm obs}–t)$. The average of this quantity,

$$\langle \Sigma[x] \rangle = \int \mathscr{D}x \mathscr{P}[x] \ln \frac{\mathscr{P}[x]}{\mathscr{P}[x^{\rm R}]} \tag{3.83}$$

is called the total entropy produced over the time window $[0, t_{\rm obs}]$. Equilibrium is achieved iff, in a stationary state, $\langle \Sigma \rangle = 0$.

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

$$D(p \parallel q) \geq 0 \text{ with equality iff } \forall i,\ p_i = q_i \tag{3.84}$$

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

$$\ln(\sum_j t_j x_j) \geq \sum_j t_j \ln x_j \tag{3.85}$$

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

$$\ln(\sum_j p_j \frac{q_j}{p_j}) \geq \sum_j p_j \ln \frac{q_j}{p_j} \tag{3.86}$$

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

Hence the entropy production $\langle \Sigma[x] \rangle$ measures how the time-reversed process differs from the time-forward one. It's a measure of the length of the arrow of time.

In practice, for a Langevin process (Markov, overdamped) of the form $\dot{\mathbf{r}} = \mathbf{F} + \sqrt{2T}\boldsymbol{\eta}$, where $\mathbf{F} = -\partial_{\mathbf{r}} V + \mathbf{f}$ is the sum of a conservative force $-\partial_{\mathbf{r}} V$ and of a nonconservative one $\mathbf{f}$, we see that

$$\mathscr{P}[\mathbf{r}] = P_{\rm init}(\mathbf{r}(0)) \mathrm{e}^{-\frac{1}{4T}\int_0^{t_{\rm obs}} \mathrm{d}t (\dot{\mathbf{r}}–\mathbf{F})^2 – \frac{1}{2}\int_0^{t_{\rm obs}} \mathrm{d}t \partial_{\mathbf{r}}\cdot\mathbf{F}} \tag{3.87}$$

and using $\mathbf{r}^{\rm R}(t) = \mathbf{r}(t_{\rm obs} – t)$, we also have

$$\mathscr{P}[\mathbf{r}^{\rm R}] = P_{\rm fin}(\mathbf{r}(t_{\rm obs})) \mathrm{e}^{-\frac{1}{4T}\int_0^{t_{\rm obs}} \mathrm{d}t (-\dot{\mathbf{r}}–\mathbf{F})^2} \tag{3.88}$$

so that

$$\Sigma[\mathbf{r}] = \frac{1}{T}\int_0^{t_{\rm obs}} \mathrm{d}t \mathbf{F}\cdot\dot{\mathbf{r}} + \ln\frac{P_{\rm init}(\mathbf{r}(0))}{P_{\rm fin}(\mathbf{r}(t_{\rm obs}))} \tag{3.89}$$

In a stationary state we have $\langle \ln \frac{P_{\rm init}(\mathbf{r}(0))}{P_{\rm fin}(\mathbf{r}(t_{\rm obs}))}\rangle = 0$ and thus

$$\langle\Sigma[\mathbf{r}]\rangle = \frac{1}{T}\int_0^{t_{\rm obs}} \mathrm{d}t\langle \mathbf{F}\cdot\dot{\mathbf{r}}\rangle = t_{\rm obs}\langle \mathbf{F}\cdot\dot{\mathbf{r}}\rangle \tag{3.90}$$

has a very transparent interpretation: this is the power injected into the system by $\mathbf{F}$. Of course, if $\mathbf{F} = -p_{\mathbf{r}} V$ is conservative, then the entropy production vanishes owing to $\int \mathrm{d}t\cdot\partial_{\mathbf{r}} V = V(t_{\rm obs}) - V(0)$ which vanishes on average in a steady-state. The corresponding steady-state, without any entropy production, is an equilibrium state. When the non conservative force $\mathbf{f}$ is nonzero, then the entropy production rate is $\langle\dot{\mathbf{r}}\cdot\mathbf{f}\rangle/T$, which is the power of the dissipative forces divided by temperature (exactly what we would expect on the basis of thermodynamics, except that not only we proved the second principle, $\langle\Sigma\rangle \geq 0$, but also we see that it applies much beyond the usual framework of extensive systems).

The definition of equilibrium we have used matches others that may have been encountered, such as the detailed balance condition that states

$$\mathrm{Prob}x(t) = x \to x(t+\Delta t) = x' = \mathrm{Prob}x(t) = x' \to x(t+\Delta t) = x \tag{3.91}$$

3.4.4 An application of the path integral formulation to barrier crossing

A traditional and interesting application of the path integral formulation of the dynamics is barrier crossing. Think again of an overdamped particle $\dot{x} = -V' + \sqrt{2T}\eta$ evolving in a potential landscape with a minimum at its starting point x_0 and a barrier at $x_M > x_0$, such that $\Delta V = V(x_M) - V(x_0) \gg k_{\rm B}T$. The typical rate τ_K^{-1} of crossing over the barrier is proportional to the fraction of trajectories $x(t)$ sarting from x_0 and reach x_M, namely,

$$\tau_K^{-1} \simeq \int \mathscr{D}x \mathrm{e}^{-\frac{1}{4T}\int(\dot{x}+V')^2 - \frac{1}{2}\int \mathrm{d}t V''} \tag{3.92}$$

ut since we are interested in the $T \ll V$ limit, the second contribution in the exponential can safely be neglected. We now rewrite $(\dot{x}+V')^2 = \dot{x}^2 + V'^2 + 2\dot{x}V'$ and we use that $\int \dot{x}V' = V(x_M) - V(x_0) = \Delta V$. Next, since,

$$\tau_K^{-1} \simeq \mathrm{e}^{-\frac{\beta}{2}\Delta V}\int \mathscr{D}x \mathrm{e}^{-\frac{1}{4T}\int(\dot{x}^2+V'^2)^2} \tag{3.93}$$

we search for the path x_c that minimizes S. This is because the $1/T$ prefactor inside the exponential tells us that out of all paths, the one that minimizes $\int(\dot{x}^2 + V'^2)$ contributes the most and that, eventually,

$$\tau_K^{-1} \simeq \mathrm{e}^{-\frac{\beta}{2}\Delta V}\int \mathscr{D}x \mathrm{e}^{-\frac{1}{4T}\int(\dot{x}_c^2+V'^2(x_c))} \tag{3.94}$$

We search for the path x_c:

$$\frac{\delta}{\delta x}\int \mathrm{d}t(\dot{x}^2 + V'^2) = 2\ddot{x}\dot{x} + 2V'V''\dot{x} \tag{3.95}$$

or $\ddot{x} = -\frac{\mathrm{d}}{\mathrm{d}x}(-V'^2)$. We recognize the Hamiltonian equation of motion of a particle in a a potential $-V'^2$ and we know $\dot{x}^2 + V'^2$ is a constant of motion. This number isis zero at the initial time, so that throughout time $\dot{x}^2 + V'^2 = 0$, which tells us that either $\dot{x} = -V'$ or $\dot{x} = V'$. The former solution is the gradient descent one, while the latter is the gradient ascent of interest, so that $\dot{x}_c = V'(x_c)$. We don't need to solve for x_c as a function of time, because our interest goes to $\int(\dot{x}_c^2 + V'^2(x_c)) = 2\int \dot{x}_c V'(x_c) = 2\Delta V$, and the concludion is

$$\tau_K^{-1} \simeq \mathrm{e}^{-\beta\Delta V},\ \tau_K \sim \mathrm{e}^{\beta\Delta V} \tag{3.96}$$

This is the celebrated Arrhenius formula derived by Kramers.

M2 PCS 2023-2024

Nonequilibrium and Active Systems

First Semester F. van Wijland

Chapter 4

The Fokker-Planck Equation

4.1 From Langevin to Fokker-Planck

4.1.1 A direct application of Itō's lemma

We begin the discussion with a simple goal in mind. Given an Itō-discretized Langevin equation $\dot{x} \overset{0}{=} f + g\eta$, how can we find an equation for the probability density $p(X,t)$ such that $p(X,t)\mathrm{d}X = \mathrm{Prob}\{X \leq x(t) \leq X + \mathrm{d}X\}$. The idea is to remark that

$$p(X,t) = \langle \delta(X - x(t)) \rangle \tag{4.1}$$

because indeed, for any physical quantity $A(x(t))$, its average is given by

$$\langle A \rangle(t) = \int \mathrm{d}X A(X) p(X,t) = \langle \int \mathrm{d}X A(X) \delta(X - x(t)) \rangle \tag{4.2}$$

We directly apply Itō's lemma, namely

$$\dot{u} = U'(f + g\eta) + \frac{1}{2} g^2 U'' \tag{4.3}$$

to $u(t) = U(x(t)) = \delta(X - x(t))$, and then we take the average:

$$\langle \dot{u} \rangle = \langle U' f + \frac{1}{2} g^2 U'' \rangle \tag{4.4}$$

This directly tells us that

$$\partial_t p = \langle f \frac{\partial}{\partial x} \delta(X - x) + \frac{1}{2} g^2 \frac{\partial^2}{\partial x^2} \delta(X - x) \rangle \tag{4.5}$$

so that, using that $\frac{\partial}{\partial x}\delta(X - x) = -\frac{\partial}{\partial X}\delta(X - x)$, we arrive at

$$\partial_t p = -\partial_X (fp) + \frac{1}{2} \partial_X^2 (g^2 p) \tag{4.6}$$

A direct application is thus that for a Langevin equation in the Markov approximation and the overdamped limit,

$$\dot{\mathbf{r}} = \mu\mathbf{F} + \sqrt{2\mu T}\boldsymbol{\eta},\ \mu = \gamma^{-1} \tag{4.7}$$

where $\mathbf{F} = -\partial_{\mathbf{r}} V + \mathbf{f}$ is an external force field comprising a conservative part and a nonconservative one, we have

$$\partial_t p = \mu\partial_{\mathbf{r}} \cdot ([\partial_{\mathbf{r}} V - \mathbf{f}]p) + \mu T\partial_{\mathbf{r}} p \tag{4.8}$$

Of course, one can check that when $\mathbf{f} = \mathbf{0}$ we have that $p_{\rm eq}(\mathbf{r}) = \mathrm{e}^{-\beta V(\mathbf{r})}/Z$ is a stationary solution of Eq. (4.8).

4.1.2 Higher-dimensional Fokker-Planck equation

Suppose that we start from a higher-dimensional process

$$\dot{x}_\mu \overset{0}{=} f_\mu + g_{\mu i}\eta_i \tag{4.9}$$

where the noises verify $\langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\delta(t-t')$. While the dimensionality index μ runs from 1 to d, the noise index i doesn't have to run up to d. In other words the matrix $g_{\mu i}$ doesn't have to be square, but it cannot have more columns than lines. Itō's lemma for a function $u(t) = U(x_1(t), \ldots, x_d(t))$ takes a somewhat more complex form:

$$\dot{u} = \partial_\mu U \dot{x}_\mu + \frac{1}{2} g_{\mu j} g_{\nu j} \partial_\mu \partial_\nu U \tag{4.10}$$

One way to verify this formula is to *a posteriori* determine $\frac{\langle \Delta u\rangle}{\Delta t}$ in the $\Delta t \to 0$ limit directly from the equation on x_μ. The reason why we may need such an extension of Itō's lemma is that we'd like to be able to find the Fokker-Planck equation for more complex processes than an overdamped Langevin particle. But actually, the simplest situation where this extension is need is for the underdamped particle:

$$\dot{\mathbf{r}} = \mathbf{v},\ m\dot{\mathbf{v}} = -\gamma\mathbf{v} - \partial_{\mathbf{r}} V + \sqrt{2\gamma T}\boldsymbol{\eta} \tag{4.11}$$

then the joint variable $\mathbf{X} = \begin{pmatrix} \mathbf{r} \\ \mathbf{v} \end{pmatrix}$ is Markovian and its evolution reads

$$\dot{X}_\mu = F_\mu(\mathbf{r}, \mathbf{v}) + g_{\mu j}(\mathbf{r}, \mathbf{v})\eta_j \tag{4.12}$$

with $\mathbf{F} = \begin{pmatrix} \mathbf{v} \\ -\partial_{\mathbf{r}} V/m - \gamma\mathbf{v}/m \end{pmatrix}$ and the matrix $g_{\mu j}$ given by (for $d = 3$)

$$g_{\mu j} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \sqrt{2\gamma T}/m & 0 & 0 \\ 0 & \sqrt{2\gamma T}/m & 0 \\ 0 & 0 & \sqrt{2\gamma T}/m \end{pmatrix} \tag{4.13}$$

The index μ runs from 1 to $2d$ (where d is the position space dimension), while the noise index $i = 1$ runs only from 1 to d. We now apply Itō's lemma to $u(t) = U(\mathbf{x}(t)) = \delta(\mathbf{x}–\mathbf{r}(t))\delta(\mathbf{w}–\mathbf{v}(t))$ and we take the average. Denoting by

$$p(\mathbf{x}, \mathbf{w}, t) = \langle u(t) \rangle = \langle \delta(\mathbf{x} - \mathbf{r}(t))\delta(\mathbf{w} - \mathbf{v}(t)) \rangle \tag{4.14}$$

we readily arrive at the Fokker-Planck equation

$$\partial_t p = \frac{1}{m}\partial_{\mathbf{w}}((\gamma \mathbf{w} + \partial_{\mathbf{r}} V)p) - \mathbf{w} \cdot \partial_{\mathbf{r}} p + \frac{T}{m}\partial^2_{\mathbf{w}} p \tag{4.15}$$

Needless to say, $p_{\rm eq}(\mathbf{x}, \mathbf{w}) = \mathrm{e}^{-\frac{1}{T}\left(m\mathbf{w}/2 + V(\mathbf{x})\right)}$ is a stationary solution of that Fokker-Planck equation.

4.1.3 Infinitesimal moments, and more complex averages

Once a Fokker-Planck equation for a process $x(t)$ is known, say of the form

$$\partial_t p = -\partial_\mu (a^{(1)}_\mu p) + \frac{1}{2}\partial_\mu \partial_\nu (a^{(2)}_{\mu\nu} p) = -\mathbb{H} p \tag{4.16}$$

then we can ask about the statistics of the infinitesimal jump $\Delta x_\mu = x_\mu(t_0 + \Delta t) - x_\mu(t_0)$ starting from a fixed value $x(t_0) = x_0$ at $t = t_0$, and averaging over the realizations of the noise during the $[t_0, t_0 + \Delta t]$ interval. Here the notation $\mathbb{H}$ refers to the differential operator acting on p. Let us denote by $p(x, t|x_0, t_0)$ the solution of the Fokker-Planck equation with the initial condition $p(x, t_0|x_0, t_0) = \delta(x - x_0)$. Then, for instance,

$$\langle \Delta x_\mu \rangle = \int \mathrm{d}x' x'_\mu p(x_0 + x', t_0 + \Delta t|x_0, t_0) \tag{4.17}$$

But for Δt very small, we can write

$$p(x_0 + x', t_0 + \Delta t|x_0, t_0) = p(x_0 + x', t_0|x_0, t_0) + \Delta t \partial_t p(x_0 + x', t_0|x_0, t_0) + O(\Delta t^2) \tag{4.18}$$

so that, using that $p(x_0 + x', t_0|x_0, t_0) = \delta(x')$, we immediately find that

$$\langle \Delta x_\mu \rangle = \Delta t \int \mathrm{d}x' x'_\mu \underbrace{\partial_t p(x_0 + x'|t_0|x_0, t_0)}_{-\partial_\nu (a^{(1)}_\nu)(x_0+x')p + \frac{1}{2}\partial_\mu \partial_\nu (a^{(2)}_{\mu\nu})(x_0+x')p} + O(\Delta t^2) \tag{4.19}$$

With a couple of integration by parts we then arrive at

$$\langle \Delta x_\mu \rangle = \Delta t a^{(1)}_\mu (x_0) + O(\Delta t^2) \tag{4.20}$$

and a similar reasoning leads to

$$\langle \Delta x_\mu \Delta x_\nu \rangle = \Delta t a^{(2)}_{\mu\nu} (x_0) + O(\Delta t^2) \tag{4.21}$$

while any higher moment of Δx is negligible with respect to Δt. This gives us a recipe to work a Langevin equation backwards from a Fokker-Planck one:

$$\dot{x}_\mu \overset{0}{=} a_\mu^{(1)} + \xi_\mu,\ \langle \xi_\mu(t)\xi_\nu(t')\rangle = a_{\mu\nu}^{(2)}(x)\delta(t-t') \tag{4.22}$$

where the Itō-discretization was used.

Of course, the average of a given observable $A(t) = A(x(t))$ that depends on the random variable x is given by

$$\langle A\rangle(t) = \int \mathrm{d}x A(x) p(x,t) \tag{4.23}$$

and thus the average is a solution of

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \int \mathrm{d}x A(x)(-\partial_\mu(a_\mu^{(1)}p) + \frac{1}{2}\partial_\mu\partial_\nu(a_{\mu\nu}^{(2)}p)) \tag{4.24}$$

again, using integration by parts, one see that

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \int \mathrm{d}x \left[a_\mu^{(1)}\partial_\mu A(x) + \frac{1}{2}a_{\mu\nu}^{(2)}\partial_\mu\partial_\nu A)\right] p = -\int \mathrm{d}x (\mathbb{H}^\dagger A)p \tag{4.25}$$

Let $q(x) = 1$, then, introducing the notation $\langle f|g\rangle = \int \mathrm{d}x f(x)g(x)$ we see that

$$\langle A\rangle = \langle q|\hat{A}p\rangle,\ \hat{A} = A(x) \tag{4.26}$$

and

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = -\langle q|\mathbb{H}^\dagger \hat{A}p\rangle = \langle q|\hat{A}\mathbb{H}p\rangle = \langle q|[\mathbb{H},\hat{A}]p\rangle \tag{4.27}$$

where we have used that $\langle q|\mathbb{H}\phi\rangle = 0$ for any ϕ. Indeed, this is obvious when we make things more explicit:

$$\langle q|\mathbb{H}\phi\rangle = \int \mathrm{d}x \left(-\partial_\mu(a_\mu^{(1)}\phi) + \frac{1}{2}\partial_\mu\partial_\nu(a_{\mu\nu}^{(2)}\phi)\right) = 0 \tag{4.28}$$

after on or two integration by parts. The vector $\langle q|$ is an eigenstate of $\mathbb{H}^\dagger$ with eigenvalue 0, so that at least we know that 0 is an eigenvalue and there must be a corresponding eigenstate for $\mathbb{H}$: this eigenvector is the steady-state probability.

Suppose now that we want to determine, for $t > 0$, the correlation function $\langle B(t)A(0)\rangle$, where both A and B are x-dependent random variables. The brackets refer to an average over the initial state (whenever this was, whether at $t = 0$ or at some earlier time) and over the noise realization up until time t. Let us assume that at time $t = 0$ the value of $x(0) = x_0$ is fixed. Then $A(0) = A(x_0)$. For that initial condition, the value of x at t is $x(t)$, and $B(t) = B(x(t))$, so that the quantity $\langle B(t)\rangle|_{\text{at fixed } x(0)=x_0} A(0)$ is the product of $B(t)$ by $A(0)$, averaged over all trajectories, at fixed initial state. One can in addition average over the initial state at $t = 0$ and then

$$\int \mathrm{d}x_0 p(x_0, t=0)\ \langle B(t)\rangle|_{\text{at fixed } x(0)=x_0} A(0) = \langle B(t)A(0)\rangle \tag{4.29}$$

The quantity $J_\mu(x,t) = a_\mu^{(1)}p(x,t) - \frac{1}{2}\partial_\nu(a_{\mu\nu}^{(2)}p(x,t))$ is the probability current. For an overdamped Langevin equation $\gamma\dot{\mathbf{r}} = \mathbf{F} + \sqrt{2\gamma T}\boldsymbol{\eta}$, its first contribution $\frac{1}{\gamma}\mathbf{F}p$ is the deterministic drift, while the $-D\partial_{\mathbf{x}}p$ term (wiht $D = T/\gamma$) expresses Fick's law (in the absence of external drift, p is the solution of a diffusion equation).

4.1.4 Spectrum and relaxation

When we write $\partial_t p = -\mathbb{H}p$, the operator $\mathbb{H}$ must have certain properties. We have already seen that it conserves probability ($q(x) = 1$ is an eigenvector of $\mathbb{H}^\dagger$), but it must also conserve the positivity of p. If we start from a normalized an positive function $p(x, 0)$, how can we be sure that $p(x, t)$ remains positive at all times, just by seeing the equation (of course, we know this must be true)? How can we be sure that there will exist a steady-state? Will it be unique? All these are interesting and fundamental questions, that we will address later, by the example.

In practice, if we are able to diagonalize $\mathbb{H}$, then things will become simpler for us: assume we have found the λ's and ϕ's such that $\mathbb{H}|\phi\rangle = \lambda|\phi\rangle$. Then we know that $p(x, t) = \mathrm{e}^{-\mathbb{H}t}p(x, 0)$, with

$$\mathrm{e}^{-\mathbb{H}t} = \sum_\lambda \mathrm{e}^{-\lambda t}|\phi\rangle\langle\phi| \tag{4.30}$$

where ϕ refers to the eigenvectors of $\mathbb{H}$ with eigenvalue λ. Since $\mathbb{H}$ is not Hermitian, the λ's don't have to be real, and in general they won't be. Clearly, the eigenvalues λ have a strong physical meaning: their real parts form the set of relaxation rates that characterize the system's dynamics. When there exists a steady-state, it must correspond to $\lambda = 0$ (which is non-degenerate if the steady-state is unique). All other eigenvalues λ must have a positive real part. The lowest "excited" state of $\mathbb{H}$, that is the eigenstates whose corresponding λ has its real part the closet to 0. The reciprocal of its real part is the slowest time scale governing the relaxation to the steady-state. If $\Im(\lambda) \neq 0$ this tells us that there will be oscillations on top of exponential relaxation.

4.1.5 A simple example

Consider a one-dimensional Brownian particle on a segment of length ℓ whose ends at $x = 0$ and $x = \ell$ are absorbing, which means that the particle dies when hitting these boundaries. We want to solve $\partial_t p = D\partial_x^2 p$ with the boundary condition $p(x = 0 \text{ or } \ell, t) = 0$. The quantity $S(t) = \int_0^\ell \mathrm{d}x p(x, t)$ is the probability that the particle has survived up until time t. Sometimes S is called a survival probability. In order to find S one first diagonalizes $\mathbb{H} = -D\partial_x^2$, which, in practice, means solving

$$D\partial_x^2\phi = -\lambda\phi,\ \phi(0, t) = \phi(\ell, t) = 0 \tag{4.31}$$

whose (orthonormalized, $\int_0^\ell \mathrm{d}x\phi_n(x)\phi_m(x) = \delta_{mn}$) solutions are $\phi_n(x) = \sqrt{2/\ell}\sin k_n x$, with $k_n = n\pi/\ell$, $n \in \mathbb{N}^*$, and the corresponding eigenvalue is $\lambda_n = Dk_n^2$. These functions can be used to express the initial condition $p(x, 0)$:

$$p(x, 0) = \sum_{j\geq 1} c_j(0)\phi_j(x),\ c_n(0) = \int \mathrm{d}x\phi_n(x)p(x, 0) \tag{4.32}$$

so that, for instance when $p(x, 0) = \delta(x - x_0)$ ($x_0 \in [0, \ell]$), we have $c_n(0) = \phi_n(x_0)$ and thus

$$p(x, t) = \sum_{n\geq 1} \phi_n(0)\phi_n(x)\mathrm{e}^{-\lambda_n t} \tag{4.33}$$

and at large times the largest negative eigenvalue dominates the summation:

$$p(x,t) \simeq \frac{2}{\ell} \sin k_1 x_0 \sin k_1 x \mathrm{e}^{-D\pi^2 t/\ell^2} \tag{4.34}$$

and thus

$$S(t) \simeq \frac{4}{\pi} \sin(\pi x_0/\ell) \mathrm{e}^{-D\pi^2 t/\ell^2} \tag{4.35}$$

For a Brownian particle on a segment $[0,\ell]$ with periodic boundary conditions, and a biased motion at velocity v, $\dot{r} = v + \sqrt{2D}\eta$, the spectrum of $\mathbb{H}$ is made of the $\lambda_k = Dk^2 + ivk$, where $k = 2\pi n/\ell$, $n \in \mathbb{Z}$. The steady-state is $p_{\mathrm{ss}}(x) = 1/\ell$ and the eigenvalue whose real part is the closest to zero is $D(2\pi/\ell)^2 + iv2\pi/\ell$ (the eigenfunctions are $\phi_k(x) = \frac{1}{\sqrt{\ell}}\mathrm{e}^{ikx}$).

For the case of a particle with reflecting boundary conditions diffusing without any bias, the local particle flux $j = -D\partial_x p$ must vanish at the two boundaries, which forces the eigenfunctions to be $\cos kx$, with $k = k_n = \frac{\pi n}{\ell}$, $n \in \mathbb{N}$, hence the relaxation to the uniform steady-state is governed by $\lambda_1 = D\frac{\pi^2}{\ell^2}$, which is smaller than $D\frac{4\pi^2}{\ell^2}$, hence it takes a bit longer with reflecting boundary conditions than it does with periodic boundary conditions to reach the uniform state $p(x) = \frac{1}{\ell}$.

4.1.6 Adjoint equation and first-passage time

Interestingly, one can actually show that the mean time $\tau(y,x)$ at which the first passage to location y occurs, when starting from x, for a process evolving through $\dot{r} \overset{0}{=} f + g\eta$, is a solution of

$$a^{(1)}(x)\partial_x \tau + \frac{1}{2} a^{(2)}(x) \partial_x^2 \tau = -1 \tag{4.36}$$

with the boundary condition $\tau(x,x) = 0$.

For the mean first-passage time $\tau(x_2,x_1)$ to x_2 starting from x_1, we expect

$$\int_y \tau(x_2,y) p(y,0|x_1,-\mathrm{d}t) + \mathrm{d}t = \tau(x_2,x_1) \tag{4.37}$$

which we can phrase as follows: the time that it takes to hit x_2 starting from x_1 is the time that it takes to hit y starting from x_1 in a time $\mathrm{d}t$, to which one must add $\mathrm{d}t$, and that is regardless of y. We have denoted by $p(x',t'|x,t)$ the probability to be at x' at time t' given that one started from x at time t. We can then use that

$$p(y,0|x_1,-\mathrm{d}t) = p(y,\mathrm{d}t|x_1,0) = \delta(x_1-y) + \mathrm{d}t\partial_y(-f(y)\delta(x_1-y)) + \frac{1}{2}\partial_y^2(g^2(y)\delta(y-x_1)) \tag{4.38}$$

which results in

$$(\mathbb{H}^\dagger)_{x,x_1}\tau(x_2,x) = 1,\ f(x_1)\partial_{x_1}\tau(x_2,x_1) + \frac{g^2(x_1)}{2}\partial_{x_1}^2\tau(x_2,x_1) = -1 \tag{4.39}$$

Interestingly, $\mathbb{H}^\dagger$ appears in this equation, as it does in most reasonings involving some sort of time-reversal. In this particular situation, we know ahead of time the time it takes to reach a

target.

There are many applications of first passage times and probabilities to nonequilibrium and biophysical systems. One of them is described in [**?**] and it deals with the best strategy to efficiently find food.

4.2 Equilibrium and time-reversibility

4.2.1 Probability current

When we consider a Langevin equation of the form $\dot{x}_\mu \overset{0}{=} f_\mu + g_{\mu j}\eta_j$ the related probability current is $J_\mu(x,t) = \underbrace{f_\mu}_{a_\mu^{(1)}} p + \frac{1}{2}\partial_\nu(\underbrace{g_{\mu i}g_{\nu i}}_{a_{\mu\nu}^{(2)}} p)$. This is not exactly $\langle \dot{x}_\mu \rangle$, so it is not always easy to picture what J_μ is. What we know for sure is that in a steady-state, we must have $\partial_\mu J_\mu = 0$: the current is divergence free.

We have already noted that when $f_\mu = -\partial_\mu V$ and $g_{\mu i} = \sqrt{2T}\delta_{\mu i}$, namely for an equilibrium dynamics, the probability current $J_\mu = -\partial_\mu V p - T\partial_\mu p$ vanishes when p reaches its equilibrium value $p_{\rm eq}(x) = {\rm e}^{-V(x)/T}/Z$. This suggests that an alternative way of defining equilibrium is by requiring that the probability current vanish. In the second example of subsection 4.1.5 where $p_{\rm ss}(x) = \frac{1}{\ell}$ we have that $J = vp - D\partial_x p = vp = \frac{v}{\ell}$ and this current indeed vanishes only when there is not directed motion (when $v = 0$).

Let's look deeper into another example, that of an underdamped Langevin equation for a particle with a unit mass $m = 1$:

$$\dot{x} = v,\ \dot{v} = -\gamma v - \partial_x V + \sqrt{2\gamma T}\eta \tag{4.40}$$

with the related Fokker-Planck equation for $p(x,v,t)$:

$$\partial_t p = -v\partial_x p + \partial_v((\gamma v + \partial_x V)p) + \gamma T\partial_v^2 p \tag{4.41}$$

This is a local conservation equation in the two-dimensional (x,v) space,

$$\partial_t p = -\partial_x J_x - \partial_v J_v,\ \begin{cases} J_x = vp \\ J_v = -(\gamma v + \partial_x V)p - \gamma T\partial_v p \end{cases} \tag{4.42}$$

where $J_x = \langle \dot{x} \rangle$ is the real spatial current. In a stationary state, whether equilibrium or not, we have $\partial_x J_x + \partial_v J_v = 0$. However, we know that the dynamics of Eq. (4.40) describes some equilibrium dynamics, since its related entropy production, at fixed initial and final states, is given by

$$\Sigma = \ln\frac{\mathscr{P}[x]}{\mathscr{P}[x^{\rm R}]} = -\frac{1}{\gamma T}\int_0^{t_{\rm obs}} (\ddot{x} + \partial_x V)\gamma\dot{x} = \left[\frac{\dot{x}^2}{2} + V(x)\right]_0^{t_{\rm obs}} \tag{4.43}$$

which tells us that choosing as the initial state a Boltzmann distribution, the system remains at zero entropy production and is thus in equilibrium. Now, let's evaluate the current components,

$$J_x = vp = v\frac{\mathrm{e}^{-\beta H(x,v)}}{Z},\ H(x,v) = \frac{1}{2}v^2 + V(x) \tag{4.44}$$

is obviously nonzero, and neither is J_v:

$$J_v = -(\gamma v + \partial_x V)p - \gamma T \partial_v p = -\partial_x V \frac{\mathrm{e}^{-\beta H(x,v)}}{Z} \tag{4.45}$$

This is no big deal for several reasons: first, unless we insisted on defining equilibrium through the vanishing of probability currents, there is no contradiction with equilibrium. Second, mathematically speaking, the only thing we know is that the current is divergence free, so that it is in general defined up to a curl. If we add $\boldsymbol{\nabla} \times \mathbf{A}$ to $\mathbf{J}$ then of course the property $\boldsymbol{\nabla} \cdot \mathbf{J} = 0$ is preserved. In the example above, the choice $\mathbf{A} = Tp\mathbf{e}_z$ works fine (where z is a third direction perpendicular to x and v):

$$J'_x = J_x + \partial_v(Tp),\ J'_v = J_v - \partial_x(Tp) \tag{4.46}$$

and of course $J'_x = 0$, $J'_v = 0$. What matters eventually is only the divergence of the current, or its net flux across some surface of phase space, not the individual components of the current.

4.2.2 Detailed balance

Our definition of equilibrium is based on the fact that there is no way to distinguish a time-forward trajectory from its time-reversed counterpart. On practice this means that the joint probability $p(x,t;x',t')$ of observing the position x' at t' and x at time $t > t'$, verifies

$$p(x,t;x',t') = p(x',t;x,t') \tag{4.47}$$

In a steady-state, we have that $p(x,t;x',t') = p(x,t|x',t')p_{\mathrm{ss}}(x')$, so that we must also have the so-called detailed balance condition:

$$p(x,t|x',t')p_{\mathrm{ss}}(x') = p(x',t|x,t')p_{\mathrm{ss}}(x) \tag{4.48}$$

When this is the case one writes that $p_{\mathrm{ss}} = p_{\mathrm{eq}}$. That's a very special brand of steady-state distribution. It is interesting to see what detailed balance tells us for the evolution operator $\mathbb{H}$. For this, we consider t' and $t = t' + \Delta t$, with Δt very small:

$$(\underbrace{p(x,t'|x',t')}_{\delta(x-x')} + \Delta t\ \partial_t p(x,t|x',t')\big|_{t=t'} + \ldots)p_{\mathrm{eq}}(x') = (p(x',t'|x,t') + \Delta t\ \partial_t p(x',t|x,t')\big|_{t=t'} + \ldots)p_{\mathrm{eq}}(x) \tag{4.49}$$

Using that $\partial_t p(x,t|x',t')\big|_{t=t'} = -\mathbb{H}_x \delta(x-x')$ and we $\partial_t p(x',t|x,t')\big|_{t=t'} = -\mathbb{H}_{x'}\delta(x-x')$ we obtain

$$\mathbb{H}_x \delta(x-x')p_{\mathrm{eq}}(x') = \mathbb{H}_{x'}\delta(x-x')p_{\mathrm{eq}}(x) \tag{4.50}$$

This is a not a very transparent equality, but when translated into what it really means, namely

$$\int \mathrm{d}x\mathrm{d}x' \phi(x)\mathbb{H}_x \delta(x-x')p_{\mathrm{eq}}(x')\chi(x') = \int \mathrm{d}x\mathrm{d}x' \phi(x)\mathbb{H}_{x'}\delta(x-x')p_{\mathrm{eq}}(x)\chi(x') \tag{4.51}$$

where ϕ and χ are dummy functions, and using the definition of the Hermitian conjugate,

$$\int \mathrm{d}x\mathrm{d}x'\phi(x)\mathbb{H}_x\delta(x-x')p_{\mathrm{eq}}(x')\chi(x') = \int \mathrm{d}x\mathrm{d}x'(\mathbb{H}_x^\dagger\phi(x))\delta(x-x')p_{\mathrm{eq}}(x')\chi(x') \tag{4.52}$$

then we arrive at

$$p_{\mathrm{eq}}(x')\mathbb{H}_x^\dagger\delta(x-x') = p_{\mathrm{eq}}(x)\mathbb{H}_{x'}\delta(x-x')p_{\mathrm{eq}}(x) \tag{4.53}$$

Put more simply, $\mathbb{H}^\dagger = p_{\mathrm{eq}}^{-1}\mathbb{H}p_{\mathrm{eq}}$.

This takes a simple form for an overdamped Langevin particle

$$\mathbb{H}\bullet = -T\partial_x^2\bullet - \partial_x(V'\bullet) = -T\mathrm{e}^{-\beta V}\partial_x\left(\mathrm{e}^{\beta V(x)}\partial_x\bullet\right) \tag{4.54}$$

which is such that

$$\mathbb{H}^\dagger\bullet = -T\mathrm{e}^{+\beta V}\partial_x\left(\mathrm{e}^{-\beta V(x)}\partial_x\bullet\right) \tag{4.55}$$

This also means that $\mathbb{H}_s = p_{\mathrm{eq}}^{-1/2}\mathbb{H}p_{\mathrm{eq}}^{1/2}$ is Hermitian, which can be checked explicitly:

$$\mathbb{H}_s = -T\partial_x^2 + U(x),\ U(x) = \frac{V'^2}{4T} - \frac{1}{2}V'' \tag{4.56}$$

In retrospect, we see that in equilibrium the spectrum is thus real and $\mathbb{H}_s$ can be diagonalized in an orthogonal basis.

For a particle evolving according to an overdamped Langevin dynamics in some *a priori* arbitrary force field $\mathbf{F}$, we have that

$$\dot{\mathbf{r}} = \mathbf{F} + \sqrt{2T}\boldsymbol{\eta},\ \ \partial_t p(\mathbf{r},t) = \partial_{\mathbf{r}}\cdot(\mathbf{F}p) + T\partial_{\mathbf{r}}^2 p = -\mathbb{H}p \tag{4.57}$$

If we denote by p_{ss} the stationary distribution and if we define $H[\mathbf{r}] = -\ln p_{\mathrm{ss}}(\mathbf{r})$, then the new operator $\mathbb{H}' = p_{\mathrm{ss}}^{-1/2}\mathbb{H}p_{\mathrm{ss}}^{1/2}$ reads

$$\mathbb{H}' = \underbrace{-T\partial_{\mathbf{r}}^2 + \partial_{\mathbf{r}}\cdot\mathbf{F} - \frac{1}{2}\mathbf{F}\cdot\partial_{\mathbf{r}}H - \frac{T}{4}(\partial_{\mathbf{r}}H)^2 + \frac{T}{2}\partial_{\mathbf{r}}^2 H}_{\text{Hermitian}} + (T\partial_{\mathbf{r}}H + \mathbf{F})\cdot\partial_{\mathbf{r}} \tag{4.58}$$

and it is obviously not Hermitian, unless $\mathbf{F} = -\partial_{\mathbf{r}}V$ is conservative, and then $H(\mathbf{r}) = \beta V(\mathbf{r})$ as expected in equilibrium.

4.2.3 Stochastic thermodynamics 101

We'll focus on the the dynamics of an overdamped particle $\dot{x} = F + \sqrt{2T}\eta$ where F is some external force field. Let $S(t) = -\int \mathrm{d}x p(x,t)\ln\frac{p(x,t)}{p_{\mathrm{ss}}(x)}$ be the Shannon entropy, then we readily see that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\int \frac{1}{p}\partial_x p \times j \tag{4.59}$$

where $j = -T\partial_x p - V'p$. We'll now split the rate of variation of entropy into two bits,

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \int \mathrm{d}x \frac{j^2}{Tp} - \int \mathrm{d}x \frac{F}{T} j \tag{4.60}$$

which is easily verified using $\partial_x p = (Fp - j)/T$

$$-\frac{1}{p}\partial_x pj = \frac{j^2}{Tp} - \frac{1}{T}Fj \tag{4.61}$$

We now give a name to each of these contributions:

$$\sigma_{\mathrm{irr}} = \int \mathrm{d}x \frac{j^2}{Tp} = \frac{\mathrm{d}S_i}{\mathrm{d}t} \tag{4.62}$$

is referred to an internal entropy production rate, while

$$\frac{\mathrm{d}S_e}{\mathrm{d}t} = -\int \mathrm{d}x \frac{F}{T} j \tag{4.63}$$

is an external entropy production rate.

Let $\hat{S}(t) = -\ln p(x(t), t)$ be, for now, a strange fluctuating quantity. Using Stratonovich calculus, we see that

$$\begin{aligned} \frac{\mathrm{d}\hat{S}}{\mathrm{d}t} &\overset{1/2}{=} -\frac{\partial_t p}{p} - \frac{\partial_x p}{p}\dot{x} \\ &\overset{1/2}{=} -\frac{\partial_t p}{p} + \left(\frac{j}{Tp} - \frac{1}{T}F\right)\dot{x} \end{aligned} \tag{4.64}$$

It is interesting to see that if we attribue to $\hat{S}$ the meaning of a trajectory-dependent entropy, then the first contribution $\frac{\partial_t p}{p}$ convey a variation due to time-evolution (say towards a steady-state, or perhaps owing to a time-dependent protocol) while the $F\dot{x}$ terms represents the power injected by the force F. The quantity $\frac{\mathrm{d}S_m}{\mathrm{d}t} = \frac{F\dot{x}}{T}$ is the entropy change in the medium, so that the total entropy variation is given by

$$\frac{\mathrm{d}S_{\mathrm{tot}}}{\mathrm{d}t} = \frac{\mathrm{d}\hat{S}}{\mathrm{d}t} + \frac{\mathrm{d}S_m}{\mathrm{d}t} \tag{4.65}$$

It is not hard to realize that, upon averaging, one has

$$\langle \frac{\mathrm{d}S_{\mathrm{tot}}}{\mathrm{d}t} \rangle = \frac{\mathrm{d}S_i}{\mathrm{d}t} = \sigma_{\mathrm{irr}} \tag{4.66}$$

while, as we have already seen,

$$S_m(t) = \ln \frac{\mathscr{P}[x]}{\mathscr{P}[x^{\mathrm{R}}]} = \frac{1}{T}\int \mathrm{d}t F\dot{x} \tag{4.67}$$

is, on average, the Kullback-Leibler divergence between the forward and time-reversed trajectories,

$$\Sigma = \langle S_m \rangle = \int \mathscr{D}x \, \mathscr{P}[x] \ln \frac{\mathscr{P}[x]}{\mathscr{P}[x^{\mathrm{R}}]} \tag{4.68}$$

4.2.4 Linear response and the fluctuation-dissipation theorem

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

$$\dot{x} = -V' + f + \sqrt{2T}\eta \tag{4.69}$$

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

$$R(t,t') = \left.\frac{\delta\langle B(t)\rangle}{\delta f(t')}\right|_{f=0} \tag{4.70}$$

with

$$\langle B\rangle = \int \mathscr{D}x B(x(t)) \mathrm{e}^{-\frac{1}{4T}\int \mathrm{d}s(\dot{x}+V'-f)} \tag{4.71}$$

so that

$$R(t,t') = \frac{1}{2T}\langle B(x(t))(\dot{x}+V')(t')\rangle \tag{4.72}$$

and in a similar fashion

$$R(-t,-t') = \frac{1}{2T}\langle B(x(-t))(\dot{x}+V')(-t')\rangle \tag{4.73}$$

so that

$$R(t,t')-R(-t,-t') = \frac{1}{2T}\left[\langle B(x(t))\dot{x}(t') - B(x(-t))\dot{x}(-t')\rangle\right] + \frac{1}{2T}\langle B(x(t))\,V'(x(t')) - B(x(-t))\,V'(x(-t'))\rangle \tag{4.74}$$

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

$$\langle B(x(t))\dot{x}(t') - B(x(-t))\dot{x}(-t')\rangle = 2\frac{\mathrm{d}}{\mathrm{d}t'}\langle B(x(t))\dot{x}(t')\rangle \tag{4.75}$$

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

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

$$\sigma = \frac{1}{T}\langle \dot{x}f\rangle = \lim_{t\to 0}\frac{\mathrm{d}}{\mathrm{d}t}\Big[TR(t) + \dot{C}(t)\Big] \tag{4.76}$$

which is the Harada-Sasa equality (the proof that can be found here [48, 49] is a bit tricky). Here R and C are the position response and the position auto-correlation function.

Chapter 5

Thermal Ratchets and Stochastic Motors

5.1 Motivations

5.1.1 Back to the XIXth century, and into the XXIst

Let's examine a macroscopic system, characterized by its usual state variables (pressure P, volume V, temperature T) that is subjected to a sequence of transformations. Start from state A with temperature T_h, and let the system spontaneously expand to reach state B. By doing so it will cool down, so we decide to inject some heat into the system to maintain its temperature T_h while it expands from V_A to V_B. By expanding, we retrieved some work that the system actually gives away to the outside world. Then, we isolate the system and let the expansion continue. Now the system cools down to temperature T_c during this adiabatic step. This is an entropic expansion, up to state C at V_C. Then we compress the system to state D by keeping its temperature constant at T_c, which means the system must release heat to the outside world. Finally we get back to the initial state A via an adiabatic isoentropic compression. The first principle tells us that $\Delta U_{A\to A} = Q_{A\to B} + Q_{C\to A} + W = 0$ and the second principle tells us that $\Delta S_{A\to A} = \frac{Q_{A\to B}}{T_h} + \frac{Q_{C\to D}}{T_c}$, hence the efficiency $\eta = \frac{\text{what we get}}{\text{what we spend}}$ is given by $\eta = -\frac{W}{Q_{A\to B}}$, so that

$$\eta = 1 - \frac{T_c}{T_h} \tag{5.1}$$

and $\eta \to 0$ as $T_c \to T_h$. For macroscopic systems, there is simply no way to extract work from a single thermal bath.

Let us now enter the XXIst century and see if our conclusion can change. We follow [76] for the experiment, and [91] for the theory. Let's quote the authors of the experimental work:

> *The Carnot cycle consists of two isothermal processes, where the working substance is respectively in contact with thermal baths at different temperatures T_h and T_c, connected by two adiabatic processes, where the substance is isolated and heat is not delivered nor absorbed. An external parameter is changed in such a way that*

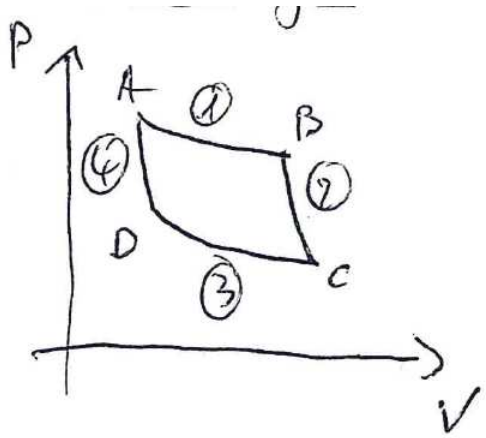


Figure 5.1: The cycle is run clockwise, so that $\oint P\mathrm{d}V > 0$ and thus $W < 0$, in accordance with the idea that some useful work is actually provided by the system. Sketch courtesy of J. Tailleur.

> *the whole cycle is carried out reversibly. Following this scheme, one could devise a progressing miniaturization of a Carnot engine and eventually reproduce the cycle with a single Brownian particle. In fact, a variety of thermodynamic processes and even a complete Stirling cycle have been already implemented in the mesoscale using micro-manipulation techniques. Interestingly, the exchange of energy between the particle and its surrounding environment becomes stochastic at the microscale and yet one can rigorously define work, heat and efficiency, within the framework of the recently developed stochastic thermodynamics.*
>
> *The experimental realization of a Carnot cycle with a single Brownian particle has remained elusive owing to the difficulties of implementing an adiabatic process. In particular, it is not clear how to isolate a particle from the surrounding fluid. A more feasible strategy is to simultaneously change the temperature and the external parameter keeping constant the Shannon entropy of the particle. However, the necessary fine-tuning of the temperature is an experimental challenge as well. Here we construct a Brownian Carnot engine putting forward an experimental technique that allows precise control of both the effective temperature and the accessible volume of a single microscopic particle. We use a particle with an inherent electric charge and apply a noisy electrostatic force that mimics a thermal bath. In this way, we can achieve temperatures ranging from room temperature (no electrostatic force) up to hundreds or even thousands of kelvins, far above the boiling point of water.*
>
> *The working substance of our engine is a single optically trapped colloidal particle immersed in water.*

For small displacements of the particle within the optical trap, the latter can be modeled by an external potential $V(x,t) = \frac{k(t)}{2}x^2$, where the stiffness k is controled in much the same

way as the volume was controled in the original Carnot cycle. The states $3, 4, 1, 2$ match the

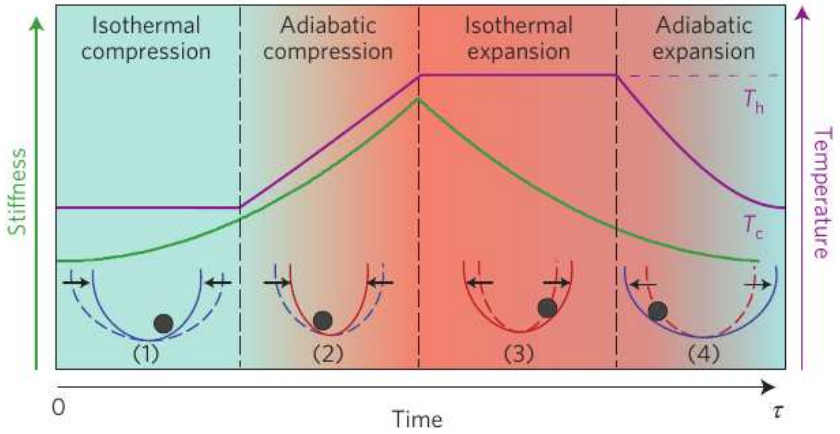


Figure 5.2: From [76].

A, B, C, D of the Carnot cycle. Let's investigate the energy balance $\mathrm{d}V = \delta W + \delta Q$ where $\delta W = \frac{1}{2}x^2 \mathrm{d}k$ and $\delta Q = T\mathrm{d}s$, with $S(t) = -\ln p_{\mathrm{eq}}(x(t))$. First, let's make sure that this is true!

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \dot{k}\frac{x^2}{2} + kx\dot{x} \tag{5.2}$$

and we see that if $p_{\mathrm{eq}}(x) = \mathrm{e}^{-\beta k x^2/2}/Z$ then $s(t) = -\beta\frac{kx(t)^2}{2} + \ln Z$ so that $\mathrm{d}s = -\beta kx\dot{x}\mathrm{d}t$. This is consistent with the idea that $0 = -kx - \dot{x} + \sqrt{2T}\eta$ and thus the work of the external force $-kx\dot{x}\mathrm{d}t$ is also the work done by the particle on the bath, namely $-kx\dot{x}\mathrm{d}t = -(-\dot{x}+\sqrt{2T}\eta)\dot{x}\mathrm{d}t = \delta Q$. From here on it should be pretty clear that taking averages will not modify anything to the Carnot efficiency!

5.1.2 Feynman's ratchet and pawl's paradox

In chapter 46 of the first volume of the Feynman Lectures on Physics [33], Feynman tricks the reader with the following thought experiment in Fig. **??**.

The question is whether the wheel will rotate anticlockwise. If the wheel had a net rotation, say with angular velocity ω_0, then this would mean that it could raise up a small body of mass m, by reducing its velocity to ω_m. We would then have an equilibrium system performing work, which contradicts the second principle of thermodynamics which states that work can be extracted only with two sources (and the highest efficiency is obtained with the Carnot cycle). We will later explore what occurs when $T_1 \neq T_2$ in the right compartment. At first sight, it appears that a fluctuation could very well lead to the wheel hopping ahead and thus peforming a net motion. As noted by Feynman, the first issue comes up when describing the pawl. For it to return in place and prevent any backward motion of the wheel, there has to be some spring pulling it back. Suppose also that the parts of the device are perfectly elastic, then this would mean that upon returning back to its initial position, the pawl would actually keep bouncing. Then, this leaves room for a fluctuation to move the wheel backward as the pawl

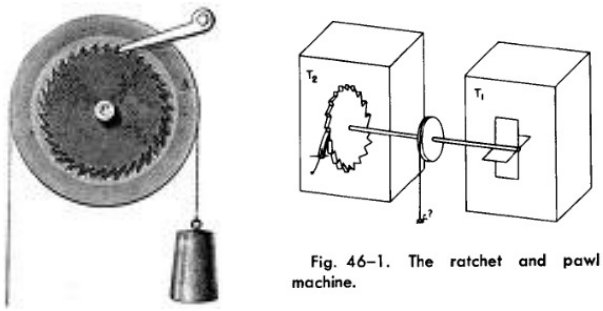


Fig. 46–1. The ratchet and pawl machine.

Figure 5.3: Left: A freely rotating ratchet (toothed wheel) is immersed in an equilibrium gas at temperature T, and a pawl is used to block the backward motion of the wheel. The net motion is used to extract work to raise a body of mass m. Right: The original discussion by Feynman, based on the same principl;e, and with $T_1 = T_2$ to begin with.

is temporarily lifted. One understands that for the pawl not to bounce, one needs some sort of dissipation. The dissipated energy will simply heat the wheel up, which will become hotter and hotter. Some of the heat will be absorbed by the surrounding gas, but not forever. As things get hotter, such a rare even by which a thermal fluctuation raises the pawl and moves the wheel backward is more and more likely. In [85] the authors have criticized some aspects of Feynman's original discussion.

We return to the right device in figure 5.3 where we now allow the two temperatures to be unequal with $T_2 < T_1$. We proceed with a standard macroscopic thermodynamics analysis. Because the wheel is cold and the fluctuations of the pawl are rather infrequent, it will be hard for the pawl to attain energy ε. In contrast, since T_1 is larger, the vane will more frequently than the ratchet reach the energy ε. The whole device will then indeed proceed with a net motion, as expected. But can it lift weights? A small mass m is hung on the ratchet-vane axis, thus exerting a torque Γ. Our questions are: how much weight can it lift and how fast does it go? In the following, ε refers to the energy necessary to lift the pawl.

We consider the forward motion. The energy needed for rotating the wheel by an angle θ is $\varepsilon + \Gamma\theta$, and this energy is taken at a rate $\gamma \mathrm{e}^{-\beta_1(\varepsilon+\Gamma\theta)}$, where γ is setting the time-scale. We now look at the opposite event. The rate at which the backward motion of the wheel occurs is $\gamma \mathrm{e}^{-\beta_2\varepsilon}$. The work W released is then $W = \Gamma\theta$. Work is indeed released since the wheel slips backward. During the latter step, the energy given to the vane at T_1 is $\varepsilon + \Gamma\theta$. In the foward motion, the needed energy is $\varepsilon + \Gamma\theta$ and it is fully taken from the vane. Work performed accounts for $\Gamma\theta$ and ε is given to the ratchet. In the backward motion, up to a sign reversal, the same energy ε is taken from the ratchet, the work $\Gamma\theta$ is released and $\Gamma\theta + \varepsilon$ is given to the vane. If the pawl is lifted up accidentally by a fluctuation, then when it falls back the spring pushes it down against the tooth, and there is a force trying to turn the wheel because the tooth is pulling on an inclined plane. This force is doing work and so is the force due to the weights. Both together make the total force and all the energy which is slowly released appers in the form of heat at the vane. For a particular value of the torque (or of the mass) the rates will be equal. If an infinitesimal weight is added to the string, work is done on the machine,

Figure 5.4: A wheat spike.

and if it is removed, heat is taken from the vane and put into the wheel. The condition at which there is perfect balance is $\frac{\varepsilon+\Gamma\theta}{T_1} = \frac{\varepsilon}{T_2}$, and it corresponds to a Carnot reversible cycle. If the machine is slowly lifting the weight, $Q_1 = \varepsilon + \Gamma\theta$ is taken from the vane and $Q_2 = \varepsilon$ is delivered to the wheel: $Q_1/Q_2 = T_1/T_2$. The work-to-energy-taken-from-the-vane ratio is $\frac{W}{Q_1} = \frac{\Gamma\theta}{\varepsilon+\Gamma\theta}$. No more work than this limiting ratio obtained from reversible conditions can be extracted. If one had $T_1 = T_2$, the angular velocity ω is θ times the rate at which a jump occurs. The forward motion has a rate $\gamma \mathrm{e}^{-\beta_1(\Gamma\theta+\varepsilon)}$ and the backward one $\gamma \mathrm{e}^{-\beta_1\varepsilon}$, hence

$$\omega = \gamma\theta \mathrm{e}^{-\beta_1\varepsilon}(\mathrm{e}^{-\beta_1\Gamma\theta} - 1) \tag{5.3}$$

which leads to $\omega(\Gamma)$ being a decreasing function of Γ, with $\omega(\Gamma < 0) > 0$ and $\omega(\Gamma > 0) < 0$. If $\Gamma > 0$, which corresponds to driving the wheel backward, the backward velocity approaches a constant $-\theta\gamma \mathrm{e}^{-\beta_1\varepsilon}$, while $\omega(\Gamma \to -\infty) \to +\infty$. If now we take the weight away and reinstate the two unequal temperatures, then, if $T_2 < T_1$ we have forward motion, as expected. The reverse case $T_2 > T_1$ leads to a backward motion, which may be harder to conceive. A hot ratchet and pawl is ideally built to go around in a direction exactly opposite to that for which it was originally designed. Indeed, with lots of heat, the ratchet keeps bouncing. If the pawl, for a moment, is on the incline somewhere then it pushed the inclined plane sideways. But is is always pushing an inclined plane, because if it happens to lift up high enough to get past the point of a tooth, then the inclined plane slides by and the pawl comes down again on an inclined plane. If the two temepratures are equal, there is no more propensity to turn one way or another.

The wheat spike

Consider a wheat spike as shown in figure 5.4. If placed in between two layers of clothing, say in between the sleeve of a coat and that of the underlying sweater, the spike will rise up the arm due to the random motion of the arm during the walk. There is a net displacement in a preferred direction, but the spike is not inequilibrium, because of an external force pulling it upwards against gravity. The force acting on the spike is random, in that it fluctuates, but the latter fluctuations are rectified, since the spike benefits only from the component of the force that drives it up. Whence the question we would like to answer: under what conditions can a fluctuating force be led to perform a net work by rectification. Curie's Principle states that the symmetry of a cause is always preserved in its effects. This makes us believe that the

wheat spike being asymmetric, its displacement along a preferred direction was expected. If that is so, why not repeating the argument for the ratchet and the pawl? The answer is no because the reversibility of the microscopic evolution equations –a symmetry property– will be preserved, which is in contradiction with the wheel rotating in a favored direction. However, out of equilibrium, in a stationary state with irreversible dynamics, the rectification of fluctuations becomes a possibility.

In what follows we'll explore several routes. One is inspired by the Carnot experiment (or the ratchet and pawl) and we will drive an energy flux through the system, say by imposing contact with thermal baths at different temperatures. Another one consists in breaking time-reversal at the microscopic level.

5.2 Fluctuating forces

5.2.1 No current in equilibrium

Our presentation is based on [70]. Before anything, let's examine what is happening with a particle in equilibrium evolving in a sawtooth potential as in Fig. 5.5. The equation of motion

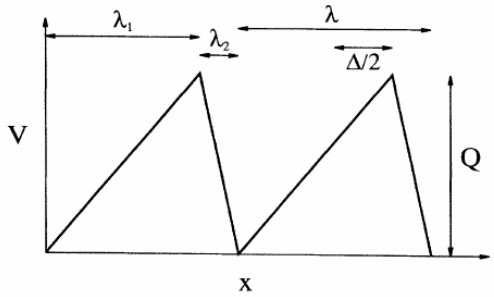


FIG. 1. A plot of the piecewise linear potential $V(x)$ as a function of position x. The width of each segment is called λ_1 and λ_2. The period of the potential is $\lambda = \lambda_1 + \lambda_2$ and the symmetry breaking amplitude is $\Delta = \lambda_1 - \lambda_2$.

Figure 5.5: Taken from [70].

is $\dot{x} = -V' + \sqrt{2T}\eta$. Is there any particle current in the steady-state? If there would be one, $j = -V'p - T\partial_x p$ would be nonzero, and thus

$$p(x) = \mathrm{e}^{-\beta V(x)} \left[p(0)\mathrm{e}\beta V(0) - \beta j \int_0^x \mathrm{d}y \mathrm{e}^{\beta V(y)} \right] \tag{5.4}$$

with $\int \mathrm{d}x p(x) = 1$. The periodicity condition $p(0) = p(\ell)$, and the fact that $V(0) = V(\ell)$, lead to $j = 0$. In the thermal equilibrium problem, the potential's asymmetric shape alone is of no help in producing a current.

5.2.2 Brownian motion in an asymmetric potential, out of equilibrium (flashing ratchet)

One way to drive the same system out of equilibrium is to replace the constant thermal bath by an oscillating temperature $T(t) = T_0 + T_1 \cos^2(\pi t/\tau)$. It remains to understand how such anoscillating thermal contact may lead to a nonvanishing current. Since an exact analytical solution is not available, we shall confine our analysis to an even simpler situation in which

$$T(t) = \begin{cases} 0 & \text{for } 0 < t < \tau/2 \\ T_0 & \text{for } \tau/2 < t/\tau \end{cases} \tag{5.5}$$

which is τ-periodic. We shall further assume that $k_\mathrm{B} T_0 \gg V(x)$. The particle starts at $t = 0$ from $x = x_0$. After a half-period, at $t = \tau/2$, at temperature $T = 0$, the particle lies at the potential well closest to x_0, which according to figure 5.6, is at $x = x_1$. At $t = \tau$, for the

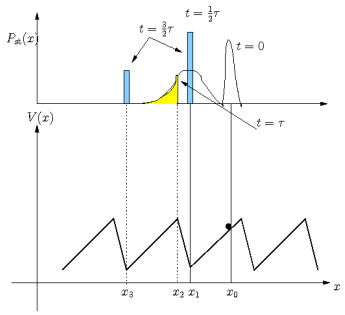


Figure 5.6: Periodic potential.

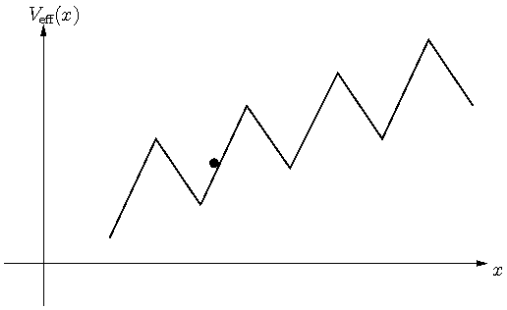


Figure 5.7: Periodic potential with a negative and constant force f.

last half-period, the particle has been executing a random walk with a temperature $k_{\rm B}T \gg V$, which leads to a wide Gaussian pdf centered around x_1. At $t = \frac{3}{2}\tau$, the particle again moves deterministically towards the closest minimum, because it has a larger probability overlap with the descending slope of the potential towards x_3. Actually, if at $t = \tau$ the particle is left of x_2, then it willmove towards x_2, and to x_1 is the particle is right of x_2. Between $t = \frac{1}{2}\tau$ and $t = \frac{3}{2}\tau$, one can see that a net probability transport has occurred to the left. Such a phenomenon survives if the temperature actually follows the periodic laws mentioned above, or if it varies randomly around a given threshold.

The same system is now in addition subjected to a constant linear force, thereby feeling the effctive potential $V_{\rm eff}(x) = V(x) - fx$, with a negative load force $f < 0$ in figure 5.7. If the temperature is constant, $T(t) = T_0$ then we just return to the solution of the Fokker-Planck equation (**??**) in which we replace $V(x)$ with $V_{\rm eff}(x)$. A nonzero current $J = \text{cst} \times f$ is now present, as shown in figure 5.8. We found in the previous section that in the absence of a load force, there already existed a nonzero current J_0, as indicated in figure 5.8. With a varying temperature, if the load force f is now imposed, we expected the $J(f)$ curve to appear roughly like the dashed line in figure 5.8 (what is shown is actually the time-averaged current), which means that there exists a regime of the load force in which the current is actually opposed to the force. The system is able to provide work against the external force: this is a molecular motor.

Note that the stationary solution in the presence of a constant temperature thermal bath

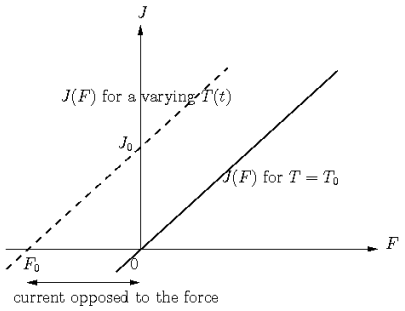


Figure 5.8: The constant temperature solution is shown is full line. The dashed line stands for the current in the presence of a varying temperature.

is given by

$$P_{\rm st}(x) = Z^{-1} \int_0^1 {\rm d}y {\rm e}^{\beta W(y,x)} \tag{5.6}$$

where

$$W(y,x) = V(y) - V(x) + \begin{cases} \int_y^x {\rm d}z f(z) & \text{if } y \leq z \\ \int_y^1 {\rm d}z f(z) + \int_0^x {\rm d}z f(z) & \text{if } y > x \end{cases} \tag{5.7}$$

is the work performed by the applied forces along the positively oriented path. The normalization factor reads $Z = \int_0^1 \int_0^1 {\rm d}x{\rm d}y {\rm e}^{\beta W(y,x)}$ and the net probability current is easily obtained by dividing $j = -\partial_x P_{\rm st} + \beta(f - V')P_{\rm st}$ by $P_{\rm st}$ and then by integrating the resulting equation over $[0,1]$, which gives

$$j = \beta \frac{W_{\rm cyle}}{\int_0^1 {\rm d}x / P_{\rm st}(x)} \tag{5.8}$$

where $W_{\rm cycle} = \int_0^1 {\rm d}z f(z)$ is the work over a complete cycle. For a constant force, this directly leads to $j = \beta f / \int_0^1 {\rm d}x / P_{\rm st}(x)$. In the experiment carried out by Mehl *et al.* [78] the potential is $V(x) = \frac{1}{2} V_0 \sin(x/R)$ (with $V_0 = 58 k_{\rm B} T$ and $f = 30 k_{\rm B} T$ is constant). The related velocity is 7 μm/s. The system is a colloidal particle of radius 0.65 μm, immersed in water, and trapped within a three-dimensional torus of radius R. The angular coordinate x of the particle is tracked between $-\pi R$ and $+\pi R$, with a time and spatial accuracy of 10 nmm and 15 ms respectively. The force f is exerted by optical tweezers.

5.2.3 Gallavotti-Cohen relation in the flashing ratchet

In this section, we draw freely from Lacoste and Mallick [61]. We take the motor to be a small particle moving in a one-dimensional space. At the initial time $t = 0$, the motor is trapped within one the wells of periodic asymmetric potential with spatial period a. Between 0 and τ_f, the asymmetric potential is erased and the particle diffuses freely and isotropically in contact with a thermostat at temperature T. At the switching time τ_f, the asymmetric potential is re-impressed and the motor slides down the nearest potential well in which it gets trapped, due to dissipation. The motor has the largest probability to fall within the same well it was in before the potential was erased, but there is a nonzero probability that it ends up to the

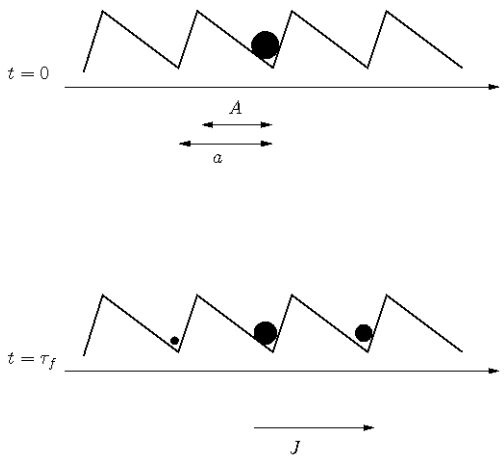


Figure 5.9: The flashing ratchet model.

right hand side well, and yet an even smaller probability to fall with the left-hand side one, as shown in figure 5.9. The fact that $a - A < A$ expresses that the potential is asymmetric. In the lower part of figure 5.9, the sizes of the disks are proportional to the presence probabilities of the particle. In practce, in order to move, ATP fuel is eaten up, at a rate r, which is broken into ADP and P,

$$\mathrm{ATP} \leftrightarrow \mathrm{ADP} + \mathrm{P} \tag{5.9}$$

The chemical energy released through the ATP hydroluysis allows the motor to detach itself from the filament it was bound to. This detachment process corresponds to the basic erasing mechanism, while the reattachment is equivalent to re-impressing the potential after τ_f. Hence the motor undergoes chemistry driven changes between strongly and weakly bound states. Energy barriers are overcome by the coupling betwwen chemistry and the interaction with the filament. The filament is a polar object, which is reflected in the asymmetric interaction potential. In general, the motor is subjected to an external force f_{ext} which further tilts the potential. If ATP is in excess, $\Delta\mu = \mu_{\mathrm{ATP}} - \mu_{\mathrm{ADP}} - \mu_{\mathrm{P}} > 0$, and we shall denote $E = \beta\Delta\mu$, with

$$E = \ln \frac{[\mathrm{ATP}]}{[\mathrm{ADP}][\mathrm{P}]} \frac{[\mathrm{ADP}]_{\mathrm{eq}}[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{ATP}]_{\mathrm{eq}}} \tag{5.10}$$

The basic question is to determine the velocity of the motor $v(f_{\mathrm{ext}}, E)$ and the ATP consumption rate $r(f_{\mathrm{ext}}, E)$ as a function of the applied forces.

In the flashing ratchet model, the switching of one potential to the other is sudden and occurs at random times generated by a Poisson process. The state of the motor is encoded in its position x and by two internal states $i = 1$ and 2 corresponding to distinct internal states. One of the states –the high energy one– corresponds to the motor being bound to the filament, and the other one –the low energy one– to a configuration where both heads are bound. In the previous discussion, U_1 is a sawtooth potential and U_2 is zero. We extend somexhat the discussion by allowing U_1 and U_2 to be arbitray asymmetric potentials with spatial period a.

The motor dynamics is given by the following Langevin equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\gamma F - \gamma \sum_i U_i \delta_{\zeta(t),i} + \sqrt{D}\xi \tag{5.11}$$

where $D = \sqrt{\gamma k_{\mathrm{B}} T}$, ζ is a dichotomous noise that can exist in two states 1 and 2, and xi is a Gaussian white noise of unit variance. The switching rates of ζ are position dependent and are given by $\omega_1(x)$ for the $1 \to 2$ transition, and by $\omega_2(x)$ for the $2 \to 1$ transition. The external force acting on the motor is denoted by F. The probability to find the motor in state i evolves according to

$$\partial_t P_1 + \partial_x J_1 = -\omega_1 P_1 + \omega_2 P_2,\ \partial_t P_2 + \partial_x J_2 = -\omega_2 P_2 + \omega_1 P_1 \tag{5.12}$$

where $J_i = -D(\partial_x P_i + k_{\mathrm{B}} T(\partial_x U_i - F)P_i)$. The transition rates are given by standard kinetics for chemical reactions,

$$\omega_1(x) = \left(\omega(x) + \psi(x)\mathrm{e}^{E}\right)\mathrm{e}^{\beta(U_1 - f_{\mathrm{ext}}x)},\ \omega_1(x) = (\omega(x) + \psi(x))\,\mathrm{e}^{\beta(U_2 - f_{\mathrm{ext}}x)} \tag{5.13}$$

with $f_{\mathrm{ext}} = Fa$ and where ω describes standard thermal transitions, while the extra ψ-dependent piece express the bias imposed by ATP hydrolysis. These two functions are periodic, but are otherwise unspecified. In the absence of any hydrolysis, there is detailed balance, $\omega_2/\omega_1 = \mathrm{e}^{-\beta U_1}/\mathrm{e}^{-\beta U_2}$. In the presence of hydrolysis, there is a generalized detailed balance condition that imposes a sort of local detailed balance,

$$\frac{\omega_2}{\omega_1} = \mathrm{e}^{-\beta(U_1 - U_2) - E} \tag{5.14}$$

For $F = 0$ and $E = 0$, the system is in equilibrium and there is no net displacement of the motor.

Let $P_i(x, q, t)$ be the probability that at time t the motor is in internal state i at position x and that q chemical units of ATP have been consumed. The master equation for $\hat{P}_i(u, \lambda, k, t) = \sum_q \mathrm{e}^{-\lambda q - k(n+u)} P_i((n+u)a, q, t)$ has the linear evolution operator

$$\mathbb{W}(\lambda, k, x) = \begin{pmatrix} \mathbb{L}_1 - \omega_1 & 0 \\ 0 & \mathbb{L}_2 - \omega_2 \end{pmatrix} + \begin{pmatrix} 0 & \omega \mathrm{e}^{\beta(U_2 - fx)} + \psi \mathrm{e}^{\beta(U_2 - fx)}\mathrm{e}^{\lambda} \\ \omega \mathrm{e}^{\beta(U_1 - fx)} + \psi \mathrm{e}^{\beta(U_1 - fx) + E}\mathrm{e}^{-\lambda} & 0 \end{pmatrix} \tag{5.15}$$

where

$$\mathbb{L}_i(q)\bullet = D_0 \partial_u^2 \bullet + \partial_u(\beta(U_i - fu)\bullet) + 2q\partial_u \bullet + q\beta(U_i' - f)\bullet + q^2 \bullet \tag{5.16}$$

The diagonal matrix $Q = \mathrm{diag}(\mathrm{e}^{-\beta U_1}, \mathrm{e}^{-\beta U_2})$ verifies

$$Q^{-1}\mathbb{W}(\lambda, q)Q = \mathbb{W}^{\dagger}(E - \lambda, f - q) \tag{5.17}$$

which leads to the Gallavotti-Cohen symmetry for the largest eigenvalue of $\mathbb{W}$.

5.2.4 With a fluctuating force

We now consider a periodic sawtooth potential with period λ as shown in Fig. 5.5 which we subject, in addition to a force $F(t)$ that has zero ensemble average (if it is fluctuating) or zero time-average (if it is deterministic). It is useful to begin with a constant F only to get back to a time-varying F afterwards, which is fine as long as F varies slowly enough.

When F is a constant, the Fokker-Planck equation $\partial_t p = \partial_x((V' - F)p) + T\partial_x^2 p$, and the current $j = -T\partial_x p + Fp - V'p$ allows us to find that

$$p(x) = p(0)\mathrm{e}^{\beta(Fx - V(x))} - \beta j \int_0^x \mathrm{d}y \mathrm{e}^{-\beta(Fx - V'(x))}\mathrm{e}^{\beta(V(y) - Fy)} \tag{5.18}$$

On the $[0, \lambda_1]$ segment we have $V(0) = 0$, $V(\lambda_1) = Q$ and thus $V(x) = \frac{Qx}{\lambda_1}$ while on the $[\lambda_1, \lambda]$ segment we have $V(x) = \frac{\lambda - x}{\lambda_2} Q$. We have so far two unknowns, $p(0$ and j. One is fixed using that $p(0) = p(\lambda)$ and the other one by imposing $\int_0^\lambda p(x) = 1$. Let's exploit periodicity,

$$p(0) = p(0)\mathrm{e}^{\beta F\lambda} - \beta j \mathrm{e}^{\beta F\lambda} \int_0^\lambda \mathrm{d}y \mathrm{e}^{\beta(V(y) - Fy)} \tag{5.19}$$

and we plit the y integral into two pieces,

$$\begin{aligned} \int_0^\lambda \mathrm{d}y \mathrm{e}^{\beta(V(y) - Fy)} &= \int_0^{\lambda_1} \mathrm{d}y \mathrm{e}^{\beta(Q/\lambda_1 - F)y} + \int_{\lambda_1}^{\lambda} \mathrm{d}y \mathrm{e}^{\beta(\lambda Q/\lambda_2 - \beta(F + + Q/\lambda_2)y)} \\ &= \frac{\mathrm{e}^{\beta(Q/\lambda_1 - F)\lambda_1} - 1}{\beta(Q/\lambda_1 - F)} + \mathrm{e}^{\beta\lambda Q/\lambda_2} \frac{\mathrm{e}^{-\beta(F + Q/\lambda_2)\lambda_1)} - \mathrm{e}^{-\beta(F + Q/\lambda_2)\lambda}}{\beta(F + Q/\lambda_2)} \end{aligned} \tag{5.20}$$

Simplifying further the condition $p(0) = p(\lambda)$ then leads to

$$p(0)(1 - \mathrm{e}^{\beta F\lambda}) = -j \left[\lambda_1 \frac{\mathrm{e}^{\beta(Q + \lambda_2 F)} - \mathrm{e}^{\beta\lambda F}}{Q - \lambda_1 F} - \lambda_2 \frac{1 - \mathrm{e}^{\beta\lambda_2 F + \lambda Q}}{Q + \lambda_2 F} \right] \tag{5.21}$$

and thus the connection between j and $p(0)$ is given by

$$j(F) = p(0) \frac{2\sinh(\beta\lambda F/2)}{\frac{\lambda_1}{Q - \lambda_1 F}\left(\mathrm{e}^{\beta(Q - \Delta F/2)} - \mathrm{e}^{\beta\lambda F/2}\right) + \frac{\lambda_2}{Q + \lambda_2 F}\left(\mathrm{e}^{\beta(Q - \Delta F/2)} - \mathrm{e}^{-\beta\lambda F/2}\right)} \tag{5.22}$$

where $\Delta = \lambda_1 - \lambda_2$.

At this stage we can get back to our original question by allowing from slow variations of F (think of $F(t)$ being a square periodic signal between $-F$ and $+F$), and by slow we mean that the typical period T of F should be much larger than the relaxation time τ of the process. If T is large enough, the steady state we have just worked out has time to be established. When the particle feels a change from F to $-F$, it will take at typical time τ for it to reach it new

steady-state with the value $-F$. We take T large enough so that $T \gg \tau$. If this is the case then the time-averaged current,

$$\bar{j} = \frac{1}{T}\int_0^T \mathrm{d}t j(t) \simeq \frac{1}{2}(j(F) + j(-F)) \tag{5.23}$$

And the question now boils down to whether $\bar{j}$ is actually nonzero.

When the sawtooth potential is symmetric, $\Delta = 0$ and $j(F)$ is an odd function of F as can be seen from Eq. (5.22),

$$j(F) = p(0)\frac{2\sinh(\beta\lambda F/2)}{\frac{\lambda/2}{Q-\lambda F/2}\left(\mathrm{e}^{\beta Q} - \mathrm{e}^{\beta\lambda F/2}\right) + \frac{\lambda/2}{Q+\lambda F/2}\left(\mathrm{e}^{\beta Q} - \mathrm{e}^{-\beta\lambda F/2}\right)} \tag{5.24}$$

where the numerator is odd in F while the denominator is even in F. If the potential is symmetric we have $\bar{j} = 0$. However, when $\Delta \neq 0$, this is not the case anymore. Of course we still have a missing ingredient, namely $p(0)$. Implementing the normalization condition leads to

$$j(F) = \frac{P_2^2 \sinh(\beta\lambda F/2)}{(\lambda/Q)^2\beta^{-1}\left(\cosh\beta(Q - \Delta F/2) - \cosh(\beta\lambda F/2)\right) - \frac{\lambda}{Q}P_1 P_2 \sinh(\beta F\lambda/2)} \tag{5.25}$$

where the notations are those of [70]:

$$P_1 = \Delta + \frac{\lambda^2 - \Delta^2}{4}\frac{F}{Q},\quad P_2 = \left(1 - \frac{\Delta F}{2Q}\right)^2 - \left(\frac{\lambda F}{2Q}\right)^2 \tag{5.26}$$

The full blown expression is not a prerequisite to witness interesting physics. Already at small F, where

$$j(F) \simeq \frac{\beta\lambda F p(0)}{\frac{\lambda_1}{Q}(\mathrm{e}^{\beta Q - 1}) + \frac{\lambda_2}{Q}(\mathrm{e}^{\beta Q} - 1)} \tag{5.27}$$

and where $p(0, F) = p(0, F = 0) + O(F)$ we see that j is nonzero!

Of course, we can do better and work at finite force by trying to find out about how asymmetry is important. This suggests to expand our formulas at small Δ. As a function of Δ we expect $p(0)$ to be even and thus $p(0, \Delta) = p(0, 0) + \frac{\Delta^2}{2}\partial_\Delta^2 p(0, 0) + \ldots$. We have to work on the denominator in Eq. (5.22),

$$\frac{\lambda_1}{Q - \lambda_1 F}\left(\mathrm{e}^{\beta(Q - \Delta F/2)} - \mathrm{e}^{\beta\lambda F/2}\right) + \frac{\lambda_2}{Q + \lambda_2 F}\left(\mathrm{e}^{\beta(Q - \Delta F/2)} - \mathrm{e}^{-\beta\lambda F/2}\right) = \text{value at } \Delta = 0 + \Delta \times \text{Cst} \tag{5.28}$$

but since the value at $\Delta = 0$ is given by

$$\frac{\lambda/2}{Q - \lambda_1 F}\left(\mathrm{e}^{\beta Q} - \mathrm{e}^{\beta\lambda F/2}\right) + \frac{\lambda/2}{Q + \lambda F/2}\left(\mathrm{e}^{\beta Q} - \mathrm{e}^{-\beta\lambda F/2}\right) \tag{5.29}$$

which, as we have already argued, is even in F, the leading term does not contribute and we find that $j \propto \Delta$.

M2 PCS 2023-2024

Nonequilibrium and Active Systems

First Semester F. van Wijland

Chapter 6

Molecular motors

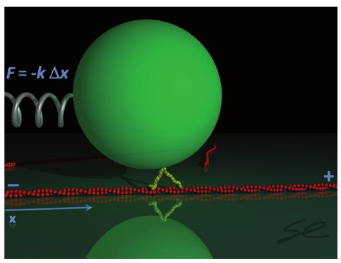
6.1 An introduction

6.1.1 Molecular machines

Motor proteins convert chemical energy into mechanical work that is then used to carry cellular material or to move. In practice, the chemical reaction

$$\mathrm{ATP} + \mathrm{H_2O} \longrightarrow \mathrm{ADP} + \mathrm{P} + \text{energy} \tag{6.1}$$

produces an energy of 30 kJ/mol (0.3 eV), about twenty times as high as the surrounding thermal excitation energy. Among the known motor proteins, we name but a few: dyneins or kinesins that move along microtubules as if along a railway track, or myosin that moves along actin filaments. Their role is to carry a load (some proteins, nucleic acids). Let's take a closer look at myosin as shown in figure 6.1. Actin filaments are long helicoidal assemblies of asymmetric monomers, which thereby possess a preferred direction. Myosin (in fact, V-myosin) is made of two interwined identical subunits. Each of the latter has a motor head by which it attaches to and pulls on the actin filament in much the same way as a rope climber would do, an arm and the tail which acts as a crook for the cargo. The idea of using a cargo to study



2. **La myosine V** (en jaune) **se déplace le long d'un filament d'actine** (en rouge) **et tire un cargo artificiel, une microbille de polystyrène** (verte). Les pinces optiques agissent comme un ressort, exercent une force sur la bille de polystyrène. De cette manière, elles opposent une force contrôlée à l'avancement du moteur.

Figure 6.1: The yellow myosin moves along a red actin filament while carrying an artificial cargo embodied by a green polystyrene bead. Optical tweezers act as a spring upon the bead. They oppose the motion of the motor.

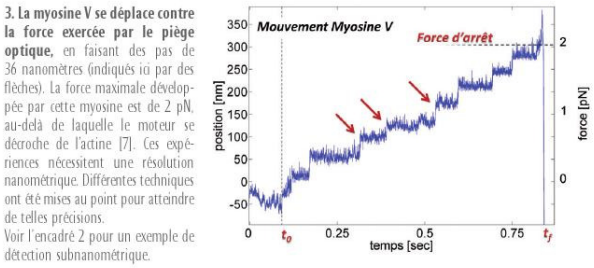


Figure 6.2: The largest force exerted by myosin is 2 pN. Beyond that threshold, the motor detaches from the actin filament. The unit step is 36 nm as myosin works against the force exerted by the optical trap.

the individual motion of a molecular motor dates back to 1983 [97], that of manipulating the bead with optical tweezers to 1990 [9]. In figure 6.2 the position of a bead attached to a myosin motor as a function of time is shown in blue. Thermal activation first has the bead fluctuate within the optical trap, and then at t_0 it connects to the actin filaments and starts moving forward. While pulled by myosin, the bead gradually escapes the trap. The curve in figure 6.2 tells us about its velocity (400 nm/s, a few tens of the motor size per second). One also realizes that the bead has a sawtooth like motion: it has rapid $\ell = 36$ nm steps followed by long pauses. The 36 nm correspond to the actin filament helix step. The pause is necessary for the chemical hydrolysis cycle to be completed and for a new ATP molecule to be loaded. In spite of the spring force increasing as the motor advances, the pace remains unchanged up to the threshold force $F = 2$ pN. A rough estimate of the work provided by the motor is thus $W \simeq F\ell = 72$ pN.nm to be compared with the energy released by breaking an ATP molecule, roughly $\Delta G_{\rm ATP} = 80$ pN.nm. The chemical energy is thus converted into mechanical energy at a yield of the order of $W/\Delta G_{\rm ATP} = 90\%$.

A significant part of the eukaryotic cellular traffic relies on motor proteins that move along filaments similar in function to railway tracks or freeways (kinesins and dyneins move along tubulin filaments; myosins move along actin filaments). The filaments are periodic (of period 10 nm) and have a fairly rigid structure; they are also polar: a given motor always moves in the same direction. These molecular motors appear in a variety of biological contexts: muscular contraction, cell division, cellular traffic, material transport along the axons of nerve cells... A biological cell forms a crowded environment in which molecular motors work together and with other proteins. In these conditions, collective effects arise due to the presence of a large number of molecular motors. These collective effects have in some cases similarities with traffic problems. We now examine one such practical example in a biological framework. Details on myosin can be explored in Cappello's presentation [15] or in the review [103].

6.2 Model and dynamics

6.2.1 A discussion of a two state model

We consider Brownian dynamics in each state and we introduce two rates ω_1 and ω_2 at which the motor hops from state 1 to state 2, and from state 2 to state 1, respectively. In each state the particle executes a Brownian motion. Denoting by $p_i(x,t)$ the probability density to find the motor in state i at position x, we have

$$\partial_t p_1 = D_1 \partial_x^2 p_1 + \omega_2 p_2 - \omega_1 p_1, \; \partial_t p_2 = D_2 \partial_x^2 p_2 + \omega_1 p_1 - \omega_2 p_2 \tag{6.2}$$

Let's begin the analysis in the absence of any motion. In the steady state $\omega_1 p_1 = \omega_2 p_2$. If we think of ω_1 or ω_2 as being the result of some thermally activated process, then we should have

$$\omega_i(x) = \omega(x) \mathrm{e}^{\beta V_i(x)} \tag{6.3}$$

and in the steady-state we will have $p_i(x) = \frac{1}{Z_i} \mathrm{e}^{-\beta V_i(x)}$. But the hop from state 1 to state 2 (and *vice versa*) can be chemically activated due to the hydrolysis of ATP, $\underbrace{\mathrm{ATP}}_{1} \Longleftrightarrow \underbrace{\mathrm{ADP} + \mathrm{P}}_{2}$, and then the rates should incorporate this chemical activity:

$$\omega_1 = \omega(x) \mathrm{e}^{\beta V_1(x)} \mathrm{e}^{\beta \Delta \mu_{\mathrm{ATP}}} \tag{6.4}$$

and

$$\omega_2 = \omega(x) \mathrm{e}^{\beta V_2(x)} \mathrm{e}^{\beta \Delta \mu_{\mathrm{ADP}} + \Delta \mu_{\mathrm{P}}} \tag{6.5}$$

where $\Delta\mu = \mu - \mu_{\mathrm{eq}}$ for each chemical species, and $\mu = \mu_{\mathrm{standard}} + \ln(\text{concentration})$ for a dilute species. If there is an excess of ATP this will favor the hydrolysis of ATP, but an excess of ADP or P will actually favor the opposite reaction. If there is no equilibrium, that is if $\beta \Delta \mu_{\mathrm{ATP}} \neq \Delta \mu_{\mathrm{ADP}} + \Delta \mu_{\mathrm{P}}$, then the resulting steady-state is out of equilibrium.

Of course, as time goes by, the various concentrations will eventually equilibrate and the system will as a whole relax to equilibrium (unless one keeps eating). However, being out of equilibrium does not warrant the existence of a spatial current.

6.2.2 A simple example

We refer interested readers to the review [55]. We take the limiting case in which $V_2 = 0$ and ω_1 and ω_2 are constant, while $V_1(x)$ is periodic with a spatial period p, with a sawtooth profile. The corresponding master equations read

$$\partial_t p_1 = \partial_x \left[T \partial_x p_1 + V_1'(x) p_1 \right] + \omega_2 p_2 - \omega_1 p_1 \tag{6.6}$$

and

$$\partial_t p_2 = T \partial_x^2 p_2 + \omega_1 p_1 - \omega_2 p_2 \tag{6.7}$$

with $p_{\mathrm{tot}} = p_1 + p_2$ evolving as

$$\partial_t p_{\mathrm{tot}} = T \partial_x^2 p_{\mathrm{tot}} + \partial_x (V_1' p_1) \tag{6.8}$$

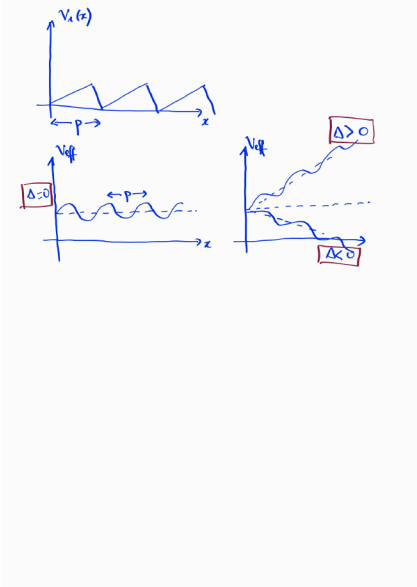


Figure 6.3: General trend of $V_{\rm eff}$ depending on the sign of Δ.

which, introducing what is, for now, a mere notation, namely $V'_{\rm eff} = V'_1\lambda$ and $\lambda = p_1/p_{\rm tot}$, becomes

$$\partial_t p_{\rm tot} = T\partial_x^2 p_{\rm tot} + \partial_x(V'_{\rm eff}p_{\rm tot}) \tag{6.9}$$

This describes a standard overdamped Langevin dynamics in an effective potential $V_{\rm eff}(x) = V_{\rm eff}(0) + \int_0^x {\rm d}y\lambda(y)\,V'_1(y)$. We shall use the notation $\Delta = \int_0^p {\rm d}y\lambda(y)\,V'_1(y)$. Since V_1 and V_2 are periodic, so p_1 and p_2 are, and thus λ is as well. If $\Delta = 0$ then we expect $V_{\rm eff}$ to be flat, while for $\Delta \neq 0$, we expect $V_{\rm eff}$ to have a nonzero slope (with the same sign as that of Δ, as shown in Fig. 6.3. When $\Delta \neq 0$ we thus expect a steady flux. The condition $\Delta = 0$ for the absence of such a flux is achieved if $V_1(x) = V_1(-x)$, because then both p_1 and p_2 are even and thus $\lambda(x) = \lambda(-x)$ which means that $\lambda(x)\,V'_1(x)$ is odd, and thus $\Delta = 0$. Otherwise, the generic situation is $\Delta \neq 0$ and there is some net current.

The emergence of the net current can be viewed as the competition between two equilibrium processes. One of them is governed by the two equations

$$\partial_t p_1 = T\partial_x^2 p_1 + \partial_x(V'_1 p_1),\ \partial_t p_2 = T\partial_x^2 p_2 \tag{6.10}$$

with equilibrium solution $p_1 \sim {\rm e}^{-V_1/T}$ and p_2 uniform. The other one is the chemical equilibrium, governed by the equations

$$\partial_t p_1 = -\partial_t p_2 = \omega_2 p_2 - \omega_1 p_1 \tag{6.11}$$

with equilibrium solution $p_1 = \omega_2/(\omega_1+\omega_2)$ and $p_2 = \omega_1/(\omega_1+\omega_2)$.

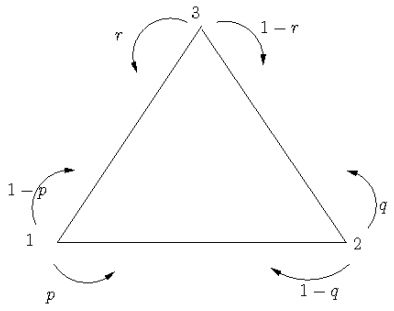


Figure 6.4: A simple three state molecular motor introduced by Lee, Allisson, Abbott and Stanley.

6.2.3 A three state model

We now present a simple three state model taken from [64] in discrete time, whose states $i = 1$, 2, and 3 are related by the transition probabilities shown in figure 6.4: The authors christened their model a minimal Brownian ratchet. The transition matrix $\mathbb{M}$ governing the evolution of the probability $P_i(t)$ that the system is in state i, $\partial_t P = \mathbb{M}P$ is contained in figure 6.4. It is not hard to search for the eigenvector with eigenvalue 1 (which describes the stationary state), and it reads

$$\begin{pmatrix} P_{\mathrm{st},1} \\ P_{\mathrm{st},2} \\ P_{\mathrm{st},3} \end{pmatrix} = \begin{pmatrix} \frac{q(r-1)+1}{D} \\ \frac{(p-1)r+1}{D} \\ \frac{p(q-1)+1}{D} \end{pmatrix} \tag{6.12}$$

where the notation $D = p(q-1) + q(r-1) + (p-1)r + 3$ was used. The stationary current flowing between states 1 and 2 is $J_{1\to 2} = P_{\mathrm{st},1}M_{1,2} - P_{\mathrm{st},2}M_{2,1} = \frac{pqr-(1-p)(1-q)(1-r)}{D}$. The nonzero current is interpreted as a reflection of the fact that teh system is subjected to an external driving force. The special parameter subspace in which $pqr = (1-p)(1-q)(1-r)$ is current free.

We now apply a zero average random perturbation defined by the following rule. With probability $1-\gamma$ the transition probabilities are those shown in figure 6.4, and with probability γ the system hops to any of the other two states (with probabilities 1/2 for each). The new transition probabilities matrix $\mathbb{M}(\gamma)$ reads

$$\mathbb{M}(\gamma) = \begin{pmatrix} 0 & (1-\gamma)(1-q) + \frac{1}{2}\gamma & (1-\gamma)r + \frac{1}{2}\gamma \\ (1-\gamma)p + \frac{1}{2}\gamma & 0 & (1-\gamma)(1-r) + \frac{1}{2}r \\ (1-\gamma)(1-p) + \frac{1}{2}\gamma & (1-\gamma)q + \frac{1}{2}\gamma & 0 \end{pmatrix} \tag{6.13}$$

The new steady state is given by

$$\begin{pmatrix} P_{\mathrm{st},1} \\ P_{\mathrm{st},2} \\ P_{\mathrm{st},3} \end{pmatrix} = \begin{pmatrix} \frac{(1-2r)\gamma^2+2(r-1)\gamma+2q(2r(\gamma-1)-\gamma+2)(\gamma-1)+4}{D(\gamma)} \\ \frac{(1-2p)\gamma^2+2(p-1)\gamma+2r(2p(\gamma-1)-\gamma+2)(\gamma-1)+4}{D(\gamma)} \\ \frac{(1-2q)\gamma^2+2(q-1)\gamma+2p(2q(\gamma-1)-\gamma+2)(\gamma-1)+4}{D(\gamma)} \end{pmatrix} \tag{6.14}$$

with

$$D(\gamma) = -4r(1-\gamma)^2 + 4q(r-1)(\gamma-1)^2 + 4p(q+r-1)(\gamma-1)^2 + 3(\gamma-1)^2 + 9 \tag{6.15}$$

which now leads to the following current

$$J(\gamma) = -\frac{(\gamma-1)\left(-(\gamma-1)^2 + 2r\gamma^2 + 2p\left(-2r(\gamma-1)^2 + 2q(2r-1)(\gamma-1)^2 + (\gamma-1)^2 + 1\right) + 2q\left(1-2r(\gamma-\right.\right.}{-4r(1-\gamma)^2 + 4q(r-1)(\gamma-1)^2 + 4p(q+r-1)(\gamma-1)^2 + 3(\gamma-1)^2 + 9} \tag{6.16}$$

In the limit for which $J(0)$ is small ($pqr \to (1-p)(1-q)(1-r)$) and for γ small of order $J(0)$, we find that

$$J(\gamma) = J(0) + \frac{\gamma}{2D(0)}(p+q+r-(1-p)-(1-q)-(1-r)) \tag{6.17}$$

It is remarkable that even if $J(0) = 0$, due to the random perturbation, a nonzero current survives. If $J(0) \neq 0$ the current is of course modified by the perturbation, but an appropriate choice of the parameters may lead to $J(\gamma)$ having a sign opposite to that of $J(0)$.

6.3 Collective behaviors of molecular motors

6.3.1 Some ideas about modeling

In practice, dealing with N motors is the same as dealing with N ratchets, that possibly interact with each other, which is of course very complicated. By coarse-graining the many microstates that encode the microscopic state of a single motor bound to a given site into one mesoscopic state (mesoscopic refers to the effective state of the motor, such bound *vs.* unbound), we may have some hope to describe how many motors interact with each other. The dynamics is then described in terms of a master equation for the probability to observe the coellection of motors in a given configuration of effective states. This is going to work on condition that the local time scales related to the fluctuations of one motor are short enough with respect to whatever time scale related to collective behavior we are interested in.

It is interesting that one of the most iconic models of nonequilibrium statistical mechanics, as een from the most mathematical side, was actually coined back in the sixties in a effort to model the motioin of ribosomes along DNA strands [66]. It has, since then, been used for the modeling of traffic, both at the biophysical level, for intracellular traffic (the crawling of dynein or kinesin along microtubules[3]) and at the macroscopic level (in terms if cars on a highway [6], or of crowds [52]). An excellent review covering much more of the interdiscplinary applications of statistical physics is [20]. The model is particularly simple to describe: particles on a one-dimensional lattice hop right or left with rates p or q, without the possibility of hopping of the target site is already occupied.

If one motor is subjected to an external force F, say for a sawtooth potential with period ℓ, rising over $\ell\delta$ up to ΔE and decreasing over $\ell(1-\delta)$, the probability of a rightward move is $p \propto \mathrm{e}^{-\beta\Delta E}$, and it becomes $p_1 \propto \mathrm{e}^{-\beta(\Delta E - F\delta\ell)}$, or $p_1 = p\mathrm{e}^{\beta F\delta\ell}$, while $q_1 \propto \mathrm{e}^{-\beta(\Delta E + F(1-\delta)\ell)} = q\mathrm{e}^{-(1-\delta)F\ell}$. The stall force F is such that the average velocity $p_1 - q_1$ vanishes, which occurs for $f = \beta F\ell = -\ln\frac{p}{q}$.

6.3.2 The Asymmetric Simple Exclusion Process (ASEP)

Let's now examine what is hapenning when more than one motor is present. We assume short-ranged repulsive interactions. Say that one is loaded and is to the right of the other one which is not, so the hopping rates are q, p and q_1, p_1. The probability $P_d(k)$ that the distance between the motors is k evolves according to

$$\partial_t P_d(k) = (p_1 + q)P_d(k-1) + (q_1 + p)P_d(k+1) - (p_1 + q_1 + p + q)P_d(k) \tag{6.18}$$

But that's only when the two particles are sufficiently far away from each other. If they are separated by a single lattice spacing, the leftward hop of the left particle is u and the rightward hop of the right particle is $v_1 = ve^{\beta\delta\ell F}$. With repsulive interactions we should have $u > q$ and $v_1 > p_1$. This means that for $k = 1$ or $k = 2$ this interaction plays some role:

$$\partial_t P_d(1) = (q_1 + p)P_d(2) - (u + v_1)P_d(1) \tag{6.19}$$

and

$$\partial_t P_d(2) = (u + v_1)P_d(1) + (q_1 + p)P_d(3) - (p + q + p_1 + q_1)P_d(2) \tag{6.20}$$

Solving for the steady-state leads to $P_d(2) = \frac{u+v_1}{p+q_1}P_d(1)$, or, with $r_1 = \frac{u+v_1}{p+q_1}$, $P_d(2) = r_1 P_d(1)$, while $P_d(3) = rP_d(2)$, with $r = \frac{p_1+q}{p+q_1}$, and thus, recursively, we get $P_d(k \geq 2) = r^{k-2}r_1 P_d(1)$. Using normalization we eventually arrive at

$$P_d(k \geq 2) = \frac{r_1(1-r)}{1-r+r_1}r^{k-2} \tag{6.21}$$

There is obviously no steady state unless $r < 1$, and then $P_d(k)$ decreases exponentially fast over a typical length $\xi \sim -1/\ln r$. The mean distsance etween motors is finite, they go at the same speed. The stall force necessary to stop two motors is bigger than the one need for a single motor, because the second motor prevents the leading one from stepping leftward. This can be seen analytically. the mean velocity of the rightmost motor is $P_d(1)v_1 + (1 - P_d(1))(p_1 - q_1)$ which vanishes for a force $-\beta\ell F = \ln\left[\frac{p}{q} + \frac{v}{u}\left(\frac{p}{q} - 1\right)\right]$. Interestingly the second motor always increases the stall force but not always the velocity.

Chapter 7

Active Particles

7.1 Models of a single active particle

7.1.1 Running

Focus on an E Coli (Escherichia coli) bacterium, made of a head an equipped with anywhere between 5 and 10 flagella [93] (depending on strain). It owes its name to its favorite location (the colon). The head itsefl is roughly 2 μm long and between 0.25 and 1 μm in diameter. The cell is overall rod-shaped with a very marked anisotropy. Each flagellum (see Fig .7.1) is at-

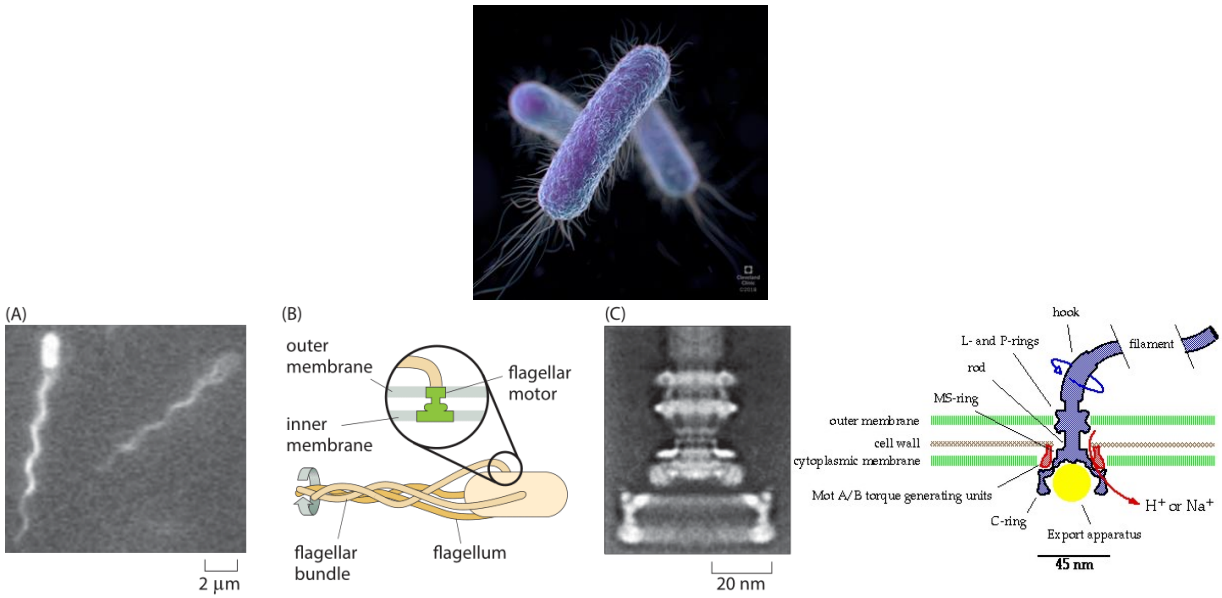


Figure 7.1: E. Coli in its full glory.

tached to the cytoplasm via a proton powered motor (a proton pump driven by an electrostatic potential across the membrane bilayer).

Of course, an important subset of cells involved in reproduction, namely sperm, works according to similar mechanims (see[53, 40, 68]): since the flagellum is made of microtubules (in an aligned bundle called the anoxem), the motors at work are dyneins.

When it comes to orders of magnitude for such an object swimming in water we can start from the Navier-stokes equation:

$$\rho \underbrace{\partial_t \mathbf{v} + \rho(\mathbf{v}\cdot\partial_{\mathbf{r}})\mathbf{v}}_{\sim v^2/L} = \underbrace{\eta\partial_{\mathbf{r}}^2\mathbf{v}}_{} \sim \eta v L^{-2} - \partial_{\mathbf{r}} P + \rho\mathbf{f} \tag{7.1}$$

where $\mathbf{f}$ are some volumic forces acting on the fluid. The typical length $L \sim 10^{-6}$ m, the typical velocity is 10^{-5} m/s and $\eta = 10^{-3}$ Pa.s. The number that compares inertial forces to viscous forces is the Reynolds number

$$\mathrm{Re} = \frac{\rho v^2 L^{-1}}{\eta v L^{-2}} = \frac{\text{density} \times \text{velocity} \times \text{length}}{\text{viscosity}} \sim \frac{10^3 \times 10^{-5} \times 10^{-6}}{10^{-3}} \sim 10^{-5} \tag{7.2}$$

When a human being swims in water the corresponding Reynolds number is

$$\mathrm{Re} = \frac{\text{density} \times \text{velocity} \times \text{length}}{\text{viscosity}} \sim \frac{10^3 \times 1 \times 1}{10^{-3}} \sim 10^6 \tag{7.3}$$

That's eleven orders of magnitude larger! This back-of-the-envelope calculation simply shows that inertial effects are way more important for us than they are for a bacterium. If the bacterium swam in honey ($\eta_{\text{honey}} \sim 10^7$ Pa.s) then we would have comparable physics. But as Purcell said [88], life occurs at low Reynolds. This tells us that the flow around a bacterium

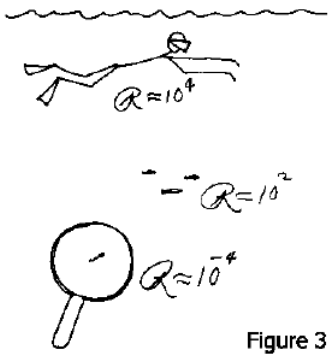


Figure 7.2: Taken from [88].

results from the instantaneous balance of the viscous force with pressure, $\eta\partial_{\mathbf{r}}^2 v - \partial_{\mathbf{r}} P = \mathbf{0}$ (in the absence of external volumic forces on the fluid). This is perfectly reversible, there is no arrow of time. Indeed, in hydrodynamics, the so-called scallop theorem (see [54] for a recent proof) states that a swimmer that exhibits time-symmetric motion cannot achieve net displacement in a low-Reynolds number fluid. By definition such a swimmer deforms its body into a

particular shape through a sequence of motions and then reverts to the original shape by going through the sequence in reverse. This is known as reciprocal motion and is invariant under time-reversal. Purcell christened the theorem after the motion of a scallop which opens and

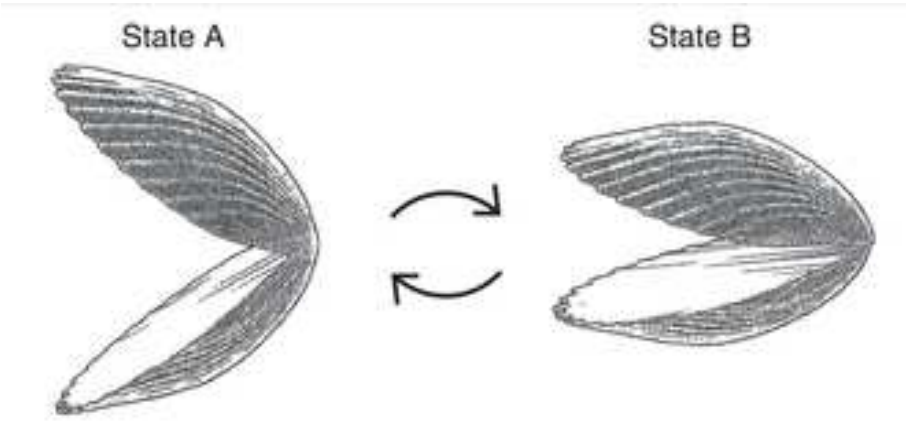


Figure 7.3: Taken from [88]. The scallop exactly retraces its trajectory and it's back where it started.

closes a simple hinge during one period without creating any net motion.

There are some hypotheses under which the scallop theorem holds (a single degree of freedom, recirprocal motion) which are of course violated by bacteria. For instance, in order to swim, they can rotate a helix which is a chiral object leading to non-reciprocal forces and then the bacteria run in straight lines. But running in straight lines is not what is observed...

7.1.2 Tumbling

What is observed in a movie tracking a single E. coli bacterium is that it runs for a typical time of 1 s and then over a time of the order of 0.1 s it changes its course–this is the tumbling step—and runs again in a straight line. The mechanism behind these tumbling events is a chemical stimulus that affects the direction of flagellar rotation and thereby modulates the swimming of the bacteria. It was identified back in 1974 [63]. Let's paraphrase [5] (these authors were ultimately interested in chemotaxis). The default direction of rotation of the flagellar motor is counterclockwise (CCW). Rotation in the other direction, clockwise (CW), is achieved by interaction of the cytoplasmic chemotaxis protein, CheY, with the switch at the base of the flagellar motor. The interaction of CheY with the switch is direct, without any mediators. Since the number of CheY molecules per cell is orders of magnitude higher than the presumed number of switch molecules, it was suggested that CheY exists in two states, active and nonactive, and that there should be a mechanism which regulates the transition between these states in response to chemotactic stimuli. A phosphorylated CheY (CheY-P) binds to the motor and changes its rotation from CCW to CW, and then Chy-P unbinds (CheZ steals the P) which causes CCW rotation a new straight run.

In terms of typical appearance, things look like in Fig .??. In one space dimension the plot

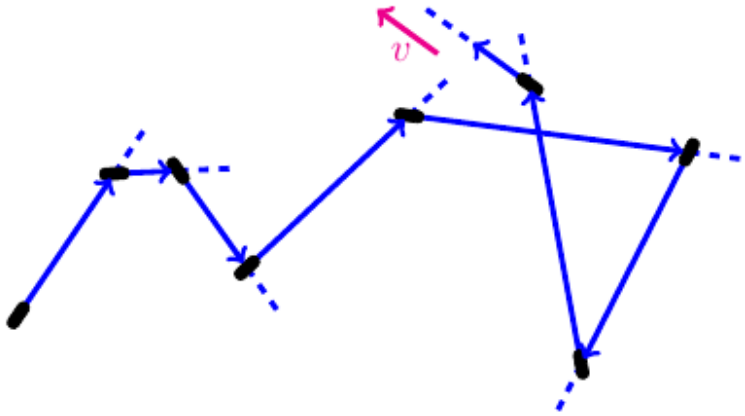


Figure 7.4: Taken from [17]. A typical run-and-tumble trajectory in two space dimensions.

of the trajectory is of course less spectacular: it looks like a random sawtooth landscape in the (t, x) plane.

The task that lies ahead of us to come up with some simple enough modeling that allows to describe such complex objects as bacteria, without disposing too much of any interesting physics.

7.1.3 Run-and-Tumble Particle

Let's begin with one space dimension. Because the dynamics is at low Reynolds, we write a balance equation

$$0 = -\dot{x} + \mu f_{\text{activ}} + \sqrt{2\mu T}\eta \tag{7.4}$$

but the order of magnitude of the typical velocity $v_0 \sim \mu f_{\text{act}}$ is much larger than the thermal energy scale. Indeed, $D = \mu T$ is the diffusion constant for a free particle, and thus $\sqrt{D\tau}$ is the diffusion length, t be compared with the run length $ell \sim v_0\tau$, where τ is the typical duration of a straight run. A rough estimate tells us that

$$D\tau \sim \frac{T}{\gamma}\tau \sim \frac{1.2\,10^{-23} \times 300 \times 1}{6\pi 10^{-3} \times 10^{-6}} \sim 10^{-13} \tag{7.5}$$

hence $\sqrt{D\tau} < .5\,\mu$s, while $\ell \sim v_0\tau \sim 10^{-5}$ m. This tells us that we can probably neglect thermal noise. We write the active force as a self-propulsion velocity, $\mu f_{\text{act}} = v_0 u$, where $u(t)$ is a random variable with unit modulus. The rate at which it flips from u to $-u$ is $\frac{1}{2\tau}$, which can be encoded in the following master equation for the probability to find the particle at x with orientation u:

$$\partial_t p(x, u, t) = -v_0 u \partial_x p + \frac{1}{2\tau} p(x, -u, t) - \frac{1}{2\tau} p(x, u, t) \tag{7.6}$$

The orientation u decorrelates from a fixed initial value u_0 exponential fast, as one can see that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle u\rangle = -2 \times \frac{1}{2\tau}\langle u\rangle \tag{7.7}$$

so that $\langle u(t)\rangle = u_0 \mathrm{e}^{-t/\tau}$. This is built into the model.

In higher space dimension $d > 1$ one writes instead

$$\dot{\mathbf{r}} = v_0 \mathbf{u} \tag{7.8}$$

where $\mathbf{u}(t)$ is a unit vector the tip of which hops randomly and uniformly from one position to another at the surface of the unit sphere of $\mathbb{R}^d$ (with area $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$, $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$). The master equation reads

$$\partial_t p(\mathbf{r}, \mathbf{y}, t) = -v_0 \mathbf{u} \cdot \partial_{\mathbf{r}} p + \frac{1}{\tau}\frac{1}{\Omega_d}\int \mathrm{d}^{d-1} u' p(\mathbf{r}, \mathbf{u}', t) - \frac{1}{\tau} p(\mathbf{r}, \mathbf{u}, t) \tag{7.9}$$

where $\int \mathrm{d}^{d-1} u'$ refers to an integral over the solild angle in which $\mathbf{u}'$ points. For instance, when dealing with a two-dimension motion, $\mathbf{u} = \cos\theta \mathbf{e}_x + \sin\theta \mathbf{e}_y$ and the master equation reads

$$\partial_t p(\mathbf{r}, \theta, t) = -v_0 \cos\theta \partial_x p - v_0 \sin\theta \partial_y + \frac{1}{\tau}\frac{1}{2\pi}\int \mathrm{d}\theta' p(\mathbf{r}, \theta', t) - \frac{1}{\tau} p(\mathbf{r}, \theta, t) \tag{7.10}$$

and again one can show that $\langle \mathbf{u}(t)\rangle = \mathrm{e}^{-t/\tau}\mathbf{u}(0)$.

[110]

7.1.4 Active Brownian Particle

Coat a spherical latex bead with platinum over half of its surface and put it in water peroxyde H_2O_2. In the presence of light, the dossiciation of water peroxyde, $H_2O_2 \to H_2 + \frac{1}{2}O_2$ is strongly catalyzed by platinum. But the surface of the bead being asymmetric, this also means the concentrations of chemicals around the bead are unevenly distributed. The non-uniform concentrations lead to an osmotic pressure gradient which, in turn, induces a hydrodynamic flow. Such a synthetic colloid is called a Janus particle. The physico-chemical reality is more complex, as electrostatic (ionic, Van der Waals, hydrophilic) forces also play a role, and there is no easy-to-phrase argument leading to a credible prediction on the direction in which these Janus particles self-propel (with respect to their symmetry plane). The experimental reality is that they indeed self-propel. Data retrieved from [83, 84] show that their typical velocity is $v_0 \simeq 1$ to $3\,\mu$m/s. Experiments with gold beads (coated with platinum) have also been carried out [102] but because they are much heavier, they sediment and are thus effectively two-dimensional swimmers instead of three-dimensional ones. They are also faster with velocities ranging from 5 to $20\,\mu$m/s.

In terms of modeling, assuming their velocity to be fixed to v_0 (and indeed fluctuations are small), we write again that

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = v_0 \mathbf{u}(t) + \sqrt{2\mu T}\boldsymbol{\xi} \tag{7.11}$$

where $\mathbf{u}(t)$ is a vector with unit norm, and where μ is the mobility and $D_t = \mu T$ is the bare translational diffusion constant, and $\boldsymbol{\xi}$ Gausian white noise with independent components. Instead of abruptly changing direction, experiments show that $\mathbf{u}$ varies continuously and the simplest modeling is to assume that the tip of $\mathbf{u}$ executes a Brownian motion at the surface of a unit sphere (a circle in $d = 2$ or a sphere in $d = 3$, with unit radius). This can be written as

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{1/2}{=} \sqrt{2D_r}\left[(\boldsymbol{\eta}\cdot\mathbf{u})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta}\right] \tag{7.12}$$

where D_r is the rotational diffusion constant governing the statistics of $\mathbf{u}$ and $\boldsymbol{\eta}$ is a Gaussian white noise with independent components. Note that this equation ensures the conservation of $||\mathbf{u}||$. When written in an Itō-discretized form it reads

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} \overset{0}{=} -(d-1)D_r\mathbf{u} + \sqrt{2D_r}\left[(\boldsymbol{\eta}\cdot\mathbf{u})\mathbf{u} - \mathbf{u}^2\boldsymbol{\eta}\right] \tag{7.13}$$

which tells us that $\langle\mathbf{u}(t)\rangle = \mathrm{e}^{-(d-1)D_r t}\mathbf{u}(0)$ when the initial condition $\mathbf{u}(0)$ is given, and thus, upon averaging over the initial condition, we get

$$\langle\mathbf{u}(t)\cdot\mathbf{u}(t')\rangle = \mathrm{e}^{-|t-t'|/\tau},\ \tau^{-1} = (d-1)D_r \tag{7.14}$$

In the presence of an external force field the Fokker-Planck/master equation reads

$$\partial_t P(\mathbf{r},\mathbf{u},t) = -v_0\mathbf{u}\cdot\partial_{\mathbf{r}}P + \mu\partial_{\mathbf{r}}\cdot(\partial_{\mathbf{r}}VP) + \mu T\partial^2_{\mathbf{r}}P + D_r\partial^2_{\mathbf{u}}P \tag{7.15}$$

where $\partial^2_{\mathbf{u}}P$ is the Laplacian on the unit sphere of $\mathbb{R}^d$ (namely the angular part of the Laplacian only).

7.1.5 Active-Ornstein Uhlenbeck particles

Here we allow for the velocity amplitude to fluctuate:

$$\dot{\mathbf{r}} = \mathbf{v},\ \dot{\mathbf{v}} = -\frac{\mathbf{v}}{\tau} + \sqrt{2v_0^2/(d\tau)}\boldsymbol{\eta} \tag{7.16}$$

where $\boldsymbol{\eta}$ is a Gaussian white noise with independent components. Because then

$$\mathbf{v}(t) = \int_{-\infty}^{t}\mathrm{d}t_1\mathrm{e}^{-(t-t_1)/\tau}\sqrt{2v_0^2/(d\tau)}\boldsymbol{\eta}(t_1) \tag{7.17}$$

and thus

$$\langle\mathbf{v}(t)\cdot\mathbf{v}(t')\rangle = \frac{2v_0^2}{d\tau}\int_{-\infty}^{t}\mathrm{d}t_1\int_{-\infty}^{t'}\mathrm{d}t_2\mathrm{e}^{-\frac{t-t_1+t'-t_2}{\tau}}d\delta(t_1-t_2) = v_0^2\mathrm{e}^{-|t-t'|/\tau} \tag{7.18}$$

Adapated to cells. Distribution of $\mathbf{v}$ is $\mathrm{e}^{-\frac{\mathbf{v}^2}{v_0^2/d}}$.

7.2 Simple results on individual particles

7.2.1 Free diffusion

Forget about thermal (translational noise) and focus on $\dot{\mathbf{r}} = v_0\mathbf{u}$ where $\mathbf{u}$ decorrelates exponentially with a time scale τ, $\langle \mathbf{u}(t)\cdot\mathbf{u}(t')\rangle = \mathrm{e}^{-|t-t'|/\tau}$, whichi is a feature common to all three models described above. Then we see that

$$\mathbf{r}(t)-\mathbf{r}(0) = v_0\int_0^t \mathrm{d}t'\mathbf{u}(t') \tag{7.19}$$

and

$$\begin{aligned}\langle(\mathbf{r}(t)-\mathbf{r}(0))^2\rangle =& v_0^2\int_0^t \mathrm{d}t_1\mathrm{d}t_2\langle\mathbf{u}(t_1)\cdot\mathbf{u}(t_2)\rangle\\ =& v_0^2\left[2\tau t + 2\tau^2\left(\mathrm{e}^{-t/\tau}-1\right)\right]\\ =& \begin{cases} v_0^2t^2 \text{ for } t\ll\tau\\ 2v_0^2\tau t \text{ for } t\gg\tau\end{cases}\end{aligned} \tag{7.20}$$

Motion is ballistic at short times but Brownian-like diffusive motion is recovered at times large with respect to the persistence time τ. If we took translational noise into account we would thus observe three regimes: a short time regime controled by thermal Brownian motion that is eventually taken over by a ballistic regime and finally diffusive motion is revovered. Let $\tau_\times$ be such that $v_0^2\tau_\times^2 = 2dD_t\tau_\times$ then $\tau_\times \sim \frac{D_t}{v_0^2}$. That's the time of the thermal-diffusion-to-ballistic crossover.

7.2.2 RTP in one space dimension with a space varying self-propulsion velocity

Consider a one-dimensional RTP with a space-dependent self-propulsion velocity $v(x)$. The master equation reads

$$\partial_t P_\pm = \mp\partial_x(vP_\pm) + \frac{1}{2\tau}(P_\mp - P_\pm) \tag{7.21}$$

Of course the total density $P = P_+ + P_-$ is locally conserved, $\partial_t P = -\partial_x J$ where the local particle current is given by

$$J(x,t) = v(P_+ - P_-) \tag{7.22}$$

This local particle current evolves in time according to

$$\begin{aligned}\partial_t J =& v\left[-\partial_x(vP) + \frac{1}{\tau}(\frac{1}{\tau}(P_- - P_+))\right]\\ =& -v\partial_x(vP)_{\frac{J}{\tau}}\end{aligned} \tag{7.23}$$

This equation can be solved

$$J(x,t) = J(x,0)\mathrm{e}^{-t/\tau} + \int_0^t \mathrm{d}t'\mathrm{e}^{-\frac{t-t'}{\tau}}(-v\partial_x(vP(x,t'))) \tag{7.24}$$

But P is a conserved field that evolves slowly, at least much slower than τ, which allows to approximate

$$J(x,t) \simeq \tau(-v\partial_x(vP(x,t))) \tag{7.25}$$

and thus $\partial_t P = -\partial_x J = \tau\partial_x(v\partial_x(vP))$. As we have discussed before, if $v(x) = v_0$ is uniform, we recover a diffusion equation with a diffusivity τv_0^2. There exists a current-free steady-state in which $P_{\rm ss}(x) \propto \frac{1}{v(x)}$. This tells us that particles accumulate in locations where the particles go slowly.

7.3 A run-and-tumble particle in a potential

7.3.1 In a potential, and the nonlocality of the steady-state distribution

This section is oversized with respect to what was done in class. It is *verbatim* taken from [82] (which also accounts for the extensive referencing).

Consider a system in equilibrium in which a small obstacle is introduced. The corresponding perturbation $\delta V(\mathbf{r})$ leads to a localized perturbation of the Boltzmann weight $P_{\rm eq}(\mathbf{r}) \propto \exp[-\beta(V(\mathbf{r}) + \delta V(\mathbf{r}))]$. In that sense, the perturbation remains local. Furthermore, TRS (*aka* time reversal symmetry) is maintained so that even systems with asymmetric obstacles cannot harbor steady currents. Both features are challenged in active systems, whose fate in the presence of obstacles and external potentials have attracted a lot of interest [2, 7, 4, 16, 19, 23, 28, 30, 35, 50, 51, 58, 59, 60, 71, 79, 80, 95, 100, 105] both for fundamental reasons, in that they probe the relationship between active and passive dynamics, but also for practical ones. External potentials and confinements are indeed the toolbox used to engineer and probe active systems, from optical & acoustic tweezers [101] to centrifuges [89] and arrays of obstacles [41]. In addition to a wealth of experimental works [24, 94, 22, 43, 44, 83], these questions have been addressed at the theoretical level by considering the overdamped dynamics

$$\dot{\mathbf{r}} = \mathbf{v} - \mu\partial_{\mathbf{r}} V(\mathbf{r}) \tag{7.26}$$

where the self-propulsion $\mathbf{v}$ evolves either through tumbles [92, 99, 2], rotational diffusion [95, 105], or as an Ornstein-Uhlenbeck process [98, 37]. In all cases, one can define a persistence time τ, a typical self-propulsion speed v_0, a persistence length $\ell_p = v_0\tau$, and a large-scale diffusivity $D_{\rm eff} \propto \ell_p^2/\tau$. In the limit $\tau \to 0$ keeping $D_{\rm eff}$ constant, the dynamics becomes equivalent to a passive one and leads to a Boltzmann distribution with an effective temperature $T_{\rm eff} \equiv D_{\rm eff}/\mu$. As the persistence time increases, active systems both develop non-Boltzmann features and exhibit TRS violations. We first review below the $\tau = 0$ limit before discussing the nonequilibrium static and dynamic features that develop as τ increases.

The $\tau = 0$ limit and the universal effective equilibrium regime

For AOUPs, the equilibrium behaviour stems from the fact that the Gaussian process $\mathbf{v}$ becomes, as $\tau \to 0$, a white noise: $\langle v_{p,\alpha}(t)v_{p,\beta}(0)\rangle = \delta_{\alpha,\beta}\frac{D}{\tau}\exp(-\frac{|t-t'|}{\tau}) \underset{\tau\to 0}{\longrightarrow} 2D\delta_{\alpha,\beta}\delta(t-t')$. The

dynamics is thus equivalent to a passive one with a temperature $T_{\rm eff} = D/\mu$. The effective equilibrium regime also exists for ABPs and RTPs, despite their non-Gaussian natures. This has been established in any dimension [16, 95] and we detail it here for RTPs in $d = 1$. In the presence of a confining potential $V(x)$, the steady-state distribution is given by [104, 96] :

$$P(x) = \frac{v_0^2 P_0}{v_0^2 - \mu^2 V'(x)^2} \exp\left[-\frac{\mu}{\tau}\int_0^x dx' \frac{V'(x')}{v_0^2 - \mu^2 V'(x')^2}\right] , \tag{7.27}$$

where τ^{-1} is the tumbling rate. Note that Eq. (7.27) exhibits, in general, a non-Boltzmann form: the forces experienced by the particle (that do not stem from the bath) are not proportional to $\nabla \log P$. Next, consider the $\tau \to 0$ limit, keeping $T_{\rm eff} = \frac{v_0^2 \tau}{\mu}$ finite. This implies a large v_0 limit, so that $v_0 \gg \mu V'(x)$ for smooth potentials, which allows one to expand (7.27) into

$$P(x) = P_0 \exp[-V(x)/T_{\rm eff}] . \tag{7.28}$$

Note that, for confining potentials, the condition $v_0 \gg \mu V'(x)$ cannot hold everywhere. To get a feeling for how small τ should be for the approximation to hold, we expand the distribution (7.28) around a minimum x_0 of V. The distribution $P(x)$ is then locally Gaussian, with a typical displacement $\sqrt{T_{\rm eff}/V''(x_0)}$. In turn, the typical force scales as $V'(x_t) \simeq \sqrt{\frac{\tau v_0^2 V''(x_0)}{\mu}}$. The condition $v_0 \gg \mu V'(x)$ then becomes $\mu V''(x_0)\tau \ll 1$: the typical time between two tumbles has to be much shorter than the relaxation time inside the potential well. These criteria generalize to $v_0 \gg \mu|\nabla V|$ and $\mu\tau\Delta V \ll 1$ in higher dimensions [95].

This effective equilibrium regime was demonstrated theoretically for sedimenting RTPs [100], ABPs [30, 109, 95, 60, 105, 51, 35] and AOUPs [98], whose sedimentation profiles have been computed theoretically and lead to Eq. (7.28) in the small τ limit. Experimentally, the effective equilibrium regime has been measured for sedimenting self-propelled diffusiophoretic colloids [83, 44, 43]. For ABPs, RTPs and AOUPs in harmonic traps, the effective equilibrium regimes have also been studied theoretically [100, 98, 101, 71] and measured in experiments [101]. Probing effective equilibrium regimes in more general experimental settings remains an open challenge [47].

Departure from the $\tau = 0$ limit: non-Boltzmann distributions

Non-thermal effects have naturally been the focus of the community and the departure from the $\tau = 0$ limit is particularly relevant from that perspective. Despite a universal $\tau = 0$ regime, different models of self-propelled particles have been shown to lead to different behaviours, both from a static and a dynamic perspective, as soon as $\tau \neq 0$. General expressions for arbitrary potentials have been obtained for a single RTP in one dimension to any order in τ, see Eq. (7.27). For AOUPs, many different approaches have been developed. Some are based on calculating the steady-state directly using either path integrals [11, 77, 108] or perturbative approaches [57, 37, 10, 74, 73]. Others rely on effective equilibrium approximations of the dynamics [38, 39, 56, 14, 69, 106, 107, 32, 72]. As a result, the steady-state distribution for N interacting AOUPs has been obtained to order τ in any dimension [69, 37, 10, 74]. For a

single AOUP, it has been obtained explicitly up to order τ^2 using a perturbative expansion that can be extended to higher orders [37, 10, 74, 73]. We use these results below to illustrate and contrast the departure of the steady-state distribution from its $\tau = 0$ limit for both RTPs and AOUPs.

In both cases, the steady-state distribution in the presence of a confining potential $V(x)$ can be written, in one dimension, as in Eq. (7.28), albeit with $V(x)$ replaced by an effective potential $V_{\rm eff}(x)$, which can be computed perturbatively. For an AOUP, one finds

$$\begin{aligned} V_{\rm eff}(x) &= V(x) - \tau\left(T_{\rm eff}\,V''(x) - \frac{V'(x)^2}{2}\right) \\ &\quad -\tau^2\left(\frac{T_{\rm eff}^2\,V^{(4)}(x)}{2} + \frac{\int^x V'(y)^2\,V^{(3)}(y)\,dy}{2} - T_{\rm eff}\,V'(x)\,V^{(3)}(x) - T_{\rm eff}\frac{V''(x)}{4}\right) + \mathcal{O}(\tau^3)\,. \end{aligned} \tag{7.29}$$

A number of interesting features can already be noted in this perturbative expansion. First, a purely repulsive potential $V(x)$ may lead to an effective potential with attractive parts, due to the term $-\tau\,T_{\rm eff}\,V''(x)$. While derived perturbatively, this gives a heuristic explanation for the accumulation of active particles close to walls, which is a trademark of active particles [28, 105, 111, 31, 29, 90]. Second, an important difference between passive and active systems can be observed at order τ^2 in Eq. (7.29): The steady-state distribution $P(x)$ is a non-local functional of V for active particles. Consider a dilute system. In thermal equilibrium, a perturbation of the potential δV localized at y does not impact $P(x \neq y) \propto e^{-\beta[V(x)+\delta V(x)]} = e^{-\beta V(x)}$, up to an overall normalization. In the active case, Eq. (7.29) reveals a completely different behaviour: $P(x \neq y)$ now depends on $V(y)$ for arbitrary large values of $|x-y|$. To see this consider the perturbation $\delta V(x) = \epsilon\delta(x-y)$. To linear order in ϵ, the effective potential at x picks up a contribution $\delta V_{\rm eff}(x) = \frac{\epsilon\tau^2}{2}[(V'(y)^2)''' + 2(V'(y)\,V'''(y))']\Theta(x-y)$, which adds a global step to the density profile at $x = y$.
This is a simple heuristic explanation of remarkable experiments conducted on swimming bacteria that show an array of asymmetric obstacles to act as a pump when placed in the middle of a microfluidic cavity [41] (See Fig. **??**).

The derivation of the steady-state distribution of a single RTP can also be carried out using Eq. (7.27), yielding

$$V_{\rm eff}(x) = V(x) - \frac{\mu\tau}{T_{\rm eff}}\left((V'(x))^2 + \frac{1}{T_{\rm eff}}\int^x dy(V'(y))^3\right) + \mathcal{O}(\tau^2)\,. \tag{7.30}$$

Again, both the emergence of effective attractive interactions out of repulsive potentials and the non-locality of $P(x)$ emerge as τ departs from 0. Contrary to AOUPs, however, both effects are already present at order τ, hence highlighting the non-universality of the departure from the $\tau = 0$ equilibrium limit across models.

7.3.2 Motility-induced phase separation as linear instability

For a fluid of noninteracting particles with a space-dependent self-propulsion velocity $v(\mathbf{r})$ one can show that the steady-state distribution is $P(\mathbf{r}) = 1/v(\mathbf{r})$. This can be verified on the ABP Fokker-Planck equation,

$$\partial_t P(\mathbf{r},\mathbf{u},t) = -\partial_{\mathbf{r}}\cdot(v\mathbf{u}P) + D_r\Delta_{\mathbf{u}}P \tag{7.31}$$

and clearly $P(\mathbf{r},\mathbf{u}) = 1/v(\mathbf{r})$ is a stationary solution. But from the point of view of a particle, repulsive interactions hinder the self-propelled motion and in a picture where $v(\mathbf{r})$ depends on $\mathbf{r}$ through the local particle density $\rho(\mathbf{r})$ then we expect v to be a decreasing function of ρ: the denser, the slower. If there is a local fluctuation $\delta\rho$ of density this will cause a variation $\delta v = v'\delta\rho$ (where $v = v(\rho)$) and thus $\rho + \delta\rho = \frac{1}{v+\delta v} \simeq \rho(1 - \frac{\delta v}{v})$ so that the density fluctuation is amplified if $v'/v < -1/\rho$.

M2 PCS 2023-2024

Nonequilibrium and Active Systems

First Semester F. van Wijland

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