Introduction to Stochastic Processes

(mostly of Langevin type)

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These lecture notes provide an introduction to Langevin processes and briefly discuss some interesting properties and simple applications. They compile material presented at the "School of Physics and Mathematics Without Frontiers" (ZigZag), held La Havana, Cuba, in March 2024, and the School "Information, Noise and Physics of Life" held at Niš, Serbia, in June 2024, both sponsored by ICTP, and in the 2012-2016 course "Out of Equilibrium Dynamics of Complex Systems" for the Master 2 program "Physics of Complex Systems" in the Paris area.

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1 Introduction

Langevin equations permeate the description of systems in contact with environments. These notes present an introduction to this kind of modelling and they discuss a number of basic properties.

Langevin proposed a stochastic equation, later named after him [1], as an alternative description to Einstein's [2] of Brownian motion [3]. One of the most spectacular applications of Brownian motion was performed by Perrin [4] who received the Nobel Prize in Physics in 1926 for his work on the discontinuous structure of matter, particularly for his experimental verification of Einstein's and Langevin's theoretical explanation of Brownian motion, and the measurement of the Avogrado number.

Many textbooks and review articles describe the Langevin equation and some of their uses [5–16]. In this Lecture Notes, we offer a modern perspective by detailing some recent applications after first addressing the fundamental aspects. We focus on simple single particle problems and we leave aside applications to many-body problems, for instance, critical dynamics [17, 18], nucleation [19, 20], coarsening [21, 22], interface motion [23], and glasses and spin-glasses [24, 25]. We discuss some applications, for example to active matter [26,27] and we refer the readers to the vast literature on the fields of stochastic thermodynamics [28–30] (including fluctuation theorems [31–39]) where Langevin processes have been especially useful.

2 Equilibrium

In this section we revisit certain aspects of equilibrium statistical physics that are not commonly discussed in usual undergraduate courses [40–46]. We then briefly discuss different sources of noise.

2.1 Canonical setting

In these lectures we consider the dynamics of a system of interest coupled to an environment with which it can exchange energy (not particles) and that can be the source of fluctuations. The total energy of the full system is conserved but the contributions from the system, bath and interaction between the two are not. See the sketch in Fig. 2.1.

The bath is usually considered to be macroscopic and not altered by the coupling to the system. This means that its statistical properties, which are assumed from the start, and

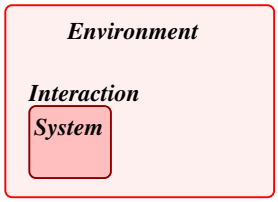

Figure 2.1: Sketch of a total systems consisting of the system of interest, the bath, and their coupling.

are typically those of equilibrium, do not change in time. The most interesting problems are those in which the system of interest is itself many-body with non-trivial collective effects.

2.2 Fluctuations

There are several possible sources of fluctuations:

- Thermal: the system is coupled to a classical environment that ensures fluctuations (noise) and dissipation (the fact that the energy of the system of interest is not conserved). Examples at the single particle level are passive colloidal particles immersed in a fluid, like in Brownian motion, or active ones also immersed in a fluid, like Janus particles used to mimic active matter. At the macroscopic level, classical coarsening, glasses and spin-glasses are passive examples, while biological matter in general are active ones.
- Quantum: the system is coupled to a quantum environment that ensures fluctuations (noise) and dissipation. The temperature of the bath can be zero or not. Some examples are atom impurities confined by optical traps in contact with an ensemble of another atomic species; coarsening, glasses, and spin-glasses at very low temperatures where quantum effects are important.
- Stochastic motors: forces that act on the particles stochastically. The energy injected in the sample is partially dissipated to the bath and partially used as work. As the system is also coupled to a bath there are also thermal fluctuations in it. Active matter provides manifold realizations.

Classical and quantum environments are usually modeled as large assemblies of non-interacting variables (oscillators [47], spins [48], fermions [49]) with chosen distributions of coupling constants and energies.

2.3 The reduced partition function

We analyze the statistical static properties of a classical canonical system in equilibrium at inverse temperature β and itself formed by two sub-parts, one that will be treated as an environment (not necessarily of infinite size) and another one that will be the (sub-)system of interest. We study the partition function or Gibbs functional, $Z_{\rm tot}$,

$$Z_{\rm tot}[\eta] = \sum_{\substack{\text{conf env}\\ \text{conf syst}}} \exp(-\beta H_{\rm tot} - \beta\eta x) \tag{2.3.1}$$

where the sum represents an integration over the phase space of the full system, i.e. the system's and the environmental ones. η is a source. We take

$$H_{\rm tot} = H_{\rm syst} + H_{\rm env} + H_{\rm int} + H_{\rm counter} = H_{\rm syst} + \tilde{H}_{\rm env} \ . \tag{2.3.2}$$

For simplicity we use as a system a single particle moving in $d = 1$: $H_{\rm syst}$ is the Hamiltonian of the isolated particle,

$$H_{\rm syst} = \frac{p^2}{2M} + V(x) \ , \tag{2.3.3}$$

with p and x its momentum and position. $H_{\rm env}$ is the Hamiltonian of a 'thermal bath' that, again for simplicity, we take to be an ensemble of $a = 1, \ldots, N$ independent harmonic oscillators [47, 52, 53] with masses m_a and frequencies ω_a,

$$H_{\rm env} = \sum_{a=1}^{N} \frac{\pi_a^2}{2m_a} + \frac{m_a\omega_a^2}{2} q_a^2 \tag{2.3.4}$$

with π_a and q_a their momenta and positions. This is indeed a very usual choice since it may represent phonons. (These oscillators could be the normal modes of a generic Hamiltonian expanded to quadratic order around its absolute minimum, written in terms of other pairs of conjugate variables; the bath could be, for instance, a chain of harmonic oscillators with nearest-neighbor couplings.) $H_{\rm int}$ is the coupling between system and environment. We will restrict the following discussion to a linear interaction in the oscillator coordinates, q_a, and in the particle coordinate,

$$H_{\rm int} = x \sum_{a=1}^{N} c_a q_a \ , \tag{2.3.5}$$

with c_a the coupling constants. The counter-term $H_{\rm counter}$ is added to avoid the generation of a negative harmonic potential on the particle due to the coupling to the oscillators (that may render the dynamics unstable). We choose it to be

$$H_{\rm counter} = \frac{1}{2} \sum_{a=1}^{N} \frac{c_a^2}{m_a\omega_a^2} x^2 \ . \tag{2.3.6}$$

We note that the addition of the counter-term makes the combination of the environmental, interaction and counter-term Hamiltonians take a rather simple and natural form

$$\tilde{H}_{\rm env} = H_{\rm env} + H_{\rm int} + H_{\rm counter} = \sum_{a=1}^{N} \frac{m_a \omega_a^2}{2} \left(q_a + \frac{c_a}{m_a \omega_a^2} x \right)^2 . \tag{2.3.7}$$

The generalization to more complex systems and/or to more complicated baths and higher dimensions is straightforward. The calculations can also be easily generalized to an interaction of the oscillator coordinate with a more complicated dependence on the system's coordinate, $\mathcal{V}(x)$, that may be dictated by the symmetries of the system at the expense of modifying the counter-term. Non-linear functions of the oscillator coordinates cannot be used since they render the problem unsolvable analytically.

Having chosen a quadratic bath and a linear coupling, the integration over the oscillators' coordinates and momenta can be easily performed. This yields the reduced partition function

$$Z_{\rm red}[\eta] \propto \sum_{\rm conf\ syst} \exp\left[-\beta \left(H_{\rm syst} + H_{\rm counter} + \eta x - \frac{1}{2} \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} \, x^2 \right) \right] . \tag{2.3.8}$$

The 'counter-term' $H_{\rm counter}$ is chosen to cancel the last term in the exponential and it avoids the renormalization of the coefficient of the quadratic term in the potential due to the coupling to the environment that could have even destabilized the potential by taking negative values. An alternative way of curing this problem would be to take a vanishingly small coupling to the bath in such a way that the last term must vanish by itself (say, all $c_a \to 0$). However, this might be problematic when dealing with the stochastic dynamics since a very weak coupling to the bath implies also a very slow relaxation. It is then conventional to include the counter-term to cancel the mass renormalization. One then finds

$$\boxed{Z_{\rm red}[\eta] \propto \sum_{\rm conf\ syst} \exp\left[-\beta \left(H_{\rm syst} + \eta x \right) \right] = Z_{\rm syst}[\eta]} \tag{2.3.9}$$

For a non-linear coupling, the counter-term has to be modified:

$$H_{\rm int} = \sum_{a=1}^{N} c_a q_a \mathcal{V}(x) \qquad\qquad H_{\rm counter} = \frac{1}{2} \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} [\mathcal{V}(x)]^2 . \tag{2.3.10}$$

Exercise 2.1 Prove the last equation.

The interaction with the reservoir does not modify the statistical properties of the particle since $Z_{\rm red} \propto Z_{\rm syst}$, independently of the choices of c_a, m_a, ω_a and N.

If one is interested in the dynamics of a coupled problem, the characteristics of the subsystem that will be considered to be the bath have an influence on the reduced dynamic equations found for the system, that are of generic Langevin kind, as explained in Sect. 3.

Quantum mechanically the reduced partition function depends explicitly on the properties of the bath. The interaction with quantum harmonic oscillators introduces non-local interactions (along the Matsubara time direction) and there is no physical way to introduce a counter-term to correct for this feature.

The dynamics of quantum systems has all these difficulties.

2.4 Ergodicity

Finally, let us discuss Boltzmann's and Gibb's interpretation of averages and the *ergodic hypothesis*. Boltzmann interpreted macroscopic observations as time averages of the form[1]

$$\overline{A} \equiv \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt\ A(\vec{x}(t), \vec{p}(t)) \tag{2.4.11}$$

(focusing on observables A that depend on the phase space variables collected in $\vec{x}$ and $\vec{p}$but are not explicitly time dependent). The fact that this limit exists is the content of a Theorem in Classical Mechanics initially proven by Birkhoff and later by Kolmogorov [50, 51]. Note that in classical mechanics the choice of the initial time is irrelevant.

With the introduction of the *concept of ensembles* Gibbs gave a different interpretation (and an actual way of computing) macroscopic observations. For Gibbs, these averages are statistical ones over all elements of the statistical ensemble,

$$\langle A\rangle = \int d\vec{x}d\vec{p}\ \rho(H(\vec{x},\vec{p}))A(\vec{x},\vec{p})\ , \tag{2.4.12}$$

with ρ the measure. In the microcanonical ensemble this is an average over micro-states on the constant energy surface taken with the microcanonical distribution:

$$\langle A\rangle = \rho_0 \int d\vec{x}d\vec{p}\ \delta(H(\vec{x},\vec{p}) - E)A(\vec{x},\vec{p})\ , \tag{2.4.13}$$

and the normalization constant $\rho_0^{-1} = \int d\vec{x}d\vec{p}\,\delta(H(\vec{x},\vec{p}) - E)$. In the canonical ensemble the average is computed with the Gibbs-Boltzmann weight:

$$\langle A\rangle = Z^{-1} \int d\vec{x}d\vec{p}\ e^{-\beta H(\vec{x},\vec{p})}A(\vec{x},\vec{p})\ . \tag{2.4.14}$$

Z is the partition function $Z = \int d\vec{x}d\vec{p}\ e^{-\beta H(\vec{x},\vec{p})}$.

[1] In practice, in an experiment or numerical simulation initiated at time $t = 0$, averages are computed over a symmetric time interval around a measuring time t, in the form $\overline{A} \equiv \lim_{t_0\ll\tau\leq t} \frac{1}{2\tau}\int_{t-\tau}^{t+\tau} dt'\ A(\vec{x}(t'),\vec{p}(t'))$ with the lower bound in the limit representing a microscopic time-scale. The result should be independent of the measuring time t, that is why we did not write it in the expression of the main text.

The *(weak) ergodic hypothesis* states that under the dynamic evolution the representative point in phase space of a classical system governed by Newton laws can get as close as desired to any point on the constant energy surface.

The *ergodic hypothesis* states that time and ensemble averages, (2.4.11) and (2.4.12), coincide in equilibrium for *all reasonable observables*:

$$\overline{A} = \langle A \rangle \ . \tag{2.4.15}$$

This hypothesis cannot be proven in general but it has been verified in a large number of cases. In general, the great success of Statistical Mechanics in predicting quantitative results has given enough evidence to accept this hypothesis.

An important activity in modern Statistical Mechanics is devoted to the study of macroscopic (non-integrable) systems that *do not satisfy the ergodic hypothesis*. A well-understood case is the one of phase transitions. Other cases are related to the breakdown of equilibration. This can occur either because they are externally driven or because they start from an initial condition that is far from equilibrium and their interactions are such that they do not manage to equilibrate. One may wonder whether certain concepts of thermodynamics and equilibrium statistical mechanics can still be applied to the latter problems. At least for cases in which the macroscopic dynamics are slow one can hope to derive an extension of equilibrium statistical mechanics concepts to describe their behaviour.

3 The Langevin equation

Here we first introduce the Langevin equation phenomenologically and then with a strict calculation. We also present several of its main characteristics and we mention some applications.

3.1 Definition

Examples of experimental and theoretical interest in condensed matter and biophysics in which quantum fluctuation can be totally neglected are manifold. In this context one usually concentrates on systems in contact with an environment: one selects some relevant degrees of freedom and treats the rest as a bath. It is a canonical view. Among these instances are colloidal suspensions which are particles suspended in a liquid, typically salted water, a 'soft condensed matter' example; spins in ferromagnets coupled to lattice phonons, a 'hard condensed matter' case; and proteins in the cell, a 'biophysics' instance. These problems are modelled as stochastic processes with Langevin equations,

the Kramers-Fokker-Planck formalism or master equations depending on the continuous or discrete character of the relevant variables and analytic convenience [5–16].

The Langevin equation was originally proposed to model the motion of a colloidal particle in a liquid but it was soon realised that generalisations of it can be used in a much wider context to describe, e.g. the motion of ions in water, the reorientation of dipolar molecules, or some collective variable of a macroscopic system. It is a stochastic differential equation that describes phenomenologically a large variety of problems. Concretely, it models the time evolution of a set of slow variables coupled to a much larger set of fast variables that are usually (but not necessarily) assumed to be in thermal equilibrium at a given temperature. We first introduce it in the context of Brownian motion in Sect. 3.1.1 and we derive it in more generality in Sect. 3.1.2.

3.1.1 Langevin's Langevin equation

The Langevin equation [1] for a particle moving in one dimension in contact with a white-noise bath reads

$$\underbrace{m\dot{v} - F}_{\text{Newton}} = \underbrace{\overbrace{-\gamma_0 v}^{\text{friction}} + \overbrace{\xi}^{\text{noise}}}_{\text{bath}} \qquad v = \dot{x} \tag{3.1.1}$$

with x and v the particle's position and velocity.

The fluctuating force ξ is supposed to come from occasional impacts of the Brownian particle with molecules of the surrounding medium. The force during an impact is assumed to vary with extreme rapidity over the time of any observation. The fluctuating force is then taken to be Gaussian, due to a time average over an infinitesimal time interval, and its first and second moments are chosen to be $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2\gamma_0 k_B T \delta(t-t')$. The delta function in time indicates that there is no correlation between impacts in any distinct time intervals around t and t'. The friction force $\gamma_0 v$ opposes the motion of the particle. The force F designates all external deterministic forces and depends, in the most common cases, on the position of the particle x only. In cases in which the force derives from a potential, $F = -dV/dx$. The generalization to higher dimensions is straightforward. Note that γ_0 is the parameter that controls the strength of the coupling to the bath (it appears in the friction term as well as in the noise term). In the case $\gamma_0 = 0$ one recovers Newton's equation of motion. The relation between the friction term and the thermal correlation is non-trivial. Langevin fixed it by requiring

$$\langle v^2(t) \rangle \to \langle v^2 \rangle_{eq} = \frac{k_B T}{m} \,. \tag{3.1.2}$$

We will give a different argument for this choice in the next section.

3.1.2 Derivation of the Langevin equation

Let us take a system in contact with an environment. The interacting system+environment ensemble is 'closed' while the system is 'open'. The nature of the environment, *e.g.* whether it can be modeled by a classical or a quantum formalism, depends on the problem under study. We focus here on the classical problem defined by $H_{\rm tot}$ in Eq. (2.3.2). A derivation of a generalized Langevin equation with memory is very simple starting from Newton dynamics of the full system [10, 14, 53]. The generalization to more complex systems and/or to more complicated baths and higher dimensions is straightforward. The calculations can also be easily generalized to an interaction of the oscillator coordinate with a more complicated dependence on the system's coordinate, $\mathcal{V}(x)$, that may be dictated by the symmetries of the system, see **Exercises 3.2-3.7**.

Hamilton's equations for the particle are

$$\dot{x}(t) = \frac{p(t)}{m} , \qquad \dot{p}(t) = -V'[x(t)] - \sum_{a=1}^{N} c_a q_a(t) - \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} x(t) \tag{3.1.3}$$

(the counter-term yields the last term) while the dynamic equations for each member of the environment read

$$\dot{q}_a(t) = \frac{\pi_a(t)}{m_a} , \qquad \dot{\pi}_a(t) = -m_a \omega_a^2 q_a(t) - c_a x(t) , \tag{3.1.4}$$

showing that they are all stable harmonic oscillators forced by the chosen particle. These equations are readily solved by

$$q_a(t) = q_a(0)\cos(\omega_a t) + \frac{\pi_a(0)}{m_a \omega_a}\sin(\omega_a t) - \frac{c_a}{m_a \omega_a}\int_0^t dt' \sin[\omega_a (t-t')] x(t') \tag{3.1.5}$$

with $q_a(0)$ and $\pi_a(0)$ the initial coordinate and position at time $t = 0$ when the particle is set in contact with the bath. It is convenient to integrate by parts the last term. The replacement of the resulting expression in the last term in the rhs of Eq. (3.1.3) yields

$$\boxed{\dot{p}(t) = \underbrace{-V'[x(t)]}_{\text{deterministic force}} + \underbrace{\xi(t) - \int_0^t dt' \; \Gamma(t-t')\dot{x}(t')}_{\text{coupling to the bath}}} \tag{3.1.6}$$

with the symmetric and stationary kernel Γ given by

$$\boxed{\Gamma(t-t') = \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} \cos[\omega_a (t-t')]} \tag{3.1.7}$$

$\Gamma(t-t') = \Gamma(t'-t)$, and the time-dependent force ξ given by

$$\boxed{\xi(t) = -\sum_{a=1}^{N} c_a \left[\frac{\pi_a(0)}{m_a\omega_a}\sin(\omega_a t) + \left(q_a(0) + \frac{c_a x(0)}{m_a\omega_a^2}\right)\cos(\omega_a t)\right]} \tag{3.1.8}$$

This is the equation of motion of the reduced system. It is still deterministic.

$\xi(t)$ is a sum of oscillating functions of time. The third term on the rhs of Eq. (3.1.6) represents a rather complicated friction force. Its value at time t depends explicitly on the history of the particle at times $0 \leq t' \leq t$ and makes the equation non-Markovian. One can rewrite it as an integral running up to a total time $\mathcal{T} > \max(t, t')$ introducing the retarded friction:

$$\boxed{\gamma(t-t') = \Gamma(t-t')\theta(t-t')} \tag{3.1.9}$$

Until this point the dynamics of the system remain deterministic and are completely determined by its initial conditions as well as those of the reservoir variables. Two important points can be make here. On the one hand, one can check, by simple numerical generation, that the function ξ at, say, fixed t resembles more and more a random variable as the number of oscillators increases (for incommensurate frequencies ω_a). The initial conditions for the oscillators are the seeds of the random number generator. This is similar to what happens with random number generators in the sense that these are, ultimately, periodic functions with a finite recurrence time that, however, can be made sufficiently long for computational purposes. Therefore, ξ is a pseudo random number. On the other hand, one can directly introduce the statistical element into play when one realizes that it is impossible to know the initial configuration of the large number of oscillators with great precision and one proposes that the initial coordinates and momenta of the oscillators have a canonical distribution at an inverse temperature β. Note that one needs to assume that the oscillators interacted in the past to establish ergodicity and reach this probability density function (pdf), though they do not do any longer. Then, one chooses $\{\pi_a(0), q_a(0)\}$ to be initially distributed according to a canonical phase space distribution:

$$\boxed{P(\{\pi_a(0), q_a(0)\}, x(0)) = \frac{1}{\tilde{\mathcal{Z}}_{\rm env}[x(0)]}\, e^{-\beta \tilde{H}_{\rm env}[\{\pi_a(0), q_a(0)\}, x(0)]}} \tag{3.1.10}$$

with $\tilde{H}_{\rm env} = H_{\rm env} + H_{\rm int} + H_{\rm counter}$, that can be rewritten as

$$\tilde{H}_{\rm env} = \sum_{a=1}^{N}\left[\frac{m_a\omega_a^2}{2}\left(q_a(0) + \frac{c_a}{m_a\omega_a^2}x(0)\right)^2 + \frac{\pi_a^2(0)}{2m_a}\right] . \tag{3.1.11}$$

Again, the presence of $H_{\rm counter}$ here is for convenience. The randomness in the initial conditions gives rise to a random force acting on the reduced system. Indeed, ξ is now a Gaussian random variable, that is to say a noise, with

$$\langle \xi(t) \rangle = 0\,, \qquad \langle \xi(t)\xi(t') \rangle = k_B T\, \Gamma(t-t')\,. \tag{3.1.12}$$

One can easily check that higher-order correlations vanish for an odd number of ξ factors and factorize as products of two time correlations for an even number of ξ factors. In consequence ξ has Gaussian statistics. Defining the inverse of Γ over the interval $[0,t]$, $\int_0^t dt''\ \Gamma(t-t'')\Gamma^{-1}(t''-t') = \delta(t-t')$, one has the Gaussian pdf:

$$P[\xi] = Z^{-1} e^{-\frac{1}{2k_BT}\int_0^t dt \int_0^t dt'\ \xi(t)\Gamma^{-1}(t-t')\xi(t')} \ . \tag{3.1.13}$$

Z is the normalization. A random force with non-vanishing correlations on a finite support is usually called a coloured noise. Equation (3.1.6) is now a genuine Langevin equation. A multiplicative retarded noise arises from a model in which one couples the coordinates of the oscillators to a generic function of the coordinates of the system, see **Exercise 3.2** and Eq. (3.1.25).

The use of an equilibrium measure for the oscillators implies the relation between the friction kernel and the noise-noise correlation, which are proportional, with a constant of proportionality of value k_BT. This is a generalized form of the fluctuation-dissipation relation, and it applies to the environment.

About the bath

One last comment is in order here. A closed ensemble of harmonic oscillators is an integrable system that does not equilibrate in strict sense. Still, we are using it as a model for a thermal bath. One can argue that the oscillators were in interaction in the past, before being connected to the system, and that this allowed them to reach the Boltzmann probability distribution that is used for their initial states in this calculation. Or else, one can follow the calculations by Mazur & Montroll and see that in the limit of a large number of degrees of freedom the Poincaré recurrence time for the system of non-interacting harmonic oscillators becomes so large that it lies beyond any relevant time for the relaxation of the system that is coupled to the oscillator bath [54].

About the counter-term

Had we not added the counter term the equation would read

$$\dot{p}(t) = -V'[x(t)] + \sum_{a=1}^{N} \frac{c_a^2}{m_a\omega_a^2} x(t) + \xi(t) - \int_0^t dt'\ \Gamma(t-t')\dot{x}(t') \ , \tag{3.1.14}$$

that is like Eq. (3.1.6) for $V \mapsto V - \frac{1}{2}\sum_{a=1}^{N} \frac{c_a^2}{m_a\omega_a^2} x^2$, as we found with the analysis of the partition sum. Note that, as we will take $c_a = \tilde{c}_a/\sqrt{N}$, with $\tilde{c}_a$ of $O(1)$, the constant resulting from the sum over a is $O(1)$. For the distribution of the initial values we can still use $\widetilde{H}_{\rm env}$ or we can choose a Maxwell-Boltzmann distribution with $H_{\rm env} + H_{\rm int}$ alone. The result will be the same, as the supplementary term goes into the normalisation constant for $P_{\rm env}(0)$.

The bath kernel Γ

Different choices of the environment are possible by selecting different ensembles of harmonic oscillators (see [52] for a detailed analysis). The simplest one, that leads to an approximate Markovian equation, is to consider that the oscillators are coupled to the particle via coupling constants $c_a = \tilde{c}_a/\sqrt{N}$ with $\tilde{c}_a$ of order one. One defines

$$\boxed{S(\omega) \equiv \frac{1}{N}\sum_{a=1}^{N} \frac{\tilde{c}_a^2}{m_a\omega_a}\,\delta(\omega-\omega_a)} \tag{3.1.15}$$

a function of ω, of order one with respect to N, and rewrites the kernel Γ as

$$\boxed{\Gamma(t-t') = \int_0^\infty d\omega\,\frac{S(\omega)}{\omega}\,\cos[\omega(t-t')]} \tag{3.1.16}$$

The spectral density $S(\omega)$ is a weighted sum over the frequencies of the oscillators in the bath. For all finite N it is then just a discrete sum of delta functions. In the limit $N \to \infty$ it can become, instead, a regular function of ω. Assuming this limit is taken, several proposals for the resulting function $S(\omega)$ are made. A common choice is

$$\boxed{\frac{S(\omega)}{\omega} = \frac{2\gamma_0}{\pi}\left(\frac{|\omega|}{\tilde{\omega}}\right)^{\alpha-1} f_c\left(\frac{|\omega|}{\Lambda}\right)} \tag{3.1.17}$$

The function $f_c(x)$ is a high-frequency cut-off of typical width Λ and is usually chosen to be an exponential. The frequency $\tilde{\omega} \ll \Lambda$ is a reference frequency that allows one to have a coupling strength γ_0 with the dimensions of viscosity. If $\alpha = 1$, the friction is said to be Ohmic, $S(\omega)/\omega$ is constant when $|\omega| \ll \Lambda$ as for a white noise. This name is motivated by the electric circuit analog exposed in Sec. 6.2. When $\alpha > 1$ ($\alpha < 1$) the bath is superOhmic (subOhmic). The exponent α is taken to be > 0 to avoid divergencies at low frequency. For the exponential cut-off the integral over ω can be computed for $\alpha = 1$ and $\alpha \neq 1$. In the former Ohmic case one finds

$$\Gamma(t) = \frac{2\gamma_0}{\pi}\,\frac{\Lambda}{[1+(\Lambda t)^2]} \qquad \alpha = 1\,. \tag{3.1.18}$$

In the $\Lambda \to \infty$ limit one approaches the Stratonovich limit and $\Gamma(t)$ becomes a delta-function, $\Gamma(t) \to 2\gamma_0\delta(t)$ such that $\int_0^t dt'\,\Gamma(t-t') = 2\gamma_0 \arctan(\Lambda t) \to \gamma_0$ for $\Lambda \to \infty$. In the latter non-Ohmic case the integral over ω yields

$$\Gamma(t) = \frac{2\gamma_0\tilde{\omega}^{-\alpha+1}}{\pi}\,\Gamma_{\rm E}(\alpha)\,\Lambda^\alpha\,\frac{\cos[\alpha\arctan(\Lambda t)]}{[1+(\Lambda t)^2]^{\alpha/2}} \qquad \alpha \neq 1 \tag{3.1.19}$$

with $\Gamma_{\rm E}(\alpha)$ the Euler Gamma-function. At long times, for any $\alpha > 0$ and $\alpha \neq 1$, one has

$$\lim_{\Lambda t\to\infty}\Gamma(t) \;=\; \frac{2\gamma_0\tilde{\omega}}{\pi}\,\cos(\alpha\pi/2)\Gamma_{\rm E}(\alpha)\,(\tilde{\omega}t)^{-\alpha}\,, \tag{3.1.20}$$

a power law decay.

Dimensional analysis

The noise ξ is a force and it should have dimensions $[\xi] = ML/T^2$ with $[m_a] = M$, $[q_a] = L$ and the frequencies $[\omega_a] = 1/T$. From their definition one finds $[c_a] = M/T^2$, $[\Gamma] = [S(\omega)] = M/T^2$ and $[\gamma_0] = M/T$.

Exercise 3.2 Prove that for a non-linear coupling $H_{\rm int} = \mathcal{V}[x]\sum_{a=1}^N c_a q_a$ there is a choice of counter-term for which the Langevin equation reads

$$\boxed{\dot{p}(t) = -V'[x(t)] + \xi(t)\mathcal{V}'[x(t)] - \mathcal{V}'[x(t)]\int_0^t dt'\ \Gamma(t-t')\mathcal{V}'[x(t')]\dot{x}(t')} \tag{3.1.21}$$

with the same Γ as in Eq. (3.1.7) and $\xi(t)$ given by Eq. (3.1.8) with $x(0) \to \mathcal{V}[x(0)]$. The noise appears now multiplying a function of the particles' coordinate. Applications of this kind of equations are manifold. For instance, the random motion of a colloid in a confined medium is mimicked with a Langevin equation in which the friction coefficient depends on the position notably close to the walls of the container.

Exercise 3.3 Take now a system made of $i = 1, \dots, n$ variables collected in two n-component vectors $\vec{p}, \vec{x}$. Use $H_{\rm int} = \sum_{i=1}^n \sum_{a=1}^N c_{ai} q_{ai} x_i$ as the coupling between system and bath and an ensemble of n independent sets of harmonic oscillators for the bath. Prove that the stochastic equation is

$$\dot{p}_i(t) = -\frac{\partial V[x(t)]}{\partial x_i(t)} + \xi_i(t) - \int_0^t dt'\ \Gamma_i(t-t')\dot{x}_i(t') \qquad\qquad i = 1, \dots, n \tag{3.1.22}$$

where there is no sum over repeated indices and Γ_i and ξ_i are given by

$$\Gamma_i(t-t') = \sum_{a=1}^N \frac{c_{ai}^2}{m_{ai}\omega_{ai}^2}\cos[\omega_{ai}(t-t')]\ , \tag{3.1.23}$$

$$\xi_i(t) = -\sum_{a=1}^N c_a \left[\frac{\pi_{ai}(0)}{m_{ai}\omega_{ai}}\sin(\omega_{ai}t) + \left(q_{ai}(0) + \frac{c_{ai}x_i(0)}{m_{ai}\omega_{ai}^2}\right)\cos(\omega_{ai}t)\right]\ . \tag{3.1.24}$$

The i dependence in Γ_i can be ignored if the ensembles of oscillators are equivalent (i.e. same distribution of parameters). Characterise next the mean $\langle \xi_i(t)\rangle$ and the correlation $\langle \xi_i(t)\xi_j(t')\rangle$ and see under which conditions $\langle \xi_i(t)\xi_j(t')\rangle = \delta_{ij}\Gamma(t-t')$.

Exercise 3.4 Take now a system made of $i = 1, \dots, n$ variables collected in $\vec{p}, \vec{x}$. Use $H_{\rm int} = \mathcal{V}[x]\sum_{a=1}^N c_a q_a$ as the coupling between system and bath, where x is the modulus of the vector $\vec{x}$. Prove that the stochastic equation is

$$\begin{aligned}\dot{p}_i(t) = &-\frac{\delta V[x(t)]}{\delta x_i(t)} + \xi(t)\frac{\delta \mathcal{V}[x(t)]}{\delta x_i(t)} \\ &-\frac{\delta \mathcal{V}[x(t)]}{\delta x_i(t)}\int_0^t dt'\ \Gamma(t-t')\sum_{j=1}^n \frac{\delta \mathcal{V}[x(t')]}{\delta x_j(t')}\ \dot{x}_j(t')\end{aligned} \tag{3.1.25}$$

with the same Γ and ξ as in Eqs. (3.1.7) and (3.1.8) with $x(0) \to \mathcal{V}[x(0)]$. There is only one noise component and it appears multiplying a function of the particles' coordinate.

Exercise 3.5 The classical phonon Hamiltonian in one dimension is

$$H = \sum_{\ell=-N/2+1}^{N/2} \frac{p_\ell^2}{2} + \sum_{\ell=-N/2+1}^{N/2} \frac{(q_\ell - q_{\ell-1})^2}{2} \tag{3.1.26}$$

where ℓ is the lattice site index and, for simplicity, we took $m_\ell = \omega_\ell = 1$. The last term is a neares-negihbour coupling. We assume periodic boundary conditions on the chain. Let us also consider a linear coupling of the form $H_I = -q_0 x$ between the central site and the system's coordinate x. Show that going to the Fourier modes $Q_k = N^{-1/2} \sum_{\ell=-N/2+1}^{N/2} e^{ik\ell} q_\ell$ all phonons decouple into independent harmonic oscillators with frequencies $\omega_k^2 = 2(1 - \cos ka) = 4\sin^2(ka/2)$, with a the lattice spacing, and the coupling constants between the variable and all Fourier modes are $c_k = N^{-1/2}$. The periodicity $q_N = q_0$ imposes the quantisation of the wave-vectors, $k = 2\pi n/(Na)$ with $n \in \mathrm{Z}$. Each k describes a normal mode of vibration and within the first Brillouin zone there are N modes.

This calculation can be extended to higher dimensions.

3.1.3 Energy conservative baths

In some situations one wishes to study a system coupled to a bath and conserve the energy of the system. This can be done with a (noiseless) 'Gaussian' [55] thermostat, extensively used in the context of entropy production and the Gallavotti-Cohen theorem, or also including a small amount of energy-preserving noise.

$$\dot{x}_i = \frac{p_i}{m} \tag{3.1.27}$$

$$\dot{p}_i = -\frac{\partial V[\vec{x}]}{\partial x_i} + \underbrace{g_{ij}(\vec{p})\xi_j}_{\substack{\text{conservative}\\ \text{noise}}} - \underbrace{f_i(\vec{x})}_{\text{forcing}} + \underbrace{\gamma(t)p_i}_{\text{bath}} \tag{3.1.28}$$

- ξ_j are white, independent noises of variance ϵ, unrelated to temperature, since the energy is fixed.
- $g_{ij} = \delta_{ij} - p_i p_j/p^2$ is the projector onto the space tangential to the energy surface.
- Multiplying Eq. (3.1.27) by $\partial V(\vec{x})/\partial x_i$, and then Eq. (3.1.28) by p_i/m, adding, and using usual rules of calculus, one concludes that energy is conserved provided

$$\gamma(t) = m(\vec{f} \cdot \vec{p})/p^2 \,. \tag{3.1.29}$$

  Note that in the absence of non-potential forces $\gamma(t) = 0$. Under non-potential forces the dissipative term compensates the work done by the force.

The product $g_{ij}(\vec{p})\xi_j$ is rather ill-defined because both g_{ij} and ξ_j are discontinuous functions of time. The ambiguity is raised by discretising time [6], or by specifying the evolution of the probability density, as in the Kramers or Fokker-Planck approaches.

3.2 Properties

In this section we discuss a number of important properties of the Langevin processes.

3.2.1 Novikov theorem

A rather trivial property of Gaussian white noises goes under the name of Novikov theorem and is a consequence of a simple integration by parts. Take the following expression

$$\left\langle \frac{\delta f_\xi[x(t),p(t)]}{\delta\xi(t')} \right\rangle = \mathcal{N}^{-1} \int \mathcal{D}\xi \; e^{-\frac{1}{4k_BT}\int_0^t dt''\xi^2(t'')} \; \frac{\delta f_\xi[x(t),p(t)]}{\delta\xi(t')} \tag{3.2.1}$$

where $f_\xi[x(t),v(t)]$ is any functional of the stochastic process ruled by a Langevin equation with white noise ξ and $\mathcal{N}$ is the normalization constant. With a simple integration by parts

$$\begin{aligned}
\left\langle \frac{\delta f_\xi[x(t),p(t)]}{\delta\xi(t')} \right\rangle &= -\mathcal{N}^{-1} \int \mathcal{D}\xi \; \frac{\delta e^{-\frac{1}{4k_BT}\int_0^t dt''\xi^2(t'')}}{\delta\xi(t')} f_\xi[x(t),p(t)] \\
&= \mathcal{N}^{-1} \int \mathcal{D}\xi \; \frac{1}{2k_BT}\xi(t') \; e^{-\frac{1}{4k_BT}\int_0^t dt''\xi^2(t'')} \; f_\xi[x(t),p(t)] \\
&= \frac{1}{2k_BT} \langle f_\xi[x(t),p(t)]\xi(t')\rangle
\end{aligned} \tag{3.2.2}$$

Exercise 3.7 Extend the relation (3.2.2) to the many variable case and also the ones in which there is memory and the noise is coloured.

3.2.2 Irreversibility

Time reversibility is the statement that $\{x(-t),-p(-t)\}$ satisfy the same equations as $\{x(t),p(t)\}$.

Time reversibility is a property that has to be respected by any set of microscopic dynamic equations. Newton equations describing the whole system, the particle and all the molecules of the fluid, *are* time reversal invariant. Indeed, the dynamics of the selected variable is still reversible, in the sense that the pair $\{x(-t),-p(-t)\}$ satisfies the same equation as $\{x(t),p(t)\}$, as long as N is kept finite *and* the oscillator positions and momenta are taken as $\{q_a(0),-\pi_a(0)\}$ (instead of $\{q_a(0),\pi_a(0)\}$). In order to prove this

statement, we can start from the equation evaluated at $-t$. The tricky terms, stemming from the integration over the oscillators, evaluated at $-t$ are:

$$\begin{aligned}
&\underbrace{-\frac{1}{m}\int_0^{-t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(-t-t')]\,\overline{p}(t')}_{\text{dissipation}} \\
&\qquad \underbrace{-c_a\left[\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(-\omega_a t)+\left(\overline{q}_a(0)+\frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(-\omega_a t)\right]}_{\text{noise}} \\
&= -\frac{1}{m}\int_0^{-t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(t+t')]\,\overline{p}(t') \\
&\qquad -c_a\left[-\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(\omega_a t)+\left(\overline{q}_a(0)+\frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(\omega_a t)\right] \\
&= +\frac{1}{m}\int_0^{t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(t-t')]\,\overline{p}(-t') \\
&\qquad -c_a\left[-\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(\omega_a t)+\left(\overline{q}_a(0)+\frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(\omega_a t)\right]
\end{aligned} \tag{3.2.3}$$

where we did not write the sum over a to alleviate the notation. The overlined variables are yet not known, they are the ones that we will later choose to get the same form as for the original terms originating in the bath coupling. It is now clear that this aim is attained if one uses $\overline{x}(t) = x(-t)$, $\overline{p}(-t) = -p(-t)$, $\overline{q}_a(t) = q_a(-t)$, $\overline{\pi}_a(-t) = -\pi_a(-t)$, and the last condition implies that $-\pi_a(0)$ has to be used in the last line.

However, time-reversal is broken in the reduced equation in which the fluid is treated in an effective statistical form. Indeed, the friction force $-\gamma_0 v$ in Eq. (3.1.1) – or its retarded extension in the non-Markovian case – explicitly breaks time-reversal ($t \to -t$) invariance. Indeed,

$$-\gamma_0 v \qquad \mapsto \qquad \gamma_0 v \tag{3.2.4}$$

3.2.3 Dissipation

Even in the case in which all forces derive from a potential, $F = -dV/dx$, the energy of the particle, $H_{\text{syst}} = mv^2/2 + V$, is not conserved by Eq. (3.1.1). This can be easily seen by taking $dH_{\text{syst}}/dt = mv\dot{v} + V'v = v(-\gamma_0 v + \xi)$, say, in the case of additive white noise. (Note that we used the standard rules of calculus here, the Stratonovich convention. We will say more about discretization subtleties later.) The second member does not vanish in general. Its sign is not determined either unless at zero-temperature, when it is negative semi-definite, $-\gamma_0 v^2$, indicating that the dynamics are of gradient descent. On average, in the absence of non-potential energy injecting forces, and for confining potentials, one finds that the energy flows to the bath leading to dissipation. At very long times, however,

the particle may reach a stationary regime in which the particle gives and receives energy from the bath at equal rate, on average. We will see this mechanism at work in some examples.

Exercise 3.8 Prove the time-irreversibility of the Langevin equation and the fact that the symmetry is restored if $\gamma_0 = 0$.

Exercise 3.9 Show that $d\langle H_{\rm syst}\rangle/dt \neq 0$ when $\gamma_0 \neq 0$. Prove that for a single variable, the non-zero terms can be found from the analysis of $t' \to t^-$ and $t' \to t^+$ limits of $\gamma_0\langle \dot{x}(t)\dot{x}(t')\rangle - 2\gamma_0 T\langle \xi(t)\dot{x}(t')\rangle$. Relate the last term to the linear response function. Discuss the equilibrium case, in which $m\langle \dot{x}^2(t)\rangle = k_B T$ (equipartition).

3.2.4 Smoluchowski (over-damped) limit

In many situations in which friction is very large, the characteristic time for the relaxation of the velocity degrees of freedom to their Maxwell distribution, t_r^v, is very short (see the examples in Sect. 2.5). In consequence, observation times are very soon longer than this time-scale, the inertia term $m\dot{v}$ can be dropped, and the Langevin equation becomes

$$\gamma_0 \dot{x} = F + \xi \tag{3.2.5}$$

(for simplicity we wrote the white-noise case). Indeed, this over-damped limit is acceptable whenever the observation times are much longer than the characteristic time for the velocity relaxation. Inversely, the cases in which the friction coefficient γ_0 is small are called under-damped.

In the over-damped limit with white-noise the friction coefficient γ_0 can be absorbed in a rescaling of time. One defines the new time τ

$$t = \gamma_0 \tau \ , \tag{3.2.6}$$

the new position, $\tilde{x}(\tau) = x(\gamma_0\tau)$, and the new noise $\eta(\tau) = \xi(\gamma_0\tau)$. In the new variables the Langevin equation reads $\dot{\tilde{x}}(\tau) = F(\tilde{x}, \tau) + \eta(\tau)$ with $\langle \eta(\tau)\eta(\tau')\rangle = 2k_B T\delta(\tau - \tau')$.

Exercise 3.10 Redefine time as $\tau = k_B T \gamma_0^{-1}\, t$ and $\tilde{x}(\tau) = x(\gamma_0 \beta t)$, and similarly for the other function of time, to transform the Langevin equation into

$$\dot{\tilde{x}} = \beta \tilde{F} + \tilde{\xi} \ , \qquad\qquad \langle \tilde{\xi}(\tau)\tilde{\xi}(\tau')\rangle = 2\delta(\tau - \tau') \ . \tag{3.2.7}$$

This equation is not well adapted to take the $T \to 0$ limit.

3.2.5 Markov character and generation of memory

In the case of a white noise (delta correlated) the full set of equations defines a Markov process, that is a stochastic process that depends on its history only through its very last step.

The Langevin equation (3.1.1) is actually a set of two first order differential equations. Notice, however, that the pair of first-order differential equations could also be described by a single second-order differential equation:

$$m\ddot{x} + \gamma_0 \dot{x} = F + \xi \ . \tag{3.2.8}$$

Having replaced the velocity by its definition in terms of the position $x(t)$ depends now on $x(t-\delta)$ and $x(t-2\delta)$. This is a very general feature: by integrating away some degrees of freedom (the velocity in this case) one generates memory in the evolution. Generalizations of the Langevin equation, such as the one that we have just presented with colored noise, and the ones that will be generated to describe the slow evolution of super-cooled liquids and glasses in terms of correlations and linear responses, do have memory [24].

A simple solvable example that illustrates this feature is the under-damped white-noise Langevin equation for a harmonic oscillator:

$$m\dot{x} = p \ , \qquad\qquad \dot{p} = -m\omega^2 x - \frac{\gamma_0}{m}\ p + \xi \ , \tag{3.2.9}$$

with initial condition $p(0) = 0$ and white noise such that $\langle \xi(t)\xi(t')\rangle = 2\gamma k_B T \delta(t-t')$. The second equation can be solved exactly

$$p(t) = \int_0^t dt'\ e^{-\frac{\gamma_0}{m}(t-t')}\ [-m\omega^2 x(t') + \xi(t')] \tag{3.2.10}$$

and when this solution is put back into the equation for $\dot{x}$ one finds an equation with memory,

$$\dot{x}(t) = -\int_0^t dt'\ K(t-t')x(t') + \xi_x(t) \ , \tag{3.2.11}$$

with

$$K(t) = \omega^2\ e^{-\frac{\gamma_0}{m}t} \qquad \text{and} \qquad \xi_x(t) = \frac{1}{m}\int_0^\infty dt'\ e^{-\frac{\gamma_0}{m}(t-t')}\ \xi(t') \ . \tag{3.2.12}$$

The statistical properties of the new noise can be derived from the ones of the original noise ξ. It keeps the zero average and its correlations are

$$\langle \xi_x(t)\xi_x(t')\rangle = \frac{k_B T}{m\omega^2}\ K(|t-t'|) \ . \tag{3.2.13}$$

The solution of this problem will be developed in Sect. 3.4.2.

Whenever a variable is integrated out from a Markov set of equations a non-Markov equation is obtain. Proceeding in the reverse sense one can transform a non-Markov equation with exponentially correlated noise into a set of Markov equations that are easier to integrate numerically.

3.2.6 Distinction between relaxation and equilibration

A system coupled to an environment can relax to a non-equilibrium steady state, usually called a NESS, that is not the one of thermal equilibrium, $P(v,x;t) \to P_{\rm NESS}(v,x) \neq P_{\rm GB}(v,x)$, that is, that is different from the Gibbs-Boltzmann measure.

3.2.7 Discretization of stochastic differential equations

The way in which the stochastic differential equation (3.2.5) (with no inertia and with white noise) is to be discretized is a subtle matter. Two schemes are the most popular ones, called the Itô and Stratonovich calculus, and are rather well documented in the literature [11, 12].

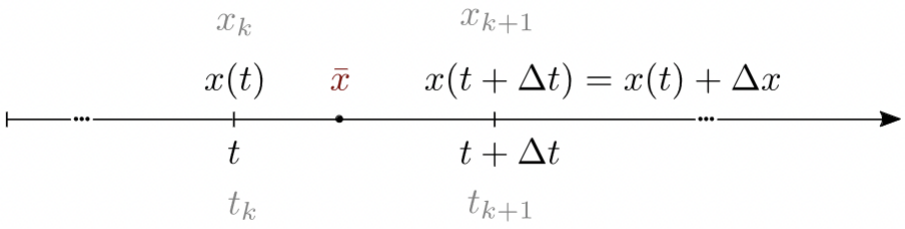

Figure 3.2: A sketch of the time axis, discretized with step Δt.

Let us try to explain, in a simple way, the origin of the subtleties and how they are controlled. We discretize time according to $t_n = n\Delta t + t_0$ with n an integer running as $n = 0, \ldots, \mathcal{N}$. The continuous time limit corresponds to $\Delta t \to 0$, $\mathcal{N} \to \infty$ while keeping $\mathcal{N}\Delta t = \mathcal{T} - t_0$ fixed and $t_{\mathcal{N}} = \mathcal{T}$. We now take a single real variable x the dynamics of which is governed by the following stochastic equation

$$\boxed{d_t x(t) = f(x) + g(x)\xi(t)} \tag{3.2.14}$$

with multiplicative white noise distributed according to a Gaussian pdf with zero mean and variance $\langle \xi(t)\xi(t')\rangle = 2k_B T\delta(t-t')$. This stochastic differential equation makes sense only when a discretization rule is explicitly given to define it.

We use the short-hand notation $x_n = x(t_n)$ and $\xi_n = \xi(t_n)$ The white noise statistics correspond to $\langle \xi_n \rangle = 0$ and $\langle \xi_n \xi_m \rangle = (2k_B T/\Delta t)\ \delta_{nm}$ that implies $\xi_n^2 \simeq 2k_B T/\Delta t$ and $\xi_n \simeq \mathcal{O}(\Delta t^{-1/2})$ (we use here the step realisation of the Dirac delta function as being identical to 0 away from the interval $[-\Delta t/2, \Delta t/2]$ and equal to $1/\Delta t$ within this interval). We will use the generic α prescription [7]

$$\boxed{x_{n+1} - x_n = f(\overline{x}_n)\Delta t + g(\overline{x}_n)\xi_n \Delta t} \tag{3.2.15}$$

with

$$\boxed{\overline{x}_n \equiv \alpha x_{n+1} + (1-\alpha)x_n} \tag{3.2.16}$$

and $0 \leq \alpha \leq 1$ in the following. $\alpha = 0$ is the Itô prescription while $\alpha = 1/2$ is the Stratonovich one.

The definition of $\overline{x}_n$ implies

$$\begin{aligned} \overline{x}_n &= x_n + \alpha(x_{n+1} - x_n) && (3.2.17)\\ \overline{x}_n &= x_{n+1} - (1-\alpha)(x_{n+1} - x_n) && (3.2.18) \end{aligned}$$

and

$$\begin{aligned} x_n &= \overline{x}_n - \alpha(x_{n+1} - x_n) && (3.2.19)\\ x_{n+1} &= \overline{x}_n + (1-\alpha)(x_{n+1} - x_n) && (3.2.20) \end{aligned}$$

which allow one to rewrite the α-prescription equation as

$$\begin{aligned} x_{n+1} - x_n &= [f(x_n) + f'(x_n)\alpha(x_{n+1} - x_n) + \mathcal{O}((x_{n+1} - x_n)^2)]\ \Delta t \\ &\quad +[g(x_n) + \alpha g'(x_n)(x_{n+1} - x_n) + \mathcal{O}((x_{n+1} - x_n)^2)]\ \xi_n \Delta t \\ &\simeq f(x_n)\Delta t + g(x_n)\xi_n \Delta t + \alpha g'(x_n)(x_{n+1} - x_n)\xi_n \Delta t \end{aligned} \tag{3.2.21}$$

where we used $\xi_n = \mathcal{O}(\Delta t^{-1/2})$ to estimate the relevant contributions up to $\mathcal{O}(\Delta t)$ and we dropped terms $\mathcal{O}(\Delta t^{3/2})$. Replacing $x_{n+1} - x_n$ in the last term by the outcome of the same equation to order $\Delta t^{1/2}$:

$$\Delta x_n \equiv x_{n+1} - x_n \simeq f(x_n)\Delta t + g(x_n)\xi_n \Delta t + \alpha g'(x_n) g(x_n)(\xi_n \Delta t)^2\ . \tag{3.2.22}$$

As $(\xi_n \Delta t)^2 \simeq 2k_B T \Delta t$, all terms in the rhs are of order Δt. We will use this expression to derive the Fokker-Planck equation.

The force term in the stochastic equation is also sometimes written as

$$\begin{aligned} f(\overline{x}_n) &= \alpha f(\overline{x}_n) + (1-\alpha) f(\overline{x}_n) \\ &= \alpha f(x_n + \alpha \Delta x_n) + (1-\alpha) f(x_{n+1} - (1-\alpha)\Delta x_n) \\ &= \alpha [f(x_n) + \alpha f'(x_n)\Delta x_n + \dots] \\ &\qquad +(1-\alpha)[f(x_{n+1} - (1-\alpha) f'(x_{n+1})\Delta x_n + \dots] \\ &= \alpha f(x_n) + (1-\alpha) f(x_{n+1}) + \mathcal{O}(\Delta x_n) \end{aligned}$$

and dropping the $\mathcal{O}(\Delta x_n)$ terms that appear multiplied by Δt and give rise to negligible terms of $\mathcal{O}(\Delta t^{3/2})$, one has

$$f(\overline{x}_n) = \alpha f(x_n) + (1-\alpha) f(x_{n+1}) \tag{3.2.23}$$

This is ultimately equivalent to writing the force term as $f(x_n)\Delta t$ in the Langevin equation.

The chain rule

As explained in [7], the chain-rule for the time-derivative of a function V of the variable x depends on the stochastic equation governing the evolution of x; we call it the x-chain rule and for Eq. (3.2.14) it reads

$$\boxed{d_t V = \dot{x}\, V' + (1-2\alpha) k_B T g^2 V''} \tag{3.2.24}$$

where $\dot{x} = d_t x = dx/dt$, $v' = \partial_x V$ and $V'' = \partial_x^2 V$. Note that the chain rule is independent of $f(x)$ (that is to say, it will take the same form for a Langevin equation with the drift term, Eq. (4.1.38), to be discussed below). Somehow surprisingly, the second term is still present for $g = 1$, the additive noise case. It only disappears and one recovers normal calculus for $\alpha = 1/2$.

We now prove Eq. (3.2.24). Let us write the difference between a generic function V evaluated at x at two subsequent times $n+1$ and n. We expand x_n around the generic α point $\bar{x}_n$ we get

$$\begin{aligned} V(x_{n+1}) - V(x_n) &= V(\bar{x}_n + (1-\alpha)(x_{n+1} - x_n)) - V(\bar{x}_n - \alpha(x_{n+1} - x_n)) \\ &= (x_{n+1} - x_n) V'(\bar{x}_n) + \tfrac{1}{2}(1-2\alpha)(x_{n+1} - x_n)^2 V''(\bar{x}_n) + \mathcal{O}(\Delta t^{3/2}) \end{aligned}$$

where $\Delta x_n = x_{n+1} - x_n$. Using $\boxed{(x_{n+1} - x_n)^2 = 2k_B T g(\bar{x}_n)^2 \Delta t + \mathcal{O}(\Delta t^{3/2})}$ from Eq. (3.2.15) after setting $(\xi_n \Delta t)^2 = 2k_B T \Delta t$, where the crucial fact is that this square is of order Δt (instead to Δt^2) we obtain

$$V(x_{n+1}) - V(x_n) = (x_{n+1} - x_n) V'(\bar{x}_n) + (1-2\alpha) k_B T g(\bar{x}_n)^2 V''(\bar{x}_n) \Delta t + \mathcal{O}(\Delta x^3)$$

and dropping terms of order $\Delta t^{1/2}$ or higher,

$$\boxed{\frac{V(x_{n+1}) - V(x_n)}{\Delta t} = \frac{x_{n+1} - x_n}{\Delta t} V'(\bar{x}_n) + (1-2\alpha) k_B T g(\bar{x}_n)^2 V''(\bar{x}_n)} \tag{3.2.25}$$

which is the chain-rule. As above, at this order one can replace the $\overline{x}_n$ in g, V' and V'' by any x in the interval. This expression is next written as in Eq. (3.2.24).

Influence of the discretisation on the trajectories

One can estimate the importance of the discretisation on the actual trajectories found by computing the difference between the two terms in the right-hand-side of the Langevin equation obtained for a discretisation α and another discretisation $\overline{\alpha}$.

Let us start with the first term, the one equal to f.

$$\begin{aligned} & f(\overline{x}_\alpha(t_k)) - f(\overline{x}_{\overline{\alpha}}(t_k)) \\ &\quad = f(x(t_k)) + f'(x(t_k)) \alpha \Delta x_k - f(x(t_k)) - f'(x(t_k)) \overline{\alpha} \Delta x_k + \mathcal{O}(\Delta x_k^2) \\ &\quad = f'(x(t_k))(\alpha - \overline{\alpha}) \Delta x_k + \mathcal{O}(\Delta x_k^2) \to 0 \qquad \text{for} \qquad \Delta t \to 0 \end{aligned} \tag{3.2.26}$$

the last results being due to the fact that $\Delta x_k = \mathcal{O}(\Delta t^{1/2})$.

Now, we will find that the difference between the two noise-dependent terms evaluated at different discretisation parameters does not vanish in the same limit:

$$\begin{aligned} & g(\overline{x}_\alpha(t_k))\xi(t_k) - g(\overline{x}_{\overline{\alpha}}(t_k))\xi(t_k) \\ & \quad = [g(x(t_k)) + g'(x(t_k))\alpha\Delta x_k - g(x(t_k)) - g'(x(t_k))\overline{\alpha}\Delta x_k + \mathcal{O}(\Delta x_k^2)]\xi(t_k) \\ & \quad = g'(x(t_k))(\alpha - \overline{\alpha})\xi(t_k)\Delta x_k + \mathcal{O}(\Delta x_k^2)\xi(t_k) = \mathcal{O}(\Delta t^0) \end{aligned} \tag{3.2.27}$$

In consequence, there is a difference of order one in the trajectories found with one and the another discretisation scheme.

Numerical integration of the Langevin equation

The numerical integration of the Langevin equation requires the discretisation of time, $t_k = k\Delta t$ where k is an integer and Δt the time-step. The choice of the optimal value of Δt has to be gauged depending on the accuracy of the numerical integration desired (the smallest the Δt the best) and the length of the time-interval wished to be analysed (one cannot take it to be so small because otherwise only too short time-scales are explored). Several algorithms are described in [56].

In the over-damped limit with additive white noise the most common algorithm used is just the simple iteration of the Ito relation

$$x(t_k) = x(t_{k-1}) - \Delta t\, V'(x(t_{k-1})) + \Delta t\, \xi(t_{k-1})\ . \tag{3.2.28}$$

The only practical issue to stress here is that one needs to consider the time-discretised version of the delta-correlated white noise ξ:

$$\langle \xi(t_k)\xi(t_n)\rangle = \frac{2k_BT}{\Delta t} \qquad \text{if} \qquad |t_k - t_n| = \Delta t|k-n| < dt/2 \tag{3.2.29}$$

that implies $\xi(t_k) = \sqrt{2k_BT/\Delta t}\ \eta_k$ with $\langle \eta_k\eta_n\rangle = \delta_{kn}$.

The inertial Langevin equation

Take now the generic stochastic system

$$d_t x = \frac{\partial H}{\partial p} = \frac{p}{m} \tag{3.2.30}$$

$$d_t p = -\frac{\partial H}{\partial x} - \gamma d_t x + g(x,p)\xi(t) \tag{3.2.31}$$

with $\xi(t)$ a white noise with zero average and correlations $\langle \xi(t)\xi(t')\rangle = 2\gamma k_BT\delta(t-t')$ which imply $\xi_n = \mathcal{O}(\Delta t^{-1/2})$. Write it in discretized form

$$x_{n+1} - x_n = h(\overline{x}_n, \overline{p}_n)\,\Delta t \tag{3.2.32}$$

$$p_{n+1} - p_n = f(\overline{x}_n, \overline{p}_n)\,\Delta t - \gamma(x_{n+1} - x_n) + g(\overline{x}_n, \overline{p}_n)\xi_n\Delta t \tag{3.2.33}$$

where we introduced the names h and f for the two first terms in the right-hand-sides for notation convenience and to make contact with what we discussed in the case without inertia. Take $\overline{x}_n = x_n + \alpha \Delta x_n$ and $\overline{p}_n = p_n + \alpha' \Delta p_n$. One can repeat the calculations done so far to show that the chain rule becomes

$$\frac{dV(x,p)}{dt} = \frac{\partial V(x,p)}{\partial x}\,\dot{x} + \frac{\partial V(x,p)}{\partial p}\,\dot{p} + (1-2\alpha')\frac{\partial^2 V(x,p)}{\partial p^2} k_B T g(x,p)^2 \tag{3.2.34}$$

What about the trajectories? Do they depend on α and/or α'? Let us compare the expressions of h and f for two processes, one with α, α' and the other with $\overline{\alpha}, \overline{\alpha}'$:

$$\begin{aligned}
&h(\overline{x}_\alpha(t_k), \overline{p}_{\alpha'}(t_k)) - h(\overline{x}_{\overline{\alpha}}(t_k), \overline{p}_{\overline{\alpha}'}(t_k)) \\
&\quad \sim h(x(t_k),p(t_k)) + \frac{\partial h(x(t_k),p(t_k))}{\partial x(t_k)}\alpha \Delta x_k + \frac{\partial h(x(t_k),p(t_k))}{\partial p(t_k)}\alpha' \Delta p_k \\
&\quad\quad -h(x(t_k),p(t_k)) - \frac{\partial h(x(t_k),p(t_k))}{\partial x(t_k)}\overline{\alpha} \Delta x_k - \frac{\partial h(x(t_k),p(t_k))}{\partial p(t_k)}\overline{\alpha}' \Delta p_k \\
&\quad = (\alpha - \overline{\alpha})\frac{\partial h(x(t_k),p(t_k))}{\partial x(t_k)}\Delta x_k + (\alpha' - \overline{\alpha}')\frac{\partial h(x(t_k),p(t_k))}{\partial p(t_k)}\overline{\alpha}' \Delta p_k
\end{aligned}$$

The first term is $\mathcal{O}(\Delta t)$ and the second $\mathcal{O}(\Delta t^{1/2})$. Therefore, for $\Delta t \to 0$, the full difference vanishes. This also applies to the first term in the right hand side of Eq. (3.2.31), the f term in the discretized version. Care should be taken with the noise term, and a similar analysis yields

$$g(\overline{x}_\alpha(t_k), \overline{p}_{\alpha'}(t_k))\xi(t_k)dt \sim \frac{\partial g(x(t_k),p(t_k))}{\partial p(t_k)}(\alpha' - \overline{\alpha}')\xi(t_k)\Delta p_k \sim \mathcal{O}(\Delta t^0)$$

Thus, for processes with a multiplicative noise such that the function g depends on the momentum the trajectories will diverge. Otherwise they will not.

Exercise 3.11 Write an algorithm that integrates the Langevin equation and reproduce and check the claims made about the trajectories in this Section.

3.3 Observables

As usual in statistical and quantum mechanics meaningful quantities are averaged observables. For an equilibrated system, due to ergodicity, one can either take an ensemble average or an average over a sufficiently long time-window. Out of equilibrium these do not coincide in general.

The interaction with the environment induces fluctuations and the Langevin equation is solved in a probabilistic sense,

$$x^{\rm sol}_{\xi_k}(t) = \mathcal{F}[(\xi_k), x_0, t]\,. \tag{3.3.35}$$

The index k labels different realizations of the thermal history, *i.e.* different realizations of the noise at each instant. x_0 is the initial condition $x_0 = q(0)$ and (ξ_k) encodes all noise values in the interval $[0, t]$. Equation (3.3.35) means that there is a different solution for each noise history.

3.3.1 One-time averages

Any *one-time* functional of x, $A[x](t)$, must be averaged over all histories of the thermal noise to obtain a deterministic result

$$\langle A[x](t)\rangle = \lim_{\mathcal{N}\to\infty} \sum_{k=1}^{\mathcal{N}} A[x^{\rm sol}_{\xi_k}](t) P(\xi_k) = \int \mathcal{D}\xi\, P[\xi]\, A[x^{\rm sol}_{\xi}](t)\ . \tag{3.3.36}$$

$\mathcal{N}$ is here the number of noise realizations. $P(\xi_k)$ is the probability distribution of the k-th thermal history. For a Gaussian noise

$$P(\xi_k) \propto \exp\left[-\frac{1}{2k_BT}\sum_{ab}\xi_k(t_a)\Gamma^{-1}(t_a - t_b)\xi_k(t_b)\right]\ . \tag{3.3.37}$$

The measure of the functional integral is just $\mathcal{D}\xi \equiv \prod_a d\xi(t_a)$.

3.3.2 Two-time correlations

Two-time functions characterize the out of equilibrium dynamics in a more detailed way and they are defined as

$$C_{AB}(t,t') \equiv \langle A[x](t)B[x](t')\rangle = \int \mathcal{D}\xi\, P[\xi]\, A[x^{\rm sol}_{\xi}](t) B[x^{\rm sol}_{\xi}](t')\ . \tag{3.3.38}$$

The observable $B[x]$ is measured at time t', the observable $A[x]$ is measured at time t for each noise realization and the average is taken afterwards.

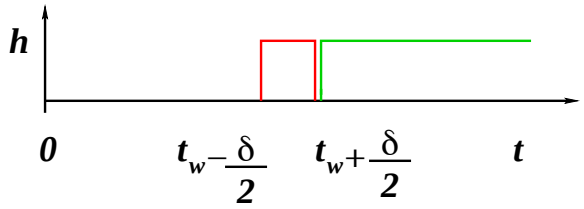

Figure 3.3: Left: an instantaneous perturbation applied at t_a. Right: a step perturbation applied at t_a and held constant for all subsequent times.

3.3.3 The averaged linear response

The instantaneous linear response is also a two-time function. Imagine that x represents the position of a Brownian particle that one *kicks* with a weak perturbing force at time $t' = t_a$ (see Fig. 3.3). The subsequent position of the particle is modified by the perturbation. The linear response is given by the comparison of the perturbed dynamics with the unperturbed one, in which no force has been applied, up to linear order in the perturbation:

$$R_{AB}(t,t') \equiv \left. \frac{\delta \langle A[x] \rangle(t)}{\delta h_B(t')} \right|_{h_B=0} . \tag{3.3.39}$$

The subindex B indicates that the perturbation applied at t' is conjugated to the observable $B[x]$ when the Hamiltonian is modified as $H \to H - h_B B[x]$. The subindex A indicates that we examine how the observable $A[x]$ at time t reacts to the perturbation. At the end of the calculation we set $h_B = 0$ to extract the linear response. Keeping $h_B \neq 0$ yields information about the nonlinear terms in the response function. For *causal* systems the response function vanishes if $t' > t$.

One is also interested in the integrated linear response rather than the instantaneous one. This quantity represents the linear response of the system to a *step*-like perturbation of duration $t - t'$ that starts at t', as represented on the right panel of Fig. 3.3:

$$\chi_{AB}(t,t') \equiv \int_{t'}^{t} dt''\, R_{AB}(t,t'') . \tag{3.3.40}$$

Rather often results are presented in the frequency domain. One defines the Fourier transform and its inverse

$$\tilde{A}(\omega) = \int_{-\infty}^{\infty} dt\, \exp(-i\omega t)\, A(t) , \qquad A(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \exp(i\omega t)\, \tilde{A}(\omega) . \tag{3.3.41}$$

For a stationary process, the linear susceptibility, $\tilde{\chi}(\omega)$, is simply given by the Fourier transform of the linear response (3.3.39). However $R_{AB}(t,t')$ is not necessarily stationary out of equilibrium. Hence, we define two generalized linear susceptibilities,

$$\tilde{\chi}^{(1)}_{AB}(\omega,t') \equiv \int_0^{\infty} d\tau\, \exp(-i\omega\tau)\, R_{AB}(t'+\tau,t') , \tag{3.3.42}$$

$$\tilde{\chi}^{(2)}_{AB}(\omega,t) \equiv \int_0^{\infty} d\tau\, \exp(-i\omega\tau)\, R_{AB}(t,t-\tau) , \tag{3.3.43}$$

that reduce to the well-known expression for $\tilde{\chi}_{AB}(\omega)$ in a stationary system. Note that in the first line we kept the shorter time (t') fixed while in the second line we kept the longer time (t) fixed. These expressions have a real and an imaginary part that yield the in-phase ($\tilde{\chi}'$) and the out-of-phase ($\tilde{\chi}''$) susceptibilities, respectively. The integrations run over positive values of τ only due to causality.

The linear response as a correlation with the noise

Thanks to the Novikov theorem, one can derive a useful expression for the linear response in the absence of an applied field. Take the simple case in which one is interested in the linear response of a generic function of the stochastic variable to a linear perturbation applied to the stochastic variable:

$$R(t,t') = \left.\frac{\partial\langle x(t)\rangle}{\partial h(t')}\right|_{h=0} \tag{3.3.44}$$

for the Langevin process with $F \mapsto F + h$

$$m\dot{x} = p \qquad\qquad \dot{p} + \frac{\gamma_0}{m}p = F + h + \xi \tag{3.3.45}$$

Then, it is clear that

$$\left\langle \frac{\delta f_\xi[x(t),p(t)]}{\delta h(t')} \right\rangle = \left\langle \frac{\delta f_\xi[x(t),p(t)]}{\delta \xi(t')} \right\rangle \tag{3.3.46}$$

for any $f_\xi[x(t),p(t)]$ and using Novikov's theorem

$$2k_BTR_{fx}(t,t') = \langle f_\xi[x(t),p(t)]\xi(t')\rangle \tag{3.3.47}$$

To compute the linear response from its definition can be hard. One needs to apply a sufficiently strong field to have a signal but also take it to zero to ensure the linear response regime. For these reasons several expressions of the linear response as correlation of observables in the absence of perturbation have been derived and used. We refer to them in Sec. 3.3.5.

3.3.4 Higher-order correlations

Up to now we have only discussed one-point and two-point functions. In general problems, higher order functions are not trivially related to the previous ones and bear richer information. These are *four-point functions*, $\langle A(t)B(t')C(t'')D(t'')\rangle$, or any other form of a more general type. In most of the solvable models we shall discuss below, and in most of the approximations used to analyze realistic models, higher-order functions do not appear. The reasons for their disappearance are manifold. In simplified models one can simply prove that higher order functions are exactly given in terms of one and two-point functions. In more realistic cases, higher order functions are approximated with expressions that depend on one and two-point functions only. This is done, for instance, in Gaussian approximations and mode-coupling theory [24]. However, a complete solution to a finite dimensional model should be able to predict the behavior of such higher order correlations.

3.3.5 The fluctuation dissipation theorem

The fluctuation dissipation theorem (FDT) is a model independent relation between the linear response and the correlation function. It states that in equilibrium the induced and spontaneous fluctuations have the same origin [57]. Out of equilibrium the FDT does not need to hold. Modifications of this relation with an interesting structure have been found in the slow relaxation of spin-glass models [58] and later in a variety of other probelms [59–61]. These modifications turn out of have a therodynamic interpretation with temperature replaced by an effective temperature [109], see the reviews [62, 64, 65].

The FDT and its violation can be partially understood from the following considerations. For simplicity, let us look at a single particle system in one dimension by described a variable $y(t)$ which satisfies the Langevin equation

$$\frac{d}{dt}y(t) = -F[y](t) + \xi(t) \tag{3.3.48}$$

where ξ is a Gaussian random noise with zero mean and correlation

$$\langle \xi(t)\, \xi(t') \rangle = 2k_B T\, \delta(t-t') \ , \tag{3.3.49}$$

T being the temperature.

Taking $t > t'$ for definiteness, the equation of motion (3.3.48) implies

$$\left(\frac{\partial}{\partial t'} - \frac{\partial}{\partial t} \right) C(t,t') = 2k_B T R(t,t') + A(t,t') \tag{3.3.50}$$

where we have used $\langle y(t)\, \xi(t') \rangle = 2k_B T\, R(t,t')$ and we defined

$$A(t,t') \equiv \langle F[y](t)\, y(t') - F[y](t')\, y(t) \rangle \ . \tag{3.3.51}$$

At equilibrium the correlation functions satisfy $\langle B(t) D(t') \rangle = \langle B(t') D(t) \rangle$, if $B(t)$ and $D(t')$ are any two functions of $y(t)$. This is a consequence of the time reversal symmetry. Hence the asymmetry A vanishes and the fluctuation-dissipation theorem may be recovered by using the invariance under translations in time of the correlation functions at equilibrium:

$$C(t,t') \ = \ C(t-t') \ \Rightarrow \ \left(\frac{\partial}{\partial t'} + \frac{\partial}{\partial t} \right) C(t,t') \ = \ 0 \tag{3.3.52}$$

for $t \geq t'$ and

$$R(t,t') = \beta\, \frac{\partial C(t,t')}{\partial t'} \ . \tag{3.3.53}$$

A system can be out of equilibrium still respecting time-translational invariance but keeping the asymmetry A as in a NESS, or it can also break this time-translational invariance.In both cases Eq. (3.3.53) is not valid and a generalization has to be considered.

The argument above was applied to the Markov Langevin equation in the Smoluchowski limit. The FDT in the very same form (3.3.53) holds also for more complex processes (non-Markov, with inertia) provided they take the system to equilibrium.

In mean-field spin-glass models the auto-correlation and response functions are defined as $C(t,t') = (1/N)\sum_{i=1}^{N}\langle s_i(t)s_i(t')\rangle$ and $R(t,t') = (1/N)\sum_{i=1}^{N}\delta\langle s_i(t)\rangle/\delta h_i(t')$, respectively. In the analysis of the asymptotic dynamics, that $t,t' \to \infty$ after $N \to \infty$, it has been proposed that, for long enough times and small time differences, $t,t' \to \infty$ and $(t-t')/t \ll 1$, FDT is satisfied, while for long enough times and long time differences, $t,t' \to \infty$ and $(t-t')/t \sim O(1)$,

$$R(t,t') = \beta\theta(t-t')\, X[C(t,t')]\, \frac{\partial C(t,t')}{\partial t'} \ . \tag{3.3.54}$$

A self-consistent asymptotic solution for the mean-field out of equilibrium dynamics within this assumption has been found both for the p-spin spherical and the Sherrington-Kirkpatrick models [64, 65].

Equation (3.3.50) - and its generalizations for other types of stochastic processes [66] - has been used to measure the linear response function without the application of a perturbation [67–71].

In the following section we will see some simple examples where FDT holds and is violated. Interestingly enough, the FDT serves as a very stringent test of equilibration. It is much more sensitive than simply looking at the convergence of one-time observables, or the stationarity of correlation functions. Indeed, one can have non-equilibrium steady states in which FDT is violated. Experiments in which FDT has been tested in biological systems are used to test the dead/alive state.

3.3.6 Fluctuations

All quantities defined in this Section were averaged over the noise. One can also be interested in studying their distribution functions over the realizations of the noise. For example,

$$P(A[x^{\rm sol}_\xi](t)) \qquad P(A[x^{\rm sol}_\xi](t)B[x^{\rm sol}_\xi](t')) \qquad P(A[x^{\rm sol}_\xi](t)\xi(t')) \ . \tag{3.3.55}$$

This is the route followed in [72] and references therein in the study of dynamic fluctuations in glassy systems.

3.4 The basic processes

We will discuss the motion of the particle in some $1d$ representative potentials: under a constant force, in a harmonic potential, in the flat limit of these two (Fig. 3.4) and the escape from a metastable state and the motion in a double well potential (Fig. 3.14).

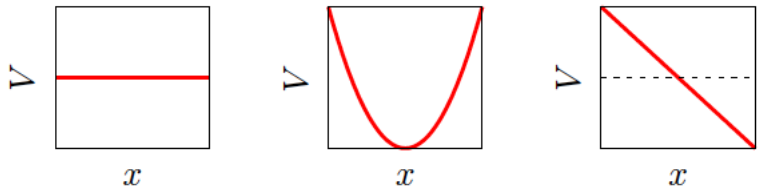

Figure 3.4: Three representative one-dimensional potentials.

3.4.1 A constant force

Let us first consider the case of a constant force, F. The first thing to notice is that the Maxwell-Boltzmann measure

$$P_{\rm GB}(v,x) \propto e^{-\beta\left(\frac{v^2}{2m}+V(x)\right)} \tag{3.4.1}$$

is not normalizable if the size of the line is infinite, due to the $\exp[-\beta V(x)] = \exp(\beta F x)$ term. Let us then study the evolution of the particle's velocity and position to show how these variables behave and the fact that they do very differently.

The problem to solve is a set of two coupled stochastic first order differential equations on $\{v(t), x(t)\}$, one needs two initial conditions v_0 and x_0.

The velocity

The time-dependent velocity follows from the integration of Eq. (3.1.1) over time

$$v(t) = v_0\ e^{-\frac{\gamma_0}{m}t} + \frac{1}{m}\int_0^t dt'\ e^{-\frac{\gamma_0}{m}(t-t')}\ [\,F + \xi(t')\,]\ , \qquad\qquad v_0 \equiv v(t=0)\ .$$

The velocity is a Gaussian variable that inherits its average and correlations from the ones of ξ. Using the fact that the noise has zero average

$$\langle v(t)\rangle = v_0\ e^{-\frac{\gamma_0}{m}t} + \frac{F}{\gamma_0}\left(1 - e^{-\frac{\gamma_0}{m}t}\right)\ .$$

In the short time limit, $t \ll t_r^v = m/\gamma_0$, this expression approaches the Newtonian result ($\gamma_0 = 0$) in which the velocity grows linearly in time $v(t) \approx v_0(1 - \gamma_0/m\ t) + F/m\ t = v_0 + (F\gamma_0^{-1} - v_0)\ \gamma_0 m^{-1}\ t$. In the opposite long time limit, $t \gg t_r^v = m/\gamma_0$, for all initial conditions v_0 the averaged velocity decays exponentially to the constant value F/γ_0. The saturation when the bath is active ($\gamma_0 \neq 0$) is due to the friction term.

$$\langle v(t)\rangle = \begin{cases} v_0 + \left(\frac{F}{m} - \frac{v_0\gamma_0}{m}\right)\ t & t \ll t_r^v \\ \frac{F}{\gamma_0} & t \gg t_r^v \end{cases}$$

The relaxation time separating the two regimes is

$$\boxed{t_r^v = \frac{m}{\gamma_0}} \tag{3.4.2}$$

The velocity mean-square displacement is

$$\sigma_v^2(t) \equiv \langle (v(t) - \langle v(t) \rangle)^2 \rangle = \frac{k_B T}{m} \left(1 - e^{-2\frac{\gamma_0}{m} t} \right) \tag{3.4.3}$$

independently of F. This is an example of the regression theorem according to which the equilibrium fluctuations decay in time following the same law as the average value. The short and long time limits yield

$$\sigma_v^2(t) \equiv \langle (v(t) - \langle v(t) \rangle)^2 \rangle \simeq \frac{k_B T}{m} \begin{cases} \dfrac{2\gamma_0}{m}\, t & t \ll t_r^v \\ 1 & t \gg t_r^v \end{cases} \tag{3.4.4}$$

and the two expressions match at $t \simeq t_r^v/2$. The asymptotic limit is the result expected from equipartition of the velocity mean-square displacement, $\langle (v(t) - \langle v(t) \rangle)^2 \rangle \to \langle (v(t) - \langle v \rangle_{\rm stat})^2 \rangle_{\rm stat}$ that implies for the 'kinetic energy' $\langle K \rangle_{\rm stat} = k_B T/2$ only if the velocity is measured with respect to its average. In the heuristic derivation of the Langevin equation for $F = 0$ the amplitude of the noise-noise correlation, say A, is not fixed. The simplest way to determine this parameter is to require that equipartition for the kinetic energy holds $A/(\gamma_0 m) = T/m$ and hence $A = \gamma_0 T$. This relation is known under the name of fluctuation–dissipation theorem (FDT) of the second kind in Kubo's nomenclature. It is important to note that this FDT characterizes the surrounding fluid and not the particle, since it relates the noise-noise correlation to the friction coefficient. In the case of the Brownian particle this relation ensures that after a transient of the order of t_r^v, the bath maintains the fluctuations of the velocity, σ_v^2, constant and equal to its equilibrium value.

The velocity two-time connected correlation reads

$$\langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle] \rangle = \frac{k_B T}{m} \left[e^{-\frac{\gamma_0}{m}|t-t'|} - e^{-\frac{\gamma_0}{m}(t+t')} \right] .$$

This is sometimes called the Dirichlet correlator. This and all other higher-order velocity correlation functions approach a stationary limit when the shortest time involved is longer than t_r^v. At $t = t'$ one recovers the mean-square displacement computed in Eq. (3.4.3). When both times are short compared to t_r^v the two-time correlator behaves as $\sim 2 k_B T \gamma_0 / m^2 \ \max(t, t')$. When at least one of the two times is much longer than t_r^v the second term vanishes and one is left with an exponential decay as a function of time delay:

$$C_{vv}^c(t, t') \equiv \langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle] \rangle \to \frac{k_B T}{m} e^{-\frac{\gamma_0}{m}|t-t'|} \qquad t, t' \gg t_r^v \, . \tag{3.4.5}$$

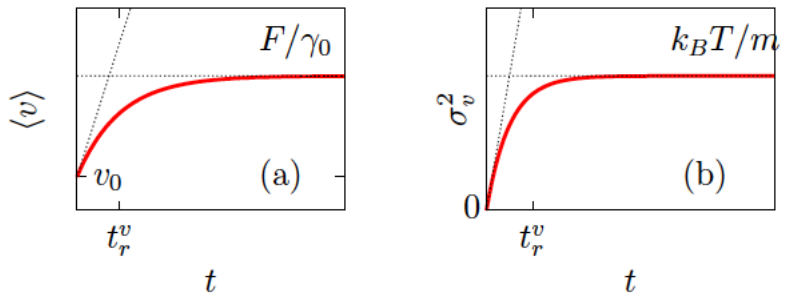

Figure 3.5: Results for the constant force problem. (a) Mean velocity as a function of time. (b) Velocity mean-square displacement as a function of time. In both cases the linear behavior at short times, $t \ll t_r^v$, and the saturation values are shown. The slopes are F/m and $k_BT/m \times 2\gamma_0/m$, respectively.

The two-time connected correlation falls off to, say, $1/e$ in a decay time

$$\boxed{t_d^v = \frac{m}{\gamma_0}} \tag{3.4.6}$$

In this simple case $t_r^v = t_d^v$ but this does not necessarily happen in more complex cases.

More generally one can show that for times $t_1 \geq t_2 \geq \cdots \geq t_n \geq t_r^v$:

$$\boxed{\langle \delta v(t_1 + \Delta) \dots \delta v(t_n + \Delta) \rangle = \langle \delta v(t_1) \dots \delta v(t_n) \rangle \quad \text{(TTI)}} \tag{3.4.7}$$

with $\delta v(t) = v(t) - \langle v \rangle(t)$, for all delays Δ. Time-translation invariance (TTI) or stationarity is one generic property of equilibrium dynamics. Another way of stating (3.4.7) is

$$\langle v(t_1) \dots v(t_n) \rangle = f(t_1 - t_2, \dots, t_{n-1} - t_n) \; . \tag{3.4.8}$$

Another interesting object is the linear response of the averaged velocity to a small perturbation applied to the system in the form of $V \to V - fx$, i.e. a change in the slope of the potential in this particular case. One finds

$$R_{vx}(t,t') \equiv \left. \frac{\delta \langle v(t) \rangle_f}{\delta f(t')} \right|_{f=0} = \frac{1}{m} \, e^{-\frac{\gamma_0}{m}(t-t')} \, \theta(t-t') \tag{3.4.9}$$

$$\simeq \frac{1}{k_BT} \langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle] \rangle \, \theta(t-t') \tag{3.4.10}$$

the last identity being valid in the limit t or $t' \gg t_r^v$. This is an fdt relation between a linear response, $R_{vx}(t,t')$, and a connected correlation, $C_{vv}^c(t,t')$, that holds for one of the particle variables, its velocity, when this one reaches the stationary state.

$$\boxed{k_BT \; R_{vx}(t,t') = C_{vv}^c(t,t') \; \theta(t-t') \qquad \text{(FDT)} \; .} \tag{3.4.11}$$

In conclusion, the velocity is a Gaussian variable that after a characteristic time t_r^v verifies 'equilibrium'-like properties: its average converges to a constant (determined by F), its multi-time correlation functions become stationary and a fluctuation-dissipation theorem links its linear response to the connected correlation at two times.

The position

The particle's position, $x(t) = x_0 + \int_0^t dt' v(t')$ is still a Gaussian random variable:

$$\begin{aligned} x(t) &= x_0 + v_0\, t_r^v + \frac{F}{\gamma_0}(t - t_r^v) + t_r^v \left(\frac{F}{\gamma_0} - v_0\right) e^{-\frac{\gamma_0}{m}t} \\ &\quad + \frac{1}{m}\int_0^t dt' \int_0^{t'} dt''\; e^{-\frac{\gamma_0}{m}(t'-t'')}\; \xi(t'') \; . \end{aligned} \tag{3.4.12}$$

Its noise-average behaves as the Newtonian result, ballistic motion,

$$\boxed{\langle x(t)\rangle \simeq x_0 + v_0 t + \frac{\gamma_0}{2m}\left(\frac{F}{\gamma_0} - v_0\right) t^2 \qquad \text{for} \qquad t \ll t_r^v} \tag{3.4.13}$$

at short times and it crossover to

$$\boxed{\langle x(t)\rangle \to x_0 + v_0\, t_r^v + \frac{F}{\gamma_0}(t - t_r^v) \qquad \text{for} \qquad t \gg t_r^v} \tag{3.4.14}$$

at long times. Note the reduction with respect to ballistic motion ($x \propto Ft^2$) due to the friction drag and the fact that this one-time observable does not saturate to a constant.

An interesting result, that we will use later, is the fact that the coordinate and the noise have vanishing correlation at equal times: $\langle x(t)\xi(t)\rangle = 0$. This can be easily proven by multiplying the expression for $x(t)$ by $\xi(t)$ and taking the average.

The position mean-square displacement approaches

$$\boxed{\sigma_x^2(t) \equiv \langle (x(t) - \langle x(t)\rangle)^2\rangle \to 2D_x t \quad \text{with} \quad D_x \equiv \frac{k_B T}{\gamma_0} \quad \text{(Diffusion)}} \tag{3.4.15}$$

in the usual $t \gg t_r^v$ limit, that is to say normal diffusion with the diffusion constant D_x. This expression can be computed using $x(t) - \langle x(t)\rangle$ as obtained from the $v(t) - \langle v(t)\rangle$ above (and it is quite a messy calculation) or one can simply go to the Smoluchowski limit, taking advantage of the knowledge of what we have just discussed on the behaviour of velocities, and obtain diffusion in two lines.

Exercise 3.12 Do the calculation sketched above.

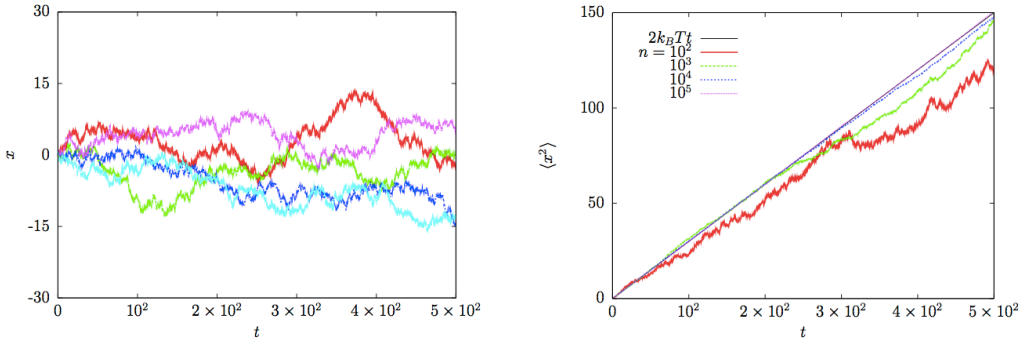

Figure 3.6: Left panel: five runs of the Langevin equation in the over-damped limit with no external force and a Gaussian white noise at temperature T and $\gamma_0 = 1$. Right panel: the average $\langle x^2 \rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. The straight line represents the normal diffusion $\langle x^2 \rangle \simeq 2k_B T t$.

When the friction coefficient γ_0 is given by the Stokes law, $\gamma_0 = 6\pi\eta a$ for a spherical particle with radius a in a liquid with dynamic viscosity η, the diffusion constant is given by the Stokes-Einstein relation $D_x = k_B T/(6\pi\eta a)$.

The searched result can also be found as follows. Multiply the Langevin equation evaluated at t by x evaluated at the same instant and use an obvious identity to find

$$m x \dot{v} = m\left(\frac{d}{dt}(xv) - v^2\right) = -\gamma_0 v x + xF + x\xi \tag{3.4.16}$$

Take now the noise average. Use the fact that the average of $x\xi$, when the two factors are evaluated at the same time, vanishes identically, and exchange time-derivative and noise-average (assuming this operation is permitted). The resulting equation is

$$\frac{d}{dt}\langle xv \rangle = -\frac{\gamma_0}{m}\langle vx \rangle + \frac{F}{m}\langle x \rangle + \langle v^2 \rangle \ . \tag{3.4.17}$$

The last two terms in the right-hand-side are a known time-dependent function, $A(t)$:

$$A \equiv \frac{F}{m}\langle x \rangle + \langle v^2 \rangle \ , \tag{3.4.18}$$

$$\frac{F}{m}\langle x \rangle = \frac{F}{m}\left[x_0 + v_0 t_r^v + \frac{F}{\gamma_0}\left(t - t_r^v\right) + t_r^v\left(\frac{F}{\gamma_0} - v_0\right)e^{-\frac{\gamma_0}{m}t}\right] \ , \tag{3.4.19}$$

$$\langle v^2 \rangle = \frac{k_B T}{m}\left(1 - e^{-2\frac{\gamma_0}{m}t}\right) + \left[v_0 e^{-\frac{\gamma_0}{m}t} + \frac{F}{\gamma_0}\left(1 - e^{-\frac{\gamma_0}{m}t}\right)\right]^2 \ . \tag{3.4.20}$$

One can now integrate Eq. (3.4.17) over time

$$\langle xv \rangle = x_0 v_0\ e^{-\frac{\gamma_0}{m}t} + \int_0^t dt'\ e^{-\frac{\gamma_0}{m}(t-t')} A(t') \tag{3.4.21}$$

to find a rather lengthy expression. In the long time limit, $t \gg t_r^v$, we drop all exponentially decaying terms to obtain

$$\langle xv \rangle \quad \to \quad \frac{k_B T}{\gamma_0} + \frac{F}{\gamma_0}\left(t_r^v v_0 + x_0\right) + \frac{F^2}{\gamma_0^2}\left(t - t_r^v\right) \tag{3.4.22}$$

Now, using $\langle xv \rangle = \frac{1}{2}\frac{d}{dt}\langle x^2 \rangle$ one finally finds

$$\langle x^2 \rangle \to 2\frac{k_B T}{\gamma_0} t + 2\frac{F}{\gamma_0}\left(t_r^v v_0 + x_0\right) t + \frac{F^2}{\gamma_0^2}\left[\left(t - t_r^v\right)^2 - t_r^2\right] \tag{3.4.23}$$

The last two terms are $\langle x \rangle^2$ in the same regime of times. Therefore, Eq. (3.4.15) is recovered.

Another way to measure the diffusion coefficient directly from the velocity that is commonly used in the literature is

$$\boxed{D_x = \lim_{\tau\to\infty} \lim_{t'\to\infty} \int_0^\tau dt' \ \langle \delta v(\tau + t') \delta v(t') \rangle \ .} \tag{3.4.24}$$

One can check that it gives the same result.

In contrast to the velocity mean-square displacement this quantity does not saturate at any finite value. Similarly, the particle displacement between two different times t and t' is

$$\Delta_{xx}(t, t') \equiv \langle [x(t) - x(t')]^2 \rangle \to 2D_x |t - t'| \ . \tag{3.4.25}$$

It is interesting to note that the force dictates the mean position but it does not modify the fluctuations about it (similarly to what it did to the velocity). Δ_{xx} is stationary for time lags longer than t_r^v.

The two-time position-position connected correlation reads

$$C_{xx}^c(t, t') = \langle (x(t) - \langle x(t) \rangle)(x(t') - \langle x(t') \rangle) \rangle = \dots \tag{3.4.26}$$

Exercise 3.13 compute this correlation function.

The linear response of the particle's position to a kick linearly applied to itself at a previous time, in the form $V \to V - fx$ at $t' < t$, is

$$R_{xx}(t, t') \equiv \left. \frac{\delta \langle x(t) \rangle_f}{\delta f(t')} \right|_{f=0} = \frac{1}{\gamma_0} \left[1 - e^{-\frac{\gamma_0}{m}(t - t')}\right] \theta(t - t') \ , \tag{3.4.27}$$

with the limits

$$R_{xx}(t, t') \to \begin{cases} m^{-1} \ (t - t') \ \theta(t - t') & t - t' \ll t_r^v \ , \\ \gamma_0^{-1} \ \theta(t - t') & t - t' \gg t_r^v \ . \end{cases} \tag{3.4.28}$$

A simple calculation proves that in the short time-differences limit this is the result for Newton dynamics.

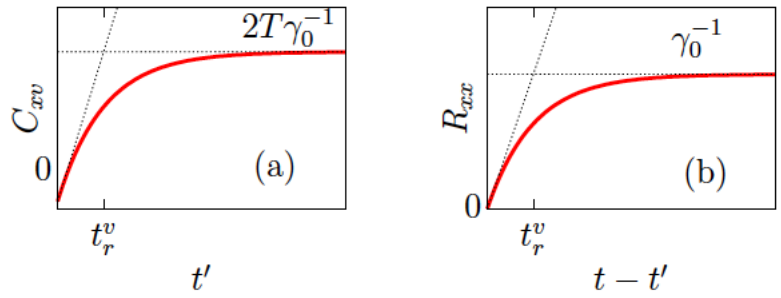

Figure 3.7: Results for the constant force problem. (a) The correlation between the position and the velocity of the particle measured at different times. (b) The linear response of the position to a kick applied linearly to itself at a previous time. In both cases the linear behavior at short times, $t \ll t_r^v$ and the saturation values are shown.

Exercise 3.14 show the property mentioned above.

The correlation between the position and the velocity reads

$$\langle (x(t) - \langle x(t) \rangle)(v(t') - \langle v(t') \rangle) \rangle = \frac{2k_B T}{m} \left[\frac{m}{\gamma_0} - \left(1 + \frac{m}{\gamma_0} \right) e^{-\frac{\gamma_0}{m} t'} \right]$$
$$\to \frac{2k_B T}{\gamma_0} \tag{3.4.29}$$

and it is only a function of t'. One notices that in the asymptotic limit in which both sides of the equation saturate

$$\boxed{2k_B T \; R_{xx}(t,t') = C^c_{xv}(t,t') \quad \text{for } \; t - t' \gg t_r^v \; \text{ and } \; t' \gg t_r^v \; ,} \tag{3.4.30}$$

with a factor of 2 different from the relation in Eq. (3.4.11).

In conclusion, the position is also a Gaussian variable but it is explicitly out of equilibrium. Its average and variance grow linearly in time, the latter as in normal diffusion, and the fluctuation-dissipation relation has an additional factor of $1/2$ (or 2, depending on on which side of the equality one writes it) with respect to the form expected in equilibrium.

A measure for the time dependent fluctuating position and velocity can be written down, taking advantage of the fact that both variables are Gaussian:

$$P(v,x) \propto \exp\left[-\frac{1}{2} \int dt \int dt' \; \delta y^t(t) A(t,t') \delta y(t') \right] \tag{3.4.31}$$

with the 2×2 matrix A being the inverse of the matrix of correlations, ${A^{-1}}_{ij}(t,t') = \langle \delta y_i(t) \delta y_j(t') \rangle$ with $i,j = 1,2$, $\delta y^t(t) = (\delta v(t) \; \delta x(t))$ and $\delta v(t) = v(t) - \langle v(t) \rangle$ (similarly for x). The correlations are given above so the dynamic pdf can be easily constructed. There will be elements in the matrix that remain time-dependent for all times.

Exercise 3.15 Confront

$$\langle v^m(t)x^n(t)x^k(t')\rangle \qquad \text{and} \qquad \langle v^m(t)x^n(t)kx^{k-1}(t')v(t')\rangle \ , \tag{3.4.32}$$

conclude.

The energy

The averaged kinetic energy can be computed using $\langle v^2(t)\rangle = \sigma_v^2(t) + \langle v(t)\rangle^2$ and the results already derived. It reaches, in the $t \gg t_r^v$ limit, a constant value: $\langle K(t)\rangle \to k_BT/2 + F/(2\gamma_0)$. The averaged potential energy diverges in the long-time limit if $F \neq 0$ since the potential is unbounded in the $x \to \infty$ limit: $\langle V(t)\rangle = -F\langle x(t)\rangle \simeq -F^2/\gamma_0 t$ for $t \gg t_r^v$. In the particular case $F = 0$ the total energy is just kinetic and it approaches the constant expected from equipartition asymptotically $\langle K(t)\rangle \to k_BT/2$.

It is also interesting to investigate the sign of dE/dt on the mean, $\langle dE/dt\rangle = -\gamma_0\langle v^2\rangle + \langle v\xi\rangle$. The first term tends to $-\gamma_0 k_BT/m - F$. The second term also yields a non-trivial contribution $\langle v\xi\rangle \to m^{-1}\int_0^t dt' e^{-\gamma_0(t-t')/m}\langle \xi(t)\xi(t')\rangle = \gamma_0 k_BT/m$. Adding these two together one finds $\langle dE/dt\rangle \to -F$ asymptotically, for $t \gg t_r^v$.

Two kinds of variables

This example shows that even in this very simple problem the velocity and position variables have distinct behavior: the former is in a sense trivial, after the transient t_r^v and for longer times, all one-time functions of $v - F/\gamma_0$ saturate to their equilibrium-like values and the correlations are stationary. Instead, the latter remains non-trivial and evolving out of equilibrium. One can loosely ascribe the different behavior to the fact that the velocity feels a confining kinetic energy $K = mv^2/2$ while the position feels an unbounded potential $V = -Fx$ in the case in which a force is applied, or a flat potential $V = 0$ if F is switched off. In none of these cases the potential is able to take the particle's position to equilibrium with the bath. The particle slides on the slope and its excursions forward and backward from the mean get larger and larger as time increases.

Over-damped (Smoluchowski) limit

Quite generally, the classical problems we are interested in are such that the friction coefficient γ_0 is large and the inertia term can be neglected, in other words, all times are much longer than the characteristic time t_r^v.

Ergodicity

The ergodic hypothesis states that, in equilibrium, one can exchange ensemble averages by time averages and obtain the same results. Out of equilibrium this hypothesis is not expected to hold and one can already see how dangerous it is to take time-averages in these cases by focusing on the simple velocity variable. Ensemble and time averages coincide only if the time-averaging is done over a time-window that lies after t_r^v but it does not if

the integration time-interval goes below t_r^v. Moreover, in the case of the position variable, there is no finite t_r^x.

Tests of equilibration have to be done very carefully in experiments and simulations. One can be simply mislead by, for instance, looking just at the velocities statistics.

Effect of a colored bath: anomalous diffusion

The anomalous diffusion ($F = 0$) of a particle governed by the generalized Langevin equation, Eq. (3.1.6), with colored noise characterized by power-law correlations as the ones given in Eq. (3.1.7), a problem also known as fractional Brownian motion, was studied in detail by N. Pottier [73]. The particle's velocity equilibrates with the environment although it does at a much slower rate than in the Ohmic case: its average and mean-square displacement decay as a power law - instead of exponentially - to their asymptotic values (still satisfying the regression theorem). The particle's mean square displacement is determined by the exponent of the noise-noise correlation,

$$\Gamma(t) \simeq t^{-\alpha} \qquad \text{and} \langle x^2(t) \rangle \simeq t^{\alpha} \ , \tag{3.4.33}$$

the dynamics is subdiffusive for $\alpha < 1$, diffusive for $\alpha = 1$ and superdiffusive for $\alpha > 1$. A time-dependent diffusion coefficient verifies $D_x(t) \equiv 1/2 \ d\langle x^2(t) \rangle / dt \propto t^{\alpha-1}$: it is finite and given by Eq. (3.4.25) for normal diffusion, it diverges for superdiffusion and it vanishes for subdiffusion. The ratio between the linear response and the time-derivative of the correlation ratio reads $TR_{xx}(t,t')/\partial_{t'} C_{xx}(t,t') = D_x(t-t')/[D_x(t-t') + D_x(t')]$. It approaches $1/2$ for normal diffusion and the two-time dependent function $1/[1 + (t'/(t-t'))^{\alpha-1}]$ in other cases.

Exercise 3.16 Work out these results.

Perrin's experiment

Jean-Baptiste Perrin used these results to measure the Avogadro number experimentally and, more importantly, give evidence for the discrete character of matter. The idea is already described in Lucretius's poem *De rerum natura, On the nature of things*. The reasoning goes as follows. Take a spherical tracer particle with radius a and immerse it in a liquid with viscosity η. These two quantities can be measured. Assume that the liquid behaves as a white noise. Stokes law states that the friction coefficient for this particle is

$$\gamma_0 = 6\pi\eta a \ . \tag{3.4.34}$$

The Boltzmann constant k_B is given by the gas constant R, that is also known, divided by the Avogadro number since $k_B = nR/N = R/N_A$ with n the number of moles and N the number of atoms in a gas. Therefore

$$\sigma_x^2(t) \simeq 2D_x t = \frac{R}{3\pi\eta a} \frac{T}{N_A} t \tag{3.4.35}$$

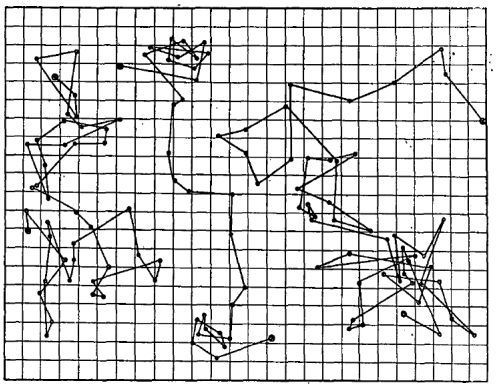

Figure 3.8: Colloidal particle trajectories. The radius of the particles is 0.53 μm, the points are successive positions taken at intervals of 30 s. The grid has spacing 3.2 μm. Image taken from Perrin's original article.

and, by measuring the tracer's diffusion one can extract N_A.

3.4.2 A harmonic potential and white additive noise

Full analysis

The Hamiltonian of a one-dimensional harmonic oscillator of mass m and spring constant k is

$$H_{\rm syst} = \frac{p^2}{2m} + \frac{kx^2}{2} \ . \tag{3.4.36}$$

The Langevin equation of motion reads

$$m\ddot{x}(t) = -\gamma_0 \dot{x}(t) - kx(t) + h(t) + \xi(t) \ . \tag{3.4.37}$$

with $h(t)$ a time-dependent deterministic force. By setting $k = 0$ one recovers the motion of a Brownian particle, see Sect. 3. ξ is the white noise with zero mean and correlations $\langle \xi(t)\xi(t')\rangle = 2k_B T\gamma_0 \delta(t-t')$.

Qualitative analysis: time-scales

From an order of magnitude analysis of the the three terms in the homogeneous equation one can extract the time-scales that rule the dynamics of this problem. The easiest way to determine these time scales is to first Fourier transform the homogeneous equation that determines the Green function

$$-m\omega^2 \tilde{x}(\omega) - i\gamma_0 \omega \tilde{x}(\omega) + k\tilde{x}(\omega) \ . \tag{3.4.38}$$

For the sake of completeness, we present this analysis for a coloured noise with power-law correlations, Eq. (3.1.17), in the limit in which the cut-off has been sent to infinity, for

which the equation above generalises to

$$-m\omega^2\tilde{x}(\omega) - i\gamma_0\omega^\alpha\tilde{\omega}^{\alpha-1}\tilde{x}(\omega) + k\tilde{x}(\omega)\ . \tag{3.4.39}$$

In the absence of dissipation ($\gamma_0 = 0$) the particle oscillates within the harmonic well, and the parameter dependence of the frequency and period of oscillation is determined with an order of magnitude argument

$$m\omega_{\rm osc}^2 \approx k \qquad \Rightarrow \qquad \omega_{\rm osc}^2 \approx \frac{k}{m} \quad \Rightarrow \qquad \boxed{t_{\rm osc} \approx \left(\frac{m}{k}\right)^{1/2}} \tag{3.4.40}$$

Under the action of the dissipative force new time-scales appear. First, one can expect that the competition between inertia and dissipation gives rise to the velocity relaxation time, t_r^v. Therefore,

$$m\omega_r^{v2} \approx \gamma_0\omega_r^{v\alpha}\tilde{\omega}^{\alpha-1} \qquad \Rightarrow \qquad \omega_r^v \approx \left(\frac{\gamma_0}{m}\ \tilde{\omega}^{1-\alpha}\right)^{1/(2-\alpha)} \tag{3.4.41}$$

and

$$\boxed{t_r^v \approx \left(\frac{m}{\gamma_0}\ \tilde{\omega}^{\alpha-1}\right)^{1/(2-\alpha)}} \tag{3.4.42}$$

In the particular case $\alpha = 1$ the bath becomes Ohmic and $t_r^v \approx m/\gamma_0$ as in Eq. (3.4.2).

Second, the comparison between dissipation and harmonic force yields

$$\gamma_0\omega_r^{x\alpha}\tilde{\omega}^{\alpha-1} \approx k \qquad \Rightarrow \qquad \omega_r^x \approx \left(\frac{k}{\gamma_0}\tilde{\omega}^{1-\alpha}\right)^{1/\alpha} \tag{3.4.43}$$

and

$$\boxed{t_r^x \approx \left(\frac{\gamma_0}{k}\ \tilde{\omega}^{\alpha-1}\right)^{1/\alpha}} \tag{3.4.44}$$

that for $\alpha = 1$ becomes $t_r^x \approx \gamma_0/k$ a time-scale that we will see appearing in the exact calculation below.

Now, we can compare these time-scales and conclude about the possible types of particle motion. If $t_{\rm osc} < t_r^x$ the particle continues to oscillate during its dissipative evolution while, on the contrary, if $t_{\rm osc} > t_r^x$, the oscillations are damped and the relaxation of observables is monotonic. One has

$$\begin{array}{lcll} t_{\rm osc} & < & t_r^x & \text{Underdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^\alpha > \gamma_0^2\ , \\ t_{\rm osc} & > & t_r^x & \text{Overdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^\alpha < \gamma_0^2\ . \end{array} \tag{3.4.45}$$

The crossover occurs at parameters such that $\gamma_0^2 \approx km$ for $\alpha = 1$, see below.

Finally, the comparison between the oscillation time, $t_{\rm osc}$, and the velocity relaxation time, t_r^v, yields

$$\begin{array}{lcll} t_{\rm osc} & < & t_r^v & \text{Underdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)} k^{2-\alpha} m^\alpha > \gamma_0^2 \ , \\ t_{\rm osc} & > & t_r^v & \text{Overdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)} k^{2-\alpha} m^\alpha < \gamma_0^2 \ , \end{array} \tag{3.4.46}$$

exactly the same conditions as for the position, as it should. The difference in behaviour between position and velocity is decided by the comparison between the relaxation time of the velocity and position. If $t_r^v \ll t_r^x$ the velocity equilibrates with the environment well before the position.

Quantitative analysis in the white noise case

The full differential equation (3.4.37) can be easily solved by first evaluating the Green function $G(t)$ from

$$m\ddot{G}(t) + \gamma_0 \dot{G}(t) + kG(t) = \delta(t) \ , \tag{3.4.47}$$

that, after Fourier transforming, implies

$$\tilde{G}(\omega) = 1/(-m\omega^2 - i\gamma_0\omega + k) \ . \tag{3.4.48}$$

The right-hand-side has two poles:

$$\omega_\pm = -\frac{i\gamma_0}{2m} \pm \sqrt{\frac{k}{m} - \frac{\gamma_0^2}{4m^2}} \ , \tag{3.4.49}$$

that are complex or imaginary depending on the relative values of the parameters:

$$4km - \gamma_0^2 > 0 \qquad \omega_\pm \ \text{complex (under-damped case)} \ , \tag{3.4.50}$$

$$4km - \gamma_0^2 \leq 0 \qquad \omega_\pm \ \text{imaginary (over-damped)} \ . \tag{3.4.51}$$

It is important to note that in both cases the poles are located in the lower half complex plane.

Using Cauchy's formula to transform back in time one finds that, for $t > 0$, the Green function reads

$$G(t) \ = \ \begin{cases} \dfrac{1}{m\omega_R} \sin\omega_R t \ e^{-|\omega_I| t} & \text{if } \ \omega_\pm = \pm\omega_R - i|\omega_I| \\ \dfrac{i}{m(\omega_+ - \omega_-)} \left(e^{-|\omega_I^{(+)}| t} - e^{-|\omega_I^{(-)}| t} \right) & \text{if } \ \omega_\pm = -i|\omega_I^{(+,-)}| \end{cases}$$

and it vanishes identically for $t < 0$. Two other important properties of $G(t)$ are $G(0) = 0$ and $m\dot{G}(0) = 1$ that follow from integrating (3.4.47) between $t = -\delta$ and $t = \delta$ and taking $\delta \to 0$. One also checks $2|\omega_I|\dot{G}(0) + \ddot{G}(0) = 0$ in the under-damped case.

In the under-damped case the time-dependent position of the particle is given by

$$x(t) = e^{-|\omega_I|t}\left\{[\dot{x}(0) + x(0)|\omega_I|]\ \frac{\sin\omega_R t}{\omega_R} + x(0)\cos\omega_R t\right\} + \int_0^\infty dt'\ G(t-t')\,[\xi(t') + h(t')] \tag{3.4.52}$$

and this can be rewritten as

$$x(t) = [\dot{x}(0) + x(0)|\omega_I|]mG(t) + x(0)[m\dot{G}(t) + |\omega_I|mG(t)] + \int_0^\infty dt'\ G(t-t')\,[\xi(t') + h(t')] \tag{3.4.53}$$

The first two terms on the RHS represent the effect of the initial conditions. Note that $G(t)$ is proportional to a Heaviside theta function and hence the integration over time has an effective upper limit at $t' = t$. One can find corresponding expression for the over-damped case.

Let us first discuss the asymptotic values of one-time quantities. The simplest cases are the averaged position and momentum themselves. In the absence of an external field, the potential is symmetric with respect to $x \to -x$ and $p \to -p$. Since the noise ξ has zero average, after a characteristic-time needed to forget the initial conditions, the average of both x and p vanish if $k \neq 0$. This is consistent with the result expected in equilibrium, $\langle x\rangle_{eq} = \langle p\rangle_{eq} = 0$, though it is not sufficient to prove that the particle equilibrates with its environment. The way in which this zero limit is approached depends strongly on the value of $4km - \gamma_0^2$ and we shall discuss it later.

When $k = 0$ the result is different. In the absence of external forces, while the average momentum vanishes, the average coordinate approaches a non-zero value for $t \gg t_c^v$, $\langle x(t)\rangle \to x(0) + p(0)/\gamma_0$: the initial condition is remembered forever by the particle's motion. It is a first indication of the non-equilibration of the coordinate for a flat potential.

Independently of the parameters k, γ_0 and T and as long as $m \neq 0$, after a tedious but straighforward calculation one finds that

$$\lim_{t\gg t_c^v} C_{pp}(t,t) = \lim_{t\gg t_c^v}\langle p(t)p(t)\rangle = mk_BT = \langle p^2\rangle_{eq}\ , \qquad t_c^v \equiv \frac{m}{\gamma_0}$$

where the last term indicates the static average. The same kind of calculation can be pursued to show that the average of any function of the momentum approaches its equilibrium limit asymptotically. This is good evidence for establishing the equilibration of the momentum. [Note that even if one of the characteristic times that determine the relaxation of the Green function diverges when $k = 0$, the velocity-velocity correlation is well-behaved since it only involves $\dot{G}(t)$.]

The observables that are functions of the position depend on the value of k. As long as $k > 0$ there is a confining harmonic potential for the position and all equal-time functions

of it approach an asymptotic limit that coincides with the one dictated by the equilibrium distribution. For instance,

$$\lim_{t\gg t_c^v} C_{xx}(t,t) = \lim_{t\gg t_c^v} \langle x(t)x(t)\rangle = \frac{k_B T}{k} = \langle x^2\rangle_{eq} \ .$$

Instead, if $k = 0$ there is no confining potential and the particle diffuses to infinity. If $k < 0$ the potential pushes the particle away from the origin towards $\pm\infty$ depending on the sign of the initial position. In none of these cases one can define a normalisable measure over the full infinite space and the position of the particles does not equilibrate with its environment. We discuss these two cases in detail below focusing on the study of the temporal evolution of correlation functions that depend on two times. We analyse the auto-correlation

$$C_{xx}(t,t') = \text{Effect of initial cond} + 2k_B T\gamma_0 \int_0^\infty ds\ G(t-s)G(t'-s) \ ,$$

and the linear response of the position of the particle at time t after a kick to this same variable has been applied at a previous time t'. From eqn (3.4.53), this is given by the Green function itself:

$$R_{xx}(t,t') \equiv \delta\langle x(t)\rangle/\delta h(t')|_{h=0} = G(t-t') \tag{3.4.54}$$

We distinguish the relaxation with different damping arising from different values of the parameters.

Relaxation in the under-damped limit

When $\omega_R \neq 0$, see eqn (3.4.50), the self correlation and linear response *oscillate* with frequency $\omega_R = \sqrt{k/m - \gamma_0^2/(4m^2)}$ and *decay exponentially* with a characteristic time $t_c = |\omega_I|^{-1} = 2m/\gamma_0$. They are displayed with dashed lines in Fig. **??**. The Fourier representation of the response function is shown in Fig. 3.9-left where we plot χ'_{xx} and χ''_{xx} as functions of ω. We observe that χ' changes sign at $\omega = \pm k/m$ and $\chi''(\omega)$ has peaks at $\omega = \pm\sqrt{k^2/m^2 - \gamma_0^2/4}$ with half-width at half maximum equal to $\gamma_0/2$. If $\gamma_0 \to 0$ these peaks approach the frequencies $\pm k/m$ of the undamped oscillator.

Relaxation in the over-damped limit

If, instead, we take the case in eqn (3.4.51) for which $\omega_R = 0$ (and $k \neq 0$) the self correlation and linear response have *pure exponential* decays with two time constants:

$$\begin{aligned} t_{fast} = \omega_-^{-1} &= \frac{2m}{\gamma_0 + \sqrt{\gamma_0^2 - 4km}} \to \frac{m}{\gamma_0} \equiv t_c^v \\ t_{slow} = \omega_+^{-1} &= \frac{2m}{\gamma_0 - \sqrt{\gamma_0^2 - 4km}} \to \frac{\gamma_0}{k} \equiv t_c^x \end{aligned} \quad \text{when } \ 4km \ll \gamma_0^2 \tag{3.4.55}$$

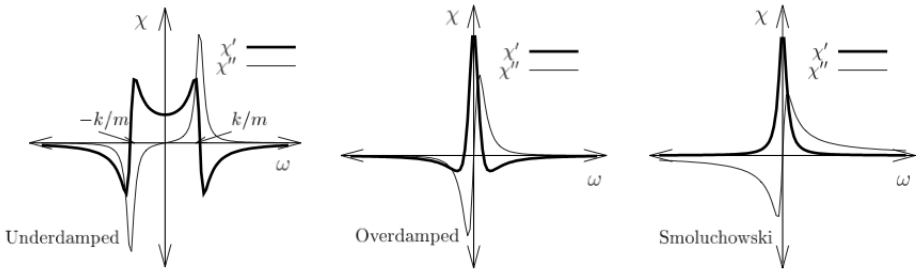

Figure 3.9: Green functions of the damped harmonic oscillator in different limits.

When $km \ll \gamma_0^2$ the fast decay time, which is the caracteristic time for relaxation of the velocity correlations, is much shorter than the slow one, $t_{fast} \ll t_{slow}$. For long observation times compared to t_{slow} one can neglect the fast mode. This is equivalent to neglecting the inertial term in the original Langevin equation and using the Smoluchowski limit to construct the properties of the coordinate.

The real and imaginary parts of the Fourier transform of the linear response are usually called χ' and χ''. χ' is peaked at the origin. In the extreme over-damped limit in which one can neglect inertia χ''/ω is a Lorentzian centered at the origin with width t_{slow}^{-1}.

Relaxation in the Smoluchowski limit

In this purely viscous case, where $m = 0$, there is only one characteristic time left, $t_c^x = \gamma_0/k$. The response decays exponentially, $R(t) = \gamma_0^{-1} e^{-t/t_c^x}$ and the susceptibility is then given by

$$\tilde{\chi}(\omega) = \frac{1}{-i\gamma_0\omega + k} = \frac{k}{k^2 + \gamma_0^2\omega^2} + i\frac{\gamma_0\omega}{k^2 + \gamma_0^2\omega^2} \ .$$

Its real part is positive for all values of ω and the imaginary part is usually said to take a *Debye* form. See the right panel in Fig. 3.9.

Diffusion in the random walk limit

When $k \to 0$ the coordinate x does not have a confining potential and a normalized equilibrium distribution cannot be defined for this degree of freedom. In this case there is no reason to expect that any equilibrium property will apply to this variable. Indeed, when $k \to 0$ the characteristic time t_{slow} diverges: there is no relaxation and a Brownian particle diffuses. The Green function approaches, exponentially in $t - t'$, a finite limit:

$$G(t - t') \sim \frac{1}{\gamma_0} \left(1 - e^{-\frac{\gamma_0}{m}(t-t')}\right) \ . \tag{3.4.56}$$

For any fixed time-difference, the correlation function diverges linearly with the shorter time. If $t' \leq t$, for $t' \gg t_c^v$ and $t - t'$ fixed, choosing the simplest initial condition

$x(0) = p(0) = 0$, we have

$$\lim_{t' \gg t_c^v,\ t-t' \text{ fixed}} C_{xx}(t,t') = -\frac{2mk_BT}{\gamma_0^2}\left(1 - \frac{1}{2}e^{-\frac{\gamma_0}{m}|t-t'|}\right) + \frac{2k_BT}{\gamma_0}\min(t,t')$$

In particular, at equal long times $t = t' \gg m/\gamma_0$, $C_{xx}(t,t) \sim 2k_BT/\gamma_0\ t$. This demonstrates the breakdown of stationarity and hence the fact that the system is far from equilibrium. For $\min(t,t')$ fixed, $C_x x(t,t')$ decays exponentially with the time-difference towards the constant $2k_BT/\gamma_0(\min(t,t') - m/\gamma_0)$.

The displacement Δ_{xx} instead is a simpler function of $t-t'$, and for long time-differences it becomes the usual diffusion law.

Over-damped limit

Another relevant example is the relaxation of a particle in a harmonic potential, with its minimum at $x^* \neq 0$:

$$V(x) = \frac{k}{2}(x - x^*)^2\ , \tag{3.4.57}$$

in contact with noise that we take to be white as the simpler starting case. The potential confines the particle and one can then expect the coordinate to reach an equilibrium distribution.

This problem can be solved exactly keeping inertia for all values of γ_0 but the calculation is slightly tedious. The behavior of the particle velocity has already been clarified in the constant force case. We now focus on the over-damped limit,

$$\gamma_0\dot{x} = -k(x - x^*) + \xi\ , \tag{3.4.58}$$

with k the spring constant of the harmonic well, that can be readily solved,

$$x(t) = x_0\ e^{-\frac{k}{\gamma_0}t} + \gamma_0^{-1}\int_0^t dt'\ e^{-\frac{k}{\gamma_0}(t-t')}\ [\xi(t') + kx^*]\ , \qquad x_0 = x(0)\ . \tag{3.4.59}$$

This problem becomes formally identical to the velocity dependence in the previous example.

Convergence of one-time quantities

The averaged position is

$$\boxed{\langle x(t) - x^*\rangle = (x_0 - x^*)e^{-\frac{k}{\gamma_0}t} \to 0 \qquad t_r^x \gg \gamma_0/k \quad \text{(Convergence)}} \tag{3.4.60}$$

Of course, one-time quantities should approach a constant asymptotically if the system equilibrates with its environment.

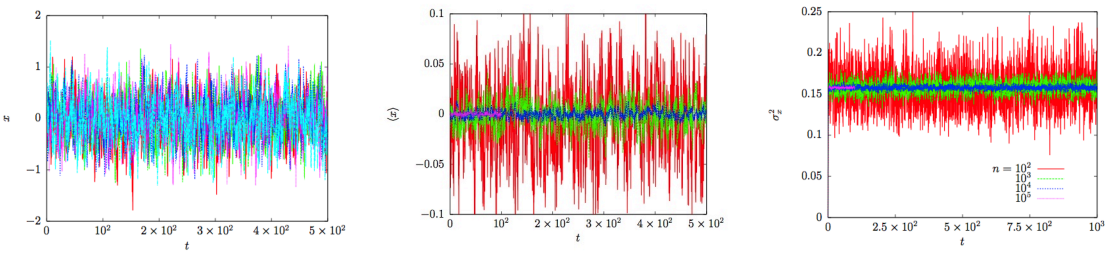

Figure 3.10: Left panel: five runs of the Langevin equation in the over-damped limit with a quadratic external potential (oscillator) and a Gaussian white noise at temperature T. Central panel: the average $\langle x \rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. Right panel: the variance $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = k_B T/k$.

Two-time quantities

The two-time connected correlation (where one extracts, basically, the asymptotic position x^*) reads

$$\langle \delta x(t) \delta x(t') \rangle = k_B T \ k^{-1} \ e^{-\frac{k}{\gamma_0}(t+t')} \left[e^{2\frac{k}{\gamma_0} \min(t,t')} - 1 \right] \ . \tag{3.4.61}$$

Again, the Dirichlet correlator ($\delta x(t) = x(t) - \langle x(t) \rangle$). For at least one of the two times going well beyond the position relaxation time $t_r^x = \gamma_0/k$ the memory of the initial condition is lost and the connected correlation becomes stationary:

$$C_c(t,t') = \langle \delta x(t) \delta x(t') \rangle \to k_B T \ k^{-1} \ e^{-\frac{k}{\gamma_0}|t-t'|} \qquad \min(t,t') \gg t_r^x \ . \tag{3.4.62}$$

For time-differences that are longer than $t_d^x = \gamma_0/k$ the correlation decays to $1/e$ and one finds $t_d^x = t_r^x$. Interestingly enough, the relaxation and decay times diverge when $k \to 0$ and the potential becomes flat.

Note that when the time-difference $t - t'$ diverges the average of the product factorizes, in particular, for the correlation one gets

$$\langle x(t) x(t') \rangle \to \langle x(t) \rangle \langle x(t') \rangle \to x^* \langle x(t') \rangle \tag{3.4.63}$$

for any t', even finite. We will see this factorization property at work later in more complicated cases.

Fluctuation-dissipation theorem (FDT)

One can also compute the linear response to an infinitesimal perturbation that couples linearly to the position changing the energy of the system as $H \to H - fx$ at a given time t':

$$R(t,t') = \left. \frac{\delta \langle x(t) \rangle_f}{\delta f(t')} \right|_{f=0} \ . \tag{3.4.64}$$

The explicit calculation yields

$$R(t,t') = \gamma_0^{-1}\ e^{-k\gamma_0^{-1}(t-t')}\ \theta(t-t')$$
$$\boxed{R(t,t') = \frac{1}{k_BT}\ \frac{\partial C_c(t,t')}{\partial t'}\ \theta(t-t') \quad \text{(FDT)}} \tag{3.4.65}$$

The last equality holds for times that are longer than t_r^x. It expresses the fluctuation-dissipation theorem (fdt), a model-independent relation between the two-time linear response and correlation function. Similar - though more complicated - relations for higher-order responses and correlations also exist in equilibrium. There are many ways to prove the fdt for stochastic processes. We will discuss one of them in Sect. 3.1.2 that is especially interesting since it applies easily to problems with correlated noise.

It is instructive to examine the relation between the linear response and the correlation function in the limit of a flat potential ($k \to 0$). The linear response is just $\gamma_0^{-1}\theta(t-t')$. The Dirichlet correlator approaches the diffusive limit:

$$\langle \delta x(t)\delta x(t')\rangle = 2\gamma_0^{-1}k_BT\ \min(t,t') \qquad \text{for} \qquad k \to 0 \tag{3.4.66}$$

and its derivative reads $\partial_{t'}\langle \delta x(t)\delta x(t')\rangle = 2\gamma_0^{-1}k_BT\ \theta(t-t')$. Thus,

$$R(t,t') = \frac{1}{2k_BT}\ \frac{\partial}{\partial t'}\langle \delta x(t)\delta x(t')\rangle\ \theta(t-t')$$
$$\boxed{R(t,t') = \frac{1}{2k_BT}\ \partial_{t'}C_c(t,t')\ \theta(t-t') \quad \text{(FDR for diffusion)}} \tag{3.4.67}$$

A factor 1/2 is now present in the relation between R and C_c. It is another signature of the fact that the coordinate is not in equilibrium with the environment in the absence of a confining potential.

Exercise 3.17 Evaluate the two members of the FDT, Eq. (3.4.65), in the case of the tilted potential $V(x) = -Fx$. Conclude.

Exercise 3.18 Compute $\langle x^n(t)x(t')\rangle$ and $\delta\langle x^n(t)\rangle/\delta h(t')|_{h=0}$ and compare. Discuss.

Exercise 3.19 Take the diffusive problem in the over-damped limit, $\dot{x} = \xi$, where the friction coefficient has been absorbed with a redefinition of time. Compute the linear response of the n-th moment of the coordinate position $\langle x^n(t)\rangle_h$ under a perturbation that modifies the energy according to $V \mapsto V - hx$. Compute the time-derivative of the correlation $\langle x^n(t)x(t')\rangle$. Compare the two and conclude about the pre factor that relates them. Does it depend on n? Is it equal to $(k_BT)^{-1}$?

Reciprocity or Onsager relations

Let us compare the two correlations $\langle x^3(t)x(t')\rangle$ and $\langle x^3(t')x(t)\rangle$ within the harmonic example. One finds $\langle x^3(t)x(t')\rangle =$

$3\langle x^2(t)\rangle\langle x(t)x(t')\rangle$ and $\langle x^3(t')x(t)\rangle = 3\langle x^2(t')\rangle\langle x(t')x(t)\rangle$. Given that $\langle x^2(t)\rangle = \langle x^2(t')\rangle \to \langle x^2\rangle_{eq}$ and the fact that the two-time self-correlation is symmetric,

$$\langle x^3(t)x(t')\rangle = \langle x^3(t')x(t)\rangle \ . \tag{3.4.68}$$

With a similar argument one shows that for any functions A and B of x:

$$\begin{aligned} &\langle A(t)B(t')\rangle = \langle A(t')B(t)\rangle \\ &\boxed{C_{AB}(t,t') = C_{AB}(t',t) \quad \text{(Reciprocity)}} \end{aligned} \tag{3.4.69}$$

This equation is known as Onsager relation and applies to A and B that are even under time-reversal (e.g. they depend on the coordinates but not on the velocities or they have an even number of verlocities).

All these results remain unaltered if one adds a linear potential $-Fx$ and works with connected correlation functions.

3.4.3 A harmonic potential and white multiplicative noise

Take the equation

$$\frac{dx(t)}{dt} = -kx(t) + x(t)\xi(t) \tag{3.4.70}$$

with zero average Gaussian white noise. Use the Stratonovich convention in which usual rules of calculus apply. In order to solve this stochastic differential equation, first absorb the first term in the rhs with the redefinition $y(t) = e^{kt}x(t)$ and write

$$\frac{dy}{dt} = y(t)\xi(t) \tag{3.4.71}$$

with the solution

$$y(t) = y(0)\ e^{\int_0^t dt'\ \xi(t')} \qquad \Rightarrow \qquad x(t) = x(0)\ e^{-kt+\int_0^t dt'\ \xi(t')} \tag{3.4.72}$$

For a Gaussian noise the average yields

$$\langle x(t)\rangle = x(0)\ e^{-kt}\ e^{\frac{1}{2}\langle(\int_0^t dt'\ \xi(t'))^2\rangle} = x(0)\ e^{-kt}e^{k_BTt} = x(0)e^{-(k-k_BT)t} \tag{3.4.73}$$

interestingly enough, the average particle position vanishes or diverges depending upon $k > k_BT$ or $k < k_BT$. It is clear from this example that in the latter case the particle does not equilibrate with the potential $V(x) = x^2/2$ as one could have expected. We will see how the departing equation has to be modified, by an additional drift term, to ensure equilibration to a quadratic potential, after discussing the Fokker-Planck equation for the stochastic process with multiplicative noise in Sec. 7. The equation ensuring this fact is

$$\frac{dx(t)}{dt} = -V'_{\text{eff}} + x(t)\xi(t) = k_BTx(t) - kx^3(t) + x(t)\xi(t) \tag{3.4.74}$$

but this one is no longer solvable analytically. Note the double well structure induced by the noise in the effective potential

$$V_{\rm eff} = -k_B T \frac{x^2}{2} + \frac{x^4}{4} \tag{3.4.75}$$

that gives rise to drifted force

$$f_{\rm drifted} = -g^2 V' + 2k_B T(1-\alpha) g g' = -kx^3 + k_B T x \ . \tag{3.4.76}$$

We will justify the generic form of $f_{\rm drifted}$ in Sec. 7. In interacting many-body problems as the ones described by field equations this phenomenon can induce a phase transition [83].

One can still compute the linear response by using the solution under a perturbation linearly coupled to the particle's position ($-kx \mapsto -kx + h$)

$$x(t) = x_0 \ e^{-kt + \int_0^t dt' \ \xi(t')} + \int_0^t dt' \ e^{-k(t-t') + \int_{t'}^t dt'' \ \xi(t'')} \ h(t') \tag{3.4.77}$$

from where

$$\begin{aligned} R(t,t') &= e^{-k(t-t')} \langle e^{\int_{t'}^t dt'' \ \xi(t'')} \rangle = e^{-k(t-t')} \ e^{\frac{1}{2}\langle (\int_{t'}^t dt'' \ \xi(t''))^2 \rangle} \\ &= e^{-k(t-t')} \ e^{k_B T (t-t')} = e^{-(k-k_B T)(t-t')} \end{aligned} \tag{3.4.78}$$

where we ignored the $\theta(t-t')$ factor assuming $t \geq t'$. The linear response is a stationary function, in the sense that it only depends upon $t-t'$. What about the position-position correlation and mean-share displacement? They read

$$\begin{aligned} C(t,t') &= \langle x(t) x(t') \rangle = x_0^2 \ e^{-k(t+t')} \ e^{k_B T [\max(t,t')]} \\ \Delta(t,t') &= \langle (x(t) - x(t'))^2 \rangle \end{aligned} \tag{3.4.79}$$

and they both behave very weirdly.

3.4.4 Colored noise

Colored noise with exponential correlation

Exercise 3.20 Solve the stochastic dynamics of a particle in a harmonic potential with a exponentially decaying memory kernel $\Gamma(t-t') = \gamma_0 e^{-|t-t'|/\tau_D}$. Hint: use Laplace transform techniques.

Figure 3.11 shows the solution to the Langevin equations:

$$\dot{x} = -\lambda x + \eta \ , \tag{3.4.80}$$

$$\dot{\eta} = -\eta/\tau + \xi \ , \tag{3.4.81}$$

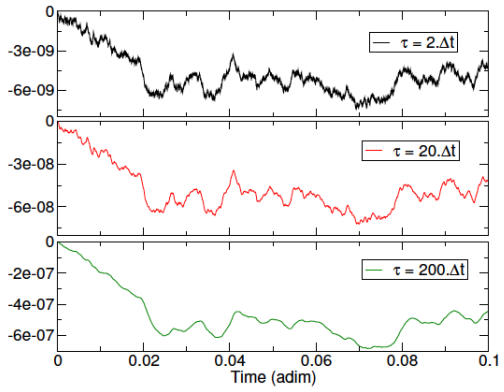

Figure 3.11: Random walk under the effect of a noise with exponential decaying correlations controlled by the parameter τ_D given as labels in the figure, see Eqs. (3.4.81). The time-step for the integration is $\Delta t = 10^{-4}$, temperature fixed by $2k_BT = 0.5$, and the damping parameter is $\lambda = 10^{-2}$. Figure taken from [84].

with $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2k_BT/\tau_D \; \delta(t-t')$. This white noise induces an exponentially decaying correlation function of the noise η that appears in the first equation. (Note, however, that this first equation lacks the memory kernel that should be present in the left-hand-side to ensure the approach to equilibrium of such an equation under a potential.) The three panels in the equation show the trajectories $x(t)$ for the same realization of the white noise ξ. The smoothing effect of correlation is quite clear.

Colored noise with power law correlation

Let us now take a power-law correlated noise. The Langevin equation can be solved by using the Laplace transform. Correlation and linear responses can be computed. As the system should equilibrate – there is confining potential – the FDT holds. However, the decay of these two functions (and more complex ones involving more times) are not trivial in the sense that their temporal dependence is not exponential. Instead, the position correlation function and its linear response are given by the Mittag-Leffer function

$$C_{xx}(t,t') = \frac{1}{k} E_{\alpha,1}\left(\frac{k|t-t'|^\alpha}{\overline{\gamma}_0} \right) , \tag{3.4.82}$$

$$R_{xx}(t,t') = \frac{1}{\overline{\gamma}_0} E_{\alpha,\alpha}\left(\frac{k|t-t'|^\alpha}{\overline{\gamma}_0} \right) \theta(t-t') , \tag{3.4.83}$$

where $\overline{\gamma}_0$ is a constant that is proportional to γ_0 and all other pre-factors in $\Gamma(t-t')$. For the Ohmic $\alpha = 1$ case the Mittag-Leffer function becomes an exponential, as expected. For $\alpha \neq 1$ the decay is algebraic, $E_{\alpha,1}(x) \simeq x^{-1}$ that implies $C_{xx}(t-t') \simeq |t-t'|^{-\alpha}$. The

ratio between linear response and time derivative of the correlation function is

$$\frac{k_B T R_{xx}(t-t')}{\partial_{t'} C_{xx}(t-t')} = 1 + \left(\frac{t}{t'} - 1\right)^{1-\alpha} \frac{E_{\alpha,1}(-kt^\alpha/\overline{\gamma}_0) E_{\alpha,\alpha}(-kt'^\alpha/\overline{\gamma}_0)}{E_{\alpha,\alpha}(-k(t-t')^\alpha/\overline{\gamma}_0)} \tag{3.4.84}$$

In the long time limit, $t \geq t' \gg 1$, the second term vanishes as long as $k > 0$ and one recovers the equilibrium result.

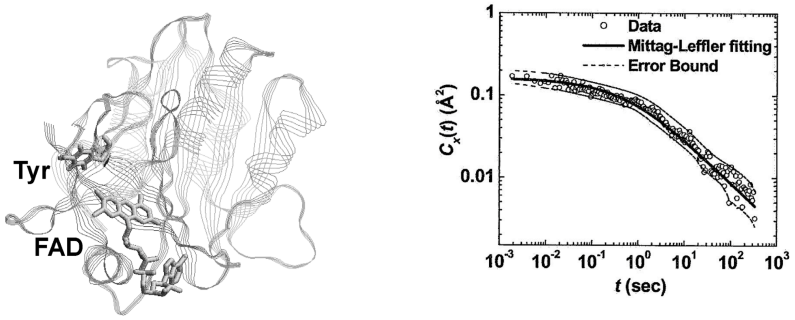

Figure 3.12: Sketch of the experiment. Correlation function measured in [85] and [86], $\alpha = 0.51 \pm 0.07$.

3.4.5 A two-dimensional example

Take a point-like particle with mass m moving in a two dimensional space. The position of this particle is $\vec{r} = (x, y) = x\hat{e}_x + y\hat{e}_y$ in a Cartesian coordinate system. The particle feels a potential $V(x, y) = kx^2/2$ and it is in contact with a generic environment in thermal equilibrium at temperature T.

Using what we have already computed for one dimensional problems we can guess the asymptotic behaviour of the phase space variables $(\vec{p}, \vec{r})$. For simplicity, we will use a white bath with friction coefficient γ_0. The momentum (or velocity) should equilibrate to its Maxwellian form, $\propto \exp(-\beta m v^2/2)$, after a characteristic time $\tau_r^v = m/\gamma_0$. The position $\vec{r} = (x, y)$ will have different behaviour in the x (confined) and y (flat) directions. The x component should reach equilibrium after a characteristic time $\tau_r^x = \gamma_0/k$. This means that it will reach a pdf $\propto \exp(-\beta k x^2/2)$. The y component of the position, instead, should undergo normal diffusion and it will not equilibrate.

The expectations exposed in the previous paragraph can be shown analytically. Take the over-damped (Smoluchowski) limit in which the inertia term in the dynamic equation is neglected. In this limit the Langevin equation becomes

$$\begin{aligned} \gamma_0 \dot{x}(t) &= -kx(t) + \xi_x(t) \ , \\ \gamma_0 \dot{y}(t) &= \xi_y(t) \ . \end{aligned}$$

The solutions are

$$x(t) = x(0)e^{-kt/\gamma_0} + \gamma_0^{-1}\int_0^t dt'\ e^{-k(t-t')/\gamma_0}\ \xi_x(t')\ .$$
$$y(t) = y(0) + \gamma_0^{-1}\int_0^t dt'\ \xi_y(t')\ .$$

The four correlations are given by

$$\begin{aligned}
C_{xx}(t,t') &= \langle x(t)x(t')\rangle = x^2(0)e^{-k(t+t')/\gamma_0} + k_BT\gamma_0^{-1}\ [e^{-k|t-t'|/\gamma_0} - e^{-k(t+t')/\gamma_0}]\ ,\\
C_{xy}(t,t') &= \langle x(t)y(t')\rangle = x(0)y(0)e^{-kt/\gamma_0}\ ,\\
C_{yx}(t,t') &= \langle y(t)x(t')\rangle = x(0)y(0)e^{-kt'/\gamma_0}\ ,\\
C_{yy}(t,t') &= \langle y(t)y(t')\rangle = y^2(0) + 2k_BT\gamma_0^{-1}\min(t,t')\ ,
\end{aligned}$$

where we used $\langle\xi_x(t)\xi_x(t')\rangle = \langle\xi_y(t)\xi_y(t')\rangle = 2k_BT\gamma_0\delta(t-t')$, and the fact that different noise components are uncorrelated, $\langle\xi_x(t)\xi_y(t')\rangle = 0$. As already announced, in the long times limit, $t \gg \gamma_0/k$ and $t' \gg \gamma_0/k$, one finds stationarity for the xx correlation, $C_{xx}(t,t') \to k_BT\gamma_0^{-1}e^{-k|t-t'|/\gamma_0}$, decorrelation of the crossed functions, $C_{xy}(t,t') \to 0$ and $C_{yx}(t,t') \to 0$, and diffusion along the y direction, $C_{yy}(t,t') \to 2k_BT\gamma_0^{-1}\min(t,t')$.

Apply now a small perturbation to the particle that modifies the potential V according to $V \to V - \vec{h}\cdot\vec{r}$. The solutions under the perturbation are

$$\langle x\rangle_{\vec{h}} = x(0)e^{-kt/\gamma_0} + \gamma_0^{-1}\int_0^t dt'\ e^{-k(t-t')/\gamma_0}\ [\xi_x(t') + h_x(t')]\ ,$$
$$\langle y\rangle_{\vec{h}} = y(0) + \gamma_0^{-1}\int_0^t dt'\ [\xi_y(t') + h_y(t')]\ ,$$

and these imply

$$\begin{aligned}
R_{xx}(t,t') &= \delta\langle x(t)\rangle_{\vec{h}}/\delta h_x(t')|_{\vec{h}=\vec{0}} = \gamma_0^{-1}\ e^{-k(t-t')/\gamma_0}\ \theta(t-t')\ ,\\
R_{yy}(t,t') &= \delta\langle y(t)\rangle_{\vec{h}}/\delta h_y(t')|_{\vec{h}=\vec{0}} = \gamma_0^{-1}\ \theta(t-t')\ ,\\
R_{xy}(t,t') &= \delta\langle x(t)\rangle_{\vec{h}}/\delta h_y(t')|_{\vec{h}=\vec{0}} = R_{yx}(t,t') = \delta\langle y(t)\rangle_{\vec{h}}/\delta h_x(t')|_{\vec{h}=\vec{0}} = 0\ .
\end{aligned}$$

The comparison to the time-derivatives of the associated correlation functions yields

$$\begin{aligned}
&k_BTR_{xx}(t,t') = \partial_{t'}C_{xx}(t,t')\theta(t-t') && \text{and FDT holds}\ ,\\
&k_BTR_{yy}(t,t') = \frac{1}{2}\partial_{t'}C_{yy}(t,t')\theta(t-t') && \text{there is a factor of } 1/2\ ,\\
&k_BTR_{xy}(t,t') = \partial_{t'}C_{xy}(t,t')\theta(t-t') = 0\ ,\\
&k_BTR_{yx}(t,t') = 0 \ \text{ and } \ \partial_{t'}C_{yx}(t,t')\theta(t-t') \to 0 \ \text{ for } t' \gg \gamma_0/k\ .
\end{aligned}$$

3.4.6 Perturbation theory

For the moment we only treated cases in which the potential was, at most, quadratic, and the Langevin equation was, therefore, linear in the variable. Quite generally one faces non-linear stochastic differential equations that cannot be solved exactly.

In some fortunate cases, perturbation theory can be easily formulated in this context. Take, for instance, the case of a quartic potential $V(x) = kx^2/2 + \lambda x^4/2$ with $k > 0$ and $\lambda > 0$ and let us focus on the over-damped dynamics of a particle that starts from the position x_0 initially. The Langevin equation for $\lambda = 0$ has already been solved. Let us then take the trajectory (3.4.59) as the zero-th order of a systematic expansion in powers of the coupling constant λ:

$$x(t) = \sum_{n=0} x_n(t)\lambda^n \tag{3.4.85}$$

with

$$x(0) = x_0 = \sum_{n=0} x_n(0)\lambda^n \ . \tag{3.4.86}$$

Quite naturally, we choose

$$x_0(0) = x_0 \qquad \text{and} \qquad x_{n>0}(0) = 0 \ . \tag{3.4.87}$$

Order by order in λ we then have

$$O(\lambda^0): \qquad \gamma_0 \dot{x}_0(t) = -kx_0(t) + \xi(t) \tag{3.4.88}$$
$$O(\lambda^1): \qquad \gamma_0 \dot{x}_1(t) = -kx_1(t) - x_0^3(t) \tag{3.4.89}$$
$$O(\lambda^2): \qquad \gamma_0 \dot{x}_2(t) = -kx_2(t) - 3x_0^2(t)x_1(t) \tag{3.4.90}$$
$$O(\lambda^3): \qquad \gamma_0 \dot{x}_3(t) = -kx_3(t) - 3x_2(t)x_0^2(t) - 3x_1^2(t)x_0(t) \tag{3.4.91}$$

etc. The structure of these equations is the same, with a linear operator $\gamma_0 d_t + k$ acting on the unknown functions at each order and a source term that is known (as a functional of ξ) from the previous orders. Their solutions are

$$x_n(t) = x_n(0)e^{-kt/\gamma_0} + \int_0^t dt' \ e^{-k(t-t')/\gamma_0} \ \text{source}(t') \tag{3.4.92}$$

Note that the power expansion in λ transforms into a power expansion in ξ. The averages can be easily computed by using the factorization properties of the noise averages for Gaussian statistics (Wick's theorem).

Exercise 3.21 Compute the first terms in the expansion above. Compare the outcome for σ^2 to the numerical result shown in Fig. 3.13 generated with $\gamma_0 = 1$ and $k_B T = 0.15$ for a pure quartic potential with $\lambda = 1$ and for a potential with $k = -1.$ and $\lambda = 0.1$.

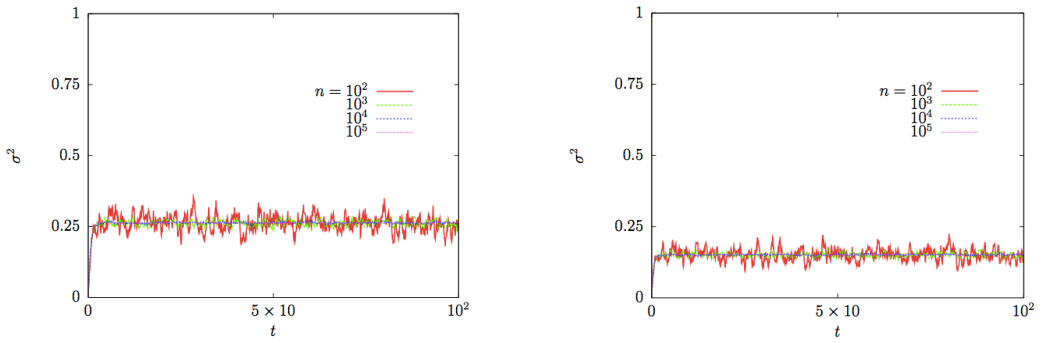

Figure 3.13: Dynamics in a quartic potential $V(x) = kx^2/2 + \lambda x^4/4$ with $k = 0$ and $\lambda = 1$ (left) and $k = 1$ and $\lambda = 0.1$ (right). In both cases $\gamma_0 = 1$ and $k_B T = 0.15$. Different curves are for different number of samples as explained in the key.

With this perturbative method one cannot, however, access non-perturbative processes as the ones leading to the thermal activation over barriers discussed below.

3.4.7 Thermally activated processes

The phenomenological Arrhenius law [74] yields the typical time needed to escape from a potential well as an exponential of the ratio between the height of the barrier and the thermal energy scale $k_B T$, (with prefactors that can be calculated explicitly, see below). This exponential is of crucial importance for understanding slow (glassy) phenomena, since a mere barrier of $30\, k_B T$ is enough to transform a microscopic time of 10^{-12} s into a macroscopic time scale. See Fig. 3.14-right for a numerical study of the Coulomb glass that demonstrates the existence of an Arrhenius time-scale in this problem. In the glassy literature such systems are called strong glass formers as opposed to weak ones in which the characteristic time-scale depends on temperature in a different way.

In 1940 Kramers estimated the escape rate from a potential well as the one shown in Fig. 3.14-center due to thermal fluctuations that give sufficient energy to the particle to allow it to surpass the barrier [75]. After this seminal paper this problem has been studied in great detail given that it is of paramount importance in many areas of physics and chemistry [76]. An example is the problem of the dissociation of a molecule where x represents an effective one-dimensional reaction coordinate and the potential energy barrier is, actually, a free-energy barrier.

Kramers assumed that the reaction coordinate is coupled to an equilibrated environment with no memory and used the probability formalism in which the particle motion is described in terms of the time-dependent probability density $P(x, v, t)$ (that for such a stochastic process follows the Kramers partial differential equation).

If the thermal energy is at least of the order of the barrier height, $k_B T \sim \Delta V$, the

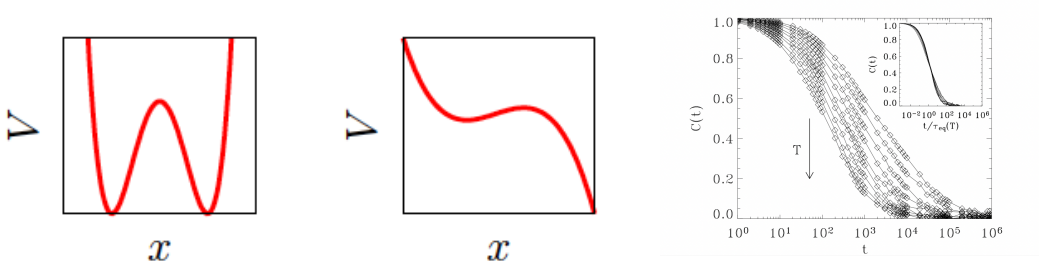

Figure 3.14: Left: sketch of a double-well potential. Center: sketch of a potential with a local minimum. Right: correlation function decay in a classical model of the $3d$ Coulomb glass at nine temperatures ranging from $T = 0.1$ to $T = 0.05$ in steps of 0.05 and all above T_g. In the inset the scaling plot $C(t) \sim f(t/t_A)$ with a characteristic time-scale, t_A, that follows the Arrhenius activated law, $t_A \simeq 0.45/T$. Figure due to Kolton, Domínguez and Grempel [77].

reaction coordinate, x, moves freely from the vicinity of one well to the vicinity of the other.

The treatment we discuss applies to the opposite weak noise limit in which the thermal energy is much smaller than the barrier height, $k_B T \ll \Delta V$, the random force acts as a small perturbation, and the particle current over the top of the barrier is very small. Most of the time x relaxes towards the minimum of the potential well where it is located. Eventually, the random force drives it over the barrier and it escapes to infinity if the potential has the form in Fig. 3.14-center, or it remains in the neighbourhood of the second well, see Fig. 3.14-left.

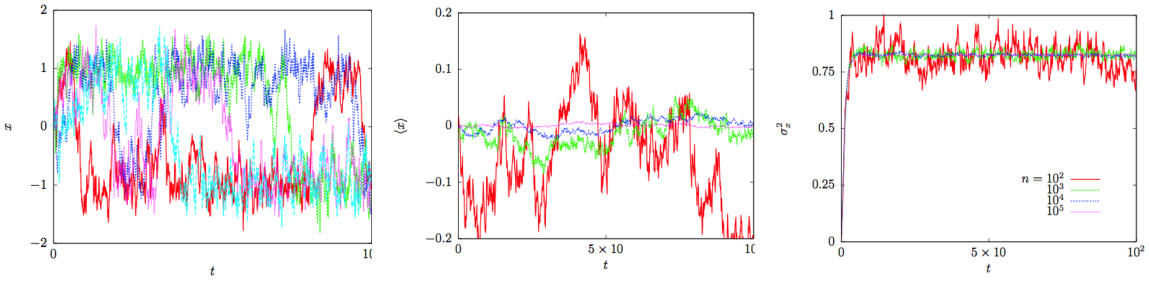

Figure 3.15: Left panel: five runs of the Langevin equation in the over-damped limit with a double well external potential (oscillator) and a Gaussian white noise at temperature T. Central panel: the average $\langle x \rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. Right panel: the variance $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$.

The treatment is simplified if a constant current can be imposed by injecting particles within the metastable well and removing them somewhere to the right of it. In these

conditions Kramers proposed a very crude approximation whereby P takes the stationary canonical form

$$P_{\rm st}(x,v) = \mathcal{N} e^{-\beta\frac{v^2}{2} - \beta V(x)} \ . \tag{3.4.93}$$

($m = 1$ for simplicity here.) If there is a sink to the right of the maximum, the normalization constant $\mathcal{N}$ is fixed by further assuming that $P_{\rm st}(x,v) \sim 0$ for $x \geq \tilde{x} > x_{\rm max}$. The resulting integral over the coordinate can be computed with a saddle-point approximation justified in the large β limit. After expanding the potential about the minimum and keeping the quadratic fluctuations one finds

$$\mathcal{N}^{-1} = \frac{2\pi}{\beta\sqrt{V''(x_{\rm min})}}\, e^{-\beta V(x_{\rm min})} \ .$$

The escape rate, r, over the top of the barrier can now be readily computed by calculating the outward flow across the top of the barrier:

$$\boxed{r \equiv \frac{1}{t_A} \equiv \int_0^\infty dv\ v P(x_{\rm max}, v) = \frac{\sqrt{V''(x_{\rm min})}}{2\pi}\, e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))}} \tag{3.4.94}$$

Note that we here assumed that no particle comes back from the right of the barrier. This assumption is justified if the potential quickly decreases on the right side of the barrier.

The crudeness of the approximation (3.4.93) can be grasped by noting that the equilibrium form is justified only near the bottom of the well. Kramers estimated an improved $P_{\rm st}(x,v)$ that leads to

$$r = \frac{\left(\frac{\gamma^2}{4} + V''(x_{\rm max})\right)^{1/2} - \frac{\gamma}{2}}{\sqrt{V''(x_{\rm max})}}\, \frac{\sqrt{V''(x_{\rm min})}}{2\pi}\, e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))} \ . \tag{3.4.95}$$

This expression approaches (3.4.94) when $\gamma \ll V''(x_{\rm max})$, *i.e.* close to the under-damped limit, and

$$r = \frac{\sqrt{V''(x_{\rm max})V''(x_{\rm min})}}{2\pi\gamma}\, e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))} \tag{3.4.96}$$

when $\gamma \gg V''(x_{\rm max})$, *i.e.* in the over-damped limit (see Sect. 3.2.4 for the definition of these limits).

The inverse of (3.4.95), t_A, is called the Arrhenius time needed for thermal activation over a barrier $\Delta V \equiv V(x_{\rm max}) - V(x_{\rm min})$. The prefactor that characterises the well and barrier in the harmonic approximation is the attempt frequency with which the particles tend to jump over the barrier. In short,

$$\boxed{t_A \simeq \tau\, e^{\beta|\Delta V|} \qquad \text{(Arrhenius time)}} \tag{3.4.97}$$

The one-dimensional reaction coordinate can be more or less easily identified in problems such as the dissociation of a molecule. In contrast, such a single variable is much

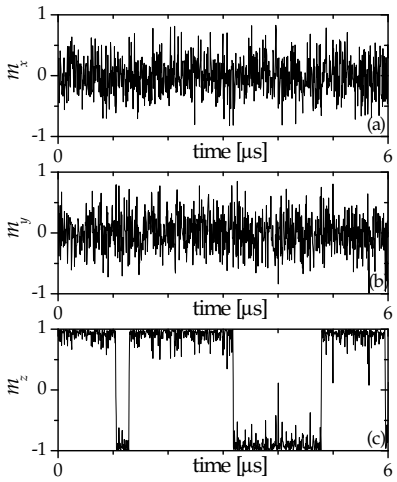

Figure 3.16: Magnetization reversal (an activated process) in the LLGB equation (picture taken from [78].

harder to visualize in an interacting problem with many degrees of freedom. The Kramers problem in higher dimensions is highly non-trivial and, in the infinite-dimensional phase-space, is completely out of reach.

The Arrhenius time can be derived within the path-integral formalism [20].

3.4.8 Driven systems

In the introduction we mentioned that systems can be externally maintained out of equilibrium We list here two solvable examples, in the form of exercises, that illustrate this point.

Exercise 3.22 Study the Langevin equation for a single particle moving in $d = 1$ under no external potential, in a case in which the friction kernel is $\gamma_1(t-t')$ and the noise-noise correlation in $\Gamma_2(t-t')$.

Exercise 3.23 Take a harmonic oscillator, in its over-damped limit to make the calculations simpler, and couple it to two external reservoirs, at different temperatures, T_1 and T_2, and different memory kernels, for instance, a delta function (white noise) and an exponential decay (Ornstein-Uhlenbeck process). The Langevin relaxation of the particle can be solved exactly and it is quite interesting. The particle inherits the two time-scales ($\tau_1 \to 0$ and τ_2 finite) from the baths as can be seen from the decay, in two steps, of the position correlation function or linear response. The temperatures of the environments appear in the fluctuation dissipation relation between these two functions in the

corresponding time regimes [80, 81]. Moreover, these temperatures appear also in the fluctuation theorem [82].

Exercise 3.24 Take now a symmetric two-dimensional harmonic oscillator $V(x, y) = k(x^2+y^2)/2$ and apply the non-potential force $\vec{f}(x, y) = a(y, -x)$ on it, with a a parameter. This force makes a particle turn within the potential well. Describe the trajectories and compute mean-square displacement, correlation function and linear response. One can check, by direct calculation, that the fluctuation-dissipation theorem does not hold.

4 The Kramers/Fokker-Planck approach

The Kramers or Fokker-Planck approach is useful to prove that a given Langevin equation with white noise takes the system to equilibrium at the working temperature. It is a deterministic partial differential equation on the probability distribution for the stochastic variable at time t to take a given value, say y, that can be closed as such for problems with white (additive or multiplicative) noise. The stochastic variables can be both velocity and position and then one speaks about the Kramers equation or just the position variables, in the Smoluchowski $t \gg t_I$ limit and one speaks about the Fokker-Planck equation. here, for the sake of simplicity, we focus on the latter case.

4.1 Derivation for the Smoluchowski case

Consider the probability density of finding the particle close to y at time t and call it $P(y, t + \Delta t)$. We start from the identity for Markov processes,

$$P(y, t + \Delta t) = \int dx_0 \; P(y, t + \Delta t|x_0, t) \; P(x_0, t) \; , \tag{4.1.1}$$

where $P(y, t + \Delta t|x_0, t)$ is the conditional probability of finding y at time $t + \Delta t$ provided the system was in the state x_0 at the previous time t (note that x_0 is not necessarily the initial value here). The probability density of this last event is $P(x_0, t)$. The integral runs over all accessible values of x_0. This equation holds for any value of the time increment Δt but we will later focus on infinitesimal ones. It is also called the Chapman-Kolmogorov equation.

To make contact with the stochastic process in the Langevin description, it is convenient to define the conditional probability in the following way:

$$P(y, t + \Delta t|x_0, t) = \langle \delta(y - x(t + \Delta t)) \rangle \tag{4.1.2}$$

where the mean value is taken over the noise ξ weighted with its probability distribution $P[\xi]$, and $x(t + \Delta t)$ is determined by the Langevin equation with the 'initial condition' $x(t) = x_0$. Expanding Eq. (4.1.2) in powers of $\Delta x \equiv x(t + \Delta t) - x(t) = y - x_0$ we

immediately obtain

$$P(y,t+\Delta t|x_0,t) = \delta(y-x_0) - d_y\delta(y-x_0)\langle\Delta x\rangle + \frac{1}{2}d_y^2\delta(y-x_0)\langle(\Delta x)^2\rangle + \dots \quad (4.1.3)$$

where the ellipsis indicate terms involving higher order moments of Δx. The idea is to compute the averages $\langle\Delta x\rangle$ and $\langle(\Delta x)^2\rangle$ to leading order in Δt and then take the limit $\Delta t \to 0$. To do this, we need to use the Langevin equation of motion and it is at this point that its form (additive or multiplicative noise) will play a role.

We recall the discretization of the stochastic different equations with white noise discussed in Sec. 7:

$$\gamma_0(x_{n+1}-x_n) = f(\overline{x}_n)\Delta t + g(\overline{x}_n)\xi_n\Delta t \quad (4.1.4)$$

where we reintroduced the friction coefficient γ_0. The overline variables are defined as $\overline{x}_n = \alpha x_{n+1} + (1-\alpha)x_n$, and $\langle\xi_n\Delta t\rangle = 0$ and $\langle(\xi_n\Delta t)^2\rangle = 2k_BT\gamma_0\Delta t$.

4.1.1 Additive white noise

We will here present an evaluation of Δx obtained from the integration of the Langevin equation over the interval $[t, t+\Delta t]$. It reads

$$\Delta x \equiv x(t+\Delta t) - x(t) = x_{n+1} - x_n = -\frac{1}{\gamma_0}V'(\overline{x}_n) + \frac{1}{\gamma_0}\xi_n\Delta t \quad (4.1.5)$$

and x_n being set to the 'reference value' x_0. From here the averages are readily computed:

$$\langle\Delta x\rangle = -\frac{\Delta t}{\gamma_0}V'(x_0) \quad (4.1.6)$$

$$\langle(\Delta x)^2\rangle = \frac{2k_BT\Delta t}{\gamma_0} + O(\Delta t^2) \quad (4.1.7)$$

where, in the second line, we identified the contribution from the deterministic force as being $O(\Delta t^2)$ and we used the fact that $x(t) = x_n$ will be fixed to x_0 to set to zero the contribution from the cross product. Interestingly enough, the mean value as well as the second moment are of order Δt. Higher momenta of the distribution such as $\langle(\Delta x)^3\rangle$ and so on and so forth are of higher order in Δt and do not contribute to the expansion for sufficiently small Δt. It is important to note that these results depend on x_0. Replacing now these averages in (4.1.3), next in (4.1.1),

$$\begin{aligned} P(y,t+\Delta t) &= P(y,t) + \frac{\Delta t}{\gamma_0}\partial_y\int dx_0\ V'(x_0)\ \delta(y-x_0)\ P(x_0,t) \\ &\quad + \frac{2k_BT\Delta t}{2\gamma_0}\partial_y^2\int dx_0\ \delta(y-x_0)\ P(x_0,t)\ , \end{aligned} \quad (4.1.8)$$

performing the integrals over x_0, and taking the $\Delta t \to 0$ limit

$$\gamma_0\partial_t P(y,t) = \partial_y[V'(y)\ P(y,t)] + k_BT\partial_y^2 P(y,t) \quad (4.1.9)$$

This is the Fokker-Planck (or Smoluchowski) equation for a one variable Langevin process with white additive noise. The limit γ_0 can then be safely taken to recover the dissipationless limit.

Stationary solution

We look now for a solution that is time-independent, $P_{\rm st}(y)$, and normalizable. We have

$$0 = \partial_y[V'(y)\ P_{\rm st}(y)] + k_BT\partial_y^2 P_{\rm st}(y)\ . \tag{4.1.10}$$

A first integration over y implies

$$\text{cst} = V'(y)\ P_{\rm st}(y) + k_BT\ \partial_y P_{\rm st}(y)\ . \tag{4.1.11}$$

To ensure the normalization of the pdf it is natural to impose $\lim_{y\to\infty} P_{\rm st}(y) = 0$ and $\lim_{y\to\infty} \partial_y P_{\rm st}(y) = 0$. Therefore, the constant must vanish and we find

$$\frac{\partial_y P_{\rm st}(y)}{P_{\rm st}(y)} = -\frac{V'(y)}{k_BT} \qquad \Rightarrow \qquad P_{\rm st}(y) \propto e^{-V(y)/(k_BT)} = e^{-\beta V(y)} \tag{4.1.12}$$

Approach to the stationary solution

The question remains as to whether the dynamics of the system takes it to this stationary solution asymptotically or not. An elegant way to prove this fact is to consider the 'dynamic free-energy functional'

$$\mathcal{F}[P] = \int dy\ P(y,t)\ [k_BT \ln P(y,t) + V(y)] \tag{4.1.13}$$

where P is a generic solution of the Fokker-Planck equation. The time derivative of $\mathcal{F}$ reads

$$d_t\mathcal{F}[P] = \int dy\ \partial_t P(y,t)\ \ [k_BT \ln P(y,t) + V(y) + k_BT] \tag{4.1.14}$$

Using now the FP equation to replace $\partial_t P(y,t)$

$$\begin{aligned} \gamma_0 d_t\mathcal{F}[P] \ &= \ \int dy\ \left\{\partial_y[V'(y)P(y,t)] + k_BT\partial_y^2 P(y,t)\right\} \\ &\qquad \times [k_BT \ln P(y,t) + V(y) + k_BT] \end{aligned} \tag{4.1.15}$$

We now integrate by parts and drop the border terms as P and $\partial_y P$ are expected to vanish at infinity to obtain

$$\begin{aligned} \gamma_0 d_t\mathcal{F}[P] \ &= \ -\int dy\ \ [V'(y)P(y,t) + k_BT\partial_y P(y,t)] \\ &\qquad \times\partial_y\left[k_BT \ln P(y,t) + V(y) + k_BT\right] \\ &= \ -\int dy\ \ [V'(y)P(y,t) + k_BT\partial_y P(y,t)]^2\ \frac{1}{P(y,t)} \le 0 \end{aligned}$$

Moreover, one sees that the numerator in the integrand vanishes identically only for $P_{\rm eq} \propto e^{-\beta V}$. For the Boltzmann equilibrium distribution function, therefore, $d_t\mathcal{F}[P_{\rm eq}] = 0$.

As V is bounded from below for a potential that may lead to equilibrium, $\mathcal{F}$ is also bounded from below. In the course of time, for any $P \neq P_{\rm eq}$, its derivative is always negative. Therefore, $\mathcal{F}$ has to approach its asymptotic value where $d_t\mathcal{F}$ must vanish. As we also showed that $d_t\mathcal{F}[P_{\rm eq}] = 0$ then

$$\lim_{t\to\infty} P(y,t) = P_{\rm eq}(y)\ . \tag{4.1.16}$$

Connection to the Schrödinger equation

The FP equation looks very similar to the Schrödinger equation for imaginary time, apart from a term proportional to $V'(y)\partial_y P(y,t)$. One can, however, eliminate it by introducing the function

$$P(y,t) = \psi_0(y)\rho(y,t) \qquad \text{with} \qquad \psi_0(y) = \text{ct}\ e^{-\frac{\beta}{2}V(y)} \tag{4.1.17}$$

with $\beta = (k_B T)^{-1}$. After a simple calculation one finds

$$\gamma_0\partial_t\rho(y,t) = \left[k_B T\partial_y^2 - U_{\rm FP}(y)\right]\rho(y,t) \tag{4.1.18}$$

with

$$U_{\rm FP}(y) = -\frac{1}{2}V''(y) + \frac{\beta}{4}(V'(y))^2 \tag{4.1.19}$$

where FP stands for Fokker-Planck. This is a Schrödinger equation in imaginary time, with the linear Schrödinger operator

$$H_{\rm FP}(y) = k_B T\partial_y^2 - U_{\rm FP}(y) \tag{4.1.20}$$

that is a symmetric operator on the space of real functions ($\int dx\ (H_{\rm FP}\Phi_1(x))\Phi_2(x) = \int dx\ \Phi_1(x)(H_{\rm FP}\Phi_2(x))$). A number of properties follow:

- The eigenvalues of $H_{\rm FP}$ are real.
- If $U_{\rm FP}$ grows rapidly to infinity for $y \to \pm\infty$ the spectrum of $H_{\rm FP}$ is discrete.
- It is easy to check that $\psi_0(y)$ is an eigenvector of $H_{\rm FP}$ with zero eigenvalue, $H_{\rm FP}(y)\psi_0(y) = E_0\psi_0(y) = 0$, implying $E_0 = 0$.
- $\psi_0(y)$ is non-negative (cst is taken to be positive). Hence, it must be the ground state of $H_{\rm FP}$. All other eigenvalues E_n are strictly positive, $E_n > 0$ for $n > 0$.
- The eigenvectors of $H_{\rm FP}$ associated to different eigenvalues are orthogonal.
- The solution is

$$\rho(y,t) = \sum_{n=0}^{\infty} c_n\psi_n(y)e^{-E_n t} \tag{4.1.21}$$

(where we absorbed the γ_0 in a redefinition of time, for simplicity) with $H_{\rm FP}\psi_n(y) = E_n\psi_n(y)$ and $c_n = \int dy\ \psi_n(y)\rho(y,0)$.

– When $t \to \infty$ all terms vanish exponentially apart from the one associated to $n = 0$. Thus,

$$\lim_{t\to\infty} \rho(y,t) = c_0\psi_0(y) = \psi_0(y) \tag{4.1.22}$$

since $c_0 = \int dy\ \psi_0(y)\rho(y,0) = \int\ dy\ P(y,0) = 1$.

– The property above implies

$$\lim_{t\to\infty} P(y,t) = \psi_0^2(y) = \mathrm{cst}^2 e^{-\beta V(y)} \tag{4.1.23}$$

– One can easily show that the probability is normalized at all times

$$\begin{aligned}\int dy\ P(y,t) &= \int dy\ \psi_0(y)\rho(y,t) = \int dy\ \psi_0(y)\sum_n c_n\psi_n(y)e^{-E_n t} \\ &= \sum_n c_n e^{-E_n t}\int dy\ \psi_0(y)\psi_n(y) = \sum_n c_n e^{-E_n t}\delta_{n0} = c_0 = 1\end{aligned} \tag{4.1.24}$$

– Finally,

$$\lim_{t\to\infty} P(y,t) = \frac{e^{-\beta V(y)}}{\int dx\ e^{-\beta V(x)}} \tag{4.1.25}$$

and this is another way of proving the approach to Boltzmann equilibrium.

Relaxation time

The longest relaxation time is then the inverse of the energy of the first excited state

$$\tau_{\mathrm{eq}} = E_1^{-1}\ . \tag{4.1.26}$$

This time can, however, diverge. In particular, if it scales with the size of the system.

4.1.2 Multiplicative white noise

In this calculation we will be more careful with the discrete time analysis. We rely heavily on the fact that $\langle \xi_n \xi_m \rangle = 2D/\Delta t\ \delta_{nm}$ implies $\xi_n \simeq \mathcal{O}(\Delta t^{-1/2})$ and $\xi_n \Delta t \simeq \mathcal{O}(\Delta t^{1/2})$. We work with the generic equation $\gamma_0 d_t x = f(x) + g(x)\xi$.

As discussed in Sec. 7 the discretized equation reads

$$\gamma_0 \Delta x \equiv \gamma_0(x_{n+1} - x_n) = f(x_n)\Delta t + g(x_n)\xi_n \Delta t + g'(x_n)\alpha \Delta x \xi_n \Delta t\ . \tag{4.1.27}$$

We replace Δx in the last term by this very same equation to get

$$\begin{aligned}\gamma_0 \Delta x \ &= \ f(x_n)\Delta t + g(x_n)\xi_n \Delta t \\ &\quad + g'(x_n)\alpha \xi_n \Delta t \gamma_0^{-1}[f(x_n)\Delta t + g(x_n)\xi_n \Delta t + g'(x_n)\alpha \Delta x \xi_n \Delta t]\ .\end{aligned} \tag{4.1.28}$$

Keeping now all terms that will contribute to the average up to $\mathcal{O}(\Delta t)$

$$\gamma_0 \Delta x = f(x_n)\Delta t + g(x_n)\xi_n \Delta t + \alpha g(x_n) g'(x_n) \gamma_0^{-1} (\xi_n \Delta t)^2 \tag{4.1.29}$$

If we fix x_n to take the value $x(t) = x_0$ in the expansion for $P(y, t + \Delta t|x_0, t)$, x_n is not correlated with the noise ξ_n. Therefore, under the noise average the third term vanishes. Using $\langle (\xi_n \Delta t)^2 \rangle = 2D\Delta t$,

$$\gamma_0 \langle \Delta x \rangle = f(x_n)\Delta t + 2D\gamma_0^{-1} \alpha g(x_n) g'(x_n) \Delta t \ . \tag{4.1.30}$$

Let us examine $(\Delta x)^2$. Keeping terms that will contribute to the average up to $\mathcal{O}(\Delta t)$ we have

$$\gamma_0^2 \langle \Delta x^2 \rangle \simeq \langle [g(x_n)\xi_n \Delta t]^2 \rangle = 2k_B T \gamma_0 g^2(x_n) \ \Delta t \tag{4.1.31}$$

Once again, the mean value as well as the two point correlation are of order Δt. These results depend on $x_n = x_0$. Replacing now in (4.1.3), next in (4.1.1),

$$\gamma_0 P(y, t + \Delta t) = \gamma_0 P(y, t) - \Delta t \ \partial_y \int dx_0 \ [f(x_0) + 2k_B T \alpha g(x_0) g'(x_0)] \ \delta(y - x_0) \ P(x_0, t)$$
$$+ k_B T \Delta t \partial_y^2 \int dx_0 \ \delta(y - x_0) \ g^2(x_0) \ P(x_0, t) \ , \tag{4.1.32}$$

and performing the integrals over x_0, in the $\Delta t \to 0$ limit

$$\boxed{\gamma_0 \partial_t P(y, t) = -\partial_y \left\{ [f(y) + 2k_B T \alpha g(y) g'(y)] \ \ P(y, t) \right\} + k_B T \partial_y^2 \Big[g^2(y) P(y, t) \Big]} \tag{4.1.33}$$

This is the Fokker-Planck (or Smoluchowski) equation for the stochastic process $\gamma_0 d_t x = f(x) + g(x)\xi$ with white noise. For $g(x) = 1$ we recover Eq. (4.1.9) for additive noise.

Stationary solution

The stationary solution to Eq. (4.1.33) with vanishing current, $J = 0$, is

$$P_{\rm st}(x) = \frac{N}{g^2(x)} \exp \left[\frac{1}{k_B T} \int_x dx' \ \frac{f(x') + 2k_B T \alpha g(x) g'(x))}{g^2(x')} \right] \tag{4.1.34}$$

with N a normalization constant. This stationary probability depends upon α and $g(x)$. In order to get rid of this undesired feature, we chose to work with the drifted force

$$\boxed{f(x) = -g^2(x) V'(x) + 2k_B T (1 - \alpha) g(x) g'(x)} \ . \tag{4.1.35}$$

The associated FP equation reads

$$\begin{aligned} \partial_t P(x, t) &= -\partial_x [-g^2(x) V'(x) + 2k_B T g(x) g'(x)) P(x, t)] \\ &\quad + k_B T \ \partial_x^2 [g^2(x) P(x, t)] \\ &= \partial_x \{ [(g^2(x) V'(x) - 2k_B T g(x) g'(x)) P(x, t)] \\ &\quad + k_B T \ \partial_x [g^2(x) P(x, t)] \} \\ &= \partial_x \{ g^2(x) [V'(x) P(x, t) + k_B T \ \partial_x P(x, t)] \} \ . \end{aligned} \tag{4.1.36}$$

It is still independent of α though it depends on $g(x)$. However, its asymptotic solution with vanishing current does not and it reads

$$P_{\rm st}(x) = P_{\rm GB}(x) = N \exp\left[-\beta\ V(x)\right] \tag{4.1.37}$$

independently of α and g, the desired result. Note that the effect of the extra term is to correct the prefactor in the measure, not what goes in the exponential, that would be the same $-\beta V$ even without the additional $2k_BTgg'$ term in the drift.

Therefore, meaning physical applications in the sense that the stochastic dynamics tends to equilibrium at the Boltzmann measure, need the drifted Langevin equation

$$\boxed{d_t x(t) = -g^2 V'(x) + 2k_BT(1-\alpha)g(x)g'(x) + g(x)\xi(t)} \tag{4.1.38}$$

Note that with this force, there is a drift in the Langevin equation even in the Stratonovich convention. The extra term *is not* the one needed to build the generalized derivative appearing in the chain rule (3.2.24), since the factor $2k_BT(1-\alpha)$ in the drift is different from the factor $k_BT(1-2\alpha)$ in the chain-rule The Fokker-Planck equation takes a simple form given in Eq. (4.1.36).

In Sec. 7 we saw an explicit realization of this phenomenon, with the study of a particle in harmonic potential under a white noise multiplied by the particle's position.

The Langevin equation (4.1.38) is equivalent to

$$\boxed{g^{-2}(x)\gamma_0 d_t x(t) = -V'(x) + 2k_BT(1-\alpha)g'(x)g^{-1}(x) + g^{-1}(x)\xi(x)} \tag{4.1.39}$$

in the sense that the term responsible for dissipation (lhs) is proportional to g^{-2} while the noise is accompanied by just one factor g^{-1} and there is no g factor in the deterministic force along the gradient descent direction. The second term in the rhs is the drift. This form has the same structure as the form of the Langevin equations derived from the non-linear coupling of the particle to the oscillator coordinates in the bath modelling.

4.2 Kramers equation and colored noise

In the previous section we worked in the Smoluchowski limit. A partial differential equation for $P(\vec{x},\vec{p},t)$ can also be derived. This is the Kramers equation

$$\begin{aligned}\frac{\partial P(\vec{x},\vec{p};t)}{\partial t} = \frac{\partial}{\partial p_\mu}\left\{\left[-\frac{\partial V}{\partial x_\mu} + \gamma_0\frac{\partial H}{\partial p_\mu}\right]P(\vec{x},\vec{p};t)\right\} - \frac{\partial}{\partial x_\mu}\left[\frac{\partial H}{\partial p_\mu}P(\vec{x},\vec{p};t)\right] \\ + \gamma_0 k_BT\ \frac{\partial^2 P(\vec{x},\vec{p};t)}{\partial p_\mu^2}\ .\end{aligned} \tag{4.2.40}$$

which we have written for a particle in $\mu = 1,\ldots,d$ dimensions.

Exercise 4.1 Derive the Kramers equation. Show that it admits the stationary solution $P_{\rm st} \propto \exp\{-\beta[p^2/(2m) + V(x)]\}$.

4.3 Colored noise

The coloured noise case is more tricky. As no Markov property can be used there is no closed partial differential equation for $P(y,t)$. Some approximations exists [87].

4.4 Master equation

For the moment we have only treated problems with continuous variables and in the rest of the notes we will stick to this kind of problems as well. However, here, we wish to present the master equation that is, basically, the partner of the Fokker-Planck equation for discrete Markov stochastic processes.

The Chapman-Kolmogorox equation (4.1.1) applies also to problems with discrete variables with the simplification of replacing the integral by a sum over discrete states. The conditional or transition probability over an infinitesimal time interval dt can be written as

$$P(y,t+\Delta t|x_0,t) = \underbrace{\left(1-\Delta t\sum_z W_{zy}\right)}_{\text{probabilty of no transition}}\delta_{zy} + \Delta t\, W_{yx_0}$$

The possibility of there being more than one transition in the interval dt has been neglected; a conjecture that is valid in the limit $dt \to 0$. The first term represents the probability for the system to stay in the state x_0 between t and dt while the second term is the probability that the system leaves the state x_0 to go to y in this same interval. Consistently, this expression satisfies $\sum_y P(y,t+\Delta t|x_0,t) = 1$.

Replacing now (4.4.41) in (4.1.1) and arranging terms in such a way to have a time-derivative in the left-hand-side,

$$\frac{dP_x}{dt} = \sum_z (W_{xz}P_z - W_{zx}P_x) \tag{4.4.41}$$

The first term in the right-hand-side is a gain, in the sense that it increases the probability P_x while the second term in the right-hand-side is a loss since it contains the contribution of all processes that take from x to any z and makes P_x diminish. This is the master equation.

4.5 Concluding remarks

The Langevin equation and its relation to the Fokker-Planck formalism have been described in many textbooks on stochastic processes including Risken's [6], Gardiner's [7] and van Kampen's [8]. Many applications can be found in Coffrey et al.'s [9]. Another

derivation of the Langevin equation uses collision theory and admits a generalization to relativistic cases [88]. The alternative master equation description of stochastic processes, more adapted to deal with discrete variables, is also very powerful but we will not use it is these lectures.

5 Functional formalism

Until here we presented the Langevin equation and, in white noise cases, the corresponding Fokker-Planck equation. Yet, within the study of Markov but also non-Markov stochastic processes there exists also the possibility of approaching the problem via the path integral formulation of generating functionals [89]. The use of generating functionals is an elegant and powerful method to derive generic properties of dynamical systems. A path-integral is handy for computing moments, probability distribution functions, transition probabilities and responses. It is also particularly well suited when it comes to perturbation theory and renormalization group analysis, as one can easily set up a diagrammatic expansion.

The classical path integral formalism for stochastic processes governed by the Langevin equation goes under the name of Martin-Siggia-Rose [90] but it was first constructed by Janssen [91–93]. Many subtleties have been identified in processes with multiplicative white noise [94–100] and with the difficulty of performing non-linear transformation of variables [79, 95, 101].

A covariant generating functional that allows to perform non-linear changes of variables and use the conventional rules of calculus was constructed in the past [102] and more recently rederived with an explicit higher order discretization scheme for one dimensional processes [103] and higher dimensional ones [104].

6 Applications

In this Section we briefly present a number of recent uses of Langevin equation in different contexts, including biophysics and quantum matter.

6.1 Stochastic thermodynamics

Thermodynamics is a phenomenological theory of equilibrium macroscopic systems which deals with heat, work, and temperature, and their relation to energy and entropy. It developed from the will to increase the efficiency of early steam engines in the XIXth and it was later justified microscopically by the equilibrium Statistical Physics of Boltzmann and Gibbs. Linear response theory allows to express transport properties caused by small external fields through equilibrium correlation functions. This applies to weak perturbations away from equilibrium only.

General laws applicable to non-equilibrium systems were derived in the last 20 years or so. They concern fluctuations and typically characterize the distribution functions of thermodynamic quantities like exchanged heat, applied work or entropy production.

These results are particularly relevant for small systems with appreciable (typically non-Gaussian) fluctuations, which are now accessible thanks to improvements in spatio-temporal resolution in nanotechnology. Stochastic energetics quantifies individual realizations of a stochastic process on the mesoscopic scale of thermal fluctuations. They helped to better understand the non-equilibrium dynamics of microscopic systems such as colloidal particles, biopolymers, enzymes, and molecular motors.

Sekimoto introduced the idea of stochastic energetics [28] and this was combined with the idea that entropy can consistently be assigned to a single fluctuating trajectory to build the stochastic thermodynamics [28, 29] framework.

Many exact relations for out of equilibrium processes have been proven. These include the fluctuation theorem, the Jarzynski relation, the Crooks relation, etc. Possibly, the easiest derivations are those that concern Langevin processes. We very briefly introduce some of these.

Stochastic energetics.

Let's multiply the generic Langevin equation by $v(t)$.[2] We find

$$\frac{d}{dt}\left[\frac{1}{2}mv^2 + V(x)\right] = v(t)\xi(t) - v(t)\int_0^t dt'\ \Gamma(t-t')v(t')\ . \tag{6.1.1}$$

Now integrate over time between t_1 and t_2

$$H_{\rm syst}(t_2) - H_{\rm syst}(t_1) = \int_{t_1}^{t_2} dt\ \xi(t)v(t) - \int_{t_1}^{t_2} dt\ \int_0^t dt'\ v(t)\Gamma(t-t')v(t')\ . \tag{6.1.2}$$

As there is no reason to suppose that the rhs be identical to zero, one finds that the energy of the system fluctuates and is not constant. Note also that, although the velocity is a Gaussian random variable, the kinetic energy, being given by its square, is not.

Non potential forces.

Time-dependent, $f(t)$, and constant non-potential forces, $f^{\rm np}$ (in higher dimensions), as the ones applied to granular matter and in rheological measurements, respectively, are simply included in the right-hand-side (rhs) as part of the deterministic force.

The energy balance under non-potential forces can be done as above, by multiplying the Langevin equation by $v(t)$. One gets an additional term due to the work done by the

[2] Subtle issues about the chain-rule for derivatives of functions of stochastic variables were discussed in the text. For equations with inertia and/or coloured noise, these problems do not usually pose, see however [105, 106].

non-potential force over the interval $[t_1, t_2]$:

$$H_{\rm syst}(t_2) - H_{\rm syst}(t_1) = \int_{t_1}^{t_2} dt\ f(t)v(t) + \int_{t_1}^{t_2} dt\ \xi(t)v(t) - \int_{t_1}^{t_2} dt \int_0^t dt'\ v(t)\Gamma(t-t')v(t') \tag{6.1.3}$$

The first term on the rhs is the work done by the time-dependent force. The second and third terms can be associated to the heat given or taken from the bath, if a fluctuating energy balance relation

$$\Delta H_{\rm syst} = W^f_{t_1 \to t_2} + \Delta Q \tag{6.1.4}$$

is proposed. This is the first law of thermodynamics at the trajectory level.

The sign of the dissipated heat is opposite to the sign convention in classical thermodynamics, where heat transfer from the system to the environment has a negative sign. Here,

$$\Delta Q = \begin{cases} \text{positive, heat goes from the system to the bath} \\ \text{negative, heat goes from the bath to the system} \end{cases} \tag{6.1.5}$$

Heat is viewed from the perspective of the heat bath, since the amount of dissipated heat from the system leads to an increase in entropy of the environment. For the work the usual sign convention applies, i.e., work applied to the system has a positive sign and work done by the system has a negative sign.

Exercise 6.1 Calculate all terms in Eq. (6.1.4) for the Langevin dynamics in the Smoluchowski over-damped limit of a particle in a one dimensional harmonic potential and driven by a constant force F. Take their averages and verify that the energy balance equation is satisfied. Check that in the long-time limit, the deterministic potential energy is increased by the thermal energy provided by the heat bath, whereas the pure mechanical dissipation is reduced correspondingly.

Interest in computing the probability distribution functions of each of these terms is current in the literature. This is part of the so-called stochastic thermodynamics, or the idea to extend notions of thermodynamics such as work, heat and entropy, to individual trajectories [28]. These pdfs are of relevance in the study of small systems, especially biological molecules and the like, but also in microfluidics, nanomachines, nano sensing devices, a many other fields. Exact relation for the probability of measuring a positive over the probability of measuring a negative quantity such as the work or heat, have been derived and are special cases of the so-called fluctuation theorems.

6.2 Phenomenological Langevin equations

In so far we have discussed a system with position and momentum degrees of freedom. Many fields in physics and other sciences use Langevin-like equations to describe the dynamic behavior of a selected set of variables, of different kind, in contact with an environment. Sometimes, these equations look different from the one that we derived above.

The electric analog.

Take an LRC circuit. The resistance is of the usual Ohmic type, that is to say, the potential drop, V_R, across it is given by $V_R = IR$ with I the current and R the resistance. The potential drop, V_L, across the inductor L is given by $V_L = LdI/dt$. Finally, the potential drop across the capacitor is $V_C = -C^{-1}\int Idt$. The balance between these potentials implies a Langevin type equation for the current circulating across the circuit:

$$L\frac{d^2I}{dt^2} + R\frac{dI}{dt} + C^{-1}I = 0\,. \tag{6.2.1}$$

This analogy justifies the Ohmic name given to a dissipative term proportional to the velocity in the general presentation.

Classical Ising spins: the soft spin description

A continuous Langevin equation for classical spins can also be used if one replaces the hard Ising constraint, $s_i = \pm 1$, by a soft one implemented with a potential term of the form $V(s_i) = u(s_i^2 - 1)^2$ with u a coupling strength (that one eventually takes to infinity to recover a hard constraint). The soft spins are continuous unbounded variables, $s_i \in (-\infty, \infty)$, but the potential energy favors the configurations with s_i close to ± 1. Even simpler models are constructed with spherical spins, that are also continuous unbounded variables globally constrained to satisfy $\sum_{i=1}^{N} s_i^2 = N$. The extension to fields is straightforward and we will discuss one when dealing with the $O(N)$ model.

Classical Heisenberg spins

Another example is the Landau-Lifshitz-Gilbert-Brown equation for the stochastic dynamics of a magnetic moment with constant magnitude:

$$\dot{\vec{M}} = -\frac{\zeta}{1+\zeta^2\gamma_0^2}\,\vec{M}\wedge\left(\vec{H}_{\rm eff} + \vec{H} + \frac{\gamma_0\zeta}{M_s}\,\vec{M}\wedge(\vec{H}_{\rm eff}+\vec{H})\right)\,, \tag{6.2.2}$$

in the Landau formulation or

$$\dot{\vec{M}} = -\zeta\vec{M}\wedge\left(\vec{H}_{\rm eff} + \vec{H} - \frac{\gamma_0}{M_s}\dot{\vec{M}}\right) \tag{6.2.3}$$

in the Gilbert formulation. $\vec{H}$ is a Gaussian white noise with zero mean and delta correlations. γ_0 is friction coefficient. Noise is multiplicative and, as they are written, these equations conserve the modulus of the magnetization only if the Stratonovich calculus is used. Otherwise a drift term has to be added [79]. Note that this is not an irrelevant detail. Numerical codes written with the discretised stochastic differential equation in a different from Stratonovich scheme do not conserve the modulus of the magnetisation.

Exercise 6.2 Show that a connection between the two formalisms is possible after the adequate identification of parameters.

Classical dipoles

The translational motion of a particle i is characterized by its time-dependent position $\vec{r}_i$ and velocity $\vec{v}_i$. Imagine that each particle carries an electric dipole orientation $\vec{p}_i$. Although constant in modulus, the orientation of the dipole is time-dependent and can be characterized by an angular velocity vector $\vec{\omega}_i$ such that $d\vec{p}_i/dt = \vec{\omega}_i \times \vec{p}_i$. It is subjected to an external force $\vec{F}_i$ and to an external torque $\vec{\Gamma}_i$. For a particle of mass m and inertia tensor I (one can have thin rods in mind) one has

$$m\ \dot{\vec{v}}_i = -\gamma_0 \vec{v}_i + \vec{F}_i + \vec{\xi}_i\ , \tag{6.2.4}$$

$$I\ \dot{\vec{\omega}}_i = -\zeta_0 \vec{\omega}_i + \vec{\Gamma}_i + \vec{\lambda}_i\ . \tag{6.2.5}$$

Here $\vec{\xi}_i$ and $\vec{\lambda}_i$ are Gaussian random forces and torques, respectively, introduced to account for the thermal exchanges with the surrounding medium. The friction coefficients γ_0 and ζ_0 govern the dissipation into the thermal bath. Just as γ_0 and $\vec{\xi}_i$ are related by a Stokes-Einstein relation, a similar relation between ζ_0 and $\vec{\lambda}_i$ exists. The Gaussian random contributions $\vec{\xi}_i$ and $\vec{\lambda}_i$ have δ-correlations in time, the amplitude of which is constrained by the condition that for conservative forces the equilibrium distribution should be the standard Boltzmann-Gibbs exponential factor, $\langle \xi_i^\mu(t) \xi_j^\nu(t') \rangle = 2\gamma_0 k_B T \delta_{ij} \delta^{\mu\nu} \delta(t-t')$, and similarly for $\vec{\lambda}_i(t)$ with γ_0 replaced by ζ_0. In physical conditions under which inertial effects can be discarded, at low Reynolds numbers, one obtains a set of over-damped Langevin equations

$$\gamma_0\ \dot{\vec{r}}_i = \vec{F}_i + \vec{\xi}_i\ , \tag{6.2.6}$$

$$\zeta_0\ \dot{\vec{p}}_i = \vec{\Gamma}_i \times \vec{p}_i + \vec{\lambda}_i \times \vec{p}_i\ , \tag{6.2.7}$$

in which the latter equation, which features a multiplicative noise, is to be understood with the Stratonovich, mid-point, discretization scheme, that ensures the conservation of the modulus of the dipole, as can be seen directly from (6.2.7). The ingredients entering the force $\vec{F}_i$ felt by particle i include an external force field and possible interactions with other colloids. Similarly, the torque $\vec{\Gamma}_i$ felt by particle i can include the effect of an external field. In general, the interparticle interaction energy $u(\vec{r}_i - \vec{r}_j, \vec{p}_i, \vec{p}_j)$ between particles i and j depends on the distance between these particles and on the orientation of the dipoles

they carry, as is the case in the well-known dipole-dipole interaction $u(\vec{r}_i - \vec{r}_j, \vec{p}_i, \vec{p}_j) = (4\pi\epsilon_0)^{-1}[\vec{p}_i \cdot \vec{p}_j / r_{ij}^3 - 3(\vec{p}_i \cdot \vec{r}_{ij})(\vec{p}_j \cdot \vec{r}_{ij})/r_{ij}^5]$. Both the force $\vec{F}_i$ and the torque then derive from the total potential energy $V = \frac{1}{2}\sum_{i \neq j} u(\vec{r}_i - \vec{r}_j, \vec{p}_i, \vec{p}_j)$ according to

$$\vec{F}_i = -\frac{\partial V}{\partial \vec{r}_i} , \qquad \vec{\Gamma}_i = -\vec{p}_i \times \frac{\partial V}{\partial \vec{p}_i} . \tag{6.2.8}$$

The combination $\vec{\Gamma}_i \wedge \vec{p}_i$ can also be written in the form

$$\vec{\Gamma}_i \wedge \vec{p}_i = \vec{E}_i p_i^2 - (\vec{p}_i \cdot \vec{E}_i)\vec{p}_i , \qquad \vec{E}_i = -\frac{\partial V}{\partial \vec{p}_i} . \tag{6.2.9}$$

6.3 Active Matter

A field of use of Langevin process which is currently attracting much attention is the one of active matter. The constituents of active matter, be them particles, lines or other, absorb energy from their environment or internal fuel tanks and use it to carry out motion. In this new type of soft condensed matter energy is partially transformed into mechanical work and partially dissipated in the form of heat [26, 27]. The units interact directly or through disturbances propagated in the medium. In systems of biological interest, conservative forces (and thermal fluctuations) are complemented by non-conservative forces. Realizations of active matter in biology are thus manifold and exist at different scales. Some of them are: bacterial suspensions, the cytoskeleton in living cells, or even swarms of different animals. Clearly enough, active matter is far from equilibrium and typically kept in a non-equilibrium steady state. The difference between active matter and other driven systems, such as sheared fluids, vibrated granular matter and driven vortex lattices is that the energy input is located on internal units (e.g. motors) and therefore homogeneously distributed in the sample. In the other driven systems mentioned above, the energy input occurs on the boundaries of the sample. Moreover, the effect of the motors can be dictated by the state of the particle and/or its immediate neighborhood and it is not necessarily fixed by an external field.

The dynamics of active matter presents a number of interesting features that are worth mentioning here. Active matter displays out of equilibrium phase transitions that may be absent in their passive counterparts. The dynamic states display large scale spatio-temporal dynamical patterns and depend upon the energy flux and the interactions between their constituents. Active matter often exhibits unusual mechanical properties, very large responses to small perturbations, and very large fluctuations – not consistent with the central limit theorem. Much theoretical effort has been recently devoted to the description of different aspects of these systems, such as self-organization of living microorganisms, the identification and analysis of states with spatial structure, such as bundles, vortices and asters, the study of the rheological properties of active particle suspensions with the aim of grasping which are the mechanical consequences of biological activity.

A rather surprisingly result was obtained with a variational solution to the many-body master equation of the motorized version of the standard hard sphere fluid often used to model colloids: instead of stirring and thus destabilize ordered structures, the motors do, in some circumstances enlarge the range of stability of crystalline and amorphous structures relative to the ones with purely thermal motion.

6.3.1 Active Brownian Particles

The Active Brownian Particles (ABP) model is a mesoscopic particle-based model that mimics the self-propelled motion of a particle in a dissipative environment [117]. It considers a collection of interacting objects coupled with the surrounding medium through stochastic effective interactions. The microscopic mechanisms for self-driven motion are not manifestly treated and only an effective self-propulsion is proposed, which results in a directional persistency in the motion.

The self-propulsion results from a force that acts on the particle's center of mass and points in the direction of an intrinsic body axis (the particle orientation). There are, therefore, positional, $\vec{r}_i$ and orientational, $\mathbf{n}_i$, degrees of freedom. $\mathbf{n}_i$ is a unit vector pointing in a direction fixed along a preferred axis of the particle. The particles are assumed to be immersed in a bath and therefore they are subject to friction and white noise, acting on both their position and the orientation.

In their simplest realization the particles are spherical and the propulsive force has constant magnitude, $F_{\rm act}$. Again for simplicity this model is usually considered in two dimensions. The equations of motion are then

$$m\ddot{\vec{r}}_i + \gamma\dot{\vec{r}}_i = F_{\rm act}\vec{n}_i - \vec{\nabla}_i \sum_{j(\neq i)} V(r_{ij}) + \vec{\xi}_i \,, \qquad \dot{\theta}_i = \eta_i \,, \tag{6.3.1}$$

where $\vec{n}_i = (\cos\theta_i, \sin\theta_i)$. Here V is a two-body potential that quantifies the interactions between the particles and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the inter-part distance. The potential is typically short-range and taken to be hardly repulsive. In relevant applications the parameters are such that one can safely take the over-damped limit, since $m/\gamma \ll 1$. The units of length and energy are σ and ε, respectively.

The noises $\vec{\xi}$ and η are Gaussian with $\langle \xi_i^\mu(t)\rangle = \langle \eta_i(t)\rangle = 0$ and $\langle \xi_i^\mu(t)\, \xi_j^\nu(t')\rangle = 2\gamma k_B T \delta_{ij}^{\mu\nu}\delta(t-t')$ and $\langle \eta_i(t)\, \eta_j(t')\rangle = 2D_\theta \delta_{ij}\delta(t-t')$. Temperature and the rotational diffusion coefficient D_θ are, in principle, independent parameters. However, the latter can be related to the temperature of the bath via $D_\theta = 3k_BT/(\gamma\sigma_d^2)$ assuming that rotational diffusion is of thermal origin. This follows from the Navier-Stokes equations assuming Stokes flow in the solvent and stick boundary conditions on the particle surface.

It is also worth noticing that dynamics is explicitly out of equilibrium due to the active force term. It also couples the evolution of the velocity $\dot{r}$ to the angular diffusion. In the passive limit $F_{\rm act} \to 0$, one recovers the motion of a usual Brownian particle and the position and angular degrees of freedom decouple.

The control parameters are the Péclet number $\mathrm{Pe} = F_{\mathrm{act}}\sigma/(k_BT)$ which compares the work done by the active force when translating a particle but its diameter to the typical energy scale of the bath, and the packing friction $\phi = \pi\sigma^2 N/(4S)$, with S the surface of the available space.

The particles undergo a persistent Brownian motion, that is, a tendency to continue moving in the same direction for a prolonged period of time. This is illustrated in the right panel of Fig. 6.17. The origin of the persistence is that the active force acquire a memory. More precisely, the integration of the second Eq. (6.3.1) yields

$$\begin{aligned}\langle \vec{F}_{\mathrm{act}}(t)\cdot\vec{F}_{\mathrm{act}}(t')\rangle &= F_{\mathrm{act}}^2\langle \vec{n}(t)\cdot\vec{n}(t')\rangle = \langle\cos(\theta(t)-\theta(t')\rangle \\ &= F_{\mathrm{act}}^2 e^{-(t-t')/t_p} \qquad \text{with} \qquad t_p = 1/D_\theta \end{aligned} \tag{6.3.2}$$

Therefore, the active force points in the same direction for a time proportional to t_p.

The persistence time $\tau_p = D_\theta^{-1} = \gamma\sigma^2/(3k_BT)$ is related to the persistence length $l_p = F_{\mathrm{act}}\tau_p/\gamma = \mathrm{Pe}\sigma_d/3$ which grows proportionally to Pe.

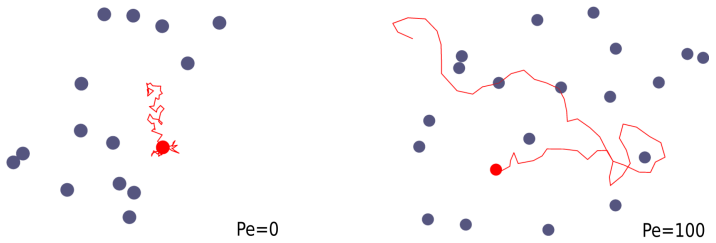

Figure 6.17: The typical trajectories of a passive Brownian particle (Pe = 0) and an active Brownian particle (Pe = 100).

Information about the translational motion of a single ABP is obtained from the mean-square displacement, $\Delta^2(t,t_0) \equiv \langle(\vec{r}(t)-\vec{r}(t_0))^2\rangle$, calculated from Eq. (6.3.1). Dropping the inertial term, an approximation that makes the solution easier, the ABP position is

$$\vec{r}(t) = \vec{r}(t_0) + \frac{1}{\gamma}\int_{t_0}^{t} dt' \left[\vec{F}_{\mathrm{act}}(t') + \vec{x}i(t')\right] \ . \tag{6.3.3}$$

from where we obtain

$$\begin{aligned}\Delta^2(t,t_0) &= \frac{4K_BT}{\gamma}(t-t_0) + \left(\frac{F_{\mathrm{act}}}{\gamma}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\ e^{-D_\theta(t'+t''-2\min(t',t''))} \\ &= \frac{4K_BT}{\gamma}(t-t_0) + \left(\frac{F_{\mathrm{act}}}{\gamma}\right)^2 \frac{1}{D_\theta^2}\left[D_\theta(t-t_0) + e^{-D_\theta(t-t_0)} - 1\right]. \end{aligned} \tag{6.3.4}$$

The mean-square displacement of the complete equation (with the inertial term) will then show four regimes:

- Ballistic regime. In this regime the velocity approaches the Maxwell distribution at the bath temperature T, and the mean-square displacement is ballistic, $\Delta^2 \sim (t-t_0)^2$, irrespective of there being an applied active force or not. This extremely short time regime ends at the time $t_v \sim m/\gamma$ that is typically the shortest time-scale in the problem. For this reason it can be ignored and the strict over-damped limit taken, as we did above.
- Thermal diffusive. At time scales longer than m/γ but still short with respect to the time-scale induced by $F_{\rm act}$, that we identify in the next item, the particle diffuses as in the absence of the active force,

$$\Delta^2 \sim D_T(t-t_0) \quad \text{with} \quad D_T = k_B T/\gamma \quad \text{for} \quad \frac{m}{\gamma} \ll t-t_0 \ll \frac{\gamma k_B T}{F_{\rm act}^2} \,. \tag{6.3.5}$$

- Active ballistic. The active force starts acting strongly on the particle motion. The Taylor expansion of the exponential term between the square brackets two second order, valid for $D_\theta(t-t_0) \ll 1$, yields $D_\theta^2(t-t_0)^2/2$ and the cross-over to this new ballistic regime occurs when this term becomes of the same order as the one linear in $(t-t_0)$:

$$\frac{k_B T}{\gamma}(t-t_0) \approx \left(\frac{F_{\rm act}}{\gamma}\right)^2 (t-t_0)^2 \quad \Longrightarrow \quad (t-t_0) \sim \frac{\gamma k_B T}{F_{\rm act}^2} \tag{6.3.6}$$

  The quadratic term then dominates and

$$\Delta^2 \sim \frac{F_{\rm act}^2}{\gamma^2}(t-t_0)^2 \quad \text{for} \quad \frac{\gamma k_B T}{F_{\rm act}^2} \ll t-t_0 \ll D_\theta \,. \tag{6.3.7}$$

  Active diffusive. For sufficiently long time delays so that the exponential contribution vanishes, the particle starts diffusing again with a new diffusion constant

$$\Delta^2 \sim D_{\rm eff}(t-t_0) \quad \text{with} \quad D_{\rm eff} = D_T + \left(\frac{F_{\rm act}}{\gamma}\right)^2 \frac{1}{D_\theta} \quad \text{for} \quad D_\theta \ll t-t_0 \,. \tag{6.3.8}$$

Of course, if the time scales identified from the equation are not well separated the crossovers between the various time-regimes will not be sharp.

The motion of a Janus colloid, which is quite well represented by an Active Brownian Particle, in contact with an environment and confined by a harmonic potential has been studied in great detail experimentally, numerically and analyticially [118].

The collective behavior of large ensembles of these particles leads to a very rich phase diagram, with active liquid, hexatic and solid phases, supplemented with a Motility Induced Phase Separation at large values of the activity [119].

6.3.2 Active Uhlenbeck Particles

In the Active Uhlenbeck Particle (AOUP) model, the Gaussian white noise of the overdamped Brownian colloids is replaced by a Gaussian colored noise, with no corresponding friction memory kernel. This sets the particle explicitly out of equilibrium because it is coupled to an out of equilibrium bath.

The position of generic active particles are determined by

$$\dot{\vec{r}}_i = -\mu\vec{\nabla}_i V + \vec{v}_i \tag{6.3.9}$$

where $\vec{v}_i$ are the self-propulsion velocities, μ is the particle mobility, and V is a inter-particle interaction potential. The self-propulsion velocities of the AOUP are given by N independent Ornstein-Uhlenbeck processes:

$$\tau\vec{v}_i = -\vec{v}_i + (2D)\vec{\eta}_i \tag{6.3.10}$$

with $\vec{\eta}_i$ zero-mean Gaussian white noises with delta correlations, $\langle\eta_i^\mu\eta_j^\nu\rangle = \delta_{ij}\delta_{\mu\nu}\delta(t-t')$. From direct integration It follows that $\vec{v}_i$ are a set of zero-mean colored Gaussian noises with correlations

$$\langle v_i^\mu v_j^\nu\rangle = \frac{D}{\tau}\,\delta_{ij}\delta_{\mu\nu}\,e^{|t-t'|/\tau} \tag{6.3.11}$$

Now, D controls the noise amplitude in $\vec{v}$ and τ its persistence.

In the limit $\tau \to 0$, the self- propulsion velocities become Gaussian white noises of correlation. For finite τ instead, the temporal correlations of the $\vec{v}_i$ are not matched by a corresponding memory kernel for the damping in Eq. (6.3.9) and the system is explicitly out of equilibrium [120].

6.3.3 Active Brownian Dumbbells

Active particles can take different forms and a simple model beyond the spherical ones is the one of a dumbbell, that is to say, a diatomic molecule formed by two spherical colloids with diameter σ_d and mass m_d linked together [121,122]. The atomic positions are noted $\vec{r}_1$ and $\vec{r}_2$ in a Cartesian system of coordinates fixed to the laboratory. Typically, one assumes that there is an elastic link between the colloids modelled by the finite extensible non-linear elastic form

$$\vec{F}_\mathrm{fene} = -\frac{k\vec{r}}{1-(r^2/r_0^2)} \tag{6.3.12}$$

with $k > 0$. The denominator ensures that the spheres cannot go beyond the distance r_0 with r the distance between their centres of mass. An additional repulsive force is added to ensure that the two colloids do not overlap. This is the Weeks-Chandler-Anderson (WCA) potential

$$V_\mathrm{wca}(r) \;=\; \begin{cases} V_\mathrm{LJ}(r) - V_\mathrm{LJ}(r_c) & r < r_c \\ 0 & r > r_c \end{cases}$$

with

$$V_{\rm LJ}(r) = 4\epsilon \left[\left(\frac{\sigma_{\rm d}}{r}\right)^{12} - \left(\frac{\sigma_{\rm d}}{r}\right)^{6} \right] , \tag{6.3.13}$$

where ϵ is an energy scale and r_c is the minimum of the Lennard-Jones potential, $r_c = 2^{1/6}\sigma_{\rm d}$. The active forces are polar and act along the main molecular axis $\hat{\vec{n}}$, are constant in modulus, and are the same for the two spheres belonging to the same molecule,

$$\vec{F}_{\rm act} = F_{\rm act}\ \hat{\vec{n}} . \tag{6.3.14}$$

The dynamic equations for one dumbbell are

$$m_d \ddot{\vec{r}}_i(t) = -\gamma_0 \dot{\vec{r}}_i(t) + \vec{F}_{\rm fene}(\vec{r}_{i,i+1}) - \frac{\partial V_{\rm wca}^{i\,i+1}}{\partial r_{i\,i+1}} \frac{\vec{r}_{i\,i+1}}{r_{i\,i+1}} + \vec{F}_i^{\rm act} + \vec{\xi}_i , \tag{6.3.15}$$

$$m_d \ddot{\vec{r}}_{i+1}(t) = -\gamma_0 \dot{\vec{r}}_{i+1}(t) - \vec{F}_{\rm fene}(\vec{r}_{i,i+1}) - \frac{\partial V_{\rm wca}^{i+1,i}}{\partial r_{i+1,i}} \frac{\vec{r}_{i+1,j}}{r_{i+1,i}} + \vec{F}_i^{\rm act} + \vec{\xi}_{i+1} , \tag{6.3.16}$$

with $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$ and $V_{\rm wca}^{ij} \equiv V_{\rm wca}(r_{ij})$ with $V_{\rm wca}$ defined in Eq. (6.3.13). Once the active force is attached to a molecule a sense of back and forth atoms is attributed to them; $\vec{F}_{\rm act}$ is directed from the ith colloid (tail) to the $i+1$th colloid (head). $\vec{F}_{\rm act}$ changes direction together with the molecule's rotation. The coupling to the thermal bath is modelled as usual, with a friction and a noise term added to the equation of motion. γ_0 is the friction coefficient. The noise $\vec{\xi}$ is a Gaussian random variable with

$$\langle \xi_{i\mu}(t) \rangle = 0 , \tag{6.3.17}$$

$$\langle \xi_{i\mu}(t) \xi_{j\nu}(t') \rangle = 2\gamma_0 k_B T \delta_{ij} \delta_{ab} \delta(t - t') , \tag{6.3.18}$$

with k_B the Boltzmann constant and T the temperature of the equilibrium environment in which the dumbbells move. a and b label the coordinates in d dimensional space. An effective rotational motion is generated by the random torque due to the white noise acting independently on the two beads.

6.4 Dynamic constraints

In some applications, one needs to select the trajectories that satisfy a given constraint. For instance, one may be interested in the dynamics of a particle constrained to move on a given N dimensional manifold, for example, a sphere with radius $\sqrt{N}$. The strict spherical condition reads

$$\phi \equiv \sum_{\mu=1}^{N} x_\mu^2 = N , \qquad \phi' \equiv \sum_{\mu=1}^{N} x_\mu \dot{x}_\mu = 0 , \tag{6.4.1}$$

where the first expression is the primary constraint and the second expression ensures that the particle does not leave the sphere as time elapses. The index μ labels the spatial

coordinates, and runs from 1 to N. The primary constraint can be imposed with a Lagrange multiplier, that turns out to depend on the particle's position and momentum and on the noise, to ensure that the particle remains on the sphere. The equations

$$m\dot{x}^\mu = p^\mu \,, \tag{6.4.2}$$

$$\dot{p}^\mu + \gamma \dot{x}^\mu = -z(\vec{x}, \vec{p}, \vec{\xi})x^\mu - V'(\vec{x}) + \xi^\mu \,, \tag{6.4.3}$$

with ξ^μ independent white noises with zero mean, $\langle \xi^\mu(t) \rangle = 0$, and delta correlations $\langle \xi^\mu(t)\xi^\nu(t') \rangle = 2\gamma k_B T \delta^{\mu\nu}\delta(t-t')$. When the potential energy is an anisotropic quadratic potential,

$$V(\vec{x}) = -\frac{1}{2}\sum_{\mu=1}^{N} \lambda_\mu x_\mu^2 \tag{6.4.4}$$

with harmonic constants, λ_μ, taken from the Wigner semi-circle law, one recovers the Langevin dynamics [123] of the Spherical Sherrington-Kirkpatrick (SSK) [124].

Another application concerns the requirement that the stochastic paths go through a given point at a given time [125, 126]. A typical example, is the one of Brownian bridges, that is, Brownian paths that are constrained to return to the origin at some future time. These processes have wide applications in the context of behavioral ecology and financial stock markets, to name a few. Also in this context, a way to achieve the goal is to derive effective Langevin equation with an effective force that implicitly accounts for the constraint. For instance, to generate a Brownian bridge $x_B(t)$ of duration t_f with the bridge constraint $x_B(0) = x_B(t_f)$, the effective Langevin equation reads

$$\dot{x}_B(t) = -\frac{x_B(t)}{t_f - t} + \sqrt{2\,D}\,\xi(t) \,, \tag{6.4.5}$$

where the subscript B refers to "bridge" and the first term in the right-hand side is the effective force that accounts for the bridge constraint. Simulating Brownian bridges can then be easily done by discretizing the effective Langevin equation over small time increments. Other effective Langevin equations have been obtained for several constrained processes such as excursions, meanders and even for some interacting particle systems.

6.5 Inference

Biological systems are so complex that it is too difficult to understand their dynamics from first principles. Data-driven approaches are then used to quantify their dynamics, and thus try to identify the underlying mechanisms and discover emergent laws. Microscopy and tracking provide abundant trajectories from biophysical experiments. The problem is, however, to infer from these short and noisy experimental data, the physical models that reproduces them the best. In other words, the idea is to infer the best Langevin equation. Several groups are currently working in devising inference methods to achieve this goal. See, for example [127].

6.6 Field equations

In this Section we extend the Langevin stochastic equations to act on fields. In the spirit of Landau, the equations are proposed phenomenologically and are dictated by symmetry and conservation laws.

6.6.1 The Ginzburg-Landau framework

Equilibrium collective behaviour at second order phase transitions are largely independent of the microscopic details and, as a consequence, also of the particular model used to describe it. Such universality characterizes the physical behaviour close to a critical point, where the system undergoes a continuous phase transition.

The onset of collective behaviour is revealed by the correlation length ξ_{eq}, the typical distance over which the fluctuations of the microscopic variables are correlated. Far away from a critical point ξ_{eq} is of the order of the range of the microscopic interactions, whereas it diverges at the critical point. Accordingly, close enough to the transition point, ξ_{eq} provides the only relevant length-scale of a critical system.

It is then possible to study the critical behaviour in terms of suitable field-theoretical models which reflect the internal symmetries of the underlying microscopic system. The proposed free-energy functionals depend only on the order parameter (the field) and a few other slow modes, whose actual nature are chosen to represent the specific system of interest. For instance, the order parameter can be identified with the magnetization in magnetic materials, or with the particle density in fluids.

By means of field-theoretical techniques it is possible to determine the non-analytic behaviour observed in various thermodynamic quantities and structure factors upon approaching the critical point. Such non-analyticities, parametrized by the standard critical exponents, some associated amplitude ratios and scaling functions turn out to be universal quantities. The values of the universal quantities and scaling functions identify the so-called equilibrium universality class.

6.6.2 Time-dependent Ginzburg-Landau description

Upon approaching a critical point the typical time scale of the fluctuations around the equilibrium state diverges as $\xi_{eq}^{z_{eq}}$ (critical slowing down), where z_{eq} is the dynamic critical exponent. This provides the natural separation between the relevant slow evolution due to the developing collective behaviour and the fast one related to microscopic processes. This separation makes the field theoretic description of the dynamics a particularly viable approach. Indeed it allows one to compute systematically the non-analytic behaviours observed in dynamical quantities, e.g., in the low-frequency limit of the dynamic structure factor. In turn the associated universal quantities define the dynamic universality class. Each static universality class consists of several dynamic sub-universality classes which

differ, e.g., by different conserved quantities, but nonetheless exhibit the same static universal properties. Moreover, the field theoretic approach can also be used away from the critical point to characterise the dynamics within the phases.

In order to treat phase-transitions and the coarsening process analytically it is preferable to introduce a continuous coarse-grained field,

$$\phi(\vec{x},t) \equiv \frac{1}{V}\sum_{i\in V_{\vec{x}}} s_i(t) \ . \tag{6.6.1}$$

In the magnetic case, this is the fluctuating magnetization density and a particle system it can represent a local density (through, for example the identification of an occupation number $n_i = (s_i + 1)/2$).

A Landau-Ginzburg free-energy functional is introduced

$$F[\phi] = \int d^d x \ \left\{ \frac{c}{2} \left[\vec{\nabla}\phi(\vec{x},t)\right]^2 + V[\phi(\vec{x},t)] \right\} \tag{6.6.2}$$

and the elastic constant c is usually re-absorbed with a series of re-definitions.

With the choice of potential V one distinguishes between a second order and a first order phase transition. In the former case, the typical form is the double-well, ϕ^4, form:

$$V(\phi) = a\phi^4 + b(g)\phi^2 \ . \tag{6.6.3}$$

The first term in Eq. (6.6.2) represents the energy cost to create a domain wall or the elasticity of an interface. The second term depends on a parameter, g, and changes sign from positive at $g > g_c$ to negative at $g < g_c$. The other parameter a is positive. Above the critical point determined by $b(g_c) = 0$ it has a single minimum at $\phi = 0$, at g_c it is flat at $\phi = 0$, and below g_c it has a double well structure with two minima, $\phi = \pm[-b(g)/(2a)]^{1/2} = \langle\phi\rangle_{eq}(g)$, that correspond to the equilibrium states in the ordered phase.

Exercise 6.3 Equation (6.6.2) is exact for a fully connected Ising model where $V(\phi)$ arises from the multiplicity of spin configurations that contribute to the same $\phi(\vec{x}) = m$. The order-parameter dependent free-energy density reads $f(m) = -Jm^2 - hm + k_BT\{(1+m)/2\ln[(1+m)/2] + (1-m)/2\ln[(1-m)/2]$ that close to the critical point where $m \simeq 0$ becomes $f(m) \simeq (k_BT - J)/2\ m^2 - hm + k_BT/12\ m^4$ demonstrating the passage from a harmonic form at $k_BT > k_BT_c = J$, to a quartic well at $T = T_c$, and finally to a double-well structure at $T < T_c$. Prove these statements.

Exercise 6.4 With a six-order potential $V(\phi) = a + b\phi^2 + c\phi^4 + d\phi^6$ one can mimic first order phase transitions. The sign of d, $d > 0$, is fixed by the condition that the potential be confining at large values of $|\phi|$. The potential has a local minimum at $\phi = 0$ for all $b > 0$. Next, we choose $c < 0$ to allow for the existence of two maxima and two minima at $\phi = \pm[(-c \pm \sqrt{c^2 - 3bd})/(3d)]^{1/2}$. Derive all these results.

When discussing dynamics one should write down the stochastic evolution of the individual components and compute time-dependent averaged quantities. This is the procedure used in numerical simulations. Analytically it is more convenient to work with a field-theory and an evolution equation of Langevin-type. This is the motivation for the introduction of continuous field equations that regulate the time-evolution of the coarse-grained order parameter. Ideally these equations should be derived from the microscopic stochastic dynamics but in practice they are introduced phenomenologically. In the magnetic case as well as in many cases of interest, the domain wall and interface dynamics can be argued to be over-damped (i.e. $t \gg t_r^{\dot{\phi}}$) and the Smoluchowski limit assumed.

Two very similar approaches are used. Assuming T is only relevant to determine the equilibrium coarse-grained field, that is, the form of the potential V, one uses the phenomenological zero-temperature time-dependent Ginzburg-Landau equation deterministic equation

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} \tag{6.6.4}$$

(the friction coefficient has been absorbed in a redefinition of time). Initial conditions are usually chosen to be random with short-range correlations

$$[\,\phi(\vec{x},0)\phi(\vec{x}',0)\,]_{ic} = \Delta\delta(\vec{x}-\vec{x}') \tag{6.6.5}$$

thus mimicking the high-temperature configuration ($[\ldots]_{ic}$ represent the average over its probability distribution). The numeric solution to this equation with the quartic potential and $b<0$ shows that such a random initial condition evolves into a field configuration with patches of ordered region in which the field takes one of the two values $[-b/(2a)]^{1/2}$ separated by sharp walls. It ignores temperature fluctuations within the domains meaning that the field is fully saturated inside them and, consequently, one has access to the aging part of the correlations only. The phase transition is controlled by the parameter b in the potential. Importantly enough

Another, similar approach, is to add a thermal noise to the former

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} + \xi(\vec{x},t)\ . \tag{6.6.6}$$

This is the field-theoretical extension of the Langevin equation in which the potential is replaced by the order-parameter-dependent functional free-energy in Eq. (6.6.2) with a potential form with fixed parameters leading to the double well form (independent of T). The noise ξ is taken to be Gaussian distributed with zero mean and correlations

$$\langle \xi(\vec{x},t)\xi(\vec{x}',t')\rangle = 2k_B T\delta^d(\vec{x}-\vec{x}')\delta(t-t')\ . \tag{6.6.7}$$

The friction coefficient has been absorbed in a redefinition of time. For a quartic potential a dynamic phase transition arises at a critical T_c; above T_c the system freely moves above

the two minima and basically ignores the double well structure while below T_c this is important. Within the growing domains the field ϕ fluctuates about its mean also given by $[-b/(2a)]^{1/2}$ and the fluctuations are determined by T. One can describe the rapid relaxation at times such that the domain walls do not move with this approach.

These equations act on a scalar order parameter and do not conserve it neither locally nor globally. They are called model A in the classification of Hohenberg-Halperin [17].

Extensions for cases in which a scalar order parameter is locally conserved (model B) are adequate to describe phase separation in particle problems in which the particles cannot be eliminated nor created. The equilibrium free-energy density is the same as the one above but the stochastic equation must be such that the conservation law is enforced.

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -\nabla^2 \frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} \tag{6.6.8}$$

which can be written in the form of a continuity equation with a current $\vec{J}$:

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = \vec{\nabla}\cdot\vec{J}(\vec{x},t) \qquad\qquad \vec{J}(\vec{x},t) = -\vec{\nabla}\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} \; . \tag{6.6.9}$$

The effect of the noise is incorporated by adding a random vector term with i.i.d. components white noise characteristics to the current:

$$\vec{J}(\vec{x},t) \mapsto \vec{J}(\vec{x},t) + \vec{\xi}(\vec{x},t) \; . \tag{6.6.10}$$

This equation is also called the Cahn-Hilliard equation.

Cases with vectorial or even tensorial order parameters can be treated similarly and are also of experimental relevance, notably for vectorial magnets or liquid crystals.

These equations are the starting point to study the critical dynamics with renormalization group methods [17]. Details on their solutions of these equations and the phase ordering kinetics that they describe can be found in [21, 22].

In active matter modelling, an active model B was introduced [27]. It starts from the continuity equation in (6.6.9) and it modifies the current

$$\vec{J}(\vec{x},t) = -\vec{\nabla}\left\{\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} + \lambda[\vec{\nabla}\phi(\vec{x},t)]^2\right\} + \vec{\xi}(\vec{x},t) \; . \tag{6.6.11}$$

The current has a term which is the gradient of the standard non-equilibrium chemical potential/free-energy (6.6.2) but the last term added is $\neq \delta F[\phi]/\delta\phi$ for any $F[\phi]$. The model was then modified into the so-called active model B+ in which other terms which also break detailed balance are added to the current [27]

$$\vec{J} \mapsto \vec{J} + \zeta(\nabla^2\phi)\vec{\nabla}\phi - \frac{1}{2}\vec{\nabla}(\vec{\nabla}\phi)^2 \tag{6.6.12}$$

which are the allowed terms in an expansion to order ∇^3 and ϕ^2. Now the terms proportional to ζ and λ are of the same order, and the ζ term vanishes for a flat interface so it does not affect the bulk contributions.

6.7 Dean-Kawasaki equation

The Dean-Kawasaki equation is a stochastic field equation obeyed by the density function for a system of Langevin processes interacting via a pairwise potential. This equation was first proposed by Kawasaki on phenomenological grounds [112] and it was then proven by Dean in a very elegant paper [113]. Differently from the phenomenological equations usually used to describe the dynamics of non-conserved (model A) and conserved (model B) particle systems described in Sec. 6.6, the spatial white noise for this system appears not additively but multiplicatively. This is a consequence of the fact that the density cannot fluctuate in regions devoid of particles. The steady state for the density function takes the form of a functional integral over the coursed grained free energy of the system.

We now briefly review how to introduce a single differential equation with all the information content of the system of Langevin equations describing the Brownian particles. The stochastic ordinary differential equation for each particle are

$$\dot{\vec{x}}_j = -V'(\vec{x}_i - \vec{x}_j) + \vec{\eta}_j \ , \qquad\qquad j = 1, \dots, N$$

The strict over-damped limit in which the inertial term is discarded is usually considered in this context. The $\vec{\eta}_i$ are independent time-dependent white noises η_j with zero mean and correlations $\langle \eta_i^a(t)\eta_j^b(t')\rangle = 2k_BT\delta_{ij}\delta_{ab}\delta(t-t')$. The friction coefficient has been absorbed in a redefinition of time. V is the interaction potential between the particles which is assumed to depend only on the inter-particle distance.

The number density field $\varrho(x,t)$ is defined as

$$\varrho(\vec{x},t) = \sum_{j=1}^{N} \delta(\vec{x} - \vec{x}_j(t)) \qquad \text{or} \qquad \varrho_{\vec{k}}(t) = \frac{1}{V}\sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{x}_j(t)} \tag{6.7.1}$$

Defining the density field as in (6.7.1), the system of equations can be formally translated into a partial differential equation governing the evolution of the density field

$$\begin{aligned} \partial_t \varrho(\vec{x},t) \ &= \ \vec{\nabla}\cdot\left(\vec{\xi}\sqrt{\varrho(\vec{x},t)}\right) + T\nabla^2\varrho(\vec{x},t) \\ &\quad + \vec{\nabla}\varrho(\vec{x},t)\cdot\int d^d y\, \varrho(\vec{y},t)\vec{\nabla}V(\vec{x}-\vec{y}) \end{aligned} \tag{6.7.2}$$

In the process, the N independent noises $\vec{\eta}_j(t)$ have been turned into a single vector field $\vec{\xi}(x,t)$ with self-correlation:

$$\langle \xi_a(\vec{x},t)\xi_b(\vec{x}',t')\rangle = 2T\delta_{ab}\delta(t-t')\delta(\vec{x}-\vec{x}')$$

Since in (6.7.2) the noise multiplies the density field, the differential equation becomes a meaningful string of symbols only once a proper interpretation for the noise term is given.

It should be stressed that, due to the singular nature of the density field, the natural setting of Dean's equation is a distribution space. In such a setting the equation has been derived exactly, without any coarse-graining assumptions or cut-off scales which are not necessary to obtain the differential equation [113].

This equation turned out to be extremely useful to analyze passive (as well as active with the necessary extensions) Brownian particle systems. For example, the Poisson statistics of the density-density correlation functions of the Brownian gas were derived in [114]. The formation of periodic clusters in systems of Brownian particle interacting via repulsive soft-core potentials is due the interplay among diffusion, the intracluster forces, and the forces between neighboring clusters. This surprising phenomenon is captured by the deterministic part of the Dean-Kawasaki equation (neglecting fluctuation effects) [115]. Onsager's results for strong electrolyte conductivity can be derived in a relatively straightforward fashion using the Kawasaki-Dean equation [116]. These are just a few examples where this equation has been successfully applied.

6.8 Quantum

Sometimes open quantum mechanical system are treated in an approximate way with Generalized Langevin Equations [54,128–130], in which the quantum Bose-Einstein energy distribution is enforced by tuning the random and friction forces, while the system degrees of freedom remain classical. Although these baths have been formally justified only for harmonic oscillators, they perform well for several systems, while keeping the cost of the simulations comparable to the classical ones [131].

In other cases, dissipation and noise are added to the deterministic quantum equations (either the SchrÃ¶dinger equation itself or the equation for the density matrix). Often, these approaches break the constraint of unitarity of the evolution, necessary for the conservation of the total probability in the statistical interpretation of quantum mechanics.

A generating functional framework [14] in which the system and the bath are both treated quantum mechanically and the bath integrated out (since assumed to be simple, made of oscillators [47], free fermions or free bosons) is fully consistent. It yields to a reduced dynamic generating functional called closed time path or Schwinger-Keldysh which in the classical limit approaches the Martin-Siggia-Rose-Janssen one.

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