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An Introduction to Computational Statistical Physics

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Part I

Introduction to statistical physics

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Introduction to statistical physics

This chapter presents the physical and mathematical frameworks to understand the basic notions of molecular simulation and statistical physics. Section 1.1 recalls the aims of computational statistical physics, gives some historical landmarks, and provides the orders of magnitude of the quantities to be computed. Section 1.2 discusses how physical systems are described at the microscopic level: unknowns, boundary conditions, interaction potentials, etc. Section 1.3 is a short summary of the most important concepts of statistical physics which will be of constant use throughout these lecture notes, in particular elements on thermodynamic ensembles. For a more comprehensive introduction to statistical physics, the reader can for instance refer to [21], as well as textbooks on molecular simulation [5, 223, 97, 269].

1.1 Computational statistical physics: some landmarks

Before giving a detailed mathematical framework for computational statistical physics, we first describe the scientific context, by recalling in Section 1.1.1 some order of magnitudes for the quantities under investigation, and by making explicit in Section 1.1.2 what we understand to be the current aims of molecular simulation.

1.1.1 Some orders of magnitude

In the framework of statistical physics, matter is most often described at the atomic level, either in a quantum or classical framework. Some of the concepts developed in this introduction may however

Physical constant	Usual notation	Value
Avogadro number	$\mathcal{N}_A$	6.02×10^{23}
Boltzmann constant	k_{B}	1.381×10^{-23} J/K
Reduced Planck constant	$\hbar$	1.054×10^{-34} Js
Elementary charge	e	1.602×10^{-19} C
Electron mass	m_{e}	9.11×10^{-31} kg
Proton mass	m_{p}	1.67×10^{-27} kg
Electron-Volt	eV	1.602×10^{-19} J

Table 1.1. Some important physical constants or quantities in quantum and statistical physics.

be used in other physical frameworks than molecular simulation (for instance, the Hamiltonian dynamics presented in Section 2.1 is the fundamental evolution equation in celestial mechanics).

In these lecture notes, only classical systems are considered. Some important physical constants are recalled in Table 1.1. From those constants, the orders of magnitudes of the classical description of matter at the microscopic level can be inferred. The typical distances ℓ_0 are of the order of 1 Å (10^{-10} m), the energies ε_0 are of the order of $k_{\mathrm{B}}T \simeq 4 \times 10^{-21}$ J at room temperature, so that, using the equality (1.8) below, the typical times t_0 are of the order of 6×10^{-13} s when the proton mass is the reference mass m_0. The precise choice of the reference values for the length, mass, time and energy depends on the system of interest; see the discussion following (1.8).

The orders of magnitude used in the microscopic description of matter are far from the orders of magnitude of the macroscopic quantities we are used to. For instance, the number of particles under consideration in a macroscopic sample of material is of the order of the Avogadro number $\mathcal{N}_A \sim 10^{23}$. For practical numerical computations of matter at the microscopic level, the dynamics has to be discretized, the timestep to be used being a fraction of the typical time t_0 introduced above, typically of the order of 10^{-15} s. Following the dynamics of every atom on a time of the order of a second would therefore require simulating $\mathcal{N}_A$ atoms and performing $\mathrm{O}(10^{15})$ time steps, which is of course impossible! These numbers should be compared with the current orders of magnitude of the problems that can be tackled with classical molecular simulation, such as the simulation of a bacterial cytoplasm of 100 million atoms over 100 ns [281], the simulation of an entire gene locus of 1 billion atoms over 1 ns [146], or the simulation of a polycrystalline microstructure of 100 billion atoms for 500 ps [251]. Smaller system in sizes could also be integrated over times of the order of milliseconds [250, 205].

To give some insight into such large numbers, it is helpful to compute the number of moles of water on earth. Recall that one mole of water corresponds to 18 mL, so that a standard glass of water contains roughly 10 moles, and a typical bathtub contains 10^5 mol. On the other hand, there are approximately 1.3×10^{18} m^3 of water in the oceans, *i.e.* 7.2×10^{22} mol, a number comparable to the Avogadro number. This means that inferring the macroscopic behavior of physical systems described at the microscopic level by the dynamics of several millions of particles only is like inferring the ocean's dynamics from hydrodynamics in a large bathtub or a small pond...

Describing the macroscopic behavior of matter knowing its microscopic description therefore seems out of reach. Statistical physics allows us to bridge the gap between microscopic and macroscopic descriptions of matter, at least at a conceptual level. The question is whether the estimated quantities for a system of N particles correctly approximate macroscopic properties, formally obtained in the thermodynamic limit $N \to +\infty$ (the density being kept fixed). In some cases, in particular for simple homogeneous systems, the macroscopic behavior is well approximated by small-scale simulations, see Section 1.1.2. However, the convergence of the estimated quantities as a function of the number of particles involved in the simulation should be checked in all cases.

1.1.2 Aims of molecular simulations

Despite its intrinsic limitations in terms of spatial and timescales, molecular simulation has been used and developed over the past 70 years, and its number of users keeps increasing. As we understand it, it has two major aims nowadays.

First, it can be used as a *numerical microscope*, which allows us to perform "computer" experiments. This was the initial motivation for simulations at the microscopic level: physical theories were tested on computers. This use of molecular simulation is particularly clear in its historic development, which was triggered and sustained by the physics of simple liquids. Indeed, there was no good analytical theory for these systems, and the observation of computer trajectories was very helpful to guide the physicists' intuition about what was happening in the system, for instance the mechanisms leading to molecular diffusion. In particular, the pioneering works on Monte-Carlo methods [195], and the first molecular dynamics simulation [4] were performed because of such motivations. Today, understanding the behavior of matter at the microscopic level can still be difficult from an experimental viewpoint (because of the high resolution required, both in time and in space), or because we simply do not know what to look for! Numerical simulations are then a valuable tool to test some ideas or obtain some data to process and analyze in order to help assessing experimental setups. This is particularly true for current nanoscale systems in electronics, or for biological systems which can nowadays be imaged with nanometer precision.

Another major aim of molecular simulation, maybe even more important than the previous one, is to compute macroscopic quantities or thermodynamic properties, typically through averages of some functionals of the system. In this case, molecular simulation is a way to obtain *quantitative* information on a system, instead of resorting to approximate theories, constructed for simplified models, and giving only qualitative answers. Sometimes, these properties are accessible through experiments, but in some cases only numerical computations are possible since experiments may be unfeasible or too costly (for instance, when high pressure or large temperature regimes are considered, or when studying materials not yet synthesized).

More generally, molecular simulation is a tool to explore the links between the microscopic and macroscopic properties of a material, allowing to address modelling questions such as "Which microscopic ingredients are necessary (and which are not) to observe a given macroscopic behavior?", or "How do the particles organize themselves to create a macroscopic state of matter?"

An example: the equation of state of Argon

Let us make precise to some extent the second aim mentioned above, namely the computation of average properties. We illustrate it with a simple but realistic example. We consider microscopic systems composed of N particles in dimension 3 (typically atoms, *i.e.* nuclei together with their electronic clouds), described by the positions of the particles $q = (q_1, \cdots, q_N) \in \mathcal{D}$ and the associated momenta $p = (p_1, \cdots, p_N) \in \mathbb{R}^{3N}$. The set $\mathcal{D}$, which is called the configuration space, is typically an open subset (possibly the whole) of $\mathbb{R}^{3N}$, or $\mathcal{D} = (L\mathbb{T})^{3N}$ for some parameter $L > 0$ (where $\mathbb{T} = \mathbb{R}/\mathbb{Z}$ denotes the one-dimensional torus). The choice of $\mathcal{D}$ depends on the boundary conditions at hand, see Section 1.2.1. The vector (q, p) is called the *microscopic state* or the *configuration* of the system. The set of all possible microscopic configurations (q, p) is called the *phase space*.

In the framework of statistical physics, macroscopic quantities of interest are written as averages over thermodynamic ensembles, which are probability measures over the admissible microscopic configurations:

$$\mathbb{E}_\mu(\varphi) = \int_{\mathcal{E}} \varphi(q,p)\, \mu(dq\, dp). \tag{1.1}$$

In this expression, the function φ is called an *observable*. The probability measure μ has support on the phase space and depends on the thermodynamic ensemble used, see Section 1.2 for further precisions on the most common choices.

Remark 1.1 (Generalization to other configuration spaces). *All the results presented in these notes may be generalized to the case when the configuration space $\mathcal{D}$ is not $\mathbb{R}^n$, but some subset of $\mathbb{R}^n$, with appropriate boundary conditions on the frontier $\partial\mathcal{D}$ (for instance, reflecting boundary conditions). One could also consider systems with molecular constraints (for instance, some interatomic distances being fixed), in which case $\mathcal{D}$ is a submanifold of $\mathbb{R}^{3N}$ and the phase-space is the*

cotangent space $T^*\mathcal{D}$. We however refrain from doing so in order to keep the presentation simpler; see for instance [178, Chapter 3] for discussions on how to handle molecular constraints.

A statistical description through a probability measure μ is a convenient description since the complete microscopic information is both unimportant (what matters are average quantities, and not the positions of all particles composing the system) and too large to be processed.

An example of property of interest for Argon is the bulk pressure P. For particles of masses m_i, described by their positions q_i and their momenta p_i, it is given by $P = \mathbb{E}_\mu(\varphi)$ with

$$\varphi(q,p) = \frac{1}{3|\mathcal{D}|} \sum_{i=1}^{N} \left(\frac{|p_i|^2}{m_i} - q_i \cdot \frac{\partial V}{\partial q_i}(q) \right), \tag{1.2}$$

where $|\mathcal{D}|$ is the physical volume of the box occupied by the fluid, and the potential energy function V is made precise below, see (1.5)-(1.6).

In practice, such averages may yield results that are very close to experimental measurements, even for systems which are small in comparison to the actual sizes of macroscopic systems (provided the interaction potentials are short-ranged). For example, the equation of state of Figure 1.1, which relates the density and the pressure at a fixed temperature, has been computed with a system of a few thousand particles only, a number which is 20 orders of magnitude lower than the Avogadro number. To obtain these results, a cubic system with periodic boundary conditions and fixed temperature was considered, with a box size chosen to match the desired density, and the pressure was computed as $P = \mathbb{E}_\mu(\varphi)$ with φ given in (1.2) (techniques to do will be extensively presented in these lecture notes). The computed results are compared with experimental measurements.[1] The agreement is very good in the case of Argon. Notice also that high-pressure results, not easily obtained from experiments, can be computed.

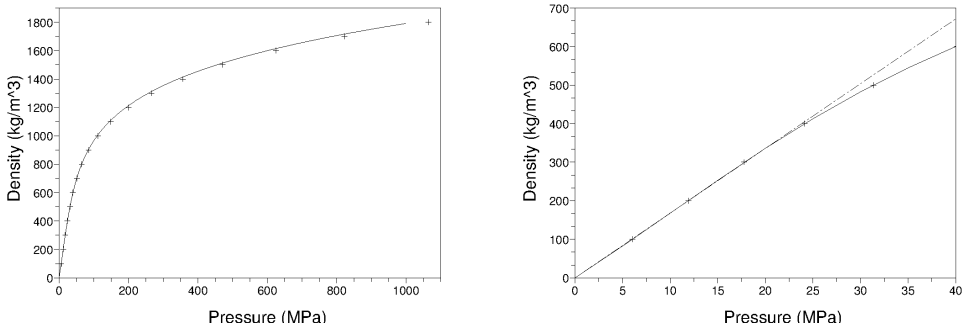

Fig. 1.1. Numerical equation of state of argon at $T = 300$ K ('+') and experimental reference curve (solid line). The picture on the right is a zoom on the low density/low pressure part of the curve, where the ideal gas regime is plotted in dash-dotted line.

Besides static equilibrium properties of the form of (1.1), it is also possible to consider dynamical properties depending on the actual time evolution of the system (correlation functions, transport coefficients such as thermal conductivity, exit times from a region in phase space,...); see for instance Chapters 8 and 9.

1.2 Microscopic description of physical systems

The description of systems in statistical physics requires a fundamental ingredient: microscopic interaction laws between the constituents of matter and possibly the environment. The interactions

[1] See for instance the NIST webpage `http://webbook.nist.gov/chemistry/fluid/`

between the particles are taken into account through a potential function V, depending on the positions q only. The total energy of the system is then given by the Hamiltonian

$$H(q,p) = U(p) + V(q), \tag{1.3}$$

where the kinetic energy is

$$U(p) = \frac{1}{2}\, p^T M^{-1} p, \qquad M = \begin{pmatrix} m_1 \,\mathrm{Id}_3 & & 0 \\ & \ddots & \\ 0 & & m_N \,\mathrm{Id}_3 \end{pmatrix}.$$

The matrix M is called the mass matrix. A Hamiltonian such as (1.3) is said to be *separable* since it writes as the sum of two terms, depending only on the momenta and the positions, respectively. Most Hamiltonians encountered in applications are separable, and we will in any case restrict ourselves to separable Hamiltonians in these notes. An instance of a non-separable Hamiltonian is the case when the mass-matrix depends on the configuration q of the system, which is for example the case when the configuration is described in terms of so-called internal variables (angles, distances between atoms, etc). Non-separable Hamiltonians can also be considered for mathematical proofs, as the modified Hamiltonians used in the backward analysis of Hamiltonian dynamics (see Section 2.2).

In order to describe more precisely the interactions between the elementary constituents of the system, several points have to be made precise. First, the boundary conditions of the system must be specified (see Section 1.2.1). We next discuss the interaction potential V in Section 1.2.2. This function is very important since it incorporates almost all the physics of the problem. It is therefore no surprise that obtaining reliable potential functions is still a very active research field.

1.2.1 Boundary conditions

Several boundary conditions can be imposed onto the system:

(i) Many current simulations are performed using periodic boundary conditions, so that surface effects can be avoided and configurations typically encountered in the bulk of the system can be obtained. In this case, a particle interacts not only with all the particles in the systems, but also with their periodic images (see Figure 1.2). In practice, interactions with a finite interaction range are set to 0 when the distance between two or several particles exceeds a given cut-off radii r_{cut}. When cubic domains of length L are considered as in Figure 1.2, *i.e.* $\mathcal{D} = (L\mathbb{T})^{3N}$, the domain length should be chosen so that $r_{\mathrm{cut}} < L/2$. This ensures that a particle interacts either with the primitive particle, or at most one of its periodic images. Long-range interactions such as Coulomb interactions require a dedicated treatment, where the potential energy function is decomposed into a short range part with finite interaction range, and a long range part where particles and all of their periodic images are taken into account using dedicated techniques such as Ewald's sum [255];

(ii) In some simulations, the system is allowed to visit the entire physical space ($\mathcal{D} = \mathbb{R}^{3N}$). This is the case for isolated systems, such as molecules *in vacuo*. It may be convenient however to quotient out translations in this case since the potential energy is usually invariant under these transformations;

(iii) It is sometimes necessary to consider confined systems. In this case, the positions of the particles are restricted to some predefined region of space, and some rules have to be set when the particles attain the boundary (such as specular reflection of the momenta).

Let us finally mention that open systems with inflows or outflows of energy, particles etc., are sometimes considered. In this case, there may be some exchanges or forcing at the boundaries. Such situations are not considered in these notes.

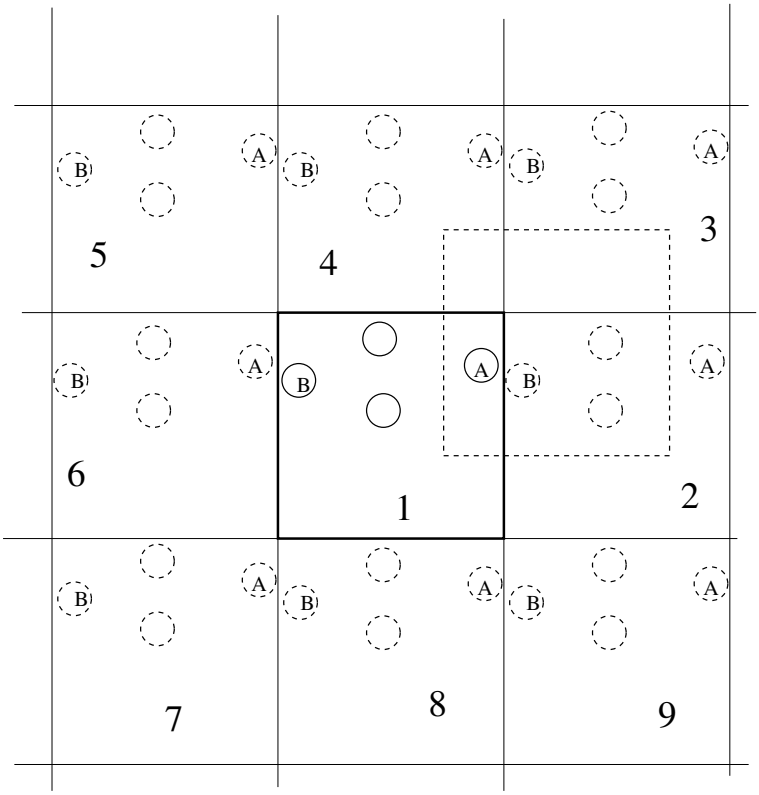

Fig. 1.2. System with periodic boundary conditions. The simulation cell is numbered "1", and the other cells are obtained by translation. The particles inside the primitive cell have interactions with particles in all the other cells.

1.2.2 Potential functions

Ab initio interaction potentials.

Ideally, the interaction potentials between the particles should be obtained in a non-empirical approach by resorting to *ab initio* computations. To reduce the computational cost of the simulations, it is customary to rely on the Born–Oppenheimer assumption, which assumes that, due to the very large difference in mass between nuclei and electrons, the evolution of the electronic and nuclear degrees of freedom can be decoupled, more precisely that the electronic degrees of freedom can be described by a wavefunction where only the positions of the nuclei enter as parameters (in particular, it is not necessary to take the nuclear momenta into account). Moreover, the wavefunction is the ground state of the Schrödinger operator associated with the fixed nuclei. More mathematical precisions on this approximation can be found in [264] for instance. Under the Born–Oppenheimer assumption, the energy of the system of nuclei of charges Z_i at positions q_i is therefore obtained by adding the Coulomb interaction energies between the nuclei, and the electronic ground-state energy:

$$V(q_1, \ldots, q_N) = \sum_{1 \leqslant i < j \leqslant N} \frac{Z_i Z_j}{|q_i - q_j|} + V_{\mathrm{elec}}(q_1, \ldots, q_N). \tag{1.4}$$

Denote by $M = Z_1 + \cdots + Z_N$ the number of electrons. The system is assumed to be neutral. The electronic ground-state energy is obtained by minimizing the electronic problem over the Hilbert space $\mathcal{H}$ of admissible wavefunctions, which is a subset of the space of antisymmetric functions in $\mathrm{L}^2(\mathbb{R}^3, \mathbb{C})$. We omit the spin variable for notational simplicity although this variable is very important for quantitative computations. The electronic problem then reads

$$V_{\rm elec}(q_1,\dots,q_N) = \inf\Big\{ \big\langle \psi, \widehat{H}_{q_1,\dots,q_N}\psi\big\rangle_{\mathcal{H}} \;\Big|\; \psi\in\mathcal{H},\ \|\psi\|_{L^2}=1\Big\},$$

where the electronic Hamiltonian operator reads

$$\widehat{H}_{q_1,\dots,q_N} = -\sum_{m=1}^{M}\frac{1}{2}\Delta_{x_m} - \sum_{m=1}^{M}\sum_{i=1}^{N}\frac{Z_i}{|x_m-q_i|} + \sum_{1\leqslant n<m\leqslant M}\frac{1}{|x_n-x_m|}.$$

We refer for instance to [46] for further precision on the computation of *ab initio* interaction potentials. Such computations are however very time-consuming, so that only small systems can be simulated this way (using Born-Oppenheimer molecular dynamics [206] or the Car-Parrinello approach [50]).

Empirical potentials.

In practice, empirical formulas for the potential energy function are used to study larger systems. These empirical formulae are obtained by assuming a functional form for the interaction potential, which depends on a set of parameters. These parameters may be chosen so that the potential energy function is as close as possible to the function (1.4) obtained from small *ab initio* computations. Alternatively, the parameters may be such that average properties computed from molecular simulations match experimental thermodynamic properties such as the equation of state of the material, its heat capacity, etc.

A very simple example of an empirical potential is the potential function of a fluid composed of N particles, interacting through a pairwise additive potential depending only on the distance between the particles:

$$V(q_1,\dots,q_N) = \sum_{1\leqslant i<j\leqslant N}\mathcal{V}(|q_i-q_j|). \tag{1.5}$$

For example, noble gases are well described using (1.5) when $\mathcal{V}$ is the Lennard-Jones potential (depicted in Figure 1.3)

$$\mathcal{V}(r) = 4\,\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right). \tag{1.6}$$

This potential depends on two parameters: an energy ε and a distance σ. For Argon for instance, a good model is obtained with $\varepsilon = 1.66\times10^{-21}$ J, and $\sigma = 3.405$ Å. The model (1.5)-(1.6) is suitable for noble gases since these systems are monatomic and the corresponding atoms have closed electronic shells. Therefore, the dominant physical interaction is the weakly attractive long-range van der Waals contribution, which scales as r^{-6}.

Potential functions for molecules.

Many systems of interest contain molecules. Their description requires interaction potentials accounting for covalent bonds between atoms and various bending or torsion angles between subsequent covalent bonds. This is modelled through elementary interactions involving two atoms or more. In order to present some typical elementary interactions used to describe molecules, it is convenient to introduce the vectors $r_{i,j} = q_j - q_i$ for $1\leqslant i,j\leqslant N$.

(1) The interactions between two atoms involved in a covalent bond can be modelled *via* a harmonic potential energy

$$\mathcal{V}_2(q_i,q_{i+1}) = \frac{k_2}{2}\big(|r_{i,i+1}|-\ell_{\rm eq}\big)^2,$$

where $\ell_{\rm eq}$ is the equilibrium length, and k_2 is a stiffness parameter;

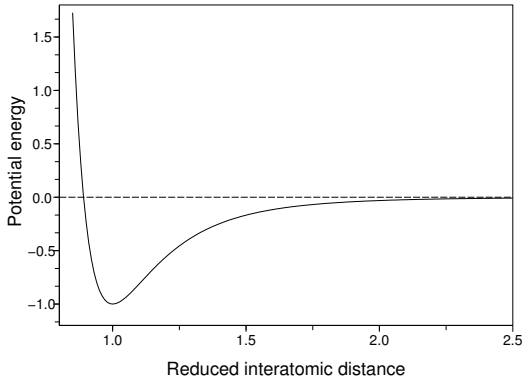

Fig. 1.3. Lennard-Jones potential (1.6) where the distance and the energy are expressed in terms of the equilibrium distance $2^{1/6}\sigma$ and the reference energy ε.

(2) Three atoms linked by two successive covalent bonds sharing a common atom (typically, three carbon atoms along the backbone of a polymer chain) can interact *via* the three-body interaction potential energy

$$\mathcal{V}_3(q_i, q_{i+1}, q_{i+2}) = \frac{k_3}{2}(\theta_i - \theta_{\rm eq})^2,$$

where the bond angle θ_i is

$$\theta_i = \arccos\left(\frac{r_{i,i+1}}{|r_{i,i+1}|} \cdot \frac{r_{i+1,i+2}}{|r_{i+1,i+2}|}\right),$$

while $\theta_{\rm eq}$ is the equilibrium bond angle, and k_3 is a stiffness parameter;

(3) Likewise, four atoms linked by three successive covalent bonds may experience the four-body interaction potential energy

$$\mathcal{V}_4(q_i, q_{i+1}, q_{i+2}, q_{i+3}) = u_{\rm tors}(\cos\phi_i), \tag{1.7}$$

where the dihedral angle ϕ_i is obtained from the relation

$$\cos\phi_i = -\frac{r_{i,i+1} \times r_{i+1,i+2}}{|r_{i,i+1} \times r_{i+1,i+2}|} \cdot \frac{r_{i+1,i+2} \times r_{i+2,i+3}}{|r_{i+1,i+2} \times r_{i+2,i+3}|}.$$

Such local interactions have to be complemented by non-bonded interactions, *e.g.* van der Waals forces modelled by Lennard–Jones potentials, and Coulomb interactions; see [246] for further precisions.

A typical example of a simple molecular system is depicted in Figure 1.4 (left), which corresponds to the pentane molecule in the so-called united-atom representation (see [244]). In this representation, the hydrogen atoms are not explicitly taken into account. We label by $q_1, \ldots, q_5$ the positions of the carbon atoms in the pentane molecule, while $q_6, \ldots, q_N$ are the positions of the solvent particles. The solvent particles are assumed to interact with all the other atoms through a pairwise potential $\mathcal{V}_{\rm sol}$ depending only on the relative distance. The total interaction energy then reads

$$V(q) = V_{\rm pentane}(q_1, \ldots, q_5) + V_{\rm solvent}(q_6, \ldots, q_N) + V_{\rm interaction}(q),$$

with

$$V_{\rm solvent}(q_6, \ldots, q_N) = \sum_{6 \leqslant i < j \leqslant N} \mathcal{V}_{\rm sol}(|q_i - q_j|),$$

and

$$V_{\text{interaction}}(q) = \sum_{i=1}^{5} \sum_{j=6}^{N} \mathcal{V}_{\text{sol}}(|q_i - q_j|).$$

The interactions within the molecule are typically modelled by

$$V_{\text{pentane}}(q_1, \ldots, q_5) = \sum_{i=1}^{4} \mathcal{V}_2(q_i, q_{i+1}) + \sum_{i=1}^{3} \mathcal{V}_3(q_i, q_{i+1}, q_{i+2}) + \sum_{i=1}^{2} \mathcal{V}_4(q_i, q_{i+1}, q_{i+2}, q_{i+3}),$$

where the dihedral potential function u_{tors} in (1.7) is given by an expression of the form

$$u_{\text{tors}}(x) = c_1(1-x) + 2c_2(1-x^2) + c_3(1+3x-4x^3).$$

The parameters c_i $(i = 1, 2, 3)$ used in the united-atom model of [244] are such that there are three stable dihedral angles, the one at $\phi = 0$ being energetically more favorable than the others (see Figure 1.4, right).

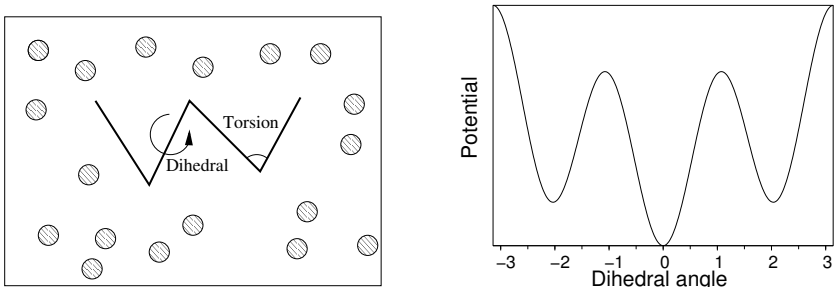

Fig. 1.4. Left: Schematic representation of a pentane molecule in a solvent (projected on a two-dimensional plane), and definition of the bond angles and dihedral angles. Right: Typical shape of the torsion potential for the dihedral angle.

More realistic force fields.

Pairwise additive potentials such as (1.5), and two-, three- or four-body bonded interactions may not be a good approximation of the many-body *ab initio* potential function (1.4). Many studies aim at proposing better empirical potential functions (or force fields). Various works in the nineties constructed empirical potentials whose expressions are motivated by the underlying physics, such as the (Modified) Embedded-Atom Model potentials [24], or bond-order potentials of REBO [263] or ReaxFF [270] types, which contain term depending on the local coordination of the atoms. The latter potentials can even account for chemical reactions (*i.e.* bond breakings and bond formations). More recently, machine learning approaches were used to construct numerical potentials which have an accuracy comparable to ab-initio potentials; see for instance the review article [106].

Non-dimensional units.

In practice, it is more convenient (and numerically more stable) to work with non-dimensional quantities, so that all quantities that appear in the numerical computations are of order 1. In general, reduced units require the following reference quantities:

- a reference mass m_0, for instance the mass of the heaviest or the lightest atom in the system;

- a reference energy ε_0, given by the magnitude of a typical interaction energy, or alternatively by $k_B T$. This energy is therefore of the order of 10^{-21} J;
- a reference length ℓ_0, given by the typical interaction distance, for instance a covalent bond length when molecules are present in the system. Usually, ℓ_0 is of the order of several Angströms.

Moreover, other reference quantities can be derived from the above fundamental reference quantities. For instance, a reference time t_0 is obtained by requiring that the typical kinetic energy is of the order of magnitude of the reference energy:

$$m_0 \left(\frac{\ell_0}{t_0}\right)^2 = \varepsilon_0,$$

so that

$$t_0 = \frac{m_0^{1/2}\,\ell_0}{\varepsilon_0^{1/2}}. \tag{1.8}$$

This time is typically of the order of the pico-second.

For the sake of concreteness, let us consider two examples. The first one is Argon, which has a molar mass $M = 39.95$ g/mol. Interactions within this system are well described by the Lennard-Jones potential (1.5)-(1.6), with the parameters $\varepsilon = 1.66 \times 10^{-21}$ J and $\sigma = 3.405$ Å. The reference mass is the mass of an atom $m_0 = 6.64 \times 10^{-26}$ kg, the equilibrium interaction distance $\ell_0 = 2^{1/6}\sigma = 3.82$ Å can be chosen as a reference length, and the reference energy may be chosen as $\varepsilon_0 = 1.66 \times 10^{-21}$ J. The time unit obtained from (1.8) is then $t_0 = 2.42 \times 10^{-12}$ s.

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A second example corresponds to covalent bonds.

1.3 Thermodynamic ensembles

The macroscopic state of a system is described, within the framework of statistical physics, by a probability measure μ on the phase space $\mathcal{E} = \mathcal{D} \times \mathbb{R}^{3N}$. Macroscopic features of the system are then computed as averages of an observable φ with respect to this measure, as given by (1.1):

$$\mathbb{E}_\mu(\varphi) = \int_{\mathcal{E}} \varphi(q,p)\,\mu(dq\,dp).$$

We therefore call the measure μ the *macroscopic state* of the system – also know as thermodynamic ensemble. The motivation for switching from a microscopic to such a macroscopic description is provided in Section 1.3.1.

We present more thoroughly in this section two very commonly used thermodynamic ensembles, namely the microcanonical ensemble (Section 1.3.2) and the canonical ensemble (Section 1.3.3). These ensembles describe respectively isolated systems, and systems at a fixed temperature (in contact with a so-called thermostat or energy reservoir). We also mention some other thermodynamic ensembles in Section 1.3.4, for the sake of completeness.

Let us already emphasize the mathematical challenge in computing ensemble averages such as (1.1): the very high dimensionality of the integral under consideration prevents the use of standard quadrature methods. In practice, the only realistic option is to rely on ergodic averages, where configurations (q^n, p^n) are generated according to the probability measure μ (or possibly according to a measure $\tilde{\mu}$ very close to μ, the difference between μ and $\tilde{\mu}$ originating from errors in the numerical integration of a continuous dynamics for instance) by integrating a time-discrete dynamics. The ensemble average (1.1) is then approximated by

$$\lim_{N_{\rm iter}\to+\infty} \frac{1}{N_{\rm iter}} \sum_{n=1}^{N_{\rm iter}} A(q^n,p^n). \tag{1.9}$$

Let us already emphasize that the successive configurations are not independent in general. The numerical techniques of course depend on the thermodynamic ensemble at hand.

1.3.1 Motivation

The first point to mention is that the complete knowledge of a system at the atomistic level is impossible by the Heisenberg uncertainty principle: momenta and positions cannot be simultaneously determined with absolute precision. The second point is that very small discrepancies in the initial conditions are usually exponentially magnified in time due to the chaotic nature of the underlying dynamics (such as the Hamiltonian dynamics presented in Section 2.1.1). The notion of trajectory is therefore not relevant.

Next, note that the number of degrees of freedom is overwhelmingly large: assume that 1 octet of data is sufficient to encode the position and momentum of a single particle. Then, a current standard harddrive of 1 To $= 10^{12}$ octet would allow to store the configuration of 10^{12} particles. Encoding the configuration of a macroscopic system composed of $\mathrm{O}(\mathcal{N}_A)$ particles would require 100 billion of harddrives... which is way too much for practical computations! In fact, it turns out that, in many situations, considering so many degrees of freedom is also unnecessary since we are only interested in a few average properties (pressure, heat capacity, etc), and these averages turn out to converge quite fast with the system size when the interaction potentials are sufficiently short-ranged.

Finally, when looking at a trajectory (q^n, p^n) for a Lennard-Jones fluid evolving according to a deterministic dynamics such as the Hamiltonian dynamics, we see that a tagged particle seems to move in a random fashion, and that the instantaneous values of observables $\varphi(q^n, p^n)$ are erratically distributed around some average value. This is the final motivation for replacing a deterministic description in terms of a full knowledge of the miscropic configuration by a probabilistic one, where we only define the probability to observe collections of microscopic configurations.

1.3.2 The microcanonical ensemble

The thermodynamic ensemble naturally associated with the Hamiltonian dynamics (2.6) is the *microcanonical ensemble*, which describes isolated systems at constant energy. This ensemble is also often termed *NVE ensemble*, the capital letters referring to the invariants of the system, namely the number of particles N, the volume of the simulation box V, and the energy E.

The corresponding probability measure is the normalized uniform probability measure on the set $\mathcal{S}(E)$ of configurations at the given energy level E:

$$\mathcal{S}(E) = \Big\{(q,p) \in \mathcal{E} \;\Big|\; H(q,p) = E\Big\}. \tag{1.10}$$

We present two ways to understand this idea. A more practical construction, which provides the basis for numerical methods, is postponed to Section 2.1.4.

An explicit construction

The building block for the construction of the microcanonical measure is the measure $\delta_{H(q,p)-E}(dq\,dp)$, where the conditioning relies on level sets of constant total energy. This measure can be obtained by an explicit construction, using a limiting procedure. Consider a given energy level E, some small energy variation $\Delta E > 0$, and define

$$\mathcal{N}_{\Delta E}(E) = \Big\{(q,p) \in \mathcal{E} \;\Big|\; E \leqslant H(q,p) \leqslant E + \Delta E\Big\}. \tag{1.11}$$

Then, the following integral of a given test function φ expresses the fact that the set $\mathcal{N}_{\Delta E}(E)$ is endowed with a uniform measure:

$$\Pi_{E,\Delta E}(\varphi) = \frac{1}{\Delta E} \int_{\mathcal{N}_{\Delta E}(E)} \varphi(q,p)\, dq\, dp.$$

In the limit $\Delta E \to 0$, a measure supported on the submanifold $\mathcal{S}(E)$ is recovered. Notice that this measure is not normalized to 1 *a priori*. The measure $\delta_{H(q,p)-E}(dq\,dp)$ is defined through the expectations of any observable φ as

$$\int_{\mathcal{S}(E)} \varphi(q,p)\, \delta_{H(q,p)-E}(dq\, dp) = \lim_{\Delta E \to 0} \frac{1}{\Delta E} \int_{\mathcal{N}_{\Delta E}(E)} \varphi(q,p)\, dq\, dp. \tag{1.12}$$

The construction highlights the fact that the regions where $|\nabla H|$ is large have a lower weight in the average since the volume of the infinitesimal domain included in $\mathcal{N}_{\Delta E}(E)$ and centered at $(q,p) \in \mathcal{S}(E)$ is proportional to $|\nabla H(q,p)|^{-1}$, see Figure 1.5. This observation is consistent with the result (1.15) below, obtained with the co-area formula, and motivates the factor $|\nabla H(q,p)|^{-1}$ on the right-hand side of (1.15).

Once the measure $\delta_{H(q,p)-E}(dq\, dp)$ is defined, the microcanonical measure is obtained by a suitable normalization:

$$\mu_{\mathrm{mc},E}(dq\, dp) = Z_E^{-1}\, \delta_{H(q,p)-E}(dq\, dp), \tag{1.13}$$

where the partition function used in the normalization

$$Z_E = \int_{\mathcal{S}(E)} \delta_{H(q,p)-E}(dq\, dp)$$

is assumed to be finite. See the discussion after (1.17) for some sufficient conditions to this end.

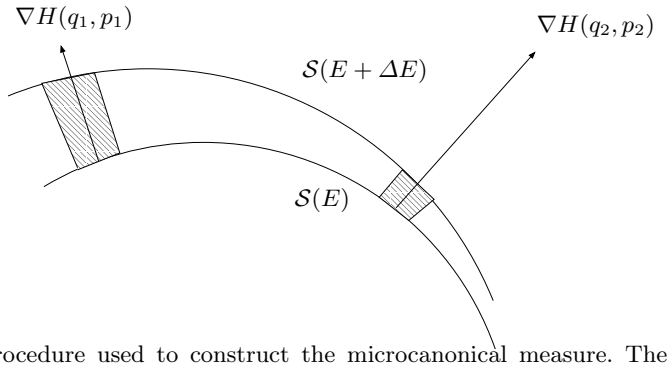

Fig. 1.5. Limiting procedure used to construct the microcanonical measure. The volume of the infinitesimal domain between $\mathcal{S}(E)$ and $\mathcal{S}(E+\Delta E)$ centered at a given point $(q,p) \in \mathcal{E}$ is proportional to $|\nabla H|^{-1}$.

An alternative definition of the microcanonical measure

The measure $\delta_{H(q,p)-E}(dq\, dp)$ for a given energy level E has support in $\mathcal{S}(E)$, and is defined by the following relation: for all test functions $f : \mathcal{E} \to \mathbb{R}$ and $g : \mathbb{R} \to \mathbb{R}$,

$$\int_{\mathcal{E}} g(H(q,p))\, f(q,p)\, dq\, dp = \int_{\mathbb{R}} g(E) \int_{\mathcal{S}(E)} f(q,p)\, \delta_{H(q,p)-E}(dq\, dp)\, dE. \tag{1.14}$$

By the co-area formula [88, 7], an alternative expression of the measure $\delta_{H(q,p)-E}(dq\, dp)$ is

$$\delta_{H(q,p)-E}(dq\, dp) = \frac{\sigma_{\mathcal{S}(E)}(dq\, dp)}{|\nabla H(q,p)|}, \tag{1.15}$$

where $\sigma_{\mathcal{S}(E)}(dq\, dp)$ is the area measure induced by the Lebesgue measure on the manifold $\mathcal{S}(E)$ when the phase space is endowed with the standard Euclidean scalar product.

The microcanonical measure can then be rewritten as

$$\mu_{\mathrm{mc},E}(dq\,dp) = Z_E^{-1}\,\delta_{H(q,p)-E}(dq\,dp) = Z_E^{-1}\,\frac{\sigma_{\mathcal{S}(E)}(dq\,dp)}{|\nabla H(q,p)|}, \tag{1.16}$$

with

$$Z_E = \int_{\mathcal{S}(E)} \delta_{H(q,p)-E}(dq\,dp) = \int_{\mathcal{S}(E)} \frac{\sigma_{\mathcal{S}(E)}(dq\,dp)}{|\nabla H(q,p)|}. \tag{1.17}$$

The partition function Z_E is finite for instance when $\mathcal{S}(E)$ is bounded and $|\nabla H| \neq 0$ on this set. Since we consider only separable Hamiltonians, the condition $|\nabla H(q,p)| = 0$ is equivalent to $p = 0$ and $\nabla V(q) = 0$. Therefore, $|\nabla H| \neq 0$ is ensured as soon as $\nabla V(q) \neq 0$ for all configurations $(q,0) \in \mathcal{S}(E)$.

1.3.3 The canonical ensemble

In many physical situations, systems in contact with some energy thermostat are considered, rather than isolated systems with a fixed energy. In this case, the energy of the system fluctuates. The temperature (a notion to be defined in this context...) is however fixed. In this situation, the microscopic configurations are distributed according to the so-called *canonical measure*. The canonical ensemble is also often termed *NVT ensemble*, since the number of particles N, the volume V and the temperature T are fixed.

We first define the canonical measure, then give some elements on its derivation from a principle of entropy maximization under constraints, and close this section with a brief presentation of some techniques to sample the canonical measure.

Definition of the canonical measure

We assume in the sequel that $\mathrm{e}^{-\beta V} \in L^1(\mathcal{D})$. The canonical probability measure μ on $\mathcal{E}$ reads

$$\mu(dq\,dp) = Z_\mu^{-1} \exp(-\beta H(q,p))\,dq\,dp, \tag{1.18}$$

where $\beta = 1/(k_{\mathrm{B}}T)$ (T denotes the temperature and k_{B} the Boltzmann constant). The normalization constant

$$Z_\mu = \int_{\mathcal{E}} \exp(-\beta H(q,p))\;dq\,dp$$

in (1.18) is called the *partition function*. When the Hamiltonian H is separable, the canonical measure is of the tensorized form

$$\mu(dq\,dp) = \nu(dq)\,\kappa(dp),$$

where ν and κ are the two following probability measures:

$$\nu(dq) = Z_\nu^{-1}\mathrm{e}^{-\beta V(q)}\,dq, \qquad Z_\nu = \int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\,dq, \tag{1.19}$$

and

$$\kappa(dp) = \left(\frac{\beta}{2\pi}\right)^{3N/2} \prod_{i=1}^{N} m_i^{-3/2} \exp\left(-\frac{\beta}{2} p^T M^{-1} p\right)\,dp. \tag{1.20}$$

Under μ, the position q and the momentum p are independent random variables. Therefore, sampling configurations (q,p) according to the canonical measure $\mu(dq\,dp)$ can be performed by independently sampling positions according to $\nu(dq)$ and momenta according to $\kappa(dp)$.

It is straightforward to sample from κ since the momenta are Gaussian random variables. The actual issue is therefore to sample from ν. Appropriate methods to this end are presented in Section 1.4.

Some elements on the derivation of the canonical measure

A standard way to derive the expression (1.18) of the canonical probability in physics textbooks is to consider a large system in the NVE ensemble, and determine the distribution of the configuration in a small subset of it (see for instance [269, Section 4.3] among many other similar references). The large system should be considered as the system of interest and the environment, which acts as some thermostat, and with which the smaller system of interest exchanges energy.

An alternative derivation, mathematically more satisfactory but physically less intuitive, is based on maximizing the entropy under the constraint that the energy is fixed *in average*. Such a derivation is performed in [21] for instance. The constraint that the average energy of the system is fixed formalizes the idea that the system under study exchanges energy with the thermostat or energy reservoir to which it is coupled. The energy is therefore not fixed, but it has nonetheless a well-defined average value.

Consider a measure which has a density $\rho(q,p)$ with respect to the Lebesgue measure. The constraints on the admissible functions $\rho(q,p)$ are

$$\rho \geqslant 0, \qquad \int_{\mathcal{E}} \rho(q,p)\, dq\, dp = 1, \qquad \int_{\mathcal{E}} H(q,p)\rho(q,p)\, dq\, dp = E \tag{1.21}$$

for some energy level E. The first two conditions ensure that ρ is the density of a probability measure, while the last one expresses the conservation of the energy in average.

Statistical entropy.

The statistical entropy is defined as

$$\mathfrak{S}(\rho) = -\int_{\mathcal{E}} \rho(q,p) \ln \rho(q,p)\, dq\, dp. \tag{1.22}$$

It quantifies the amount of information missing, or the "degree of disorder" as is sometimes stated in a more physical language. We refer to Chapter 3 in [21] for a detailed discussion on the properties of $\mathfrak{S}$. The statistical entropy allows us to give a rigorous meaning to the idea that a thermodynamic measure is (quoting [21, Section 4.1.3]) "*the most disordered macrostate possible compatible with the data*," or, equivalently, the measure which "*contains no more information than is strictly necessary to take the data into account*." The amount of information or disorder is quantified by the entropy.

Let us motivate the fact that large values of the statistical entropy (1.22) indeed correspond to probability measures which are the least informative. We quantify this by showing that the maximizer of the statistical entropy for bounded phase spaces $\mathcal{E}$ is unique, and corresponds to the uniform probability distribution (the expression of this maximiser can be found by writing the formal Euler–Lagrange equations associated with the maximization problem, as we do below to derive the expression of the canonical measure). Assume momentarily that $|\mathcal{E}| < +\infty$ and consider the density $\rho_{\mathcal{E}}(q,p) = |\mathcal{E}|^{-1}\mathbf{1}_{\mathcal{E}}(q,p)$ of the uniform probability measure on $\mathcal{E}$. A simple computation first shows that

$$\mathfrak{S}(\rho_{\mathcal{E}}) = \ln |\mathcal{E}|. \tag{1.23}$$

Then, for any probability density ρ,

$$\mathfrak{S}(\rho) - \mathfrak{S}(\rho_{\mathcal{E}}) = -\int_{\mathcal{E}} \rho \ln \rho + \int_{\mathcal{E}} \rho_{\mathcal{E}} \ln \rho_{\mathcal{E}} = \int_{\mathcal{E}} \rho \ln\left(\frac{\rho_{\mathcal{E}}}{\rho}\right) \leqslant \int_{\mathcal{E}} \rho\left(\frac{\rho_{\mathcal{E}}}{\rho} - 1\right) = 0,$$

where we used the inequality $\ln x \leqslant x - 1$ for all $x > 0$, with equality if and only if $x = 1$. This proves therefore that

$$\rho_{\mathcal{E}} = \operatorname{argmin}\left\{\mathfrak{S}(\rho),\ \rho \in L^1(\mathcal{E}),\ \rho \geqslant 0,\ \int_{\mathcal{E}} \rho = 1\right\} \tag{1.24}$$

is the unique maximiser of the statistical entropy.

Remark 1.2 (Physical relevance of the statistical entropy). *The main point in the above derivation is that the maximiser of* (1.22) *is the uniform probability measure on* $\mathcal{E}$ *when this set is finite. However, there are various other functionals whose maximizer is the uniform probability measure. One interest of the statistical entropy is its extensivity. This is discussed in [21, Chapter 3]. It can also be seen on the expression* (1.23) *of the maximal entropy in simple systems, such as independent particles in a bounded phase space. In this situation,* $\mathcal{E} = \mathscr{E}^N$ *for some bounded domain* $\mathscr{E}$*, so that the statistical entropy is indeed proportional to* N*.*

Maximization of the statistical entropy under constraints.

We come back to the case when $\mathcal{E}$ is not necessarily bounded. The canonical measure is recovered as the solution to the following optimization problem, similar to (1.24) but with an additional constraint on the average energy:

$$\sup \left\{ \mathfrak{S}(\rho),\ \rho \in L^1(\mathcal{E}),\ \rho \geqslant 0,\ \int_{\mathcal{E}} \rho = 1,\ \int_{\mathcal{E}} H\rho = E \right\}. \tag{1.25}$$

Formally, the Euler-Lagrange equation satisfied by an extremum reads

$$\mathfrak{S}'(\rho) + \lambda + \gamma H = 0,$$

where λ, γ are the Lagrange multipliers associated with the two constraints in (1.25) (normalization and average energy fixed). Since $\mathfrak{S}'(\rho) = -1 - \ln \rho$, a candidate maximizer in (1.25) is the measure with density

$$\exp\left(1 + \lambda + \gamma H(q,p)\right).$$

Usually, the Lagrange multiplier γ associated with the energy constraint is denoted by $-\beta$ (with $\beta > 0$ in order for the measure to be normalizable), and $\exp(1+\lambda) = Z^{-1}$ is a normalization constant. The Lagrange multiplier β exists and is unique since

$$\beta \mapsto \mathcal{E}(\beta) = \frac{\displaystyle\int_{\mathcal{E}} H\, \mathrm{e}^{-\beta H}}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H}}$$

is an increasing function. This is a consequence of the negativity of the derivative of the average energy

$$\mathcal{E}'(\beta) = -\frac{\displaystyle\int_{\mathcal{E}} (H - \mathcal{E}(\beta))^2\, \mathrm{e}^{-\beta H}}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H}}$$

when H is not constant.

It is easy to verify that the canonical measure with density $Z^{-1}\mathrm{e}^{-\beta H}$ is indeed the unique maximizer of (1.25), as shown in [21, Section 4.2]. For the sake of completeness, we sketch the proof of this statement. Consider two functions ρ_1, ρ_2 satisfying (1.21). Using again the inequality $\ln x \leqslant x - 1$ (with equality if and only if $x = 1$),

$$\int_{\mathcal{E}} \rho_1 \ln \rho_2 - \int_{\mathcal{E}} \rho_1 \ln \rho_1 = \int_{\mathcal{E}} \rho_1 \ln\left(\frac{\rho_2}{\rho_1}\right) \leqslant \int_{\mathcal{E}} \rho_1 - \rho_2 = 0.$$

Equality holds if and only if $\rho_1(q,p) = \rho_2(q,p)$ almost everywhere. Then, choosing $\rho_2(q,p) = Z^{-1}\exp(-\beta H(q,p))$, it holds, for any ρ satisfying the constraints (1.21):

$$-\int_{\mathcal{E}} \rho \ln \rho \leqslant -\int_{\mathcal{E}} \rho \ln\left(Z^{-1}\mathrm{e}^{-\beta H}\right) = \ln Z + \beta \int_{\mathcal{E}} H\, \rho.$$

In view of the energy constraint (last condition in (1.21)), we therefore obtain

$$\mathfrak{S}(\rho) \leqslant \ln Z + \beta E = \mathfrak{S}\left(Z^{-1}\mathrm{e}^{-\beta H}\right),$$

with equality if and only if $\rho(q,p) = Z^{-1}\exp(-\beta H(q,p))$. This shows that the canonical measure is indeed the unique maximizer of the entropy under the constraints (1.21).

1.3.4 Other thermodynamic ensembles (complements)

We saw in Section 1.3.3 that the Boltzmann-Gibbs probability measure (1.18) can be seen as the phase space probability measure maximizing the statistical entropy among the set of phase space probability measures compatible with the observed macroscopic data (in this case, average energy given). The derivation performed for an average energy fixed may be performed for any average thermodynamic quantity, leading to other thermodynamic ensembles. The choice of the ensemble amounts to choosing which quantities are fixed exactly or in average. This is in accordance with the general philosophy that thermodynamic ensembles are probability measures on the set of all possible microscopic configurations, consistent with the macroscopic state of the system.

We present in this section a general derivation of thermodynamic ensembles associated with a given set of constraints, and next focus on two examples, the isobaric-isothermal ensemble (NPT) where the number of particles, the pressure and the temperature are fixed, and the grand-canonical ensemble (μVT) where the chemical potential, the volume and the temperature are fixed. Many other cases could be treated in a similar fashion (fixed temperature and magnetization for a spin system, fixed temperature and average velocity for a fluid, etc.). This section is not necessary for understanding the remainder of these notes, and can be omitted in a first reading.

General derivation

Assume that the microscopic state of the system is described by (q, p, x), where (q, p) denotes as above a phase space configuration, and where $x \in \mathcal{X}$ is some additional degree of freedom. We denote by $\mathcal{D}_x$ and $\mathcal{E}_x$ the set of admissible positions q and configurations (q, p) for a given value of x, so that the set of admissible configurations (q, p, x) is the space

$$\mathcal{E} = \bigcup_{x \in \mathcal{X}} \mathcal{E}_x \times \{x\}.$$

Denote by $\lambda(dq\, dp\, dx)$ some reference measure on $\mathcal{E}$. This measure expresses the *a priori* information available on the system. Here, we will consider a reference measure of the form

$$\lambda(dq\, dp\, dx) = \mathbf{1}_{(q,p) \in \mathcal{E}_x}\, dq\, dp\, \pi(dx).$$

The conditional measure with respect to the parameter x (*i.e.* the measure obtained in the (q, p) variables when the parameter x is kept fixed) is the usual Lebesgue measure on the set of admissible configurations. The reference measure π on the variable x depends on the problem at hand.

Consider then a measure $\rho(dq\, dp\, dx)$ describing the macroscopic state of the system, and several observables $\varphi_1, \ldots, \varphi_M$, functions of (q, p, x), whose averages are fixed. We assume that the measure $\rho(dq\, dp\, dx)$ is absolutely continuous with respect to the reference measure $\lambda(dq\, dp\, dx)$, and denote, with an abuse of notation, by $\rho(q, p, x)$ the corresponding density. In this setting, the statistical entropy is defined as

$$\mathfrak{S}_\lambda(\rho) = -\int_{\mathcal{E}} \rho(q, p, x) \ln \rho(q, p, x)\, \lambda(dq\, dp\, dx),$$

and the probability measure describing the system is obtained as the solution of the following maximization problem:

$$\sup_{\rho \in \mathcal{S}(\varphi_1^0, \ldots, \varphi_M^0)} \Big\{ \mathfrak{S}_\lambda(\rho) \Big\}, \tag{1.26}$$

with

$$\mathcal{S}(\varphi_1^0, \ldots, \varphi_M^0) = \left\{ \rho \in L^1(\lambda) \;\middle|\; \rho \geqslant 0,\ \int_{\mathcal{E}} \rho\, d\lambda = 1,\ \int_{\mathcal{E}} \varphi_i \rho\, d\lambda = \varphi_i^0,\ \ \forall i \in \{1, \ldots, M\} \right\}.$$

The necessary condition to be satisfied by an extremum of (1.26) is the following: there exist $(\alpha_0, \ldots, \alpha_M) \in \mathbb{R}^{M+1}$ such that

$$\mathfrak{S}'_\lambda(\rho) + \alpha_0 + \sum_{i=1}^{M} \alpha_i \varphi_i = 0.$$

Therefore,

$$\rho(q,p,x) = Z^{-1} \exp\left(\sum_{i=1}^{M} \alpha_i \varphi_i(q,p,x) \right). \tag{1.27}$$

Remark 1.3 (Nonequilibrium steady states). *Let us stress that the above derivation is performed under the assumption that the system is at equilibrium. In particular,* no notion of dynamics is required. *For nonequilibrium systems in a steady state, the dynamics has to be made precise. It is not always clear whether a stationary probability measure exists, and, when it exists, whether it is unique and whether the distribution of the microscopic configurations converges to it. In general, no explicit expression of the invariant measure is available, in contrast to formulas such as* (1.27)*. See Chapter 8 for a more precise discussion.*

Isobaric-isothermal ensemble (NPT)

Let us now present a first application of the above general derivation. Isobaric-isothermal ensembles are characterized by the fact that the energy and the volume of the system are fixed in average only. Consider for example a periodic system for which the size of the unit cell can vary in one direction, and denote by $x > 0$ the length of unit cell in this direction (while it is fixed to L in the two remaining directions). Then,

$$\mathcal{D}_x = \left[x\mathbb{T} \times (L\mathbb{T})^2 \right]^N, \qquad \mathcal{E}_x = \left[x\mathbb{T} \times (L\mathbb{T})^2 \right]^N \times \mathbb{R}^{3N}.$$

We choose a uniform measure on all possible volumes:

$$\mathcal{X} = (0, +\infty), \qquad \lambda(dq\, dp\, dx) = \mathbf{1}_{(q,p) \in \mathcal{E}_x} \mathbf{1}_{x>0}\, dq\, dp\, dx.$$

The constraints to be taken into account are $\varphi_1 = H$ (average energy fixed), and $\varphi_2(x,q,p) = xL^2$ (average volume fixed).

Applying the results of the general derivation to the NPT case, it is easily seen that the probability measure describing the equilibrium is

$$\rho_{\mathrm{NPT}}(dq\, dp\, dx) = Z_{\mathrm{NPT}}^{-1}\, \mathrm{e}^{-\beta P L^2 x}\, \mathrm{e}^{-\beta H(q,p)}\, 1_{\{q \in [x\mathbb{T} \times (L\mathbb{T})^2]^N\}}\, dq\, dp\, dx,$$

where the Lagrange multiplier associated with the volume constraint is written as βP. The quantity P can be identified with the pressure.

Grand canonical ensemble (μVT)

We now describe a second application of the above general derivation. Consider a fluid of N indistinguishable particles. The additional variable describing the microscopic state of the system is the number $N \in \mathbb{N}^*$ of particles contained in a periodic cubic box of volume L^3. For a given number N of particles, the set of admissible configurations is

$$\mathcal{E}_N = (L\mathbb{T})^{3N} \times \mathbb{R}^{3N}.$$

The reference measure for the number N of particles

$$\sum_{n=1}^{+\infty} \frac{1}{n!}\, \delta_n(dN)$$

is the uniform measure on the set of positive integers, up to factors $n!$ which are related to the indistinguishability of the particle (see for instance [199, Chapter 3] for further precision on the construction of the reference measure for the grand-canonical ensemble). Therefore,

$$\lambda(dq\,dp\,dN) = \sum_{n=1}^{+\infty} \frac{1}{n!}\,\mathbf{1}_{(q,p)\in\mathcal{E}_n}\,dq\,dp\,\delta_n(dN).$$

We denote by H_n the Hamiltonian function on each space $\mathcal{E}_n$, which is a function of the variables $(q_1,\dots,q_n,p_1,\dots,p_n)$. The Hamiltonian H is then defined as $H(q,p,n) = H_n(q,p)$ for $(q,p)\in\mathcal{E}_n$.

The constraints to be taken into account are $\varphi_1 = H$ (average energy fixed) and $\varphi_2(x,q,N) = N$ (average number of particles fixed). Applying the results of the general derivation, the grand-canonical equilibrium measure reads:

$$\rho_{\mu\mathrm{VT}}(dq\,dp\,dN) = Z_{\mu\mathrm{VT}}^{-1} \sum_{n=1}^{+\infty} \frac{\mathrm{e}^{\beta\mu n}}{n!}\,\mathrm{e}^{-\beta H_n(q,p)}\,\mathbf{1}_{(q,p)\in\mathcal{E}_n}\,dq\,dp\,\delta_n(dN), \tag{1.28}$$

where $\beta\mu$ is the Lagrange multiplier associated with the average number constraint.[2] The parameter μ can be identified with the chemical potential.

1.4 A review of dynamics to sample the canonical ensemble

a ecrire

We present in this section various other ways to sample the canonical ensemble, not necessarily efficient or mainstream approaches. The aim is to give a feeling for the diversity of the techniques which can be used – including purely deterministic approaches, stochastic differential equations, and piecewise deterministic Markov processes.

add also Metropolis here?

We do not discuss the efficiency of the various methods.

1.4.1 Deterministic dynamics

The original idea of Nosé was to introduce an extra variable ξ mimicking the influence of an energy reservoir. This variable can act as a friction or anti-friction term depending on the sign of ξ, and has an associated "mass" parameter $Q > 0$. It in fact provides a feedback mechanism: the friction is increased if the kinetic temperature is too large, and decreased otherwise. More precisely,

$$\begin{cases} \dot q = M^{-1}p, \\ \dot p = -\nabla V(q) - \xi p, \\ \dot\xi = \dfrac{1}{Q}\left(p^T M^{-1} p - \dfrac{3N}{\beta}\right) \end{cases} \tag{1.29}$$

The generator of this dynamics reads $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \mathcal{L}_{\mathrm{NH}}$ with $\mathcal{L}_{\mathrm{ham}} = p^T M^{-1}\nabla_q - \nabla V(q)^T\nabla_p$ and

$$\mathcal{L}_{\mathrm{NH}} = -\xi p^T\nabla_p + \frac{1}{Q}\left(p^T M^{-1}p - \frac{3N}{\beta}\right)\partial_\xi.$$

A simple computation shows that $\mathcal{L}^* = -\mathcal{L} + 3N\xi$ and

$$\mathcal{L}\left(H(q,p) + \frac{Q\xi^2}{2}\right) = -\frac{3N}{\beta}\xi$$

An invariant probability measure is

$$\pi(dq\,dp\,d\xi) = Z_Q^{-1}\mathrm{e}^{-\beta H(q,p)}\mathrm{e}^{-\beta Q\xi^2/2}\,dq\,dp\,d\xi,$$

as follows from the fact that $\mathcal{L}^\dagger\left(\mathrm{e}^{-\beta H(q,p)}\mathrm{e}^{-\beta Q\xi^2/2}\right) = 0$. Note that the marginal in the variables (q,p) of this distribution is the canonical measure (1.18).

[2] The notation μ for the chemical potential, standard in the physics and chemistry literature, should not be confused with the notation used for the canonical measure throughout these lecture notes.

This dynamics is typically discretized using time reversible and measure preserving splittings, or using a Hamiltonian reformulation. Time averages typically converge faster than for stochastic dynamics but possibly to a wrong value. Ergodicity is the key issue for this technique. In fact, proofs of non-ergodicity were obtained in limiting regimes (KAM tori). In practice, difficulties are encountered for heterogeneous systems (*e.g.* two populations of atoms with very different masses).

Various (unsatisfactory) remedies were suggested, ranging from Nosé-Hoover chains, massive Nosé-Hoover thermostatting, etc [269]. A more satisfactory remedy consists in adding some stochasticity by considering an additional Ornstein-Uhlenbeck process on ξ, ergodic for $\mathrm{e}^{-\beta Q \xi^2/2}\, d\xi$. The corresponding dynamics, known as Langevin Nosé-Hoover, reads

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_t = (-\nabla V(q_t) - \xi_t p_t) \, dt \\ d\xi_t = \left[Q^{-1} \left(p_t^T M^{-1} p_t - \dfrac{3N}{\beta} \right) - \gamma \xi_t \right] dt + \sqrt{\dfrac{2\gamma}{\beta Q}} \, dW_t \end{cases}$$

Its generator is $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \mathcal{L}_{\mathrm{NH}} + \gamma \mathcal{L}_{\mathrm{thm}}$ with

$$\mathcal{L}_{\mathrm{thm}} = -\xi \partial_\xi + \frac{1}{\beta Q} \partial_\xi^2.$$

This dynamics is ergodic for π.

1.4.2 Langevin-like dynamics

works of Brown and Einstein, see the first chapters in [204], the latter reference also provides many interesting results on the Langevin equation and its overdamped limit

REVOIR REF

Overdamped Langevin dynamics

Langevin dynamics

Generalized Langevin dynamics

A Mori-Zwanzig derivation is provided in [159] from a generalized Hamiltonian system: a particle coupled to harmonic oscillators with a distribution of frequencies.

For $M = \mathrm{Id}$,

$$\begin{cases} dq = p_t \, dt \\ dp_t = -\nabla V(q_t) \, dt + R_t \, dt \\ \varepsilon \, dR_t = -R_t \, dt - \gamma p_t \, dt + \sqrt{\dfrac{2\gamma}{\beta}} \, dW_t \end{cases}$$

The unique invariant probability measure of the system is

$$\pi(dq \, dp \, dR) = Z_{\gamma,\varepsilon}^{-1} \exp\left(-\beta \left[H(q,p) + \frac{\varepsilon}{2\gamma} R^2 \right] \right)$$

The Langevin dynamics is recovered in the limit $\varepsilon \to 0$. Proofs of convergence follow the same scheme as for Langevin dynamics. See **??** for estimates similar to the ones obtained in Section 5.5.1.

Dissipative Particle Dynamics

The Langevin dynamics is not Galilean invariant, hence not consistent with hydrodynamics. A simple remedy is to consider friction forces depending on relative velocities.

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_{i,t} = -\nabla_{q_i} V(q_t) \, dt + \sum_{i \neq j} \left(-\gamma \chi^2(r_{ij,t}) v_{ij,t} \, dt + \sqrt{\frac{2\gamma}{\beta}} \chi(r_{ij,t}) \, dW_{ij} \right) \end{cases}$$

with $\gamma > 0$, $r_{ij} = |q_i - q_j|$, $v_{ij} = \dfrac{p_i}{m_i} - \dfrac{p_j}{m_j}$, $\chi \geqslant 0$, and $W_{ij} = -W_{ji}$. A simple computation shows that the canonical measure is invariant and the total momentum

$$\sum_{i=1}^{N} p_i$$

is an preserved by the dynamics.

Ergodicity is an issue [249]. Numerical discretizations are typically obtained by a splitting strategy [248].

1.4.3 Piecewise deterministic Markov processes

We present in this section deterministic dynamics, where particles evolve in straight lines with some velocities, interrupted by stochastic modifications of the velocities at random times. Such processes fall into the class of piecewise deterministic Markov processes (PDMP). The model considered here was initially proposed in the physics literature [220] but was also independently introduced in the mathematics literature [202].

quote also Andersen

Andersen dynamics and the like

We consider the case when the mass matrix is diagonal. Andersen dynamics amount to resampling individual components of the momenta at rate γ/D. This corresponds to the generator

$$\mathcal{L} = \mathcal{L}_{\rm ham} + \gamma \mathcal{L}_{\rm AR}, \qquad \mathcal{L}_{\rm AR} = \frac{1}{D} \sum_{i=1}^{D} (P_D - 1), \tag{1.30}$$

where

$$(P_i \varphi)(q,p) = \sqrt{\frac{\beta}{2\pi m_i}} \int_{\mathbb{R}} \varphi(q, p_1, \ldots, p_{i-1}, \xi, p_{i+1}, \ldots, p_D) \, \mathrm{e}^{-\beta \xi^2/(2m_i)} \, d\xi.$$

Linear Boltzmann dynamics resampling all components of the momenta at the same time:

$$\mathcal{L} = \mathcal{L}_{\rm ham} + \gamma \mathcal{L}_{\rm LB}, \qquad \mathcal{L}_{\rm LB} = \mathscr{P} - 1, \qquad \mathscr{P} = P_1 \ldots P_D. \tag{1.31}$$

BPS

The stochastic modifications of the velocities have two origins: (i) changes in the potential energy landscape the particles visit, which leads to velocities being changed from p to $R(q,p)$; (ii) momenta resampling at exponential times in order to ensure that ergodicity holds. More precisely, the generator of the dynamics writes $\mathcal{L} = \mathcal{L}_{\rm j/d} + \gamma \mathcal{L}_{\rm thm}$ with

$$\begin{aligned} \mathcal{L}_{\rm j/d} \varphi(q,p) &= p^T \nabla_q \varphi(q,p) + \lambda(q,p) \Big(\varphi(q, R(q)p) - \varphi(q,p) \Big), \\ \mathcal{L}_{\rm thm} \varphi(q,p) &= \int_{\mathbb{R}^D} \Big(\varphi(q,p') - \varphi(q,p) \Big) \kappa(dp'), \end{aligned}$$

with the jump rate and the post-collisional velocity respectively given by

$$\lambda(q,p) = \max\left(0, p^T \nabla V(q)\right), \qquad R(q)p = p - 2 \Pi_{\nabla V(q)} p,$$

where the projector Π_a reads

$$\Pi_a p = \frac{(p^T a)a}{|a|^2}.$$

A simple computation shows that $R(q)^2 = \mathrm{Id}_{\mathbb{R}^D}$.

To check the invariance of the canonical measure by this dynamics, we check that each part preserves the invariant measure. For the thermalization part,

$$\int_{\mathcal{E}} \mathcal{L}_{\mathrm{thm}}\varphi \, d\mu = \int_{\mathcal{D}} \Big(\int_{\mathbb{R}^D} \varphi(q,p') \, \kappa(dp') \Big) \, \nu(dq) - \int_{\mathcal{E}} \varphi \, d\mu = 0.$$

For the jump/drift part, we use the fact that κ is invariant by $R(q)$ to write

$$\begin{aligned}\int_{\mathcal{E}} \mathcal{L}_{\mathrm{j/d}}\varphi \, d\mu &= \int_{\mathcal{E}} \lambda(q,p)\Big(\varphi(q,R(q)p) - \varphi(q,p)\Big)\mu(dq\,dp) + \int_{\mathcal{E}} p^T \nabla V(q) \varphi(q,p) \, \mu(dq\,dp) \\ &= \int_{\mathcal{E}} \Big(\lambda(q,R(q)p) - \lambda(q,p)\Big)\varphi(q,p) \, \mu(dq\,dp) + \int_{\mathcal{E}} p^T \nabla V(q) \varphi(q,p) \, \mu(dq\,dp).\end{aligned}$$

Now, note that $\lambda(q,R(q)p) = \max(0, -p^T \nabla V(q))$ so that $\lambda(q,R(q)p) - \lambda(q,p) = -p^T \nabla V(q)$. This allows to conclude to the invariance of μ by $\mathcal{L}_{\mathrm{j/d}}$.

Remark 1.4. *The proof of the invariance of the canonical measure can be extended to any measure of the form $\nu(dq)\widetilde{\kappa}(dp)$ upon two conditions: (i) appropriately changing the thermalization part by resampling the new velocity from $\widetilde{\kappa}$, i.e. upon considering the thermalization operator*

$$\mathcal{L}_{\mathrm{thm}}\varphi(q,p) = \int_{\mathbb{R}^D} \Big(\varphi(q,p') - \varphi(q,p)\Big)\widetilde{\kappa}(dp');$$

(ii) ensuring that $\widetilde{\kappa}$ is invariant by $R(q)$.

In fact, exponential convergence rates in certain metrics can also be obtained [202].

2

Longtime integration of the Hamiltonian dynamics

This chapter focuses on the longtime integration of the Hamiltonian dynamics. The motivation for performing such simulations is that average properties with respect to the microcanonical measure (1.13) are approximated in practice using averages over such trajectories. The consistency of this approach relies on an ergodic assumption (see (2.21) below), which can be proved to hold only for sufficiently simple systems, and provided no other invariants than the energy are present.

From a numerical perspective, a minimal requirement for integration schemes is that they preserve well the energy over very long times. This means that energy cannot increase or decrease in a systematic way as the number of integration steps goes to infinity, for a fixed and finite timestep; although it can oscillate around some average value, with an amplitude diminishing as the timestep is reduced. (Near)Energy preservation motivates the notion of stability we will consider for these schemes. Ergodicity however always remains a concern.

Section 2.1 presents the Hamiltonian dynamics, and gives its properties. In particular, ergodicity is discussed in Section 2.1.4. We then turn to numerical methods dedicated to the computation of longtime averages in Section 2.2. Some extensions, in particular to stiff and constrained systems, are hinted at in Section 2.3. Our presentation is based on the review article [113], which is an excellent introduction to the domain of geometric numerical integration, which studies schemes preserving invariants or characteristic features of the continuous system at hand (a typical quantity being the energy). Another nice introduction to the geometric numerical integration of Hamiltonian systems is the book by Leimkuhler and Reich [170]. A more advanced reference, which provides an extensive treatment of the topic, is the monograph by Hairer, Lubich and Wanner [114].

2.1 The Hamiltonian dynamics and its properties

We consider in this section the time evolution of isolated systems described at the microscopic level. We denote by D the dimension of the positions q and momenta p variables, so that the phase-space $\mathcal{E}$ is of dimension $2D$. For instance, $D = 3N$ when the system is composed of N

particles in a 3-dimensional physical space. We assume in all this chapter that the system has an energy described by a Hamiltonian function $H(q,p)$, which is as smooth as needed.

After a general presentation of the Hamiltonian dynamics in its usual form in Section 2.1.1, an equivalent reformulation is proposed in Section 2.1.3. We then recall some important properties of the dynamics in Section 2.1.2, and conclude with a discussion on its (non)ergodic properties in Section 2.1.4.

2.1.1 The Hamiltonian dynamics

General formulation

Hamiltonian dynamics describe the evolution of isolated physical systems. They are a system of ordinary differential equations which reads in general

$$\begin{cases} \dfrac{dq(t)}{dt} = \quad \nabla_p H(q(t),p(t)), \\ \dfrac{dp(t)}{dt} = -\nabla_q H(q(t),p(t)). \end{cases} \tag{2.1}$$

Initial conditions

$$(q(0),p(0)) = (q^0,p^0) \tag{2.2}$$

should be provided. Introducing the matrix

$$J = \begin{pmatrix} 0 & \mathrm{Id}_D \\ -\mathrm{Id}_D & 0 \end{pmatrix}, \tag{2.3}$$

and denoting by $y = (q,p) \in \mathcal{E}$, the Hamiltonian dynamics can be rewritten as the first-order ordinary differential equation:

$$\frac{dy}{dt} = J\nabla H(y) = J \begin{pmatrix} \nabla_q H(q,p) \\ \nabla_p H(q,p) \end{pmatrix}. \tag{2.4}$$

Let us discuss the existence and uniqueness of trajectories. We assume to this end that ∇H is locally Lipschitz continuous. Then, $J\nabla H$ is locally Lipschitz continuous, and the Cauchy–Lipschitz theorem ensures the existence and uniqueness of C^1 trajectories for positive times up to an explosion time that depends a priori on the initial condition. In order to prove that the solution is globally well defined, more assumptions are needed. We give below some sufficient conditions for the global well posedness of the dynamics for separable potentials.

We always assume in the sequel that the Cauchy problem (2.1)-(2.2) is well-posed for any initial condition $(q^0,p^0) \in \mathcal{E}$. A mathematical object which will be of constant use in this chapter is the flow of the Hamiltonian dynamics.

Definition 2.1. *Fix $t \geqslant 0$. The flow ϕ_t the application which associates to some initial condition (q^0,p^0) the solution $(q(t),p(t)) = \phi_t(q^0,p^0)$ to (2.1) at time $t \geqslant 0$.*

Let us emphasize that (2.1) is an autonomous equation since the system is assumed to be isolated, so that the flow only depends on the duration time t of the trajectory, and not on the initial and final times separately.

The flow is a semi-group: $\phi_{t+u} = \phi_t \circ \phi_u$ for all $t,u \geqslant 0$. Actually, it is possible to define the backward evolution ϕ_{-t} for $t \geqslant 0$, using for instance the reversibility of the dynamics (see (2.15) below), so that $\phi_{t+u} = \phi_t \circ \phi_u$ for all $t,u \in \mathbb{R}$.

Another important property, which we will repeatedly use, is the following phase-space volume preservation (see Section 2.1.2 below for a proof and further comments): For all measurable subsets $B \subset \mathbb{R}^{2D}$,

$$\int_{\phi_t(B)} dq\,dp = \int_B dq\,dp.$$

This identity, often referred to as Liouville's theorem, motivates the fact that the Hamiltonian dynamics is naturally written in terms of the momenta rather than velocities. It allows to change variables by replacing (q,p) by $\phi_t(q,p)$, without the addition of Jacobian terms.

Hamiltonian dynamics for separable potentials

A physically very relevant situation in practice corresponds to separable Hamiltonians of the form (1.3), namely

$$H(q,p) = \frac{1}{2}\, p^T M^{-1} p + V(q). \tag{2.5}$$

In this case, the Hamiltonian dynamics reduces to

$$\begin{cases} \dfrac{dq(t)}{dt} = \quad \nabla_p H(q(t),p(t)) = M^{-1}p(t), \\ \dfrac{dp(t)}{dt} = -\nabla_q H(q(t),p(t)) = -\nabla V(q(t)). \end{cases} \tag{2.6}$$

When reformulating this dynamics in terms of the positions only, one obtains

$$M\,\frac{d^2q(t)}{dt^2} = -\nabla V(q(t)),$$

which is Newton's second law.

A sufficient condition for the dynamics (2.6) to be well posed for all times $t \geqslant 0$ is that ∇V is locally Lipschitz continuous (so that the existence and uniqueness of the trajectories is granted for small positive times) and that V is bounded below. In order to prove this statement, we denote by $V_- = \inf_{\mathcal{D}} V$. We first note that the total energy is conserved when the solution is well defined, see (2.8) below. This shows that $|p(t)| \leqslant \sqrt{H(q^0,p^0) - V_-}$ is uniformly bounded, and hence positions grow at most linearly in time. Therefore, $y(t)$ cannot explode in finite time and the dynamics is globally well posed. In fact, as the above elementary proof shows, a sufficient condition for the trajectory starting from any initial (q^0,p^0) to be globally well defined is that V is bounded below and ∇V is locally Lipchitz continuous on the set $\{q \in \mathcal{D} \,|\, V(q) \leqslant H(q^0,p^0)\}$.

2.1.2 Properties of the Hamiltonian dynamics

The Hamiltonian dynamics (2.1) has several interesting mathematical and structural properties:

(1) *Symmetry.* Since $\phi_t \circ \phi_{-t} = \mathrm{Id}$,

$$\phi_{-t} = \phi_t^{-1}. \tag{2.7}$$

(2) *Energy conservation.* The choice $\varphi = H$ in the reformulation of the Hamiltonian dynamics (2.16) leads to $\dfrac{dH(q(t),p(t))}{dt} = 0$, which means that

$$\forall t \geqslant 0, \qquad H(q(t),p(t)) = H(q^0,p^0). \tag{2.8}$$

(3) *Volume preservation.* For all measurable sets $B \subset \mathcal{E}$, and for all $t \in \mathbb{R}$,

$$\int_{\phi_t(B)} dq\, dp = \int_B dq\, dp. \tag{2.9}$$

The volume conservation (2.9) is a consequence of the equality

$$\mathrm{Jac}\,\phi_t(q,p) = 1, \tag{2.10}$$

where[1] $\mathrm{Jac}\,\phi_t(q,p) = |\det(\nabla\phi_t(q,p))|$. In the latter expression, our convention for defining the gradient of a mapping $g(q,p) = (g_1(q,p),\ldots,g_{2D}(q,p))^T$ is the following:

[1] In fact, as can seen from proof of Lemma 2.1 below, it actually holds that $\det(\nabla\phi_t(q,p)) = 1$.

$$\nabla g(q,p) = \begin{pmatrix} \frac{\partial g_1}{\partial q_1} & \cdots & \frac{\partial g_1}{\partial q_D} & \frac{\partial g_1}{\partial p_1} & \cdots & \frac{\partial g_1}{\partial p_D} \\ & \ddots & & & \ddots & \\ \frac{\partial g_{2D}}{\partial q_1} & \cdots & \frac{\partial g_{2D}}{\partial q_D} & \frac{\partial g_{2D}}{\partial p_1} & \cdots & \frac{\partial g_{2D}}{\partial q_{2D}} \end{pmatrix}.$$

For a given vector $h \in \mathbb{R}^{2D}$, the vector $\nabla g(q,p)h$ therefore has components $\nabla g_i(q,p)^T h$, which is consistent with the fact that $\nabla g(q,p)h$ approximates $g((q,p)+h) - g(q,p)$. We will also write in the sequel, using the notation $y = (q,p)$,

$$\frac{\partial g}{\partial y} = \nabla g.$$

The proof of (2.10) relies on the fact that the Hamiltonian vector field is divergence-free:

$$\operatorname{div}(J\nabla H) = \operatorname{div}_q(\nabla_p H) - \operatorname{div}_p(\nabla_q H) = \sum_{i=1}^{D} \left(\partial_{q_i}\partial_{p_i} - \partial_{p_i}\partial_{q_i}\right) H = 0.$$

The following lemma then allows us to conclude.

Lemma 2.1 ([Lemma VII.3.1 in [114]). *The flow of a differential equation $\dot{y} = f(y)$ in $\mathbb{R}^n$ is volume-preserving if and only if $\operatorname{div} f(y) = 0$ for all $y \in \mathbb{R}^n$.*

In fact, as the following proof shows, a stronger property than valume preservation holds true since $\det(\nabla\phi_t(y)) = 1$ for all $y \in \mathbb{R}^n$ and $t \geqslant 0$.

Proof. Fix an initial condition $y_0 \in \mathbb{R}^n$ and introduce $Y(t) = \nabla\phi_t(y_0)$. Then, a simple computation shows that

$$\dot{Y}(t) = A(t)Y(t), \qquad A(t) = \nabla f(\phi_t(y_0)), \tag{2.11}$$

with $Y(0) = \mathrm{Id}$. Now, the Abel–Liouville–Ostrogradskii identity implies that

$$\frac{d}{dt}\Big(\det Y\Big) = \operatorname{Tr}(A)\det Y. \tag{2.12}$$

This identity is obtained by noting that, for a matrix $B \in \mathbb{R}^{n\times n}$,

$$\det(Y + \varepsilon BY) = \det(\mathrm{Id} + \varepsilon B)\det Y = \big(1 + \varepsilon\operatorname{Tr}(B) + \mathrm{O}(\varepsilon^2)\big)\det Y,$$

and using the differential equation on $Y(t)$ to write

$$Y(t+h) = Y(t) + \int_0^h A(t+s)Y(t+s)\,ds = Y(t) + h\,A(t)Y(t) + \mathrm{O}(h^2).$$

Since $\operatorname{Tr}(A(t)) = (\operatorname{div} f)(\phi_t(y_0))$, we deduce from (2.12) that the requirement $\det Y(t) = \det Y(0) = 1$ for all $t \in \mathbb{R}$ is equivalent to $(\operatorname{div} f)(\phi_t(y_0)) = 0$ for all $t \in \mathbb{R}$. The conclusion follows since y_0 is arbitrary. □

When $D = 1$, *i.e.* for 2-dimensional Hamiltonian systems, we discuss in the following Remark 2.1 that the preservation of signed volumes (and not just volumes themselves) can be reformulated in a seemingly more complicated way, which however allows to characterize Hamiltonian systems (as made clear in Theorem 2.2 below).

Remark 2.1 (Preservation of signed volumes by linear maps in dimension 2). *Consider the linear mapping $\Phi(y) = Ay$ for $y \in \mathbb{R}^2$ and $A \in \mathbb{R}^{2\times 2}$. The signed volume of the parallelogram generated by two vectors $y = (y_1, y_2)$ and $z = (z_1, z_2)$ is $y \wedge z = y_1 z_2 - y_2 z_1 = y^T J z$. Under the mapping Φ, the parallelogram generated by y and z is transformed into the parallelogram generated by Ay and Az, whose signed volume is $(Ay)^T J(Az)$. The equality of these volumes for all possible vectors $y, z \in \mathbb{R}^2$ is thus equivalent to $A^T J A = J$. The latter equality implies in particular $|\det A| = 1$,* i.e. *the linear mapping Φ is volume preserving.*

(4) *Symplecticity.* The matrix J defined by (2.3) is antisymmetric and orthogonal since $J^T = -J = J^{-1}$. In particular, $J^2 = -\mathrm{Id}$. The following property may be seen as an appropriate generalization of the preservation of signed volumes, for general nonlinear mappings, and dimensions $D \geqslant 1$ (recall the criterion for the preservation of signed volumes obtained for linear mappings in dimension $2D = 2$ at the end of Remark 2.1).

Definition 2.2. *For an open set $U \subset \mathcal{E}$, a mapping $g : U \to \mathbb{R}^{2D}$ of class C^1 is symplectic if $\nabla g(q,p)$ satisfies*

$$\forall (q,p) \in U, \qquad (\nabla g)^T J \nabla g = J. \tag{2.13}$$

It is easily shown that the flow ϕ_t associated with (2.1) is symplectic for all $t \in \mathbb{R}$ (this is a result due to Poincaré); see Theorem 2.1 below. Note that the volume preservation property (2.9) of the flow ϕ_t is recovered as a consequence of the symplecticity property since (2.13) with $g = \phi_t$ implies that $(\det \nabla \phi_t)^2 = 1$ (in fact, in view of the initial condition $\det \nabla \phi_0 = 1$, it holds $\det \nabla \phi_t = 1$). The symplecticity property is stronger than volume preservation, and can be understood as the conservation of the signed volume of elementary parallelograms, see [170, Section 3.5] or [114, Section VI.2] for pedagogical presentations. Remark 2.1 shows that symplecticity is equivalent to the preservation of the signed volume in dimension 2.

Theorem 2.1 (Symplecticity of the Hamiltonian flow). *Let $H(q,p)$ be a $C^2(U)$ function, for an open set $U \subset \mathbb{R}^{2D}$. Then for any fixed $t \in \mathbb{R}$ such that the flow ϕ_t of (2.1) exists, the mapping ϕ_t is symplectic.*

Proof. Note first that

$$\frac{d}{dt}\left(\frac{\partial \phi_t(y)}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{d\phi_t(y)}{dt}\right) = \frac{\partial}{\partial y}\big(J\nabla H(\phi_t(y))\big) = J\nabla^2 H(\phi_t(y))\frac{\partial \phi_t(y)}{\partial y}.$$

Let us now fix y and introduce $\Psi : t \mapsto \dfrac{\partial \phi_t(y)}{\partial y}$. Then, using that $(\nabla^2 H)^T = \nabla^2 H$,

$$\frac{d}{dt}\big(\Psi(t)^T J \Psi(t)\big) = \Psi(t)^T \nabla^2 H(\phi_t(y)) J^T J \Psi(t) + \Psi(t)^T J^2 \nabla^2 H(\phi_t(y)) \Psi(t) = 0,$$

where we used $J^T = -J$. This shows that $\Psi(t)^T J \Psi(t) = \Psi(0)^T J \Psi(0) = J$, which gives the claimed result. □

Actually, the symplecticity of the flow is indeed a characteristic feature of Hamiltonian systems. To prove this, we introduce the notion of locally Hamiltonian systems: the differential equation $\dot{y} = f(y)$ is locally Hamiltonian on an open set U if, for every $y_0 \in U$, there exists an open neighborhood $\mathcal{N}$ of y_0 and a function $H : \mathcal{N} \to \mathbb{R}$ (depending possibly on y_0) such that the force field can be written $f(y) = J\nabla H(y)$ for all $y \in \mathcal{N}$.

Theorem 2.2 (Theorem VI.2.6 in [114]). *Let $f : U \to \mathbb{R}^{2D}$ be continuously differentiable. Then, the differential equation $\dot{y} = f(y)$ is locally Hamiltonian on U if and only if its flow $\phi_t : U \to \mathbb{R}^{2D}$ is symplectic for all sufficiently small $t \geqslant 0$.*

Proof. In view of Theorem 2.1, we only need to prove that if the flow is symplectic, then the differential equation is locally Hamiltonian, *i.e.* for any initial condition y_0, there exists a function H such that $f = J\nabla H$ in the neighborhood of y_0. To this end, we differentiate the symplecticity condition

$$(\nabla \phi_t)^T J \nabla \phi_t = J$$

with respect to time, and use (2.11) to obtain (using again the notation $Y(t) = \nabla \phi_t(y_0)$)

$$Y(t)^T \big(A(t)^T J + J A(t)\big) Y(t) = 0.$$

At time $t = 0$, since $J^T = -J$, this condition means that $JA(0) = J\nabla f(y_0)$ is a symmetric matrix for all $y_0 \in U$. Upon introducing the function $h(y_0) = -Jf(y_0)$, the latter condition

can be restated as $\nabla h(y_0)$ being a symmetric matrix for all $y_0 \in U$. Let us show that this implies that, for any $y_0 \in U$, there exists a neighborhood $\mathcal{N} \subset U$ of y_0 and a function H such that $h(y) = \nabla H(y)$ for any $y \in \mathcal{N}$. This indeed proves the theorem since $f = Jh = J\nabla H$. We next define the following function H in an open ball centered at y_0 and contained in U:

$$H(y) = \int_0^1 (y - y_0)^T h(y_0 + t(y - y_0))\, dt. \tag{2.14}$$

The latter formula is natural because the right hand side of the previous equality is indeed equal to $H(y) - H(y_0)$ when h is the gradient of some function H integrated along the straight path going from y_0 to y. In order to check that it indeed holds that $h = \nabla H$ for the function H defined in (2.14), we use the symmetry property $\partial_{y_k} h_i = \partial_{y_i} h_k$, to write, for a component y_k $(1 \leqslant k \leqslant n)$,

$$\begin{aligned}
\partial_{y_k} H(y) &= \int_0^1 \left(h_k(y_0 + t(y - y_0)) + t \sum_{i=1}^{2D} (y_i - y_{0,i}) \partial_{y_k} h_i(y_0 + t(y - y_0)) \right) dt \\
&= \int_0^1 \left(h_k(y_0 + t(y - y_0)) + t \sum_{i=1}^{2D} (y_i - y_{0,i}) \partial_{y_i} h_k(y_0 + t(y - y_0)) \right) dt \\
&= \int_0^1 \frac{d}{dt} \Big(t h_k(y_0 + t(y - y_0)) \Big) dt = h_k(y),
\end{aligned}$$

which allows to conclude. □

Additional properties can hold true in specific situations. For instance, the Hamiltonian dynamics (2.6) associated with the separable Hamiltonian (2.5) (or more generally with separable Hamiltonians with kinetic energies which are even) is reversible in the following sense.

(5) *Reversibility.* Assume that H is of the separable form (2.5), and consider the momentum reversal function

$$S(q, p) = (q, -p).$$

Then, the time-reversed evolution ϕ_{-t} for $t \geqslant 0$, defined by (2.7), coincides with a forward evolution with momenta reversed (the so-called backward flow):

$$\phi_{-t} = S \circ \phi_t \circ S. \tag{2.15}$$

This statement can be proved as follows. Consider initial conditions $(q_0, p_0) \in \mathcal{E}$, denote by $(q(t), p(t))$ the solution of the Hamiltonian dynamics starting from this initial condition, and by $(\widehat{q}(t), \widehat{p}(t))$ the solution of the Hamiltonian dynamics starting from the momenta-reversed initial condition $(q_0, -p_0)$. Note that

$$\frac{d}{dt} \begin{pmatrix} q(-t) \\ -p(-t) \end{pmatrix} = \begin{pmatrix} -\dot{q}(-t) \\ \dot{p}(-t) \end{pmatrix} = \begin{pmatrix} -M^{-1} p(-t) \\ -\nabla V(q(-t)) \end{pmatrix} = J \nabla H(q(-t), -p(-t)).$$

Therefore, $(q(-t), -p(-t)) = (S \circ \phi_{-t})(q_0, p_0)$ and $(\widehat{q}(t), \widehat{p}(t)) = (\phi_t \circ S)(q_0, p_0)$ are both solutions of the Hamiltonian dynamics, starting from the same initial condition $(q_0, -p_0)$; hence they are equal: $\phi_t \circ S = S \circ \phi_{-t}$. The conclusion (2.15) follows by composing both sides with S and using $S^2 = \mathrm{Id}$.

Exercise 2.1. *Prove that* (2.15) *holds for separable Hamiltonians of the form* $H(q, p) = V(q) + U(p)$ *with* U *even (*i.e. $U(-p) = U(p)$*). More generally, prove that the flow of the dynamics*

$$\begin{cases} \dot{q}(t) = F(q(t), p(t)), \\ \dot{p}(t) = G(q(t), p(t)), \end{cases}$$

is reversible when $F(q, -p) = -F(q, p)$ *and* $G(q, -p) = G(q, p)$.

2.1.3 Equivalent reformulations

We present in this section a more abstract reformulation of (2.1) in terms of semigroups, which will be useful to determine the order of certain integration schemes, and, maybe more importantly, allows to make contact with the infinitesimal generators of stochastic differential equations we will encounter in Chapters 4 and 5.

Let us introduce the first order differential operator

$$\mathcal{L}_{\mathrm{ham}} = \nabla_p H^T \nabla_q - \nabla_q H^T \nabla_p,$$

considered for instance as an operator on $C^0(\mathcal{E})$, with domain $C^1(\mathcal{E})$ (recall that we assumed H to be as smooth as needed in order to simplify the presentation; here, $H \in C^1(\mathcal{E})$ is a sufficient condition for the statement on the domain of $\mathcal{L}_{\mathrm{ham}}$). A simple computation shows that, for any $\varphi \in C^1(\mathcal{E})$,

$$\frac{d}{dt}\big[\varphi(q(t),p(t))\big] = (\mathcal{L}_{\mathrm{ham}}\varphi)\,(q(t),p(t)). \tag{2.16}$$

This means that $\mathcal{L}_{\mathrm{ham}}$ can be seen as the infinitesimal generator[2] of the following semigroup on $C^0(\mathcal{E})$:

$$(P_t\varphi)(q,p) = \varphi(\phi_t(q,p)). \tag{2.17}$$

refaire topo sur semi-groupes et les notations associees ?

The operator $\mathcal{L}_{\mathrm{ham}}$ is therefore called the *generator* of the dynamics.

The transport equation (2.16) (or equivalently the Hamiltonian equation (2.6)) may also be restated as an evolution equation for the phase space density of the particles. Assume that the initial conditions (q^0,p^0) are random variables distributed according to some probability measure with density $\psi_0(q,p)$ with respect to the phase space Lebesgue measure $dq\,dp$ (the associated expectation being denoted by $\mathbb{E}$), and that each initial phase space configuration is evolved according to the dynamics (2.6). Then the configurations $\phi_t(q^0,p^0)$ at time t are distributed according to a measure with density $\psi(t,q,p)$, whose evolution is governed by the following partial differential equation (called the Liouville equation), understood in the distributional sense:

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$$\partial_t\psi = \nabla_q H^T \nabla_p \psi - \nabla_p H^T \nabla_q \psi = \mathcal{L}_{\mathrm{ham}}^\dagger \psi = -\mathcal{L}_{\mathrm{ham}}\psi, \qquad \psi(0,q,p) = \psi_0(q,p), \tag{2.18}$$

where $\mathcal{L}_{\mathrm{ham}}^\dagger = -\mathcal{L}_{\mathrm{ham}}$ is the adjoint of $\mathcal{L}_{\mathrm{ham}}$ on $L^2(\mathcal{E})$ (we used here the fact that the Hamiltonian vector field is divergence-free). The Liouville equation (2.18) can be derived using (2.16). Indeed, for any $\varphi \in C^1(\mathcal{E})$ with compact support,

$$\begin{aligned}\frac{d}{dt}\left(\int_{\mathcal{E}} \varphi(q,p)\psi(t,q,p)\,dq\,dp\right) &= \frac{d}{dt}\mathbb{E}\Big(\varphi(q(t),p(t))\Big)\\ &= \mathbb{E}\Big(\mathcal{L}_{\mathrm{ham}}\varphi(q(t),p(t))\Big) = \int_{\mathcal{E}} \mathcal{L}_{\mathrm{ham}}\varphi(q,p)\psi(t,q,p)\,dq\,dp,\end{aligned}$$

so that

$$\int_{\mathcal{E}} (\partial_t\psi - \mathcal{L}_{\mathrm{ham}}^\dagger\psi)\varphi = 0,$$

which leads to (2.18). Finally, note that the method of characteristics allows to solve (2.18) as $\psi(t,q,p) = \psi_0(\phi_{-t}(q,p))$.

[2] Recall that the generator $\mathcal{L}$ of a continuous semigroup P_t is characterized by the following strong limit:

$$\forall \varphi \in D(\mathcal{L}), \qquad \frac{P_t - \mathrm{Id}}{t}\varphi \xrightarrow[t\to 0]{} \mathcal{L}\varphi.$$

2.1.4 The microcanonical measure as an ergodic limit

Practitioners often want to compute microcanonical averages as ergodic limits over Hamiltonian trajectories. Notice first that the measure $\mu_{\mathrm{mc},E}(dq\,dp)$, which is supported on the submanifold $\mathcal{S}(E)$ defined in (1.10), is invariant by the flow ϕ_t of the Hamiltonian dynamics for all energy levels E. Indeed, by the conditioning formula (1.14), and using the fact that $\operatorname{Jac}\phi_t = 1$ (see (2.10)), we obtain, for two bounded measurable functions $\varphi : \mathbb{R}^{2D} \to \mathbb{R}$ and $\psi : \mathbb{R} \to \mathbb{R}$ and any time $t \in \mathbb{R}$,

$$\begin{aligned}
&\int_{\mathbb{R}} \psi(E) \int_{\mathcal{S}(E)} \varphi(\phi_t(q,p))\, \delta_{H(q,p)-E}(dq\,dp)\, dE \\
&\quad = \int_{\mathcal{E}} \psi(H(q,p))\, \varphi(\phi_t(q,p))\, dq\,dp \\
&\quad = \int_{\mathcal{E}} \psi(H\circ\phi_{-t}(Q,P))\, \varphi(Q,P)\, dQ\,dP \\
&\quad = \int_{\mathcal{E}} \psi(H(Q,P))\, \varphi(Q,P)\, dQ\,dP \\
&\quad = \int_{\mathbb{R}} \psi(E) \int_{\mathcal{S}(E)} \varphi(q,p)\, \delta_{H(q,p)-E}(dq\,dp)\, dE,
\end{aligned}$$

where we have used the change of variables $(Q,P) = \phi_t(q,p)$ and the invariance of the Hamiltonian by the flow ϕ_t. Therefore,

$$\int_{\mathcal{S}(E)} \varphi(q,p)\, \delta_{H(q,p)-E}(dq\,dp) = \int_{\mathcal{S}(E)} (\varphi\circ\phi_t)\,(q,p)\, \delta_{H(q,p)-E}(dq\,dp) \tag{2.19}$$

for all times $t \in \mathbb{R}$ and all test functions φ, which shows the claimed invariance.

Remark 2.2. *A more intuitive way to understand the equality* (2.19) *is to perform the same change of variables as above when integrating the bounded measurable function f over the domain $\mathcal{N}_{\Delta E}$ defined in* (1.11)*. In view of the property $\phi_t^{-1} = \phi_{-t}$, it holds $\phi_t^{-1}(\mathcal{N}_{\Delta E}(E)) = \mathcal{N}_{\Delta E}(E)$ (the inclusion $\phi_t^{-1}(\mathcal{N}_{\Delta E}(E)) = \mathcal{N}_{\Delta E}(E)$ is clear by energy preservation; for the equality, note that for any $(q,p) \in \mathcal{N}_{\Delta E}(E)$, the configuration $(Q,P) = \phi_t(q,p)$ belongs to $\phi_t^{-1}(\mathcal{N}_{\Delta E}(E))$ and is such that $\phi_t^{-1}(Q,P) = (q,p)$). Then,*

$$\frac{1}{\Delta E}\int_{\mathcal{N}_{\Delta E}(E)} \varphi(Q,P)\, dQ\,dP = \frac{1}{\Delta E}\int_{\mathcal{N}_{\Delta E}(E)} (\varphi\circ\phi_t)\,(q,p)\, dq\,dp.$$

The argument is concluded by using (1.12) *to obtain* (2.19) *in the limit $\Delta E \to 0$.*

The invariance of the microcanonical measure by the Hamiltonian flow can be reformulated using the generator $\mathcal{L}_{\mathrm{ham}}$ introduced in Section 2.1.3 as: for any $\varphi \in C^\infty(\mathcal{E})$ with compact support,

$$\int_{\mathcal{S}(E)} \mathcal{L}_{\mathrm{ham}}\varphi\, d\mu_{\mathrm{mc},E}(dq\,dp) = 0. \tag{2.20}$$

In view of the preservation of the microcanonical measure by the Hamiltonian flow, the following ergodicity assumption can therefore be considered: Thermodynamic integrals of the form (1.1) are computed as trajectory averages

$$\int_{\mathcal{S}(E)} \varphi(q,p)\, \mu_{\mathrm{mc},E}(dq\,dp) = \lim_{T\to+\infty} \frac{1}{T}\int_0^T \varphi(\phi_t(q^0,p^0))\, dt, \tag{2.21}$$

where ϕ_t is the flow of the Hamiltonian dynamics (2.6), and the initial condition (q^0,p^0) is such that $H(q^0,p^0) = E$.

Ergodicity can be rigorously shown to hold for completely integrable systems and their perturbations (see for instance [15]). In general however, no convergence result can be stated, and

examples of non-ergodicity can be found. A simple instance of non-ergodicity is the following. Consider the one-dimensional double-well potential

$$V(q) = \left(q^2 - 1\right)^2. \tag{2.22}$$

The submanifolds $\mathcal{S}(E)$ for $E < 1$ are composed of two simply connected subdomains, and ergodicity can only be expected in a given connected component (see Figure 2.1). Other instances of non-ergodicity are situations when there are other invariants than the energy (such as the total momentum of the system, for instance). In those cases, ergodicity is possible only with respect to the Lebesgue measure conditioned to the set of all the invariants of the dynamics.

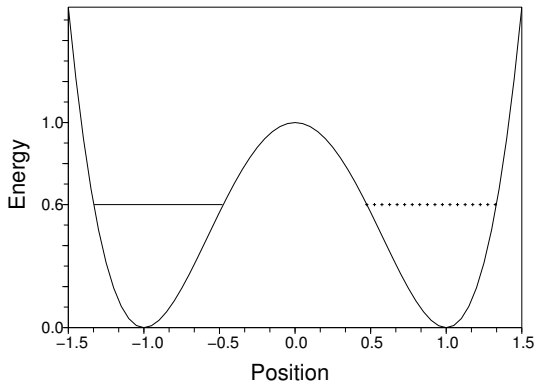

Fig. 2.1. When $H(q,p) = 0.6$ for the double-well potential (2.22), the only positions which can be obtained are in the union of two disjoint intervals $\{q < 0 \,|\, V(q) \leqslant 0.6\}$ and $\{q > 0 \,|\, V(q) \leqslant 0.6\}$. If the Hamiltonian dynamics starts with an energy $H(q^0, p^0) = 0.6$ and a negative value of q^0, it cannot explore positive positions.

Remark 2.3 (Rate of convergence of ergodic averages). *We highlight on a specific example the statement that, when ergodic averages converge to the correct value, they do so with a fast convergence rate, scaling as the inverse of the integration time – in contrast to stochastic dynamics, for which the error is much larger since it is inversly proportional to the square-root of the time (see for instance Section 4.2.2). More precisely, consider a function $\varphi \in C^1(\mathcal{E})$, bounded and with bounded derivatives to simplify the discussion. Note first that the average of φ against the microcanonial measure is 0 in view of* (2.20)*. Next, by* (2.16)*,*

$$\frac{1}{\tau}\int_0^\tau \left(\mathcal{L}_{\rm ham}\varphi\right)(q(t),p(t))\,dt = \frac{1}{\tau}\Big[\varphi(q(\tau),p(\tau)) - \varphi(q(0),p(0))\Big]. \tag{2.23}$$

This shows the trajectory average of φ converges to 0, so that the ergodic assumption holds in this case. Moreover, the error is of order $1/\tau$. It is in fact a general practical observation that deterministic methods allow for a faster convergence, although the limit of trajectory averages may not correspond to the average with respect to the canonical measure when ergodicity does not hold.

Remark 2.4 (Viriel's theorem, taken from [113]). *Consider the separable Hamiltonian* (2.5) *and the observable $\varphi(q,p) = p \cdot q$, for which $\mathcal{L}_{\rm ham}\varphi(q,p) = p^T M^{-1} p - q \cdot \nabla V(q)$. We assume in this remark that the Hamiltonian dynamics is ergodic. Under appropriate assumptions on the potential energy function (for instance, growth conditions on V ensuring that $|\varphi| \leqslant aH + b$ for some constants $a, b \geqslant 0$), the right-hand side of* (2.23) *converges to 0 as $\tau \to +\infty$, so that*

$$\lim_{\tau\to+\infty} \frac{1}{\tau}\int_0^\tau p(t)^T M^{-1} p(t)\,dt = \lim_{\tau\to+\infty} \frac{1}{\tau}\int_0^\tau q(t)\cdot\nabla V(q(t))\,dt.$$

This equality states that the potential part of the pressure is proportional to the kinetic energy (recall the definition (1.2) *of the pressure observable), an equipartition theorem known as the Viriel relation in the physics and chemistry literature.*

From a numerical viewpoint, the computation of averages according to the right-hand side of (2.21) requires very stable algorithms allowing a longtime integration of the Hamiltonian dynamics with a very good preservation of the energy, such as the Verlet algorithm (2.28). This is the subject of Section 2.2. The numerical analysis of microcanonical sampling methods based on these properties (in the very particular case of completely integrable systems) can be read in [44, 45]. There exist also stochastic methods based on constrained diffusion processes to sample the microcanonical measure, see [89, 90]. The aim of these methods is to destroy all invariants of the dynamics, except the energy.

2.2 Numerical integration of the Hamiltonian dynamics

We discuss in this section numerical schemes to integrate (2.6). We restrict the discussion to separable Hamiltonians with qudratic kinetic energies for simplicity of exposition and because this is the most common situation in practice, but various arguments can be adapted to cover more general situation (separable Hamiltonians with non-quadratic kinetic energies, or non-separable Hamiltonians). We denote by (q^n, p^n) an approximation of $(q(t_n), p(t_n))$ at time $t_n = n\Delta t$ for a given, fixed timestep $\Delta t > 0$. A numerical scheme is characterized by a mapping $\Phi_{\Delta t} : \mathcal{E} \to \mathcal{E}$ such that

$$\forall n \in \mathbb{N}, \qquad \left(q^{n+1}, p^{n+1}\right) = \Phi_{\Delta t}(q^n, p^n).$$

Let us first mention a few reasons why it is both hopeless and useless to integrate precisely the Hamiltonian dynamics in the context of molecular simulation:

use word "chaotic"? what would be a good reference?

(i) The Hamiltonian dynamics is known to be strongly sensitive to the initial conditions, or to numerical errors such as round-off errors: Small differences between two initially close configurations are exponentially magnified as time passes. Since the initial conditions can never be known exactly for physical reasons in molecular systems (in particular because there are too many atoms whose positions and momenta are required) and very long integration times are needed, this is a first reason not to try to integrate too precisely the Hamiltonian dynamics. The situation may of course be different in other application fields where Hamiltonian dynamics are used for systems with less degrees of freedom, such as celestial mechanics.

(ii) Moreover, given the large number of particles in molecular simulations (hence the numerical cost of evaluating forces), the very small time-steps that would be needed to integrate precisely the trajectory are prohibitive.

(iii) Finally, the aim of many current computations in computational statistical physics is the evaluation of average properties along a long trajectory (see the ergodicity assumption (2.21) above). Therefore, it is sufficient to ensure a correct sampling rather than integrating precisely the trajectory. In particular, a basic requirement is the preservation of the energy over long trajectories.

The above arguments led to the development of numerical techniques dedicated to Hamiltonian systems, fully taking into account the energy preservation as a basic first requirement, and as a definition of stability. This requirement is different from the usual finite time error analysis for discretizations of ODEs (see *e.g.* [115]), which gives results on the error at finite times in the limit when the discretization timestep goes to 0. The numerical analysis of Hamiltonian dynamics rather considers the regime where the time step is fixed (possibly to a relatively small value) and the integration time goes to infinity. In this context, the order of the numerical scheme (*i.e.* the integer α such that the error between the exact solution over a time interval Δt and the numerical solution after one step of the numerical scheme is of order $\Delta t^{\alpha+1}$) is not used to quantify the magnitude of the error of the numerical approximation compared to the reference dynamics on finite-time intervals, but rather to determine bounds on the error on the energy of the system.

We first show that standard integration schemes fail to preserve the energy in the longtime limit in Section 2.2.1. We next present in Section 2.2.2 dedicated numerical schemes to integrate the Hamiltonian dynamics, which turn out to have very nice long time properties, as explained from a mathematical viewpoint in Section 2.2.3.

2.2.1 Failure of standard integration schemes

In view of (2.4), the Hamiltonian dynamics is a standard ordinary differential equation (ODE). Therefore, all standard integration schemes can be used to approximate its solution. However, the standard numerical analysis of such schemes only provides error estimates on trajectories over finite time intervals, and focuses on the order of the scheme with the aim of improving the precision of the integration. The proofs of such finite time approximation results rely on stability properties over finite integration times, typically obtained using a (discrete) Gronwall inequality. Such analysis does not provide information over long times, and actually many integration schemes which are perfectly valid to approximate the solution over finite time intervals $[0,T]$ when $\Delta t \to 0$ do not correctly preserve the energy over very long times – namely, for $\Delta t > 0$ fixed, looking at the solution at time $n\Delta t$ when $n \to +\infty$. Moreover, the quest for high order schemes is not as relevant in molecular simulation as for standard ODE problems: a much more relevant issue is the ability to (approximately) preserve the energy.

We motive in this section why dedicated numerical techniques are needed to integrate the Hamiltonian dynamics by showing how various standard integration schemes fail to preserve the energy. We perform the analysis on an analytical case, but let us emphasize that numerical experiments show that the conclusions drawn in this section remain valid for generic nonlinear systems (see for instance [114, Chapter 1]).

Consider the one-dimensional harmonic oscillator with unit mass and pulsation ω, for which the Hamiltonian $H : \mathbb{R}^2 \to \mathbb{R}$ reads

$$H(q,p) = \frac{\omega^2 q^2}{2} + \frac{p^2}{2}.$$

One-step integrators then reduce to linear evolutions of the form

$$y^{n+1} = \begin{pmatrix} q^{n+1} \\ p^{n+1} \end{pmatrix} = A_{\Delta t} y^n, \tag{2.24}$$

the matrix $A_{\Delta t}$ depending on the numerical scheme at hand. For the explicit Euler scheme for example,

$$A_{\Delta t} = \begin{pmatrix} 1 & \Delta t \\ -\omega^2 \Delta t & 1 \end{pmatrix}.$$

This matrix has eigenvalues $\lambda_{\Delta t,\pm} = 1 \pm \mathrm{i}\omega\Delta t$ (as can be checked from the fact that the sum of the eigenvalues is 2, while their product is $1 + \omega^2\Delta t^2$). Since $|\lambda_{\Delta t,\pm}| = \sqrt{1+\omega^2\Delta t^2} > 1$, the energy exponentially increases in time: indeed, writing

$$A_{\Delta t} = P_{\Delta t}^{-1} \Lambda_{\Delta t} P_{\Delta t}, \qquad \Lambda_{\Delta t} = \begin{pmatrix} \lambda_{\Delta t,+} & 0 \\ 0 & \lambda_{\Delta t,-} \end{pmatrix},$$

and noting that

$$H(y) = y^T K y, \qquad K = \frac{1}{2}\begin{pmatrix} \omega^2 & 0 \\ 0 & 1 \end{pmatrix},$$

the energy can be written as

$$H(q^n,p^n) = z_0^T \Lambda_{\Delta t}^n \widetilde{K}_{\Delta t} \Lambda_{\Delta t}^n z_0,$$

where $z_0 = P_{\Delta t} y_0$ and $\widetilde{K}_{\Delta t} = P_{\Delta t}^{-T} K P_{\Delta t}^{-1}$ is symmetric definite positive. In particular, there exists $\alpha > 0$ (independent of $\Delta t > 0$) such that $H(q^n,p^n) \geqslant \alpha \|\Lambda_{\Delta t}^n z_0\|$.

For the implicit Euler scheme, the energy exponentially decreases in time. A simple computation indeed allows to rewrite this scheme in the explicit form (2.24) (thanks again to the quadratic nature of the Hamiltonian) with

$$A_{\Delta t} = \frac{1}{1+\omega^2\Delta t^2}\begin{pmatrix} 1 & \Delta t \\ -\omega^2\Delta t & 1 \end{pmatrix}.$$

The eigenvalues of this matrix are $\lambda_{\Delta t,\pm} = (1 \pm \mathrm{i}\omega\Delta t)^{-1}$, which are such that $|\lambda_{\Delta t,\pm}| = \left(1+\omega^2\Delta t^2\right)^{-1/2} < 1$.

Let us consider one last example: the 4th order Runge-Kutta scheme, which is a default scheme for the integration of many ODEs since it is quite precise while still being relatively cheap from a computational viewpoint (it has order $\alpha = 4$, as the name indicates). The iterations read:

$$y^{n+1} = y^n + \Delta t\frac{f(Y^n) + 2f(Y^{n+1}) + 2f(Y^{n+2}) + f(Y^{n+3})}{6}. \tag{2.25}$$

with

$$\begin{cases} Y^n = y^n, \\ Y^{n+1} = y^n + f(Y^n)\Delta t/2, \\ Y^{n+2} = y^n + f(Y^{n+1})\Delta t/2, \\ Y^{n+3} = y^n + f(Y^{n+2})\Delta t. \end{cases}$$

For the simple situation considered here, simple computations reveal that the matrix $A_{\Delta t}$ in (2.24) reads

$$A_{\Delta t} = \mathrm{Id}_2 + \Delta t B + \frac{\Delta t^2}{2}B^2 + \frac{\Delta t^3}{6}B + \frac{\Delta t^4}{24}B^4, \qquad B = \begin{pmatrix} 0 & 1 \\ -\omega^2 & 0 \end{pmatrix}.$$

Since $M^2 = -\omega^2\mathrm{Id}_2$, we finally obtain

$$A_{\Delta t} = \begin{pmatrix} 1 - \dfrac{(\omega\Delta t)^2}{2} + \dfrac{(\omega\Delta t)^4}{24} & \Delta t\left(1 - \dfrac{(\omega\Delta t)^2}{6}\right) \\ -\omega^2\Delta t\left(1 - \dfrac{(\omega\Delta t)^2}{6}\right) & 1 - \dfrac{(\omega\Delta t)^2}{2} + \dfrac{(\omega\Delta t)^4}{24} \end{pmatrix}.$$

The eigenvalues of $A_{\Delta t}$ are

$$\lambda_{\Delta t,\pm} = 1 - \frac{(\omega\Delta t)^2}{2} + \frac{(\omega\Delta t)^4}{24} \pm \mathrm{i}\omega\Delta t\left(1 - \frac{(\omega\Delta t)^2}{6}\right),$$

so that

$$|\lambda_{\Delta t,\pm}| = \sqrt{1 - \frac{(\omega\Delta t)^6}{72} + \frac{(\omega\Delta t)^8}{576}}.$$

This shows that for $\omega\Delta t > 0$ sufficiently small (numerically, $\omega\Delta t \leqslant 2.828427$), it holds $|\lambda_{\Delta t,\pm}| < 1$, hence the energy is exponentially decreasing.

The lesson from the above failures to preserve the energy over long times is that we really must take into account the specific properties of the Hamiltonian dynamics in order to come up with good integrators. Among the five properties listed in Section 2.1.2, which can be readily extended to numerical schemes (for example, time reversibility corresponding to $S \circ \Phi_{\Delta t} \circ S = \Phi_{-\Delta t}$, while symmetry is expressed as $(\Phi_{\Delta t})^{-1} = \Phi_{-\Delta t}$), time reversibility for sure is not sufficient since the standard integrators above satisfy this property. For instance, the numerical flow of the explicit Euler method

$$\Phi^{\mathrm{Euler}}_{\Delta t}(q,p) = \big(q + \Delta t M^{-1}\, p, p - \Delta t\nabla V(q)\big)$$

satisfies

$$\begin{aligned}\Phi^{\mathrm{Euler}}_{\Delta t}(q,-p) &= \big(q - \Delta t M^{-1}\, p, -p - \Delta t\nabla V(q)\big) \\ &= S\left(q - \Delta t M^{-1}\, p, p + \Delta t\nabla V(q)\right) = S\big(\Phi^{\mathrm{Euler}}_{-\Delta t}(q,p)\big).\end{aligned}$$

The crucial property turns out to be symplecticity, which, as we have seen, is equivalent to the fact that the dynamics is locally Hamiltonian. It may therefore be of no surprise that the preservation of the symplectic structure provides some form of preservation of the Hamiltonian nature of the dynamics. Let us however mention that there are some results on the longtime energy preservation for schemes which are not symplectic, in particular for symmetric numerical methods (such that $\Phi_{\Delta t} \circ \Phi_{-\Delta t} = \Phi_{-\Delta t} \circ \Phi_{\Delta t} = \mathrm{Id}$) applied to integrable systems; see [113, Chapter XI].

2.2.2 Symplectic schemes

We show in this section one way to construct symplectic schemes for the Hamiltonian dynamics (2.6) associated with separable Hamiltonians, and derive in particular the most common numerical integrator used in practice for Hamiltonian dynamics: the Störmer-Verlet scheme.

Construction of symplectic schemes

A systematic and nice way to construct symplectic schemes relies on a splitting strategy where the Hamiltonian of the system is decomposed into elementary Hamiltonians, chosen such that the associated Hamiltonian dynamics are analytically integrable. The one-step integrator is then obtained by composition of the time evolutions of the elementary Hamiltonian dynamics. The resulting numerical scheme is automatically symplectic in view of Theorem 2.1 and the following result.

Theorem 2.3. *The composition $g \circ h$ of two symplectic mappings $h : U \to \mathbb{R}^n$ and $g : h(U) \to \mathbb{R}^n$ is symplectic.*

Proof. The proof relies on the equality $\nabla(g \circ h) = [(\nabla g) \circ h] \nabla h$. Therefore,

$$[\nabla(g \circ h)]^T J[\nabla(g \circ h)] = [\nabla h]^T [(\nabla g) \circ h]^T J [(\nabla g) \circ h] [\nabla h] \quad = [\nabla h]^T J [\nabla h] = J,$$

where we successively used the symplecticity of g and h. □

A simple and nice splitting is based upon the decomposition of the total Hamiltonian into its potential and kinetic parts:

$$H(q,p) = H_1(q,p) + H_2(q,p), \qquad H_1(q,p) = \frac{1}{2} p^T M^{-1} p, \qquad H_2(q,p) = V(q).$$

This corresponds to the decomposition of the original dynamics as

$$\begin{cases} \dot q = M^{-1} p, \\ \dot p = 0, \end{cases} \qquad \begin{cases} \dot q = 0, \\ \dot p = -\nabla V(q). \end{cases}$$

Each of the above dynamics is Hamiltonian and analytically integrable, with respective flows

$$\phi_t^1(q,p) = (q + t\, M^{-1} p, p), \qquad \phi_t^2(q,p) = (q, p - t \nabla V(q)).$$

A Trotter splitting where positions are updated first leads to the following scheme

$$(q^{n+1}, p^{n+1}) = \left(\phi_{\Delta t}^2 \circ \phi_{\Delta t}^1\right)(q^n, p^n),$$

called "symplectic Euler A", and which reads more explicitly

$$\begin{cases} q^{n+1} = q^n + \Delta t M^{-1} p^n, \\ p^{n+1} = p^n - \Delta t \nabla V(q^{n+1}). \end{cases} \tag{2.26}$$

When the flows are composed the other way round, a different symplectic scheme is obtained ("symplectic Euler B"):

$$\begin{cases} p^{n+1} = p^n - \Delta t \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t M^{-1} p^{n+1}. \end{cases} \tag{2.27}$$

Both schemes are explicit and of order $\alpha = 1$, time reversible but not symmetric.

Exercise 2.2. *Check that the numerical methods* (2.26) *and* (2.27) *are symplectic by a direct computation based on the definition* (2.13).

The Verlet scheme

There is some arbitrariness in the choice of the operation to perform first in the symplectic Euler schemes. It is natural to make the operations more symmetric by relying on a Strang splitting, which can be seen as a symmetrization of the symplectic Euler schemes. The so-obtained scheme is called the Störmer-Verlet scheme since it was rediscovered by Verlet in the context of molecular dynamics [271]; and was in fact already known by Störmer in the context of celestial mechanics at the beginning of the 20th century, and even by Newton (see [113, Section 1.3] for historical precisions). The Verlet algorithm is nowadays the standard integration scheme for Hamiltonian dynamics. It reads

$$\begin{cases} p^{n+1/2} = p^n - \dfrac{\Delta t}{2}\nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\ M^{-1}p^{n+1/2}, \\ p^{n+1} = p^{n+1/2} - \dfrac{\Delta t}{2}\nabla V(q^{n+1}). \end{cases} \tag{2.28}$$

The numerical flow associated with this scheme is denoted by $\Phi_{\Delta t}^{\mathrm{Verlet}}$ in the sequel. Note that

$$\Phi_{\Delta t}^{\mathrm{Verlet}} = \phi_{\Delta t/2}^2 \circ \phi_{\Delta t}^1 \circ \phi_{\Delta t/2}^2.$$

It is easy to check that the scheme is time reversible and symmetric. It is of course symplectic by construction. It also requires only one force evaluation per timestep upon saving the force $\nabla V(q^{n+1})$ at used in the last update of the n-th timestep to re-use in the first update of the $(n+1)$-th timestep.

Determination of the order of the Verlet scheme

The Verlet scheme can be shown to be of order $\alpha = 2$, *i.e.*

$$\Phi_{\Delta t}^{\mathrm{Verlet}} = \phi_{\Delta t} + \mathrm{O}(\Delta t^3), \tag{2.29}$$

where ϕ_t is the flow of the Hamiltonian dynamics (2.6). This can be proved by simple Taylor expansions, as usually done to determine the local consistency error of numerical schemes for ODEs (see for instance [167, Section 2.2.3]).

We present here an alternative approach to proving (2.29). Let us emphasize that this approach is unnecessarily complicated if the only aim was to prove (2.29), but we insist on presenting it since it allows to introduce concepts and manipulations which are crucial for the numerical analysis of discretizations of stochastic differential equations (see in particular Sections 6.1 and 6.2.4). The analysis in this section can therefore be seen as some investment for the chapters to come.

The first step is to rewrite the equality (2.29) as an equality of appropriate semigroups. Introduce to this end the following operators:

$$A = p^T M^{-1}\nabla_q, \qquad B = -\nabla V(q)^T \nabla_p,$$

and consider the following evolution operators:

$$\begin{aligned} \left(\mathrm{e}^{tA}\varphi\right)(q,p) &= \varphi(\phi_t^1(q,p)) = \varphi(q + tM^{-1}p, p), \\ \left(\mathrm{e}^{tB}\varphi\right)(q,p) &= \varphi(\phi_t^2(q,p)) = \varphi(q, p - t\nabla V(q)). \end{aligned} \tag{2.30}$$

As the notation suggests, the evolution operators e^{tA} and e^{tB} respectively admit A and B as infinitesimal generators, all these operators being defined on appropriate functional spaces (for instance, e^{tA} and e^{tB} are bounded operators on $C^0(\mathbb{R}^{2D})$ while A and B can be defined as unbounded operators with domain $C^1(\mathbb{R}^{2D})$). The symplectic Euler schemes and the Verlet scheme can be equivalently written in terms of the evolution operators $\mathrm{e}^{tA}, \mathrm{e}^{tB}$. Consider for instance the symplectic Euler scheme (2.26), and denote by $P_{\Delta t}^{A,B}$ its evolution operator:

$$\left(P_{\Delta t}^{A,B}\varphi\right)(q,p) = \left(\varphi\circ\phi_{\Delta t}^2\circ\phi_{\Delta t}^1\right)(q,p) = \left(\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B}\varphi\right)(q,p).$$

The last equality is easily obtained by a direct computation based on the expressions (2.30). Note that the order of the operations is changed when passing from flows to semigroups (e^{tB}, which is associated with ϕ_t^2, acts first). This inversion is known as *Vertauschungssatz* (see for instance the discussion in [114, Section III.5.1]). It arises from the fact that the numerical method modifies the distribution of the variables, whereas the evolution operator encodes the evolution of observables (determined by the adjoint of the operator encoding the evolution of the distribution). Similarly, the evolution operators for the symplectic Euler B scheme and the Verlet scheme respectively read

$$P_{\Delta t}^{B,A} = \mathrm{e}^{\Delta t B}\mathrm{e}^{\Delta t A}, \qquad P_{\Delta t}^{B,A,B} = \mathrm{e}^{\Delta t B/2}\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B/2}.$$

Remark 2.5 (Stochastic integrators). *The above ordering of the integrators is also the correct one for stochastic evolutions. We will see such dynamics in greater detail in the following chapters, but let us already present a simple example illustrating the above discussion on the ordering of the evolution operators. Consider for instance a numerical scheme of the form*

$$\begin{cases} q^{n+1/2} = \Phi_1(q^n, Z_1^n), \\ q^{n+1} = \Phi_2(q^{n+1/2}, Z_2^n), \end{cases}$$

where $(Z_1^n)_{n\geqslant 0}$ and $(Z_2^n)_{n\geqslant 0}$ are sequences of independent variables, the variables (Z_i^n) being sampled from distributions μ_i for $i = 1, 2$. Define also the evolution operators

$$(P_i\varphi)(q) = \mathbb{E}_{Z_i}\Big(\varphi(\Phi_i(q, Z_i))\Big),$$

where expectations are taken with respect to all realizations of the random variable $Z_i \sim \mu_i$. Then,

$$\begin{aligned}(P\varphi)(q) &= \mathbb{E}\Big[\varphi(q^{n+1}) \,\Big|\, q^n = q\Big] = \mathbb{E}_{Z_1^n}\left(\mathbb{E}_{Z_2^n}\Big[\varphi\big(\Phi_2(q^{n+1/2}, Z_2^n)\big)\Big] \,\Big|\, q^n = q\right) \\ &= \mathbb{E}_{Z_1^n}\Big((P_2\varphi)(q^{n+1/2}) \,\Big|\, q^n = q\Big) \\ &= (P_1P_2\varphi)(q).\end{aligned}$$

The local consistency orders α of the schemes are, from an algebraic viewpoint, most conveniently obtained with the Baker-Campbell-Hausdorff (BCH) formula. For Trotter splittings, we formally have

$$\mathrm{e}^{tX}\mathrm{e}^{tY} = \mathrm{e}^{Z_t}, \qquad Z_t = t(X+Y) + \frac{t^2}{2}[X,Y] + \mathrm{O}(t^3), \tag{2.31}$$

where

$$[X,Y] = XY - YX \tag{2.32}$$

is the commutator between the operators X and Y. Upon iterating (2.31) (writing first $\mathrm{e}^{tX/2}\mathrm{e}^{tY/2} = \mathrm{e}^{tZ_t}$, noting that $\mathrm{e}^{tY/2}\mathrm{e}^{tX/2} = \mathrm{e}^{-tZ_{-t}}$ and finally using (2.31) again for $\mathrm{e}^{tZ_t}\mathrm{e}^{-tZ_{-t}}$), the following equality holds for Strang splittings:

$$\mathrm{e}^{tX/2}\mathrm{e}^{tY}\mathrm{e}^{tX/2} = \mathrm{e}^{S_t}, \qquad S_t = t(X+Y) + \frac{t^3}{12}\left(-\frac{1}{2}\big[X,[X,Y]\big] + \big[Y,[Y,X]\big]\right) + \mathrm{O}(t^5). \tag{2.33}$$

We next prove the formulas (2.31)-(2.32) for bounded operators, and then make precise how (2.31) and (2.33) should be understood for unbounded operators.

To prove the equality (2.31) for bounded operators X, Y (in particular matrices; see [114, Section III.4.2]), we start by writing

$$\mathrm{e}^{tX} = \mathrm{Id} + tX + \frac{t^2}{2}X^2 + t^3R_{X,t}, \qquad R_{X,t} = X^3\sum_{n=0}^{+\infty}\frac{t^n}{(n+3)!}X^n.$$

Note that $R_{X,t}$ is a bounded operator, whose norm can be uniformly controlled for t in finite time intervals. A similar expansion holds for e^{tY}. Then,

$$\begin{aligned} \mathrm{e}^{tX}\mathrm{e}^{tY} &= \left(\mathrm{Id} + tX + \frac{t^2}{2}X^2 + t^3 R_{X,t}\right)\left(\mathrm{Id} + tY + \frac{t^2}{2}Y^2 + t^3 R_{Y,t}\right) \\ &= \mathrm{Id} + t(X+Y) + \frac{t^2}{2}\left(X^2 + 2XY + Y^2\right) + t^3 \widetilde{R}_{X,Y,t}, \end{aligned} \tag{2.34}$$

where $\widetilde{R}_{X,Y,t}$ is a family of bounded operators, whose norms can be uniformly controlled on finite time intervals. Now,

$$X^2 + 2XY + Y^2 = (X+Y)^2 + [X,Y].$$

On the other hand, writing $Z_t = t(X+Y) + t^2\mathcal{Z} + t^3\widehat{R}_{X,Y,t}$ with $\mathcal{Z}$ bounded and where $\widehat{R}_{X,Y,t}$ is a family of bounded operators whose norms can be uniformly controlled on finite time intervals,

$$\begin{aligned} \mathrm{e}^{Z_t} &= \mathrm{Id} + Z_t + \frac{Z_t^2}{2} + t^3 R_{Z_t,t} \\ &= \mathrm{Id} + t(X+Y) + \frac{t^2}{2}\Big((X+Y)^2 + 2\mathcal{Z}\Big) + t^3 \widehat{R}_{Z,t}, \end{aligned}$$

where again $\widehat{R}_{Z,t}$ is a family of bounded operators whose norms can be uniformly controlled on finite time intervals. Comparing this equality with (2.34) shows that the choice

$$\mathcal{Z} = \frac{1}{2}[X,Y],$$

allows to recover (2.31)-(2.32). The higher order terms in the expansion of Z_t in powers of t can be found by induction.

For unbounded operators, the equalities (2.31)-(2.33) should be seen as a convenient way to obtain the expressions of the first terms of the expansion of the semigroup in powers of t, upon formally writing the exponential as a series: for $U_t = \mathrm{e}^{tX}$,

$$\begin{aligned} U_t &= U_0 + t\left.\frac{dU_t}{dt}\right|_{t=0} + \frac{t^2}{2}\left.\frac{d^2U_t}{dt^2}\right|_{t=0} + \cdots + \frac{t^n}{n!}\left.\frac{d^nU_t}{dt^n}\right|_{t=0} + \frac{t^{n+1}}{n!}\int_0^1 (1-\theta)^n \left.\frac{d^{n+1}U_s}{ds^{n+1}}\right|_{s=\theta t} d\theta \\ &= \mathrm{Id} + tX + \frac{t^2}{2}X^2 + \cdots + \frac{t^n}{n!}X^n + \frac{t^{n+1}}{n!}\int_0^1 (1-\theta)^n U_{\theta t} X^{n+1}\, d\theta. \end{aligned}$$

Equality holds in the strong sense for sufficiently smooth functions, belonging to $\bigcap_{k=1}^{n+1} D(X^k)$, where $D(X^k)$ is the domain of the operator X^k, considered for instance on $C^0(\mathcal{E})$. For the operators A, B and $\mathcal{L}_{\mathrm{ham}}$ we consider here, note that $\mathrm{i}A$, $\mathrm{i}B$ and $\mathrm{i}\mathcal{L}_{\mathrm{ham}}$ are symmetric and in fact self-adjoint on $L^2(\mathcal{E})$, so that their semigroups can be defined by calculus; or simply from formulas such as (2.30).

As an application,

$$\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B} = \mathrm{Id} + \Delta t(A+B) + \frac{\Delta t^2}{2}\Big((A+B)^2 + [A,B]\Big) + \Delta t^3 R_t,$$

where R_t is a differential operator involving a finite number of derivatives. This should be compared to the semigroup (2.17) associated with the exact evolution: using $\mathcal{L}_{\mathrm{ham}} = A + B$,

$$\mathrm{e}^{\Delta t(A+B)} = \mathrm{Id} + \Delta t(A+B) + \frac{\Delta t^2}{2}(A+B)^2 + \Delta t^3 \widetilde{R}_t,$$

so that $(\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B} - \mathrm{e}^{\Delta t(A+B)})\varphi = \mathrm{O}(\Delta t^2)$ when φ is sufficiently smooth. A careful inspection of the remainder term shows that it depends on derivatives of φ up to order 2. The choice $\varphi(q,p) = (q,p)$ shows that the local truncation error is of order Δt^2, so that the first order splittings given by the symplectic Euler method lead to first order schemes. Similarly,

$$P_{\Delta t}^{\mathrm{Verlet}} = \mathrm{e}^{\Delta t B/2}\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B/2} = \mathrm{e}^{\Delta t(A+B)} + \mathrm{O}(\Delta t^3),$$

so that the Verlet scheme is of order 2.

Remark 2.6. *Higher-order splittings can be considered, although stability then becomes an issue since operations with negative timesteps are introduced. We refer to [114, Section II.4] for a complete discussion of these issues.*

Linear stability analysis of the Verlet scheme

We consider again the one-dimensional example treated in Section 2.2.1. The iterates of the Verlet scheme can be formulated as

$$\begin{pmatrix} q^{n+1} \\ p^{n+1} \end{pmatrix} = A_{\Delta t} \begin{pmatrix} q^n \\ p^n \end{pmatrix}, \quad A_{\Delta t} = \begin{pmatrix} 1 - \dfrac{(\omega \Delta t)^2}{2} & \Delta t \\ -\omega^2 \Delta t \left(1 - \dfrac{(\omega \Delta t)^2}{4} \right) & 1 - \dfrac{(\omega \Delta t)^2}{2} \end{pmatrix}.$$

The eigenvalues of the matrix $A_{\Delta t}$ are the solutions of the following equation in x:

$$\left(1 - \frac{(\omega \Delta t)^2}{2} - x \right)^2 + \frac{(\omega \Delta t)^2}{2} \left(2 - \frac{(\omega \Delta t)^2}{2} \right) = 0.$$

Setting $\xi = (\omega \Delta t)^2/2$, the latter equation is of the form $(1 - \xi - x)^2 = -\xi(2 - \xi)$, with solutions $x_\pm = 1 - \xi \pm \mathrm{i}\sqrt{\xi(2-\xi)}$ when $\xi(2-\xi) \geqslant 0$, and $x_\pm = 1 - \xi \pm \sqrt{\xi(\xi - 2)}$ when $\xi(2-\xi) \leqslant 0$. The eigenvalues of $A_{\Delta t}$ therefore have modulus 1 if and only if

$$\omega \Delta t \leqslant 2. \tag{2.35}$$

In this case, the trajectory $(q^n, p^n)_{n \geqslant 0}$ is bounded. Otherwise, one eigenvalue has a modulus strictly larger than 1, so that the trajectory $(q^n, p^n)_{n \geqslant 0}$ is not bounded in general. Besides, a straightforward computation shows that the modified energy

translate into actual orders of magnitude

$$H_{\Delta t}(q, p) = H(q, p) - \frac{(\omega \Delta t)^2}{4} \omega^2 q^2$$

is preserved exactly: $H_{\Delta t}(q^n, p^n) = H_{\Delta t}(q^0, p^0)$ for all $n \geqslant 0$. Therefore, when $\omega \Delta t < 2$, the boundedness of the trajectory implies immediately that the energy is preserved at second order in the timestep, for all times:

$$\sup_{n \in \mathbb{N}} \left| H(q^n, p^n) - H(q^0, p^0) \right| \leqslant C \Delta t^2.$$

We will see below in Section 2.2.3 that this is in fact a general property of symplectic schemes: the exact energy is preserved approximately as a consequence of an approximate energy being conserved exactly.

Exercise 2.3. *Study the stability of the symplectic Euler schemes, and find a modified energy $H_{\Delta t}(q, p) = H(q, p) + a \Delta t q p$ exactly preserved by the numerical scheme for the one-dimensional harmonic oscillator.*

For general potential energy functions beyond purely quadratic ones, there is no simple rule to place an upper bound on the time-step. However, the linear stability requirement suggests that an admissible time-step should be a fraction of the fastest vibration period in the system. For molecular systems, this corresponds to timesteps of the order of a femtosecond (10^{-15} s) – a fraction of the typical times hinted at in Section 1.1.1.

2.2.3 Longtime stability of symplectic schemes

The Verlet scheme can be rewritten in a seamingly more direct form: a simple computation indeed shows that the positions q^n obtained by the Verlet scheme (2.28) satisfy

$$M\frac{q^{n+1}-2q^n+q^{n-1}}{\Delta t^2}=-\nabla V(q^n),$$

which is the simple centered finite-difference discretization for the equation $M\dfrac{d^2q}{dt^2}(t)=-\nabla V(q(t))$. However, the very good properties of the numerical method cannot be understood from this perspective. It is important to keep both variables q and p, and study the numerical flow $\Phi_{\Delta t}^{\mathrm{Verlet}}$ of (2.28).

The longtime stability properties of symplectic numerical methods applied to Hamiltonian systems can be proved with the help of the so-called backward analysis. Contrarily to standard error analysis where the numerical trajectory is considered as an approximation of the true trajectory of the exact problem

$$\dot y=f(y),\qquad y(0)=y^0,$$

backward analysis consists in interpreting the numerical trajectory generated by a numerical method $\Phi_{\Delta t}$ as the *exact trajectory of some modified ordinary differential equation*

$$\dot z=f_{\Delta t}(z),\qquad z(0)=y^0. \tag{2.36}$$

By this we mean that $y^k=z(k\Delta t)$; see Figure 2.2 for a graphical illustration. The modified force field $f_{\Delta t}$ is therefore chosen such that $z(\Delta t)$ coincides with $\Phi_{\Delta t}(y^0)$ for any y^0. In practice, only the first orders of $f_{\Delta t}$ with respect to Δt are computed, with corrections chosen such that $|z(\Delta t)-\Phi_{\Delta t}(y^0)|$ is much smaller than $|y(\Delta t)-\Phi_{\Delta t}(y^0)|$.

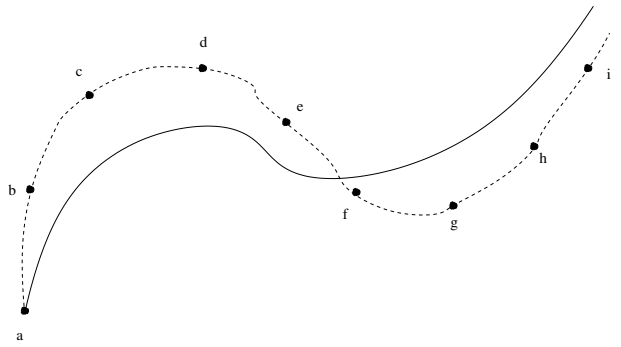

Fig. 2.2. Exact trajectory $y(t)$ (solid line) and numerical trajectory y^k (dots), interpolated by the trajectory of the modified dynamics $z(t)$ (dashed line).

The next step is to study the properties of the modified problem in order to deduce properties of the numerical scheme. For symplectic methods approaching symplectic flows, the modified equation is still Hamiltonian. Therefore, *some modified energy is preserved exactly.* This property is finally used to show that the *exact energy is preserved approximately.* In fact, some rather involved analysis has to be used since the modified Hamiltonian is defined as a formal series, which does not converge in general. Optimal truncations should then be considered, and the modified energy is therefore not strictly preserved, but the error terms are very small.

We present an introduction to the backward analysis of symplectic methods in this section, by first computing the first order term in the modified equation for two simple schemes, namely the explicit Euler and a symplectic Euler scheme. We then prove that any truncation of the modified equation for symplectic methods is of Hamiltonian type. This allows to conclude to the longtime energy preservation, which is the last step of our proof. For the last two steps, we rely on the presentation of [113, Sections 4 and 5]; see also [114] for an extensive presentation of backward analysis for Hamiltonian systems.

Explicit expressions of the leading order terms in the modified equations

The fundamental idea behind the construction of the modified force field $f_{\Delta t}$ in (2.36) is to compare the Taylor expansion of the numerical method $\Phi_{\Delta t}$ to the Taylor expansion of the solution to the modified equation $z(\Delta t)$ after one step. Let us consider the explicit Euler and the symplectic Euler schemes. Both are of order 1, meaning that $\Phi_{\Delta t}(y^0) - y(\Delta t) = \mathrm{O}(\Delta t^2)$. Our aim is to find a modified force field $f_{\Delta t}$ such that $\Phi_{\Delta t}(y^0) - z(\Delta t) = \mathrm{O}(\Delta t^3)$. To this end, we make the ansatz

$$f_{\Delta t}(y) = f(y) + \Delta t F(y).$$

We generalize this procedure in the sequel.

A Taylor expansion of the solution of the modified equation gives

$$\begin{aligned} z(\Delta t) &= z(0) + \Delta t\, \dot z(0) + \frac{\Delta t^2}{2} \ddot z(0) + \dots \\ &= y^0 + \Delta t [f(y^0) + \Delta t F(y^0)] + \frac{\Delta t^2}{2} \nabla f_{\Delta t}(y^0) \dot z(0) + \dots \\ &= y^0 + \Delta t f(y^0) + \Delta t^2 \left[\frac{1}{2} \nabla f(y^0) f(y^0) + F(y^0) \right] + \mathrm{O}(\Delta t^3). \end{aligned}$$

Now, for the explicit Euler scheme,

$$\Phi^{\mathrm{EE}}_{\Delta t}(y^0) = y^0 + \Delta t f(y^0).$$

The choice $F(y) = -\frac{1}{2} \nabla f(y) f(y)$ ensures that $\Phi^{\mathrm{EE}}_{\Delta t}(y^0) - z(\Delta t) = \mathrm{O}(\Delta t^3)$. For Hamiltonian dynamics, one finds

$$F(y) = -\frac{1}{2} \begin{pmatrix} 0 & M^{-1} \\ -\nabla^2 V(q) & 0 \end{pmatrix} \begin{pmatrix} M^{-1} p \\ -\nabla V(q) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} M^{-1} \nabla V(q) \\ \nabla^2 V(q) M^{-1} p \end{pmatrix}. \tag{2.37}$$

This force is not of Hamiltonian type. Indeed, if there existed $\widetilde H$ such that

$$F(q,p) = J \nabla \widetilde H(q,p) = \begin{pmatrix} \nabla_p \widetilde H(q,p) \\ -\nabla_q \widetilde H(q,p) \end{pmatrix},$$

then we would have $\mathrm{div}_{(q,p)} F = 0$, which is clearly not the case for (2.37).

For the symplectic Euler scheme (2.26), it holds

$$\begin{cases} q^{n+1} = q^n + \Delta t M^{-1} p^n, \\ p^{n+1} = p^n - \Delta t \nabla V(q^n) - \Delta t^2 \nabla^2 V(q^n) M^{-1} p^n + \mathrm{O}(\Delta t^3), \end{cases}$$

which shows that

$$F(q,p) = \frac{1}{2} \begin{pmatrix} M^{-1} \nabla V(q) \\ -\nabla^2 V(q) M^{-1} p \end{pmatrix} = J \nabla \widetilde H(q,p),$$

with

$$\widetilde H(q,p) = \frac{1}{2} p^T M^{-1} \nabla V(q). \tag{2.38}$$

The leading order term of the modified dynamics is therefore of Hamiltonian type (but not separable).

Exercise 2.4. *Show that the leading order term of the modified dynamics for the other symplectic Euler scheme* (2.26) *corresponds to the opposite of* (2.38).

Exercise 2.5. *Show, by following the approach presented in [113, Section 4.2], that the leading order of the modified Hamiltonian for the Verlet scheme reads*

$$\widetilde H(q,p) = \frac{1}{12} p^T M^{-1} \nabla^2 V(q) M^{-1} p - \frac{1}{24} \nabla V(q)^T M^{-1} \nabla V(q).$$

Truncations of the modified equation for symplectic methods

We prove here that the fact that the modified dynamics is Hamiltonian for symplectic schemes is not an accident. We follow the pedagogical account of [113, Section 4].

Consider first a general differential equation $\dot{y} = f(y)$. Assuming that the numerical method admits a Taylor series expansion of the form

$$\Phi_{\Delta t}(y) = y + \Delta t f(y) + \Delta t^2 \Psi_2(y) + \Delta t^3 \Psi_3(y) + \dots$$

with smooth vector fields Ψ_j, we can iterate the argument presented on two simple examples in the previous section and construct vector fields $F_1, F_2, \dots$ such that the flow $\varphi_{N,t}$ associated with the modified force field

$$f_{N,\Delta t} = f + \Delta t F_1 + \dots + \Delta t^N F_N$$

coincides with the numerical solution up to error terms of order Δt^{N+2} over one timestep:

$$\Phi_{\Delta t}(y) = \varphi_{N,\Delta t}(y) + \mathrm{O}(\Delta t^{N+2}). \tag{2.39}$$

Remark 2.7. *Of course, if the numerical method is of order α (i.e. $\Phi_{\Delta t}(y) = \phi_{\Delta t}(y) + \mathrm{O}(\Delta t^{\alpha+1})$), then the $\alpha - 1$ first order correction terms vanish: $F_1 = \dots = F_{\alpha-1} = 0$. Moreover, if the leading order term of the local trunction error is $E_{\alpha+1}$, namely*

$$\Phi_{\Delta t}(y) = \phi_{\Delta t}(y) + \Delta t^{\alpha+1} E_{\alpha+1}(y) + \mathrm{O}(\Delta t^{\alpha+2}),$$

and since $\varphi_{\alpha,\Delta t} = \varphi_{\Delta t} + \Delta t^{\alpha+1} E_{\alpha+1}$ when choosing $F_\alpha = E_{\alpha+1}$, it follows that (2.39) *holds with $N = \alpha$.*

Consider now a symplectic method $\Phi_{\Delta t}$, which is of order $\alpha \geqslant 1$. We proceed by induction, and assume that, at order N, the modified force field is of Hamiltonian type:

$$f_{N,\Delta t} = J\nabla H + \Delta t J \nabla H_1 + \dots + \Delta t^N J \nabla H_N.$$

The aim is to prove that $F_{N+1} = J\nabla H_{N+1}$ for some Hamiltonian H_{N+1}. This is satisfied at order $N = 0$. Now, the induction assumption implies that the flow $\varphi_{N,t}$ is symplectic since it is associated with a Hamiltonian dynamics. In addition,

$$\varphi_{N+1,\Delta t}(y) = \varphi_{N,\Delta t}(y) + \Delta t^{N+2} F_{N+1}(y) + \mathrm{O}(\Delta t^{N+3}),$$

so that (2.39) implies

$$\begin{aligned}
\Phi_{\Delta t}(y) &= \varphi_{N,\Delta t}(y) + \Delta t^{N+2} F_{N+1}(y) + \mathrm{O}(\Delta t^{N+3}),\\
\nabla\Phi_{\Delta t}(y) &= \nabla\varphi_{N,\Delta t}(y) + \Delta t^{N+2} \nabla F_N(y) + \mathrm{O}(\Delta t^{N+3}).
\end{aligned}$$

The symplecticity condition $\nabla\Phi_{\Delta t}(y)^T J \nabla\Phi_{\Delta t}(y) = J$ therefore leads to

$$\begin{aligned}
J &= \left[\nabla\varphi_{N,\Delta t}(y) + \Delta t^{N+2}\nabla F_{N+1}(y) + \mathrm{O}(\Delta t^{N+3})\right]^T J \left[\nabla\varphi_{N,\Delta t}(y) + \Delta t^{N+2}\nabla F_{N+1}(y) + \mathrm{O}(\Delta t^{N+3})\right]\\
&= \nabla\varphi_{N,\Delta t}(y)^T J \nabla\varphi_{N,\Delta t}(y) + \Delta t^{N+2}\left(\nabla\varphi_{N,\Delta t}(y)^T J \nabla F_{N+1}(y) + \nabla F_{N+1}(y)^T J \nabla\varphi_{N,\Delta t}(y)\right) + \mathrm{O}(\Delta t^{N+3})\\
&= J + \Delta t^{N+2}\left(J\nabla F_{N+1}(y) + \nabla F_{N+1}(y)^T J\right) + \mathrm{O}(\Delta t^{N+3}),
\end{aligned}$$

where we have used $\nabla\varphi_{N,\Delta t}(y) = \mathrm{Id} + \mathrm{O}(\Delta t)$ and the symplecticity of $\varphi_{N,\Delta t}$ in the second and third lines. Since the last equality is true for all $\Delta t > 0$ and $y \in \mathcal{E}$, it holds

$$\forall y \in \mathcal{E}, \qquad J\nabla F_{N+1}(y) + \nabla F_{N+1}(y)^T J = 0.$$

Therefore, $J\nabla F_{N+1}(y)$ is a symmetric matrix for all $y \in \mathcal{E}$, so that $JF_{N+1}(y) = -\nabla H_{N+1}(y)$ for some Hamiltonian H_{N+1} (see the proof of Theorem 2.2 for a proof of the latter statement), which gives the claimed result.

Remark 2.8. *In fact, the above proof only shows that the modified dynamics is locally Hamiltonian. In order to have some globally defined Hamiltonian, one should add some extra assumptions, typically that the domain on which the Hamiltonian dynamics is defined is simply connected, in order for the construction* (2.14) *to make sense over all the domain; see the discussion in [114, Sections VI.2 and IX.3].*

Longtime energy preservation

The previous results in this section show that a symplectic method applied to a Hamiltonian evolution admits a modified equation which is Hamiltonian at all orders. Moreover, the Hamiltonian correction terms are locally bounded (see the explicit construction in (2.14)). We can then show that the energy is very well preserved over very long times provided the trajectory remains in a compact set of $\mathcal{E}$.

Theorem 2.4. *Consider a symplectic numerical method of order $\alpha \geqslant 1$, and assume that the numerical trajectory (q^n, p^n) remains in a compact subset of $\mathcal{E}$. Then, there exists $C > 0$ such that, for any $a \geqslant \alpha + 1$, there is $C_a > 0$ for which*

$$\left|H(q^n, p^n) - H(q^0, p^0)\right| \leqslant C\Delta t^\alpha + C_a \Delta t^a t, \qquad 0 \leqslant t = n\Delta t \leqslant \frac{1}{\Delta t^a}.$$

A careful proof shows that C_a depends on derivatives of H up to order a in the compact subset where the trajectory remains. The precise interpretation of this result is the following: for physical times $t \ll \Delta t^{\alpha - a}$ which are very large when Δt is small, the dominant term in the error is $C\Delta t^\alpha$. Therefore, the energy typically oscillates around the initial energy, with an amplitude related to the order of the numerical method. In fact, under additional technical conditions, precise estimates can be obtained on C_a. Upon resorting to some optimal truncation of the series (*i.e.* optimizing the error bound with respect to a), Theorem 2.4 can be improved by stating a near energy conservation over time intervals which grow exponentially with the timestep.

Theorem 2.5 (Theorem IX.8.1 in [114]). *Consider an analytic Hamiltonian H and a symplectic method $\Phi_{\Delta t}$ of order α. If the numerical trajectory remains in a compact subset, there exists $\tau > 0$ and $\Delta t^* > 0$ such that, for $\Delta t \in (0, \Delta t^*]$,*

$$H(q^n, p^n) = H(q^0, p^0) + \mathrm{O}(\Delta t^\alpha)$$

for exponentially long times $n\Delta t \leqslant \mathrm{e}^{\tau/\Delta t}$.

Proof (of Theorem 2.4). Consider the modified equation of order $a - 1$. Since $\alpha \geqslant 1$, the modified Hamiltonian dynamics is generated by the modified Hamiltonian

$$\widetilde{H}_{a-1}(q, p) = H(q, p) + \Delta t^\alpha H_\alpha(q, p) + \cdots + \Delta t^{a-1} H_{a-1}(q, p).$$

By construction, the flow of the modified dynamics $\varphi_{a-1,t}$ preserves $\widetilde{H}_{a-1}$ and is such that $\varphi_{a-1,t}(q^k, p^k) = (q^{k+1}, p^{k+1}) + \mathrm{O}(\Delta t^{a+1})$. Therefore, the variations in the modified energy over one timestep are

$$\left|\widetilde{H}_{a-1}(q^{k+1}, p^{k+1}) - \widetilde{H}_{a-1}(q^k, p^k)\right| \leqslant C_a \Delta t^{a+1}.$$

Then,

$$\left|\widetilde{H}_{a-1}(q^n, p^n) - \widetilde{H}_{a-1}(q^0, p^0)\right| = \left|\sum_{k=0}^{n-1} \widetilde{H}_{a-1}(q^{k+1}, p^{k+1}) - \widetilde{H}_{a-1}(q^k, p^k)\right| \leqslant C_a \Delta t^a \, n\Delta t.$$

The claimed result follows by a triangular inequality since $\left|\widetilde{H}_a(q^n, p^n) - H(q^n, p^n)\right| \leqslant C\Delta t^a$. □

Let us however, one last time, emphasize again that the near energy preservation is a only necessary condition for the statistical correctness of ergodic averages. The results presented in this section do not guarantee the convergence of trajectorial averages towards ensemble averages: ergodicity remains a pending issue. As acknowledged in [113, Section 5.3]:

> The success of the Störmer-Verlet method in [molecular dynamics] lies in the observation that the method is apparently able to reproduce the correct statistical behaviour over long times. Since Verlet (1967), this has been confirmed in countless computational experiments. Backward error analysis gives indications as to why this might be so, but to our knowledge there are as yet no rigorous mathematical results in the literature explaining the favourable statistical behaviour.

To the best of our knowledge, the last statement still holds...

2.3 Extensions

needs to be completed...

The timestep in the Verlet method is limited by the stability requirement (2.35). In actual systems such as biological molecules, it is common to have very stiff bonds (covalent bonds), which therefore severely limit the timesteps which can be used. In order to alleviate this limitation, several techniques have been developped, in particular

- the replacement of very stiff bonds by rigid bonds. This requires simulating constrained systems, using appropriate generalizations of the Verlet scheme such as the RATTLE method, see [171];
- multiple timestep strategies, where the stiff parts of the system are evolved using a small timestep, while the less stiff degrees of freedom are evolved with a larger timestep. There are however resonance issues.

In addition, there are situations in which non-separable systems should be considered. The Verlet algorithm then needs to be generalized. There are also ways to add randomness to the Hamiltonian evolution in order to ensure ergodicity [90].

Part II

Sampling the canonical ensemble

3

The Metropolis–Hastings algorithm

We present in this chapter the Metropolis algorithm [195] and some of its variants. This algorithm can be understood as a Markov chain on a continuous state space. We therefore start this chapter by recalling in Section 3.1 some background material on Markov chains in such spaces. This complements Lecture ??. We next present the Metropolis algorithm in Section 3.2, in its general form, and give some versions which are commonly used in molecular simulation. The longtime convergence of the law of the associated Markov chain is discussed in Section 3.3, relying on a general result by Hairer and Mattingly [118] which provides a more analytical point of view on Markov chains than the maybe more standard approach by Meyn and Tweedie [196]. The implication of the convergence analysis of the law in terms of the convergence of trajectory averages is finally discussed in Section 3.4, where a central limit theorem allows in particular to asymptotically quantify the statistical error.

add reference

quote also recent book by Moulines and co'

3.1 Some background material on Markov chains

We present Markov chains in terms of the positions only, for notational simplicity and in order to introduce the simplest versions of the Metropolis–Hastings algorithm. We denote by $\mathcal{D}$ the configuration space, which may be either $\mathbb{R}^D$ or a compact domain such as $(L\mathbb{T})^D$ (see Chapter 1). Extensions to Markov chains involving more degrees of freedom, for instance Markov chains in phase space where the unknowns are the positions and momenta of particles, are straightforward.

3.1.1 Definition of Markov chains in a continuous state space

A time-homogeneous Markov chain $(q^n)_{n\geqslant 0}$ is a sequence of random variables sampled from a *probability transition kernel* $P(q, dq')$: At each iteration n, the new state q^{n+1} is sampled knowing

only q^n (and not the previous iterations), according to the probability distribution $P(q^n, dq')$. Notice that, since $P(q^n, dq')$ is a probability distribution, the following normalization condition is satisfied:

$$\forall q \in \mathcal{D}, \qquad \int_{\mathcal{D}} P(q, dq') = 1.$$

When $P(q, dq')$ has a density with respect to the Lebesgue measure dq', with a slight abuse of notation, we still denote by P the *probability transition density*, so that the transition kernel is in this case $P(q, q')\, dq'$.

Remark 3.1. *When the transition kernel depends on the time index n, the chain is called time-inhomogeneous.*

More constructively, a Markov chain can generically be written as follows:

$$q^{n+1} = F(q^n, \Theta_n),$$

where $(\Theta_n)_{n \geqslant 0}$ is a sequence of independent identically distributed random variables. In this case, the transition kernel is characterized by the following equality: For any state q and for any observable φ (*i.e.* a bounded measurable function),

$$(P\varphi)(q) = \int_{\mathcal{D}} \varphi(q')\, P(q, dq') = \mathbb{E}\Big[\varphi\big(F(q, \Theta_1)\big)\Big], \tag{3.1}$$

where the expectation is with respect to Θ_1. Again, with some abuse of notation, we use the same notation for the evolution operator and the integral kernel of this operator.

3.1.2 Properties of Markov chains

To study the longtime properties of a time homogeneous chain, two features are of interest:

- *Stationarity.* A probability distribution π is a stationary probability distribution of P (or is said invariant for P) when

  $$\int_{q \in \mathcal{D}} P(q, dq')\, \pi(dq) = \pi(dq'),$$

  which may be equivalently restated as the following equality of averages for any bounded measurable test function φ:

  $$\int_{\mathcal{D}} \int_{\mathcal{D}} \varphi(q')\, P(q, dq')\, \pi(dq) = \int_{\mathcal{D}} \varphi(q)\, \pi(dq). \tag{3.2}$$

  This condition means that, if the random variable q^0 is distributed according to π, then so is q^1, and, by induction, q^n as well.

compare with the concepts introduced in the lectures by Lelièvre/Reygner

- *Irreducibility.* A Markov chain is said to be irreducible with respect to some measure ρ when, for any Borel subset $S \subset \mathcal{D}$ such that $\rho(S) > 0$, and any initial condition $q^0 \in \mathcal{D}$, it holds $\mathbb{P}_{q^0}(\tau_S < +\infty) > 0$, where $\tau_S = \inf\{n \geqslant 0, q^n \in S\}$ is the first entry time into the set S.
  It is often useful to formulate irreducibility in terms of the nth step transition probability, defined by induction as

  $$P^n(q, dq') = \int_{Q \in \mathcal{D}} P(q, dQ)\, P^{n-1}(Q, dq'),$$

  with $P^1(q, dq') := P(q, dq')$. Irreducibility can then be formulated as follows: For any Borel subset $S \subset \mathcal{D}$ such that $\rho(S) > 0$ and any initial condition $q^0 \in \mathcal{X}$, there exists $n \geqslant 0$ (depending on q^0 and S) such that $P^n(q^0, S) > 0$.
  In particular, the Markov chain P is aperiodically irreducible with respect to ρ if for any measurable set S such that $\rho(S) > 0$, and π-almost all initial condition q^0, there exists $n_0 > 0$ such that for any $n \geqslant n_0$,

  $$P^n(q^0, S) > 0. \tag{3.3}$$

  This means that the set S can be reached in n steps with positive probability starting from q^0.

Additional features can be of interest, which give a more detailed information on the structure of the Markov chain. This is the case of the following notion of reversibility.

- *Reversibility.* The chain P is said to be reversible with respect to π as soon as the following *detailed balance condition* is satisfied:

$$P(q, dq')\,\pi(dq) = P(q', dq)\,\pi(dq'). \tag{3.4}$$

The reversibility condition implies the stationarity of π. Indeed, a simple computation shows that, for a bounded measurable function φ and using (3.4),

$$\begin{aligned}\int_{\mathcal{D}}\int_{\mathcal{D}} \varphi(q')\,P(q, dq')\,\pi(dq) &= \int_{\mathcal{D}}\int_{\mathcal{D}} \varphi(q')\,P(q', dq)\,\pi(dq') \\ &= \int_{\mathcal{D}} \left(\int_{\mathcal{D}} P(q', dq)\right) \varphi(q')\,\pi(dq') \\ &= \int_{\mathcal{D}} \varphi(q')\,\pi(dq'),\end{aligned}$$

which is the stationarity condition (3.2). The detailed balance condition (3.4) is equivalent to the following statement: If q^0 is distributed according to π, then for any n, the sequence $(q^0, \dots, q^n)$ has the same probability distribution as the time-reversed sequence $(q^n, \dots, q^0)$.

3.1.3 Convergence of trajectory averages

An important result is that stationarity and aperiodic irreducibility imply ergodicity, understood as the almost-sure convergence of averages along realizations of the Markov chain (see [196, Theorem 17.1.7]):

Proposition 3.1. *Let $(q^n)_{n\geqslant 0}$ be a Markov chain in $\mathcal{D}$ with invariant probability measure π. If $(q^n)_{n\geqslant 0}$ is aperiodically irreducible, then it is* pathwise ergodic, *meaning that for any bounded measurable function φ and π-almost all initial conditions q^0:*

$$\lim_{n\to+\infty} \frac{1}{n}\sum_{k=1}^{n} \varphi(q^k) = \int_{\mathcal{D}} \varphi(q)\,\pi(dq) \quad \text{a.s.}$$

Two comments are in order:

(i) we will see in Theorem 3.1 one way to prove the existence of an invariant probability measure in situations where there is no obvious candidate (as is the case when considering discretizations of stochastic differential equations, see for instance Section 6.1). Some Markov chains such as the Metropolis–Hastings algorithm discussed in Section 3.2 have by construction an invariant measure whose expression is explicitly known. Note also that π is automatically absolutely continuous with respect to the measure ρ with respect to which irreducibility holds.

(ii) the restriction that the ergodic average converges only for almost all initial conditions can be strengthened to hold for all initial conditions under some regularity conditions on the transition kernel; more precisely that the transition kernel $P(q, dq')$ is absolutely continuous with respect to the invariant probability measure π for all $q \in \mathcal{D}$, and that the Markov chain is irreducible with respect to π (see [266, Corollary 1], based on [207]).

Example 3.1. Consider a system with a finite state space $\mathbb{T}_N = \{1, 2, \dots, N\}$ with periodic boundary conditions, *i.e.* $m + kN$ is identified with m for any $1 \leqslant m \neq N$ and $k \in \mathbb{Z}$, and the following evolution rule: the current state $q^n \in \mathbb{T}_N$ is changed to $q^{n+1} = q^n + 1$ with probability $a \in [0, 1]$, and to $q^{n+1} = q^n - 1$ with probability $1 - a$. Then, when $a \neq 0$, the uniform measure

$$\mu = \frac{1}{N}\sum_{m=1}^{N} \delta_m$$

this example should be in the lectures on finite state spaces

is the unique stationary measure. The Markov chain is reversible with respect to this measure if and only if $a = 1/2$. Let us also remark that the convergence is somehow the slowest in this case, since a diffusive behavior is observed; where some ballistic transport arises as soon as $a > 0$ is different from $1/2$.

3.2 The Metropolis–Hastings algorithm

The Metropolis–Hastings algorithm generates a Markov chain of the system configurations $(q^n)_{n\geqslant 0}$ having as invariant distribution the marginal of the canonical measure in the position variables (defined in (1.19))

$$\nu(dq) = Z^{-1}\mathrm{e}^{-\beta V(q)}\, dq. \tag{3.5}$$

It consists in a two-step procedure. First, a move is generated, according to some given proposition transition kernel $T(q, dq')$. Then, the latter proposal move is either accepted or rejected, according to a rule such that the probability distribution $\nu(dq)$ is an invariant measure of the corresponding Markov chain. The original Metropolis algorithm was proposed in [195], and relied on symmetric proposals in the configuration space, meaning that

$$T(q, dq')\, dq = T(q', dq)\, dq'.$$

It was later refined in [121] in order to allow for non-symmetric propositions which can bias proposals towards higher probability regions with respect to the target distribution ν.

We start by describing the method in Section 3.2.1, then present some of its mathematical properties in Section 3.2.2, and conclude by giving practical examples in Section 3.2.3.

3.2.1 Description of the algorithm

Given a target probability distribution ν and a proposition transition kernel T, the Metropolis–Hastings algorithm constructs in a systematic way a Markov chain reversible with respect to ν. The detailed balance condition (3.4) is usually not verified for T and ν, and a correction has therefore to be considered. For this correction to be possible, the proposition kernel $T(q, dq')$ must have some reversibility property, in the sense that the measures $T(q, dq')\,\nu(dq)$ and $T(q', dq)\,\nu(dq')$ have to be mutually absolutely continuous (or equivalent) for all $q, q' \in \mathcal{D}$, in order for the Metropolis–Hastings ratio to be defined and positive (see below). Under this assumption, the algorithm is the following.

Algorithm 3.1 (Metropolis–Hastings algorithm). *Assume that the two measures $T(q', dq)\,\nu(dq')$ and $T(q, dq')\,\nu(dq)$ are equivalent and introduce the Metropolis–Hastings ratio:*

$$r(q, q') = \frac{T(q', dq)\,\nu(dq')}{T(q, dq')\,\nu(dq)}.$$

The ratio $r(q, q')$ is defined and positive for almost any couple of states (q, q') with respect to the measure $T(q, dq')\,\nu(dq)$. Consider an initial configuration q^0 and iterate on $n \geqslant 0$,

(1) Propose a new state $\tilde{q}^{n+1}$ from q^n according to the proposition kernel $T(q^n, \cdot)$;
(2) Accept the proposition with probability

$$R(q^n, \tilde{q}^{n+1}) = \min\left(1, r(q^n, \tilde{q}^{n+1})\right),$$

and set in this case $q^{n+1} = \tilde{q}^{n+1}$; otherwise, set $q^{n+1} = q^n$.

In practice, the second step consists in drawing (independently) a random variable U^n with uniform law on $(0, 1)$, and accepting (resp. rejecting) the move if $U^n \leqslant \min\left(1, r(q^n, \tilde{q}^{n+1})\right)$ (resp. if $U^n > \min\left(1, r(q^n, \tilde{q}^{n+1})\right)$). The algorithm can therefore be summarized as follows:

$$q^{n+1} = q^n + \mathbf{1}_{\{U^n \leqslant R(q^n, \tilde{q}^{n+1})\}} \left(\tilde{q}^{n+1} - q^n \right).$$

An important point in this method is that the distribution ν has to be known only up to a multiplicative constant to perform this algorithm. This is fortunate for computational statistical physics, since the partition function Z in (3.5) is not usually unknown.

It may be worth emphasizing that, as for "direct" probabilistic methods such as the rejection method, proposal moves which are rejected are discarded, but, in contrast to the "direct" probabilistic methods, a new configuration q^{n+1}, equal to the previous one q^n, is obtained in any case. This is important to estimate correctly canonical averages: Configurations where many propositions are rejected are counted several times (and possibly many times) in the average.

Example 3.2 (Symmetric proposition kernels). As an example, let us consider the case of the canonical sampling of positions using a symmetric proposition kernel, which therefore satisfies:

$$T(q, dq')\, dq = T(q', dq)\, dq'.$$

It is thus reversible with respect to the Lebesgue measure (so that the Lebesgue measure is in particular an invariant measure of the Markov chain with kernel T), whereas we would like the Markov chain to be reversible with respect to the canonical measure. This is why an acceptance/rejection step is required, the corresponding Metropolis–Hastings ratio being simply the Metropolis ratio

$$r(q, q') = \exp\left[-\beta(V(q') - V(q))\right].$$

In this case, the interpretation of the algorithm is particularly simple. If the proposed move has a lower energy, it is always accepted, which allows to visit more frequently the states of higher probability. On the other hand, transitions to less likely states of higher energies are not forbidden (but accepted less often), which is important to observe transitions from one metastable region to another when these regions are separated by some energy barrier.

3.2.2 Mathematical properties of the Metropolis–Hastings algorithm

Let us first provide an expression of the transition kernel of the Metropolis–Hastings algorithm, relying on (3.1). For a given smooth test function φ,

$$\begin{aligned}\mathbb{E}_{q^n}\left[\varphi(q^{n+1})\right] &= \mathbb{E}_{q^n}\left[\varphi\left(q^n + \mathbf{1}_{U^n \leqslant R(q^n, \tilde{q}^{n+1})}\left(\tilde{q}^{n+1} - q^n\right)\right)\right] \\ &= \mathbb{E}_{q^n}\left[R(q^n, \tilde{q}^{n+1})\varphi(\tilde{q}^{n+1})\right] + \mathbb{E}_{q^n}\left[1 - R(q^n, \tilde{q}^{n+1})\right]\varphi(q),\end{aligned}$$

where the second line follows by computing the expectation with respect to U^n. Since $\tilde{q}^{n+1}$ is distributed according to $T(q, dq')$ when $q^n = q$, the probability transition kernel of the Metropolis–Hastings chain reads

$$P(q, dq') = R(q, q')T(q, dq') + (1 - \alpha(q))\, \delta_q(dq'), \tag{3.6}$$

where $\alpha(q) \in [0, 1]$ is the probability to accept a move starting from q (considering all possible propositions):

$$\alpha(q) = \int_{\mathcal{D}} R(q, Q)T(q, dQ).$$

The first part of the transition kernel corresponds to the accepted transitions from q to q', which occurs with probability $R(q, q') = \min(1, r(q, q'))$; while the term $(1 - \alpha(q))\delta_q(dq')$ encodes all the rejected steps.

A distinctive feature of Metropolis–Hastings algorithm is their built-in reversibility with respect to the target measure.

Lemma 3.1. *The Metropolis–Hastings transition kernel P is given in* (3.6) *is reversible with respect to ν. In particular, ν is an invariant probability measure for P.*

Proof. Consider

$$P(q, dq')\nu(dq) = \min\left(1, r(q,q')\right) T(q, dq')\nu(dq) + \left(1 - \alpha(q)\right) \delta_q(dq')\nu(dq). \tag{3.7}$$

Using the identity $r(q,q') = 1/r(q',q)$ and the algebraic equality for $r > 0$:

$$\min(1, r) = r \min\left(1, \frac{1}{r}\right),$$

the first term on the right-hand side of (3.7) can be rewritten as

$$\begin{aligned}\min\left(1, r(q,q')\right) T(q, dq')\nu(dq) &= \min\left(1, r(q',q)\right) r(q,q') T(q, dq')\nu(dq) \\ &= \min\left(1, r(q',q)\right) T(q', dq)\nu(dq').\end{aligned}$$

On the other hand, for a given bounded measurable function φ,

$$\begin{aligned}\int_{\mathcal{D}}\int_{\mathcal{D}} \varphi(q,q') \left(1 - \alpha(q)\right) \delta_q(dq')\nu(dq) &= \int_{\mathcal{D}} \varphi(q,q)(1-\alpha(q))\nu(dq) \\ &= \int_{\mathcal{D}}\int_{\mathcal{D}} \varphi(q,q')(1-\alpha(q'))\delta_{q'}(dq)\nu(dq'),\end{aligned}$$

so that $\left(1 - \alpha(q)\right) \delta_q(dq')\nu(dq) = (1-\alpha(q'))\delta_{q'}(dq)\nu(dq')$. This shows finally the reversibility property $P(q, dq')\nu(dq) = P(q', dq)\nu(dq')$. □

Remark 3.2. *The Metropolis–Hastings algorithm relies on the acceptance ratio $A(r) = \min(1, r) \in [0, 1]$. There are in fact (infinitely many) other functions A with values in $[0, 1]$ which satisfy $A(r) = rA(1/r)$, and thus lead to a Markov chain reversible with respect to ν by a straightforward adaptation of the proof of Lemma 3.1. For instance (see [102]), one can consider the family of acceptance functions*

$$A_\gamma(r) = \frac{r}{1+r}\left(1 + 2\left[\frac{1}{2}\min\left(r, \frac{1}{r}\right)\right]^\gamma\right),$$

indexed by a real number $\gamma \geqslant 1$. The Metropolis rule corresponds to $\gamma = 1$, while the Barker rule $A(r) = r/(r+1)$ (introduced in [23]) is formally recovered for $\gamma = +\infty$. However, it can be shown that the Metropolis rule is optimal in terms of asymptotic variance (see [219]; as well as Section 3.4 below for a discussion on asymptotic variance), which is why this algorithm is usually preferred, although the use of a Barker rule can sometimes be beneficial (see for instance [92] where the Barker rule allows to decrease the timestep bias compared to Metropolis-like dynamics when computing properties obtained from discretizations of certain stochastic differential equations).

To conclude to the pathwise ergodicity of the algorithm using Proposition 3.1, it remains to check whether the chain is aperiodically irreducible. This property depends on the proposal kernel T, and should be checked for the model at hand. Note that as soon as the Metropolis–Hastings ratio $r(q,q') > 0$ for all $(q,q') \in \mathcal{D}^2$ for instance, the aperiodic irreducibility of the proposal transition T alone (with respect to the reference measure ν) is equivalent to the aperiodic irreducibility of the Markov chain induced by the Metropolis Algorithm 3.1. We discuss the irreducibility of some concrete instances of the Metropolis–Hastings algorithms in Section 3.2.3.

Besides determining the theoretical convergence of the algorithm, the proposed kernel is also a key element in devising efficient algorithms. It is observed in practice that the optimal acceptance/rejection rate, in terms of the variance of the estimator (a mean of some functional over a trajectory) for example, is often around 0.5, ensuring some balance between

- large moves that decorrelate the iterates when they are accepted (hence reducing the correlations in the chain, which is interesting for the convergence to happen faster, see Section 3.4), but lead to high rejection rates (and thus, degenerate samples since the same position may be counted several times);
- and small moves that are less rejected but do not decorrelate the iterates much.

This trade-off between small and large proposal moves has been investigated rigorously in some simple cases in [234, 235], where some optimal acceptance rates are obtained in a limiting regime where the dimension goes to infinity, for potentials which are sums of one dimensional potentials: $V(q) = v(q_1) + \cdots + v(q_D)$. This analysis can be extended to target probability measures with some form of correlation, and to more general Markov chains than the ones considered in Section 3.2.3. In practice, it is always a good idea to run some preliminary small simulations to determine orders of magnitude for the optimal acceptance rate, based on some metric such as the mean square displacement $\mathbb{E}(|q^{n+1} - q^n|^2)$.

More precise review of literature here

3.2.3 Some examples of proposition transition kernels

We present in this section two paradigmatic choices for the proposal kernel in the Metropolis–Hastings algorithm, and hint at (the very many) extensions.

Symmetric moves

The most simple transition kernels are based on random walks. For instance, it is possible to modify the current configuration by a random perturbation, such as

$$q' = q + \sigma G, \qquad G \sim \mathcal{N}(0, \mathrm{Id}_D),$$

where $\sigma > 0$ is some scale parameter. The associated proposal probability kernel reads

$$T(q, dq') = \left(\sigma\sqrt{2\pi}\right)^{-D} \exp\left(-\frac{|q' - q|^2}{2\sigma^2}\right) dq'.$$

Of course, uniformly distributed displacements for instance could be considered as well:

$$q' = q + \sigma U, \qquad U \sim \mathcal{U}\left((-1, 1)^D\right)$$

in which case

$$T(q, dq') = (2\sigma)^{-D} \mathbf{1}_{|q'-q| \leqslant \sigma} \, dq'.$$

Both these proposals are symmetric. The problem with such proposals is that they are uninformed and therefore not well suited in general to the target probability measure at hand (creating very correlated successive configurations for small σ, or very unlikely moves for large σ).

Another symmetric proposal which may be used in the case of many particle systems for which $q = (q_1, \ldots, q_N)$ in a physical space of dimension d (so that $D = dN$) consists in applying a random walk displacement to only one particle chosen at random. This may help proposing moves which are more likely to be accepted than when updating all particles simultaneously (think for example of a relatively dense fluid). For instance, for a uniformly distributed perturbation with a typical magnitude $\sigma > 0$, the transition kernel is

$$T(q, dq') = \frac{1}{N} \sum_{i=1}^{N} \left(\prod_{j \neq i} \delta_{q_j}(dq'_j) \right) \left(\prod_{\alpha=1}^{d} \mathbf{1}_{|q'_{i,\alpha} - q_{i,\alpha}| \leqslant \sigma} \right) \frac{dq'_i}{(2\sigma)^d},$$

where $q_{i,\alpha}$ is the α-th component of q_i.

For random walk proposals, under weak assumptions on the potential energy function, it is possible to transform a given configuration into another one in a finite number of steps by moving individually one particle after another. This shows the irreducibility of the chain.

should this be made precise? painful...

Non-symmetric move

An instance of a non-symmetric proposal which may be useful to sample the canonical measure (3.5) is the one used in the so-called Metropolis-Adjusted Langevin Algorithm (MALA) in the statistics literature [235], known as Smart MC in the chemistry literature [237]:

$$q' = q - \sigma^2 \nabla V(q) + \sqrt{\frac{2\sigma^2}{\beta}}\, G, \qquad G \sim \mathcal{N}(0, \mathrm{Id}_D). \tag{3.8}$$

The proposal is built on the time discretization (with time step $\sigma^2 > 0$) of the overdamped Langevin dynamics which is ergodic with respect to the canonical measure (see Chapter 4). The acceptance-rejection step corrects the bias introduced by the time discretization. Roughly speaking, the added drift term proportional to $-\nabla V(q)$ brings back the system to regions of higher probability, while the random term adds some stochastic fluctuations. The associated transition kernel reads

$$T(q, dq') = \left(\frac{\beta}{4\pi\sigma^2}\right)^{D/2} \exp\left(-\beta \frac{|q' - q + \sigma^2 \nabla V(q)|^2}{4\sigma^2}\right) dq'.$$

Notice that in this case $T(q, dq')\, dq \neq T(q', dq)\, dq'$.

Exercise 3.1. *For practical implementation, it is numerically more stable to compute the logarithmic acceptance rate* $\log r(q, q')$*. Show that for the proposal* (3.8)*,*

$$\log r(q, q') = \beta \left[V(q) - V(q')\right] + \frac{1}{2}\left[G^2 - \mathcal{G}_\sigma(q, q')^2\right],$$

for some function $\mathcal{G}_\sigma$ *such that* $\lim_{\sigma \to 0} \mathcal{G}_\sigma(q, q') = -G$*.*

Remark 3.3. *For small values of* σ*, it can be shown that the average rejection rate*

$$1 - \int_{\mathcal{D}} \alpha(q)\, \nu(dq)$$

scales as σ *for random walk proposals, while it scales as* σ^3 *for MALA. This can be proved by straightforward Taylor expansions, see for instance [91].*

better reference?

Refinements and extensions

Since the proposal kernel T lies at the heart of the method, it is no surprise that a large fraction of the literature from the application fields (chemistry, physics, materials science, etc) deals with new and creative proposal kernels, using for instance "non-physical moves" where molecules are broken and other ones are linked together ; see for instance [97, Chapter 13] for some examples. Another important class of methods relies parallel tempering strategies [186], where several replicas of the system are simulated in parallel at different temperatures, and sometimes exchanges between two replicas at different temperatures are attempted, the probability of such an exchange being given by a Metropolis–Hastings ratio.

write exercice on this

other extensions to mention – delayed rejection and co' for instance

3.3 Convergence of the law

We present in this section a result on the exponential convergence of the evolution operator in some space of functions growing not too fast at infinity [118]. Similar results are provided in [196]; see also [228] for stochastic differential equations. We first give in Section 3.3.1 a convergence result in a general form on an abstract configuration space $\mathcal{X}$, since this result will be used in many situations in the sequel: time-discrete or time-continuous dynamics, in terms of positions or positions and momenta. The first situation we discuss concerns time-discrete dynamics (Markov chains), in positions; see Section 3.3.3.

In this section, and in the sequel, we denote by $B^\infty(\mathcal{X})$ the Banach space of bounded measurable functions on $\mathcal{X}$ endowed with the norm

$$\|\varphi\|_{B^\infty} = \sup_{x \in \mathcal{X}} |\varphi(x)|.$$

3.3.1 A general result

Consider a stochastic evolution described by its evolution operator P, with associated kernel $P(x, dx')$. Recall that bounded measurable functions are evolved as

$$(P\varphi)(x) = \int_{\mathcal{X}} \varphi(x') P(x, dx').$$

To define the evolution of probability measures, we introduce the set $\mathscr{B}(\mathcal{X})$ of Borel subsets of $\mathcal{X}$, and define

$$\forall S \in \mathscr{B}(\mathcal{X}), \qquad (P\mu)(S) = \int_{\mathcal{X}} P(x, S)\, \mu(dx).$$

Note that these definitions imply

$$\int_{\mathcal{X}} (P\varphi)\, d\mu = \int_{\mathcal{X}} \varphi\, d(P\mu). \tag{3.9}$$

Indeed, the equality is a result of the above definitions when $\varphi = \mathbf{1}_S$ for any $S \in \mathscr{B}(\mathcal{X})$, and from that we deduce the equality for any bounded measurable functions (see for instance [243]). We make the following assumptions.

Assumption 3.1 (Lyapunov condition). *There exists a function $\mathscr{W} : \mathcal{X} \to [0, +\infty)$ and constants $K \geqslant 0$ and $\gamma \in (0, 1)$ such that*

$$\forall x \in \mathcal{X}, \qquad (P\mathscr{W})(x) \leqslant \gamma \mathscr{W}(x) + K.$$

Remark 3.4. *Note that, upon replacing $\mathcal{X}$ with $\{x \in \mathcal{X} \,|\, \mathscr{W}(x) < +\infty\}$, it can be assumed that $\mathscr{W}(x) < +\infty$ for any $x \in \mathcal{X}$.*

This assumption implies that the dynamics returns to the region of the configuration space where the values of $\mathscr{W}$ are not too large. Typically, one chooses functions $\mathscr{W}$ which go to infinity at infinity, so that the Lyapunov condition ensures that the dynamics returns to a compact region around the origin. Let us also insist on the fact that we require $\mathscr{W} \geqslant 0$ (in order to be able to divide by $1 + \mathscr{W}$, see (3.10) below).

Assumption 3.2 (Minorization condition). *There exists a constant $\alpha \in (0, 1)$ and a probability measure λ such that*

$$\inf_{x \in \mathcal{C}} P(x, dy) \geqslant \alpha \lambda(dy),$$

where $\mathcal{C} = \{x \in \mathcal{X} \,|\, \mathscr{W}(x) \leqslant R\}$ for some $R > 2K/(1-\gamma)$, where γ, K are introduced in Assumption 3.1.

For compact position spaces, this condition is the standard Doeblin condition, which implies exponential convergence in total variation. Here, the condition ensures that there is a sufficiently strong coupling of the evolution in the region where the Lyapunov function is sufficiently small. It is in fact possible to replace Assumption 3.2 by weaker condition, see Remark 3.7 below.

add ref

We next introduce the functional space used to measure convergence, which we denote by $B^\infty_{\mathscr{W}}(\mathcal{X})$. It is the Banach space of measurable functions φ such that

$$\|\varphi\|_{B^\infty_{\mathscr{W}}} = \left\| \frac{\varphi}{1 + \mathscr{W}} \right\|_{B^\infty} < +\infty. \tag{3.10}$$

Theorem 3.1. *Suppose that Assumptions 3.1 and 3.2 hold. Then, P admits a unique invariant probability measure μ which satisfies*

$$\int_{\mathcal{X}} \mathscr{W}\, d\mu < +\infty. \tag{3.11}$$

Moreover, there exist $C > 0$ and $r \in (0, 1)$ such that, for any $\varphi \in B^\infty_{\mathscr{W}}(\mathcal{X})$,

$$\forall n \in \mathbb{N}, \qquad \left\| P^n \varphi - \int_{\mathcal{X}} \varphi\, d\mu \right\|_{B^\infty_{\mathscr{W}}} \leqslant C r^n \left\| \varphi - \int_{\mathcal{X}} \varphi\, d\mu \right\|_{B^\infty_{\mathscr{W}}}. \tag{3.12}$$

Let us now present a more compact reformulation of this inequality in terms of operators. Introduce

$$B^{\infty}_{\mathscr{W},0}(\mathcal{X}) = \left\{ \varphi \in B^{\infty}_{\mathscr{W}}(\mathcal{X}) \;\middle|\; \int_{\mathcal{X}} \varphi \, d\mu = 0 \right\}.$$

Then, (3.12) can be equivalently written as an inequality of bounded operators on $B^{\infty}_{\mathscr{W},0}(\mathcal{X})$:

$$\|P^n\|_{\mathcal{B}\left(B^{\infty}_{\mathscr{W},0}(\mathcal{X})\right)} \leqslant C r^n. \tag{3.13}$$

Remark 3.5 (sub-exponential convergence rates). *It is possible to weaken the Lyapunov condition* (4.55) *for instance as* $\mathcal{L}\mathscr{W} \leqslant \phi(\mathscr{W}) + b$*, where* ϕ *is a non-negative, non-decreasing, concave function such that* $\phi(x)/x \to 0$ *as* $x \to +\infty$*. In this case, algebraic rates of decay are typically obtained instead of exponential ones; see [73] or [52] for further details.*

Theorem 3.1 allows us to obtain bounds on the resolvent $\mathrm{Id} - P$, which will prove useful in various contexts (definition and quantitative estimates of the variance of Markov chains in Section 3.4, error estimates on transport coefficients in Section 8.4, etc).

Corollary 3.1. *If the assumptions of Theorem 3.12 are satisfied, the bounded operator* $\mathrm{Id} - P$ *is invertible on* $B^{\infty}_{\mathscr{W},0}(\mathcal{X})$*, and*

$$\left\| (\mathrm{Id} - P)^{-1} \right\|_{\mathcal{B}\left(B^{\infty}_{\mathscr{W},0}(\mathcal{X})\right)} \leqslant \frac{C}{1-r}.$$

Proof. The series with general term P^n is convergent in $\mathcal{B}\left(B^{\infty}_{\mathscr{W},0}(\mathcal{X})\right)$ in view of (3.13). In addition, a simple computation gives, for $N \in \mathbb{N}$ fixed,

$$(\mathrm{Id} - P) \sum_{n=0}^{N} P^n = \left(\sum_{n=0}^{N} P^n \right) (\mathrm{Id} - P) = \mathrm{Id} - P^{N+1},$$

so that, when $N \to +\infty$,

$$(\mathrm{Id} - P) \sum_{n=0}^{+\infty} P^n = \left(\sum_{n=0}^{+\infty} P^n \right) (\mathrm{Id} - P) = \mathrm{Id}.$$

This shows that $\mathrm{Id} - P$ is invertible and

$$(\mathrm{Id} - P)^{-1} = \sum_{n=0}^{+\infty} P^n. \tag{3.14}$$

Moreover,

$$\left\| (\mathrm{Id} - P)^{-1} \right\|_{\mathcal{B}\left(B^{\infty}_{\mathscr{W},0}(\mathcal{X})\right)} \leqslant \sum_{n=0}^{+\infty} \|P^n\|_{\mathcal{B}\left(B^{\infty}_{\mathscr{W},0}(\mathcal{X})\right)} \leqslant C \sum_{n=0}^{+\infty} r^n = \frac{C}{1-r},$$

which gives the desired bound. □

Remark 3.6. *In the subsequent chapters, we will in fact consider Lyapunov functions with values larger than 1, which correspond to* $\widetilde{\mathscr{W}} = 1 + \mathscr{W}$ *with the notation of this chapter. Assumption* (3.1) *should then be replaced by*

$$P\widetilde{\mathscr{W}} \leqslant \gamma \widetilde{\mathscr{W}} + \widetilde{K}, \qquad \widetilde{K} = K + 1 - \gamma,$$

while Assumption 3.2 should be checked in the set $\mathcal{C} = \left\{ x \in \mathcal{X} \;\middle|\; \widetilde{\mathscr{W}}(x) \leqslant R \right\}$ *for some* $R > 1 + 2(\widetilde{K} - 1 + \gamma)/(1-\gamma)$*.*

3.3.2 Proof of Theorem 3.1

The proof of Theorem 3.1, reproduced from [118], is divided into three steps:

(1) We first introduce a family of equivalent metrics on $B^\infty_{\mathscr{W}}(\mathcal{X})$, which allows to simplify some computations.
(2) We then prove a contraction principle in one of these equivalent metrics (see Proposition 3.3).
(3) We finally obtain the existence of the invariant measure by a fixed-point strategy (see Proposition 3.4).

We start by considering two families of equivalent norms, parameterized by $a > 0$. The first one corresponds, with the notation introduced above, to the norms $\|\cdot\|_{B^\infty_{a\mathscr{W}}}$:

$$\|\varphi\|_{B^\infty_{a\mathscr{W}}} = \left\| \frac{\varphi}{1 + a\mathscr{W}} \right\|_{B^\infty}.$$

The associated induced metric on probability measures is

$$\rho_a(\mu_1, \mu_2) = \sup_{\|\varphi\|_{B^\infty_{a\mathscr{W}}} \leqslant 1} \left\{ \int_{\mathcal{X}} \varphi(x) \Big(\mu_1(dx) - \mu_2(dx) \Big) \right\} = \int_{\mathcal{X}} (1 + a\mathscr{W}(x)) |\mu_1 - \mu_2|(dx). \tag{3.15}$$

The second one is induced by the following metrics on $\mathcal{X}$:

$$d_a(x, y) = \begin{cases} 0 & \text{if } x = y, \\ 2 + a\Big(\mathscr{W}(x) + \mathscr{W}(y) \Big) & \text{if } x \neq y. \end{cases}$$

Although this definition looks odd, it can be checked that d_a indeed is a distance. We then consider the Lipschitz seminorm on measurable functions induced by d_a:

$$\|\varphi\|_a = \sup_{x \neq y} \frac{|\varphi(x) - \varphi(y)|}{d_a(x, y)},$$

as well as the induced metric on probability measures:

$$d_a(\mu_1, \mu_2) = \sup_{\|\varphi\|_a \leqslant 1} \left\{ \int_{\mathcal{X}} \varphi(x) \Big(\mu_1(dx) - \mu_2(dx) \Big) \right\}. \tag{3.16}$$

In fact, as made precise in the following proposition, the two families of norms $\|\cdot\|_{B^\infty_{a\mathscr{W}}}$ and $\|\cdot\|_a$ are closely related, and induce the same distance on probability measures. The basic idea is that an element $\varphi \in B^\infty_{a\mathscr{W}}$ can be written as $\varphi = (1 + a\mathscr{W})\phi$ with $\phi \in B^\infty(\mathcal{X})$.

Proposition 3.2. *It holds* $\|\varphi\|_a = \min_{c \in \mathbb{R}} \|\varphi + c\|_{B^\infty_{a\mathscr{W}}}$. *Therefore,* $d_a(\mu_1, \mu_2) = \rho_a(\mu_1, \mu_2)$.

Proof. Since $|\varphi(x)| \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}} (1 + a\mathscr{W}(x))$ by definition of $\|\varphi\|_{B^\infty_{a\mathscr{W}}}$, it follows that, for any $x \neq y$,

$$\frac{|\varphi(x) - \varphi(y)|}{d_a(x, y)} \leqslant \frac{|\varphi(x)| + |\varphi(y)|}{2 + a\mathscr{W}(x) + a\mathscr{W}(y)} \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}.$$

Therefore, $\|\varphi\|_a \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}$. Now, replacing φ by $\varphi + c$, we obtain $\|\varphi\|_a = \|\varphi + c\|_a \leqslant \|\varphi + c\|_{B^\infty_{a\mathscr{W}}}$, from which we conclude that $\|\varphi\|_a \leqslant \inf_{c \in \mathbb{R}} \|\varphi + c\|_{B^\infty_{a\mathscr{W}}}$.

To prove the converse inequality, we choose φ such that $\|\varphi\|_a = 1$, and set

$$c_\varphi = \inf_{x \in \mathcal{X}} \big(1 + a\mathscr{W}(x) - \varphi(x) \big). \tag{3.17}$$

We can then prove the following facts.

- The constant c_φ is finite. Indeed, consider $y \in \mathcal{X}$ such that $\mathscr{W}(y) < +\infty$ and $|\varphi(y)| < +\infty$ (see Remark 3.4). Then,

$$|\varphi(x)| \leqslant |\varphi(y)| + |\varphi(x) - \varphi(y)| \leqslant |\varphi(y)| + 2 + a\Big(\mathscr{W}(x) + \mathscr{W}(y)\Big),$$

  so that

$$1 + a\mathscr{W}(x) - \varphi(x) \geqslant -1 - a\mathscr{W}(y) - |\varphi(y)|.$$

  This shows that c_φ is bounded from below and $|c_\varphi| < +\infty$.
- It holds $|\varphi(x) + c_\varphi| \leqslant 1 + a\mathscr{W}(x)$. Indeed, on the one hand,

$$\varphi(x) + c_\varphi \leqslant \varphi(x) + \Big(1 + a\mathscr{W}(x) - \varphi(x)\Big) = 1 + a\mathscr{W}(x),$$

  while on the other,

$$\begin{aligned}\varphi(x) + c_\varphi &= \inf_{y\in\mathcal{X}} \big(1 + a\mathscr{W}(y) + \varphi(x) - \varphi(y)\big)\\ &\geqslant \inf_{y\in\mathcal{X}} \big(1 + a\mathscr{W}(y) - d_a(x,y)\|\varphi\|_a\big)\\ &= \inf_{y\in\mathcal{X}} \big(1 + a\mathscr{W}(y) - d_a(x,y)\big) = -\big(1 + a\mathscr{W}(x)\big).\end{aligned}$$

In conclusion, $\|\varphi + c_\varphi\|_{B^\infty_{a\mathscr{W}}} \leqslant 1$ for the specific choice (3.17) when $\|\varphi\|_a = 1$. By homogeneity, for general measurable functions φ,

$$\inf_{c\in\mathbb{R}} \|\varphi + c\|_{B^\infty_{a\mathscr{W}}} \leqslant \|\varphi\|_a,$$

which allows to conclude to the equality. In fact, the infimum is a minimum since $\|\varphi+c\|_{B^\infty_{a\mathscr{W}}} \to +\infty$ as $c \to \pm\infty$

To prove the equality of the induced metrics d_a and ρ_a on the space of probability measures, we first note that

$$\{\varphi \text{ measurable} : \|\varphi\|_a \leqslant 1\} = \big\{\phi + c \,\big|\, \phi \text{ measurable}, \|\phi\|_{B^\infty_{a\mathscr{W}}} \leqslant 1\big\}.$$

It is indeed clear that the set on the right hand side of the previous equality is included in the set on the left hand side. The converse inequality follows from the fact that, for any measurable function φ such that $\|\varphi\|_a \leqslant 1$, there exists $c \in \mathbb{R}$ such that $\|\varphi\|_a = \|\varphi + c\|_{B^\infty_{a\mathscr{W}}} \leqslant 1$, which proves that φ indeed belongs to the set on the right hand side of the above equality. Therefore, the functions belonging to the sets $\{\varphi \text{ measurable} : \|\varphi\|_a \leqslant 1\}$ and $\{\varphi \text{ measurable} : \|\varphi\|_{B^\infty_{a\mathscr{W}}} \leqslant 1\}$ differ only by additive constants, which are unimportant in the integrals appearing on the right-hand sides of the definitions (3.15) and (3.16), so that the induced metrics d_a and ρ_a on the space of probability measures coincide. □

Proposition 3.3. *Suppose that Assumptions 3.1 and 3.2 hold. Then, there exists $r \in (0,1)$ and $a > 0$ such that*

$$\|P\varphi\|_a \leqslant r\|\varphi\|_a.$$

A careful inspection of the proof also allows to obtain quantitative bounds on r in terms of the various constants appearing in Assumptions 3.1 and 3.2. Note that the above inequality can be iterated to write $\|P^n\varphi\|_a \leqslant r^n\|\varphi\|_a$. In order to conclude the proof of the theorem, we will however need a final step: prove the existence of some invariant probability measure.

Proof. The result follows if we can show that there exist $a > 0$ and $r \in (0,1)$ such that

$$\forall x \neq y, \qquad |P\varphi(x) - P\varphi(y)| \leqslant r\, d_a(x,y)\|\varphi\|_a.$$

It is sufficient to prove the latter inequality with $\|\varphi\|_a$ replaced by $\|\varphi\|_{B^\infty_{a\mathscr{W}}}$ on the right hand side, and then consider the infimum over c of functions of the form $\varphi + c$ (as this does not change the left hand side). We distinguish two cases, the value of a being determined by the second condition.

(i) If $\mathscr{W}(x)+\mathscr{W}(y) \geqslant R$ (where R is defined in Assumption 3.2): in this case, x, y are typically far away from the origin and we use the Lyapunov condition to obtain some average decrease. More precisely, introduce $\gamma_0 = \gamma + 2K/R < 1$ and, for some $a \in (0,1)$, consider $\gamma_1 = (2+aR\gamma_0)/(2+aR) \in (\gamma_0, 1)$. With these choices, upon applying P to the inequality $\varphi(x) \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}(1+a\mathscr{W}(x))$, we obtain

$$\begin{aligned}|P\varphi(x) - P\varphi(y)| &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\big(2 + aP\mathscr{W}(x) + aP\mathscr{W}(y)\big)\\ &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\big(2 + \gamma a\mathscr{W}(x) + \gamma a\mathscr{W}(y) + 2aK\big)\\ &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\big(2 + \gamma_0 a\mathscr{W}(x) + \gamma_0 a\mathscr{W}(y)\big)\\ &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\gamma_1\big(2 + a\mathscr{W}(x) + a\mathscr{W}(y)\big) = \|\varphi\|_{B^\infty_{a\mathscr{W}}}\gamma_1 d_a(x,y).\end{aligned}$$

The last inequality is true as soon as $2 + a\gamma_0 R \leqslant \gamma_1(2+aR)$, which motivates the choice of γ_1.

(ii) If $\mathscr{W}(x)+\mathscr{W}(y) \leqslant R$: in this case, both x and y belong to $\mathcal{C}$, and we use the coupling condition given by the minoration property to obtain some average decrease. For $z \in \mathcal{C}$, consider the transition kernel

$$\widetilde{P}(z, dz') = \frac{1}{1-\alpha}\Big(P(z,dz') - \alpha\lambda(dz')\Big),$$

which is indeed positive and sums up to 1. Then,

$$P\varphi(x) = (1-\alpha)\widetilde{P}\varphi(x) + \alpha\int_{\mathcal{X}} \varphi\, d\lambda, \tag{3.18}$$

so that, upon applying $\widetilde{P}$ to the inequality $\varphi(x) \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}(1+a\mathscr{W}(x))$ and using $\widetilde{P}\mathscr{W}(z) \leqslant P\mathscr{W}(z)/(1-\alpha)$ for $z \in \mathcal{C}$,

$$\begin{aligned}|P\varphi(x) - P\varphi(y)| &= (1-\alpha)\Big|\widetilde{P}\varphi(x) - \widetilde{P}\varphi(y)\Big|\\ &\leqslant (1-\alpha)\|\varphi\|_{B^\infty_{a\mathscr{W}}}\Big(2 + a\widetilde{P}\mathscr{W}(x) + a\widetilde{P}\mathscr{W}(y)\Big)\\ &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\big(2(1-\alpha) + aP\mathscr{W}(x) + aP\mathscr{W}(y)\big)\\ &\leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\big(2(1-\alpha) + a\gamma[\mathscr{W}(x) + \mathscr{W}(y)] + 2aK\big).\end{aligned} \tag{3.19}$$

We now choose a sufficiently small so that $\gamma_2 = \min(1-\alpha+aK, \gamma) < 1$. Then

$$|P\varphi(x) - P\varphi(y)| \leqslant \|\varphi\|_{B^\infty_{a\mathscr{W}}}\gamma_2 d_a(x,y).$$

The proof is concluded by setting $r = \max(\gamma_1, \gamma_2)$. □

Remark 3.7 (Weaker minorization conditions). *As discussed in [116], it is possible to consider a more general assumption than the minorization condition stated in Assumption 3.2; namely: There exists a constant $\alpha \in (0,1)$ such that, for all $(x,y) \in \mathcal{X}^2$ with $\mathscr{W}(x)+\mathscr{W}(y) \leqslant R$ (for some $R > 2K/(1-\gamma)$), it holds*

$$\|P(x,\cdot) - P(y,\cdot)\|_{\mathrm{TV}} := \sup_{\|\varphi\|_{B^\infty} \leqslant 1} |(P\varphi)(x) - (P\varphi)(y)| \leqslant 2(1-\alpha).$$

It is clear from (3.18) *that Assumption 3.2 implies the latter condition. The only part of the proof which changes is the coupling estimate* (3.19) *in item (ii), for which one proceeds as follows. Consider φ such that $\|\varphi\|_{B^\infty_{a\mathscr{W}}} \leqslant 1$ and decompose it as $\varphi = \varphi_1 + \varphi_2$ with $|\varphi_1(z)| \leqslant 1$ and $|\varphi_2(z)| \leqslant a\mathscr{W}(z)$ for all $z \in \mathcal{X}$. Then,*

$$\begin{aligned}|P\varphi(x) - P\varphi(y)| &\leqslant |P\varphi_1(x) - P\varphi_1(y)| + |P\varphi_2(x) - P\varphi_2(y)|\\ &\leqslant 2(1-\alpha) + |P\varphi_2(x)| + |P\varphi_2(y)|\\ &\leqslant 2(1-\alpha) + a(P\mathscr{W}(x) + P\mathscr{W}(y))\\ &\leqslant 2(1-\alpha) + \gamma a(\mathscr{W}(x) + \mathscr{W}(y)) + 2aK,\end{aligned}$$

which leads to (3.19) *upon considering $\varphi/\|\varphi\|_{B^\infty_{\mathscr{W}}}$.*

A direct corollary of Proposition 3.3 is the following contraction result.

Corollary 3.2. *Suppose that Assumptions 3.1 and 3.2 hold. Then, there exist* $r \in (0,1)$ *and* $a > 0$ *such that, for any* $\mu_1, \mu_2 \in \mathscr{P}(\mathcal{X})$,

$$\rho_a(P\mu_1, P\mu_2) \leqslant r\rho_a(\mu_1, \mu_2).$$

Proof. Note first that, in view of (3.9) and (3.16), Proposition 3.3 implies that $d_a(P\mu_1, P\mu_2) \leqslant r\, d_a(\mu_1, \mu_2)$. The conclusion then follows from the equality of metrics $d_a = \rho_a$ given by Proposition 3.2. □

Note that this contraction principle immediately gives the uniqueness of the invariant measure provided it exits. It in fact also allows to obtain the existence of the invariant measure.

Proposition 3.4. *Suppose that Assumptions 3.1 and 3.2 hold. Then, there exists a unique invariant probability measure* μ *on* $\mathcal{X}$*, which moreover satisfies*

$$\int_{\mathcal{X}} \mathscr{W}\, d\mu \leqslant \frac{K}{1-\gamma} < +\infty.$$

Proof. Consider any probability distribution μ_0 on $\mathcal{X}$ (for instance δ_{x_0} for a given element $x_0 \in \mathcal{X}$), and define $\mu_n = P^n\mu_0$. Then, by Corollary 3.2, there exist $r \in (0,1)$ and $a > 0$ such that $\rho_a(\mu_{n+1}, \mu_n) \leqslant r^n \rho_a(\mu_1, \mu_0)$. This shows that (μ_n) is a Cauchy sequence for the metric ρ_a. Now, the space of probability measures integrating $\mathscr{W}$ is complete for ρ_a. This shows that there exists a probability measure μ_∞ such that $\mu \to \mu_\infty$ for the metric ρ_a.

add a ref or a proof? (see comments in the tex)

The invariance of μ_∞, namely $P\mu_\infty = \mu_\infty$, is obtained by passing to the limit in the inequality $\rho_a(\mu_{n+1}, P\mu_\infty) \leqslant r\rho_a(\mu_n, \mu_\infty)$, which gives $\rho_a(\mu_\infty, P\mu_\infty) = 0$. The uniqueness is easy to obtain: if $\mu_{\infty,1}$ and $\mu_{\infty,2}$ are invariant, then $\rho_a(\mu_{\infty,1}, \mu_{\infty,2}) = \rho_a(P\mu_{\infty,1}, P\mu_{\infty,2}) \leqslant r\rho_a(\mu_{\infty,1}, \mu_{\infty,2})$, which shows that $\rho_a(\mu_{\infty,1}, \mu_{\infty,2}) = 0$ and so $\mu_{\infty,1} = \mu_{\infty,2}$.

Bounds on the integral of $\mathscr{W}$ with respect to μ are deduced by integrating both sides of the Lyapunov condition with respect to μ_∞:

$$\int_{\mathcal{X}} \mathscr{W}\, d\mu_\infty = \int_{\mathcal{X}} P\mathscr{W}\, d\mu_\infty \leqslant \gamma \int_{\mathcal{X}} \mathscr{W}\, d\mu_\infty + K,$$

which gives the desired upper bound. □

Theorem 3.1 now follows by applying the contraction principle of Corollary 3.2 with μ_1 replaced by any initial distribution δ_{x_0} for $x_0 \in \mathcal{X}$, and with μ_2 replaced by the invariant measure μ given by Proposition 3.4. More precisely, for a given initial condition δ_{x_0}, it holds $\rho_a(P^n\delta_{x_0}, \mu) \leqslant r^n\rho_a(\delta_{x_0}, \mu)$. For a given function $\varphi \in B^\infty_{a\mathscr{W}}(\mathcal{X})$, this implies, by definition of ρ_a,

$$\begin{aligned}\left|P^n\varphi(x_0) - \int_{\mathcal{X}} \varphi\, d\mu\right| &= \left|P^n\left(\varphi - \int_{\mathcal{X}} \varphi\, d\mu\right)(x_0)\right| \leqslant \rho_a(P^n\delta_{x_0}, \mu)\left\|\varphi - \int_{\mathcal{X}} \varphi\, d\mu\right\|_{B^\infty_{a\mathscr{W}}} \\ &\leqslant r^n\rho_a(\delta_{x_0}, \mu)\left\|\varphi - \int_{\mathcal{X}} \varphi\, d\mu\right\|_{B^\infty_{a\mathscr{W}}}.\end{aligned}$$

Now, there exists a constant $C \in \mathbb{R}_+$ (which depends on a) such that, using the definition of $B^\infty_{a\mathscr{W}}(\mathcal{X})$,

$$\begin{aligned}\int_{\mathcal{X}} \phi(x)(\delta_{x_0}(dx) - \mu(dx)) = \phi(x_0) - \int_{\mathcal{X}} \phi\, d\mu &\leqslant \|\phi\|_{B^\infty_{a\mathscr{W}}}\left(2 + a\mathscr{W}(x_0) + a\int_{\mathcal{X}} \mathscr{W}\, d\mu\right) \\ &\leqslant C\|\phi\|_{B^\infty_{\mathscr{W}}}\big(1 + \mathscr{W}(x_0)\big).\end{aligned}$$

Therefore, $\rho_a(\delta_{x_0}, \mu) \leqslant C(1 + \mathscr{W}(x_0))$, and finally

$$\left|P^n\varphi(x_0) - \int_{\mathcal{X}} \varphi\, d\mu\right| \leqslant Cr^n\big(1+\mathscr{W}(x_0)\big)\left\|\varphi - \int_{\mathcal{X}} \varphi\, d\mu\right\|_{B^\infty_{a\mathscr{W}}} \leqslant \widetilde{C}r^n\big(1+\mathscr{W}(x_0)\big)\left\|\varphi - \int_{\mathcal{X}} \varphi\, d\mu\right\|_{B^\infty_{\mathscr{W}}},$$

which leads to (3.12).

Remark 3.8. *Note that the prefactors $C, \widetilde{C} \geqslant 1$ in the above estimates arise from some norm equivalence. We will encounter again such prefactors in the theory of hypocoercivity, see Sections 5.5.1 and 5.4.3.*

3.3.3 Application to the Metropolis–Hastings algorithm

A simple example to apply the above framework is the following. Consider the canonical measure (3.5) on a compact state space $\mathcal{D}$, for a smooth potential energy function V, and a Metropolis–Hastings algorithm with a symmetric proposal kernel with a density with respect to the Lebesgue measure such that $T(q, q') \geqslant \eta > 0$ for any $q, q' \in \mathcal{D}$. Since the potential V is bounded from above and from below, there exists $m, M > 0$ such that

$$m \leqslant \min_{q \in \mathcal{D}} \mathrm{e}^{-\beta V(q)} \leqslant \max_{q \in \mathcal{D}} \mathrm{e}^{-\beta V(q)} \leqslant M.$$

Therefore, since the acceptance rate is bounded from below by m/M, (3.7) implies that

$$P(q, dq') \geqslant \frac{m\eta}{M}\, dq'.$$

This immediately gives the minorization condition in Assumption 3.2 with $\alpha = m\eta|\mathcal{D}|/M$ and $\lambda(dq) = |\mathcal{D}|^{-1}\, dq$. Since the space is compact, the Lyapunov function can be chosen to be $\mathscr{W} = 0$ in Assumption 3.1. We can then conclude to the exponential convergence in B^∞: there exist $C > 0$ and $r \in (0, 1)$ such that, for any $\varphi \in B^\infty(\mathcal{D})$,

$$\left\| P^n \varphi - \int_{\mathcal{D}} \varphi\, d\nu \right\|_{B^\infty} \leqslant C r^n \left\| \varphi - \int_{\mathcal{D}} \varphi\, d\nu \right\|_{B^\infty}.$$

3.4 Rate of convergence of ergodic averages

For $\varphi \in L^1(\nu)$, the almost-sure convergence of the sample averages

$$\widehat{\varphi}_{N_{\mathrm{iter}}} = \frac{1}{N_{\mathrm{iter}}} \sum_{n=0}^{N_{\mathrm{iter}}-1} \varphi(q^n) \xrightarrow[N_{\mathrm{iter}} \to +\infty]{} \int_{\mathcal{D}} \varphi\, d\nu$$

is given by Proposition 3.1. A natural question is to quantify the statistical error. This can be performed using a Central Limit Theorem for Markov chains. Proving such a result requires deep tools from probability theory such as a Central Limit Theorem for discrete martingales. We will therefore only motivate here the expression of the asymptotic variance for a certain class of observables (smaller than $L^2(\nu)$), using the operator bounds derived in the previous section. In order to state the result, we introduce the operator Π defined for $\varphi \in L^1(\nu)$ as

$$\Pi\varphi = \varphi - \int_{\mathcal{D}} \varphi\, d\nu.$$

Proposition 3.5. *Suppose that Assumptions 3.1 and 3.2 hold for a Lyapunov function $\mathscr{W} \in L^2(\nu)$, and denote by ν the unique invariant measure of the Markov chain associated with P. Fix $\varphi \in B^\infty_{\mathscr{W}}(\mathcal{X})$. Then, the asymptotic variance of the random variable $\widehat{\varphi}_{N_{\mathrm{iter}}}$ is given by*

$$\begin{aligned} \lim_{N_{\mathrm{iter}} \to +\infty} N_{\mathrm{iter}} \mathrm{Var}_\nu\left(\widehat{\varphi}_{N_{\mathrm{iter}}}\right) &= \mathbb{E}_\nu\left(\Pi\varphi^2\right) + 2\sum_{n=1}^{+\infty} \mathbb{E}_\nu\left[\Pi\varphi(q^n)\Pi\varphi(q^0)\right] \\ &= \int_{\mathcal{D}} \Pi\varphi\left[\left(2(\mathrm{Id} - P)^{-1} - \mathrm{Id}\right)\Pi\varphi\right] d\nu, \end{aligned} \tag{3.20}$$

where expectations are with respect to initial conditions $q^0 \sim \nu$ and over all realizations of the Markov chain.

Note that upper bounds on (3.20) can be obtained by Corollary 3.1, as follows:

$$\left| \lim_{N_{\mathrm{iter}} \to +\infty} N_{\mathrm{iter}} \mathrm{Var}_\nu \left(\widehat{\varphi}_{N_{\mathrm{iter}}} \right) \right| \leqslant \left(1 + \frac{2C}{r-1} \right) \|\mathscr{W}\|^2_{L^2(\nu)} \|\varphi\|^2_{B^\infty_{\mathscr{W}}}.$$

In fact, it is possible to generalize the above result to any initial distribution since the law of the Markov chain converges exponentially fast to the invariant measure ν under our assumptions. For a Central Limit Theorem to hold, it suffices that the solution Φ to the Poisson equation

$$(\mathrm{Id} - P)\Phi = \Pi\varphi \tag{3.21}$$

belongs to $L^2(\nu)$; see [196, Theorem 17.4.4]. The proof is based on a Central Limit Theorem for discrete martingales. In view of Corollary 3.1, a sufficient condition for $\Phi \in L^2(\nu)$ is that $\varphi \in B^\infty_{\mathscr{W}}(\mathcal{X})$ and $\mathscr{W} \in L^2(\pi)$. The condition $\mathscr{W} \in L^2(\nu)$ can be proved by showing that a Lyapunov condition holds for $\mathscr{W}^2$ (*i.e.* Assumption 3.1 holds with $\mathscr{W}$ replaced by $\mathscr{W}^2$).

Proof. Note that when $q^0 \sim \nu$, it holds $q^n \sim \nu$ for all $n \geqslant 1$ and the following stationarity property holds:

$$\forall n, m \geqslant 0, \qquad \mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^m) \right] = \mathbb{E}_\nu \left[\Pi\varphi(q^{|n-m|}) \Pi\varphi(q^0) \right].$$

Then,

$$\begin{aligned}
N_{\mathrm{iter}} \, \mathrm{Var}_\nu \left(\widehat{\varphi}_{N_{\mathrm{iter}}} \right) &= N_{\mathrm{iter}} \, \mathbb{E}_\nu \left[\left(\Pi\widehat{\varphi}_{N_{\mathrm{iter}}} \right)^2 \right] \\
&= \frac{1}{N_{\mathrm{iter}}} \sum_{n,m=0}^{N_{\mathrm{iter}}-1} \mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^m) \right] \\
&= \frac{1}{N_{\mathrm{iter}}} \sum_{n=0}^{N_{\mathrm{iter}}-1} \mathbb{E}_\nu \left[\left(\Pi\varphi(q^n) \right)^2 \right] + \frac{2}{N_{\mathrm{iter}}} \sum_{0 \leqslant m < n \leqslant N_{\mathrm{iter}}-1} \mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^m) \right] \\
&= \mathbb{E}_\nu \left[\left(\Pi\varphi \right)^2 \right] + 2 \sum_{1 \leqslant n \leqslant N_{\mathrm{iter}}-1} \left(1 - \frac{n}{N_{\mathrm{iter}}} \right) \mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^0) \right],
\end{aligned}$$

where we used the stationary property in the last step. Note next that

$$\mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^0) \right] = \int_{\mathcal{D}} (\Pi\varphi)(P^n \Pi\varphi) \, \mathrm{d}\nu.$$

Since, by (3.13),

$$|\Pi\varphi(x)(P^n \Pi\varphi)(q)| \leqslant C \|\varphi\|^2_{B^\infty_{\mathscr{W}}} r^n (1 + \mathscr{W}(q))^2,$$

a dominated convergence argument shows that

$$N_{\mathrm{iter}} \mathrm{Var}_\nu (\widehat{\varphi}_{N_{\mathrm{iter}}}) \xrightarrow[N_{\mathrm{iter}} \to +\infty]{} \sigma^2_\varphi,$$

with

$$\begin{aligned}
\sigma^2_\varphi &= \mathbb{E}_\nu \left[(\Pi\varphi)^2 \right] + 2 \sum_{n=1}^{+\infty} \mathbb{E}_\nu \left[(\Pi\varphi)(q^n)(\Pi\varphi)(q^0) \right] = \int_{\mathcal{D}} (\Pi\varphi) \left[\mathrm{Id} + 2 \sum_{n=1}^{+\infty} P^n \right] \Pi\varphi \, \mathrm{d}\nu \\
&= \int_{\mathcal{D}} (\Pi\varphi) [2(\mathrm{Id} - P)^{-1} - \mathrm{Id}] \Pi\varphi \, \mathrm{d}\nu.
\end{aligned} \tag{3.22}$$

where we used (3.14) in the last step. □

It is instructive at this stage to compare the asymptotic variance (3.20) to the one obtained by averages of independent and identically distributed (i.i.d.) random variables $(q^n)_{n \geqslant 1}$ with common law ν. When $\varphi \in L^2(\nu)$, a Central Limit Theorem holds true for the estimator

$$\widehat{\varphi}^{\mathrm{iid}}_{N_{\mathrm{iter}}} = \frac{1}{N_{\mathrm{iter}}} \sum_{n=1}^{N_{\mathrm{iter}}} \varphi(q^n),$$

whose asymptotic variance is

$$\sigma^2_{\varphi,\mathrm{iid}} = \lim_{N_{\mathrm{iter}} \to +\infty} N_{\mathrm{iter}} \mathrm{Var}_\nu \left[\left(\widehat{\Pi\varphi}^{\mathrm{iid}}_{N_{\mathrm{iter}}} \right)^2 \right] = \int_{\mathcal{D}} (\Pi\varphi)^2 d\nu.$$

We write the asymptotic variance (3.20) for time averages estimates with ergodic SDEs in terms of the reference variance $\sigma^2_{\varphi,\mathrm{iid}}$ as

$$\sigma^2_\varphi = N_{\mathrm{corr},\varphi} \sigma^2_{\varphi,\mathrm{iid}}, \tag{3.23}$$

and interpret $N_{\mathrm{corr},\varphi}$ as some number of correlation steps. What is meant by that is that the mean-square error of the estimator $\widehat{\varphi}_{N_{\mathrm{iter}}}$ asymptotically behaves as $\sigma^2_\varphi / N_{\mathrm{iter}} = \sigma^2_{\varphi,\mathrm{iid}} N_{\mathrm{corr},\varphi} / N_{\mathrm{iter}}$, so that in order to have an estimator of the same quality as the one based on N_{iter} i.i.d. samples, $N_{\mathrm{corr},\varphi} N_{\mathrm{iter}}$ steps of the Markov chain should be performed.

add references on estimation of asymptotic variance: e.g. [94] and (references in) [178, Section 2.3.1.3]

4

The overdamped Langevin dynamics

We discuss in this lecture the overdamped Langevin dynamics presented in Section 1.4.2. We start by giving in Section 4.1 some mathematical properties of the dynamics, as well as possible extensions. We next discuss the convergence of time averages along realizations of the dynamics (see Section 4.2). We finally present in Section 4.3 various approaches to conclude to the longtime convergence of the law of the process to its invariant measure.

4.1 Description of the dynamics and mathematical properties

Overdamped processes are stochastic dynamics on the system positions $q \in \mathcal{D}$ only. We first describe in Section 4.1.1 the simplest version of overdamped Langevin dynamics, with a constant diffusion coefficient and a gradient drift. Possible extensions are reviewed in Section 4.1.2. We assume in all this lecture that the potential energy function V is smooth.

4.1.1 Simple overdamped Langevin dynamics

The simplest version of overdamped Langevin dynamics is the following stochastic differential equation:

$$dq_t = -\nabla V(q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t, \tag{4.1}$$

where $t \mapsto W_t$ is a standard D-dimensional Wiener process. As will be made clear below, the unique invariant probability measure for the process (4.1) is the canonical measure (1.19), which we recall here for convenience:

$$\nu(dq) = Z_\nu^{-1} \exp(-\beta V(q))\,dq. \tag{4.2}$$

Below: take out the basic material on SDEs already discussed in lectures from T.

Generator of the dynamics

The generator $\mathcal{L}$ associated with (4.1) acts on functions of the variable q. For a smooth function $\varphi \in C^\infty(\mathcal{D})$,

$$\mathcal{L}\varphi = \frac{1}{\beta}\Delta\varphi - \nabla V \cdot \nabla\varphi = \frac{\mathrm{e}^{\beta V}}{\beta}\mathrm{div}\left(\mathrm{e}^{-\beta V}\nabla\varphi\right). \tag{4.3}$$

The operator $\mathcal{L}$ can be considered as an unbounded operator for instance on the Banach space $C^0(\mathcal{D})$ with domain $C^2(\mathcal{D})$; or on the Hilbert space $L^2(\nu)$ with domain $H^2(\nu)$ under appropriate growth conditions on the potential energy function when the configuration space $\mathcal{D}$ is unbounded. For instance, when $\varphi \in H^2(\nu)$, the function $\nabla V^T \nabla\varphi \in L^2(\nu)$ provided there exist $C > 0$ such that

$$\forall q \in \mathcal{D}, \qquad \left|\nabla^2 V(q)\right| \leqslant C\left(1 + |\nabla V(q)|\right),$$

see [274, Lemma A.24]. This condition on V is satisfied for instance for potentials which grow polynomially at infinity. In fact, we can rewrite the generator when considered on $L^2(\nu)$ as

$$\mathcal{L} = -\frac{1}{\beta}\sum_{i=1}^{D} \partial_{q_i}^* \partial_{q_i}, \tag{4.4}$$

where adjoints are taken on $L^2(\nu)$. More precisely, for any smooth and compactly supported functions ϕ, φ and a closed operator $\mathcal{A}$,

$$\int_{\mathcal{D}} (\mathcal{A}^*\varphi)\,\phi\,d\nu = \int_{\mathcal{D}} \varphi(\mathcal{A}\phi)\,d\nu.$$

A simple computation shows that $\partial_{q_i}^* = -\partial_{q_i} + \beta\partial_{q_i}V$, which leads to (4.4) in view of (4.3).

Evolution of time averages

A first important property of the generator $\mathcal{L}$ is that it encodes the time evolution through the semigroup $\mathrm{e}^{t\mathcal{L}}$ (which will be given a rigorous meaning in Section 4.3). This semigroup is formally defined as

$$\left(\mathrm{e}^{t\mathcal{L}}\varphi\right)(q_0) = \mathbb{E}^{q_0}\left[\varphi(q_t)\right]. \tag{4.5}$$

To prove this equality, we consider a fixed time $t > 0$ and a C^∞ function φ with compact support, and introduce the solution to the following parabolic equation:

$$\partial_t \Phi = \mathcal{L}\Phi, \qquad \Phi(0) = \varphi.$$

Note that the solution to this equation can be denoted by $\Phi(t) = \mathrm{e}^{t\mathcal{L}}\varphi$ using notation from semigroup theory [216]. Then, using Itô's formula, it holds, for $s \in [0,t]$,

formal computations, cf. local martingales need estimates on $\nabla\Phi$...

$$d\left[\Phi(t-s,q_s)\right] = (-\partial_t + \mathcal{L})\Phi(t-s,q_s)\,ds + \sqrt{\frac{2}{\beta}}\nabla\Phi(t-s,q_s)\cdot dW_s,$$

so that, taking expectations,

$$\mathbb{E}^{q_0}(\varphi(q_t)) - \Phi(t,q_0) = \sqrt{\frac{2}{\beta}}\mathbb{E}^{q_0}\left[\int_0^t \nabla\Phi(t-s,q_s)\cdot dW_s\right] = 0,$$

which gives (4.5).

Evolution of the law of the process

The evolution of the law $\psi(t,q)$ of the process q_t is governed by the Fokker–Planck equation

$$\partial_t \psi = \mathcal{L}^\dagger \psi, \qquad \psi(0,\cdot) = \psi_0, \tag{4.6}$$

where ψ_0 is the distribution of initial conditions, and

$$\mathcal{L}^\dagger = \frac{1}{\beta}\Delta + \operatorname{div}(\nabla V \cdot)$$

is the adjoint of $\mathcal{L}$ on $L^2(\mathcal{D})$. We write ψ_0 for the initial distribution with some abuse of notation, but we emphasize that this initial condition is in general a probability measure, which is not necessarily absolutely continuous with respect to the Lebesgue measure (think of a Dirac mass centered at a given position q_0). Equation 4.6 should then be understood in the sense of distributions. By parabolic regularity, the equality (4.6) actually holds in the classical sense for $t > 0$. For rigorous results concerning the existence and uniqueness of a solution to (4.6) and the link with stochastic differential equations, see for example to [98].

To formally derive (4.6), we fix a test function $\varphi \in C^\infty(\mathcal{D})$ with compact support. For $h > 0$, and denoting by $\mathbb{E}_{\psi_0}$ the expectation taken over all realizations of (4.1) with initial conditions q_0 distributed according to ψ_0, we obtain from Iô's calculus on $d\varphi(q_t)$ that

$$\frac{\mathbb{E}_{\psi_0}[\varphi(q_{t+h})] - \mathbb{E}_{\psi_0}[\varphi(q_t)]}{h} = \frac{1}{h}\int_t^{t+h} \mathbb{E}_{\psi_0}[(\mathcal{L}\varphi)(q_s)]\, ds,$$

which can be restated as

$$\frac{1}{h}\left(\int_{\mathcal{D}} \varphi(q)\psi(t+h,q)\, dq - \int_{\mathcal{D}} \varphi(q)\psi(t,q)\, dq\right) = \frac{1}{h}\int_t^{t+h}\int_{\mathcal{D}} (\mathcal{L}\varphi)(q)\psi(s,q)\, dq\, ds.$$

This leads, in the limit $h \to 0$, to the following equation:

$$\frac{d}{dt} E_{\psi_0}(\varphi(q_t)) = \mathbb{E}_{\psi_0}\big[(\mathcal{L}\varphi)(q_t)\big],$$

or, equivalently,

$$\frac{d}{dt}\left(\int_{\mathcal{D}} \varphi(q)\psi(t,q)\, dq\right) = \int_{\mathcal{D}} (\mathcal{L}\varphi)(q)\psi(t,q)\, dq,$$

which is indeed the weak formulation (to be understood in the distributional sense) of (4.6).

Reversibility and self-adjointness of $\mathcal{L}$

The process (4.1) is reversible with respect to the canonical probability distribution (4.2). In probabilistic terms, this means that, for $q_0 \sim \nu$ and $t > 0$, the law of the trajectories $(q_s)_{0\leqslant s\leqslant t}$ is the same as the law of the trajectories $(q_{t-s})_{0\leqslant s\leqslant t}$ (the arrow of time cannot be read off the trajectory). From a functional analytical viewpoint, this means that the generator is self-adjoint on the Hilbert space

$$L^2(\nu) = \left\{\varphi \text{ measurable} \,\middle|\, \int_{\mathcal{D}} |\varphi|^2\, d\nu < +\infty\right\},$$

equipped with the scalar product[1]

$$\langle \varphi_1, \varphi_2 \rangle_{L^2(\nu)} = \int_{\mathcal{D}} \varphi_1\, \varphi_2\, d\nu.$$

[1] To keep the notation simple, we restrict ourselves to real-valued scalar products, although, for spectral theory, complex-valued scalar products should be considered. However, the extension to the latter case is straightforward.

To prove this statement, note first that the operator $\mathcal{L}$ is symmetric. This can be seen from (4.4), or by a direct proof based on the Dirichlet form associated with $\mathcal{L}$: for any test functions φ_1 and φ_2 (for instance C^∞ with compact support),

$$\begin{aligned}\langle \mathcal{L}\varphi_1, \varphi_2 \rangle_{L^2(\nu)} &= \int_{\mathcal{D}} \varphi_1 \, \mathcal{L}(\varphi_2) \, \frac{\mathrm{e}^{-\beta V}}{Z_\nu} = \frac{1}{\beta Z_\nu} \int_{\mathcal{D}} \varphi_1 \, \mathrm{div}\left(\mathrm{e}^{-\beta V} \nabla \varphi_2\right) \\ &= -\frac{1}{\beta} \int_{\mathcal{D}} \nabla \varphi_1^T \nabla \varphi_2 \, \frac{\mathrm{e}^{-\beta V}}{Z_\nu} = -\frac{1}{\beta} \left\langle \nabla \varphi_1, \nabla \varphi_2 \right\rangle_{L^2(\nu)}.\end{aligned} \tag{4.7}$$

The latter expression is obviously symmetric in φ_1, φ_2. In order to conclude that $\mathcal{L}$ is self-adjoint on $L^2(\nu)$, domain issues have to be considered; see *e.g.* [20].

A consequence of reversibility is that the canonical measure is invariant: the choice $\varphi_1 = 1$ indeed in the previous equality leads indeed to

$$\int_{\mathcal{D}} \mathcal{L}\varphi \, d\nu = 0 \tag{4.8}$$

for all smooth functions φ with compact support. In particular, $\mathcal{L}^\dagger \nu = 0$, which proves that the canonical measure ν recalled in (4.2) is invariant.

4.1.2 Extension of simple overdamped Langevin dynamics

We first present how to formulate overdamped Langevin dynamics in the case of multiplicative noise, and then how to incorporate non gradient forces provided these forces have some vanishing divergence. Of course, it is possible to combine both extensions.

Dynamics with multiplicative noise

In some situations, it is relevant to consider the case when the Brownian motion in (4.1) is multiplied by some diffusion matrix $B \in \mathbb{R}^{D \times D}$, taken to be symmetric. In this case, the drift has to be modified accordingly in order to ensure the invariance of the canonical measure. More precisely, introduce

$$A(q) = B(q)B(q)^T,$$

and consider

$$dq_t = \left(-A(q_t)\nabla V(q_t) + \frac{1}{\beta}\mathrm{div} A(q_t)\right) dt + \sqrt{\frac{2}{\beta}}\, B(q_t)\, dW_t. \tag{4.9}$$

The divergence of the matrix valued function A is the vector field with components $\mathrm{div}A_i = \sum_{j=1}^D \partial_{q_j} A_{ij}$, where A_i is the ith line of the matrix A (or column, which is the same since A is symmetric). The generator of the dynamics (4.9) acts on smooth functions φ as

$$\mathcal{L}\varphi = \left(-A\nabla V + \frac{1}{\beta}\mathrm{div}A\right)^T \nabla\varphi + \frac{1}{\beta}\, A : \nabla^2\varphi = -\frac{1}{\beta}\nabla^* A \nabla\varphi = -\frac{1}{\beta}\sum_{i,j=1}^D \partial_{q_j}^* A_{ij} \partial_{q_i}\varphi, \tag{4.10}$$

where adjoints are still considered on $L^2(\nu)$, and the contraction of two matrices $M, \widetilde{M} \in \mathbb{R}^{D\times D}$ is defined as

$$M : \widetilde{M} = \mathrm{Tr}\left(M^T \widetilde{M}\right) = \sum_{i,j=1}^D M_{i,j}\widetilde{M}_{i,j}.$$

The latter rewriting immediately implies that the generator is symmetric on $L^2(\nu)$, and that ν is an invariant probability measure, by the same reasoning as the one leading to (4.8).

Dynamics with non gradient drifts preserving the canonical measure

It is possible to add to (4.1) an extra drift F with values in $\mathbb{R}^D$, assumed to be smooth for simplicity:

$$dq_t = (-\nabla V(q_t) + F(q_t))\,dt + \sqrt{\frac{2}{\beta}}\,dW_t. \tag{4.11}$$

The generator of this dynamics is $\mathcal{L} + \mathcal{A}$, where $\mathcal{L}$ is defined in (4.3), and $\mathcal{A} = F^T \nabla_q$. In order to ensure that ν defined in (4.2) remains an invariant probability measure for the dynamics (4.11), we further assume that

$$\operatorname{div}\left(F \mathrm{e}^{-\beta V}\right) = 0. \tag{4.12}$$

A simple computation indeed shows that the generator associated with the extra drift term is antisymmetric:

$$\mathcal{A}^* = -\mathcal{A}.$$

Recalling that $\mathcal{L}$ is symmetric, we therefore obtain that, for any smooth and compactly supported test function φ,

$$\int_{\mathcal{D}} (\mathcal{L} + \mathcal{A})\varphi \, d\nu = \int_{\mathcal{D}} \varphi(\mathcal{L} - \mathcal{A})\mathbf{1} \, d\nu = 0,$$

which characterizes the invariance of ν by (4.11).

Examples of force fields satisfying (4.12) are for instance

$$F(q) = A(q)\nabla V(q), \qquad A(q)^T = -A(q) \in \mathbb{R}^{D\times D}, \qquad \operatorname{div}(A)^T \nabla V = 0.$$

In particular, constant antisymmetric matrices A can be considered. In order to check that the above condition is a sufficient one, we compute

$$\operatorname{div}\left(F \mathrm{e}^{-\beta V}\right) = \mathrm{e}^{-\beta V}\left[\operatorname{div}(A\nabla V) - \beta \nabla V^T A \nabla V\right] = \mathrm{e}^{-\beta V} \operatorname{div}(A)^T \nabla V = 0,$$

where we used successively that $\nabla V^T A \nabla V = 0$ and $A : \nabla^2 = 0$ by antisymmetry of A.

4.2 Convergence of trajectory averages

We discuss in this section the convergence of practical estimators of averages with respect to the target measure ν in (4.2), using the following estimator for some observable of interest φ:

$$\widehat{\varphi}_t = \frac{1}{t}\int_0^t \varphi(q_s)\,ds, \tag{4.13}$$

where, for simplicity of exposition, $(q_s)_{s\geqslant 0}$ follows the overdamped Langevin dynamics (4.1) (extensions to the dynamics discussed in Section 4.1.2 are of course possible). We first give in Section 4.2.1 sufficient conditions to guarantee the almost sure convergence of $\widehat{\varphi}_t$ to $\mathbb{E}_\nu(\varphi)$, which provides some form of Law of Large Numbers for SDEs; and then discuss in Section 4.2.2 the asymptotic quantification of statistical errors on $\widehat{\varphi}_t - \mathbb{E}_\nu(\varphi)$ through a Central Limit Theorem. The results we present here are similar in spirit (and also from a technical viewpoint) to the results given for Markov chains, see in particular Section 3.1.3 for the almost sure convergence of trajectory averages, and Section 3.4 for a Central Limit Theorem.

4.2.1 Almost sure convergence of trajectory averages

It would be possible to use a result by Kliemann [149] (discussed more precisely in Section 5.3) to directly obtain the almost sure convergence of $\widehat{\varphi}_t$ to $\mathbb{E}_\nu(\varphi)$ for any initial condition q_0. For pedagogical purposes, we will consider here a more constructive proof where we obtain the pathwise ergodicity of the overdamped process (4.1) by proving that the process is irreducible with respect

to the Lebesgue measure (a notion made precise below) and recalling that the canonical measure is by construction an invariant probability measure. The more constructive proof discussed here will also be useful to obtain the almost sure convergence of trajectory averages in situations where the expression of the invariant probability measure is not known, as for the nonequilibrium systems considered in Lecture 8.

Irreducibility corresponds here to the following property (denoting by $\mathscr{B}(\mathcal{D})$ the Borel sets of $\mathcal{D}$): for any $S \in \mathscr{B}(\mathcal{D})$ with positive Lebesgue measure, any initial condition $q_0 \in \mathcal{D}$ and any time $t > 0$, it holds $\mathbb{P}^{q_0}(q_t \in S) > 0$. The proof is conducted in two steps: first, a controllability argument shows that $\mathbb{P}^{q_0}(q_t \in S) > 0$ when $t > 0$ and S is an open set; second, this property is extended to general measurable ensembles using the continuity of the transition kernel. The proof of these statements are simpler than for dynamics with degenerate noise (see Section 5.3).

discuss somewhere Gaussian bounds de Menozzi, Malliavin approach by Pardoux

Let us first make precise the controllability argument. Fix $t > 0$, $q_0 \in \mathcal{D}$ and an open set $S \subset \mathcal{D}$, and consider $q^* \in S$. We denote by $Q(t) = (1-t)q_0 + tq^*$ the path interpolating between q_0 and q^*, and by $u(t)$ the control defined as $u(0) = 0$ and

$$u(t) = \sqrt{\frac{\beta}{2}} \int_0^t \dot{Q}(s) + \nabla V(Q(s))\, ds = \sqrt{\frac{\beta}{2}} \left[t\,(q^* - q_0) + \int_0^t \nabla V(Q(s))\, ds \right].$$

By construction,

$$\frac{dQ}{dt} = -\nabla V(Q(t)) + \sqrt{\frac{2}{\beta}}\, \dot{u}(t).$$

This shows that there exists a (very specific) realization of the Brownian motion which allows to go from q_0 to q^* in time $t > 0$. In addition, for any $\varepsilon > 0$, it holds (see [258, Theorem 4.20])

$$\mathbb{P}\left(\sup_{0 \leqslant t \leqslant 1} |W_t - u(t)| \leqslant \varepsilon \right) > 0.$$

To prove this statement, one first reduces the problem to $u = 0$ by a Girsanov transform, in which case the result is easily proved by martingale inequalities. By continuity of the solution with respect to the realizations of the Brownian motion, $\mathbb{P}^{q_0}(q_t \in S) > 0$. The precise argument relies on the Stroock–Varadhan support theorem, as reviewed in [228, Section 6].

To prove that $\mathbb{P}^{q_0}(q_t \in S) > 0$ for any measurable set of positive measure (and not just open sets), the idea is to rely on the regularity of the transition kernel. By standard results of parabolic regularity [87, Section 7.1], the integral kernel $P_t(q, dq')$ of $\mathrm{e}^{t\mathcal{L}}$ has a density $p(t, q, q')$, which is C^∞ in all its arguments on $(0, +\infty) \times \mathcal{D}^2$:

previous result on existence of the kernel

$$\left(\mathrm{e}^{t\mathcal{L}}\varphi\right)(q) = \int_{\mathcal{D}} p(t, q, q')\varphi(q')\, dq'.$$

Indeed, p satisfies the following family of Fokker-Planck equations, indexed respectively by q and q' (see [228, Section 7]):

other references?

$$\partial_t p(t, q, \cdot) = \mathcal{L}p(t, q, \cdot), \qquad \partial_t p(t, \cdot, q') = \mathcal{L}^\dagger p(t, \cdot, q'). \tag{4.14}$$

These equations have to be understood in the sense of distributions. The second one is obtained by writing

$$\frac{d}{dt}\left(\int_{\mathcal{D}} P_t(q, dq')\varphi(q') \right) = \frac{d}{dt}\left(\mathrm{e}^{t\mathcal{L}}\varphi\right)(q) = \left(\mathrm{e}^{t\mathcal{L}}\mathcal{L}\varphi\right)(q) = \int_{\mathcal{D}} P_t(q, dq')(\mathcal{L}_{q'}\varphi)(q'),$$

where the subscript q' in $\mathcal{L}_{q'}$ indicates that the differential operator acts on functions of q' (q being a parameter in the previous equation); while the first one is obtained by duality, letting $\mathrm{e}^{t\mathcal{L}^\dagger}$ act on probability distributions. The evolution equations (4.14) on the density of the transition kernel allow to show that $(t, q, q') \mapsto p(t, q, q')$ is C^∞. With this regularity result at hand, we can finally prove that the irreducibility using the following lemma, which states that open set irreducibility

implies irreducibility when the transition kernel has some continuity property (known as strong Feller).[2]

Lemma 4.1. *Consider a transition kernel $P_t(q, dq')$ which leaves invariant a probability measure ν, namely*

$$\forall S \in \mathscr{B}(\mathcal{D}), \quad \forall t \geqslant 0, \qquad \int_{\mathcal{D}} P_t(q, S)\, \nu(dq) = \nu(S). \tag{4.15}$$

Assume that

(i) ν has a positive density with respect to the Lebesgue measure;
(ii) for any set $S \in \mathscr{B}(\mathcal{D})$ and any $t > 0$, the function $q \mapsto P_t(q, S)$ is continuous;
(iii) for any open set $O \subset \mathcal{D}$ and any $t > 0$, it holds $P_t(q, O) > 0$.

Then, for any $q \in \mathcal{D}$, $t > 0$ and any measurable set S with positive Lebesgue measure, it holds $P_t(q, S) > 0$.

Proof. Fix a measurable set S with positive measure and $t > 0$. Note first that $\nu(S) > 0$, so (4.15) implies that there exists $q^* \in \mathcal{D}$ such that $P_{t/2}(q^*, S) > 0$. Moreover, there exists $r > 0$ such that $P_{t/2}(q', S) \geqslant P(q^*, S)/2$ for $q' \in B(q^*, r)$. Consider next $q \in \mathcal{D}$. Then,

$$\begin{aligned} P_t(q, S) &= \int_{q' \in \mathcal{D}} P_{t/2}(q, dq') P_{t/2}(q', S) \geqslant \int_{B(q^*, r)} P_{t/2}(q, dq') P_{t/2}(q', S) \\ &\geqslant \frac{P_{t/2}(q^*, S)}{2} P_{t/2}(q, B(q^*, r)) > 0, \end{aligned}$$

since the last factor is positive by the asssumed open set irreducibility. □

Remark 4.1. *The previous arguments extend immediately to dynamics with non gradient drifts* (4.11) *since we did not use the fact that the drift has a gradient structure. They can also be extended to dynamics with multiplicative noise* (4.9) *provided $A \geqslant a\mathrm{Id}_D$ with $a > 0$ (in the sense of symmetric matrices).*

4.2.2 Asymptotic variance and central limit theorem

Convergence rates on $\widehat{\varphi}_t - \mathbb{E}_\nu(\varphi)$ can be obtained provided a Central Limit Theorem holds. A first step is to show that the asymptotic variance is well defined. To this end, introduce the following projector:

$$\Pi\varphi = \varphi - \int_{\mathcal{D}} \varphi\, d\nu. \tag{4.16}$$

The asymptotic variance of the trajectorial average formally is

$$\sigma_\varphi^2 = \lim_{t \to +\infty} t\mathbb{E}\left(\left(\widehat{\Pi\varphi}_t\right)^2\right) = 2\int_0^{+\infty} \mathbb{E}(\Pi\varphi(q_t)\Pi\varphi(q_0))\, dt = -2\left\langle \Pi\varphi, \mathcal{L}^{-1}\Pi\varphi \right\rangle_{L^2(\nu)}. \tag{4.17}$$

The proof of the latter equalities is very similar to the proof of Proposition 3.5. For simplicity, we assume that $q_0 \sim \nu$, and denote by $\mathbb{E}_\nu$ expectations with respect to initial conditions $q_0 \sim \nu$ and realizations of (4.1). In particular, by invariance of ν, it holds $\mathbb{E}_\nu[\varphi(q_t)\varphi(q_s)] = \mathbb{E}_\nu[\varphi(q_{|t-s|})\varphi(q_0)]$. Then,

$$\begin{aligned} t\mathbb{E}\left(\left(\widehat{\Pi\varphi}_t\right)^2\right) &= \frac{1}{t}\int_0^t \int_0^t \mathbb{E}_\nu[\Pi\varphi(q_s)\Pi\varphi(q_r)]\, dr\, ds = 2\int_0^t \left(1 - \frac{\theta}{t}\right) \mathbb{E}_\nu[\Pi\varphi(q_\theta)\Pi\varphi(q_0)]\, d\theta \\ &= 2\int_0^t \left(1 - \frac{\theta}{t}\right) \left(\mathrm{e}^{\theta\mathcal{L}}\Pi\varphi\right) \Pi\varphi\, d\nu\, d\theta. \end{aligned} \tag{4.18}$$

[2] We thank Boris Nectoux and Liming Wu for teaching us this argument.

The conclusion then follows from a dominated convergence argument, provided we have good decay estimates on the semigroup $e^{t\mathcal{L}}$, in appropriate functional spaces E of functions with average 0 with respect to ν. In particular, the invertibility of the generator, and bounds on this inverse in $\mathcal{B}(E)$, can be deduced from decay estimates on the semigroup, as made precise in the following result.

Proposition 4.1. *Consider a Banach space E of measurable functions with average 0 with respect to ν, and assume that there exist $C \in \mathbb{R}_+$ and $\lambda > 0$ such that*

$$\forall t \geqslant 0, \qquad \|e^{t\mathcal{L}}\|_{\mathcal{B}(E)} \leqslant C e^{-\lambda t}. \tag{4.19}$$

Then the operator $\mathcal{L}$ is invertible on E, with

$$\mathcal{L}^{-1} = -\int_0^{+\infty} e^{t\mathcal{L}}\, dt.$$

In particular,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(E)} \leqslant \frac{C}{\lambda}. \tag{4.20}$$

The aim of the next section is precisely to provide estimates such as (4.19), in various Banach spaces E.

Proof. Introduce the operator

$$U = -\int_0^{+\infty} e^{t\mathcal{L}}\, dt,$$

which is well defined and bounded on E, in view of the estimate (4.19). Using semigroup theory [216], a simple computation shows that, for for $\varphi \in D(\mathcal{L}) = \{\phi \in E \,|\, \mathcal{L}\phi \in E\}$,

$$\mathcal{L}U\varphi = U\mathcal{L}\varphi = -\int_0^{+\infty} \frac{d}{dt}[e^{t\mathcal{L}}\varphi] = \varphi.$$

These equalities show that $\mathcal{L}$ is invertible on E, with $U = \mathcal{L}^{-1}$. From the definition of U, it follows that

$$\|U\|_{\mathcal{B}(E)} \leqslant \int_0^{+\infty} \|e^{t\mathcal{L}}\|_{\mathcal{B}(E)}\, dt \leqslant C \int_0^{+\infty} e^{-\lambda t}\, dt = \frac{C}{\lambda},$$

which proves the resolvent bound (4.20). □

Note that the manipulations performed here for continuous-in-time dynamics are quite similar to the ones used for discrete-in-time dynamics; see Corollary 3.1. As motivated in the introduction of Section 6.1, the expression (4.17) of the asymptotic variance can also be seen as a continuous limit of the asymptotic variance for Markov chains associated with numerical discretizations of the dynamics (4.1).

Correlation times

Correlation times can be defined by mimicking the approach used at the end of Section 3.4. We write the asymptotic variance (4.17) for time averages estimates with ergodic SDEs in terms of the reference variance $\sigma^2_{\varphi,\mathrm{iid}}$ as

$$\sigma^2_\varphi = \theta_{\mathrm{corr},\varphi}\sigma^2_{\varphi,\mathrm{iid}}, \tag{4.21}$$

and interpret $\theta_{\mathrm{corr},\varphi}$ as some correlation time. What is meant by that is that the mean-square error of the estimator $\widehat{\varphi}_t$ asymptotically behaves as $\sigma^2_\varphi/t = \sigma^2_{\varphi,\mathrm{iid}}\theta_{\mathrm{corr},\varphi}/t$, so that in order to have an estimator of the same quality as the one based on N i.i.d. samples, integration times of order $t = N\theta_{\mathrm{corr},\varphi}$ should be considered.

Remark 4.2. *Upper bounds on the norm of $\mathcal{L}^{-1}$ on $L^2_0(\nu)$ lead to upper bounds on the correlation time in view of the last equality in* (4.17)*. In fact, the following bound holds whatever $\varphi \in L^2(\nu)$:*

$$0 \leqslant \theta_{\mathrm{corr},\varphi} \leqslant 2\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^2_0(\nu))}. \tag{4.22}$$

We refer for instance to (4.31) *for a possible upper bound on $\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^2_0(\nu))}$. Of course, it may well be the case that $\theta_{\mathrm{corr},\varphi}$ is much smaller than $2\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^2_0(\nu))}$, due to anticorrelations in the autocorrelation function $t \mapsto \int_{\mathcal{D}} (\mathrm{e}^{t\mathcal{L}} \Pi\varphi)\Pi\varphi \, d\nu$ which is integrated in time in order to obtain* (4.17)*. Typically the bound* (4.22) *is saturated when $\mathcal{L}$ is selfadjoint with compact resolvent, and φ is an eigenvector of $-\mathcal{L}$ associated with the smallest non zero eigenvalue.*

Central Limit Theorems

The asymptotic variance can be defined without any reference to the evolution semigroup $\mathrm{e}^{t\mathcal{L}}$, by directly considering the last equality in (4.17):

$$\sigma^2_\varphi = 2 \int_{\mathcal{D}} (-\mathcal{L}^{-1}\Pi\varphi)\Pi\varphi \, d\nu.$$

The integral on the right hand side is well defined once the solution Φ of the Poisson equation

$$-\mathcal{L}\Phi = \Pi\varphi \tag{4.23}$$

belongs to a functional space $E \subset L^2(\nu)$ and $\varphi \in L^2(\nu)$. This is the case when $\varphi \in E$ and $\mathcal{L}^{-1}$ is a bounded operator on E. There are however more general frameworks to define solutions of Poisson equations, see for instance [213] and references therein.

Remark 4.3. *Note that a necessary condition for* (4.23) *to have a solution is that the right hand side of this equation has average 0 with respect to ν, since this is the case for the left hand side by* (4.8)*. This further motivates the projection operator Π on the right hand side.*

In fact, it was proved by [30] that a Central Limit Theorem holds once the Poisson equation (4.23) has a solution in $L^2(\nu)$ and the initial conditions are distributed according to ν. In this case,

$$\sqrt{t}\,(\widehat{\varphi}_t - \mathbb{E}_\nu(\varphi)) \xrightarrow[t\to+\infty]{\text{law}} \mathcal{N}(0, \sigma^2_\varphi).$$

This result can be extended to cover the case when the initial conditions are not distributed according to the invariant measure; see also [30]. The bottom line of the proof, which we write here in the general case (4.9), is to use Itô calculus to rewrite $\sqrt{t}\,(\widehat{\varphi}_t - \mathbb{E}_\nu(\varphi))$ as

$$\sqrt{t}\,(\widehat{\varphi}_t - \mathbb{E}_\nu(\varphi)) = \frac{\Phi(q_0) - \Phi(q_t)}{\sqrt{t}} + \mathcal{M}_t, \qquad \mathcal{M}_t = \frac{1}{\sqrt{t}} \int_0^t \nabla\Phi(q_s)^T B(q_s) dW_s.$$

The first term converges to 0 in law as $t \to +\infty$, while a Central Limit Theorem for martingales can be applied to obtain the asymptotic behavior of the second term (see for instance [151] or [83]): $\mathcal{M}_t$ converges in law to a Gaussian distribution with variance

$$\widetilde{\sigma}^2 = \lim_{t\to+\infty} \mathbb{E}\left(\frac{1}{t}\int_0^t \nabla\Phi(q_s)^T A(q_s)\nabla\Phi(q_s)\, ds\right).$$

By ergodicity of the dynamics,

$$\widetilde{\sigma}^2 = \int_{\mathcal{D}} \nabla\Phi^T A \nabla\Phi \, d\nu.$$

Now, recalling the expression (4.10) for the generator, a simple computation shows that

$$\mathcal{L}(\Phi^2) - 2\Phi\mathcal{L}\Phi = A : \nabla^2(\Phi^2) - 2\Phi A : \nabla^2\Phi = \nabla\Phi^T A \nabla\Phi.$$

The invariance of ν then leads to

$$\widetilde{\sigma}^2 = \int_{\mathcal{D}} \nabla\Phi^T A\nabla\Phi \, d\nu = -2\int_{\mathcal{D}} \Phi\mathcal{L}\Phi \, d\nu = \sigma^2_\varphi,$$

which allows to conclude.

4.3 Convergence of the law

Since the canonical measure is invariant for the overdamped Langevin dynamics presented in Section 4.1, it is relevant to ask whether the law $\psi(t,q)$ of the process at time t converges to ν, and, when this is the case, at which rate. Another question, closely related, is to prove convergence rates for the semigroup $\mathrm{e}^{t\mathcal{L}}$ (such as (4.19)), in order for the asymptotic variance to be well defined.

ajouter un mot sur les approches par couplage ?

We discuss in this section three ways to measure the convergence, and prove that convergence happens at an exponential rate under appropriate assumptions on the potential energy function V. After presenting two reformulations of the Fokker–Planck equation (4.6) in Section 4.3.1, we start by the converence in $L^2(\nu)$ in Section 4.3.2, where the fundamental functional inequality is the Poincaré inequality. We then turn in Section 4.3.3 to convergence in relative entropy and total variation, relying on logarithmic Sobolev inequalities. The convergence in $L^2(\nu)$ and in relative entropy is discussed for the law of the process, but the computations in these sections can be easily adapted to measure the convergence of the semigroup $\mathrm{e}^{t\mathcal{L}}$ (even for non reversible dynamics such as (4.11)). We finally turn in Section 4.3.4 to the convergence of the semigroup $\mathrm{e}^{t\mathcal{L}}$ in spaces of measurables functions growing at most like some reference Lyapunov function $\mathscr{W}$, using a Lyapunov condition of the form $\mathcal{L}\mathscr{W} \leqslant -a\mathscr{W} + b$ as a fundamental ingredient.

4.3.1 Two reformulations of the Fokker–Planck equation

We give in this section two useful reformulations of the Fokker–Planck equation (4.6). First, a simple computation shows that the function $g = \psi\,\mathrm{e}^{\beta V/2}$ satisfies the Schrödinger-type equation

$$\partial_t g = \frac{1}{\beta}\Delta g - wg, \qquad w = \frac{1}{2}\left(\frac{\beta}{2}|\nabla V|^2 - \Delta V\right), \tag{4.24}$$

together with the normalization condition

$$\forall t \geqslant 0, \qquad \int_{\mathcal{D}} g(t)\,\mathrm{e}^{-\beta V/2} = 1.$$

Equation (4.24) is not strictly a Schrödinger equation since a factor i is missing on the left hand side. Nonetheless, the operator arising on the right hand side is the opposite of a Schrödinger Hamiltonian $-\beta^{-1}\Delta + w$ with some effective potential w. The interest of the reformulation (4.24) is that many results of the mathematical literature on quantum physics [226] can be used to obtain detailed information on the Schrödinger Hamiltonian $-\beta^{-1}\Delta + w$, from which the long time behavior of (4.24) follows.

Second, the function $f = \psi\,\mathrm{e}^{\beta V}$ satisfies

$$\partial_t f = \mathcal{L}f, \qquad \int_{\mathcal{D}} f\,\mathrm{e}^{-\beta V} = 1. \tag{4.25}$$

In fact, the same equation is satisfied by the Radon–Nikodym derivative of ψ with respect to ν, *i.e.* the function f such that $\psi = f\,\nu$. This shows that, at least formally, $\psi(t) = (\mathrm{e}^{t\mathcal{L}}f_0)\nu$, where $\psi(0) = f_0\,\nu$. Therefore, the operator to study to obtain the longtime convergence of the law is the same as the one determining the convergence of time averages (4.5). In this setting, the functional space to consider is the Hilbert space $L^2(\nu)$ in order to have a self-adjoint generator, as discussed around (4.7).

4.3.2 Convergence in $L^2(\nu)$

We start by considering the Fokker-Planck equation reformulated as (4.25), for an initial condition $f_0 = \psi_0/\nu$ belonging to $L^2(\nu)$. Note that this condition is more stringent than the conditions

$$f_0 \geqslant 0, \qquad \int_{\mathcal{D}} f_0\,d\nu = 1,$$

which characterize the fact that $\psi_0 = f_0\,\nu$ is a probability measure. It is possible to consider less demanding moment conditions, upon changing the functional framework, see the discussion before Proposition 4.5 below.

The simplest setting to consider is when a so-called Poincaré inequality holds; see for instance [20, Chapter 4] for a very nice introduction to these inequalities. In this case, $f(t) = \mathrm{e}^{t\mathcal{L}} f_0$ converges exponentially fast in $L^2(\nu)$ to the constant function $\mathbf{1}$. This can be rephrased as the exponential convergence to 0 of $\mathrm{e}^{t\mathcal{L}}(f_0 - \mathbf{1})$ in $L^2(\nu)$.

In order to state the convergence result, we introduce the following definition.

Definition 4.1 (Poincaré inequality). *Consider the functional spaces*

$$L^2_0(\nu) = \left\{ \varphi \in L^2(\nu) \;\middle|\; \int_{\mathcal{D}} \varphi \, d\nu = 0 \right\},$$

and

$$H^1(\nu) = \left\{ \varphi \in L^2(\nu) \;\middle|\; \nabla\varphi \in (L^2(\nu))^D \right\}.$$

The measure ν is said to satisfy a Poincaré inequality with constant $R > 0$ when

$$\forall \varphi \in H^1(\nu) \cap L^2_0(\nu), \qquad \|\varphi\|^2_{L^2(\nu)} \leqslant \frac{1}{R} \|\nabla\varphi\|^2_{L^2(\nu)}. \tag{4.26}$$

The constant $R > 0$ depends on the potential V, the inverse temperature β and the domain $\mathcal{D}$. We discuss below various sufficient conditions for ν to satisfy a Poincaré inequality. We will also repeatedly use below that functions φ with average 0 with respect to ν are still of average 0 when evolved according to (4.25) since, at least formally,

$$\frac{d}{dt}\left(\int_{\mathcal{D}} \mathrm{e}^{t\mathcal{L}} \varphi \right) = \int_{\mathcal{D}} \mathcal{L}\left(\mathrm{e}^{t\mathcal{L}} \varphi \right) d\nu = 0, \tag{4.27}$$

by (4.8). This property is the counterpart in $L^2_0(\nu)$ of the fact that the Fokker–Planck equation (4.6) preserves the total mass (as can be seen by a direct integration over $\mathcal{D}$).

The inequality (4.26) implies (and in fact is equivalent to) the exponential convergence to 0 of the semigroup $\mathrm{e}^{t\mathcal{L}}$ considered as an operator on $L^2_0(\nu)$.

Proposition 4.2. *The measure ν satisfies a Poincaré inequality with constant $R > 0$ if and only if*

$$\left\| \mathrm{e}^{t\mathcal{L}} \right\|_{\mathcal{B}(L^2_0(\nu))} \leqslant \mathrm{e}^{-Rt/\beta}. \tag{4.28}$$

Proof. Let us first assume that the measure ν satisfies a Poincaré inequality with constant $R > 0$. In view of (4.7), we obtain, for $\varphi \in D(\mathcal{L}) \cap L^2_0(\nu)$,

$$-\langle \mathcal{L}\varphi, \varphi \rangle_{L^2(\nu)} = \frac{1}{\beta} \|\nabla\varphi\|^2_{L^2(\nu)} \geqslant \frac{R}{\beta} \|\varphi\|^2_{L^2(\nu)}. \tag{4.29}$$

Since 0 is an eigenvalue of the operator $\mathcal{L}$ (whose associated eigenvectors are constant functions), this inequality shows that the spectral gap of the self-adjoint operator $-\mathcal{L}$ on $L^2(\nu)$ is larger than or equal to R/β (using a Raylegh–Ritz principle). The inequality (4.29) also gives the exponential decrease of the semigroup on $L^2_0(\nu)$ since, using (4.27),

$$\frac{d}{dt}\left(\frac{1}{2} \left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|^2_{L^2(\nu)} \right) = \left\langle \mathrm{e}^{t\mathcal{L}} \varphi, \mathcal{L}\, \mathrm{e}^{t\mathcal{L}} \varphi \right\rangle_{L^2(\nu)} \leqslant -\frac{R}{\beta} \left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|^2_{L^2(\nu)}. \tag{4.30}$$

By a Gronwall inequality, it follows that

$$\forall \varphi \in L^2_0(\nu), \qquad \left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|_{L^2_0(\nu)} \leqslant \mathrm{e}^{-Rt/\beta} \|\varphi\|_{L^2_0(\nu)}.$$

We can finally extend the bound to all functions in $L^2_0(\nu)$ by density.

Assume now that $\|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(L^2_0(\nu))} \leqslant \mathrm{e}^{-Rt/\beta}$. Then, for a given $\varphi \in L^2_0(\nu)$ and any $t > 0$,

$$\frac{\left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|^2_{L^2_0(\nu)} - \|\varphi\|^2_{L^2_0(\nu)}}{t} \leqslant \|\varphi\|^2_{L^2_0(\nu)} \, \frac{\mathrm{e}^{-2Rt/\beta} - 1}{t}.$$

We next pass to the limit $t \to 0$, using the equalities in (4.29) and (4.30), and restrict ourselves to a C^∞ function with compact support:

$$-\frac{2}{\beta}\|\nabla\varphi\|^2_{L^2(\nu)} \leqslant -\frac{2R}{\beta}\|\varphi\|^2_{L^2_0(\nu)}.$$

The Poincaré inequality (4.26) finally follows by a density argument. □

Remark 4.4. *The following observation is made in [230]: for the non reversible dynamics* (4.11)*, when a Poincaré inequality holds for ν,*

$$\frac{d}{dt}\left(\frac{1}{2}\left\|\mathrm{e}^{t(\mathcal{L}+\mathcal{A})}\varphi\right\|^2_{L^2(\nu)}\right) = \left\langle \mathrm{e}^{t(\mathcal{L}+\mathcal{A})}\varphi, \mathcal{L}\,\mathrm{e}^{t(\mathcal{L}+\mathcal{A})}\varphi\right\rangle_{L^2(\nu)} \leqslant -\frac{R}{\beta}\left\|\mathrm{e}^{t(\mathcal{L}+\mathcal{A})}\varphi\right\|^2_{L^2(\nu)},$$

so that the law of (4.11) *converges at least as fast towards the stationary state ν as the law of the law of* (4.1)*.*

In application of Proposition 4.1, a useful corollary of the decay estimates on the semigroup is the following result. Alternatively, the invertibility of the operator $\mathcal{L}$ could be directly obtained from the coercivity inequality (4.29).[3]

Corollary 4.1. *Assume that ν satisfies a Poincaré inequality with constant R. Then the operator $\mathcal{L}$ is invertible on $L^2_0(\nu)$, and the following equality holds in $\mathcal{B}(L^2_0(\nu))$:*

$$\mathcal{L}^{-1} = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}}\, dt.$$

Moreover,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^2_0(\nu))} \leqslant \frac{\beta}{R}. \tag{4.31}$$

In fact, by a proof similar to the proof of Proposition 4.1, the decay estimate (4.28) implies that, for any $z \in \mathbb{C}$ with $\mathrm{Re}(z) < R/\beta$, the following equalities holds on $\mathcal{B}(L^2_0(\nu))$:

$$(z + \mathcal{L})^{-1} = \int_0^{+\infty} \mathrm{e}^{tz}\mathrm{e}^{t\mathcal{L}}\, dt$$

is a well defined and bounded operator. Therefore, $\sigma(\mathcal{L})\backslash\{0\} \subset \{z \in \mathbb{C} \,|\, \mathrm{Re}(z) \geqslant R/\beta\}$, and the spectral gap of the dynamics is at least R/β.

Obtaining Poincaré inequalities

Poincaré inequalities are easily obtained for probability measures equivalent to the Lebesgue measure, on bounded connected domains, as a consequence of the standard Poincaré–Wirtinger inequality. This is the case for instance when $\mathcal{D} = (L\mathbb{T})^d$. Indeed, consider a measure with density $\rho(q)$ with respect to the Lebesgue measure, and such that there exist two positive constants $\rho_{\min}$ and $\rho_{\max}$ with $0 < \rho_{\min} \leqslant \rho(q) \leqslant \rho_{\max}$ for all $q \in \mathcal{D}$. First, note that

[3] The injectivity is clear, while the surjectivity is a consequence of the fact that the image is dense (in view of $\overline{\mathrm{Ran}(\mathcal{L})} = \mathrm{Ker}(\mathcal{L})^\perp$) and closed. For the latter point, the inequality (4.29) shows that, for any Cauchy sequence $(\psi_n) = (\mathcal{L}\varphi_n)$ of the image converging to ψ, the sequence of preimages (φ_n) is also a Cauchy sequence, hence converges to some element φ. The closedness of the operator allows to conclude that $\varphi \in D(\mathcal{L})$ and $\psi = \mathcal{L}\varphi$ is in the image.

$$\min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 d\rho = \int_{\mathcal{D}} (\varphi - \mathbb{E}_\rho(\varphi))^2 d\rho, \qquad \forall \varphi \in L^2(\rho).$$

The proof of this assertion is easily obtained by writing $c = \mathbb{E}_\rho(f) + \widetilde{c}$ and expanding $(f-c)^2$. Therefore,

$$\min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 d\rho \leqslant \rho_{\max} \min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 \leqslant \frac{\rho_{\max}}{R_{\mathrm{PW}}} \int_{\mathcal{D}} |\nabla\varphi|^2 \leqslant \frac{\rho_{\max}}{R_{\mathrm{PW}}\rho_{\min}} \int_{\mathcal{D}} |\nabla\varphi|^2 d\rho,$$

where R_{PW} is the constant of the standard Poincaré–Wirtinger inequality on the bounded connected domain $\mathcal{D}$. This shows that the canonical measure ν defined in (4.2) satisfies a Poincaré inequality when the domain $\mathcal{D}$ is bounded and connected, with the following upper bound for the Poincaré constant R_ν:

$$R_\nu \leqslant R_{\mathrm{PW}}\, \mathrm{e}^{-\beta(V_{\max}-V_{\min})},$$

where

$$V_{\max} = \max_{q\in\mathcal{D}} V(q), \quad V_{\min} = \min_{q\in\mathcal{D}} V(q).$$

In fact, this argument can be made more general to show that Poincaré inequalities satisfy some stability property under bounded perturbations of the measure, similar to the result obtained in Theorem 4.4 below for logarithmic Sobolev inequalities.

On unbounded domains, some growth conditions on the potential V are required. For example, a Poincaré inequality holds when V is uniformly convex (*i.e.*, $\nabla^2 V \geqslant R\,\mathrm{Id}$ with $R > 0$), similar to the result stated in Theorem 4.3 below for logarithmic Sobolev inequalities. Another result is based on the growth at infinity of the potential, see [18, Corollary 1.6].

Theorem 4.1. *Consider $V \in C^2(\mathbb{R}^D)$. If there exists $a \in (0,1)$, $c > 0$ and $M \geqslant 0$ such that*

$$\forall q \in \mathbb{R}^d \text{such that } |q| \geqslant M, \qquad a\beta|\nabla V(q)|^2 - \Delta V(q) \geqslant c. \tag{4.32}$$

then ν satisfies a Poincaré inequality.

The above condition is satisfied, for instance, for potentials of the form

$$V(q) = K|q|^n + \widetilde{V}(q),$$

where $n > 1$ and $\widetilde{V} \in C^\infty(\mathcal{D})$ is such that

$$\lim_{|q|\to+\infty} \frac{|\widetilde{V}(q)|}{|q|^n} = 0, \quad \lim_{|q|\to+\infty} \frac{|\nabla\widetilde{V}|^2 + |\Delta\widetilde{V}|}{|q|^{2(n-1)}} = 0.$$

The first condition implies that $\mathrm{e}^{-\beta V}$ is integrable, while the second one ensures that (4.32) holds. The reader may wonder what are examples of probability measures which do not satisfy Poincaré inequalities. A necessary condition to this end is that the probability measure has an exponential moment, see [20, Proposition 4.4.2]. This is not the case for potential which grow less than linearly at infinity.

For the sake of completeness, we provide the complete proof of a result weaker than Theorem 4.1, quoted from [274, Appendix A.19] – the proof being based on an argument by Deuschel and Stroock [67].

Theorem 4.2. *Consider $V \in C^2(\mathbb{R}^D)$ such that*

$$w(q) = \frac{\beta}{2}|\nabla V(q)|^2 - \Delta V(q) \xrightarrow[|q|\to+\infty]{} +\infty. \tag{4.33}$$

Then ν satisfies a Poincaré inequality.

Note that the condition (4.33) of course implies (4.32). Note also that the function in (4.33) is the potential w in (4.24). Standard results in the theory of Schrödinger operators (see for instance [226, Theorem XIII.67]) show that $-\beta^{-1}\Delta + w + 1 - \min_{\mathbb{R}^D} w$ has a compact resolvent on $L^2(\mathbb{R}^D)$, which immediately gives the compactness of the resolvent of $\mathcal{L}$ on $L^2(\nu)$ (since these operators are unitarily related, see the discussion around (4.24)), and hence the existence of a spectral gap.

Proof. Fix $h \in C^1(\mathbb{R}^D)$ with compact support. We already have a control of the $L^2(\nu)$ norm of h on bounded domains. To control the $L^2(\nu)$ norm of h at infinity, the key observation is that

$$\int_{\mathbb{R}^D} w\, h^2\, d\nu \leqslant \frac{2}{\beta} \int_{\mathbb{R}^D} |\nabla h|^2 d\nu. \tag{4.34}$$

To derive this inequality, we note that

$$0 \leqslant \int_{\mathbb{R}^D} \left| \nabla h - \frac{\beta h}{2} \nabla V \right|^2 \mathrm{e}^{-\beta V} = \int_{\mathbb{R}^D} |\nabla h|^2\, \mathrm{e}^{-\beta V} - \frac{\beta}{2} \int_{\mathbb{R}^D} \nabla \left(h^2\right) \cdot \nabla V \mathrm{e}^{-\beta V} + \frac{\beta^2}{4} \int_{\mathbb{R}^D} |\nabla V|^2 h^2\, \mathrm{e}^{-\beta V}.$$

Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^D} |\nabla h|^2 \mathrm{e}^{-\beta V} &\geqslant \frac{\beta}{2} \int_{\mathbb{R}^D} \nabla \left(h^2\right) \cdot \nabla V \mathrm{e}^{-\beta V} - \frac{\beta^2}{4} \int_{\mathbb{R}^D} |\nabla V|^2 h^2\, \mathrm{e}^{-\beta V} \\
&= -\frac{\beta}{2} \int_{\mathbb{R}^D} h^2 \mathrm{div} \left(\nabla V \mathrm{e}^{-\beta V}\right) - \frac{\beta^2}{4} \int_{\mathbb{R}^D} |\nabla V|^2 h^2\, \mathrm{e}^{-\beta V} \\
&= \int_{\mathbb{R}^D} \left(\frac{\beta^2}{4} |\nabla V|^2 - \frac{\beta}{2} \Delta V \right) h^2\, \mathrm{e}^{-\beta V} = \frac{\beta}{2} \int_{\mathbb{R}^D} w\, h^2\, \mathrm{e}^{-\beta V}.
\end{aligned}$$

Consider next $M > 0$ such that $w(q) \geqslant 1$ for $|q| \geqslant M$, and define

$$\varepsilon(M) = \frac{1}{\min\limits_{|q| \geqslant M} w} \leqslant 1, \qquad w_- = \min_{q \in \mathbb{R}^D} w(q) > -\infty.$$

Note that $\varepsilon(M) \to 0$ as $M \to +\infty$. The inequality (4.34) implies that

$$w_- \int_{|q| \leqslant M} h^2\, d\nu + \frac{1}{\varepsilon(M)} \int_{|q| \geqslant M} h^2\, d\nu \leqslant \frac{2}{\beta} \int_{\mathbb{R}^D} |\nabla h|^2 d\nu,$$

which can be rewritten as

$$\int_{|q| \geqslant M} h^2\, d\nu \leqslant \varepsilon(M) \left(\frac{2}{\beta} \int_{\mathbb{R}^D} |\nabla h|^2 d\nu - w_- \int_{|q| \leqslant M} h^2\, d\nu \right). \tag{4.35}$$

We next control the $L^2(\nu)$ norm the bounded set $B_M = \{|q| \leqslant M\}$. The probability measure $\nu_M = Z_M^{-1} \mathbf{1}_{B_M}\, \nu$ satisfies a Poincaré inequality with constant $C_M > 0$, so that

$$\int_{B_M} h^2\, d\nu_M \leqslant C_M \int_{B_M} |\nabla h|^2\, d\nu_M + \left(\int_{B_M} h\, d\nu_M \right)^2.$$

Note that $Z_M \geqslant 1$ and $Z_M \to 1$ as $M \to +\infty$, so that, upon increasing M in order to have $Z_M \geqslant 1/2$,

$$\int_{B_M} h^2\, d\nu \leqslant C_M \int_{B_M} |\nabla h|^2\, d\nu + 2 \left(\int_{B_M} h\, d\nu \right)^2. \tag{4.36}$$

Assume now that

$$\int_{\mathbb{R}^D} h\, d\nu = 0.$$

Then, by a Cauchy–Schwarz inequality,

$$\left(\int_{B_M} h\,d\nu\right)^2 = \left(\int_{|q|>M} h\,d\nu\right)^2 \leqslant \nu\left(\mathbb{R}^D\backslash B_M\right)\int_{|q|>M} h^2\,d\nu \leqslant \int_{|q|>M} h^2\,d\nu.$$

We therefore obtain from (4.36) the following control on the $L^2(\nu)$ norm of h on B_M:

$$\int_{B_M} h^2\,d\nu \leqslant C_M\int_{B_M}|\nabla h|^2\,d\nu + 2\int_{|q|\geqslant M} h^2\,d\nu. \tag{4.37}$$

We finally add (4.35) multiplied by 3 and (4.37) to obtain

$$\int_{\mathbb{R}^D} h^2\,d\nu \leqslant \left(C_M + \frac{6\varepsilon(M)}{\beta}\right)\int_{\mathbb{R}^D}|\nabla h|^2\,d\nu - 3\varepsilon(M)w_-\int_{|q|\leqslant M} h^2\,d\nu.$$

In conclusion, provided $M > 0$ is sufficiently large so that $3\varepsilon(M)w_- < 1/2$ (a condition to be satisfied only when $w_- < 0$ in fact),

$$\int_{\mathbb{R}^D} h^2\,d\nu \leqslant \frac{1}{\min\left(1, 1+3\varepsilon(M)w_-\right)}\left(C_M + \frac{6\varepsilon(M)}{\beta}\right)\int_{\mathbb{R}^D}|\nabla h|^2\,d\nu,$$

which gives the desired estimate. □

A useful result which we use in the sequel is that it is possible to deduce Poincaré inequalities by tensorization.

Proposition 4.3. *If a probability measure is a product of d probability measures satisfying Poincaré inequalities with constants R_i, then the product measure satisfies a Poincaré inequality with constant* $\min(R_1,\dots,R_d)$.

Proof. To simplify the notation, we prove the result in the case $d = 2$, for a probability measure $\rho(dq_1\,dq_2) = \rho_1(dq_1)\,\rho_2(dq_2)$, defined on $\mathcal{D} = \mathcal{D}_1\times\mathcal{D}_2$. Consider a C^∞ function φ with compact support, and average 0 with respect to ρ. We first introduce the partial average

$$\overline{\varphi}(q_2) = \int_{\mathcal{D}_1}\varphi(q_1', q_2)\,\rho_1(dq_1').$$

Since ρ_1 satisfies a Poincaré inequality with constant R_1, and using the fact that the function $q_1\mapsto\varphi(q_1,q_2)-\overline{\varphi}(q_2)$ has average 0 with respect to $\rho_1(dq_1)$ for any value of q_2, it holds

$$\int_{\mathcal{D}_1}\left|\varphi(q_1,q_2)-\overline{\varphi}(q_2)\right|^2\rho_1(dq_1) \leqslant \frac{1}{R_1}\int_{\mathcal{D}_1}\left|\nabla_{q_1}\varphi(q_1,q_2)\right|^2\rho_1(dq_1).$$

This inequality can be rewritten as

$$\int_{\mathcal{D}_1}\left|\varphi(q_1,q_2)\right|^2\rho_1(dq_1) \leqslant \left|\overline{\varphi}(q_2)\right|^2 + \frac{1}{R_1}\int_{\mathcal{D}_1}\left|\nabla_{q_1}\varphi(q_1,q_2)\right|^2\rho_1(dq_1). \tag{4.38}$$

Now, since $\overline{\varphi}$ has average 0 with respect to ρ_2 because φ has average 0 with respect to ρ,

$$\begin{aligned}\int_{\mathcal{D}_2}\left|\overline{\varphi}(q_2)\right|^2\rho_2(dq_2) &\leqslant \frac{1}{R_2}\int_{\mathcal{D}_2}\left|\nabla_{q_2}\overline{\varphi}(q_2)\right|^2\rho_2(dq_2)\\ &\leqslant \frac{1}{R_2}\int_{\mathcal{D}}\left|\nabla_{q_2}\varphi(q_1,q_2)\right|^2\rho_1(dq_1)\,\rho_2(dq_2),\end{aligned}$$

where we used a Cauchy–Schwarz inequality in the last step. An integration of (4.38) with respect to $\rho_2(dq_2)$ finally leads to

$$\begin{aligned}\int_{\mathcal{D}}\left|\varphi(q_1,q_2)\right|^2\rho(dq) &\leqslant \frac{1}{R_1}\int_{\mathcal{D}}\left|\nabla_{q_1}\varphi(q_1,q_2)\right|^2\rho(dq) + \frac{1}{R_2}\int_{\mathcal{D}}\left|\nabla_{q_2}\varphi(q_1,q_2)\right|^2\rho(dq)\\ &\leqslant \frac{1}{\min(R_1,R_2)}\int_{\mathcal{D}}\left|\nabla_q\varphi\right|^2 d\rho,\end{aligned}$$

from which we deduce that ρ satisfies a Poincaré inequality with constant $R = \min(R_1,R_2)$. □

Finally, anticipating later discussion, we will see in Proposition 4.5 that a probability measure satisfying a logarithmic Sobolev inequality also satisfies a Poincaré inequality.

4.3.3 Convergence in relative entropy and total variation

The aim of this section is to give some background on entropy techniques with a focus on logarithmic Sobolev inequalities, which can be used to show the convergence to the equilibrium state. More material can be read in the review papers by Guionnet and Zegarlinski [112], Ledoux [163], Arnold, Markowich, Toscani and Unterreiter [14] and in [20, Section 5]. The latter two works have a PDE approach which may help readers more accustomed to analytical frameworks. Other useful introductory references include [10, 273].

The relative entropy and the Fisher information between two measures are defined as follows.

Definition 4.2 (entropy and Fisher information). *For two probability measures π_1 and π_2 defined on a space $\mathcal{D}$, and such that π_1 is absolutely continuous with respect to π_2 (denoted by $\pi_1 \ll \pi_2$ in the following), the entropy of π_1 with respect to π_2 is*

$$\mathcal{H}(\pi_1 \mid \pi_2) = \int_{\mathcal{D}} \ln\left(\frac{d\pi_1}{d\pi_2}\right) d\pi_1. \tag{4.39}$$

The Fisher information of π_1 with respect to π_2 is

$$\mathcal{I}(\pi_1 \mid \pi_2) = \int_{\mathcal{D}} \left|\nabla \ln\left(\frac{d\pi_1}{d\pi_2}\right)\right|^2 d\pi_1. \tag{4.40}$$

Note that the relative entropy is not a distance because it is not symmetric in its arguments. Moreover, using the strict convexity of $x \mapsto x \ln x$ and the fact that $x \ln x - x + 1 \geqslant 0$ (with equality if and only if $x = 1$), it is easy to check that the entropy is non-negative:

$$\mathcal{H}(\pi_1 \mid \pi_2) = \int_{\mathcal{D}} \frac{d\pi_1}{d\pi_2} \ln\left(\frac{d\pi_1}{d\pi_2}\right) d\pi_2 \geqslant \int_{\mathcal{D}} \left(\frac{d\pi_1}{d\pi_2} - 1\right) d\pi_2 = 0.$$

Moreover, the above computation shows that it is zero if and only if the two probability measures are identical. This is also true for the Fisher information.

Remark 4.5 (On the choice of the entropy function). *There are many possible definitions of the entropy besides the relative entropy $\mathcal{H}$ defined in* (4.39)*. Some mathematical motivations for the use of the relative entropy $\mathcal{H}$ can be found in [187], see also [54] for a historical perspective. This particular entropy may be of interest for the following extensivity property. The relative entropy of the distribution of D independent variables (or, in less probabilistic terms, the entropy of a tensorized measure) is the sum of the relative entropies of the distributions of each random variable. This suggests that the rate of convergence to equilibrium estimated with relative entropies for weakly dependent variables may remain stable when the number of variables becomes large (see for instance the paragraph on Kac's spectral problem in [272, Chapter 5]). This extensivity is a consequence of the extensivity of the logarithm function involved in definition* (4.39) *(by which we mean that $\ln(f_1 f_2) = \ln(f_1) + \ln(f_2)$). This extensivity property makes the logarithmic Sobolev inequality and entropy approaches much more convenient to study some nonlinear Fokker-Planck equations, as in [177] for instance.*

The total variation between two measures, which reduces to the L^1-norm of the difference between the two densities when the two measures are absolutely continuous with respect to the Lebesgue measure, can be bounded by the relative entropy. This is the Csiszár–Kullback inequality (see for example [10, 241]): recalling the total variation norm already considered in Remark 3.7, namely

$$\|\pi_1 - \pi_2\|_{\mathrm{TV}} = \sup_{\|\varphi\|_{B^\infty} \leqslant 1} \int_{\mathcal{D}} \varphi(d\pi_1 - d\pi_2), \tag{4.41}$$

it holds

$$\|\pi_1 - \pi_2\|_{\mathrm{TV}} \leqslant \sqrt{2\mathcal{H}(\pi_1 \mid \pi_2)}. \tag{4.42}$$

In other words, an upper bound for the entropy between π_1 and π_2 yields an upper bound for a distance between π_1 and π_2 (even though the relative entropy is not a distance itself).

We now present a way to obtain an estimate of the rate of convergence to zero of the entropy $\mathcal{H}(\psi(t,\cdot) \mid \nu)$ for the solutions of the Fokker–Planck equation (4.6). To this end we introduce the following functional inequality.

Definition 4.3 (logarithmic Sobolev inequality). *A probability measure π_2 satisfies a logarithmic Sobolev inequality with constant $R > 0$ (LSI(R) for short) if, for all probability measures π_1 such that $\pi_1 \ll \pi_2$,*

$$\mathcal{H}(\pi_1 \mid \pi_2) \leqslant \frac{1}{2R}\mathcal{I}(\pi_1 \mid \pi_2). \tag{4.43}$$

Remark 4.6. *Proposition 4.5 below motivates the factor $1/(2R)$ on the right hand side of* (4.43)*, compared to the factor $1/R$ considered for Poincaré inequalities* (4.26)*.*

The exponential decay of $\mathcal{H}(\psi(t,\cdot) \mid \nu)$ to 0 can then be shown provided ν satisfies a so-called logarithmic Sobolev inequality (LSI). In fact, there is some equivalence between the two notions, as made precise in the following result (which is the equivalent of Proposition 4.2 where a similar result is obtained for Poincaré inequalities and exponential decay in $L^2(\nu)$).

Proposition 4.4. *The measure ν satisfies LSI(R) if and only if, for any initial condition $\psi_0 \geqslant 0$ with integral 1 and finite relative entropy with respect to ν (*i.e. $\mathcal{H}(\psi_0 \mid \nu) < +\infty$*), the solution $\psi(t)$ of the Fokker–Planck equation* (4.6) *satisfies*

$$\forall t \geqslant 0, \qquad \mathcal{H}(\psi(t) \mid \nu) \leqslant \mathcal{H}(\psi_0 \mid \nu)\exp(-2\beta^{-1}Rt). \tag{4.44}$$

From the Csiszár–Kullback inequality (4.42), it is then possible to deduce the exponential convergence to zero with rate $\beta^{-1}R$ of the norm $\|\psi(t,\cdot) - \nu\|_{L^1}$.

Proof. Note first that the Fokker-Planck equation (4.6) can be rewritten as

$$\partial_t \psi = \mathcal{L}^\dagger \psi = \frac{1}{\beta}\mathrm{div}\left(\nu\nabla\left(\frac{\psi}{\nu}\right)\right).$$

A straightforward computation shows that

$$\frac{d}{dt}(\mathcal{H}(\psi(t,\cdot) \mid \nu)) = \int_{\mathcal{D}} \partial_t\psi \left(\ln\left(\frac{\psi}{\nu}\right) + 1\right) = \int_{\mathcal{D}} \partial_t\psi \, \ln\left(\frac{\psi}{\nu}\right),$$

since

$$\int_{\mathcal{D}} \psi(t) = 1,$$

so that the integral of $\partial_t\psi$ over $\mathcal{D}$ vanishes. Therefore,

$$\frac{d}{dt}(\mathcal{H}(\psi(t,\cdot) \mid \nu)) = \int_{\mathcal{D}} (\mathcal{L}^\dagger\psi) \, \ln\left(\frac{\psi}{\nu}\right) = -\frac{1}{\beta}\int_{\mathcal{D}} \nabla\left(\frac{\psi}{\nu}\right) \cdot \nabla\left[\ln\left(\frac{\psi}{\nu}\right)\right] d\nu,$$

which can be summarized as

$$\frac{d}{dt}(\mathcal{H}(\psi(t,\cdot) \mid \nu)) = -\frac{1}{\beta}\mathcal{I}(\psi(t,\cdot) \mid \nu). \tag{4.45}$$

If ν satisfies an LSI(R), then the estimate (4.44) directly follows from (4.45) and a Gronwall inequality.

Assume conversely that (4.44) holds for any initial condition ψ_0 with finite relative entropy with respect to ν. Then,

$$\frac{\mathcal{H}(\psi(t) \mid \nu) - \mathcal{H}(\psi_0 \mid \nu)}{t} \leqslant \mathcal{H}(\psi_0 \mid \nu) \frac{\exp(-2\beta^{-1}Rt) - 1}{t}.$$

In the limit $t \to 0$, one obtains, with (4.45),

$$-\frac{1}{\beta}\mathcal{I}(\psi_0 \mid \nu) \leqslant -\frac{2R}{\beta}\,\mathcal{H}(\psi_0 \mid \nu),$$

which indeed leads to (4.43). □

Obtaining LSI

We now present several ways to obtain LSIs for measures of the form (4.2).

(1) When the potential V satisfies a strict convexity condition of the form $\mathrm{Hess}(V) \geqslant R\,\mathrm{Id}_D$ with $R > 0$, then ν satisfies an LSI with constant βR, as first shown in [19] (see Theorem 4.3 below).

(2) When $\rho = \prod_{i=1}^d \rho^i$ and each measure $\rho^i(q)\,dq$ satisfies an LSI with constant R_i, then ρ satisfies an LSI with constant $R = \min\{R_1, \dots, R_d\}$ (see [109]). This is the equivalent of Proposition 4.3 for LSI.

(3) When an LSI with constant R is satisfied by $\nu(dq) = Z_V^{-1}\,\mathrm{e}^{-V(q)}dq$, then the modified measure

$$Z_{V+\widetilde{V}}^{-1}\,\mathrm{e}^{-(V(q)+\widetilde{V}(q))}\,dq$$

with $\widetilde{V}$ bounded satisfies an LSI with constant $\widetilde{R} = R\,\mathrm{e}^{\inf \widetilde{V} - \sup \widetilde{V}}$. This property expresses some stability with respect to bounded perturbations (see [129] and Theorem 4.4 below).

(4) There are also results on an LSI for the measure when a marginal law and the corresponding conditional laws satisfy an LSI (see [32]), or when all the conditional laws satisfy an LSI under some weak coupling assumption (see [210]). Such results can be extended to the non-linear setting, *i.e.* in the case when the marginal distribution is obtained for some variable $z = \xi(q) \in \mathbb{R}^m$ (with $m < D$): see [172].

Let us now state more precisely, and prove, two fundamental results ensuring that an LSI holds for canonical measures of the form (4.2).

Theorem 4.3 (Bakry–Emery criterion). *Assume that $\mathcal{D} = \mathbb{R}^D$ and $\nabla^2 V \geqslant R\,\mathrm{Id}_D$ for some constant $R > 0$. Then ν satisfies LSI(βR).*

Let us mention that the criterion on the Hessian is only a sufficient criterion, which can be seen as a specific case of the more general condition writen in [19].

Proof. The idea is to differentiate the Fisher information with respect to time, in order to prove its exponential convergence to 0, and then to insert it in (4.45). We present the formal argument, and refer to [14, 13] for discussions on how to make the proof below fully rigorous.

Introduce $f(t) = \psi(t)/\nu$ for an arbitrary initial condition $f_0 = \psi_0/\nu$. In view of (4.25), this function evolves according to $\partial_t f = \mathcal{L} f$, so that

$$\begin{aligned}
\frac{d}{dt}[\mathcal{I}(\psi(t) \mid \nu)] &= \frac{d}{dt}\left(\int_{\mathcal{D}} |\nabla \ln f(t)|^2 f(t)\,d\nu\right) \\
&= 2\int_{\mathcal{D}} \nabla\left(\frac{\partial_t f(t)}{f(t)}\right) \cdot \nabla f(t)\,d\nu + \int_{\mathcal{D}} |\nabla \ln f(t)|^2 \partial_t f(t)\,d\nu \\
&= 2\int_{\mathcal{D}} \nabla\left(\frac{\mathcal{L} f(t)}{f(t)}\right) \cdot \nabla f(t)\,d\nu + \int_{\mathcal{D}} |\nabla \ln f(t)|^2 \mathcal{L} f(t)\,d\nu.
\end{aligned}$$

Since

$$\mathcal{L}(\ln f) = \frac{\mathcal{L}f}{f} - \frac{|\nabla f|^2}{\beta f^2} = \frac{\mathcal{L}f}{f} - \frac{1}{\beta}|\nabla(\ln f)|^2,$$

we obtain, after some algebraic calculations,

$$\frac{1}{2}\frac{d}{dt}[\mathcal{I}(\psi(t) \mid \nu)] = \int_{\mathcal{D}} \nabla[\mathcal{L}(\ln f(t))] \cdot \nabla[\ln f(t)]\, f(t)\, d\nu - \int_{\mathcal{D}} \mathcal{L}\left[\frac{1}{2}|\nabla(\ln f(t))|^2\right] f(t)\, d\nu.$$

Now, using

$$\nabla\left(\frac{1}{2}|\nabla h|^2\right) = \nabla^2 h \cdot \nabla h, \quad \Delta\left(\frac{1}{2}|\nabla h|^2\right) = \nabla^2 h : \nabla^2 h + \nabla(\Delta h) \cdot \nabla h,$$

it follows that

$$\begin{aligned}\mathcal{L}\left(\frac{1}{2}|\nabla h|^2\right) &= \frac{1}{\beta}\left(\nabla^2 h : \nabla^2 h + \nabla(\Delta h) \cdot \nabla h\right) - (\nabla V)^T(\nabla^2 h)\nabla h \\ &\geqslant \nabla(\mathcal{L}h) \cdot \nabla h + (\nabla h)^T(\nabla^2 V)\nabla h \\ &\geqslant \nabla(\mathcal{L}h) \cdot \nabla h + R|\nabla h|^2,\end{aligned}$$

where we have used $\nabla^2 h : \nabla^2 h \geqslant 0$ in the second line, and the assumption on $\nabla^2 V$ in the third one. We next replace h with $\ln f(t)$ and obtain

$$\frac{1}{2}\frac{d}{dt}[\mathcal{I}(\psi(t) \mid \nu)] \leqslant -R\int_{\mathcal{D}} |\nabla(\ln f(t))|^2\, f(t) d\nu = -R\mathcal{I}(\psi(t) \mid \nu).$$

This shows that the Fisher information converges exponentially fast to zero:

$$\mathcal{I}(\psi(t) \mid \nu) \leqslant \mathrm{e}^{-2Rt}\mathcal{I}(\psi(0) \mid \nu). \tag{4.46}$$

The next step is to prove that $\mathcal{H}(\psi(t,\cdot) \mid \nu)$ converges to 0 as $t \to +\infty$. To this end, we use the argument provided in [14]. Note first that the inequality

$$\forall x \geqslant 0, \qquad 0 \leqslant x\ln x - x + 1 \leqslant (x-1)^2$$

implies the following bound

$$\mathcal{H}(\psi(t)\,|\,\nu) \leqslant \frac{1}{2}\left\|\frac{\psi(t)}{\nu} - \mathbf{1}\right\|^2_{L^2(\nu)} = \|f(t) - \mathbf{1}\|^2_{L^2(\nu)}\,. \tag{4.47}$$

Since the operator $-\mathcal{L}$ is self-adjoint on $L^2(\nu)$ and positive by (4.29), its spectral measure P_λ is supported by $[0, +\infty)$ (see [225] and [59] for the definition of the spectral measure). In addition, (4.29) also shows that 0 is a non-degenerate eigenvalue whose associated eigenvectors are constant functions. Therefore,

$$f(t) = \mathrm{e}^{t\mathcal{L}} f_0 = P_0 f_0 + \int_{(0,+\infty)} \mathrm{e}^{-t\lambda}\, d\,(P_\lambda f_0)\,.$$

In fact, P_0 is the projector onto the eigenspace associated with the eigenvalue 0, so that $P_0 f_0 = \int_{\mathcal{D}} f_0 d\nu = 1$. Moreover,

$$\|f(t) - \mathbf{1}\|^2_{L^2(\nu)} = \int_{(0,+\infty)} \mathrm{e}^{-2t\lambda}\, m_{f_0}(d\lambda), \qquad m_{f_0}(d\lambda) = d\left(\|P_\lambda f_0\|^2_{L^2(\nu)}\right).$$

By dominated convergence, the integral on the right-hand side of the above equality converges to 0 as $t \to +\infty$.

The conclusion now follows by a time integration of (4.45) together with the decay estimate (4.46), which leads to

$$\mathcal{H}(\psi_0 \mid \nu) - \mathcal{H}(\psi(t,\cdot) \mid \nu) = \frac{1}{\beta}\int_0^t \mathcal{I}(\psi(s) \mid \nu)\, ds \leqslant \frac{1}{2\beta R}\mathcal{I}(\psi_0 \mid \nu).$$

In the limit $t \to +\infty$, this inequality becomes

$$\mathcal{H}(\psi_0 \mid \nu) \leqslant \frac{1}{2\beta R}\mathcal{I}(\psi_0 \mid \nu),$$

which gives the claimed LSI since ψ_0 is arbitrary. □

Remark 4.7. *It is possible to prove that certain non gradient drifts lead to a faster convergence to ν for solutions of* (4.11) *compared to the reversible dynamics* (4.1)*, which allows to obtain better estimates on the LSI constant; see [13], where the computations of the proof of Theorem 4.3 are generalized to dynamics with multiplicative noise and non gradient drifts. In particular, the spectral argument based on the selfadjointness of the generator has to be modified, see [13, Theorem 2.5] whose proof relies on Vitali's convergence theorem.*

Theorem 4.4 (Holley–Stroock). *If ν satisfies LSI(R) and if $\widetilde{V} : \mathcal{D} \to \mathbb{R}$ is a bounded function, then $\widetilde{\nu} = \widetilde{Z}^{-1}\,\mathrm{e}^{-\widetilde{V}}\,\nu$ satisfies LSI($\widetilde{R}$) with $\widetilde{R} = R\,\mathrm{e}^{\inf \widetilde{V} - \sup \widetilde{V}}$.*

Proof. Introduce $\phi(x) = x\ln x - 1 + x$. Consider any function $f \geqslant 0$ such that

$$\int_{\mathcal{D}} f d\widetilde{\nu} = 1, \tag{4.48}$$

and denote by $\overline{f}$ the average of f with respect to ν:

$$\overline{f} = \int_{\mathcal{D}} f d\nu. \tag{4.49}$$

Then

$$\begin{aligned}\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) &= \int_{\mathcal{D}} f\ln f\, d\widetilde{\nu} = \int_{\mathcal{D}} \phi(f) d\widetilde{\nu} \\ &\leqslant \int_{\mathcal{D}} \left[\phi(f) - (\phi(\overline{f}) + \phi'(\overline{f})(1-\overline{f}))\right] d\widetilde{\nu} = \int_{\mathcal{D}} \left[\phi(f) - \phi(\overline{f}) + \phi'(\overline{f})(\overline{f} - f)\right] d\widetilde{\nu},\end{aligned}$$

since the convexity of ϕ implies that $\phi(1) = 0 \geqslant \phi(\overline{f}) + \phi'(\overline{f})(1-\overline{f})$, and where we have used (4.48) to obtain the last line. Note that $\phi(f(q)) - \phi(\overline{f}) + \phi'(\overline{f})(\overline{f} - f(q)) \geqslant 0$, still by the convexity of ϕ. Since the integrand is non-negative, we can therefore reintroduce ν as follows:

$$\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) \leqslant \frac{Z}{\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \int_{\mathcal{D}} \left[\phi(f) - \phi(\overline{f}) + \phi'(\overline{f})(\overline{f} - f)\right] d\nu = \frac{Z}{\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \left(\int_{\mathcal{D}} \phi(f)\, d\nu - \phi(\overline{f})\right),$$

in view of (4.49). On the other hand,

$$\int_{\mathcal{D}} \phi(f)\, d\nu - \phi(\overline{f}) = \int_{\mathcal{D}} f\ln f\, d\nu - \overline{f}\ln\overline{f} = \overline{f}\int_{\mathcal{D}} \frac{f}{\overline{f}}\ln\frac{f}{\overline{f}}\, d\nu = \overline{f}\int_{\mathcal{D}} \phi\left(\frac{f}{\overline{f}}\right) d\nu.$$

Since ν satisfies LSI(R), and $f/\overline{f}$ has integral 1 with respect to ν,

$$\int_{\mathcal{D}} \phi\left(\frac{f}{\overline{f}}\right) d\nu \leqslant \frac{1}{2R}\int_{\mathcal{D}} \left|\nabla \ln\left(\frac{f}{\overline{f}}\right)\right|^2 \left(\frac{f}{\overline{f}}\right) d\nu = \frac{1}{2R\overline{f}}\int_{\mathcal{D}} |\nabla(\ln f)|^2 f d\nu.$$

In conclusion,

$$\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) \leqslant \frac{Z}{2R\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \int_{\mathcal{D}} |\nabla(\ln f)|^2 f\, d\nu \leqslant \frac{1}{2R}\,\mathrm{e}^{\sup \widetilde{V} - \inf \widetilde{V}} \int_{\mathcal{D}} |\nabla(\ln f)|^2 f d\widetilde{\nu},$$

which gives the claimed statement. □

LSI and metastability

Theorem 4.4 gives lower bounds on the LSI constants. It suggests that the LSI constant, hence the rate of convergence to equilibrium of the overdamped Langevin dynamics, decreases exponentially as the temperature decreases and/or energetic barriers increase. Consider for instance the low-temperature regime $\beta \to +\infty$, for a reference convex potential $V_0(q) = a|q|^2/2$ with $a > 0$, perturbed by a bounded potential $\widetilde{V}$, for instance $\widetilde{V}(q) = b\exp(-|q|^2)$ with $b > 0$. In this case, Theorem 4.3 shows that the canonical measure associated with V, at inverse temperature β, satisfies LSI(βa), while the canonical measure associated with $V+\widetilde{V}$, at inverse temperature β, satisfies LSI($\beta a\,\mathrm{e}^{-\beta b}$) by Theorem 4.4. The LSI constants obtained by the Holley–Stroock perturbative argument are of course lower bounds, but it is indeed expected that the optimal constant decreases exponentially fast as the temperature decreases when the potential exhibits energetic barriers. This can be rigorously proven in one dimensional systems for example, see [193, Section 2.4].

Relationship with Poincaré inequalities

Initial conditions ψ_0 belonging to $L^2(\nu)$ also have a finite relative entropy with respect to ν in view of (4.47) (with $\psi(t)$ replaced by ψ_0). This shows that LSI allow to cover a larger set of initial conditions than Poincaré inequalities. Unsurprisingly, the following result shows that LSIs are stronger than Poincaré inequalities.

Proposition 4.5 (LSI implies Poincaré inequality). *If a measure ν satisfies an LSI with constant $R > 0$, then it satisfies a Poincaré inequality with the same constant.*

Probability measures associated with potentials growing as $|q|^\alpha$ at infinity for some $\alpha > 1$ satisfy Poincaré inequalities by Theorem 4.1. On the other hand, they satisfy LSI only for $\alpha \geqslant 2$, since it can be shown that probability measures satisfying a LSI necessarily integrate functions of the form $\exp(a|q|^2)$ for some $a > 0$ (see [20, Proposition 5.4.1]).

Proof. The idea of the proof is that the Poincaré inequality can be seen as a linearization of the logarithmic Sobolev inequality. Fix a function $\phi \in C^\infty(\mathcal{D})$ with compact support, with nonnegative values and average 1 with respect to ν, and start from the LSI

$$\int_{\mathcal{D}} \phi \ln \phi \, d\nu \leqslant \frac{1}{2R} \int_{\mathcal{D}} \frac{|\nabla \phi|^2}{\phi} \, d\nu.$$

The function ϕ can be chosen of the form $\phi = 1+\varepsilon\varphi$ where $\varphi \in C^\infty(\mathcal{D})$ has average 0 with respect to ν. For $0 < \varepsilon \leqslant 1/(2\sup_{\mathcal{D}} |\varphi|)$,

$$\int_{\mathcal{D}} (1+\varepsilon\varphi)\ln(1+\varepsilon\varphi)\, d\nu \leqslant \frac{\varepsilon^2}{2R} \int_{\mathcal{D}} \frac{|\nabla\varphi|^2}{1+\varepsilon\varphi}\, d\nu = \frac{\varepsilon^2}{2R}\left(\int_{\mathcal{D}} |\nabla\varphi|^2\, d\nu + \mathrm{O}(\varepsilon)\right). \tag{4.50}$$

Since

$$(1+\varepsilon\varphi)\ln(1+\varepsilon\varphi) = \varepsilon\varphi + \frac{1}{2}(\varepsilon\varphi)^2 + \mathrm{O}(\varepsilon^3),$$

and using the fact that φ has average 0 with respect to ν, it follows that

$$\int_{\mathcal{D}} (1+\varepsilon\varphi)\ln(1+\varepsilon\varphi)\, d\nu = \frac{\varepsilon^2}{2}\left(\int_{\mathcal{D}} \varphi^2\, d\nu + \mathrm{O}(\varepsilon)\right).$$

By dividing both sides of (4.50) by $\varepsilon^2/2$ and taking the limit $\varepsilon \to 0$, we obtain the following inequality for bounded functions φ with average 0 with respect to ν:

$$\int_{\mathcal{D}} \varphi^2\, d\nu \leqslant \frac{1}{R}\int_{\mathcal{D}} |\nabla\varphi|^2\, d\nu.$$

The Poincaré inequality (4.26) can finally be deduced by a density argument. □

4.3.4 Convergence in weighted B^∞ spaces

We discuss in this section the convergence of the semigroup $\mathrm{e}^{t\mathcal{L}}$, which describes how average properties converge to their stationary values. Convergence results in weighted B^∞ spaces very similar to the ones obtained for Markov chains (see Theorem 3.1) can be stated for diffusion processes. We will therefore be very brief, and mention only the required adpations with respect to the setting introduced in Section 3.3.1.

Let us start by emphasizing that the convergence results provided here are for the semigroup $\mathrm{e}^{t\mathcal{L}}$, which describes how average properties converge to their stationary values. Similar convergence results can then be deduced on the Fokker–Planck semigroup $\mathrm{e}^{t\mathcal{L}^\dagger}$. This semigroup is defined in a space of probability measures integrating the inverse of the weight function used to define the weighted B^∞ spaces. In some cases, as for the overdamped Langevin dynamics, the adjoints $\mathcal{L}^*$ of the generator on L^2 spaces weighted by the canonical measure is similar to $\mathcal{L}$ (equal here), which allows to easily extend convergence results stated for $\mathrm{e}^{t\mathcal{L}}$ to $\mathrm{e}^{t\mathcal{L}^*}$ and therefore to $\mathrm{e}^{t\mathcal{L}^\dagger}$.

To state the result, we consider a Lyapunov function $\mathscr{W} : \mathcal{D} \to [1, +\infty)$ (let us emphasize that the Lyapunov function has values larger than 1 here, in contrast to the setting of Section 3.3.1), and introduce the space $B^\infty_{\mathscr{W}}(\mathcal{D})$ of measurable functions φ such that

$$\|\varphi\|_{B^\infty_{\mathscr{W}}} = \left\| \frac{\varphi}{\mathscr{W}} \right\|_{B^\infty} < +\infty. \tag{4.51}$$

the notation does not refer to ν... is this an issue?

We denote by $B^\infty_{\mathscr{W},0}(\mathcal{D})$ the subspace of $B^\infty_{\mathscr{W}}(\mathcal{D})$ of functions with average 0 with respect to ν.

Theorem 4.5. *Assume that $\mathcal{D}$ is bounded or that there are $A > 0$ and $B \in \mathbb{R}$ such that*

$$q \cdot \nabla V(q) \geqslant A|q|^2 - B. \tag{4.52}$$

Then, for any $n \geqslant 2$, there exist $C_n, \kappa_n > 0$ such that the following decay estimate holds for the Lyapunov function $\mathscr{W}_n(q) = 1 + |q|^n$:

$$\forall \varphi \in B^\infty_{\mathscr{W}_n}(\mathcal{D}), \qquad \left\| \mathrm{e}^{t\mathcal{L}}\varphi - \int_{\mathcal{D}} \varphi \, d\nu \right\|_{B^\infty_{\mathscr{W}_n}} \leqslant C_n \mathrm{e}^{-\kappa_n t} \|\varphi\|_{B^\infty_{\mathscr{W}_n}}. \tag{4.53}$$

ajouter fct Lyapunov expo, cf. conditions moins fortes sur V ! calculs faits pex dans /home/gabriel/travail/NonequilibriumMD/general_refs/Presentation_ReyBellet.pdf

The condition (4.52) is satisfied for potentials $V(q)$ behaving at infinity as $|q|^k$ with $k \geqslant 2$. Note that, for simplicity, we state the result for the dynamics (4.1) with a force $-\nabla V(q)$ which is a gradient field. The results obtained below can however easily be extended to more general force fields $b(q)$, upon replacing (4.52) by $q \cdot b(q) \leqslant -A|q|^2 + B$. This is one of the main interest of weighted B^∞ estimates: they do not require structural assumptions on the type of dynamics considered. This is in sharp constrast with the analysis developed in Sections 4.3.3 and 4.3.2, and will prove useful in Lecture 8 in particular.

The key element in the proof is to define an appropriate transition kernel $P(q, dq')$ to apply the analysis of Section 3.3.1. A natural way to define a transition kernel for the overdamped Langevin dynamics (4.1) is the following, for a given time $t_0 > 0$: for any measurable set S,

$$P(q, S) = \mathbb{E}^q(\mathbf{1}_S(q_{t_0})). \tag{4.54}$$

Here $\mathbb{E}^q$ is the expectation over the realizations of (4.1) starting from $q_0 = q$, and $\mathbf{1}_S$ is the indicator function of the set S. The operator associated with the integral kernel (4.54) is therefore $P = \mathrm{e}^{t_0\mathcal{L}}$.

Proof. We first discuss how to establish the Lyapunov condition (Assumption 3.1 in Section 3.3.1). Let us start by recalling that it is trivial to satisfy a Lyapunov condition when the state space is compact, by choosing $\mathscr{W} = \mathbf{1}$. This situation is encountered for overdamped Langevin dynamics when $\mathcal{D}$ is compact. For overdamped Langevin dynamics in unbounded position spaces, the

Lyapunov condition can be established on the basis of a differential Lyapunov condition stated in terms of the generator of the dynamics. Indeed, assume that the following inequality is true for some $a_1 > 0$ and $a_2 \geqslant 0$, and a given Lyapunov function $\mathscr{W} \geqslant 1$:

$$\mathcal{L}\mathscr{W} \leqslant -a_1 \mathscr{W} + a_2. \tag{4.55}$$

Then,

$$\frac{d}{dt}\left(\mathrm{e}^{t\mathcal{L}}\mathscr{W}\right) = \mathrm{e}^{t\mathcal{L}}\mathcal{L}\mathscr{W} \leqslant -a_1 \mathrm{e}^{t\mathcal{L}}\mathscr{W} + a_2,$$

so that, by a Gronwall inequality,

$$\mathrm{e}^{t\mathcal{L}}\mathscr{W} \leqslant \mathrm{e}^{-a_1 t}\mathscr{W} + \frac{a_2}{a_1}(1 - \mathrm{e}^{-a_1 t}) \leqslant \mathrm{e}^{-a_1 t}\mathscr{W} + \frac{a_2}{a_1}. \tag{4.56}$$

In particular, for $t = t_0$, we obtain

$$P\mathscr{W} \leqslant \mathrm{e}^{-a_1 t_0}\mathscr{W} + \frac{a_2}{a_1}, \tag{4.57}$$

which is the condition of Assumption 3.1 with $\gamma = \mathrm{e}^{-a_1 t_0} \in (0,1)$ and $K = a_2/a_1 \geqslant 0$. We therefore choose $\mathscr{W}$ in order for (4.55) to be satisfied. For overdamped Langevin dynamics in unbounded spaces, a typical choice is $\mathscr{W}_n(q) = 1 + |q|^n$ for $n \geqslant 2$. In this case,

$$\mathcal{L}\mathscr{W}_n(q) = n\left(-\nabla V(q)\cdot q + \frac{D+n-2}{\beta}\right)|q|^{n-2}.$$

With (4.52), the Lyapunov condition (4.55) indeed holds since

$$\mathcal{L}\mathscr{W}_n(q) \leqslant -An\mathscr{W}_n(q) + \frac{n(D+n-2)}{\beta}|q|^{n-2} + Bn,$$

so that

$$\lim_{|q|\to+\infty} \frac{\mathcal{L}\mathscr{W}_n(q)}{\mathscr{W}_n(q)} \leqslant -An.$$

This shows that there exist $c_n \in \mathbb{R}$ such that

$$\mathcal{L}\mathscr{W}_n \leqslant -\frac{An}{2}\mathscr{W}_n + c_n. \tag{4.58}$$

The minorization condition can be obtained by an argument similar to the one used to prove Lemma 4.1, see for instance [189, Lemma 2.3]. In this part of the argument, we denote by $P_t = \mathrm{e}^{t\mathcal{L}}$. Fix first some $q^* \in \mathcal{D}$, and note that $P_{t_0/2}(q^*, B_\eta(q^*)) > 0$ for $\eta > 0$ by the open set irreducibility. There exists therefore $Q^* \in \mathcal{D}$ and $\varepsilon > 0$ such that $p(t_0/2, q^*, Q^*) \geqslant 2\varepsilon$. By continuity of the transition density, there exists $r > 0$ such that $p(t_0/2, q', Q') \geqslant \varepsilon$ for any $q' \in B_r(q^*)$ and $Q' \in B_r(Q^*)$. Then, for any $S \in \mathscr{B}(\mathcal{D})$ and any $q' \in B_r(q^*)$,

$$P_{t_0/2}(q', S) = \int_S p\left(t_0/2, q', Q\right) dQ \geqslant \int_{S\cap B_r(Q^*)} p\left(t_0/2, q', Q\right) dQ \geqslant \varepsilon \left|S \cap B_r(Q^*)\right|.$$

We also note that, for any compact set $\mathscr{C} \subset \mathcal{D}$,

$$\inf_{q\in\mathscr{C}} P_{t_0/2}(q, B_r(q^*)) \geqslant \rho > 0,$$

by the open set accessibility and the continuity of the mapping $q \mapsto P_{t_0/2}(q, B_r(q^*))$. Therefore (recalling $P = P_{t_0}$ with the notation we introduced)

$$\begin{aligned} P(q,S) &\geqslant \int_{B_r(q^*)} p(t_0/2, q, q') P_{t_0/2}(q', S)\, dq' \geqslant \varepsilon \left|S \cap B_r(Q^*)\right| \int_{B_r(q^*)} p(t_0/2, q, q')\, dq' \\ &\geqslant \rho\varepsilon \left|S \cap B_r(Q^*)\right|, \end{aligned}$$

which indeed provides the condition in Assumption 3.2 with $\alpha = \rho\varepsilon\,|B_r(Q^*)|$ and $\lambda(S) = |S \cap B_r(Q^*)|\,/\,|B_r(Q^*)|$ the uniform probability measure on $B_r(Q^*)$.

At this stage, we have discussed how to obtain Assumption 3.1 for $n \geqslant 2$ given, as well as Assumption 3.2. This already implies the decay estimates (3.12) by Theorem 3.1: there exist $C_n \in \mathbb{R}_+$ and $r_n \in (0,1)$ such that

$$\forall k \geqslant 1, \qquad \left\|\mathrm{e}^{kt_0\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}_n}} \leqslant C_n r_n^k \|\varphi\|_{B^\infty_{\mathscr{W}_n}}$$

These bounds correspond to evolutions observed at integer multiples of the reference time t_0. Let us now finally show how to deduce an exponential convergence result at all times $t \geqslant 0$. We decompose to this end the time t as $t = kt_0 + \theta$ with $\theta \in [0, t_0)$. Then, for any $\varphi \in B^\infty_{\mathscr{W},0}(\mathcal{D})$, we obtain

$$\left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}_n}} \leqslant C_n r_n^k \left\|\mathrm{e}^{\theta\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}_n}} \leqslant C_n r_n^k \sup_{0\leqslant s\leqslant t_0} \left\|\mathrm{e}^{s\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}_n}}. \tag{4.59}$$

Now, the inequality

$$\forall q \in \mathcal{D}, \qquad |\varphi(q)| \leqslant \|\varphi\|_{B^\infty_{\mathscr{W}_n}} \mathscr{W}_n(q),$$

leads to

$$\left\|\mathrm{e}^{s\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}_n}} \leqslant \|\varphi\|_{B^\infty_{\mathscr{W}_n}} \left\|\frac{\mathrm{e}^{s\mathcal{L}}\mathscr{W}_n}{\mathscr{W}_n}\right\|_{B^\infty}.$$

In view of the inequalities (4.56) and (4.58), it holds, for any $s \geqslant 0$,

$$\left\|\frac{\mathrm{e}^{s\mathcal{L}}\mathscr{W}_n}{\mathscr{W}_n}\right\|_{B^\infty} \leqslant \mathrm{e}^{-Ans/2} + \frac{2c_n}{An}\left\|\frac{1}{\mathscr{W}_n}\right\|_{B^\infty} \leqslant 1 + \frac{2c_n}{An}.$$

Upon introducing $\kappa_n = -\log(r_n)/t_0 > 0$, (4.59) implies

$$\left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|_{B^\infty_{\mathscr{W}}} \leqslant C_n\left(1 + \frac{2c_n}{An}\right)\mathrm{e}^{-\kappa_n k t_0}\|\varphi\|_{B^\infty_{\mathscr{W}}} \leqslant \widetilde{C}_n \mathrm{e}^{-\kappa_n t}\|\varphi\|_{B^\infty_{\mathscr{W}_n}},$$

with

$$\widetilde{C} = C\left(1 + \frac{2c_n}{An}\right)\mathrm{e}^{\kappa_n t_0}.$$

This allows to conclude (4.53). □

Remark 4.8 (Compactness of the evolution operator). *As made precise in [228, Theorem 8.9], the evolution operator $\mathrm{e}^{t_0\mathcal{L}}$ can be shown to be compact when the constant a in (4.55) can be chosen arbitrary large. Typical Lyapunov functions to this end are $W_\theta(q) = \mathrm{e}^{\theta V(q)}$ for $\theta < \beta$. Indeed,*

$$\frac{\mathcal{L}W_\theta}{W_\theta} = -\theta\left[\left(1 - \frac{\theta}{\beta}\right)|\nabla V|^2 - \frac{1}{\beta}\Delta V\right],$$

which converges to $-\infty$ as $|q| \to +\infty$ when $V(q)$ behaves asymptotically as $|q|^n$ with $n > 1$. This the counterpart in weighted B^∞ spaces of Sobolev inequalities which guarantee the compactness of the evolution operator (or of the resolvent) in a $L^2(\nu)$ setting (see [20, Chapter 6]).

mal dit... a garder ?

Remark 4.9 (sub-exponential convergence rates). *It is possible to weaken the Lyapunov condition (4.55) for instance as $\mathcal{L}\mathscr{W} \leqslant -\phi(\mathscr{W}) + b$, where ϕ is a non-negative, non-decreasing, concave function such that $\phi(x)/x \to 0$ as $x \to +\infty$. In this case, algebraic rates of decay are typically obtained instead of exponential ones; see [73, 52] for further details.*

The exponential convergence result (4.53) leads to the following bounds on the resolvent, by a direct application of Proposition 4.1.

Corollary 4.2. *Consider one of the following situations: the position space is compact, in which case $\mathscr{W} = \mathbf{1}$; or (4.52) holds, in which case $\mathscr{W}_n(q) = 1 + |q|^n$ for some $n \geqslant 2$. Then the operator $\mathcal{L}$ is invertible on $B^\infty_{\mathscr{W}_n,0}(\mathcal{D})$, and the following equality holds in $\mathcal{B}(B^\infty_{\mathscr{W}_n,0})$:*

$$\mathcal{L}^{-1} = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}}\, dt.$$

Moreover,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(B^\infty_{\mathscr{W}_n,0})} \leqslant \frac{C_n}{\kappa_n}, \tag{4.60}$$

where C_n, κ_n are the same constants as in Theorem 4.5.

Although it is possible to keep track of the values of the various constants until (4.53), the final rate of convergence in weighted B^∞ spaces is often not very sharp. The difficult point is in general to obtain a good control on the constant α in the minorization condition of Assumption 3.2.

4.4 Complements

pas relu

4.4.1 Convergence of general entropy functions

We present in this section convergence results in the metric formally defined by the generalized entropy

$$e_u(\pi_1, \pi_2) = \int_{\mathcal{D}} u\left(\frac{d\pi_1}{d\pi_2}\right) d\pi_2.$$

The choice $u(x) = (x-1)^2$, $\pi_2 = \nu$ and $\pi_1 = f\pi_2$ with $f \in L^2(\nu)$ corresponds to the framework considered in Section 4.3.2, while the choice $u(x) = x \ln x - x + 1$, $\pi_2 = \nu$ and $\pi_1 = f\pi_2$ with $f \ln f \in L^1(\nu)$ corresponds to the framework of Section 4.3.3. We consider here the following general entropy functions.

Assumption 4.1. *The function u belongs to $C^0([0,+\infty)) \cap C^4((0,+\infty))$, is convex with $u'' > 0$ on $(0,+\infty)$, and satisfies the following inequality:*

$$\forall x > 0, \qquad u''(x)u^{(4)}(x) - 2\left(u^{(3)}(x)\right)^2 \geqslant 0.$$

Typical examples are the Tsallis relative entropies

$$u_p(x) = \frac{x^p - px}{p-1} + 1, \qquad 1 < p \leqslant 2.$$

Most of the computations presented in this section are formal, but can be given a precise meaning as in [14, 13]. We follow the presentation in [19].

The evolution we consider is only more general than the overdamped Langevin dynamics. It is characterized by its generator $\mathcal{L}$, which defines the following differential forms (which prove useful to simplify the computations):

$$\begin{aligned}
\Gamma(f,g) &= \frac{1}{2}\left(\mathcal{L}(fg) - f\mathcal{L}g - g\mathcal{L}f\right), \\
\Gamma_2(f,g) &= \frac{1}{2}\Big(\mathcal{L}\left[\Gamma(f,g)\right] - \Gamma(\mathcal{L}f, g) - \Gamma(f, \mathcal{L}g)\Big).
\end{aligned}$$

For the SDE $dq_t = b(q_t)\,dt + B(q_t)\,dW_t$, it holds $\Gamma(f,g) = \nabla f^T A \nabla g$ with $A = BB^T$. The expression of Γ_2 is more complicated (see [19, Proposition 3]). For $B = \sqrt{2}\mathrm{Id}$, one finds

$$\Gamma_2(f,f) = \nabla^2 f : \nabla^2 f - \frac{1}{2}\nabla f^T(\nabla b + \nabla b^T)\nabla f.$$

As will be made clear in the computations below, the expression of the drift b can be more general than in (4.9), as long as the dynamics preserves the invariant measure. This freedom was used in [13] for generalize the approach of [19].

Consider now $f(t) = \mathrm{e}^{t\mathcal{L}} f_0$ for some given initial condition f_0. Note that, in contrast to the approach of Section 4.3.3 (but consistently with the approach of Section 4.3.2), we work here with the evolution operator $\mathrm{e}^{t\mathcal{L}}$ and not the semigroup associated with the Fokker–Planck equation. Since $\mathcal{L}\left[u(f(t))\right] = u'(f(t))\mathcal{L}f(t) + u''(f(t))\Gamma(f(t), f(t))$ and ν is invariant by $\mathcal{L}$, it holds

$$\frac{d}{dt}\Big[e_u(f(t)\nu, \nu)\Big] = \int_{\mathcal{D}} u'(f(t))\mathcal{L}f(t)\,d\nu = -I_u(f(t)\nu, \nu), \tag{4.61}$$

where the entropy dissipation reads

$$I_u(\pi_2, \pi_2) = \int_{\mathcal{D}} u''\left(\frac{d\pi_1}{d\pi_2}\right)\Gamma\left(\frac{d\pi_1}{d\pi_2}, \frac{d\pi_1}{d\pi_2}\right) d\pi_2.$$

Following the strategy of proof of Theorem 4.3, we derive the entropy dissipation in time:

$$\frac{d}{dt}\Big[I_u(f(t)\nu,\nu)\Big] = \frac{d}{dt}\left(\int_{\mathcal{D}} u''(f(t))\Gamma(f(t),f(t))\,d\nu\right) = -R_u(f(t)\nu,\nu),$$

with

$$R_u(\pi_1,\pi_2) = \int_{\mathcal{D}} u^{(3)}\left(\frac{d\pi_1}{d\pi_2}\right)\Gamma\left(\frac{d\pi_1}{d\pi_2},\frac{d\pi_1}{d\pi_2}\right)\mathcal{L}\left(\frac{d\pi_1}{d\pi_2}\right)d\pi_2 + 2\int_{\mathcal{D}} u''\left(\frac{d\pi_1}{d\pi_2}\right)\Gamma\left[\mathcal{L}\left(\frac{d\pi_1}{d\pi_2}\right),\frac{d\pi_1}{d\pi_2}\right]d\nu.$$

At this stage, some assumption is needed in order to obtain the decay of the entropy dissipation.

Assumption 4.2. *There exist $\rho > 0$ and $m \in [0,1)$ such that, for all smooth and compactly supported functions g, it holds*

$$\Gamma_2(g,g) \geqslant \rho\Gamma(g,g) + m(\mathcal{L}g)^2.$$

For $B = \sqrt{2}\mathrm{Id}$, the above condition reduces to

$$\nabla^2 g : \nabla^2 g - \frac{1}{2}\nabla g^T(\nabla b + \nabla b^T)\nabla g \geqslant \rho|\nabla g|^2 + m(\mathcal{L}g)^2.$$

When $b = -\beta\nabla V$ (which ensures that the canonical measure ν is indeed invariant), a sufficient condition for this inequality to hold with $m = 0$ is that $\nabla^2 V \geqslant \rho/\beta$, which coincides with the assumption in Theorem 4.3.

Assumption 4.2 ensures that the following key coercivity property holds.

Proposition 4.6. *Under Assumption 4.2, it holds, for any smooth and compactly supported function g,*

$$R_u(g\nu,\nu) \geqslant \frac{2\rho}{1-m} I_u(g\nu,\nu).$$

A Gronwall inequality then shows that $I_u(f(t)\nu,\nu) \leqslant I_u(f_0\nu,\nu)\,\mathrm{e}^{-2\rho t/(1-m)}$. We next integrate in time (4.61), and conclude as in the proof of Theorem 4.3 to the exponential decay of the entropy, and hence to the validity of some functional inequality such as a log-Sobolev inequality or a Poincaré inequality (depending on the choice of u). To prove that the entropy goes to zero (without making precise the rate), the spectral approach used in the proof of Theorem 4.3 no longer works. It was shown in [13, Theorem 2.5] how to circumvent this difficulty relying on Vitali's convergence theorem.

In order to write the proof of Proposition 4.6, we first need a technical result.

Lemma 4.2. *Assumption 4.2 implies that, for smooth and compactly supported functions v, g,*

$$\begin{aligned} v'(g)^2\Gamma_2(g,g) + v'(g)v''(g)\Gamma\Big(g,\Gamma(g,g)\Big) + v''(g)^2\Gamma(g,g)^2 \\ \geqslant \rho v'(g)^2\Gamma(g,g) + m\left[v'(g)\mathcal{L}g + v''(g)\Gamma(g,g)\right]^2. \end{aligned}$$

Proof (of Lemma 4.2). The changes on the right-hand side of the inequality to prove are obtained by straightforward computations. For the left-hand side, we note that

$$2\Gamma_2(v(g),v(g)) = \mathcal{L}\left[\Gamma(v(g),v(g))\right] - 2\Gamma(\mathcal{L}v(g),v(g)). \tag{4.62}$$

Now, $\Gamma(v(g),v(g)) = v'(g)^2\Gamma(g,g)$ so that

$$\begin{aligned} \mathcal{L}\left[\Gamma(v(g),v(g))\right] &= v'(g)^2\mathcal{L}\Gamma(g,g) + \Gamma(g,g)\mathcal{L}\left(v'(g)^2\right) + 2\Gamma\left(v'(g)^2,\Gamma(g,g)\right) \\ &= v'(g)^2\mathcal{L}\Gamma(g,g) + 2\Gamma(g,g)\left[\Gamma\left(v'(g),v'(g)\right) + v'(g)\mathcal{L}\left(v'(g)\right)\right] + 2\Gamma\left(v'(g)^2,\Gamma(g,g)\right) \\ &= v'(g)^2\mathcal{L}\Gamma(g,g) + 2\Gamma(g,g)\left[v''(g)^2\Gamma\left(g,g\right) + v'(g)v''(g)\mathcal{L}g + 2v'(g)v^{(3)}(g)\Gamma(g,g)\right] \\ &\quad + 4v'(g)v''(g)\Gamma\left(g,\Gamma(g,g)\right). \end{aligned}$$

Moreover,

$$\begin{aligned}\Gamma(\mathcal{L}v(g), v(g)) &= \Gamma(v'(g)\mathcal{L}g, v(g)) + \Gamma\Big(v''(g)\Gamma(g,g), v(g)\Big) \\ &= v'(g)v''(g)\Gamma(g,g)\mathcal{L}g + v'(g)^2\Gamma(\mathcal{L}g, g) + v'(g)v''(g)\Gamma\Big(g, \Gamma(g,g)\Big) + v'(g)v^{(3)}(g)\Gamma(g,g)^2.\end{aligned}$$

The conclusion then follows by gathering the various terms in (4.62). □

Proof (of Proposition 4.6). We use the following equality for the first term on the right-hand side of $R_u(g\nu, \nu)$ (with $v = u''$ and $g = f(t)$):

$$\begin{aligned}\int_{\mathcal{D}} v'(g)\Gamma(g,g)\mathcal{L}g\, d\nu &= \int_{\mathcal{D}} \Gamma\Big(g, v'(g)\Gamma(g,g)\Big) d\nu \\ &= -\int_{\mathcal{D}} v'(g)\Gamma\Big(g, \Gamma(g,g)\Big) d\nu - \int_{\mathcal{D}} v''(g)\Gamma(g,g)^2\, d\nu, \end{aligned} \tag{4.63}$$

and the following one for the second term (obtained from the definition of Γ_2):

$$\begin{aligned}\int_{\mathcal{D}} v(g)\Gamma(g, \mathcal{L}g)\, d\nu &= -\int_{\mathcal{D}} v(g)\Gamma_2(g,g)\, d\nu - \frac{1}{2}\int_{\mathcal{D}} v(g)\mathcal{L}\left[\Gamma(g,g)\right] d\nu \\ &= -\int_{\mathcal{D}} v(g)\Gamma_2(g,g)\, d\nu - \frac{1}{2}\int_{\mathcal{D}} v'(g)\Gamma\Big(g, \Gamma(g,g)\Big) d\nu, \end{aligned} \tag{4.64}$$

Then,

$$R_u(g\nu, \nu) = \int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\, d\nu + 2\int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g, \Gamma(g,g\Big) d\nu + 2\int_{\mathcal{D}} u''(g)\Gamma_2(g,g)\, d\nu.$$

We now use Assumption 4.2 to obtain some positiviy, relying on the change of unknown function based on Lemma 4.2 in order to account for the fact that factors $u^{(k)}(g)$ appear.

More precisely, consider the statement of Lemma 4.2 for quadratic functions v. The numbers $a = v'(g(x))$ and $b = v''(g(x))$ can take arbitrary values, so that the non-negativity property can be rephrased as

$$\forall (a,b) \in \mathbb{R}^2, \qquad \begin{pmatrix} a \\ b \end{pmatrix}^T X \begin{pmatrix} a \\ b \end{pmatrix} \geqslant 0,$$

where the matrix $X \in \mathbb{R}^{2\times 2}$ has entries

$$\begin{aligned} X_{1,1} &= \Gamma_2(g,g) - \rho\Gamma(g,g) - m(\mathcal{L}g)^2, \\ X_{1,2} = X_{2,1} &= \frac{1}{2}\Gamma\Big(g, \Gamma(g,g)\Big) - m\Gamma(g,g)\mathcal{L}g, \\ X_{2,2} &= (1-m)\Gamma(g,g)^2. \end{aligned}$$

This shows that X is symmetric non-negative. Since (4.1) implies that, for a given $\xi \in \mathbb{R}$ and any $z \in (0, +\infty)$, the matrix

$$Y_\xi(z) = \begin{pmatrix} u''(z) & \xi u^{(3)}(z) \\ \xi u^{(3)}(z) & \dfrac{\xi^2}{2} u^{(4)}(z) \end{pmatrix}$$

is also symmetric non-negative, we deduce that $F_\xi(z) = \mathrm{Tr}(XY_\xi(z)) \geqslant 0$. An integration of F_ξ with respect to ν leads to

$$\begin{aligned}&\int_{\mathcal{D}} u''(g)\Big(\Gamma_2(g,g) - \rho\Gamma(g,g)\Big) d\nu + \xi\int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g, \Gamma(g,g)\Big) d\nu \\ &+ \frac{\xi^2(1-m)}{2}\int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\, d\nu - m\int_{\mathcal{D}} u''(g)(\mathcal{L}g)^2\, d\nu - 2\xi m\int_{\mathcal{D}} u^{(3)}(g)\Gamma(g,g)\mathcal{L}g\, d\nu \geqslant 0.\end{aligned}$$

For the fourth integral on the left-hand side, we use

$$\int_{\mathcal{D}} v(g)(\mathcal{L}g)^2\,d\nu = -\int_{\mathcal{D}} \Gamma(g, v(g)\mathcal{L}g)\,d\nu = -\int_{\mathcal{D}} v(g)\Gamma(g,\mathcal{L}g)\,d\nu - \int_{\mathcal{D}} v'(g)\Gamma(g,g)\mathcal{L}g\,d\nu,$$

together with (4.63); and (4.64) for the fifth term. This gives

$$\begin{aligned}(1-m)\int_{\mathcal{D}} u''(g)\Gamma_2(g,g)\,d\nu + \Big(\xi - \frac{3m}{2} + 2\xi m\Big)\int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu \\ + \Big(\frac{\xi^2(1-m)}{2} + m(2\xi-1)\Big)\int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\,d\nu \geqslant \rho\int_{\mathcal{D}} u''(g)\Gamma(g,g)\,d\nu.\end{aligned}$$

The choice $\xi_m = (1+m/2)/(1+2m)$ allows to simplify the factor in front of the second integral on the left-hand side as

$$\begin{aligned}\int_{\mathcal{D}} u''(g)\Gamma_2(g,g)\,d\nu + \int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu \\ + \Big(\frac{\xi_m^2}{2} + \frac{m(2\xi_m-1)}{1-m}\Big)\int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\,d\nu \geqslant \frac{\rho}{1-m}\int_{\mathcal{D}} u''(g)\Gamma(g,g)\,d\nu.\end{aligned}$$

Since (using $m \leqslant 1$)

$$\xi_m(1+m) = \frac{1}{1+2m}\Big(1 + \frac{3m}{2} + \frac{m^2}{2}\Big) \leqslant 1,$$

the prefactor in front of the last integral on the left-hand satisfies

$$\frac{\xi_m^2}{2} + \frac{m(2\xi_m-1)}{1-m} = \frac{1}{2(1-m)}\big(\xi_m^2 + m\xi_m - m\big) \leqslant \frac{1}{2}.$$

It remains to note that $u^{(4)} \geqslant 0$ by Assumption 4.1, as well as $\Gamma(g,g) \geqslant 0$, which gives the claimed result since the left-hand side of the above inequality is $R_u(g\nu,\nu)/2$. □

5

The Langevin dynamics

The Langevin dynamics, presented in Section 1.4.2, can be seen as some stochastic perturbation of the Hamiltonian dynamics. From a mathematical viewpoint, it is a stochastic dynamics with degenerate noise, so that the associated generator is not elliptic. This raises several serious issues compared to the overdamped Langevin dynamics studied in Lecture 4. We start by presenting Langevin dynamics in its general form in Section 5.1, where we also relate it precisely to two limiting dynamics, namely Hamiltonian dynamics (studied in Lecture 2) and overdamped Langevin dynamics (which is the focus of Lecture 4). We next make precise some mathematical properties of Langevin dynamics in Section 5.2. We finally discuss the convergence of Langevin dynamics: first through the convergence of trajectory averages in Section 5.3, and next through the convergence of the law of the process in Section 5.4. Some key concepts used in the latter two sections are hypoellipticity and hypocoercivity. Let us also emphasize that we try as much as possible to obtain convergence estimates which allow to cover the limiting regimes of both Hamiltonian dynamics and overdamped Langevin dynamics.

5.1 Description of the Langevin dynamics

We first present Langevin dynamics in a general framework in Section 5.1.1, before considering two limiting regimes: the Hamiltonian limit (Section 5.1.2) and the overdamped limit (Section 5.1.3). We make precise the timescales involved in these limits, which proves crucial to determine the scaling of the convergence rates obtained in Section 5.4 with respect to the parameters of the dynamics.

5.1.1 General structure of the dynamics

The Langevin dynamics reads, for a general (possibly non separable) Hamiltonian $H(q,p)$,

$$\begin{cases} dq_t = \nabla_p H(q_t,p_t)\,dt, \\ dp_t = -\nabla_q H(q_t,p_t)\,dt - \gamma(q_t)\nabla_p H(q_t,p_t)\,dt + \sigma(q_t)\,dW_t, \end{cases} \tag{5.1}$$

where $t \mapsto W_t$ is a D-dimensional standard Brownian motion, and σ and γ are (possibly position dependent) $D\times D$ real matrices. Note that (5.1) can be seen as the superposition of the Hamiltonian dynamics (2.1) and some overdamped Langevin dynamics in the momenta, where the positions enter as parameters. Let us already emphasize that the noise driving (5.1) is degenerate since it acts on momenta only. The analytical translation of this fact is that the generator of the Langevin dynamics is not elliptic (see Section 5.2.1 below).

We will typically consider separable Hamiltonians with quadratic kinetic energies (although some generalizations, such as the use of non-quadratic kinetic energies, may prove benefitial to improve the sampling properties of the method, see for instance [257]). In this case,

$$H(q,p) = \frac{1}{2}p^T M^{-1} p + V(q),$$

so that the evolution equations (5.1) simplify as

$$\begin{cases} dq_t = M^{-1}p_t\,dt, \\ dp_t = -\nabla V(q_t)\,dt - \gamma(q_t)\,M^{-1}p_t\,dt + \sigma(q_t)\,dW_t. \end{cases} \tag{5.2}$$

The term $\sigma(q_t)\,dW_t$ is a fluctuation term bringing energy into the system, this energy being dissipated through the viscous friction term $-\gamma(q_t)\,M^{-1}p_t\,dt$. These two terms are related through the following *fluctuation-dissipation* relation, which ensures that the canonical measure (1.18)

$$\mu(dq\,dp) = Z_\mu^{-1}\exp(-\beta H(q,p))\,dq\,dp \tag{5.3}$$

at the correct temperature is sampled:

$$\sigma\sigma^T = \frac{2\gamma}{\beta}. \tag{5.4}$$

The proof of this statement is provided in Section 5.2.2. Let however remark that it is a quite natural statement since the Hamiltonian part of (5.2) preserves any probability measure which is a function of H, while the Ornstein–Uhlenbeck part of the dynamics forces the marginal in p of the invariant measure to be Gaussian. The combination of these two informations suggests that the canonical measure (5.3) is the only invariant probability measure, and motivates that the fluctuation dissipation relation (5.4) determines the strength of the noise in order to have a Gaussian distribution with the desired variance.

Notice (5.4) implies that γ is a symmetric matrix. Often, γ and σ are proportional to the identity matrix, or γ is proportional to the mass matrix M. It may be interesting to choose position-dependent matrices σ, γ to restrict the action of the thermostat to the boundaries only, therefore sticking to the physical Hamiltonian dynamics in the core regions of the system. In most applications, σ and γ are constant and proportional to the identity matrix. For simplicity, we will restrict ourselves to this case in the sequel, in which case Langevin dynamics further simplify as

$$\begin{cases} dq_t = M^{-1}p_t\,dt, \\ dp_t = -\nabla V(q_t)\,dt - \gamma\,M^{-1}p_t\,dt + \sqrt{\dfrac{2\gamma}{\beta}}\,dW_t, \end{cases} \tag{5.5}$$

where $\gamma > 0$ is a real number to be determined.

5.1.2 Hamiltonian limit $\gamma \to 0$

Hamiltonian dynamics are recovered by setting $\gamma = 0$ in (5.1). The Hamiltonian limit therefore corresponds to an underdamped limit, where the friction γ vanishes. In order to make this argument more precise, and determine the timescales involved in the limiting procedure, we consider (5.5). Note that, by Itô calculus,

$$dH(q_t, p_t) = -\gamma \left(p_t^T M^{-2} p_t - \frac{1}{\beta} \mathrm{Tr}(M^{-1}) \right) dt + \sqrt{\frac{2\gamma}{\beta}} p_t^T M^{-1} dW_t.$$

This suggests that the dynamics takes times of order $1/\gamma$ to change energy levels. This is made precise in [95], where the authors prove that the process $E_t^\gamma = H(q_{t/\gamma}, p_{t/\gamma})$ converges as $\gamma \to 0$ to some effective diffusion on an energy graph. The convergence rates on the law of the process, as first provided in [119], also confirm that the typical timescale to consider is $1/\gamma$ in the underdamped limit.

5.1.3 Overdamped limit of Langevin dynamics

The overdamped Langevin dynamics (4.1) can be seen as a limit of Langevin dynamics when either the mass of the particles goes to 0, or the friction is taken to infinity with an appropriate time-rescaling, see the presentation in [178, Section 2.2.4]. For simplicity, we set $M = m\mathrm{Id}$ in this section for some scalar mass $m > 0$, and consider the simple Langevin dynamics (5.5). Note first that the second equation in (5.5) can be rewritten as

$$dp_t = -\nabla V(q_t)\, dt - \gamma dq_t + \sqrt{\frac{2\gamma}{\beta}}\, dW_t,$$

so that, by an integration in time,[1]

$$q_t - q_0 = \frac{p_0 - p_t}{\gamma} - \frac{1}{\gamma} \int_0^t \nabla V(q_s)\, ds + \sqrt{\frac{2}{\gamma\beta}} W_t. \tag{5.6}$$

This solution should be considered to the solution of the overdamped Langevin dynamics driven by the same Brownian motion, namely $dQ_t = -\nabla V(Q_t)\, dt + \sqrt{2\beta^{-1}}\, dB_t$, for which

$$Q_t - Q_0 = -\int_0^t \nabla V(Q_s)\, ds + \sqrt{\frac{2}{\beta}} B_t.$$

The comparison of the latter equation with (5.6) suggests to introduce the process $(q_{\gamma t}, p_{\gamma t})$, which corresponds to considering (5.6) over times γt, and consider the Brownian motion $W_t = \sqrt{\gamma} B_{t/\gamma}$ in (5.5):

$$\begin{aligned} q_{\gamma t} - q_0 &= \frac{p_0 - p_{\gamma t}}{\gamma} - \frac{1}{\gamma} \int_0^{\gamma t} \nabla V(q_s)\, ds + \sqrt{\frac{2}{\gamma\beta}} W_{\gamma t} \\ &= \frac{p_0 - p_{\gamma t}}{\gamma} - \int_0^t \nabla V(q_{\gamma s})\, ds + \sqrt{\frac{2}{\beta}} B_t. \end{aligned}$$

When $Q_0 = q_0$, we therefore obtain

$$q_{\gamma t} - Q_t = \frac{p_0 - p_{\gamma t}}{\gamma} - \int_0^t \left[\nabla V(q_{\gamma s}) - \nabla V(Q_s) \right] ds.$$

Assuming that ∇V is K-Lipschitz and using a Gronwall inequality, the following bound follows from the latter inequality:

[1] We thank Stefano Olla for this perspective on the overdamped Langevin limit.

$$|q_{\gamma t} - Q_t| \leqslant \int_0^t \mathrm{e}^{K(t-s)} \left| \frac{p_0 - p_{\gamma t}}{\gamma} \right| ds.$$

To conclude to the convergence of $q_{\gamma t}$ to Q_t as either $m \to 0$ or $\gamma \to +\infty$, it suffices to control $|p_{\gamma t}|$, and make precise how initial conditions p_0 are chosen. The latter point depends on the limit which is taken:

- If m is fixed and $\gamma \to +\infty$, the marginal distribution in p of the canonical measure is the same for all values of γ, and it is reasonable to either fix the initial condition or consider some given initial distribution of momenta.
- When γ is fixed and $m \to 0$, the invariant probability measure of the Langevin dynamics changes in the momentum variables. More precisely, momenta are distribution in the stationary state according to a Gaussian distribution with variance m/β. The choice of initial conditions depends on whether one wants to fix the initial kinetic energy, velocity or momentum, for instance.

To control $|p_{\gamma t}|$, we rely on the fact that

$$p_t = \mathrm{e}^{-\gamma t/m} p_0 - \int_0^t \mathrm{e}^{-\gamma(t-s)/m} \nabla V(q_s)\, ds + \sqrt{\frac{2\gamma}{\beta}} \int_0^t \mathrm{e}^{-\gamma(t-s)/m}\, dW_s,$$

so that

$$\frac{p_{\gamma t}}{\gamma} = \mathrm{e}^{-\gamma t/m} \frac{p_0}{\gamma} - \frac{1}{\gamma} \int_0^{\gamma t} \mathrm{e}^{-\gamma(t-s)/m} \nabla V(q_s)\, ds + \sqrt{\frac{2}{\gamma\beta}} \int_0^{\gamma t} \mathrm{e}^{-\gamma(t-s)/m}\, dW_s.$$

Bounds on the various terms on the right hand side can then be obtained as either $m \to 0$ or $\gamma \to +\infty$, possibly using martingale inequalities for the last term, and moment bounds together with some growth assumption on ∇V for the second term; see for instance [178, Section 2.2.4] for a result on the pathwise convergence of $q_{\gamma t}$ to Q_t, and [240] for a result on the convergence of the law of the trajectories.

Write more precise convergence results ?

In any case, the appropriate timescale to consider for the convergence to the overdamped limit is either of order 1 when $\gamma > 0$ is fixed and $m \to 0$, or of order γ when $m > 0$ is fixed and $\gamma \to +\infty$. The need for observing the system over longer times in the latter situation is related to the fact that momenta can be considered to be constantly resampled according to a Gaussian distribution so that no average drift on the positions results on integration times of order 1.

5.2 Mathematical properties of the Langevin dynamics

We make precise in this section some properties of the Langevin dynamics (5.5), in particular for its generator (see Section 5.2.1). We also prove that the canonical measure (5.3) is indeed the unique invariant probability measure of the process in Section 5.2.2.

5.2.1 Some properties of the generator of the Langevin dynamics

The generator of the Langevin dynamics reads

$$\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}}, \tag{5.7}$$

where

$$\mathcal{L}_{\mathrm{ham}} = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p$$

is the generator of the Langevin dynamics (see Section 2.1.3), while the fluctuation-dissipation part of the dynamics is encoded by

$$\mathcal{L}_{\mathrm{FD}} = -p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p,$$

which is the generator of a Gaussian process on momenta (known as the Ornstein–Uhlenbeck process). Let us immediately emphasize that the generator of Langevin dynamics is not an elliptic operator since second derivatives in the position variable q are missing. This is the analytical counterpart of the fact that the noise is degenerate in SDEs such as (5.1).

As for (4.4), it is useful to rewrite the generator using elementary operators and their adjoints on $L^2(\mu)$. Recall that the adjoint T^* of an unbounded operator T with domain dense in $L^2(\mu)$ is characterized by the following property: for any C^∞ and compactly supported functions φ, ϕ,

$$\int_{\mathcal{E}} (T\varphi)\phi \, d\mu = \int_{\mathcal{E}} \varphi(T^*\phi) \, d\mu. \tag{5.8}$$

For instance, the adjoint of ∂_{p_i} for $1 \leqslant i \leqslant D$ can be found by integrations by parts as follows:

$$\begin{aligned}\int_{\mathcal{E}} (\partial_{p_i}\varphi)\, \phi \, d\mu &= -\frac{1}{Z_\mu} \int_{\mathcal{E}} \varphi \left[\partial_{p_i} \left(\phi \, \mathrm{e}^{-\beta p^T M^{-1} p/2}\right)\right] \mathrm{e}^{-\beta V} \, dq \, dp \\ &= -\int_{\mathcal{E}} \varphi \left[\partial_{p_i}\phi - \beta \left(M^{-1}p\right)_i \phi\right] d\mu,\end{aligned}$$

which shows that $\partial_{p_i}^* = -\partial_{p_i} + \beta \left(M^{-1}p\right)_i$. Simple computations then show that

$$\mathcal{L}_{\mathrm{FD}} = -\frac{1}{\beta} \sum_{i=1}^{D} \partial_{p_i}^* \partial_{p_i}$$

is a symmetric operator, while

$$\mathcal{L}_{\mathrm{ham}} = \frac{1}{\beta} \sum_{i=1}^{D} \partial_{p_i}^* \partial_{q_i} - \partial_{q_i}^* \partial_{p_i}$$

is antisymmetric. This is an important structural property of the generators of Langevin dynamics: they are the sum of an antisymmetric Hamiltonian part, and a symmetric dissipation operator, which is however degenerate. In particular,

$$\mathcal{L}^* = -\mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}} \tag{5.9}$$

has a structure very similar to the structure of generators of Langevin dynamics, although $\mathcal{L} \neq \mathcal{L}^*$ in contrast to the generators of overdamped Langevin dynamics considered in Section 4.1. Note that the generator $\mathcal{L}$ and its adjoint are both dissipative since, for any $\varphi \in C_{\mathrm{c}}^\infty(\mathcal{E})$,

$$\langle \mathcal{L}\varphi, \varphi \rangle_{L^2(\mu)} = \langle \mathcal{L}^*\varphi, \varphi \rangle_{L^2(\mu)} = -\frac{\gamma}{\beta} \|\nabla_p \varphi\|_{L^2(\mu)}^2 \leqslant 0, \tag{5.10}$$

Remark 5.1. *It can in fact be proved that $-\mathcal{L}$ and $-\mathcal{L}^*$ are maximal accretive on $L^2(\mu)$ when $V \in C^\infty(\mathcal{D})$ (see [123, Chapter 5]). This implies in particular that the associated evolution semigroups $\mathrm{e}^{t\mathcal{L}^*}$ and $\mathrm{e}^{t\mathcal{L}}$ are contraction semigroups on $L^2(\mu)$ (see for instance [60]).*

The kernel of the generator considered as an operator on $L^2(\mu)$ (or the kernel of its ajoint) can in fact be readily made precise in view of their specific structures. Consider $\varphi \in D(\mathcal{L})$ such that $\mathcal{L}\varphi = 0$. Then,

$$\langle \varphi, \mathcal{L}\varphi \rangle_{L^2(\mu)} = -\frac{\gamma}{\beta} \|\nabla_p \varphi\|_{L^2(\mu)} = 0,$$

which shows that φ is a function of q only. With this information at hand, $\mathcal{L}\varphi = \mathcal{L}_{\mathrm{ham}}\varphi = p^T M^{-1} \nabla_q \varphi(q) = 0$, which shows that $\nabla_q \varphi = 0$ and allows to conclude that φ is constant. In conclusion, $\mathrm{Ker}(\mathcal{L}) = \mathrm{Ker}(\mathcal{L}^*) = \mathbb{R}\mathbf{1}$.

The following result generalizes the manipulations we made to a broader class of generators (which is useful for dynamics which are even more degenerate than Langevin dynamics, such as the generalized Langevin dynamics presented in Section 1.4.2). To state it, we recall that the commutator of two operators T_1, T_2 is formally defined (*i.e.* ignoring domain issues) as

$$[T_1, T_2] = T_1 T_2 - T_2 T_1.$$

Proposition 5.1 (Proposition 15 in [274]). *Consider an operator*

$$\mathcal{A} = A_0 + \sum_{j=1}^{J} A_j^* A_j \tag{5.11}$$

on a Hilbert space $\mathcal{H}$, with $A_0^* = -A_0$. Then,

$$\operatorname{Ker}\mathcal{A} \subset \left(\bigcap_{0 \leqslant j \leqslant J} \operatorname{Ker} A_j \right) \cap \left(\bigcap_{n \geqslant 1} \bigcap_{1 \leqslant j \leqslant J} \operatorname{Ker} C_{n,j} \right),$$

where $C_{0,j} = A_j$ and $C_{n,j} = [C_{n-1,j}, A_0]$.

Proof. Note first that $\operatorname{Ker}\mathcal{A} \subset \operatorname{Ker} A_0 \cap \operatorname{Ker} A_1 \cdots \cap \operatorname{Ker} A_J$. Indeed, when $\varphi \in \operatorname{Ker}\mathcal{A}$,

$$\langle \varphi, \mathcal{A}\varphi \rangle_{\mathcal{H}} = \sum_{j=1}^{J} \|A_j \varphi\|_{\mathcal{H}}^2 ,$$

so that $\varphi \in \operatorname{Ker} A_j$ for any $j = 1, \ldots, J$. Next, $\mathcal{A}\varphi = A_0\varphi = 0$, which implies $\varphi \in \operatorname{Ker} A_0$.

We then proceed by induction and assume that $\varphi \in \operatorname{Ker}\mathcal{A}$ belongs to $\operatorname{Ker} C_{0,j} \cap \cdots \cap \operatorname{Ker} C_{n,j}$ for all $1 \leqslant j \leqslant J$. First, since $\varphi \in \operatorname{Ker}\mathcal{A}$, it holds

$$A_0\varphi = -\sum_{j=1}^{J} A_j^* A_j \varphi,$$

so that (recalling $A_k\varphi = 0$ for any $1 \leqslant k \leqslant J$)

$$C_{n+1,j}\varphi = C_{n,j}A_0\varphi - A_0 C_{n,j}\varphi = -C_{n,j} \sum_{k=1}^{J} A_k^* A_k \varphi = 0.$$

This gives the desired result. □

The opposite of the generator of Langevin dynamics can be written as (5.11) with

$$A_j = \sqrt{\gamma\beta^{-1}}\partial_{p_j}, \qquad A_0 = -\mathcal{L}_{\mathrm{ham}}. \tag{5.12}$$

Note that $\operatorname{Ker} A_1 \cap \cdots \cap \operatorname{Ker} A_J$ is the space of functions which do not depend on p, *i.e.* functions of q only. Now, for diagonal mass matrices (in order to simplify the notation),

$$C_{1,j} = [A_j, A_0] = -\frac{1}{m_j}\sqrt{\frac{\gamma}{\beta}}\partial_{q_j}. \tag{5.13}$$

Therefore, $\operatorname{Ker} C_{1,1} \cap \cdots \cap \operatorname{Ker} C_{1,J}$ is the space of functions which do not depend on q. In conclusion, $\operatorname{Ker}\mathcal{L} = \mathbb{R}\mathbf{1}$. Similarly, $\operatorname{Ker}\mathcal{L}^* = \mathbb{R}\mathbf{1}$.

Remark 5.2 (Spectrum of generators of Langevin dynamics). *It is possible to obtain detailed information on the spectrum of Fokker–Planck operator using subelliptic estimates [80, 128, 123]. In particular, it is possible to make precise conditions on V to ensure that $\mathcal{L}$ has a compact resolvent on the orthogonal of the kernel, with eigenvalues located in cusp region. Let us also mention that the spectrum of Langevin operators is analytically known for systems with zero potential on a torus [157], in which case there are only real eigenvalues, or for quadratic potential energy functions, in which case the spectrum has some ladder structure (see [194, 214]).*

5.2.2 Invariance of the canonical measure

The aim of this section is to prove that (5.4) ensures the invariance of the canonical measure (5.3). The bottom line is that the Hamiltonian part of the evolution preserves any measure which is a function of the energy, while the fluctuation/dissipation part forces the conditional distribution of the momenta to be $(2\pi/\beta)^{-D/2}\det(M)^{-1/2}\mathrm{e}^{-\beta p^T M^{-1} p/2}\,dp$. In fact, this forces the invariant measure to be of the form (5.3). However, we postpone the discussion on the uniqueness of the invariant measure and the ergodicity of the dynamics to Section 5.3.

Given the insights used to obtain (5.9), the proof of the invariance of μ is now straightfoward. Indeed, the invariance of this probability measure can be reformulated as follows: for any smooth test function φ with compact support,

$$\int_{\mathcal{E}} \mathcal{L}\varphi \, d\mu = 0,$$

or equivalently $\mathcal{L}^* \mathbf{1} = 0$. The result then immediately follows from (5.9). The stationarity of the canonical distribution in fact holds for the more general Langevin dynamics (5.1) associated with a non separable Hamiltonian function.

Remark 5.3 (Detailed balance up to momentum reversal). *The fluctuation-dissipation relation* (5.4) *ensures that the canonical measure is a stationary measure of the Langevin process, and that the detailed balance condition with respect to the canonical distribution holds up to momenta reversal for the dynamics* (5.2)*. We mean by this that, when* $(q_0, p_0) \sim \mu$*, the law of the trajectory* $(q_t, p_t)_{0 \leqslant t \leqslant T}$ *is the same as the law of the trajectory* $(q_{T-t}, -p_{T-t})_{0 \leqslant t \leqslant T}$*, which, from a functional analytic viewpoint, corresponds to the equality* $\mathcal{R}\mathcal{L}\mathcal{R} = \mathcal{L}^*$ *with* $\mathcal{R}$ *the momentum reversal operator acting as* $(\mathcal{R}\varphi)(q,p) = \varphi(q,-p)$ *(see [178, Sections 2.2 and 4.2] for some in-depth discussion of these aspects). Let us emphasize that time-reversibility properties depend on the Hamiltonian at hand: they are not true for kinetic energies which are not even functions of* p *and do not hold either for non separable Hamiltonians in general.*

5.3 Convergence of trajectory averages

In order to estimate $\mathbb{E}_\mu(\varphi)$ for a given observable $\varphi \in L^1(\mu)$, we consider similarly to Section 4.2 the following trajectorial average:

$$\widehat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s)\, ds. \tag{5.14}$$

We first provide in Section 5.3.1 results on the almost sure convergence of $\widehat{\varphi}_t$ to $\mathbb{E}_\mu(\varphi)$. We next discuss in Section 5.3.2 the Central Limit Theorem associated with this almost sure convergence, and provide some bounds on the associated asymptotic variance. For these two sections, we crucially rely on the techniques and approaches used in Sections 4.2.1 and 4.2.2 for non degenerate stochastic dynamics, and merely point out the necessary modifications/extensions needed to accomodate the degeneracy of the noise.

5.3.1 Almost sure convergence of trajectory averages

The almost sure convergence of $\widehat{\varphi}_t$ towards $\mathbb{E}_\mu(\varphi)$ can be deduced from a general result by Kliemann [149].

Theorem 5.1. *Consider a diffusion process* $(x_t)_{t \geqslant 0}$ *in a* d*-dimensional space* $\mathcal{X}$*, which admits an invariant probability measure* $\pi(dx)$ *with a positive density with respect to the Lebesgue measure, and whose generator can be written as*

$$\mathcal{A} = A_0 + \frac{1}{2}\sum_{j=1}^{J} A_j^2, \qquad A_j = \sum_{i=1}^{d} A_{j,i}(x)\partial_{x_i}, \tag{5.15}$$

where the vector fields $A_0, \dots, A_J$ have smooth coefficients $A_{j,i}$. Assume that the Lie algebra spanned by

$$\{A_j\}_{j=0,\dots,J}, \{[A_j, A_k]\}_{j,k=0,\dots,J}, \{[[A_j, A_k], A_\ell]\}_{j,k,\ell=0,\dots,J}, \dots$$

has maximal rank d at every point $x \in \mathcal{X}$. Then, the invariant probability measure is unique and, for a given observable $\phi \in L^1(\pi)$ and any initial condition $x_0 \in \mathcal{D}$,

$$\lim_{t\to+\infty} \frac{1}{t}\int_0^t \phi(x_s)\, ds = \int_{\mathcal{E}} \varphi \, d\mu \qquad \text{a.s.}$$

It is possible to use this result for the Langevin dynamics (5.5) since the invariant probability measure (5.3) indeed has a positive density with respect to the Lebesgue measure $dq\, dp$, and, in view of (5.13) and (5.12) the maximal rank in the Lie algebra is attained already by considering only $A_1, \dots, A_J$ and the commutators $[A_0, A_1], \dots, [A_0, A_J]$ (note however that the definition of the operators $A_0, \dots, A_J$ has to be modified compared to (5.12) in order to fit (5.15)).

Remark 5.4. *Let us insist that such convergence results provide no information on the convergence of the law of the process. This can be understood on the simple one-dimensional example $dx_t = dt$ on $\mathcal{D} = \mathbb{T}$. The Lebesgue measure is an invariant probability measure which admits a smooth density, and one can indeed check that the generator $\mathcal{L} = A_0 = \partial_x$ has full rank at every point $x \in \mathcal{D}$. Trajectory averages are also easily seen to converge, with rate $1/t$. On the other hand, the law of the process at time t simply is a translation of the law at time 0, so that no convergence can occur for this quantity.*

Instead of using the general result by Kliemann, it is possible to provide more constructive elements for the proof by showing that the process (q_t, p_t) is irreducible with respect to the Lebesgue measure. The proof of the irreductibility is not trivial since the noise acts only in the momentum variable. It is conducted in two steps, as done in Section 4.2.1: first, a controllability argument shows that $\mathbb{P}^{(q_0,p_0)}((q_t, p_t) \in O) > 0$ for any $t > 0$ and open set O; second, this property is extended to general measurable ensembles using the continuity of the transition kernel, obtained by the hypoellipticity.

The proof of the controllability argument is performed as for the overdamped Langevin dynamics. Fix an initial condition (q, p), a time $t > 0$ and an open set O. Consider $(q_*, p_*) \in O$, and introduce a polynomial interpolation $Q(s)$ on $[0, t]$ such that $Q(0) = q$, $\dot{Q}(0) = M^{-1}p$ as well as $Q(t) = q_*$, $\dot{Q}(t) = M^{-1}p_*$. It is then possible to construct a control $u : [0, t] \to \mathbb{R}^D$ such that $u(0) = 0$ and

$$M\ddot{Q}(s) = -\nabla V(Q(s)) - \gamma\dot{Q}(s) + \sqrt{\frac{2\gamma}{\beta}}\,\dot{u}(s).$$

More precisely,

$$\begin{aligned} u(s) &= \sqrt{\frac{\beta}{2\gamma}}\int_0^s M\ddot{Q}(\theta) + \nabla V(Q(\theta)) + \gamma\dot{Q}(\theta)\, d\theta \\ &= \sqrt{\frac{\beta}{2\gamma}}\left(M\dot{Q}(s) - p + \gamma(Q(s) - q) + \int_0^s \nabla V(Q(\theta))\, d\theta\right). \end{aligned}$$

By continuity of the solutions of the SDE with respect to the realizations of the Brownian motion, we can conclude that $\mathbb{P}^{(q_0,p_0)}((q_t, p_t) \in O) > 0$ (see [189, Lemma 3.4] for details).

To obtain the regularity of the transition density $p(t, (q, p), (q', p'))$, we apply Hörmander's theorem [130, 131], which involves the commutator between two operators defined in (2.32). We formulate the result on a space $\mathcal{Y}$ (compared to the space $\mathcal{X}$ of Theorem 5.1) because we will consider the case when $\mathcal{Y} = (0, +\infty) \times \mathcal{X}$ involves space and time variables. We however keep the notation $\mathcal{A}$ for the operator which, as we will see below, can for instance be $\mathcal{L}$ or $\partial_t - \mathcal{L}$.

Theorem 5.2. *Consider C^∞ vector fields on the d-dimensional space $\mathcal{Y}$*

$$A_j = \sum_{i=1}^{d} A_{j,i}(y)\partial_{y_i},$$

and introduce the operator

$$\mathcal{A} = f + A_0 + \sum_{j=1}^{J} A_j^\dagger A_j,$$

where f is a smooth function and $A_j^\dagger$ is the (formal) adjoint of A_j on $L^2(\mathcal{Y})$. Assume that the Lie algebra spanned by

$$\{A_j\}_{j=0,\dots,J}, \{[A_j, A_k]\}_{j,k=0,\dots,J}, \{[[A_j, A_k], A_\ell]\}_{j,k,\ell=0,\dots,J}, \dots$$

has maximal rank d at every point $y \in \mathcal{Y}$. Then $\mathcal{A}$ is hypoelliptic, namely there exists $\varepsilon > 0$ such that $\mathcal{A}\varphi \in H^s_{\mathrm{loc}}(\mathcal{Y})$ implies $\varphi \in H^{s+\varepsilon}_{\mathrm{loc}}(\mathcal{Y})$.

In particular, solutions φ of the equation $\mathcal{A}\varphi = 0$ are C^∞. A simple but very useful corollary of Hörmander's sufficient criterion for hypoellipticity is the following.

Corollary 5.1. *For the Langevin dynamics, with generator* (5.7)*, the operators $\mathcal{L}$, $\mathcal{L}^\dagger$, $\partial_t - \mathcal{L}$ and $\partial_t - \mathcal{L}^\dagger$ are hypoelliptic. Therefore, the densities $p(t,(q,p),(q',p'))$ of the transition kernel, which satisfy*

$$\partial_t p\Big(t,(q,p),\cdot\Big) = \mathcal{L}p\Big(t,(q,p),\cdot\Big), \qquad \partial_t p\Big(t,\cdot,(q',p')\Big) = \mathcal{L}^\dagger p\Big(t,\cdot,(q',p')\Big),$$

in the sense of distributions, are C^∞ functions.

Proof. We prove that $\partial_t - \mathcal{L}$ is hypoelliptic, the proofs for the other operators being similar and therefore omitted. We use to this end Theorem 5.2 with $\mathcal{Y} = (0,+\infty) \times \mathcal{E}$ and $d = 2D + 1$, and prove that the Lie algebra based on $-\partial_t + \mathcal{L}$ is of dimension $2D + 1$ at each state $(q,p) \in \mathcal{E}$ and for any time t. First,

$$A_j = \sqrt{\frac{\gamma}{\beta}}\partial_{p_j}, \qquad A_0 = \partial_t - p^T M^{-1}\nabla_q + \nabla V^T \nabla_p + \gamma p^T M^{-1}\nabla_p,$$

so that

$$\partial_t - \mathcal{L} = A_0 + \sum_{j=1}^{D} A_j^\dagger A_j.$$

For notational simplicity, we assume that M is diagonal with entries m_j (although the computations can be extended to account for general positive definite matrices). Since

$$[A_0, A_j] = \frac{1}{m_j}\sqrt{\frac{\gamma}{\beta}}\left(\partial_{q_j} - \gamma\partial_{p_j}\right),$$

we immediately deduce that the Lie algebra spanned by $\{A_j\}_{j=1,\dots,D}$, $\{[A_j, A_k]\}_{j,k=1,\dots,D}$ has rank $2D$ and spans all derivatives in q and p. Adding A_0, the derivative in time is recovered. This allows to conclude. □

Remark 5.5 (Hypoellipticity does not imply uniqueness of the invariant measure). *Let us insist that hypoellipticity is local property, which deals with the regularity of the objects at hand. It does not say anything about global properties such as controllability. The main difference with the uniqueness result provided by Theorem 5.1 is that the latter result requires an invariant probability measure which a positive density. The example discussed in this remark, adapted from [139, Section 5], considers a situation when invariant probability measures vanish at some points. More precisely, consider the SDE*

$$dx_t = \cos(\pi x_t)\left[1 + \frac{\pi}{2}\sin(\pi x_t)\right]dt + \sin(\pi x_t)\,dW_t,$$

on the space $\mathcal{X} = 3\mathbb{T}$. *Its generator can be written as*

$$\mathcal{L} = A_0 - \frac{1}{2}A_1^\dagger A_1, \qquad A_0 = \cos(\pi x)\left[1 - \frac{\pi}{2}\sin(\pi x)\right]\frac{d}{dx}, \qquad A_1 = \sin(\pi x)\frac{d}{dx}.$$

check algebra

Note that the Lie algebra spanned by A_1 *and*

$$[A_0, A_1] = \pi\left(1 - \frac{\pi}{2}\sin(\pi x)^3\right)\frac{d}{dx}$$

has full rank at every point, so that $\mathcal{L}$ *and* $\partial_t - \mathcal{L}$ *are hypoelliptic. On the other hand, there are two distinct invariant measures, one supported in* $[0,1]$ *and the same measure translated by 2 (hence supported in* $[2,3]$*). Indeed, from a dynamical viewpoint, the drift at* $x = 0$ *(where the diffusion vanishes) is positive while the drift at* $x = 1$ *(where the diffusion also vanishes) is negative. This shows that the dynamics started in* $(0,1)$ *remains in* $(0,1)$.

5.3.2 Central Limit Theorem and bounds on the asymptotic variance

Consider some observable $\varphi \in L^2(\mu)$, and introduce, similarly to (4.16), the following projection operator on $L^2(\mu)$:

$$\Pi\varphi = \varphi - \int_{\mathcal{E}} \varphi\, d\mu. \tag{5.16}$$

As discussed in Section 4.2.2, the results of [30] show that a Central Limit Theorem holds once the Poisson equation

$$-\mathcal{L}\Phi = \Pi\varphi \tag{5.17}$$

has a solution in $L^2(\mu)$. More precisely,

$$\sqrt{t}\,(\widehat{\varphi}_t - \mathbb{E}_\mu(\varphi)) \xrightarrow[t\to+\infty]{\text{law}} \mathcal{N}(0, \sigma_\varphi^2),$$

with

$$\sigma_\varphi^2 = 2\,\langle -\mathcal{L}\Phi, \Phi\rangle_{L^2(\mu)} = \frac{2\gamma}{\beta}\,\|\nabla_p \Phi\|_{L^2(\mu)}^2 = 2\left\langle \Pi\varphi, (-\mathcal{L})^{-1}\Pi\varphi\right\rangle_{L^2(\mu)}. \tag{5.18}$$

Denoting by

$$L_0^2(\mu) = \Pi L_0^2(\mu) = \left\{\varphi \in L^2(\mu)\,\middle|\,\int_{\mathcal{E}} \varphi\, d\mu = 0\right\},$$

the asymptotic variance can be bounded as

$$0 \leqslant \sigma_\varphi^2 \leqslant \left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}(L_0^2(\mu))}\|\Pi\varphi\|_{L_0^2(\mu)}^2.$$

In order to prove that (5.16) is well posed and to obtain bounds on $\left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}(L_0^2(\mu))}$ hence on σ_φ^2, there are essentially two paths. The first one is to rely on decay estimates of the evolution semigroup $\mathrm{e}^{t\mathcal{L}}$ and resort to Proposition 4.1. Approaches to obtaining decay estimates on $\mathrm{e}^{t\mathcal{L}}$ are discussed at length in Section 5.4. One of their drawbacks, however, is that the bounds which are deduced on the norm of $\mathcal{L}^{-1}$ are usually not completely quantitative, because of the need for changing the scalar product on $L^2(\mu)$ for the proofs. An alternative approach, which provides more quantitative bounds on the norm of $\mathcal{L}^{-1}$, is to directly work out an expression of the inverse of $\mathcal{L}$, as recently done in [27]. The latter approach leads for instance to the following explicit bounds (stated for simplicity in the case when the mass matrix is a multiple of the identity matrix).

add the proof at the end of the lecture? rather short in the end...

Theorem 5.3 (Corollary 1 and Proposition 1 in [27]). *Suppose that* $M = m\mathrm{Id}_D$ *and that* $V \in C^\infty(\mathcal{D})$ *satisfies the following assumptions:*

(1) the probability measure $\nu(dq) = Z_\nu^{-1} \mathrm{e}^{-\beta V(q)}\, dq$ *satisfies the Poincaré inequality* (4.26) *with a constant* $R_\nu > 0$*;*
(2) there exist $c_1 > 0$, $c_2 \in [0,1]$ *and* $c_3 > 0$ *such that*

$$\Delta V \leqslant c_1 D + \frac{c_2 \beta}{2} |\nabla V|^2, \qquad \left|\nabla^2 V\right|^2 = \sum_{i,j=1}^{D} \left|\partial_{q_i} \partial_{q_j} V\right|^2 \leqslant c_3^2 \left(D + |\nabla V|^2\right). \tag{5.19}$$

Then, the operator $\mathcal{L}$ *is invertible on* $L^2_0(\mu)$ *and the following bound holds:*

$$\left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}(L^2_0(\mu))} \leqslant \frac{2\beta\gamma}{R_\nu} + \frac{8m}{\gamma}\left(\frac{3}{8} + C + \frac{C'}{R_\nu}\right), \tag{5.20}$$

where C *and* C' *can be chosen as:*

(i) If V *is convex, then* $C = 1$ *and* $C' = 0$*;*
(ii) If $\nabla_q^2 V \geqslant -K\mathrm{Id}$ *for some* $K \geqslant 0$*, then* $C = 1$ *and* $C' = K$*;*
(iii) In the general case, $C = 2$ *and* $C' = 2c_3 \left[\sqrt{D} + 2\max\left(\frac{8c_3}{\beta^2}, \sqrt{\frac{c_1 D}{\beta}}\right)\right]$.

The estimate (5.20) can be seen as the counterpart of the simple resolvent estimate (4.31) for overdamped Langevin dynamics. The interest of the upper bound (5.20) is that it is fully explicit in terms of the parameters of the dynamics (in particular the friction γ and the mass m) and of the dimension D of the system, except for the dependence of the Poincaré constant on the dimension and on the potential V. Note in particular that $\left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}(L^2_0(\mu))}$ scales as $\max(\gamma, \gamma^{-1})$ as $\gamma \to 0$ and $\gamma \to +\infty$ when $m > 0$ is fixed. This is related to the discussion in Sections 5.1.2 and 5.1.3, which suggest that the convergence rates of the dynamics scales as $\min(\gamma, \gamma^{-1})$, which indeed leads to an upper bound on the operator norm of $\mathcal{L}^{-1}$ scaling as $\max(\gamma, \gamma^{-1})$ by Proposition 4.1.

Remark 5.6 (Sharpness in γ of the resolvent bounds). *It is easy to see that the resolvent should indeed scale as* $\max(\gamma, \gamma^{-1})$ *as* $\gamma \to 0$ *or* $\gamma \to +\infty$*. For the overdamped limit* $\gamma \to +\infty$*, we consider the following example:*

$$\mathcal{L}\Big(p^T \nabla V + \gamma(V - v)\Big) = p^T M^{-1} \left(\nabla^2 V\right) p - |\nabla V|^2,$$

where v *is a constant chosen such that* $p^T \nabla V + \gamma(V - v)$ *has a vanishing average with respect to* μ*. It is clear that the right hand side is of order 1, while the left-hand side is of order* γ *when* V *is not constant. For the limit* $\gamma \to 0$*, we use the same argument as in [119, Proposition 6.3], and consider a function* $\varphi = \phi \circ H$*, for which the following equality holds:*

$$\frac{1}{\gamma}\mathcal{L}\varphi = \mathcal{L}_{\mathrm{FD}}\varphi.$$

Here again, the right hand side is of order 1, while the solution to the Poisson equation is of order γ^{-1}*. These two examples show that there exists* $C > 0$ *such that* $\left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}(L^2_0(\mu))} \geqslant C \max(\gamma, \gamma^{-1})$*. In fact, it can be shown that* $\mathcal{L}^{-1}$ *is at dominant order equal to* $\gamma\mathcal{L}_{\mathrm{ovd}}$ *in the overdamped limit* $\gamma \to +\infty$ *(see [169, Theorem 2.5]).*

The scaling with respect to the dimension D of the constants in the bounds (5.19) is motivated by the case of separable potentials for which $V(q) = v(q_1) + \cdots + v(q_d)$ for some smooth one dimensional function v, which corresponds to tensorized probability measures. The bounds (5.19) then follow from the inequalities

$$v'' \leqslant c_1 + \frac{c_2 \beta}{2}(v')^2, \qquad |v''|^2 \leqslant c_3^2 \left(1 + |v'|^2\right).$$

These bounds generally hold if v has polynomial growth for example. The scaling of the constants should be similar for particles on a lattice (such as one dimensional atom chains) with finite

interaction ranges, or systems for which correlations between degrees of freedom are bounded with respect to the dimension, in the sense that each column/line of the matrix $\nabla^2 V$ has a finite number of nonzero entries.

Note finally that the condition (2) in Theorem 5.3 does not necessarily imply the Poincaré inequality (it does not imply (4.32) because of the sign of c_1; a typical example is a potential behaving as $\sqrt{|q|}$ at infinity, which satisfies (5.19) but not (4.32)) (see the discussion after Theorem 4.1).

5.4 Convergence of the law

We study in this section the evolution of the law $\psi(t)$ of the Langevin dynamics, which satisfies the Fokker–Planck equation

$$\partial_t \psi = \mathcal{L}^\dagger \psi, \tag{5.21}$$

with $\mathcal{L}^\dagger$ the adjoint on $L^2(\mathcal{E})$ of the generator $\mathcal{L}$ defined in (5.7). Results on the existence and uniqueness of solutions to this equation are discussed for instance in [274, Section 2.4]. Alternatively and somewhat equivalently, we study the convergence of averages at time t, namely $(\mathrm{e}^{t\mathcal{L}}\varphi)(q_0,p_0) = \mathbb{E}^{(q_0,p_0)}(\varphi(q_t,p_t))$, towards the limiting value $\mathbb{E}_\mu(\varphi)$ as $t \to +\infty$. Throughout this section, we assume at various places for notational simplicity that the mass matrix M is a multiple of the identity, namely

$$M = m\,\mathrm{Id}_D, \qquad m > 0. \tag{5.22}$$

When the notation M is kept, this means that the computations are performed with a general symmetric definite positive mass matrix.

The main difficulty encountered in the study of the generator $\mathcal{L}$ and its adjoint is the fact that dissipation appears only in the momentum variable. Some dissipation can be transferred to the position variable through the Hamiltonian part of the dynamics. This abstract idea has to be fleshed out differently depending on the functional setting, as we show in the following subsections. We first consider in Section 5.4.1 Lyapunov type approaches, which is a flexible technique that can be used even for Langevin dynamics with non gradient forcings. We next turn to convergence in $L^2(\mu)$, explaining first in Section 5.4.2 the difficulty arising from the lack of coercivity of $\mathcal{L}$ in the canonical scalar product on $L^2(\mu)$. We then present instances of so-called hypocoercive techniques (the denomination is motivated at the end of Section 5.4.2). More precisely, we outline in Section 5.4.3 the approach suggested in [126, 71, 72], and present entropic estimates in Section 5.4.4.

Remark 5.7. *Let us emphasize that we present a biased and limited, but hopefully still useful, perspective on hypocoercive methods. In particular, we do not review hypocoercive approaches based on $H^1(\mu)$ norms, as abstracted in [274], nor hypoelliptic regularization results allowing to transfer $H^1(\mu)$ convergence to $L^2(\mu)$ (see [127]). A short account on these aspects for generators of Langevin dynamics can be read in [180, Sections 2.3.3 and 2.3.4]. These approaches to hypocoercivity are still useful since certain dynamics, such as the generalized Langevin dynamics presented in Section 1.4.2, cannot be tackled with the L^2 hypocoercive method presented in Section 5.4.3, while they can be studied with H^1 hypocoercivity [215].*

We do not mention either probabilistic approaches based on coupling strategies which lead to convergences measured in Wasserstein distance, in particular [78] which, very interestingly, can be used for forcings which are not gradient; nor the new approach suggested in [12, 49] (see also [27, Appendix A]), which is based on space-time Poincaré inequalities and avoids changing the scalar product.

5.4.1 Convergence in weighted B^∞ spaces

We consider the same setting as for overdamped Langevin dynamics in Section 4.3.4. We prove in this section the following convergence result.

Theorem 5.4. *Assume that $\mathcal{D}$ is bounded, or that the potential energy function $V(q)$ is bounded from below by $V_- > -\infty$ and there exist $A, B > 0$ and $C \in \mathbb{R}$ such that*

$$q^T M^{-1} \nabla V(q) \geqslant A\,[V(q) - V_-] + B q^T M^{-1} q + C. \tag{5.23}$$

Then, for any $n \geqslant 2$, there exist $C_n, \kappa_n > 0$ such that the following decay estimate holds for the Lyapunov function $\mathscr{W}_n(q,p)$ defined in Lemma 5.1 below:

$$\forall \varphi \in B^\infty_{\mathscr{W}_n}(\mathcal{E}), \qquad \left\| \mathrm{e}^{t\mathcal{L}}\varphi - \int_{\mathcal{E}} \varphi \, d\mu \right\|_{B^\infty_{\mathscr{W}_n}} \leqslant C_n \mathrm{e}^{-\kappa_n t} \|\varphi\|_{B^\infty_{\mathscr{W}_n}}.$$

Similarly to condition (4.52), the condition (5.23) is satisfied for potentials growing at infinity like $|q|^{2m}$ (with $m \geqslant 1$).

In order to prove Theorem 5.4, we rely on the same strategy as for the proof of Theorem 4.5. The minorization condition is a direct consequence of the controllability and the smoothness of the density of the transition kernel, and the proof of this condition follows exactly the same lines as the proof of the corresponding minorization condition in the proof of Theorem 4.5. We therefore only need to check the Lyapunov conditions. We state such conditions in their differential form (see Section 4.3.4). As usual, two cases should be distinguished, depending on whether the position space is compact or not. In the latter case, some control on q is required, see (5.23). We quote for instance the result in [189], although other suitable Lyapunov were already proposed in [280], and also in [260].

Lemma 5.1. *For compact position spaces $\mathcal{D}$, consider the Lyapunov functions $\mathscr{W}_n(q,p) = 1 + |p|^{2n}$ for $n \geqslant 1$. When the position space is not compact, assume that $V \geqslant V_- > -\infty$ and (5.23) holds, and introduce*

$$\mathscr{W}_n(q,p) = \left(1 + H(q,p) - V_- + \frac{\gamma}{2} p^T M^{-1} q + \frac{\gamma^2}{4} q^T M^{-1} q\right)^n.$$

Then for, any $n \geqslant 1$, it holds $\mathscr{W}_n(q,p) \geqslant 1$ and $\mathscr{W}_n(q,p) \to +\infty$ as $|(q,p)| \to +\infty$. Moreover, there exists $a > 0$ such that, for any $n \geqslant 1$, there is $b_n \in \mathbb{R}$ for which

$$\mathcal{L}\mathscr{W}_n \leqslant -na\mathscr{W}_n + b_n. \tag{5.24}$$

Since dissipation happens only in the momentum variable, some coupling term between q and p should be introduced in the Lyapunov function, as first proposed in [280, 189, 260]. This is done here through some component $p^T M^{-1} q$ which allows us to retrieve some dissipation in the q-direction from the dissipation in the momenta. This is a key insight in treating the convergence of Langevin dynamics, and can be thought of twisting the Euclidean scalar product for vectors $(q,p) \in \mathbb{R}^{2D}$ – in the same way scalar products are twisted in hypocoercive approaches.

Proof. We introduce $m_+, m_- > 0$ such that $m_- \mathrm{Id} \leqslant M \leqslant m_+ \mathrm{Id}$ in the sense of symmetric matrices, and fix $n \geqslant 2$. Let us start with compact position spaces. Since

$$\Delta\left(|p|^{2n}\right) = 2n \mathrm{div}\left(p|p|^{2(n-1)}\right) = 2n(2n - 2 + D)|p|^{2(n-1)},$$

we find, for $\mathscr{W}_n(q,p) = 1 + |p|^{2n}$,

$$\begin{aligned}
\mathcal{L}\mathscr{W}_n(q,p) &= -2n|p|^{2(n-1)} \nabla V(q)^T p + 2\gamma n \left(-p^T M^{-1} p + \frac{D + 2n - 2}{\beta}\right) |p|^{2(n-1)} \\
&\leqslant -\frac{2\gamma n}{m_+} |p|^{2n} + 2n \|\nabla V\|_{B^\infty} |p|^{2n-1} + \frac{2\gamma n(2n + D - 2)}{\beta} |p|^{2(n-1)}.
\end{aligned}$$

Therefore,

$$\lim_{|p| \to +\infty} \frac{\mathcal{L}\mathscr{W}_n(q,p)}{\mathscr{W}_n(q,p)} \leqslant -\frac{2\gamma n}{m_+},$$

so that the inequality (5.24) holds with $a = \gamma/m_+$ for instance.

Consider now the case of position spaces which are not compact. We first consider the case $n = 1$. A simple computation shows that

$$\begin{aligned}\mathcal{L}\mathscr{W}_1(q,p) &= \frac{\gamma}{2}\mathcal{L}_{\rm ham}\left[q^T M^{-1}\left(p+\frac{\gamma}{2}q\right)\right] + \gamma\mathcal{L}_{\rm FD}\left[\frac{1}{2}p^T M^{-1}(p+\gamma q)\right] \\ &= \frac{\gamma}{2}\left(p^T M^{-2}p - q^T M^{-1}\nabla V(q) + \gamma p^T M^{-2}q\right) + \gamma\left(-p^T M^{-2}p + \frac{\mathrm{Tr}(M)}{\beta}\right) - \frac{\gamma^2}{2}p^T M^{-2}q \\ &= -\frac{\gamma}{2}\left(p^T M^{-2}p + q^T M^{-1}\nabla V(q)\right) + \frac{\gamma \mathrm{Tr}(M)}{\beta}.\end{aligned}$$

On the other hand, a Cauchy–Schwarz inequality and (5.23) show that

$$\begin{aligned}\mathscr{W}_1(q,p) &\leqslant 1 + \frac{1}{2}\left(1+\frac{\gamma}{2}\right)p^T M^{-1}p + V(q) - V_- + \frac{\gamma(1+\gamma)}{4}q^T M^{-1}q \\ &\leqslant 1 + \frac{m_+}{2}\left(1+\frac{\gamma}{2}\right)p^T M^{-2}p + \max\left(\frac{1}{A}, \frac{\gamma(1+\gamma)}{4B}\right)\left[q^T M^{-1}\nabla V(q) - C\right].\end{aligned}$$

Since the function $\mathcal{L}\mathscr{W}_1/\mathscr{W}_1$ converges to a negative constant as $|(q,p)| \to +\infty$, we obtain as before the existence of $a_1 > 0$ and $b_1 \in \mathbb{R}$ such that $\mathcal{L}\mathscr{W}_1 \leqslant -a_1\mathscr{W}_1 + b_1$. For the general case $n \geqslant 2$, a simple computation gives

$$\begin{aligned}\mathcal{L}\mathscr{W}_n &= n(\mathcal{L}\mathscr{W}_1)\mathscr{W}_1^{n-1} + \frac{n(n-1)\gamma}{\beta}|\nabla_p\mathscr{W}_1|^2\mathscr{W}_1^{n-2} \\ &\leqslant n\left(-a_1\mathscr{W}_1 + b_1\right)\mathscr{W}_1^{n-1} + \frac{n(n-1)\gamma}{\beta}\left(p+\frac{\gamma}{2}q\right)^T M^{-2}\left(p+\frac{\gamma}{2}q\right)\mathscr{W}_1^{n-2} \\ &\leqslant n\left[-a_1\mathscr{W}_n + b_1\mathscr{W}_1^{n-1} + \frac{2(n-1)\gamma}{\beta m_-}\left(p^T M^{-1}p + \frac{\gamma^2}{4}q^T M^{-1}q\right)\mathscr{W}_1^{n-2}\right].\end{aligned}$$

We finally use the upper bound

$$\left|\frac{\gamma}{2}p^T M^{-1}q\right| \leqslant \frac{\eta}{2}p^T M^{-1}p + \frac{\gamma^2}{8\eta}q^T M^{-1}q,$$

to deduce, with $\eta = 3/4$,

$$\mathscr{W}_1(q,p) \geqslant 1 + \frac{1}{8}p^T M^{-1}p + \frac{\gamma^2}{12}q^T M^{-1}q. \tag{5.25}$$

Then,

$$\mathcal{L}\mathscr{W}_n \leqslant n\left[-a_1\mathscr{W}_n + b_1\mathscr{W}_1^{n-1} + \frac{16(n-1)\gamma}{\beta m_-}\left(\mathscr{W}_1 - 1\right)\mathscr{W}_1^{n-2}\right].$$

Since $\mathscr{W}_1(q,p) \to +\infty$ as $|(q,p)| \to +\infty$ in view of (5.25), we deduce that

$$\lim_{|(q,p)|\to+\infty} \frac{\mathcal{L}\mathscr{W}_n(q,p)}{\mathscr{W}_n(q,p)} \leqslant -na_1 < 0.$$

This shows that (5.24) holds and concludes the proof. □

5.4.2 Lack of coercivity in $L^2(\mu)$ with canonical scalar product

In order to consider convergence in a $L^2(\mu)$ setting, which allows to use tools and techniques for Hilbert spaces, we first proceed as in Section 4.3.1, and rewrite $\psi(t)$, the law at time t, as $\psi(t) = f(t)\,\mu$. The Fokker–Planck equation (5.21) can then be reformulated in terms of the operator $\mathcal{L}^*$ made precise in (5.9) as

$$\partial_t f = \mathcal{L}^* f, \tag{5.26}$$

where the initial condition $f(0) = f_0 = \psi_0/\mu$ satisfies

$$f_0 \geqslant 0, \quad \int_{\mathcal{E}} f_0 \, \mathrm{d}\mu = 1. \tag{5.27}$$

Note that there is a slight inconsistency in this rewriting: the initial condition f_0 should be considered in $L^1(\mu)$, whereas the functional framework considered here requires the stronger integrability condition $f_0 \in L^2(\mu)$. This situation can be improved by using relative entropies; see Section 5.4.4 below. The well posedness of (5.26) for $f_0 \in L^2(\mu)$ is ensured by the fact that $\mathcal{L}^*$ is maximal dissipative, see Remark 5.1.

In any case, $\mathrm{e}^{t\mathcal{L}^*} = (\mathrm{e}^{t\mathcal{L}})^*$, so decay estimates obtained for the bounded operator $\mathrm{e}^{t\mathcal{L}}$ immediately transfer to its adjoint. For simplicity of notation, some convergence results (as in Theorem 5.5) are stated for the semigroup $\mathrm{e}^{t\mathcal{L}}$, but the reader should bear in mind that the results equally apply to the semigroup $\mathrm{e}^{t\mathcal{L}^*}$, which then yields results on the long-time behaviour of the Fokker–Planck equation by (5.26).

Note also that solutions to the Fokker–Planck equation (5.26) are expected to converge to the constant function $\mathbf{1}$. Upon subtracting this constant function from the initial condition f_0, the convergence of the law amounts to the convergence to 0 of $\mathrm{e}^{t\mathcal{L}^*}(f_0 - \mathbf{1})$. This motivates the introduction of the following functional space:

$$L^2_0(\mu) = \left\{ \varphi \in L^2(\mu) \;\middle|\; \int_{\mathcal{E}} \varphi \, d\mu = 0 \right\}.$$

The same functional space is considered when studying the convergence of $\mathrm{e}^{t\mathcal{L}}\varphi$ towards its limiting value $\mathbb{E}_\mu(\varphi)$, since $\mathrm{e}^{t\mathcal{L}}\varphi - \mathbb{E}_\mu(\varphi) = \mathrm{e}^{t\mathcal{L}}\Pi\varphi$ (with Π the projector defined in (5.16)), so that it is sufficient to prove that $\mathrm{e}^{t\mathcal{L}}\varphi$ converges to 0 for functions $\varphi \in L^2_0(\mu)$.

The important remark which motivates the title of this section is that the generator $\mathcal{L}$ of Langevin dynamics, defined in (5.7), fails to be coercive on $L^2_0(\mu)$ since second derivatives in q are missing. In fact, for C^∞ and compactly supported test functions φ, we obtain from (5.10) that

$$-\langle \mathcal{L}\varphi, \varphi \rangle_{L^2(\mu)} = \frac{\gamma}{\beta} \|\nabla_p \varphi\|^2_{L^2(\mu)}, \tag{5.28}$$

which should be compared to (4.29) for overdamped Langevin dynamics. The key idea of hypocoercivity is to introduce some mixed derivatives in q and p in a modified scalar product in order to retrieve some dissipation in q through some commutator identities. This idea was already present in the computations performed in [260, Section 3], and was later generalized in [274]. This motivates the name for the technique in view of the analogy with hypoellipticity, since some (more or less explicit) commutator identities allow to recover some form of coercivity for operators with degenerate diffusion parts, in the same way commutators identities (as given by Theorem 5.2) imply hypoellipticity and therefore allow to recover regularity results for operators with degenerate diffusion parts similar to the regularity results for elliptic operators.

5.4.3 Hypocoercivity in a $L^2(\mu)$ setting

We present in this section a way to prove the exponential decay of the semigroup $\mathrm{e}^{t\mathcal{L}}$ in $L^2(\mu)$, by modifying the scalar product with some operator involving the generator of the Hamiltonian part of the dynamics. This approach was first proposed in [126] and then extended in [71, 72]. It is more direct than first proving a decay estimate in $H^1(\mu)$ and then to transfer this decay to $L^2(\mu)$ by hypoelliptic regularization (see [274, 127] as well as the review of these approaches in [180]), or by some spectral argument (using the bounded self-adjoint operators $Q_t = \mathrm{e}^{t\mathcal{L}^*}\mathrm{e}^{t\mathcal{L}}$, as done in [63] by resorting to [120, Lemma 2.9]). It also turns out to be more robust to perturbations, since it can be used for nonequilibrium systems in a perturbative framework [40, 137] or for spectral discretization of the Langevin dynamics [238]. It also allows to quantify more easily the convergence rate in terms of the parameters of the dynamics, in particular the friction rate [70, 110].

Statement of the convergence result

As mentioned above, for notational simplicity, we study the convergence to 0 of $\mathrm{e}^{t\mathcal{L}}\varphi$ for $\varphi \in L^2_0(\mu)$ rather than the convergence to 0 of $\mathrm{e}^{t\mathcal{L}^*}(f_0 - 1)$ for $f_0 \in L^2(\mu)$ (see Remark 5.8 below).

Theorem 5.5 (Hypocoercivity in $L^2(\mu)$). *Suppose that $V \in C^\infty(\mathcal{D})$ satisfies* (5.19) *and that $\nu(dq) = Z_\nu^{-1}\mathrm{e}^{-\beta V(q)}\,dq$ satisfies the Poincaré inequality* (4.26) *with a constant $R_\nu > 0$. Then there exist $C > 1$ and $\lambda_\gamma > 0$ (which are explicitly computable in terms of the parameters of the dynamics, C being independent of $\gamma > 0$) such that, for any $\varphi \in L^2_0(\mu)$,*

$$\forall t \geqslant 0, \qquad \left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|_{L^2(\mu)} \leqslant C\mathrm{e}^{-\lambda_\gamma t}\|\varphi\|_{L^2(\mu)}. \tag{5.29}$$

Moreover, the convergence rate is of order $\min(\gamma, \gamma^{-1})$*: there exists $\overline{\lambda} > 0$ such that*

$$\lambda_\gamma \geqslant \overline{\lambda}\min(\gamma, \gamma^{-1}).$$

This result calls for several comments. The first one is that some prefactor $C > 1$ appears in (5.29), compared to similar estimates for overdamped Langevin dynamics (see (4.28)). It is not possible to choose $C = 1$, otherwise, by the argument used to prove Proposition 4.2, this would mean that $-\mathcal{L}$ is coercive on $L^2_0(\mu)$ for the canonical scalar product on $L^2(\mu)$, which is not the case as discussed in Section 5.4.2.

Let us next comment on the scaling of the lower bound for the exponential convergence rate. Since the Langevin dynamics becomes singular in the limit $\gamma \to 0$ (where it reduces to the Hamiltonian dynamics, which is not ergodic with respect to the canonical measure) and in the limit $\gamma \to +\infty$ (where it converges to the overdamped Langevin dynamics after rescaling in time, see the discussion in Section 5.1.3), it is expected that the convergence rate to equilibrium of the Langevin dynamics degrades as $\gamma \to 0$ or $\gamma \to +\infty$. In both cases, the decay is apparent only at long time scales, of order t/γ as $\gamma \to 0$ (the fluctuation/dissipation is so small that energy diffusion is only observed at long times; see Section 5.1.2) and γt as $\gamma \to +\infty$ (the fluctuation/dissipation is so large that the momenta are continuously randomized, which leads to some effective Brownian motion on the positions over long times).

Finally, we mention that the convergence result of Theorem 5.5 can be extended to more general Hamiltonian functions, in particular separable Hamiltonians $H(q,p) = V(q) + U(p)$ under appropriate assumptions on U, namely some moment conditions for derivatives of U and a Poincaré inequality for the probability measure with density proportional to $\mathrm{e}^{-\beta U}$; see [257] for precise statements. Let us emphasize that we do not need the generator to be hypoelliptic, though, and can allow for instance for kinetic energy functions which vanish on open sets. In fact, Theorem 5.5 can be extended to certain Piecewise Deterministic Markov Processes, see [71, 72, 9].

Remark 5.8. *Theorem 5.5 admits a dual version in terms of probability measures. Consider an initial condition $f_0 \in L^2(\mu)$, which represents the density with respect to μ of a probability measure $\psi_0 = f_0\mu$. In particular, conditions* (5.27) *are satisfied. Then the time-evolved probability measure $\psi_t = f_t\mu$ with $f_t = \mathrm{e}^{t\mathcal{L}^*}f_0$ converges exponentially fast to μ in the following sense:*

$$\forall t \geqslant 0, \qquad \|f_t - \mathbf{1}\|_{L^2(\mu)} \leqslant C\mathrm{e}^{-\lambda_\gamma t}\|f_0 - \mathbf{1}\|_{L^2(\mu)}.$$

The proof of this convergence result can be obtained either by duality from (5.29)*, or by mimicking the proof of Theorem 5.5 upon changing the sign of the Hamiltonian part in the modified scalar product (which amounts to changing the sign of the second term in* (5.31) *below).*

General structure of the proof of Theorem 5.5

We give here the roadmap for the proof of Theorem 5.5, proving the results we need along the way later on in this section. We consider for simplicity of notation that the mass matrix is of the form (5.22), although the proof can easily be extended to account for more general cases.

The first key point in the proof is to use a modified squared norm equivalent to the $L^2(\mu)$ squared norm. To introduce it, we need to define the orthogonal projector in $L^2_0(\mu)$ onto the subspace of functions depending only on positions:

$$\forall \varphi \in L^2(\mu), \qquad (\mathscr{P}\varphi)(q) = \int_{\mathbb{R}^D} \varphi(q,p)\,\kappa(dp), \tag{5.30}$$

where we recall that $\kappa(dp)$ is the marginal of the canonical measure (5.3) in the p variables.

Definition 5.1 (Entropy functional). *Fix $\varepsilon \in (-1,1)$. For any smooth function φ with compact support,*

$$\mathcal{H}[\varphi] = \frac{1}{2}\|\varphi\|^2_{L^2(\mu)} - \varepsilon \langle A\varphi, \varphi\rangle_{L^2(\mu)}, \qquad A = \Big(1 + (\mathcal{L}_{\rm ham}\mathscr{P})^*(\mathcal{L}_{\rm ham}\mathscr{P})\Big)^{-1}(\mathcal{L}_{\rm ham}\mathscr{P})^*. \tag{5.31}$$

A more explicit expression of the operator A is provided in (5.45). Some of the properties of A are gathered in the following lemma.

Lemma 5.2. *It holds $A = \mathscr{P}A(1-\mathscr{P})$. Moreover, for any $\varphi \in L^2(\mu)$,*

$$\|A\varphi\|_{L^2(\mu)} \leqslant \frac{1}{2}\|(1-\mathscr{P})\varphi\|_{L^2(\mu)}, \qquad \|\mathcal{L}_{\rm ham}A\varphi\|_{L^2(\mu)} \leqslant \|(1-\mathscr{P})\varphi\|_{L^2(\mu)}.$$

In particular, the operator A is in fact bounded in $L^2(\mu)$ with operator norm smaller than 1, so that $\sqrt{\mathcal{H}}$ is a norm equivalent to the canonical norm of $L^2(\mu)$ for $-1 < \varepsilon < 1$:

$$\frac{1-\varepsilon}{2}\|\varphi\|^2_{L^2(\mu)} \leqslant \mathcal{H}[\varphi] \leqslant \frac{1+\varepsilon}{2}\|\varphi\|^2_{L^2(\mu)}. \tag{5.32}$$

The second key element is the coercivity of $-\mathcal{L}$ in the scalar product $\langle\langle \cdot,\cdot\rangle\rangle$ associated by polarization with $\mathcal{H}$, namely

$$\langle\langle \varphi_1, \varphi_2\rangle\rangle = \langle \varphi_1, \varphi_2\rangle_{L^2(\mu)} - \varepsilon \langle A\varphi_1, \varphi_2\rangle_{L^2(\mu)} - \varepsilon \langle \varphi_1, A\varphi_2\rangle_{L^2(\mu)}.$$

Proposition 5.2. *There exists $\overline{\varepsilon} \in (0,1)$ and $\overline{\lambda} > 0$, such that, by considering $\varepsilon = \overline{\varepsilon}\min(\gamma, \gamma^{-1})$ in* (5.31)*,*

$$\forall \varphi \in C^\infty_{\rm c}(\mathcal{E}) \cap L^2_0(\mu), \qquad \mathscr{D}[\varphi] := \langle\langle -\mathcal{L}\varphi, \varphi\rangle\rangle \geqslant \widetilde{\lambda}_\gamma \|\varphi\|^2_{L^2(\mu)}, \tag{5.33}$$

with $\widetilde{\lambda}_\gamma \geqslant \overline{\lambda}\min(\gamma, \gamma^{-1})$.

The coercivity property (5.33) and a Gronwall inequality then allow to conclude to the exponential convergence to 0 of $\mathcal{H}[\mathrm{e}^{t\mathcal{L}}\varphi]$, from which (5.29) follows by the norm equivalence of $\sqrt{\mathcal{H}}$ and $\|\cdot\|_{L^2(\mu)}$. Let us make these arguments more precise. Consider $\varphi_0 \in \mathrm{Dom}(\mathcal{L}) \cap L^2_0(\mu)$ (which contains $H^2(\mu) \cap L^2_0(\mu)$) and introduce $\mathscr{H}(t) = \mathcal{H}[\varphi(t)]$, where $\varphi(t) = \mathrm{e}^{t\mathcal{L}}\varphi_0 \in \mathrm{Dom}(\mathcal{L})$ for any $t \geqslant 0$. Then,

$$\mathscr{H}'(t) = -\mathscr{D}[\varphi(t)] \leqslant -\widetilde{\lambda}_\gamma \|\varphi(t)\|^2_{L^2(\mu)}.$$

Using the norm equivalence (5.32) and the choice (5.43) for $\overline{\varepsilon} < 1$, it follows that

$$\mathscr{H}'(t) \leqslant -\frac{2\widetilde{\lambda}_\gamma}{1 + \overline{\varepsilon}\min(\gamma, \gamma^{-1})}\mathscr{H}(t),$$

so that, by a Gronwall estimate,

$$\mathscr{H}(t) \leqslant \mathrm{e}^{-2\lambda_\gamma t}\mathscr{H}(0), \qquad \lambda_\gamma = \frac{\widetilde{\lambda}_\gamma}{1 + \overline{\varepsilon}\min(\gamma, \gamma^{-1})}.$$

Using again the norm equivalence (5.32), it holds

$$\|\varphi(t)\|^2_{L^2(\mu)} \leqslant \frac{1+\overline{\varepsilon}}{1-\overline{\varepsilon}}\,\mathrm{e}^{-2\lambda_\gamma t}\|\varphi(0)\|^2_{L^2(\mu)},$$

from which the estimate (5.29) finally follows by density of $\mathrm{Dom}(\mathcal{L})$ in $L^2(\mu)$.

The remainder of this section is devoted to the proof of Proposition 5.2 and of some technical estimates – Lemma 5.2 but also other technical estimates used in the proof of Proposition 5.2.

Proof of Proposition 5.2

The key element to prove Proposition 5.2 are the following coercivity estimates, respectively called "microscopic" and "macroscopic" coercivity in [71, 72].

Proposition 5.3 (Coercivity properties). *The operators $\mathcal{L}_{\mathrm{FD}}$ and $\mathcal{L}_{\mathrm{ham}}\mathscr{P}$ satisfy the following coercivity properties:*

$$\forall \varphi \in C_{\mathrm{c}}^{\infty}(\mathcal{E}), \qquad -\langle \mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle_{L^2(\mu)} \geqslant \frac{1}{m}\|(1-\mathscr{P})\varphi\|_{L^2(\mu)}^2, \tag{5.34}$$

$$\forall \varphi \in C_{\mathrm{c}}^{\infty}(\mathcal{E}) \cap L_0^2(\mu), \qquad \|\mathcal{L}_{\mathrm{ham}}\mathscr{P}\varphi\|_{L^2(\mu)}^2 \geqslant \frac{DR_\nu}{\beta m}\|\mathscr{P}\varphi\|_{L^2(\mu)}^2. \tag{5.35}$$

As a corollary, the following inequality holds in the sense of symmetric operators on $L_0^2(\mu)$:

$$A\mathcal{L}_{\mathrm{ham}}\mathscr{P} \geqslant \lambda_{\mathrm{ham}}\mathscr{P}, \qquad \lambda_{\mathrm{ham}} = 1 - \left(1 + \frac{DR_\nu}{\beta m}\right)^{-1} > 0. \tag{5.36}$$

Proof. The inequality (5.34) directly results from the fact that the Gaussian measure κ satisfies a Poincaré inequality with constant $R_\kappa = \beta/m$ (in view of Theorem 4.3 and Proposition 4.5), the position q being seen as a parameter. Indeed, for a given $\varphi \in C_{\mathrm{c}}^{\infty}(\mathcal{E})$,

$$\forall q \in \mathcal{D}, \qquad \int_{\mathbb{R}^D} |\nabla_p \varphi(q,p)|^2 \, \kappa(dp) \geqslant \frac{\beta}{m}\int_{\mathbb{R}^D} |(1-\mathscr{P})\varphi(q,p)|^2 \, \kappa(dp). \tag{5.37}$$

Integrating against ν and noting that $-\langle \mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle_{L^2(\mu)} = \beta^{-1}\|\nabla_p\varphi\|_{L^2(\mu)}^2$ leads to the desired inequality.

To prove (5.35), we note that

$$\mathcal{L}_{\mathrm{ham}}\mathscr{P} = \frac{1}{\beta}\nabla_q\nabla_p^*\mathscr{P} = \left(\frac{p}{m}\right)^T \nabla_q\mathscr{P}, \tag{5.38}$$

which leads to

$$\|\mathcal{L}_{\mathrm{ham}}\mathscr{P}\varphi\|_{L^2(\mu)}^2 = \frac{1}{m^2}\|\nabla_q\mathscr{P}\varphi\|_{L^2(\nu)}^2 \, \|p\|_{L^2(\kappa)}^2 = \frac{D}{\beta m}\|\nabla_q\mathscr{P}\varphi\|_{L^2(\nu)}^2. \tag{5.39}$$

The conclusion then follows from the Poincaré inequality (4.26) satisfied by ν, since, for $\varphi \in C_{\mathrm{c}}^{\infty}(\mathcal{E}) \cap L_0^2(\mu)$, the function $\mathscr{P}\varphi$ has average 0 with respect to ν (namely, $\mathbb{E}_\nu[\mathscr{P}\varphi] = \mathbb{E}_\mu[\varphi] = 0$).

The macroscopic coercivity (5.35) allows to write the following inequality in the sense of symmetric operators on $L_0^2(\mu)$:

$$(\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*(\mathcal{L}_{\mathrm{ham}}\mathscr{P}) \geqslant \frac{DR_\nu}{\beta m}\mathscr{P}.$$

Moreover,

$$A\mathcal{L}_{\mathrm{ham}}\mathscr{P} = [1 + (\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*(\mathcal{L}_{\mathrm{ham}}\mathscr{P})]^{-1}\,(\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*(\mathcal{L}_{\mathrm{ham}}\mathscr{P}).$$

Since $(\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*(\mathcal{L}_{\mathrm{ham}}\mathscr{P})$ is self-adjoint and the function $x \mapsto x/(1+x) = 1 - 1/(1+x)$ is increasing, the inequality (5.36) follows by spectral calculus. □

Another technical argument is the boundedness of certain operators, which appear in the proof of Proposition 5.2.

Proposition 5.4 (Boundedness of auxiliary operators). *There exist $K_{\mathrm{ham}} > 0$ such that*

$$\forall \varphi \in C_{\mathrm{c}}^{\infty}(\mathcal{E}), \qquad \begin{aligned} \|A\mathcal{L}_{\mathrm{ham}}(1-\mathscr{P})\varphi\|_{L^2(\mu)} &\leqslant K_{\mathrm{ham}}\|(1-\mathscr{P})\varphi\|_{L^2(\mu)}, \\ \|A\mathcal{L}_{\mathrm{FD}}\varphi\|_{L^2(\mu)} &\leqslant \frac{1}{2m}\|(1-\mathscr{P})\varphi\|_{L^2(\mu)}. \end{aligned} \tag{5.40}$$

We can now proceed with the proof of Proposition 5.2.

Proof (of Proposition 5.2). Note first that, for a given $\varphi \in C_c^\infty(\mathcal{E})$, the entropy dissipation $\mathscr{D}[\varphi]$ can be explicitly written as

$$\begin{aligned}\mathscr{D}[\varphi] = &\langle -\gamma \mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle_{L^2(\mu)} + \varepsilon \langle A\mathcal{L}_{\mathrm{ham}}\mathscr{P}\varphi, \varphi\rangle_{L^2(\mu)} + \varepsilon \langle A\mathcal{L}_{\mathrm{ham}}(1-\mathscr{P})\varphi, \varphi\rangle_{L^2(\mu)} \\ &+ \varepsilon\gamma \langle A\mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle_{L^2(\mu)} - \varepsilon \langle \mathcal{L}_{\mathrm{ham}}A\varphi, \varphi\rangle_{L^2(\mu)},\end{aligned} \tag{5.41}$$

since $\mathcal{L}_{\mathrm{FD}}A = \mathcal{L}_{\mathrm{FD}}\mathscr{P}A = 0$. Using respectively the properties (5.34), (5.36), (5.40) and Lemma 5.2, it follows

$$\begin{aligned}\mathscr{D}[\varphi] \geqslant \frac{\gamma}{m}\|(1-\mathscr{P})\varphi\|^2_{L^2(\mu)} + \varepsilon\lambda_{\mathrm{ham}}\|\mathscr{P}\varphi\|^2_{L^2(\mu)} - \varepsilon\left(K_{\mathrm{ham}} + \frac{\gamma}{2m}\right)\|(1-\mathscr{P})\varphi\|_{L^2(\mu)}\,\|\mathscr{P}\varphi\|_{L^2(\mu)} \\ - \varepsilon\langle \mathcal{L}_{\mathrm{ham}}A\varphi, \varphi\rangle_{L^2(\mu)}.\end{aligned} \tag{5.42}$$

Since, by Lemma 5.2,

$$\langle \mathcal{L}_{\mathrm{ham}}A\varphi, \varphi\rangle_{L^2(\mu)} = \langle (1-\mathscr{P})\mathcal{L}_{\mathrm{ham}}\mathscr{P}A(1-\mathscr{P})\varphi, \varphi\rangle_{L^2(\mu)} \leqslant \|(1-\mathscr{P})\varphi\|^2_{L^2(\mu)},$$

it holds $\mathscr{D}[\varphi] \geqslant X^T S X$, where

$$X = \begin{pmatrix} \|\mathscr{P}\varphi\|_{L^2(\mu)} \\ \|(1-\mathscr{P})\varphi\|_{L^2(\mu)}\end{pmatrix}, \qquad S = \begin{pmatrix} S_{--} & S_{-+}/2 \\ S_{-+}/2 & S_{++}\end{pmatrix},$$

with

$$S_{--} = \varepsilon\lambda_{\mathrm{ham}}, \qquad S_{-+} = -\varepsilon\left(K_{\mathrm{ham}} + \frac{\gamma}{2m}\right), \qquad S_{++} = \frac{\gamma}{m} - \varepsilon.$$

The smallest eigenvalue of S is

$$\Lambda(\gamma,\varepsilon) = \frac{S_{--}+S_{++}}{2} - \frac{1}{2}\sqrt{(S_{--}-S_{++})^2 + (S_{-+})^2}.$$

In the limit $\gamma \to 0$, the parameter ε should be chosen of order γ in order for $\Lambda(\gamma,\varepsilon)$ to be positive (in particular for S_{++} to remain positive). When $\gamma \to +\infty$, the parameter ε should be chosen of order $1/\gamma$ in order for the determinant of S to remain positive. We therefore consider the choice

$$\varepsilon = \bar{\varepsilon}\min(\gamma, \gamma^{-1}). \tag{5.43}$$

It is then easy to check that there exists $\bar{\varepsilon} > 0$ sufficiently small such that $\Lambda(\gamma, \bar{\varepsilon}\min(\gamma,\gamma^{-1})) > 0$ for all $\gamma > 0$. Moreover, it can be proved that $\Lambda(\gamma, \bar{\varepsilon}\min(\gamma,\gamma^{-1}))/\gamma$ converges to a positive value as $\gamma \to 0$, while $\gamma\Lambda(\gamma, \bar{\varepsilon}\min(\gamma,\gamma^{-1}))$ converges to a positive value as $\gamma \to +\infty$. This gives the claimed result with $\widetilde{\lambda}_\gamma = \Lambda(\gamma, \bar{\varepsilon}\min(\gamma,\gamma^{-1}))$. □

Proofs of technical estimates

We gather here the proofs of two technical estimates, namely Lemma 5.2 and Proposition 5.4.

Proof (Proof of Lemma 5.2). Consider $\varphi \in C_c^\infty(\mathcal{E})$. In view of (5.38), the function $\mathcal{L}_{\mathrm{ham}}\mathscr{P}\varphi$ has average 0 with respect to $\kappa(dp)$ for any $q \in \mathcal{D}$. Therefore, $\mathscr{P}\mathcal{L}_{\mathrm{ham}}\mathscr{P} = 0$, which implies $A = A(1-\mathscr{P})$.

By definition of the operator A, it also holds

$$A\varphi + (\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*(\mathcal{L}_{\mathrm{ham}}\mathscr{P})A\varphi = (\mathcal{L}_{\mathrm{ham}}\mathscr{P})^*\varphi.$$

This identity immediately implies that $\mathscr{P}A = A$. Taking the scalar product with $A\varphi$, we obtain, using $\mathcal{L}_{\mathrm{ham}}A = \mathcal{L}_{\mathrm{ham}}\mathscr{P}A = (1-\mathscr{P})\mathcal{L}_{\mathrm{ham}}A$:

$$\begin{aligned}\|A\varphi\|^2_{L^2(\mu)} + \|\mathcal{L}_{\rm ham} A\varphi\|^2_{L^2(\mu)} &= \langle \mathcal{L}_{\rm ham} A\varphi, \varphi\rangle_{L^2(\mu)} = \langle \mathcal{L}_{\rm ham} A\varphi, (1-\mathscr{P})\varphi\rangle_{L^2(\mu)} \\ &\leqslant \|(1-\mathscr{P})\varphi\|_{L^2(\mu)} \, \|\mathcal{L}_{\rm ham} A\varphi\|_{L^2(\mu)} \\ &\leqslant \frac{1}{4}\|(1-\mathscr{P})\varphi\|^2_{L^2(\mu)} + \|\mathcal{L}_{\rm ham} A\varphi\|^2_{L^2(\mu)}.\end{aligned} \tag{5.44}$$

The last inequality gives $\|A\varphi\|_{L^2(\mu)} \leqslant \|(1-\mathscr{P})\varphi\|_{L^2(\mu)}/2$, while the second one implies that $\|\mathcal{L}_{\rm ham} A\varphi\|_{L^2(\mu)} \leqslant \|(1-\mathscr{P})\varphi\|_{L^2(\mu)}$. The conclusion is finally obtained by density of $C^\infty_{\rm c}(\mathcal{E})$ in $L^2(\mu)$. □

Proof (of Proposition 5.4). The first task is to give a more explicit expression of the operator A. In the following we use frequently the fact that operators acting only on the variables q (such as ∇_q and ∇_q^*) commute with operators acting only on variables p (such as ∇_p, ∇_p^* and $\mathscr{P}$). Moreover the relations $\partial_{p_i}\mathscr{P} = 0$, $\mathscr{P}\partial^*_{p_i} = 0$ and $\mathscr{P}\partial_{p_i}\partial^*_{p_j} = \partial_{p_i}\partial^*_{p_j}\mathscr{P} = \frac{\beta}{m}\mathscr{P}\delta_{ij}$ allow to simplify the action of $(\mathcal{L}_{\rm ham}\mathscr{P})^*(\mathcal{L}_{\rm ham}\mathscr{P})$ as follows:

$$\begin{aligned}(\mathcal{L}_{\rm ham}\mathscr{P})^*(\mathcal{L}_{\rm ham}\mathscr{P}) &= -\frac{1}{\beta^2}\sum_{i,j=1}^D \mathscr{P}(\partial^*_{p_i}\partial_{q_i} - \partial^*_{q_i}\partial_{p_i})(\partial^*_{p_j}\partial_{q_j} - \partial^*_{q_j}\partial_{p_j})\mathscr{P} \\ &= \frac{1}{\beta^2}\sum_{i,j=1}^D \mathscr{P}\partial^*_{q_i}\partial_{p_i}\partial^*_{p_j}\partial_{q_j}\mathscr{P} = -\frac{1}{m}\mathcal{L}_{\rm ovd}\mathscr{P},\end{aligned}$$

where

$$\mathcal{L}_{\rm ovd} = \frac{1}{\beta}\sum_{i=1}^D \partial^*_{q_i}\partial_{q_i}$$

is the generator (4.4) of the overdamped Langevin dynamics. The operator A can therefore be reformulated as

$$A = \frac{1}{\beta}\left(1 - \frac{1}{m}\mathcal{L}_{\rm ovd}\right)^{-1} \mathscr{P}\sum_{i=1}^D \partial^*_{q_i}\partial_{p_i}. \tag{5.45}$$

To obtain bounds on the operator $A\mathcal{L}_{\rm ham}(1-\mathscr{P})$, we next consider its adjoint:

$$\begin{aligned}-(1-\mathscr{P})\mathcal{L}_{\rm ham}A^* &= -\frac{1}{\beta^2}(1-\mathscr{P})\sum_{i,j=1}^D (\partial^*_{p_i}\partial_{q_i} - \partial^*_{q_i}\partial_{p_i})\partial_{q_j}\partial^*_{p_j}\mathscr{P}\left(1 - \frac{1}{m}\mathcal{L}_{\rm ovd}\right)^{-1} \\ &= -\frac{1}{\beta^2}(1-\mathscr{P})\left[\sum_{i,j=1}^D \partial^*_{p_i}\partial^*_{p_j}\mathscr{P}\partial_{q_i}\partial_{q_j} - \frac{\beta}{m}\sum_{i=1}^D \partial^*_{q_i}\partial_{q_i}\mathscr{P}\right]\left(1 - \frac{1}{m}\mathcal{L}_{\rm ovd}\right)^{-1} \\ &= -\frac{1}{\beta^2}(1-\mathscr{P})\sum_{i,j=1}^D \partial^*_{p_i}\partial^*_{p_j}\mathscr{P}\partial_{q_i}\partial_{q_j}\left(1 - \frac{1}{m}\mathcal{L}_{\rm ovd}\right)^{-1},\end{aligned}$$

where we used $(1-\mathscr{P})\partial^*_{q_i}\partial_{q_i}\mathscr{P} = 0$ in the last line. In order to bound the operator appearing on the right hand side of the previous equality, we proceed as follows:

- first, for any $1 \leqslant i,j \leqslant D$, the operators $\partial^*_{p_i}\partial^*_{p_j}\mathscr{P}\partial_{q_i}\partial_{q_j}$ are bounded from $H^2(\nu)$ to $L^2(\mu)$ since the operators $\partial^*_{p_i}\partial^*_{p_j}\mathscr{P}$ are bounded on $L^2(\mu)$. To prove the latter statement, we prove in fact that the adjoint operators $\mathscr{P}\partial_{p_i}\partial_{p_j}$ are bounded. Consider to this end $\varphi \in C^\infty_{\rm c}(\mathcal{E})$, and note that

$$\begin{aligned}\left|\left(\mathscr{P}\partial_{p_i}\partial_{p_j}\varphi\right)(q)\right| &= \left|\int_{\mathbb{R}^D} (\partial_{p_i}\partial_{p_j}\varphi)(q,\cdot)\, d\kappa\right| = \left|\int_{\mathbb{R}^D} \varphi(q,\cdot)(\partial^*_{p_j}\partial^*_{p_i}\mathbf{1})\, d\kappa\right| \\ &\leqslant \|\varphi(q,\cdot)\|_{L^2(\kappa)} \left\|\partial^*_{p_j}\partial^*_{p_i}\mathbf{1}\right\|_{L^2(\kappa)}.\end{aligned}$$

By taking the square of the previous inequality, and integrating with respect to ν, we finally obtain

$$\forall \varphi \in C_{\rm c}^\infty(\mathcal{E}), \qquad \left\| \mathscr{P} \partial_{p_i} \partial_{p_j} \varphi \right\|_{L^2(\mu)} \leqslant \left\| \partial_{p_j}^* \partial_{p_i}^* \mathbf{1} \right\|_{L^2(\kappa)} \|\varphi\|_{L^2(\mu)},$$

which indeed establishes that $\mathscr{P}\partial_{p_i}\partial_{p_j}$ is bounded on $L^2(\mu)$.

- second as proved in [72, Proposition 5] (see also [49, Lemma 2.3] and [27, Lemma 1] for more precise estimates, based on Bochner's formula), the conditions (5.19) ensure that the operator $\mathscr{P}(1 - m^{-1}\mathcal{L}_{\rm ovd})^{-1}$ is bounded from $L^2(\mu)$ to $H^2(\nu)$.

In conclusion, $-(1-\mathscr{P})\mathcal{L}_{\rm ham}A^*$ is bounded on $L^2(\mu)$, and so is $A\mathcal{L}_{\rm ham}(1-\mathscr{P})$.

The boundedness of the operator $A\mathcal{L}_{\rm FD}$ comes from the fact that

$$\begin{aligned}\mathscr{P}\mathcal{L}_{\rm ham}\mathcal{L}_{\rm FD} &= -\frac{1}{\beta^2}\sum_{i,j=1}^D \mathscr{P}(\partial_{p_i}^*\partial_{q_i} - \partial_{q_i}^*\partial_{p_i})\partial_{p_j}\partial_{p_j}^* = \frac{1}{\beta^2}\sum_{i,j=1}^D \mathscr{P}\partial_{q_i}^*\partial_{p_i}\partial_{p_j}\partial_{p_j}^* \\ &= \frac{1}{\beta m}\sum_{i=1}^D \mathscr{P}\partial_{q_i}^*\partial_{p_i} = -\frac{1}{m}\mathscr{P}\mathcal{L}_{\rm ham}.\end{aligned}$$

Alternatively, it is possible to compute the action of $\mathcal{L}_{\rm FD}\mathcal{L}_{\rm ham}\mathscr{P}$, since $(\mathcal{L}_{\rm ham}\mathscr{P}\varphi)(q,p) = p^T M^{-1}(\nabla_q \mathscr{P}\varphi)(q)$ and use the fact that $\mathcal{L}_{\rm FD}(M^{-1}p) = -p/m^2$ when (5.22) holds (as assumed for simplicity in this proof). In any case, $A\mathcal{L}_{\rm FD} = -A/m$, which gives the claimed result in view of Lemma 5.2. □

Exercise 5.1. *Theorem 5.5 can be extended to the linear Boltzmann and Andersen dynamics,* i.e. *the piecewise deterministic Markov process with generators* (1.31) *and* (1.30) *(see Section 1.4.3). The only part of the proof that needs to be modified is the proof of Proposition 5.2. Prove that* (5.33) *holds when the generator is given by* (1.31) *or* (1.30)*. For the latter operator, the key point is to check that a coercivity property such as* (5.34) *still holds. Note to this end that*

$$\begin{aligned}\|(P_1 \dots P_D - 1)\varphi\|_{L^2(\mu)}^2 &= \|P_1(P_2 \dots P_D - 1)\varphi\|_{L^2(\mu)}^2 + \|(P_1 - 1)\varphi\|_{L^2(\mu)}^2 \\ &\leqslant \|(P_2 \dots P_D - 1)\varphi\|_{L^2(\mu)}^2 + \|(P_1 - 1)\varphi\|_{L^2(\mu)}^2,\end{aligned}$$

and proceed by induction.

5.4.4 Hypocoercivity in the entropic sense

We show in this section how to adapt the convergence estimates in relative entropy discussed for overdamped Langevin dynamics in Section 4.3.3. The interest of this approach is that initial conditions (5.27) can be considered in a functional space larger than $L^2(\mu)$ (although still not for the whole space $L^1(\mu)$ as one would like). Logarithmic Sobolev inequalities are still a key tool, but the entropy functional needs to be modified.

Entropic estimates for Fokker–Planck operators were initiated in [66] and abstracted in [274, Section 6], however under conditions stronger than those for other hypocoercive frameworks, requiring in particular that the Hessian of the potential is bounded. The approach can be generalized to various entropies besides logarithmic ones [2], under the same assumption about the boundedness of the Hessian of V. It was recently shown in [53] how to remove the latter assumption and allow $\nabla^2 V$ to grow at infinity as V^η for some power $\eta \geqslant 0$, provided a weighted log-Sobolev inequality holds. Let us also mention that the computations in [274] can be simplified for Langevin-type dynamics; see [209, Appendix D].

We state here convergence results in the case when the law $\psi(t)$ of the process at time t can be written as as $f(t)\mu$. This is the case when the initial law is $f_0\mu$, with $f_0 \geqslant 0$ and $\int_{\mathcal{E}} f_0 {\rm d}\mu = 1$. In this case, the function $f(t)$ evolves according to the Fokker–Planck equation (5.26), *i.e.*, $f(t) = {\rm e}^{t\mathcal{L}^*} f_0$. It is expected that $f(t)$ converges to the constant function $\mathbf{1}$.

To quantify the convergence rate, we introduce the entropy functional

$$\mathscr{E}(f) = \int_{\mathcal{E}} f \, \ln f \, d\mu + \int_{\mathcal{E}} \frac{\nabla f^T S \nabla f}{f} \, d\mu, \tag{5.46}$$

where $S \in \mathbb{R}^{2d \times 2d}$ is a nonnegative symmetric matrix which is not assumed to be positive definite at this stage. Note that the functional $\mathscr{E}$ mixes the relative entropy and a generalization of the Fisher information introduced in Definition 4.2. It is sufficient for our purposes to restrict ourselves to the case when S is constant (but see [274, Remark 29] for a context where a dependence on the position q may be useful). In fact, we will consider the choice made in [209, Appendix D], namely

$$S = a \begin{pmatrix} \mathrm{Id}_D & \mathrm{Id}_D \\ \mathrm{Id}_D & \mathrm{Id}_D \end{pmatrix} \in \mathbb{R}^{2D \times 2D}$$

for some parameter $a > 0$. The associated entropy function is denoted by $\mathscr{E}_a$:

$$\mathscr{E}_a(f) = \int_{\mathcal{E}} f \, \ln f \, d\mu + a \int_{\mathcal{E}} \frac{|\nabla_q f + \nabla_p f|^2}{f} \, d\mu.$$

Note that $\mathscr{E}_a(\mathbf{1}) = 0$, so that the entropy is expected to converge to 0 as $t \to +\infty$.

Theorem 5.6. *Assume that $\nabla^2 V$ is bounded:*

$$K = \sup_{q \in \mathcal{D}} \left\| \nabla^2 V(q) \right\|_{\mathcal{B}(\ell^2)} < +\infty, \qquad \left\| \nabla^2 V(q) \right\|_{\mathcal{B}(\ell^2)} = \sup_{\xi \in \mathbb{R}^D} \frac{\left| \nabla^2 V(q) \xi \right|}{|\xi|}, \tag{5.47}$$

where $|\cdot|$ is the standard Euclidean norm in $\mathbb{R}^D$. Then, there exists $\overline{a} > 0$ and $\alpha > 0$ such that, for the choice

$$a(\gamma) = \overline{a} \min\left(\gamma, \frac{1}{\gamma}\right), \tag{5.48}$$

it holds

$$\forall \gamma > 0, \quad \forall t \geqslant 0, \qquad \frac{d}{dt} \left[\mathscr{E}_{a(\gamma)}(f(t)) \right] \leqslant -\alpha \min\left(\gamma, \frac{1}{\gamma}\right) \int_{\mathcal{E}} \frac{|\nabla f(t)|^2}{f(t)} \, d\mu. \tag{5.49}$$

If in addition $\nu(dq)$ satisfies a logarithmic Sobolev inequality (4.43) *with constant R_ν, then there exists $\lambda > 0$ such that*

$$\forall \gamma > 0, \quad \forall t \geqslant 0, \qquad \frac{d}{dt} \left[\mathscr{E}_{a(\gamma)}(f(t)) \right] \leqslant -\lambda \min\left(\gamma, \frac{1}{\gamma}\right) \mathscr{E}_{a(\gamma)}(f(t)). \tag{5.50}$$

In particular, $0 \leqslant \mathscr{E}_{a(\gamma)}(f(t)) \leqslant \mathscr{E}_{a(\gamma)}(f_0) \, \mathrm{e}^{-\lambda \min(\gamma, \gamma^{-1}) t}$ for any $t \geqslant 0$ and any $\gamma > 0$.

Note that we recover a convergence rate of order $\min(\gamma, \gamma^{-1})$, as in Theorem 5.5. A careful inspection of the proof shows that final decay rate λ can be made quite explicit in terms of the various parameters in the model (LSI constant R_ν, bounds on $\nabla^2 V$, etc).

Proof. For simplicity, we write the proof in the simple case (5.22) when the mass matrix is isotropic. One of the main ideas in the proof is to rewrite the time derivative of the second term in the expression of $\mathscr{E}_a$ as a sum of terms similar to the ones appearing in the proof of H^1 coercivity [274]. To this end, consider $g(t) = \sqrt{f(t)}$, so that

$$\int_{\mathcal{E}} \frac{\nabla f(t)^T S \nabla f(t)}{f(t)} d\mu = 4 \int_{\mathcal{E}} \nabla g(t)^T S \nabla g(t) \, d\mu. \tag{5.51}$$

In order to determine the time evolution of this quantity, we first write the time evolution for $g(t)$, obtained from the equality

$$\partial_t f(t) = \partial_t \left(g(t)^2 \right) = \mathcal{L}^* \left(g(t)^2 \right) = 2 g(t) \mathcal{L}^* g(t) + \frac{2\gamma}{\beta} \left| \nabla_p g(t) \right|^2,$$

so that

$$\partial_t g(t) = \mathcal{L}^* g(t) + \frac{\gamma}{\beta} \frac{|\nabla_p g(t)|^2}{g(t)}. \tag{5.52}$$

We next compute the time derivatives of the various terms in $\mathscr{E}_a(f(t))$. First,

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} f(t)\,\ln f(t)\,d\mu\right) &= \int_{\mathcal{E}} (1+\ln f(t))\mathcal{L}^* f(t)\,d\mu \\
&= \int_{\mathcal{E}} \mathcal{L}_{\rm ham}(1+\ln f(t)) f(t)\,d\mu - \frac{\gamma}{\beta}\int_{\mathcal{E}} \nabla_p f(t)\cdot\nabla_p(\ln f(t))\,d\mu \\
&= \int_{\mathcal{E}} \mathcal{L}_{\rm ham} f(t)\,d\mu - \frac{\gamma}{\beta}\int_{\mathcal{E}} \frac{|\nabla_p f(t)|^2}{f(t)}\,d\mu = -\frac{4\gamma}{\beta}\int_{\mathcal{E}} |\nabla_p g(t)|^2\,d\mu,
\end{aligned}$$

in view of the invariance of μ by $\mathcal{L}_{\rm ham}$. To compute the various terms in the time derivative of the Fisher information, we rely on the reformulation (5.51), and use the following commutator identities:

$$\begin{aligned}
[\partial_{p_i}, \mathcal{L}^*]\varphi &= -\left[\partial_{p_i}, \frac{p_i}{m}\partial_{q_i}\right]\varphi - \frac{\gamma}{\beta}\left[\partial_{p_i}, \partial^*_{p_i}\partial_{p_i}\right]\varphi = -\frac{1}{m}\left(\partial_{q_i} + \gamma\partial_{p_i}\right)\varphi, \\
[\partial_{q_i}, \mathcal{L}^*]\varphi &= [\partial_{q_i}, \nabla V^T \nabla_p]\varphi = \nabla\left(\partial_{q_i} V\right)^T \nabla_p \varphi.
\end{aligned} \tag{5.53}$$

Then, by (5.52),

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} |\partial_{p_i} g(t)|^2\,d\mu\right) &= 2\int_{\mathcal{E}} \partial_{p_i} g(t)\,\partial_{p_i}(\mathcal{L}^* g(t))\,d\mu + \frac{2\gamma}{\beta}\int_{\mathcal{E}} \partial_{p_i} g(t)\,\partial_{p_i}\left(\frac{|\nabla_p g(t)|^2}{g(t)}\right)d\mu \\
&= 2\int_{\mathcal{E}} \partial_{p_i} g(t)\,\mathcal{L}^*(\partial_{p_i} g(t))\,d\mu - \frac{2}{m}\int_{\mathcal{E}} \partial_{p_i} g(t)\,(\partial_{q_i} + \gamma\partial_{p_i}) g(t)\,d\mu \\
&\quad + \frac{2\gamma}{\beta}\int_{\mathcal{E}} \partial_{p_i} g(t)\left(\frac{2\nabla_p(\partial_{p_i} g(t))\cdot\nabla_p g(t)}{g(t)} - \frac{|\nabla_p g(t)|^2}{g(t)^2}\partial_{p_i} g(t)\right)d\mu \\
&= -\frac{2}{m}\int_{\mathcal{E}} \partial_{p_i} g(t)\,(\partial_{q_i} + \gamma\partial_{p_i}) g(t)\,d\mu \\
&\quad - \frac{2\gamma}{\beta}\int_{\mathcal{E}} |\nabla_p \partial_{p_i} g(t)|^2 - 2\nabla_p(\partial_{p_i} g(t))\cdot\frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)} + \frac{|\nabla_p g(t)|^2(\partial_{p_i} g(t))^2}{g(t)^2}\,d\mu,
\end{aligned}$$

where we have used

$$\int_{\mathcal{E}} \partial_{p_i} g(t)\,\mathcal{L}^*(\partial_{p_i} g(t))\,d\mu = -\int_{\mathcal{E}} \partial_{p_i} g(t)\,\mathcal{L}_{\rm ham}(\partial_{p_i} g(t))d\mu - \frac{\gamma}{\beta}\sum_{j=1}^{D}\int_{\mathcal{E}} \partial_{p_i} g(t)\,\partial^*_{p_j}\partial_{p_j}(\partial_{p_i} g(t))\,d\mu,$$

the first integral on the right-hand side vanishing since $\mathcal{L}_{\rm ham}$ is antisymmetric. Therefore,

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{\mathcal{E}} |\partial_{p_i} g(t)|^2\,d\mu\right) \\
&\quad = -\frac{2}{m}\int_{\mathcal{E}} \partial_{p_i} g(t)\,(\partial_{q_i} + \gamma\partial_{p_i}) g(t)\,d\mu - \frac{2\gamma}{\beta}\int_{\mathcal{E}} \left|\nabla_p\partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)}\right|^2 d\mu.
\end{aligned}$$

Similar computations give

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} |\partial_{q_i} g(t)|^2\,d\mu\right) &= 2\int_{\mathcal{E}} \partial_{q_i} g(t)\,(\nabla\partial_{q_i} V)\cdot\nabla_p g(t)\,d\mu \\
&\quad - \frac{2\gamma}{\beta}\int_{\mathcal{E}} \left|\nabla_p\partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t))\nabla_p g(t)}{g(t)}\right|^2 d\mu,
\end{aligned}$$

and

$$\frac{d}{dt}\left(\int_{\mathcal{E}} \partial_{p_i} g(t)\, \partial_{q_i} g(t)\, d\mu\right) = \int_{\mathcal{E}} \partial_{p_i} g(t)\, (\nabla \partial_{q_i} V)\cdot \nabla_p g(t)\, d\mu - \frac{1}{m}\int_{\mathcal{E}} \partial_{q_i} g(t)\, (\partial_{q_i} + \gamma \partial_{p_i}) g(t)\, d\mu$$
$$- \frac{2\gamma}{\beta}\int_{\mathcal{E}} \left(\nabla_p \partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t))\nabla_p g(t)}{g(t)}\right)\cdot\left(\nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)}\right) d\mu.$$

Let us emphasize that, among the various terms produced by the last time derivative, there is in particular a term of the form $-m^{-1}\left\|\partial_{q_i} g(t)\right\|^2_{L^2(\mu)}$, which allows to retrieve some missing dissipation in the direction q_i.

By gathering all time derivatives, it follows that

$$\frac{d}{dt}\left[\mathscr{E}_{a(\gamma)}(f(t))\right] = -\frac{4\gamma}{\beta}\int_{\mathcal{E}} |\nabla_p g(t)|^2\, d\mu$$
$$+ 8a(\gamma)\sum_{i=1}^{D}\left(\int_{\mathcal{E}} (\partial_{q_i} + \partial_{p_i}) g(t)\, (\nabla \partial_{q_i} V)\cdot \nabla_p g(t)\, d\mu - \frac{1}{m}\sum_{i=1}^{D}\int_{\mathcal{E}} (\partial_{q_i} + \partial_{p_i}) g(t)\, (\partial_{q_i} + \gamma\partial_{p_i}) g(t)\, d\mu\right)$$
$$- \frac{8\gamma a(\gamma)}{\beta}\sum_{i=1}^{D}\int_{\mathcal{E}} \left|\nabla_p (\partial_{q_i} + \partial_{p_i}) g(t) - \frac{[(\partial_{q_i} + \partial_{p_i}) g(t)]\nabla_p g(t)}{g(t)}\right|^2 d\mu.$$

Therefore, recalling the definition of the constant K in (5.47),

$$\frac{d}{dt}\left[\mathscr{E}_{a(\gamma)}(f(t))\right] \leqslant -\frac{4\gamma}{\beta}\left\|\nabla_p g(t)\right\|^2_{L^2(\mu)}\, d\mu + 8Ka(\gamma)\left\|(\nabla_p + \nabla_q) g(t)\right\|_{L^2(\mu)}\left\|\nabla_p g(t)\right\|_{L^2(\mu)}$$
$$- \frac{8a(\gamma)}{m}\left[\left\|\nabla_q g(t)\right\|^2_{L^2(\mu)} + \gamma\left\|\nabla_p g(t)\right\|^2_{L^2(\mu)} - (\gamma+1)\left\|\nabla_q g(t)\right\|_{L^2(\mu)}\left\|\nabla_p g(t)\right\|_{L^2(\mu)}\right].$$

The right hand side of the previous inequality can be bounded as

$$\frac{d}{dt}\left[\mathscr{E}_{a(\gamma)}(f(t))\right] \leqslant -8X(t)^T \mathcal{M} X(t), \qquad X(t) = \begin{pmatrix} \left\|\nabla_p g(t)\right\|_{L^2(\mu)} \\ \left\|\nabla_q g(t)\right\|_{L^2(\mu)}\end{pmatrix} \in \mathbb{R}^2,$$

where $\mathcal{M} \in \mathbb{R}^{2\times 2}$ has entries

$$\mathcal{M}_{11} = \gamma\left(\frac{1}{2\beta} + \frac{a(\gamma)}{m}\right) - Ka(\gamma), \quad \mathcal{M}_{21} = \mathcal{M}_{12} = -\frac{a(\gamma)}{2}\left(\frac{\gamma+1}{m} + K\right), \quad \mathcal{M}_{22} = \frac{a(\gamma)}{m}.$$

Necessary and sufficient conditions for $\mathcal{M}$ to be positive definite are that $\mathcal{M}_{11}, \mathcal{M}_{22} > 0$ and $\det \mathcal{M} > 0$. The condition $\mathcal{M}_{11} > 0$ implies that $a(\gamma)$ has to be of order at most γ when $\gamma \to 0$, while the determinant condition requires $\gamma a(\gamma)$ not to be too large as $\gamma \to +\infty$. This motivates the choice (5.48), for some value $\overline{a} > 0$ chosen small enough so that $\mathcal{M}_{11}, \mathcal{M}_{22} > 0$ and $\det \mathcal{M} > 0$ for any $\gamma > 0$. With such a choice, the smallest eigenvalue $\Lambda(\gamma)$ of $\mathcal{M}$ is positive. In fact,

$$\Lambda(\gamma) = \frac{\mathcal{M}_{11} + \mathcal{M}_{22}}{2} - \frac{1}{2}\sqrt{(\mathcal{M}_{11} - \mathcal{M}_{22})^2 + 4\mathcal{M}_{12}^2} = \frac{2\left(\mathcal{M}_{11}\mathcal{M}_{22} - \mathcal{M}_{12}^2\right)}{\mathcal{M}_{11} + \mathcal{M}_{22} + \sqrt{(\mathcal{M}_{11} - \mathcal{M}_{22})^2 + 4\mathcal{M}_{12}^2}}.$$

Given that all the entries of $\mathcal{M}$ are of order γ as $\gamma \to 0$, it is easily seen that there exists $\lambda_0 > 0$ such that $\Lambda(\gamma) \geqslant \lambda_0 \gamma$ for all $\gamma \leqslant 1$. For γ large, $\mathcal{M}_{11}$ is of order γ, $\mathcal{M}_{12}$ is of order 1, while $\mathcal{M}_{22}$ is of order $1/\gamma$. A simple inspection of the formula for $\Lambda(\gamma)$ shows that there exists $\lambda_\infty > 0$ such that $\Lambda(\gamma) \geqslant \lambda_\infty/\gamma$ for all $\gamma \geqslant 1$. Upon setting $\lambda = \min(\lambda_0, \lambda_\infty)$, and noting that

$$|X(t)|^2 = \left\|\nabla_p g(t)\right\|^2_{L^2(\mu)} + \left\|\nabla_q g(t)\right\|^2_{L^2(\mu)} = \frac{1}{4}\int_{\mathcal{E}} \frac{|\nabla f(t)|^2}{f(t)}\, d\mu,$$

we obtain (5.49).

To deduce (5.50), we note that, by tensorization of LSI, the following inequality holds for any C^∞ function $h \geqslant 0$ with integral 1 with respect to μ:

$$\int_{\mathcal{E}} h \ln h \, d\mu \leqslant \frac{1}{2\min(R_\nu, \beta/m)} \int_{\mathcal{E}} \frac{|\nabla_p h|^2 + |\nabla_q h|^2}{h} \, d\mu.$$

Then,

$$\mathscr{E}_{a(\gamma)}(h) \leqslant \left(\frac{1}{2\min(R_\nu, \beta/m)} + 2a(\gamma) \right) \int_{\mathcal{E}} \frac{|\nabla_p h|^2 + |\nabla_q h|^2}{h} \, d\mu.$$

In view of (5.49), we therefore obtain

$$\frac{d}{dt}(\mathscr{E}_{a(\gamma)}(f(t))) \leqslant -\alpha \min\left(\gamma, \frac{1}{\gamma}\right) \left(\frac{1}{2\min(R_\nu, \beta/m)} + 2a(\gamma) \right)^{-1} \mathscr{E}_{a(\gamma)}(f(t))$$

which indeed leads to (5.50). The exponential decay follows by a Gronwall inequality. □

Remark 5.9. *The computations performed in the proof of Theorem 5.6 are very close to the ones performed to prove $H^1(\mu)$ coercivity. This is not a suprise, since convergence in $H^1(\mu)$ can be seen as working with an entropy function $(x-1)^2$ instead of $x \ln x - x + 1$. More precisely, the functional* (5.46) *is replaced by*

$$\mathscr{E}(f) = \int_{\mathcal{E}} (f-1)^2 \, d\mu + \int_{\mathcal{E}} \nabla f^T S \nabla f \, d\mu.$$

Note that the second term in this functional is some generalization of the dissipative term which arises in (4.30) *for overdamped Langevin dynamics – similarly to the fact that the second term in* (5.46) *is some Fisher information, which corresponds to the dissipation of entropy for overdamped Langevin dynamics (see* (4.45)*). The $H^1(\mu)$ framework however more easily allows for less stringent conditions on V to obtain the convergence – for instance a bound of the form $|\nabla^2 V(q)| \leqslant \rho(1 + |\nabla V(q)|)$ for some $\rho \in \mathbb{R}_+$ (see [274] as well as the presentation in [180] which is dedicated to Langevin dynamics).*

5.5 Complements

TO DISCARD

5.5.1 Hypocoercivity and convergence in $H^1(\mu)$

A first setting to retrieve coercivity is to consider the Hilbert space $H^1(\mu) \cap L^2_0(\mu)$, where

$$H^1(\mu) = \left\{ \varphi \in L^2(\mu) \, \middle| \, \nabla_p \varphi, \nabla_q \varphi \in \left(L^2(\mu)\right)^D \right\}$$

is endowed with a scalar product different from the canonical one:

$$\langle \varphi_1, \varphi_2 \rangle_{H^1(\mu)} = \langle \varphi_1, \varphi_2 \rangle_{L^2(\mu)} + \langle \nabla_q \varphi_1, \nabla_q \varphi_2 \rangle_{L^2(\mu)} + \langle \nabla_p \varphi_1, \nabla_p \varphi_2 \rangle_{L^2(\mu)}.$$

It is then possible to resort to some Gronwall estimates and deduce the longtime convergence of $f(t)$ when a Poincaré inequality holds for μ (as in the proof of Proposition 4.2).

Although hypocoercivity eventually provides decay estimates in $H^1(\mu)$, it turns out to be convenient, for the proof, to work with a specific scalar product equivalent to the canonical scalar product on $H^1(\mu)$. We introduce the following scalar product:

$$\langle\langle u, v \rangle\rangle = \langle u, v \rangle + a \langle \nabla_p u, \nabla_p v \rangle - b \langle \nabla_p u, \nabla_q v \rangle - b \langle \nabla_q u, \nabla_p v \rangle + c \langle \nabla_q u, \nabla_q v \rangle, \tag{5.54}$$

where, for simplicity of notation, we denote by $\langle \cdot, \cdot \rangle$ the standard scalar product on $L^2(\mu)$. In order for the above scalar product to be equivalent to the canonical scalar product on $H^1(\mu)$, we assume in the remainder of this section that

$$a, c > 0, \quad \text{and} \quad ac - b^2 > 0. \tag{5.55}$$

Lemma 5.3. *Assume that* (5.55) *holds. Then the bilinear form* $(u, v) \mapsto \langle\langle u, v \rangle\rangle$ *induces a scalar product equivalent to the canonical scalar product on* $H^1(\mu)$.

Proof. Of course,

$$|\langle\langle u, u \rangle\rangle| \leqslant \max(1, a + |b|, c + |b|) \|u\|^2_{H^1(\mu)}.$$

It therefore remains to prove that $\|u\|^2_{H^1(\mu)}$ can be controlled by $\langle\langle u, u \rangle\rangle$. Note first that, by a Cauchy-Schwarz inequality,

$$\begin{aligned} a \langle \nabla_p u, \nabla_p u \rangle - b \langle \nabla_p u, \nabla_q u \rangle - b \langle \nabla_q u, \nabla_p u \rangle + c \langle \nabla_q u, \nabla_q u \rangle & \\ \geqslant \begin{pmatrix} \|\nabla_p u\|_{L^2(\mu)} \\ \|\nabla_q u\|_{L^2(\mu)} \end{pmatrix}^T \begin{pmatrix} a & -|b| \\ -|b| & c \end{pmatrix} \begin{pmatrix} \|\nabla_p u\|_{L^2(\mu)} \\ \|\nabla_q u\|_{L^2(\mu)} \end{pmatrix} & \\ \geqslant \alpha \left(\|\nabla_p u\|^2_{L^2(\mu)} + \|\nabla_q u\|^2_{L^2(\mu)} \right), & \end{aligned}$$

where

$$\alpha = \frac{1}{2} \left(a + c - \sqrt{(a-c)^2 + 4b^2} \right) = \frac{2(ac - b^2)}{a + c + \sqrt{(a-c)^2 + 4b^2}} > 0. \tag{5.56}$$

This shows that

$$\langle\langle u, u \rangle\rangle \geqslant \min(1, \alpha) \|u\|^2_{H^1(\mu)},$$

which allows us to conclude the proof. □

As mentioned above, for notational simplicity, we study the convergence to 0 of $\mathrm{e}^{t\mathcal{L}}\varphi$ for $\varphi \in L^2_0(\mu)$ rather than the convergence to 0 of $\mathrm{e}^{t\mathcal{L}^*}(f_0 - 1)$ for $f_0 \in L^2(\mu)$. The results of this section can however be straightforwardly extended to the latter case by changing the sign of the antisymmetric part of the operator (which is handled by changing the sign of b in the definition of the scalar product $\langle\langle \cdot, \cdot \rangle\rangle$). The following result can then be stated.

Theorem 5.7 (hypocoercivity). *Fix $\gamma > 0$, and assume either that the domain $\mathcal{D}$ is bounded, or that there exists $\rho > 0$ such that*

$$\forall q \in \mathcal{D}, \qquad |\nabla^2 V(q)| \leqslant \rho(1 + |\nabla V(q)|), \tag{5.57}$$

when $\mathcal{D}$ is not bounded. Then there exist $a, b, c \in \mathbb{R}$ satisfying (5.55) and $K > 0$ such that, for any $\varphi \in H^1(\mu) \cap L^2_0(\mu)$ and any $t \geqslant 0$,

$$\frac{d}{dt}\Big[\langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle\Big] \leqslant -K\left(\|\nabla_p \mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\mu)} + \|\nabla_q \mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\mu)}\right). \tag{5.58}$$

If in addition a Poincaré inequality holds for the measure $\nu(dq) = Z_\nu^{-1}\,\mathrm{e}^{-\beta V(q)}\,dq$, then there exists $\kappa > 0$ such that, for any $t \geqslant 0$,

$$\forall \varphi \in H^1(\mu) \cap L^2_0(\mu), \qquad \langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle \leqslant \mathrm{e}^{-2\kappa t}\langle\langle \varphi, \varphi\rangle\rangle. \tag{5.59}$$

As a consequence, there exists $C \geqslant 1$ such that

$$\forall t \geqslant 0, \qquad \|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(H^1(\mu)\cap L^2_0(\mu))} \leqslant C\,\mathrm{e}^{-\kappa t}. \tag{5.60}$$

In the last inequality, $H^1(\mu)$ is endowed with the canonical scalar product. The operator bound (5.60) is obtained from (5.59) by taking the supremum over functions $\varphi \in H^1(\mu) \cap L^2_0(\mu)$ and using the equivalence of norms provided by Lemma 5.3. Note that this implies that $C \geqslant 1$.

An immediate consequence of the above convergence result is the following corollary.

Corollary 5.2. *Under the same assumptions as in Theorem 5.7, the operator $\mathcal{L}$ is invertible on $H^1(\mu) \cap L^2_0(\mu)$, and the following equality holds in $\mathcal{B}(H^1(\mu) \cap L^2_0(\mu))$:*

$$\mathcal{L}^{-1} = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}} \mathrm{d}t.$$

Moreover,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(H^1(\mu)\cap L^2_0(\mu))} \leqslant \frac{C}{\kappa}, \tag{5.61}$$

where C and κ are the same constants as in (5.60).

Let us now present the proof of Theorem 5.7.

Proof. Note that, formally,

$$\frac{d}{dt}\left(\frac{1}{2}\langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle\right) = \langle\langle \mathrm{e}^{t\mathcal{L}}\varphi, \mathcal{L}\,\mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle.$$

Our aim is to find nonnegative constants a, b, c such that (5.55) holds and, for all C^∞ functions with compact support,

$$\langle\langle \varphi, \mathcal{L}\varphi\rangle\rangle \leqslant -\kappa\langle\langle \varphi, \varphi\rangle\rangle.$$

This allows us to obtain (5.58) and thus the desired exponential decrease, using the Poincaré inequality and a Gronwall argument, together with some density argument in order to extend inequalities from smooth functions with compact support to all elements of $H^1(\mu) \cap L^2_0(\mu)$. The idea of hypocoercivity is thus to find a scalar product equivalent to the canonical $H^1(\mu)$ scalar product and such that $-\mathcal{L}$ is coercive with respect to this scalar product (while it fails to be coercive with respect to the canonical $H^1(\mu)$ scalar product, see (5.28)).

Let us first compute the various terms in $\langle\langle \varphi, \mathcal{L}\varphi\rangle\rangle$. It is useful to first establish some commutator identities:

$$\begin{aligned}
&[\partial_{p_i}, \mathcal{L}]\varphi = \left[\partial_{p_i}, \frac{p_i}{m_i}\partial_{q_i}\right]\varphi - \frac{\gamma}{\beta}\left[\partial_{p_i}, \partial^*_{p_i}\partial_{p_i}\right]\varphi = \frac{1}{m_i}\left(\partial_{q_i} - \gamma\partial_{p_i}\right)\varphi,\\
&[\partial_{q_i}, \mathcal{L}]\varphi = -[\partial_{q_i}, \nabla V^T \nabla_p]\varphi = -\nabla\left(\partial_{q_i} V\right)^T \nabla_p \varphi.
\end{aligned} \tag{5.62}$$

First,

$$\langle \varphi, \mathcal{L}\varphi \rangle = -\frac{\gamma}{\beta} \|\nabla_p \varphi\|^2_{L^2(\mu)}.$$

Now, using (5.62),

$$\begin{aligned}\langle \partial_{p_i}\varphi, \partial_{p_i}\mathcal{L}\varphi \rangle &= \langle \partial_{p_i}\varphi, \mathcal{L}\partial_{p_i}\varphi \rangle + \frac{1}{m_i} \langle \partial_{p_i}\varphi, (\partial_{q_i} - \gamma\partial_{p_i})\,\varphi \rangle \\ &= -\frac{\gamma}{\beta} \|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\|\partial_{p_i}\varphi\|^2_{L^2(\mu)} + \frac{1}{m_i}\langle \partial_{p_i}\varphi, \partial_{q_i}\varphi \rangle .\end{aligned}$$

Moreover,

$$\begin{aligned}\langle \partial_{q_i}\varphi, \partial_{q_i}\mathcal{L}\varphi \rangle &= \langle \partial_{q_i}\varphi, \mathcal{L}\partial_{q_i}\varphi \rangle - \left\langle \partial_{q_i}\varphi, \nabla(\partial_{q_i}V)^T \nabla_p \varphi \right\rangle \\ &= -\frac{\gamma}{\beta} \|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)} - \left\langle \partial_{q_i}\varphi, \nabla(\partial_{q_i}V)^T \nabla_p \varphi \right\rangle .\end{aligned}$$

In addition,

$$\begin{aligned}\langle \partial_{p_i}\varphi, \partial_{q_i}\mathcal{L}\varphi \rangle &= \langle \partial_{p_i}\varphi, \mathcal{L}\partial_{q_i}\varphi \rangle - \left\langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T \nabla_p \varphi \right\rangle \\ &= \langle \partial_{p_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi \rangle - \frac{\gamma}{\beta} \left\langle \nabla_p\left(\partial_{p_i}\varphi\right), \nabla_p\left(\partial_{q_i}\varphi\right) \right\rangle - \left\langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T \nabla_p \varphi \right\rangle .\end{aligned}$$

Finally, the last term provides some dissipation in q since

$$\begin{aligned}\langle \partial_{q_i}\varphi, \partial_{p_i}\mathcal{L}\varphi \rangle &= \langle \partial_{q_i}\varphi, \mathcal{L}\partial_{p_i}\varphi \rangle + \frac{1}{m_i} \langle \partial_{q_i}\varphi, (\partial_{q_i} - \gamma\partial_{p_i})\,\varphi \rangle \\ &= \langle \partial_{q_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{p_i}\varphi \rangle - \frac{\gamma}{\beta} \langle \nabla_p(\partial_{q_i}\varphi), \nabla_p(\partial_{p_i}\varphi) \rangle + \frac{1}{m_i}\|\partial_{q_i}\varphi\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\langle \partial_{q_i}\varphi, \partial_{p_i}\varphi \rangle .\end{aligned}$$

Note that

$$\langle \partial_{p_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi \rangle = \langle \partial_{p_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi \rangle + \langle \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi, \partial_{p_i}\varphi \rangle = \langle \partial_{p_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi \rangle - \langle \partial_{q_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{p_i}\varphi \rangle .$$

which implies that

$$\langle \partial_{p_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{q_i}\varphi \rangle + \langle \partial_{q_i}\varphi, \mathcal{L}_{\mathrm{ham}}\partial_{p_i}\varphi \rangle = 0,$$

Gathering all terms, we obtain Some straightforward computations then show that

$$\begin{aligned}\langle\langle \varphi, \mathcal{L}\varphi \rangle\rangle &= -\frac{\gamma}{\beta}\|\nabla_p\varphi\|^2_{L^2(\mu)} \\ &\quad + a\sum_{i=1}^{D}\left(-\frac{\gamma}{\beta}\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\|\partial_{p_i}\varphi\|^2_{L^2(\mu)} + \frac{1}{m_i}\langle \partial_{p_i}\varphi, \partial_{q_i}\varphi \rangle\right) \\ &\quad + c\sum_{i=1}^{D}\left(-\frac{\gamma}{\beta}\|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)} - \langle \partial_{q_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi \rangle\right) \\ &\quad - b\sum_{i=1}^{D}\left(-\frac{\gamma}{\beta}\langle \nabla_p(\partial_{p_i}\varphi), \nabla_p(\partial_{q_i}\varphi) \rangle - \langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi \rangle\right) \\ &\quad - b\sum_{i=1}^{D}\left(-\frac{\gamma}{\beta}\langle \nabla_p(\partial_{q_i}\varphi), \nabla_p(\partial_{p_i}\varphi) \rangle + \frac{1}{m_i}\|\partial_{q_i}\varphi\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\langle \partial_{q_i}\varphi, \partial_{p_i}\varphi \rangle\right).\end{aligned}$$

Note in particular that dissipation terms $\|\partial_{q_i}\varphi\|^2_{L^2(\mu)}$ appear in the last line. This motivates choosing the parameter b positive.[2] The next step is to bound the right-hand side of the previous equality from above using Cauchy-Schwarz inequalities (recall that we assume $b \geqslant 0$), by

[2] When working with $\mathcal{L}^*$ instead of $\mathcal{L}$, the parameter b should be negative.

$$\begin{aligned}\langle\langle\varphi,\mathcal{L}\varphi\rangle\rangle \leqslant -\gamma\left(\frac{1}{\beta}+\frac{a}{m_+}\right)\|\nabla_p\varphi\|_{L^2(\mu)}^2 - \frac{b}{m_+}\|\nabla_q\varphi\|_{L^2(\mu)}^2 \\ + \frac{a+b\gamma}{m_-}\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)} \\ - \frac{a\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}^2 - \frac{c\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)}^2 \\ + \frac{2b\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)} \\ + \langle(b\nabla_p - c\nabla_q)\varphi,(\nabla^2 V)\nabla_p\varphi\rangle,\end{aligned}$$

where

$$m_+ = \max(m_1,\dots,m_d), \qquad m_- = \min(m_1,\dots,m_d). \tag{5.63}$$

Condition (5.55) shows that (by a computation similar to the one performed in the proof of Lemma 5.3)

$$\begin{aligned}a\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}^2 + c\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)}^2 - 2b\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)} \\ \geqslant \alpha(\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}^2 + \|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)}^2),\end{aligned} \tag{5.64}$$

with $\alpha > 0$ defined in (5.56). Therefore, the upper bound on $\langle\langle\varphi,\mathcal{L}\varphi\rangle\rangle$ simplifies as

$$\begin{aligned}\langle\langle\varphi,\mathcal{L}\varphi\rangle\rangle \leqslant -\gamma\left(\frac{1}{\beta}+\frac{a}{m_+}\right)\|\nabla_p\varphi\|_{L^2(\mu)}^2 - \frac{b}{m_+}\|\nabla_q\varphi\|_{L^2(\mu)}^2 \\ + \frac{a+b\gamma}{m_-}\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)} \\ - \frac{\alpha\gamma}{\beta}\sum_{i=1}^D(\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}^2 + \|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)}^2) \\ + \langle(b\nabla_p - c\nabla_q)\varphi,(\nabla^2 V)\nabla_p\varphi\rangle.\end{aligned} \tag{5.65}$$

In order to control the term $\langle(b\nabla_p - c\nabla_q)\varphi,(\nabla^2 V)\nabla_p\varphi\rangle$, two cases have to be distinguished.

(i) *The position space $\mathcal{D}$ is compact.* Here $\nabla^2 V$ is uniformly bounded, and there exists a constant $C_V > 0$ such that

$$\begin{aligned}|\langle(b\nabla_p - c\nabla_q)\varphi,(\nabla^2 V)\nabla_p\varphi\rangle| &\leqslant C_V\|\nabla_p\varphi\|_{L^2(\mu)}\|(b\nabla_p - c\nabla_q)\varphi\|_{L^2(\mu)} \\ &\leqslant bC_V\|\nabla_p\varphi\|_{L^2(\mu)}^2 + cC_V\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)}.\end{aligned}$$

(ii) *The position space is not compact.* Conditions must be imposed on the potential energy function in order to control the growth of the Hessian at infinity. One possible condition is that $\nabla^2 V$ (considered as a multiplication operator acting on vectors) is relatively bounded by ∇_q on $L^2(\mu)$, *i.e.*, there exist $A_V, B_V \geqslant 0$ such that

$$\forall\phi\in H^1(\mu), \qquad \|\phi\nabla^2 V\|_{L^2(\mu)} \leqslant A_V\|\phi\|_{L^2(\mu)} + B_V\|\nabla_q\phi\|_{L^2(\mu)}.$$

This condition is satisfied when (5.57) holds (see [274, Lemma A.24]). In this case,

$$\begin{aligned}&|\langle(b\nabla_p - c\nabla_q)\varphi,(\nabla^2 V)\nabla_p\varphi\rangle| \\ &\quad\leqslant (A_V\|\nabla_p\varphi\|_{L^2(\mu)} + B_V\|\nabla_p\nabla_q\varphi\|_{L^2(\mu)})\|(b\nabla_p - c\nabla_q)\varphi\|_{L^2(\mu)}.\end{aligned}$$

The term involving derivatives in both q and p can be controlled by the dissipative terms $-\frac{\alpha\gamma}{\beta}\|\partial_{p_j}\partial_{q_i}\varphi\|_{L^2(\mu)}^2$ in (5.65).

For simplicity, we consider the case when $\mathcal{D}$ is compact. Then,

$$\begin{aligned}\langle\langle\varphi,\mathcal{L}\varphi\rangle\rangle &\leqslant \left[bC_V-\gamma\left(\frac{1}{\beta}+\frac{a}{m_+}\right)\right]\|\nabla_p\varphi\|^2_{L^2(\mu)}-\frac{b}{m_+}\|\nabla_q\varphi\|^2_{L^2(\mu)}\\ &\quad+\left(\frac{a+b\gamma}{m_-}+cC_V\right)\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)}\\ &= -X^T\mathcal{M}X,\end{aligned}$$

where

$$X=\begin{pmatrix}\|\nabla_p\varphi\|_{L^2(\mu)}\\ \|\nabla_q\varphi\|_{L^2(\mu)}\end{pmatrix},\quad \mathcal{M}=\begin{pmatrix}A & C/2\\ C/2 & B\end{pmatrix}.$$

with

$$A=\gamma\left(\frac{1}{\beta}+\frac{a}{m_+}\right)-bC_V,\quad B=\frac{b}{m_+},\quad C=\frac{a+b\gamma}{m_-}+cC_V.$$

In addition to (5.55), the values of a,b,c should be such that

$$4AB>C^2, \tag{5.66}$$

in order for $\mathcal{M}$ to be positive definite. If this is the case, (5.58) follows. The condition (5.66) is satisfied for instance when

$$a=c=\varepsilon,\qquad b=\varepsilon^{1+\delta},\qquad \delta\in(0,1), \tag{5.67}$$

for $\varepsilon>0$ sufficiently small. Note also that this choice is compatible with (5.55) as soon as $\varepsilon<1$.

Let us now discuss how to obtain (5.59) from (5.58), assuming that ν satisfies a Poincaré inequality. This requires us to retrieve some control on the $L^2(\mu)$-norm of φ from the norms of the gradient. We use to this end the fact that, by the tensorization argument stated in Proposition 4.3, the canonical measure μ satisfies a Poincaré inequality, whose constant we denote by R. Therefore, $X^TSX\geqslant\langle\langle\varphi,\varphi\rangle\rangle$ with

$$S=\begin{pmatrix}a+1/(2R) & -b\\ -b & c+1/(2R)\end{pmatrix}.$$

We finally define κ as the largest positive constant such that $X^T\mathcal{M}X\geqslant\kappa X^TSX$. In fact, κ is the smallest eigenvalue of $S^{-1/2}\mathcal{M}S^{-1/2}$ (or equivalently of $\mathcal{M}S^{-1}$). Since S is symmetric definite positive, this shows that $\kappa>0$ since $\mathcal{M}$ is also definite positive thanks to (5.55). This concludes the proof of (5.59). □

Remark 5.10 (Degenerate scalar product). *The standard hypocoercive approach relies on estimates in $H^1(\mu)$, obtained under the non-degeneracy condition* (5.55)*. However, in the situation when ∇^2V is bounded, it is possible with a slight modification of the above argument to state an exponential convergence in the degenerate case $a=b=c$, for which the associated squared norm is $\|f\|^2_{L^2(\mu)}+a\|(\nabla_p-\nabla_q)f\|^2_{L^2(\mu)}$; see [137] for the complete argument.*

One interest of the hypocoercive approach is that the constants κ and C in (5.60) can be made quite explicit in terms of the various factors (related to the potential such as the bound on the Hessian C_V and the Poincaré constant R, or to the masses). We discuss this in Section 5.5.1 for the limits where $\gamma\to0$ and $\gamma\to+\infty$, and in Remark 5.11 for the small temperature limit.

Remark 5.11 (Small temperature limit). *Consider the limit where $\beta\to+\infty$. The constant R typically decreases exponentially with the temperature, with a lower bound scaling as $\mathrm{e}^{\beta(\inf\widetilde{V}-\sup\widetilde{V})}$ when $V=V_{\rm convex}+\widetilde{V}$. In this decomposition, the potential is separated into a strongly convex part $V_{\rm convex}$ whose Hessian is uniformly lower bounded by a positive constant, while $\widetilde{V}$ is some bounded perturbation. On the other hand, upon rescaling the values a,b,c in the definition of the scalar product by a factor $1/\beta$ (which amounts to considering $a=\overline{a}/\beta$,* etc.*), it can be shown that the smallest eigenvalue α of $\mathcal{M}$ is of order $1/\beta$. Therefore, the smallest eigenvalue κ of $S^{-1/2}\mathcal{M}S^{-1/2}$ admits a lower bound which decreases exponentially with β.*

Convergence in $L^2(\mu)$

The passage from bounds in $H^1(\mu)$ to bounds in $L^2(\mu)$ follows from hypoelliptic regularization results. Such results are presented in [274, Theorem A.8] or [119, Section 6.1], and are based on the idea of F. Hérau [127]. We follow the latter approach, which is more straightforward, although the so-obtained results are not as strong as the results presented in [274].

other motivation: integration Langevin with zero forces, and obtain some heat kernel with t^3 for positions...

Theorem 5.8 (hypoelliptic regularization). *Assume that $\nabla^2 V \in L^\infty(\mathcal{D})$ or that (5.57) holds. Then there exists $K > 0$ such that, for any $\varphi \in L^2(\mu)$,*

$$\forall 0 < t \leqslant 1, \qquad \|\nabla_p \mathrm{e}^{t\mathcal{L}}\varphi\|_{L^2(\mu)} + \|\nabla_q \mathrm{e}^{t\mathcal{L}}\varphi\|_{L^2(\mu)} \leqslant \frac{K}{t^{3/2}}\|\varphi\|_{L^2(\mu)}.$$

Combining this inequality with $t = 1$ and Theorem 5.7, we can conclude that, for $t \geqslant 1$ and $\varphi \in L^2_0(\mu)$,

$$\|\mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\mu)} \leqslant \langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle \leqslant \mathrm{e}^{-2\kappa(t-1)}\langle\langle \mathrm{e}^{\mathcal{L}}\varphi,\, \mathrm{e}^{\mathcal{L}}\varphi\rangle\rangle \leqslant \widetilde{C}\,\mathrm{e}^{-2\kappa t}\|\varphi\|^2_{L^2(\mu)},$$

which gives an exponential decay in $L^2(\mu)$. For completeness, let us recall the proof of Theorem 5.8, as presented in [119].

Proof. As at the end of the proof of Theorem 5.7, we consider for simplicity the case when $\nabla^2 V$ is bounded. We denote $\mathrm{e}^{t\mathcal{L}}\varphi$ by $\varphi(t)$ in this proof. Define

$$N_\varphi(t) = \frac{1}{2}\left[\|\varphi(t)\|^2_{L^2(\mu)} + c_1 t\|\nabla_p\varphi(t)\|^2_{L^2(\mu)} - c_2 t^2\langle\nabla_q\varphi(t), \nabla_p\varphi(t)\rangle_{L^2(\mu)} + c_3 t^3\|\nabla_q\varphi(t)\|^2_{L^2(\mu)}\right], \tag{5.68}$$

for some positive constants c_1, c_2, c_3 to be determined later on. Note that $2N_\varphi(t)$ corresponds to the norm induced by the scalar product (5.54) for time dependent coefficients $a(t) = c_1 t$, $2b(t) = c_2 t^2$ and $c(t) = c_3 t^3$. This choice is motivated in Remark 5.12 below. The time derivative of this quantity reads

$$\begin{aligned}
\frac{dN_\varphi(t)}{dt} &= \langle\varphi(t), \mathcal{L}\varphi(t)\rangle + \frac{c_1}{2}\|\nabla_p\varphi(t)\|^2_{L^2(\mu)} + c_1 t\sum_{i=1}^D \langle\partial_{p_i}\varphi(t), \partial_{p_i}\mathcal{L}\varphi(t)\rangle \\
&\quad - c_2 t\langle\nabla_q\varphi(t), \nabla_p\varphi(t)\rangle - \frac{c_2 t^2}{2}\sum_{i=1}^D[\langle\partial_{q_i}\varphi(t), \partial_{p_i}\mathcal{L}\varphi(t)\rangle + \langle\partial_{p_i}\varphi(t), \partial_{q_i}\mathcal{L}\varphi(t)\rangle] \\
&\quad + \frac{3c_3 t^2}{2}\|\nabla_q\varphi(t)\|^2_{L^2(\mu)} + c_3 t^3\sum_{i=1}^D\langle\partial_{q_i}\varphi(t), \partial_{q_i}\mathcal{L}\varphi(t)\rangle.
\end{aligned}$$

Using computations similar to those in the proof of Theorem 5.7, we obtain

$$\begin{aligned}
\frac{dN_\varphi(t)}{dt} &= -\left(\frac{\gamma}{\beta} - \frac{c_1}{2}\right)\|\nabla_p\varphi(t)\|^2_{L^2(\mu)} \\
&\quad - c_1 t\sum_{i=1}^D\left[\frac{\gamma}{\beta}\|\nabla_p(\partial_{p_i}\varphi(t))\|^2_{L^2(\mu)} + \frac{\gamma}{m_i}\|\partial_{p_i}\varphi(t)\|^2_{L^2(\mu)}\right] \\
&\quad + \sum_{i=1}^D\left[t\left(\frac{c_1}{m_i} - c_2\right) + \frac{\gamma c_2 t^2}{2m_i}\right]\langle\partial_{p_i}\varphi(t), \partial_{q_i}\varphi(t)\rangle \\
&\quad + \frac{c_2 t^2}{2}\sum_{i=1}^D\frac{2\gamma}{\beta}\langle\nabla_p(\partial_{p_i}\varphi(t)), \nabla_p(\partial_{q_i}\varphi(t))\rangle + \langle\partial_{p_i}\varphi(t), \nabla(\partial_{q_i}V)^T\nabla_p\varphi(t)\rangle \\
&\quad + t^2\sum_{i=1}^D\left(\frac{3c_3}{2} - \frac{c_2}{m_i}\right)\|\partial_{q_i}\varphi(t)\|^2_{L^2(\mu)} \\
&\quad - c_3 t^3\sum_{i=1}^D\left[\frac{\gamma}{\beta}\|\nabla_p(\partial_{q_i}\varphi(t))\|^2_{L^2(\mu)} + \langle\partial_{q_i}\varphi(t), \nabla(\partial_{q_i}V)^T\nabla_p\varphi(t)\rangle\right].
\end{aligned} \tag{5.69}$$

We now choose c_1, c_2, c_3 such that $dN_\varphi/dt \leqslant 0$. First, we restrict ourselves to coefficients such that

$$\forall (x,y) \in \mathbb{R}^2, \qquad c_2 t^2 xy \leqslant c_1 t x^2 + c_3 t^3 y^2.$$

which is satisfied once

$$c_1, c_3 \geqslant 0, \qquad 4c_1 c_3 > c_2^2. \tag{5.70}$$

Note that we keep a strict inequality in the second condition in order to have some norm equivalence between $N_\varphi(t)$ and $\|\varphi(t)\|^2_{H^1(\mu)}$, which is crucial to conclure the proof. Then,

$$\begin{aligned} -c_1 t \sum_{i=1}^D \frac{\gamma}{\beta} \|\nabla_p(\partial_{p_i}\varphi(t))\|^2_{L^2(\mu)} + \frac{c_2 t^2}{2} \sum_{i=1}^D \frac{2\gamma}{\beta} \langle \nabla_p(\partial_{p_i}\varphi(t)), \nabla_p(\partial_{q_i}\varphi(t))\rangle \\ - c_3 t^3 \sum_{i=1}^D \frac{\gamma}{\beta} \|\nabla_p(\partial_{q_i}\varphi(t))\|^2_{L^2(\mu)} \leqslant 0, \end{aligned}$$

so that, with $C_V = \|\nabla^2 V\|_{L^\infty}$, **NEED TO CHECK FACTORS HERE (REMARQUE JULIEN)**

$$\begin{aligned} \frac{dN_\varphi(t)}{dt} \leqslant & -\left(\frac{\gamma}{\beta} + \frac{\gamma c_1 t}{m_+} - \frac{c_1}{2} - C_V \frac{c_2 t^2}{2}\right) \|\nabla_p \varphi(t)\|^2_{L^2(\mu)} \\ & - t^2 \left(\frac{c_2}{m_+} - \frac{3c_3}{2}\right) \|\nabla_q \varphi(t)\|^2_{L^2(\mu)} \\ & + \left[t\left(\frac{c_1}{m_-} + c_2\right) + \frac{\gamma c_2 t^2}{2m_-} + C_V c_3 t^3\right] \|\nabla_p \varphi(t)\|_{L^2(\mu)} \|\nabla_q \varphi(t)\|_{L^2(\mu)}. \end{aligned}$$

On the time interval $[0,1]$, we finally obtain the following upper bound:

$$\begin{aligned} \frac{dN_\varphi(t)}{dt} \leqslant & -\left(\frac{\gamma}{\beta} - \frac{c_1}{2} - C_V \frac{c_2}{2}\right) \|\nabla_p \varphi(t)\|^2_{L^2(\mu)} - t^2 \left(\frac{c_2}{m_+} - \frac{3c_3}{2}\right) \|\nabla_q \varphi(t)\|^2_{L^2(\mu)} \\ & + t\left[\frac{c_1}{m_-} + \frac{\gamma c_2}{2m_-} + C_V c_3\right] \|\nabla_p \varphi(t)\|_{L^2(\mu)} \|\nabla_q \varphi(t)\|_{L^2(\mu)}. \end{aligned}$$

We next consider coefficients c_1, c_2, c_3 all of order ε for $\varepsilon > 0$ sufficiently small, satisfying (5.70) and $c_2/m_+ - 3c_3/2 > 0$. For instance, $c_1 = \varepsilon$, $c_2 = \bar{c}_2 \varepsilon$ and $c_3 = \bar{c}_3 \varepsilon$, with $\bar{c}_2, \bar{c}_3$ sufficiently small so that $\bar{c}_2 > 3m_+\bar{c}_3/2$ and $4\bar{c}_3 \geqslant \bar{c}_2^2$. We can then deduce that $dN_\varphi(t)/dt \leqslant 0$, which implies $N_\varphi(t) \leqslant N_\varphi(0) = \|\varphi\|^2_{L^2(\mu)}/2$. The desired conclusion immediately follows. □

Remark 5.12. *Let us now motivate more precisely the definition* (5.68)*. As discussed after this equation, the choice* (5.68) *corresponds to the scalar product* (5.54) *with time dependent coefficients* $a(t), b(t), c(t)$*. First, in order to only have the* $L^2(\mu)$*-norm of* φ *at time* $t = 0$*, it is necessary that* $a(0) = b(0) = c(0) = 0$*. Second, when generalizing the computations leading to* (5.69)*, the prefactors of the third and fifth terms on the right-hand side of (E) now read* $a(t)/m_i - b'(t) + \gamma b(t)/(2m_i)$ *instead of* $t(c_1/m_i - c_2) + \gamma c_2 t^2/(2m_i)$ *and* $c'(t)/2 - 2b(t)/m_i$ *instead of* $t^2(3c_3/2 - c_2/m_i)$*. This suggests that* $a(t)$ *and* $b'(t)$ *should be of the same order of magnitude, as well as* $b(t)$ *and* $c'(t)$*. When* $a(t)$ *is linear in* t*, this implies that* $b(t)$ *is quadratic and* $c(t)$ *cubic.*

Hamiltonian and overdamped limits

The results stated in Theorem 5.7 are obtained for a given value of γ. Hypocoercivity allows to quantify the degradation of the convergence rate. Let κ_γ denote the exponential decay rate given by Theorem 5.7 for a given value of γ. By tracking the dependency of all estimates on γ in the proofs of Theorems 5.7 and 5.8, it is possible to show the following result.

Proposition 5.5. *Under the same assumptions as for Theorem 5.7, there exist $C, \overline{\kappa} > 0$ such that, for all $\gamma > 0$,*

$$\left\| \mathrm{e}^{t\mathcal{L}} \right\|_{\mathcal{B}(H^1(\mu) \cap L^2_0(\mu))} \leqslant \overline{C} \mathrm{e}^{-\overline{\kappa} \min(\gamma, \gamma^{-1})t}.$$

As a consequence,

$$\left\| \mathcal{L}^{-1} \right\|_{\mathcal{B}\left(L^2_0(\mu)\right)} \leqslant \frac{\overline{C}}{\overline{\kappa}} \max\left(\gamma, \frac{1}{\gamma}\right). \tag{5.71}$$

On the other hand, the Langevin dynamics becomes singular in the limit $\gamma \to 0$, where it reduces to the Hamiltonian dynamics (which is not ergodic with respect to the canonical measure); and in the limit $\gamma \to +\infty$, where it converges to the overdamped Langevin dynamics (see the discussion after (5.1)). It is therefore expected that the convergence rate to equilibrium of the Langevin dynamics degrades as $\gamma \to 0$ or $\gamma \to +\infty$. The decay rate therefore becomes singular both in the Hamiltonian and overdamped limits. In both cases, the decay is apparent only at long time scales, of order t/γ as $\gamma \to 0$ (the fluctuation/dissipation is so small that energy diffusion is only observed at long times: see [119] for a precise statement) and γt as $\gamma \to +\infty$ (the fluctuation/dissipation is so large that the momenta are continuously randomized, which leads to some effective Brownian motion on the positions over long times). Proposition 5.5 shows that in the limiting regimes of very low or very large frictions, time should be renormalized in order to observe some macroscopic diffusion. Note also that the resolvents bounds are sharp, see [119, Proposition 6.3] for the Hamiltonian limit. For the overdamped limit, consider the following example:

$$\mathcal{L}\Big(p^T \nabla V + \gamma(V - v)\Big) = p^T M^{-1} \left(\nabla^2 V\right) p - |\nabla V|^2,$$

where v is a constant chosen such that $p^T \nabla V + \gamma(V - v)$ has a vanishing average with respect to μ. It is clear that the right hand side is of order 1, while the left-hand side is of order γ when V is not constant. In fact, it can be shown that $\mathcal{L}^{-1}$ is at dominant order equal to $\gamma \mathcal{L}_{\mathrm{ovd}}$ (see [169, Theorem 2.5] and Theorem ??for precise statements). This results relies on the fact that the norm of $\mathcal{L}^{-1}$ can be uniformly controlled for functions whose conditional averages with respect to the momentum distribution vanish for all possible configurations q.

Proof (of Proposition 5.5). We study separately the Hamiltonian and the overdamped limits.

- *Hamiltonian limit.* When $\gamma \to 0$, it is no longer possible to choose a, b, c in (5.54) of order 1 since the condition (5.66) cannot be verified. This motivates choosing a, b, c of order γ by writing $a = \gamma \overline{a}$, etc. In this case, the smallest eigenvalue of M transforms into $\alpha = \gamma \overline{\alpha}$ with

$$\overline{\alpha} = \frac{1}{2} \cdot \frac{4\overline{A}\overline{B} - \overline{C}^2}{\overline{A} + \overline{B} + \sqrt{(\overline{A} - \overline{B})^2 + \overline{C}^2}},$$

and

$$\overline{A} = \frac{1}{\beta} + \frac{\overline{a}}{m_+} - \overline{b} C_V, \qquad \overline{B} = \frac{\overline{b}}{m_+}, \qquad \overline{C} = \frac{\overline{a} + \overline{b}\gamma}{m_-} + C_V \overline{c}.$$

On the other hand, S^{-1} is close to a diagonal matrix with $2m_+/\beta$ and R_V^{-1} on the diagonal. This shows that there exists $\overline{\kappa} > 0$ such that, for any $0 < \gamma \leqslant 1$,

$$\left\langle \left\langle \mathrm{e}^{t\mathcal{L}} \varphi, \mathrm{e}^{t\mathcal{L}} \varphi \right\rangle \right\rangle_\gamma \leqslant \mathrm{e}^{-2\gamma\overline{\kappa}t} \left\langle \langle \varphi, \varphi \rangle \right\rangle_\gamma, \tag{5.72}$$

where the subscript γ in $\langle\langle \cdot, \cdot \rangle\rangle_\gamma$ emphasizes the dependence on γ of the bilinear form. In particular,

$$\left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|^2_{L^2(\mu)} \leqslant \mathrm{e}^{-2\gamma\overline{\kappa}t} \left\langle \langle \varphi, \varphi \rangle \right\rangle_\gamma.$$

We next choose $c_i = \gamma \overline{c_i}$ in (5.68). We can then find $\overline{C} > 0$ (independent of the friction γ) such that, for any $0 < \gamma \leqslant 1$,

$$\left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|_{L^2(\mu)} \leqslant \overline{C} \mathrm{e}^{-\gamma\overline{\kappa}t} \left\| \varphi \right\|_{L^2(\mu)}.$$

- *Overdamped limit.* As in the Hamiltonian case, it is no longer possible to choose a, b, c of order 1 when $\gamma \to +\infty$ since the condition (5.66) cannot be verified. In order to temper the increase of the off-diagonal coefficient of the matrix M, we choose a, b, c of order $1/\gamma$ by writing $a = \overline{a}/\gamma$, etc. In this scaling, α becomes of order γ^{-1}. We next choose $c_i = \overline{c_i}/\gamma$ in (5.68). By a reasoning similar to the one performed for the Hamiltonian limit, we obtain the existence of $\overline{C}, \overline{\alpha} > 0$ such that, for any $\gamma \geqslant 1$,
$$\left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\|_{L^2(\mu)} \leqslant \overline{C} \mathrm{e}^{-\overline{\kappa} t/\gamma} \left\| \varphi \right\|_{L^2(\mu)}.$$

This allows to conclude the proof of Proposition 5.5. □

Remark 5.13. *A result similar to Proposition 5.5 cannot be stated in a $H^1(\mu)$ setting since the constant C appearing in* (5.60) *becomes singular since the prefactor arising from the norm equivalence scales as* $\max(\gamma, \gamma^{-1})$.

Going from $H^1(\mu)$ to $L^2(\mu)$ without hypoelliptic regularization

Instead of using Theorem 5.8 (which however has the benefit of providing explicit regularization estimates), we can in fact infer the exponential convergence in $L^2_0(\mu)$ directly from the one in $H^1(\mu) \cap L^2_0(\mu)$, by considering the family of bounded self-adjoint operators $Q_t = \mathrm{e}^{t\mathcal{L}^*} \mathrm{e}^{t\mathcal{L}}$. The argument below is taken from [63].

We rely to this end on (5.72) and its analogue in the overdamped limit, which can be rephrased as follows: there exists $\overline{\kappa} > 0$ such that, for any $\gamma > 0$,
$$\forall \varphi \in H^1(\mu) \cap L^2_0(\mu), \quad \forall t \geqslant 0, \qquad \left\langle\!\left\langle \mathrm{e}^{t\mathcal{L}} \varphi, \mathrm{e}^{t\mathcal{L}} \varphi \right\rangle\!\right\rangle_\gamma \leqslant \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left\langle\!\left\langle \varphi, \varphi \right\rangle\!\right\rangle_\gamma .$$

A similar inequality holds for $\mathrm{e}^{t\mathcal{L}^*}$, with the same rate but with a scalar product $((\cdot,\cdot))_\gamma$ for which the cross term involving ∇_q and ∇_p term has the same coefficient with an opposite sign:
$$\forall \varphi \in H^1(\mu) \cap L^2_0(\mu), \quad \forall t \geqslant 0, \qquad \left(\left(\mathrm{e}^{t\mathcal{L}^*} \varphi, \mathrm{e}^{t\mathcal{L}^*} \varphi \right) \right)_\gamma \leqslant \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left((\varphi, \varphi) \right)_\gamma .$$

From the asymptotic choices for the coefficients of $((\cdot,\cdot))_\gamma$ and $\langle\langle \cdot, \cdot \rangle\rangle_\gamma$ discussed above, there exists $C > 0$ (independent of γ) such that
$$\forall \gamma > 0, \quad \forall \varphi \in H^1(\mu), \qquad \frac{1}{C} \left\langle\!\left\langle \varphi, \varphi \right\rangle\!\right\rangle_\gamma \leqslant \left((\varphi, \varphi) \right)_\gamma \leqslant C \left\langle\!\left\langle \varphi, \varphi \right\rangle\!\right\rangle_\gamma .$$

Then, for any $t \geqslant 0$,
$$\begin{aligned} \left((Q_t \varphi, Q_t \varphi) \right)_\gamma &\leqslant \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left((P_t \varphi, P_t \varphi) \right)_\gamma \leqslant C \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left\langle\!\left\langle P_t \varphi, P_t \varphi \right\rangle\!\right\rangle_\gamma \\ &\leqslant C \mathrm{e}^{-4\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left\langle\!\left\langle \varphi, \varphi \right\rangle\!\right\rangle_\gamma \leqslant C^2 \mathrm{e}^{-4\overline{\kappa} \min(\gamma, \gamma^{-1}) t} \left((\varphi, \varphi) \right)_\gamma . \end{aligned}$$

Fix now $t > (\ln C)/(2\overline{\kappa} \min(\gamma, \gamma^{-1}))$ and define $\rho_{\gamma,t} = C \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t} < 1$. The above inequality implies that, for $\varphi \in H^1(\mu) \cap L^2_0(\mu)$,
$$\forall n \geqslant 0, \qquad \| Q_t^n \varphi \|^2_{L^2(\mu)} \leqslant \left((Q_t^n \varphi, Q_t^n \varphi) \right)_\gamma \leqslant \rho_{\gamma,t}^{2n} \left((\varphi, \varphi) \right)_\gamma .$$

From [120, Lemma 2.9], we deduce that we have in fact
$$\| Q_t \varphi \|_{L^2(\mu)} \leqslant \rho_{\gamma,t} \| \varphi \|_{L^2(\mu)}.$$

Since $\| P_t \|^2_{\mathcal{B}(L^2_0(\mu))} \leqslant \| Q_t \|_{\mathcal{B}(L^2_0(\mu))}$, we finally obtain, by density of $H^1(\mu)$ in $L^2(\mu)$, that
$$\| P_t \|_{\mathcal{B}(L^2_0(\mu))} \leqslant \rho_{\gamma,t} = C \mathrm{e}^{-2\overline{\kappa} \min(\gamma, \gamma^{-1}) t}.$$

This property was proved for any $t > (\ln C)/(2\overline{\kappa} \min(\gamma, \gamma^{-1}))$, but can be extended to all times $t \geqslant 0$ in view of the trivial bound $\| P_t \|_{\mathcal{B}(L^2_0(\mu))} \leqslant 1$.

6

Discretization of (overdamped) Langevin dynamics

We discuss in this lecture how to discretize the (overdamped) Langevin dynamics studied in Lectures 4 and 5. We start in Section 6.1 by a general presentation of time discretization issues in the context of computational statistical physics, focusing in particular on the approximation of trajectory averages by numerical methods operating with a finite timestep but integrated over long times (very much in the spirit of numerical methods discussed in Lecture 2 to integrate the Hamiltonian dynamics). We next focus in Section 6.2 on the systematic error which persists in the regime of infinitely long simulations, namely the bias on the invariant probability measure sampled by the Markov chains discretizing the underlying continuous dynamics. We conclude in Section 6.3 by a discussion on the statistical error of trajectory averages of discretizations of continuous stochastic dynamics, and mention some options to reduce it.

6.1 Time discretization of ergodic stochastic dynamics

In order to approximate time averages such as (4.13) or (5.14), the continuous stochastic dynamics (4.1) and (5.5) are discretized in time using a numerical scheme. We present in this section elements on discretizations of SDEs more general than the latter ones, and come back to these specific dynamics in Sections 6.2.3 and 6.2.4 respectively. More precisely, we consider the following continous dynamics, with values in some space $\mathcal{X}$, to be discretized:

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t. \tag{6.1}$$

We assume in the sequel that this dynamics admits a unique invariant probability measure $\pi(dx)$. Overdamped Langevin dynamics correspond to $x = q$ and $\mathcal{X} = \mathcal{D}$ with π given by (4.2); while $x = (q, p)$ and $\mathcal{X} = \mathcal{E}$ for Langevin dynamics, with π given by (5.3). The simplest choice to discretize

it is to resort to an Euler–Maruyama discretization with a fixed time step $\Delta t > 0$. In this case $x_{n\Delta t}$ is approximated by x^n, constructed iteratively from a given initial condition $x^0 = x_0$ as

$$x^{n+1} = x^n + b(x^n)\,\Delta t + \sigma(x^n)\sqrt{\Delta t}\,G^n, \tag{6.2}$$

where G^n is a sequence of i.i.d. Gaussian random variables with covariance matrix Id_D. We denote in the sequel by $P_{\Delta t}$ the evolution operator (also called transition operator) associated with a general one-step numerical scheme:

$$\left(P_{\Delta t}\varphi\right)(x) = \mathbb{E}\left(\varphi(x^{n+1})\middle| x^n = x\right). \tag{6.3}$$

It is the discrete equivalent of the semigroup $\mathrm{e}^{\Delta t\mathcal{L}}$, with $\mathcal{L}$ the generator of (6.1). The transition operator $P_{\Delta t}$ describes how the values of a given function evolve in average over one time step.

We discuss in this section the various types of errors arising from the discretization. We first recall in Section 6.1.1 the standard measures of error on finite time intervals (weak vs. strong errors). We then turn to our main concern, error estimates on long time averages. After providing conditions under which long time averages converge (see Section 6.1.2), we discuss in Section 6.1.3 how to decompose the error, for sufficiently long times, into

(i) a systematic part, related to errors on the invariant measure due to the time discretization;
(ii) a statistical error dictated by a Central Limit Theorem, with an asymptotic variance close to the one of the underlying continuous process.

The quality of the numerical schemes for ergodic dynamics is therefore mainly determined by the size of the systematic errors, as well as their stability.

6.1.1 Standard numerical analysis of SDEs

There are many good review articles and textbooks on the numerical analysis of SDEs, such as [150, 221, 198]. Two types of errors are considered for discretizations of SDEs, as follows.

(1) *Weak error estimates.* There exists $\alpha > 0$ such that, for any C^∞ test function φ with compact support and finite time horizon $T > 0$, there are $C \geqslant 0$ and $\Delta t^* > 0$ (the latter two constants depending on φ and T *a priori*) such that, for any $\Delta t \in (0, \Delta t^*]$,

$$\sup_{0 \leqslant n \leqslant T/\Delta t} \left|\mathbb{E}[\varphi(x^n)] - \mathbb{E}[\varphi(x_{n\Delta t})]\right| \leqslant C\Delta t^\alpha. \tag{6.4}$$

In fact, when the numerical method is stable (which is the case when b and σ are globally Lipschitz), such error estimates can be deduced from the error over one time step, as stated in [198, Theorem 2.1]. In essence, the order α is determined by the formal equality

$$P_{\Delta t} = \mathrm{e}^{\Delta t\mathcal{L}} + \mathrm{O}(\Delta t^{\alpha+1}).$$

To make the functional setting more precise, this equally can for instance be understood as $P_{\Delta t}\varphi = \mathrm{e}^{\Delta t\mathcal{L}}\varphi + \Delta t^{\alpha+1} r_{\varphi,\Delta t}$ for a function φ growing at most polynomially and whose derivatives of order at most $2\alpha + 2$ grow at most polynomially, and with a remainder term $r_{\varphi,\Delta t}$ such that there exists $a \in \mathbb{N}$ for which $\|r_{\varphi,\Delta t}/(1 + |x|^a)\|_{B^\infty} \leqslant K$ for Δt sufficiently small.

(2) *Strong error estimates in L^r-norm for $r \geqslant 1$.* There exists $\alpha \in \mathbb{R}_+$ such that, for any time horizon T, there is $C \geqslant 0$ and $\Delta t^* > 0$ (the latter two constants depending on T *a priori*) such that, for any $0 \leqslant \Delta t \leqslant \Delta t^*$,

$$\sup_{0 \leqslant n \leqslant T/\Delta t} \left(\mathbb{E}|x^n - x_{n\Delta t}|^r\right)^{1/r} \leqslant C\Delta t^\alpha. \tag{6.5}$$

In this case the Gaussian increments used in a numerical scheme such as (6.2) must be induced by the Brownian motion for the continuous dynamics (6.1), *i.e.*,

$$G^n = \frac{W_{(n+1)\Delta t} - W_{n\Delta t}}{\sqrt{\Delta t}}.$$

Typically, the constant C in (6.4) and (6.5) are obtained via some (discrete) Gronwall estimate, as in the standard numerical analysis of ordinary differential equations, and hence increase exponentially with time.

As an example, let us mention that, when the functions b and σ in (6.1) are globally Lipschitz, the weak and strong errors of the Euler–Maruyama scheme (6.2) are respectively 1 and 1/2.

Note that it is also possible to reduce errors due to the time discretization by resorting to extrapolation methods as in [161] or multilevel Monte Carlo methods [104, 105].

6.1.2 Convergence of time averages

The error estimates (6.4) and (6.5) are not relevant to long-time convergence since the prefactor C is not uniformly controlled in time. Therefore, additional techniques should be introduced to control the quality of the approximation of average properties presented by the time averages traditionally considered in molecular simulation:

$$\widehat{\varphi}_{N_{\rm iter},\Delta t} = \frac{1}{N_{\rm iter}} \sum_{n=0}^{N_{\rm iter}-1} \varphi(x^n). \tag{6.6}$$

We discuss here the long time convergence of $\widehat{\varphi}_{N_{\rm iter},\Delta t}$ to some limit. We first resort to Proposition 3.1 to conclude to the almost sure convergence of the trajectory averages. This requires first checking whether the Markov chain induced by the numerical scheme indeed admits an invariant probability measure. We next discuss sufficient conditions for a Central Limit Theorem to hold.

Existence and uniquess of an invariant probability measure

A first issue is to prove that the Markov chain induced by the numerical scheme is indeed ergodic with respect to some probability measure, which depends in general on the time step Δt. Even if the associated continuous dynamics is ergodic, the ergodicity of the discretized dynamics cannot be guaranteed in general. A common obstruction is the presence of non-globally Lipschitz drifts which induce a transient behaviour of the Markov chain. A typical case is reported in [189, Section 6.3] for $x \in \mathbb{R}$ with $b(x) = -x^3$ and $\sigma(x) = 1$. Note first that the associated continuous dynamics

$$dx_t = -(x_t)^3 dt + dW_t$$

admits the probability measure $Z^{-1}\mathrm{e}^{-x^4/2}\,dx$ as a unique invariant measure (by the results of Lecture 4). The Euler–Maruyama scheme for this dynamics reads

$$x^{n+1} = x^n - \Delta t\,(x^n)^3 + \sqrt{\Delta t}\,G^n.$$

It can be shown that

$$\mathbb{P}\left(|x^n| \geqslant \frac{2^n}{\sqrt{\Delta t}} \ \forall n \geqslant 1\right) = \alpha > 0. \tag{6.7}$$

Assume that the Markov chain has an invariant measure $\mu_{\Delta t}$. There exists $R > 0$ such that $\mu_{\Delta t}([-R,R]) \geqslant 3/4$. Consider next $\varphi(x) = 1_{|x|>R}$. In view of (6.7), there exists $N_{\rm iter}$ such that

$$\frac{1}{N_{\rm iter}} \sum_{n=1}^{N_{\rm iter}} \varphi(x^n)$$

is larger than 1/2 with probability α; while, on the other hand, this quantity would converge almost surely to $\mathbb{E}_{\mu_{\Delta t}}(\varphi) \leqslant 1/4$ by Proposition 3.1. The contradiction shows that there cannot be an invariant probability measure.

In order to prove the existence of an invariant probability measure $\pi_{\Delta t}$ for the numerical scheme, it is standard to resort to results such as Theorem 3.1. Proving that a minorization condition holds on any compact set (see Assumption 3.2) is usually not too difficult, thanks to the presence of

Gaussian increments; see for instance Lemma ?? below for an Euler–Maruyama discretization of the overdamped Langevin dynamics. It can also often be shown that the measure $\pi_{\Delta t}$ is absolutely continuous with respect to the Lebesgue measure since the transition kernel has a smooth density with respect to the Lesbesgue measure.

update ref

Some assumptions on the drift, on the other hand, are usually required to state a Lyapunov condition such as Assumption 3.1; see [189]. When these conditions are met, the convergence of the law of x^n to the invariant measure is exponentially fast (with respect to the iteration index, the time step Δt being fixed, as stated in Theorem 3.1).

Ergodicity of time averages

The next step is to prove that the numerical scheme is aperiodically irreducible, and in fact that (3.3) holds. For discretizations of SDEs, the latter property is usually easy to prove, taking the Lebesgue measure as a reference measure. It holds for instance with $n = 1$ for the Euler–Maruyama scheme (6.2) when σ has full rank d at each point $x \in \mathcal{X}$ since

$$G^1 = \sigma(x^0)^{-1} \left(\frac{x^1 - x^0 - \Delta t\, b(x^0)}{\sqrt{\Delta t}} \right) := \mathcal{G}_{\Delta t, x^0}(x^1),$$

so that

$$P_{\Delta t}(x^0, S) = \mathbb{P}\left(G^1 \in \mathcal{G}_{\Delta t, x_0}^{-1}(S) \right) > 0.$$

When σ is degenerate, several iterates may be necessary; see for instance [36] where it is proved that $P_{\Delta t}^2(x^0, S) > 0$ for some discretization of Langevin dynamics. Once the existence of an invariant probability measure and the irreducibility of the scheme are proved, the almost-sure convergence of long-time averages over one realization already follows by Proposition 3.1.

add a reference to later on

Asymptotic variance and Central Limit Theorem

As in the continuous case, when decay estimates on the evolution operator $P_{\Delta t}$ hold as in Theorem 3.1, it can easily be shown that the asymptotic variance is well defined provided $\mathscr{W} \in L^2(\pi_{\Delta t})$ and $\varphi \in B^\infty_{\mathscr{W}}(\mathcal{X})$; and that a Central Limit Theorem holds in fact. The discussion follows the same lines the presentation in Section 3.4, upon replacing $\nu(dq)$ by the invariant probability measure $\pi_{\Delta t}(dx)$ for the Markov chain under consideration, and Π by the projection operator $\Pi_{\Delta t}$ defined as

$$\Pi_{\Delta t}\varphi = \varphi - \int_{\mathcal{X}} \varphi \, d\pi_{\Delta t}.$$

A way to prove that $\mathscr{W} \in L^2(\pi_{\Delta t})$ is check whether the assumptions of Theorem 3.1 are satisfied for the Lyapunov function $\mathscr{W}^2$ instead of $\mathscr{W}$, so that the integrability condition follows from (3.11). In practice, it can be convenient to establish minorization conditions on arbitrary compact sets, and to obtain Lyapunov conditions for the family of functions $\mathscr{W}_n(x) = 1 + |x|^n$ (for integers $n \geqslant n_0$ sufficiently large). Note that $\mathscr{W}_n^2 = \mathscr{W}_{2n} + 2(\mathscr{W}_n - 1)$, so that the $L^2(\pi_{\Delta t})$ integrability of $\mathscr{W}_n$ follows as soon as Lyapunov estimates hold for $\mathscr{W}_{2n}$.

The expression of the asymptotic variance suggests a definition of a correlation time, as for continuous dynamics. By the same reasoning as the one leading to (3.23),

$$\sigma^2_{\varphi,\Delta t} = N_{\mathrm{corr},\Delta t,\varphi} \sigma^2_{\varphi,\mathrm{iid},\Delta t}, \quad \text{where} \quad \sigma^2_{\varphi,\mathrm{iid},\Delta t} = \int_{\mathcal{X}} (\Pi_{\Delta t}\varphi)^2 \, d\pi_{\Delta t}.$$

As discussed below, the correlation time $\theta_{\mathrm{corr},\varphi}$ is related to the number of correlation steps $N_{\mathrm{corr},\Delta t,\varphi}$ for the discrete dynamics as $\theta_{\mathrm{corr},\varphi} \simeq N_{\mathrm{corr},\Delta t,\varphi} \Delta t$ since $\theta_{\mathrm{corr},\varphi} \simeq N_{\mathrm{corr},\Delta t,\varphi} \Delta t$ in the limit of small timesteps Δt.

6.1.3 Error analysis on time averages: general decomposition

Let us now discuss the topic of main interest for this section, namely error estimates for the computation of thermodynamic averages $\mathbb{E}_\pi(\varphi) = \int_{\mathcal{X}} \varphi \, d\pi$ with (6.6), for a given one step discretization of the continuous dynamics (6.1) ergodic with respect to π. We decompose the error as the sum of two contributions:

$$\widehat{\varphi}_{N_{\rm iter},\Delta t} - \mathbb{E}_\pi(\varphi) = \Big(\widehat{\varphi}_{N_{\rm iter},\Delta t} - \mathbb{E}_{\pi_{\Delta t}}(\varphi)\Big) + \Big(\mathbb{E}_{\pi_{\Delta t}}(\varphi) - \mathbb{E}_\pi(\varphi)\Big). \tag{6.8}$$

The first term is a statistical error arising from the finiteness of the number of time steps $N_{\rm iter}$, while the second term is a systematic error (or bias), which persists in the limit $N_{\rm iter} \to +\infty$, and is due to the use of finite time steps $\Delta t > 0$. Let us discuss each term more precisely.

Statistical error

According to the Central Limit Theorem for Markov chains (which holds when the Poisson equation (3.21) can be solved in $L^2(\pi_{\Delta t})$, see the discussion after Proposition 3.5), the statistical error behaves in the limit $N_{\rm iter} \to +\infty$ as a Gaussian random variable with asymptotic variance given by (3.22). In practice, this asymptotic regime is attained when $N_{\rm iter} \gg N_{{\rm corr},\Delta t,\varphi}$. However, $N_{{\rm corr},\Delta t,\varphi}$ is often very large because of the metastability of the underlying continuous dynamics (so that $\theta_{{\rm corr},\varphi}$ is large), which makes it difficult in practice to ensure that the Central Limit Theorem actually holds for the values of $N_{\rm iter}$ which can be achieved with computer simulations.

When the asymptotic regime can be considered to be reached, $\widehat{\varphi}_{N_{\rm iter},\Delta t} - \mathbb{E}_{\pi_{\Delta t}}(\varphi)$ is of order

$$\frac{\sigma_{\varphi,\Delta t}}{\sqrt{N_{\rm iter}}} = \frac{\sigma_{\varphi,\Delta t}\sqrt{\Delta t}}{\sqrt{T}}.$$

This reformulation highlights the fact that the statistical error is of the order of the inverse of the square root of the 'physical' simulation time $T = N_{\rm iter}\Delta t$. Indeed, weakly consistent discretizations of SDEs are such that

$$\frac{{\rm Id} - P_{\Delta t}}{\Delta t}\varphi = -\mathcal{L}\varphi + {\rm O}(\Delta t),$$

In addition, the variance $\sigma^2_{\varphi,\Delta t}$ can be rewritten as

$$\Delta t \, \sigma^2_{\varphi,\Delta t} = 2 \int_{\mathcal{X}} (\Pi_{\Delta t}\varphi) \left(\frac{{\rm Id} - P_{\Delta t}}{\Delta t}\right)^{-1} \Pi_{\Delta t}\varphi \, d\pi_{\Delta t} + {\rm O}(\Delta t). \tag{6.9}$$

In view of the expression σ^2_φ of the asymptotic variance of the continuous dynamics, namely (the proof being the same as for (4.17))

$$\sigma^2_\varphi = 2 \int_{\mathcal{X}} (\Pi\varphi) \left(-\mathcal{L}\Pi\varphi\right)^{-1} d\pi, \tag{6.10}$$

where Π is the projection associated with the invariant probability measure π of the reference dynamics with generator $\mathcal{L}$, this suggests the following convergence result:

$$\Delta t \, \sigma^2_{\varphi,\Delta t} \xrightarrow[\Delta t \to 0]{} \sigma^2_\varphi. \tag{6.11}$$

A rigorous proof of this convergence is provided by Theorem 8.2. In fact, it typically holds that $\theta_{\rm corr} = N_{{\rm corr},\Delta t}\Delta t + {\rm O}(\Delta t)$.

The interpretation of (6.11) is that the asymptotic variance of time averages computed using numerical methods is, to first order in Δt, related to the asymptotic variance of the time averages computed with the continuous process. This motivates to directly study the asymptotic variances of the continuous processes, such as (4.17) or (5.18), rather than their discrete counterparts, which we therefore do in Section 6.3.

Systematic error

The second term in (6.8) is a systematic error (or bias) related to the fact that the invariant measure of the numerical scheme $\pi_{\Delta t}$ is different from the canonical measure π. Although this is not obvious, the expression of the formal correction function $h_{\Delta t}$ defined as $\pi_{\Delta t} = h_{\Delta t}\pi$ is encoded in the asymptotic expansion of the one-step evolution operator $P_{\Delta t}$, provided some ergodicity conditions are met. A typical result is that $h_{\Delta t} = 1 + \mathrm{O}(\Delta t^a)$ for some integer a. In fact, it is often possible to make precise the leading term in the bias as follows (see Theorem 6.1 below):

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \, d\pi + \Delta t^a \int_{\mathcal{X}} \varphi f \, d\pi + \mathrm{O}(\Delta t^{a+1})$$

for some function f solving a PDE. As made clear in Theorem 6.1, $a \geqslant \alpha$, where α is the weak order of the method (in the sense that $P_{\Delta t} = \mathrm{e}^{\Delta t \mathcal{L}} + \mathrm{O}(\Delta t^{\alpha+1})$). In some cases, it even holds $a \geqslant \alpha + 1$.

An important remark is that the bias becomes noticeable only for sufficiently long integration times $T = N_{\mathrm{iter}}\Delta t$, namely when $\sigma_\varphi/\sqrt{T} \sim \Delta t^a$. More precisely,

$$N_{\mathrm{iter}} \sim \frac{\sigma_\varphi^2}{\Delta t^{2a+1}}.$$

The small denominator on the right hand side of the previous equality motivates N_{iter} is often too small for the bias to be of the same order of magnitude, or even larger, than the statistical error, so that the statistical error often dominates in actual simulations. However, it is desirable to have biases as small as possible in order to use larger time steps (while still satisfying stability constraints). We now analyse the bias in the next section.

Remark 6.1. *In practice, a more relevant way to determine the time step may be to minimize the mean square error*

$$C_1 \Delta t^{2a} + C_2 \frac{\sigma_\varphi^2}{N_{\mathrm{iter}} \Delta t}$$

for N_{iter} fixed. A simple computation shows that the two errors should be equilibrated to this end, with Δt scaling as $\left(\sigma_\varphi^2/N_{\mathrm{iter}}\right)^{1/(2a+1)}$ – subject to upper bounds on the time step related to stability issues, of course.

6.2 Error estimates on the invariant measure

We present in this section how to analyse the bias, *i.e.* the second term on the right-hand side of (6.8). We first describe in Section 6.2.1 a general framework to quantify the bias on the invariant measure for discretizations of ergodic SDEs; see in particular the error expansion provided by Theorem 6.1. We next discuss in Section 6.2.2 how to rely on the error expansion to reduce the bias. We then turn to applications to overdamped Langevin dynamics in Section 6.2.3 and Langevin dynamics in Section 6.2.4. Some schemes for Langevin dynamics are preferred since they behave well in the limit of large frictions γ where they reduce to consistent schemes for the overdamped Langevin dynamics, in accordance with the overdamped limit at the continuous level discussed in Section 5.1.3.

6.2.1 A general result

Assume that the continuous dynamics, with generator $\mathcal{L}$, admits a unique invariant probability measure π. Consider next a given numerical scheme, described in terms of its discrete evolution operator $P_{\Delta t}$ defined in (6.3), and admitting an invariant measure $\pi_{\Delta t}$ (we do not make any uniqueness assumption on $\pi_{\Delta t}$ at this stage).

Assume that, for a C^∞ function φ and a given integer α, the evolution operator can be expanded as

$$P_{\Delta t}\varphi = \varphi + \Delta t\, \mathcal{A}_1\varphi + \Delta t^2 \mathcal{A}_2\varphi + \cdots + \Delta t^{\alpha+1}\mathcal{A}_{\alpha+1}\varphi + \Delta t^{\alpha+2} r_{\varphi,\Delta t}, \tag{6.12}$$

for some remainder term $r_{\varphi,\Delta t}$ (which depends on α, although we henceforth omit this dependence). The operators $\mathcal{A}_k$ are identified in practice by Taylor expansions of $\varphi(x^{n+1})$ around $\varphi(x^n)$, with a remainder term typically expressed as an integral remainder. Note that, by consistency of the discretization, it typically holds that

$$\mathcal{A}_1 = \mathcal{L},$$

although in principle it is possible to construct numerical schemes approximating π for which this is not the case. More generally, the method is of weak order α when $\mathcal{A}_k = \mathcal{L}^k/k!$ for $1 \leqslant k \leqslant \alpha$. However, there may be discrete dynamics for which $\mathcal{A}_k = a_k\mathcal{L}^k$ with a prefactor $a_k \neq 1/k!$ for some $1 \leqslant k \leqslant p$. In this case the dynamics is not of weak order α, but the invariant measure may nonetheless be correct up to error terms of order $\Delta t^{\alpha+1}$. Moreover, as made precise in Theorem 6.1, there are situations in which the operators $\mathcal{A}_k$ are different from $\mathcal{L}^k$ but the invariant measure $\pi_{\Delta t}$ is still close to π; see for instance [1] in the context of Langevin dynamics.

We next need some functional estimates on the operator $\mathcal{A}_1$ appearing in (6.12). We introduce to this end the following set of C^∞ functions.

Definition 6.1 (Smooth functions). *Consider scale functions $\mathscr{W}_n : \mathcal{X} \to [1, +\infty)$ such that, for any $n \geqslant 0$, there exists $C_n \in \mathbb{R}_+$ such that*

$$\mathscr{W}_n \leqslant C_n \mathscr{W}_{n+1}.$$

The space $\mathcal{S}$ is composed of all functions $\varphi \in C^\infty(\mathcal{X})$ for which, for any $k \in \mathbb{N}^d$, there exists $m \in \mathbb{N}$ such that $\partial^k\varphi \in B^\infty_{\mathscr{W}_m}(\mathcal{X})$.

In the simple case when $\mathcal{X}$ is bounded, it is possible to choose $\mathscr{W}_n = \mathbf{1}$ for all $n \geqslant 0$, in which case $\mathcal{S} = C^\infty(\mathcal{X})$. For unbounded spaces, a typical choice is $\mathscr{W}_n(x) = 1 + |x|^n$. In this case, the above definition means that the functions in $\mathcal{S}$, as well as all their derivatives, grow at most polynomially. The set $\mathcal{S}$ can then be shown to dense in $L^2(\pi)$ when π has moments of all orders, so that all the operators arising in the error estimations can be considered as operators on $L^2(\pi)$, defined on the core $\mathcal{S}$.

In order to state the regularity result we rely on, we restrict the space of smooth functions to those with average 0 with respect to the invariant measure π of the continuous process, namely

$$\mathcal{S}_0 = \Pi\mathcal{S} = \left\{ \varphi \in \mathcal{S} \;\middle|\; \int_{\mathcal{X}} \varphi \, d\pi = 0 \right\}, \tag{6.13}$$

where Π is the counterpart of the projection operator defined in (4.16):

$$\Pi\varphi = \varphi - \int_{\mathcal{X}} \varphi \, d\pi. \tag{6.14}$$

We next consider the following assumption on the generator of the continuous dynamics. Recall that operators are considered on $L^2(\pi)$ and that adjoints are taken with respect to the corresponding scalar product.

Assumption 6.1 (Stability of smooth functions by inverse operators). *The space $\mathcal{S}$ is dense in $L^2(\pi)$ (in particular $\mathscr{W}_n \in L^2(\pi)$ for any $n \geqslant 0$) and the operators $\mathcal{A}_1^{-1}$ and $(\mathcal{A}_1^*)^{-1}$ leave $\mathcal{S}_0$ invariant.*

Here $\mathcal{A}_1^*$ denotes the adjoint of $\mathcal{A}_1$ with respect to the scalar product in $L^2(\pi)$. Typically $\mathcal{A}_1 = \mathcal{L}$. The invariance of $\mathcal{S}_0$ by an operator $\mathcal{T}^{-1}$ has to be understood in the following sense: when $\varphi \in \mathcal{S}_0$, the unique solution Φ of the equation $\mathcal{T}\Phi = \varphi$ belongs to $\mathcal{S}_0$.

Error estimates on averages of smooth functions can finally be stated as follows.

Theorem 6.1 (Error estimates on the invariant measure). *Suppose that Assumption 6.1 is satisfied, and that an expansion such as* (6.12) *holds for any* $\varphi \in \mathcal{S}$ *and a given* $\alpha \in \mathbb{N}$*, with a remainder* $r_{\varphi,\Delta t}$ *for which there exist* $K \geqslant 0$*,* $m \in \mathbb{N}$ *and* $\Delta t^* > 0$ *(all depending on* φ *and* α*) such that*

$$\forall \Delta t \leqslant \Delta t^*, \qquad \|r_{\varphi,\Delta t}\|_{B^\infty_{\mathscr{W}_m}} \leqslant K.$$

Assume in addition that the operators $\mathcal{A}_k$ *leave* $\mathcal{S}$ *invariant for any* $k \geqslant 1$*, that*

$$\forall k \in \{1, \dots, \alpha\}, \quad \forall \varphi \in \mathcal{S}, \qquad \int_{\mathcal{X}} \mathcal{A}_k \varphi \, d\pi = 0, \tag{6.15}$$

and that $g_{\alpha+1} = \mathcal{A}^*_{\alpha+1}\mathbf{1} \in \mathcal{S}_0$*. Finally, assume that the numerical scheme admits an invariant measure* $\pi_{\Delta t}$ *which integrates all scale functions:*

$$\forall n \geqslant 0, \qquad \int_{\mathcal{X}} \mathscr{W}_n \, d\pi_{\Delta t} < +\infty.$$

Then, there exists $L > 0$ *such that, for any* $\Delta t \in (0, \Delta t^*]$*,*

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \, d\pi + \Delta t^\alpha \int_{\mathcal{X}} \varphi f_{\alpha+1} \, d\pi + \Delta t^{\alpha+1} R_{\varphi,\Delta t}, \tag{6.16}$$

with $|R_{\varphi,\Delta t}| \leqslant L$ *and where*

$$f_{\alpha+1} = -\left(\mathcal{A}^*_1\right)^{-1} g_{\alpha+1} \in \mathcal{S}_0. \tag{6.17}$$

Let us first comment the assumptions of the theorem. The condition that the operators $\mathcal{A}_k$ leave $\mathcal{S}$ invariant is usually very easy to check since these operators typically are differential operators with C^∞ coefficients when b and σ in (6.1) are C^∞. Moreover, in order to obtain the expression of $g_{\alpha+1} = \mathcal{A}^*_{\alpha+1}\mathbf{1}$, it is convenient to resort to integrations by parts to determine the function $g_{\alpha+1}$ such that, for any test function $\varphi \in \mathcal{S}$,

$$\int_{\mathcal{X}} \mathcal{A}_{\alpha+1} \varphi \, d\pi = \int_{\mathcal{X}} g_{\alpha+1} \varphi \, d\pi. \tag{6.18}$$

It can usually be checked by direct inspection that $g_{\alpha+1} \in \mathcal{S}$. In addition, by considering $\varphi = \mathbf{1}$ in (6.18), it follows that $g_{\alpha+1}$ automatically has average 0 with respect to π when $\mathcal{A}_{\alpha+1}\mathbf{1} = 0$, which is the case for differential operators. Finally, let us emphasize once again that the important condition which determines the order of the error is (6.15). This condition holds when $\mathcal{A}_k$ is proportional to $\mathcal{L}^k$, but can be satisfied for more general operators.

The interpretation of Theorem 6.1 is as follows. First, averages with respect to $\pi_{\Delta t}$ are correct up to errors of order Δt^α. Second, we can give an explicit expression of the leading-order term in the error, which can then be eliminated either by Romberg extrapolation or by a numerical estimate (see (6.24) below). Let us finally mention that it is possible to obtain bounds on $R_{\varphi,\Delta t}$ in terms of weighted B^∞ norms of φ and a given number of its derivatives when more precise estimates for $\mathcal{L}^{-1}$ are available. There are also results extending the error expansion (6.16) to non-smooth functions, in particular indicator functions, using techniques from Malliavin calculus [22].

Proof. The proof is obtained by a generalization of the proof of [169, Theorem 2.13]. Similar results are provided in [1, 61]. Note first that, since $f_{\alpha+1}$ has average 0 with respect to π, it is sufficient to establish (6.16) for functions with average 0 with respect to π, upon considering $\varphi - \mathbb{E}_\pi(\varphi)$.

The first step of the proof is to prove (6.16) for functions $\varphi \in (P_{\Delta t} - \mathrm{Id})\mathcal{S}$. This step motivates the expression for the correction function $f_{\alpha+1}$. Consider $\phi \in \mathcal{S}$. The invariance of $\pi_{\Delta t}$ by the discretized dynamics implies that

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \phi \right] d\pi_{\Delta t} = 0. \tag{6.19}$$

On the other hand, (6.12) and (6.15) give

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\phi\right] d\pi = \Delta t^{\alpha}\int_{\mathcal{X}} \mathcal{A}_{\alpha+1}\phi\, d\pi + \Delta t^{\alpha+1}\int_{\mathcal{X}} r_{\phi,\Delta t}\, d\pi,$$

while, for a given function $f \in \mathcal{S}$,

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\phi\right] f\, d\pi = \int_{\mathcal{X}} (\mathcal{A}_1\phi) f\, d\pi + \Delta t\int_{\mathcal{X}} \left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right] f\, d\pi,$$

so that

$$\begin{aligned}\int_{\mathcal{X}} &\left[\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\phi\right](1+\Delta t^{\alpha} f)\, d\pi \\ &= \Delta t^{\alpha}\int_{\mathcal{X}} (\mathcal{A}_{\alpha+1}\phi + (\mathcal{A}_1\phi) f)\, d\pi + \Delta t^{\alpha+1}\int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right] f\right) d\pi.\end{aligned}$$

The second term on the right-hand side of the previous equality is indeed of order $\Delta t^{\alpha+1}$ since the integrand of the corresponding integral is bounded in some weighted B^{∞} space. In order to choose f so that the first term on the right-hand side vanishes for all test functions $\phi \in \mathcal{S}$, we rewrite it as

$$\int_{\mathcal{X}} (\mathcal{A}_{\alpha+1}\phi + (\mathcal{A}_1\phi) f)\, d\pi = \int_{\mathcal{X}} (g_{\alpha+1} + \mathcal{A}_1^{*} f)\phi\, d\pi.$$

This suggests choosing $f = f_{\alpha+1} = -(\mathcal{A}_1^{*})^{-1} g_{\alpha+1}$, which is well defined by our assumptions on $\mathcal{A}_1$ since $g_{\alpha+1} \in \mathcal{S}_0$. With this choice,

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\phi\right](1+\Delta t^{\alpha} f_{\alpha+1})\, d\pi = \Delta t^{\alpha+1}\int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right] f_{\alpha+1}\right) d\pi, \tag{6.20}$$

so that (6.16) holds for $\varphi = (\mathrm{Id}-P_{\Delta t})\phi/\Delta t$.

The second step of the proof is to extend (6.16) to all functions in $\mathcal{S}_0$. Of course, we would like to replace ϕ with $\Delta t(\mathrm{Id}-P_{\Delta t})^{-1}\varphi$ in the previous estimates. There are however two obstructions to this approach: (i) the inverse $\Delta t(\mathrm{Id}-P_{\Delta t})^{-1}$ is well defined only on spaces of functions with average 0 with respect to $\pi_{\Delta t}$, and (ii), when this is the case, we typically do not have any control on the derivatives of $\Delta t(\mathrm{Id}-P_{\Delta t})^{-1}\varphi$, but only on the function itself (by results such as Corollary 3.1). Our strategy is to construct an operator $Q_{\Delta t}$ which leaves $\mathcal{S}_0$ invariant and is an approximate inverse of $(\mathrm{Id}-P_{\Delta t})/\Delta t$ on $\mathcal{S}_0$. Since $(\mathrm{Id}-P_{\Delta t})\varphi/\Delta t = \mathcal{A}_1\varphi + \mathrm{O}(\Delta t)$, we expect the inverse operator to be $\mathcal{A}_1^{-1}$ at dominant order in Δt.

The first task is to restrict $\mathrm{Id}-P_{\Delta t}$ to $\mathcal{S}_0$ as $\Pi(\mathrm{Id}-P_{\Delta t})\Pi$ using the projection operator Π defined in (6.14). The equality (6.19) implies, for $\phi \in \mathcal{S}_0$ (so that $\Pi\phi = \phi$),

$$\int_{\mathcal{X}} \left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right] d\pi_{\Delta t} = -\frac{1}{\Delta t}\int_{\mathcal{X}} (P_{\Delta t}\phi)\, d\pi, \tag{6.21}$$

while, using the fact that $f_{\alpha+1}$ is of average 0 with respect to π, (6.20) leads to

$$\begin{aligned}\int_{\mathcal{X}} \left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right](1+\Delta t^{\alpha} f_{\alpha+1})\, d\pi &= -\frac{1}{\Delta t}\int_{\mathcal{X}} (P_{\Delta t}\phi)\, d\pi \\ &\quad + \Delta t^{\alpha+1}\int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right] f_{\alpha+1}\right) d\pi.\end{aligned} \tag{6.22}$$

This shows that, for any $\phi \in \mathcal{S}_0$,

$$\begin{aligned}\int_{\mathcal{X}} \left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right] d\pi_{\Delta t} &= \int_{\mathcal{X}} \left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right](1+\Delta t^{\alpha} f_{\alpha+1})\, d\pi \\ &\quad - \Delta t^{\alpha+1}\int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right] f_{\alpha+1}\right) d\pi.\end{aligned}$$

We next consider an approximate inverse operator $Q_{\Delta t}$ which leaves $\mathcal{S}_0$ invariant, and is such that

$$\forall \varphi \in \mathcal{S}_0, \qquad \Pi \left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \Pi Q_{\Delta t} \varphi = \varphi + \Delta t^{\alpha+1} \widetilde{r}_{\varphi,\Delta t}. \tag{6.23}$$

with $\|\widetilde{r}_{\varphi,\Delta t}\|_{B^\infty_{\mathscr{W}_m}}$ uniformly bounded with respect to Δt for some integer m. Such operators are constructed as follows. The fundamental idea is to truncate the formal series expansion of the inverse of the operator $A + \Delta t\, B = A(\mathrm{Id} + \Delta t\, A^{-1}B)$ in powers of $A^{-1}B$:

$$A^{-1} - \Delta t\, A^{-1}BA^{-1} + \Delta t^2\, A^{-1}BA^{-1}BA^{-1} + \cdots .$$

In the present situation, we set $A = \Pi \mathcal{A}_1 \Pi$ and $B = \Pi \mathcal{A}_2 \Pi + \cdots + \Delta t^{\alpha-1} \Pi \mathcal{A}_{\alpha+1} \Pi$. Note that perturbative arguments cannot be used to make sense of the formal infinite series since B usually involves differential operators of higher order than A, so that B cannot be controlled by A (in contrast to the situation we will encounter later on in Theorem 8.1). Introducing $\widetilde{\mathcal{A}}_k = \Pi \mathcal{A}_k \Pi$ for notational simplicity, we consider

$$\widetilde{Q}_{\Delta t} = \widetilde{\mathcal{A}}_1^{-1} \sum_{n=0}^{\alpha} (-1)^n \Delta t^n \, (B \widetilde{\mathcal{A}}_1^{-1})^n.$$

We next remove operators with powers of Δt larger than or equal to $\alpha+1$ (arising from the higher-order terms in the expression of $B\widetilde{\mathcal{A}}_1^{-1}$) in order to write down an expression for $Q_{\Delta t}$ involving only powers of Δt smaller than or equal to α. Finally, the so-constructed operator,

$$Q_{\Delta t} = \widetilde{\mathcal{A}}_1^{-1} - \Delta t \widetilde{\mathcal{A}}_1^{-1} \widetilde{\mathcal{A}}_2 \widetilde{\mathcal{A}}_1^{-1} + \Delta t^2 \left(\widetilde{\mathcal{A}}_1^{-1} \widetilde{\mathcal{A}}_2 \widetilde{\mathcal{A}}_1^{-1} \widetilde{\mathcal{A}}_2 \widetilde{\mathcal{A}}_1^{-1} - \widetilde{\mathcal{A}}_1^{-1} \widetilde{\mathcal{A}}_3 \widetilde{\mathcal{A}}_1^{-1} \right) + \Delta t^3 \mathcal{Q}_3 + \cdots + \Delta t^\alpha \mathcal{Q}_\alpha,$$

is a well defined operator which leaves $\mathcal{S}_0$ invariant (since its action is given by the application of at most α operations of the form $\widetilde{\mathcal{A}}_k \widetilde{\mathcal{A}}_1^{-1}$, and a final application of $\widetilde{\mathcal{A}}_1^{-1}$) and is such that (6.23) holds true.

In order to conclude, it remains to replace ϕ with $Q_{\Delta t}\varphi$, and gather all the higher-order terms in $R_{\varphi,\Delta t}$. This gives the desired equality (6.16) for functions in $\mathcal{S}_0$.

We postpone a numerical illustration of the results of Theorem 6.1 to Figure 8.1 in Section 8.4. Indeed, as explained in Section 6.2.2, the leading order correction term can be computed as some integrated correlation function, for which we provide elements of numerical analysis later on, in Section 8.4.1.

6.2.2 Removing or reducing the systematic error

We discuss in this section two ways of decreasing the bias corresponding to the second term in (6.8): first by leveraging the a priori error estimate (6.16), and second by resorting to a Metropolis procedure.

Reducing the systematic error

The estimate (6.16) not only allows us to estimate the order of magnitude of the error on average properties arising from the discretization of the dynamics, but also provides an expression of the leading-order term in the difference as

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} - \int_{\mathcal{X}} \varphi \, d\pi = \Delta t^\alpha \int_{\mathcal{X}} \varphi f_{\alpha+1} \, d\pi + \mathrm{O}(\Delta t^{\alpha+1}).$$

There are two principal strategies for reducing/removing the leading order term on the right-hand side of the above equality.

(1) Using Romberg extrapolation as already suggested in [261], by performing simulations with two different time steps, in order to eliminate the leading-order error term by an appropriate linear combination of the associated estimators.

(2) Directly estimating the correction term by reformulating it as an integrated correlation function when $\mathcal{A}_1 = \mathcal{L}$ (which corresponds to scheme of weak order at least one). Indeed, the expression (6.17) for $f_{\alpha+1}$ leads to

$$\begin{aligned}\int_{\mathcal{X}} \varphi f_{\alpha+1}\, d\pi &= \int_{\mathcal{X}} \Pi\varphi f_{\alpha+1}\, d\pi = -\int_{\mathcal{X}} (\mathcal{L}^{-1}\Pi\varphi) g_{\alpha+1}\, d\pi \\ &= \int_0^{+\infty} \int_{\mathcal{X}} \left(\mathrm{e}^{t\mathcal{L}}\Pi\varphi\right) g_{\alpha+1}\, d\pi\; dt = \int_0^{+\infty} \mathbb{E}_\pi[\varphi(x_t) g_{\alpha+1}(x_0)]\, dt, \end{aligned} \tag{6.24}$$

where we have implicitly assumed that decay estimates hold for the semigroup $\mathrm{e}^{t\mathcal{L}}$ (which allows us to rewrite the resolvent $-\mathcal{L}^{-1}$ as a time integral of the semigroup), and where the expectation $\mathbb{E}_\pi$ is over all initial conditions $x_0 \sim \pi$ and for all realizations of the dynamics with generator $\mathcal{L}$. Recall that the expression of the function $g_{\alpha+1}$ is usually not too difficult to obtain once the expansion (6.12) has been worked out, see the discussion after (6.18). The integrated correlation on the right-hand side is then approximated as described in Section 8.4.1 (see Theorem 8.2). This strategy has been tested on a simple case in [169]: see Figure 8.1.

An issue with both approaches is that the statistical error on the estimated properties has to be sufficiently small, otherwise the linear combination mentioned in the first item, or the addition of the integration correlation (6.24), increase the statistical error of the final estimate of $\mathbb{E}_\pi(\varphi)$ and degrade the overall error.

Removing the bias by a Metropolis procedure

An alternative strategy consists in using a Metropolis–Hastings algorithm with the numerical scheme as a proposal, in order to completely remove the systematic error due to the time discretization. This is straightforward for reversible dynamics such as overdamped Langevin dynamics. When an Euler–Maruyama scheme is used, one obtains the so-called Metropolis-adjusted Langevin algorithm (MALA) in the statistics literature, known as smart MC in the chemistry literature [237, 235]. This corresponds in fact to the proposal function associated with (3.8). It is however possible to use more accurate schemes at no extra cost, as made precise in [92, Section 3]. Another advantage of superimposing a Metropolis–Hastings procedure upon a discretization of overdamped Langevin dynamics is that it stabilizes the numerical scheme even for non-globally Lipschitz forces ∇V: an invariant probability measure exists by construction, which ensures the recurrence of the Markov chain. In contrast, numerical discretizations which are not stabilized by a Metropolis–Hastings procedure may be transient, as discussed in Section 6.1.2.

For Langevin dynamics, some care has to be taken since the transition kernel associated with the Hamiltonian dynamics is irregular (because the noise acts only on momenta), which raises some difficulties in the definition of the Metropolis–Hastings ratio. It is nonetheless possible to use a Metropolis–Hastings procedure for schemes based on a splitting between the Ornstein–Uhlenbeck process on the momenta and a reversible discretization of the Hamiltonian part, upon reverting momenta when rejecting proposed moves; see [178, Section 2.2.3.2] for a precise discussion, as well as Section ?? below.

add reference

However, it is not always possible or desirable to use any Metropolis correction. First, the average acceptance probability in the Metropolis step for MALA or related algorithms in general decreases exponentially with the dimension of the system for a *fixed* time step. In fact, the time step should be reduced as some inverse power of the system size in order to maintain a constant acceptance rate (see [234, 235]). There are ways to limit the decrease of the acceptance probability:

(i) Change the dynamics or the measure used to compute the Metropolis ratio. For the Metropolization of the Hamiltonian dynamics, see the works [141, 3] where the Hamiltonian

H in the canonical measure is changed to $H + \Delta t^2 \widetilde{H}$, with $\widetilde{H}$ the first order correction arising from backward error analysis. For the Metropolization of overdamped Langevin dynamics, see [92].

(ii) Evolve only subparts of the system as advocated by [39].

However, the latter strategy may complicate the implementation of parallel algorithms for the simulation of very large systems, especially if long-range potentials are used (as acknowledged in [39, Remark 2.5]). Second, the variance of the computed averages may increase since rejections occur, and the samples along the numerical trajectory are therefore more correlated in general than for rejection-free dynamics. Lastly, the Metropolis procedure requires that the invariant probability measure π of the continuous dynamics is known. This is the case for Langevin and overdamped Langevin dynamics with forces $-\nabla V(q)$. However, for non-reversible systems subjected to external forcings such as a temperature gradient or a non-gradient force (see Lecture 8), the invariant measure of the continuous dynamics is not known.

6.2.3 Application to overdamped Langevin dynamics

For overdamped Langevin dynamics, we consider for simplicity the case of a simple Euler–Maruyama discretization:

$$q^{n+1} = q^n - \Delta t \, \nabla V(q^n) + \sqrt{\frac{2\Delta t}{\beta}} \, G^n, \tag{6.25}$$

where $(G^n)_{n \geqslant 0}$ is a sequence of i.i.d. D-dimensional standard Gaussian random variables. The results below can be easily generalized to other discretization schemes.

The first task is to find an expansion of the transition operator $P_{\Delta t}$ defined in (6.3) in powers of Δt, see (6.12). We next apply Theorem 6.1 with $p = 1$. There are three types of assumptions to be checked:

(1) assumptions on the generator $\mathcal{L} = \mathcal{A}_1 = -\nabla V^T \nabla + \beta^{-1} \Delta$ of the continuous dynamics;

(2) assumptions on the operator $\mathcal{A}_2$, whose action is given by (6.28);

(3) assumptions on the invariant measure of the numerical scheme.

Let us successively consider all these items in the remainder of this section.

Expansion of the transition operator

We consider a C^∞ function φ. We rewrite the numerical scheme as $q^{n+1} = \Phi_{\Delta t}(q^n, G^n)$. A Taylor expansion shows that

$$\varphi(q+\delta) = \varphi(q) + \delta^T \nabla \varphi(q) + \frac{1}{2} \delta^T \nabla^2 \varphi(q) \delta + \frac{1}{6} D^3 \varphi(q) : \delta^{\otimes 3} + \frac{1}{24} D^4 \varphi(q) : \delta^{\otimes 4} + \frac{1}{120} D^5 \varphi(q) : \delta^{\otimes 5} + \frac{1}{120} \int_0^1 (1-\theta)^5 D^6 \varphi(q+\theta\delta) : \delta^{\otimes 6} \, d\theta,$$

where we use the short-hand notation

$$D^n \varphi(q) : (x_1 \otimes \cdots \otimes x_n) = \sum_{i_1, \ldots, i_n = 1}^{D} \partial^n_{i_1, \ldots, i_n} \varphi(q) \, x_{1,i_1} \ldots x_{n,i_n}.$$

Replacing δ with $\Phi_{\Delta t}(q, G) - q = \sqrt{2\Delta t \beta^{-1}} \, G - \Delta t \, \nabla V(q)$ and gathering terms according to powers of Δt, we obtain

$$\begin{aligned}\varphi\left(\Phi_{\Delta t}(q,G)\right) = \varphi(q) &+ \sqrt{\frac{2\Delta t}{\beta}} G^T \nabla\varphi(q) + \Delta t \left(\frac{1}{\beta} G^T \left(\nabla^2\varphi(q)\right) G - \nabla V(q)^T \nabla\varphi(q)\right) \\ &+ \Delta t^{3/2} \left(\frac{\sqrt{2}}{3\beta^{3/2}} D^3\varphi(q) : G^{\otimes 3} - \sqrt{\frac{2}{\beta}} G^T \nabla^2\varphi(q) \nabla V(q)\right) \\ &+ \Delta t^2 \left(\frac{1}{6\beta^2} D^4\varphi(q) : G^{\otimes 4} - \frac{1}{\beta} D^3\varphi(q) : \left(G^{\otimes 2} \otimes \nabla V(q)\right) + \frac{1}{2} \nabla V(q)^T \nabla^2\varphi(q) \nabla V(q)\right) \\ &+ \Delta t^{5/2} \xi_{5/2}(q,G) + \Delta t^3 \widetilde{\xi}_{\Delta t}(q,G).\end{aligned}$$

Note that we have an expansion with fractional powers of Δt. However, the terms corresponding to non-integer powers of Δt (such as $\xi_{5/2}(q,G)$) contain an odd number of occurences of G, so that their expectations with respect to G vanish. Since $\left(P_{\Delta t}\varphi\right)(q) = \mathbb{E}_G\left[\varphi\left(\Phi_{\Delta t}(q,G)\right)\right]$, a simple computation shows that

$$P_{\Delta t}\varphi = \varphi + \Delta t\, \mathcal{L}\varphi + \Delta t^2 \mathcal{A}_2 \varphi + \Delta t^3 r_{\varphi,\Delta t} \tag{6.26}$$

where

$$\mathcal{A}_2 = \frac{1}{2}\left(\frac{1}{\beta^2}\Delta^2 - \frac{2}{\beta}\nabla V(q)^T \nabla(\Delta\varphi) + \nabla V(q)^T \nabla^2\varphi(q) \nabla V(q)\right),$$

and $r_{\varphi,\Delta t}(q) = \mathbb{E}_G\left[\widetilde{\xi}_{\Delta t}(q,G)\right]$ is such that $\|r_{\varphi,\Delta t}\|_{B^\infty} \leqslant K$ for Δt sufficiently small. It can be checked that $\mathcal{A}_2 \neq \frac{1}{2}\mathcal{L}^2$. Indeed,

$$\mathcal{L}^2\varphi = \frac{1}{\beta^2}\Delta^2\varphi - \frac{2}{\beta}\nabla V \cdot \nabla(\Delta\varphi) + \left(\nabla V \otimes \nabla V - \frac{2}{\beta}\nabla^2 V\right) : \nabla^2\varphi + \left(\nabla^2 V \nabla V - \frac{1}{\beta}\nabla(\Delta V)\right) \cdot \nabla\varphi, \tag{6.27}$$

so that

$$\mathcal{A}_2 = \frac{1}{2}\left(\mathcal{L}^2 + \mathcal{R}_2\right), \tag{6.28}$$

with

$$\mathcal{R}_2\varphi = \frac{2}{\beta}\nabla^2 V : \nabla^2\varphi + \frac{1}{\beta}\nabla(\Delta V) \cdot \nabla\varphi - \nabla V^T (\nabla^2 V) \nabla\varphi.$$

Assumptions on the generator $\mathcal{L}$

First, recall that, as discussed after Definition 6.1, $\mathscr{W}_n(q) = \mathbf{1}$ for all $n \geqslant 0$ when $\mathcal{D}$ is bounded, so that $\mathcal{S} = C^\infty(\mathcal{D})$. Standard results of elliptic regularity (see *e.g.* [87, Section 6.3]) then show that $\mathcal{L}^{-1}$ is a well-defined operator from

$$\mathcal{S}_0 = \left\{ f \in C^\infty(\mathcal{D}) \,\middle|\, \int_{\mathcal{D}} f \, d\nu = 0 \right\}$$

to itself. For dynamics in the full space $\mathcal{D} = \mathbb{R}^d$, additional assumptions on the potential are needed to obtain the stability of $\mathcal{S}$ with the choice $\mathscr{W}_n(q) = 1 + |q|^n$, and the proof of this stability result are much more involved; see [156].

Expression of the correction function

Thanks to (6.28), it can be easily checked that g_2 is well defined and belongs to $\mathcal{S}$ (recall that, as discussed after Theorem 6.1, it automatically has average 0 with respect to π). To obtain the precise expression for g_2, we use integration by parts to compute

$$\int_{\mathcal{D}} \mathcal{R}_2\varphi \, d\nu = -\frac{1}{\beta}\int_{\mathcal{D}} \nabla\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right) \cdot \nabla\varphi \, d\nu = \int_{\mathcal{D}} \mathcal{L}\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right)\varphi \, d\nu.$$

Using that, for all $\varphi \in \mathcal{S}$,

$$\int_{\mathcal{D}} \mathcal{A}_2\varphi \, d\nu = \frac{1}{2}\int_{\mathcal{D}} \mathcal{R}_2\varphi \, d\nu = \int_{\mathcal{D}} g_2\varphi \, d\nu,$$

one obtains

$$g_2 = \frac{1}{2}\mathcal{L}\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right).$$

Since $\mathcal{A}_1 = \mathcal{L} = \mathcal{L}^*$ on $L^2(\nu)$, we in fact obtain the analytical expression of the correction function f_2 defined in (6.17):

$$f_2 = -\frac{1}{2}\left(\Delta V - \frac{\beta}{2}|\nabla V|^2 - \frac{a_{\beta,V}}{2}\right),$$

where

$$a_{\beta,V} = \int_{\mathcal{D}} \Delta V \, d\nu = \beta \int_{\mathcal{D}} |\nabla V|^2 \, d\nu$$

is a constant ensuring that f_2 has average 0 with respect to ν.

Existence of an invariant probability measure for the numerical scheme

To prove that an invariant probability measure $\pi_{\Delta t}$ exists for the numerical scheme, we rely on Theorem 3.1, and distinguish two cases:

(i) For compact position spaces, the Lyapunov condition of Assumption 3.1 is trivially satisfied. Therefore, the only property to prove is the minorization condition of Assumption 3.2. Since the space is bounded, it readily follows from (6.25) that, for any Borel subset $S \subset \mathcal{D}$,

$$\begin{aligned}
\mathbb{P}(q^1 \in S \,|\, q^0 = q) &\geqslant \mathbb{P}\left(\sqrt{\frac{2\Delta t}{\beta}}G^1 \in S - q + \Delta t \nabla V(q)\right) \\
&\geqslant \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{B^\infty}} \mathbb{P}\left(\sqrt{\frac{2\Delta t}{\beta}}G^1 \in S - \mathcal{Q}\right) \\
&= \left(\frac{\beta}{4\pi\Delta t}\right)^{d/2} \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{B^\infty}} \int_{S-\mathcal{Q}} \exp\left(-\frac{\beta|g|^2}{4\Delta t}\right) dg, \qquad (6.29)
\end{aligned}$$

where the first inequality is due to the fact that the contributions associated with periodic images of q are not taken into account. The minorization condition then follows by defining the measure

$$\widetilde{\lambda}_{\Delta t}(S) = \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{B^\infty}} \int_{S-\mathcal{Q}} \exp\left(-\frac{\beta|g|^2}{4\Delta t}\right) dg,$$

normalizing it as $\lambda_{\Delta t}(S) = \widetilde{\lambda}_{\Delta t}(S)/\widetilde{\lambda}_{\Delta t}(\mathcal{D})$, and introducing $\eta_{\Delta t} = (4\pi\Delta t/\beta)^{-d/2}\widetilde{\lambda}_{\Delta t}(\mathcal{D})$.

(ii) For unbounded spaces, the Euler–Maruyama scheme is typically transient for non-globally Lipschitz forces, as discussed in Section 6.1.2. Implicit schemes should then be considered, see for instance [189]. Lyapunov functions for the numerical schemes can be inherited from the Lyapunov function of the continuous dynamics. Minorization measures for initial positions q^0 in a compact set can still be constructed as above.

The minorization conditions sketched here for discretizations of SDEs on unbounded spaces are not uniform with respect to the time step Δt, and hence the exponential convergence to the invariant measure happens exponentially for each Δt, but with a rate which itself depends on the time step. Some more work however allows to recover some uniformity in the convergence, for specific numerical schemes and up to small error terms [156]; and even to obtain a convergence rate uniform with respect to the time step (see Section ??).

reference to add

6.2.4 Application to Langevin dynamics

Many numerical schemes have been proposed for Langevin dynamics. The first ones, such as the BBK scheme proposed in [41], were often obtained by modifications of numerical schemes for deterministic Hamiltonian dynamics. Various other schemes have been proposed since then; see for instance [253, 190, 42, 265, 165] for recent suggestions.

One systematic way to derive numerical schemes of arbitrary order is to resort to splitting schemes to integrate the various parts of the dynamics analytically; see [36, 165, 169]. However, proving rigorous ergodicity results on the corresponding numerical schemes has so far been done only for compact position spaces [169]. For unbounded position spaces, implicit schemes should be considered (see [189, 155]), in which case some geometric convergence can be achieved. Alternatively, it is possible, as discussed at the end of this section, to superimpose a Metropolis–Hastings step upon the discretization under consideration in order to stabilize the numerical method and ensure the existence of an invariant measure.

Description of the numerical schemes

In order to describe more conveniently splitting schemes, it is useful to introduce the elementary dynamics with generators

$$A = p^T M^{-1} \nabla_q, \qquad B = -\nabla V(q)^T \nabla_p, \qquad C = -p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p. \tag{6.30}$$

The generator $\mathcal{L}$ of the equilibrium Langevin dynamics (5.5), defined on the core $\mathcal{S}$, is the sum of the generators of the elementary dynamics:

$$\mathcal{L} = A + B + \gamma C,$$

where $\mathcal{L}_{\rm ham} = A + B$ is the generator associated with the Hamiltonian part of the dynamics. The motivation for the splitting (6.30) is that all elementary evolutions are analytically integrable. By computing $d(\mathrm{e}^{\gamma M^{-1} t} p_t)$, it is easily seen that the elementary dynamics associated with γC, namely

$$dp_t = -\gamma M^{-1} p_t + \sqrt{\frac{2\gamma}{\beta}}\, dW_t,$$

can be integrated as

$$p_t = \mathrm{e}^{-\gamma M^{-1} t} p_0 + \sqrt{\frac{2\gamma}{\beta}} \int_0^t \mathrm{e}^{-\gamma M^{-1}(t-s)}\, dW_s,$$

which is a Gaussian random variable with mean $\mathrm{e}^{-\gamma M^{-1} t} p_0$ and variance

$$\frac{2\gamma}{\beta} \int_0^t \mathrm{e}^{-2\gamma M^{-1}(t-s)}\, ds = \frac{1 - \mathrm{e}^{-2\gamma M^{-1} t}}{\beta}.$$

First-order splitting schemes

First-order schemes are obtained by a Lie–Trotter splitting of the elementary evolutions generated by $A, B, \gamma C$ (see Section 2.2.2 for a discussion of Lie–Trotter splittings). There are 6 possible schemes, whose evolution operators (defined on the core $\mathcal{S}$) are of the general form

$$P_{\Delta t}^{Z,Y,X} = \mathrm{e}^{\Delta t Z} \mathrm{e}^{\Delta t Y} \mathrm{e}^{\Delta t X},$$

with all possible permutations (Z, Y, X) of $(A, B, \gamma C)$. For instance, the numerical scheme associated with $P_{\Delta t}^{B,A,\gamma C}$ is

$$\begin{cases} \widetilde{p}^{n+1} = p^n - \Delta t\, \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\, M^{-1} \widetilde{p}^{n+1}, \\ p^{n+1} = \alpha_{\Delta t} \widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}^2}{\beta} M}\, G^n, \end{cases} \tag{6.31}$$

where $\alpha_{\Delta t} = \exp(-\gamma M^{-1} \Delta t)$, and (G^n) are independent and identically distributed Gaussian random vectors with identity covariance. Let us recall that, as already mentioned in Section 2.2.2, the order of the operations performed on the configuration of the system is the inverse of the order of the operations mentioned in the superscript of the evolution operator $P_{\Delta t}^{B,A,\gamma C}$ when read from right to left.

Remark 6.2. *The simulation of the dynamics with generator C is very simple when the mass matrix M is diagonal since $\alpha_{\Delta t}$ is a diagonal matrix. In the case when M is not diagonal, which may happen for instance when molecular constraints are considered, the analytic integration of the Ornstein–Uhlenbeck process should be replaced by an approximate integration, such as a mid-point scheme; see the discussion in [179, 178].*

The iterations of the three schemes associated with $P_{\Delta t}^{\gamma C,B,A}, P_{\Delta t}^{B,A,\gamma C}, P_{\Delta t}^{A,\gamma C,B}$ share a common sequence of update operations, as for $P_{\Delta t}^{\gamma C,A,B}, P_{\Delta t}^{A,B,\gamma C}, P_{\Delta t}^{B,\gamma C,A}$. More precisely, we mean that equalities of the following form hold:

$$\left(P_{\Delta t}^{A,B,\gamma C}\right)^n = T_{\Delta t} \left(P_{\Delta t}^{\gamma C,A,B}\right)^{n-1} U_{\gamma,\Delta t}, \qquad U_{\gamma,\Delta t} = \mathrm{e}^{\gamma \Delta t C}, \qquad T_{\Delta t} = \mathrm{e}^{\Delta t A} \mathrm{e}^{\Delta t B}. \tag{6.32}$$

It is therefore not surprising that the invariant measures of the schemes with operators composed in the same order have very similar properties, as can be made precise using Lemma 6.1 below.

Second-order schemes

Second-order schemes are obtained by a Strang splitting of the elementary evolutions generated by $A, B, \gamma C$. There are also 6 possible schemes, which are of the general form

$$P_{\Delta t}^{Z,Y,X,Y,Z} = \mathrm{e}^{\Delta t Z/2} \mathrm{e}^{\Delta t Y/2} \mathrm{e}^{\Delta t X} \mathrm{e}^{\Delta t Y/2} \mathrm{e}^{\Delta t Z/2},$$

with the same possible orderings as for first-order schemes. Again, these schemes can be classified into three groups depending on the ordering of the operators once the elementary one-step evolution is iterated: (i) $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}, P_{\Delta t}^{A,B,\gamma C,B,A}$, (ii) $P_{\Delta t}^{\gamma C,A,B,A,\gamma C}, P_{\Delta t}^{B,A,\gamma C,A,B}$, and (iii) $P_{\Delta t}^{B,\gamma C,A,\gamma C,B}, P_{\Delta t}^{A,\gamma C,B,\gamma C,A}$. We discard the latter category since the invariant measures of the associated numerical schemes are not consistent with ν in the overdamped limit (see below).

Geometric Langevin Algorithms

In fact, as proved in [36, 169], a second-order accuracy on the invariant measure can be obtained by resorting to a first-order splitting between the Hamiltonian and the Ornstein–Uhlenbeck parts, and discretizing the Hamiltonian part with a second-order scheme. This corresponds to the following evolution operators of Geometric Langevin Algorithm (GLA) type:

$$\begin{aligned} P_{\Delta t}^{\gamma C,A,B,A} &= \mathrm{e}^{\gamma \Delta t C} \mathrm{e}^{\Delta t A/2} \mathrm{e}^{\Delta t B} \mathrm{e}^{\Delta t A/2}, & P_{\Delta t}^{\gamma C,B,A,B} &= \mathrm{e}^{\gamma \Delta t C} \mathrm{e}^{\Delta t B/2} \mathrm{e}^{\Delta t A} \mathrm{e}^{\Delta t B/2}, \\ P_{\Delta t}^{A,B,A,\gamma C} &= \mathrm{e}^{\Delta t A/2} \mathrm{e}^{\Delta t B} \mathrm{e}^{\Delta t A/2} \mathrm{e}^{\gamma \Delta t C}, & P_{\Delta t}^{B,A,B,\gamma C} &= \mathrm{e}^{\Delta t B/2} \mathrm{e}^{\Delta t A} \mathrm{e}^{\Delta t B/2} \mathrm{e}^{\gamma \Delta t C}, \end{aligned} \tag{6.33}$$

which amounts to composing a Verlet-like scheme for the Hamiltonian part, preceded or followed by an integration of the Ornstein–Uhlenbeck part.

Error estimates on the invariant measure

Among all the splitting schemes introduced for Langevin dynamics, some lead to smaller errors on the invariant measure; see [169] for more precise statements. The key tool in this analysis is, as for overdamped Langevin dynamics, Theorem 6.1, and in particular the error estimate (6.16) on the invariant measure. If only the order of magnitude of the correction is of interest, and not the expression of the leading order error term, no regularity on the derivatives is required (see [36]), in contrast to situations where such corrections are explicitly considered, as in [260] for instance.

In order to apply Theorem 6.1, we consider $\alpha = 1$ for first-order splitting schemes or $\alpha = 2$ for second-order splitting schemes and GLA, and the hierarchy of scale functions $\mathscr{W}_n(q,p) = 1 + |p|^{2n}$ when the position space is compact. There are three types of assumptions to be checked.

(i) *Assumptions on the generator $\mathcal{A}_1 = \mathcal{L}$ of the continuous dynamics.* The stability of the space of smooth functions $\mathcal{S}_0$ under $\mathcal{L}^{-1}$ and its adjoint is a highly non trivial statement, which follows from a careful analysis of the proof presented in [260], as provided in [155, Appendix A] for unbounded position spaces under some conditions on the potential energy function V. The adaption to compact position spaces allows to simplify some arguments.

(ii) *Assumptions on the invariant measure $\mu_{\Delta t}$ of the numerical scheme.* In order to prove that splitting schemes admit a unique invariant probability measure, a first step is to prove that $\mathscr{W}_n$ are Lyapunov functions for splitting schemes in compact position spaces (see [169, Lemma 2.7]). Let us mention that the existence of Lyapunov functions for splitting schemes in unbounded position spaces is an open issue, to our knowledge. For such spaces, implicit schemes should be considered, in which case a slight modification of the Lyapunov function introduced in Lemma 5.1 for the continuous dynamics is a Lyapunov function for the numerical scheme (see [189, Lemma 8.1] for precise statements).
The second step is to prove that a minorization condition similar to (6.29) holds. However, there are many schemes for which the operator C appears only once (all first order and GLA schemes, and also certain second order schemes), so that there is only one D-dimensional noise per time step. This prevents from controlling both positions and momenta. Therefore, the argument leading to (6.29) has to be modified by considering the transition kernel $P_{\Delta t}^2$ corresponding to an evolution over two time steps, as done in [189, 36] for instance.

(iii) *Assumptions on the differential operators arising in the expansion in powers of Δt of the evolution operator $P_{\Delta t}$.* The expressions of these operators are conveniently obtained for splitting schemes with the Baker–Campbell–Hausdorff formula already encountered in Section 2.2.2; see for instance the presentation in [114, Section III.4.2]. Such computations are reported in [165, 169].

Remark 6.3 (Stability). *Stability is a necessary condition for the existence of an invariant measure $\mu_{\Delta t}$ for the numerical scheme under consideration. This property is guaranteed by the existence of a Lyapunov function $\mathscr{W}$ for the transition operator $P_{\Delta t}$, which typically requires the time step Δt to be sufficiently small. For discretizations of Langevin dynamics, the stability conditions are similar to the ones obtained for discretizations of the Hamiltonian dynamics, which correspond to $\gamma = 0$; see [166, 167]. Note indeed that all the splitting schemes introduced above reduce to a symplectic discretization of the Hamiltonian dynamics when $\gamma = 0$.*

Relating invariant measures of two numerical schemes

We classified the numerical schemes according to the order of appearance of the elementary operators. More precisely, we considered schemes to be similar when the global ordering of the operators is the same but the operations are started and ended differently, as in (6.32) above (see also (6.34) below for an abstract definition). This choice of classification is motivated by the following lemma which demonstrates how we may straightforwardly obtain the expression of the invariant measure of one scheme when the expression for another one is given.

We state the result in an abstract fashion for two schemes $P_{\Delta t} = U_{\Delta t} T_{\Delta t}$ and $Q_{\Delta t} = T_{\Delta t} U_{\Delta t}$ (which implies the condition (6.34) below). See (6.32) for a concrete example.

Lemma 6.1 (Here and elsewhere: TU lemma). *Consider two numerical schemes with associated evolution operators $P_{\Delta t}, Q_{\Delta t}$ bounded on $B^\infty(\mathcal{E})$, for which there exist bounded operators $U_{\Delta t}, T_{\Delta t}$ on $B^\infty(\mathcal{E})$ such that, for all $n \geqslant 1$,*

$$Q_{\Delta t}^n = T_{\Delta t} P_{\Delta t}^{n-1} U_{\Delta t}. \tag{6.34}$$

We also assume that both schemes are ergodic with associated invariant measures denoted respectively by $\mu_{P,\Delta t}$, $\mu_{Q,\Delta t}$: For any $\varphi \in B^\infty(\mathcal{E})$ and almost all $(q,p) \in \mathcal{E}$,

$$\lim_{n\to+\infty} \left(P_{\Delta t}^n \varphi\right)(q,p) = \int_{\mathcal{E}} \varphi \, d\mu_{P,\Delta t}, \qquad \lim_{n\to+\infty} \left(Q_{\Delta t}^n \varphi\right)(q,p) = \int_{\mathcal{E}} \varphi \, d\mu_{Q,\Delta t}. \tag{6.35}$$

Then, for all $\varphi \in B^\infty(\mathcal{E})$,

$$\int_{\mathcal{E}} \varphi \, d\mu_{Q,\Delta t} = \int_{\mathcal{E}} \left(U_{\Delta t}\varphi\right) d\mu_{P,\Delta t}. \tag{6.36}$$

Proof. The proof of this result relies on the simple observation that, for a given initial measure ρ with a smooth density with respect to the Lebesgue measure, the ergodicity assumption ensures that, for a bounded measurable function φ,

$$\int_{\mathcal{E}} \varphi \, d\mu_{Q,\Delta t} = \lim_{n\to+\infty} \int_{\mathcal{E}} Q_{\Delta t}^n \varphi \, d\rho = \lim_{n\to+\infty} \int_{\mathcal{E}} T_{\Delta t} P_{\Delta t}^{n-1} \left(U_{\Delta t}\varphi\right) d\rho.$$

Now, we use the ergodicity property (6.35) with f replaced by $U_{\Delta t}\varphi$ to obtain the following convergence for almost all $(q,p) \in \mathcal{E}$:

$$\lim_{n\to+\infty} P_{\Delta t}^{n-1} \left(U_{\Delta t}\varphi\right)(q,p) = \int_{\mathcal{E}} U_{\Delta t}\varphi \, d\mu_{P,\Delta t} = a_{\Delta t}.$$

Since $T_{\Delta t}$ preserves constant functions, there holds

$$\int_{\mathcal{E}} T_{\Delta t}(a_{\Delta t}\mathbf{1}) \, d\rho = a_{\Delta t} \int_{\mathcal{E}} \mathbf{1} \, d\rho = a_{\Delta t},$$

which finally gives (6.36). □

Overdamped limit of the numerical schemes

We discuss in this section the behavior of the splitting schemes in the overdamped limit γ. Recall that, under some time rescaling, solutions to the Langevin dynamics converge to solutions of overdamped Langevin dynamics (see Section 5.1.3). It would therefore be desirable that the invariant measure of the numerical schemes for Langevin dynamics converges to some approximation of the canonical measure in position $\nu(dq)$ given by (4.2).

The only part of the numerical schemes where the friction enters is the Ornstein–Uhlenbeck process on momenta. The limit $\gamma \to +\infty$ for $\Delta t > 0$ fixed amounts to resampling momenta according to the Gaussian distribution $\kappa(dp)$ at all timesteps. For instance, the numerical scheme associated with the evolution operator $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$ reduces to

$$q^{n+1} = q^n - \frac{\Delta t^2}{2} \nabla V(q^n) + \frac{\Delta t}{\sqrt{\beta}} G^n,$$

where (G^n) are independent and identically distributed Gaussian random vectors with identity covariance. This is indeed a consistent discretization of the overdamped process (4.1) with an effective timestep $h = \Delta t^2/2$, and the invariant measure of this numerical scheme is close to ν. Other schemes may have non-trivial large friction limits and invariant measures close to ν. This is the case for the scheme associated with the evolution operator $P_{\Delta t}^{B,A,\gamma C,A,B}$, for which the limiting discrete dynamics reads (see [165])

$$q^1 = q^0 - \frac{\Delta t^2}{4}\nabla V(q^0) + \frac{\Delta t}{2\sqrt{\beta}}(G^0 + G^1),$$
$$q^{n+1} = q^n - \frac{\Delta t^2}{2}\nabla V(q^n) + \frac{\Delta t}{2\sqrt{\beta}}(G^n + G^{n+1}), \quad \text{for } n > 0.$$

Note that (q^n) is not a Markov chain due to the correlations in the random noises. Nonetheless, and somewhat suprisingly, this schemes turns out to have an invariant measure correct at second order in the effective time step; see [169, Section 2.6] for precise statements.

On the other hand, the limits of the invariant measures associated with certain schemes are not consistent with the canonical measure ν. This is the case for the first-order schemes, as well as the second order splittings listed in item (iii) in Section 6.2.4. For instance, the limit of the scheme associated with $P_{\Delta t}^{\gamma C,A,B}$ reads

$$q^{n+1} = q^n + \frac{\Delta t}{\sqrt{\beta}}\, G^n.$$

The invariant measure of this Markov chain is the uniform measure on $\mathcal{D}$, and is therefore very different from the invariant measure ν of the continuous dynamics (4.1) (it amounts to setting $V = 0$). As another example, consider the limit of the scheme associated with $P_{\Delta t}^{\gamma C,B,A}$:

$$q^{n+1} = q^n - \Delta t^2 \nabla V(q^n) + \frac{\Delta t}{\sqrt{\beta}}\, G^n.$$

This is the Euler-Maruyama discretization of (4.1) with an effective timestep $h = \Delta t^2$ but an inverse temperature 2β rather than β.

Generalized Hybrid Monte Carlo schemes

We discuss in this section how to superimpose a Metropolis acceptance/rejection procedure to certain splitting schemes for Langevin dynamics, which allows to guarantee the existence of an invariant probability measure by construction, and also removes the bias on the invariant measure sampled by the algorithm. The method is a version of Hybrid Monte Carlo (HMC) schemes, initially proposed in [74], which can be understood as Metropolis–Hastings algorithms with proposal moves computed using one or several steps of Hamiltonian dynamics. These algorithms have been analyzed from a mathematical viewpoint in various works, including [247, 47, 184, 77]. HMC is now a popular method in computational statistics [203], where it was introduced early on, and where it is known as Hamiltonian Monte Carlo. We refer to [37] for some overview of HMC and its many current extensions.

We focus our attention here on the so-called one-step HMC method, where only one step of the integrator for the Hamiltonian dynamics is performed, together with some partial refreshment of momenta, as in generalized HMC [132]. This allows to construct consistent discretizations of Langevin dynamics [38] and of various extensions of the standard Langevin dynamics, including constrained dynamics restricted to submanifolds (see [179, 168] and [178, Section 3.3.5.4]), Langevin dynamics with even non-quadratic kinetic energies [257], etc.

We present for simplicity the simplest one step HMC scheme based on first partially resampling momenta, for instance by an analytic integration of the dynamics of generator C, as done in the last step of (6.31); then performing one step of the Verlet scheme; and finally reverting the momentum upon rejection. This is made precise in Algorithm 6.1 below. Various extensions are possible, for instance by symmetrizing the evolution and adding another update of the momentum at the end in order to have a method which is weakly second order consistent. See also [178, Section 2.1.4] for a more abstract presentation of generalized HMC methods.

Algorithm 6.1 (Metropolis correction to splitting schemes for Langevin dynamics). *Fix $\gamma > 0$, $\Delta t > 0$ and introduce $\alpha_{\Delta t} = \exp(-\gamma M^{-1}\Delta t)$, as a well as families of i.i.d. standard D-dimensional Gaussian random variables $(G^n)_{n\geqslant 0}$ and uniform random variables $(U^n)_{n\geqslant 0}$ on $[0,1]$. Consider an initial configuration (q^0, p^0) and iterate on $n \geqslant 0$,*

(1) Update the momentum as $p^{n+1/2} = \alpha_{\Delta t} p^n + \sqrt{\beta^{-1}(1-\alpha_{\Delta t}^2)M}\, G^n$*;*
(2) Compute $(\widetilde{q}^{n+1}, \widetilde{p}^{n+1}) = \Phi_{\Delta t}(q^n, p^{n+1/2})$ *where* $\Phi_{\Delta t}$ *corresponds to the Verlet scheme* (2.28)*;*
(3) If $U^n \leqslant \exp\left(-\beta\left[H(\widetilde{q}^{n+1}, \widetilde{p}^{n+1}) - H(q^n, p^{n+1/2})\right]\right)$*, set* $(q^{n+1}, p^{n+1}) = (\widetilde{q}^{n+1}, \widetilde{p}^{n+1})$*; otherwise set* $(q^{n+1}, p^{n+1}) = (q^n, -p^{n+1/2})$*.*

Since the Verlet scheme is second order accurate, the energy difference $H(\widetilde{q}^{n+1}, \widetilde{p}^{n+1}) - H(q^n, p^{n+1/2})$ is of order Δt^3, and so the rejection rate itself scales as Δt^3; see for instance [257, Lemma 3.1] for precise statements.

Exercise 6.1. *Prove that Algorithm 6.1 reduces to MALA with an effective timestep* $\Delta t^2/2$ *when* $\gamma = +\infty$ *(*i.e. $\alpha_{\Delta t} = 1$*).*

Let us emphasize that momenta need to be reverted when the proposal is rejected. In order to understand this point, and in fact to prove that the Markov chain induced by Algorithm 6.1 preserves the canonical measure (5.3), we write the numerical method as the composition of three steps: (i) updating the momenta; (ii) performing a Verlet step and reverting the momentum, before performing an acceptance/rejection according to the Metropolis rule given in the algorithm; (iii) reverting the momenta. Note that if the proposal is accepted in Step (ii), momenta are reverted twice, so that the final configuration is indeed the one obtained by one step of the Verlet scheme.

It is clear that Steps (i) and (iii) preserve the canonical measure, so it suffices to check that Step (ii) does too. The motivation for composing the Verlet step with some momentum reversal is that this provides some built-in reversibility for this (deterministic) proposal. To make this point precise, we introduce $\Psi_{\Delta t}(q,p) = (S \circ \Phi_{\Delta t})(q,p)$ where $S(q,p) = (q,-p)$ is the momentum reveral already considered in Section 2.1.2. Note that, crucially, $\Psi_{\Delta t}$ is an involution:

$$\Psi_{\Delta t} \circ \Psi_{\Delta t} = \mathrm{Id},$$

which moreover preserves the Lebesgue measure $dq\, dp$ (since $\Phi_{\Delta t}$ preserves it as a consequence of symplecticity, while S also obviously preserves this measure). With this notation, Step (ii) outputs a configuration (q', p') from (q,p) as

$$(q',p') = (q,p) + \mathbf{1}_{U \leqslant r_{\Delta t}(q,p)} \left[\Psi_{\Delta t}(q,p) - (q,p)\right], \quad r_{\Delta t}(q,p) = \min\left\{1, \mathrm{e}^{-\beta[(H\circ\Psi_{\Delta t})(q,p) - H(q,p)]}\right\}.$$

The associated transition kernel reads

$$P_{\Delta t}((q,p), dq'\, dp') = r_{\Delta t}(q,p)\delta_{\Psi_{\Delta t}(q,p)}(dq'\, dp') + (1 - r_{\Delta t}(q,p))\delta_{(q,p)}(dq'\, dp'). \tag{6.37}$$

The proof that the Markov chain induced by Algorithm 6.1 preserves the canonical measure is then a consequence of the following result.

Lemma 6.2. *The Markov chain with transition kernel* (6.37) *leaves the canonical measure* (5.3) *invariant.*

Proof. Consider a bounded measurable function $\varphi : \mathcal{E} \to \mathbb{R}$. For simplicity of notation, we write $x = (q,p)$. Note first that

$$\int_{\mathcal{E}} \varphi(x') P_{\Delta t}(x, dx')\mu(dx) = \int_{\mathcal{E}} r_{\Delta t}(x)\left[\varphi(\Psi_{\Delta t}(x)) - \varphi(x)\right]\mu(dx) + \int_{\mathcal{E}} \varphi(x)\,\mu(dx),$$

so it suffices to prove that the first integral vanishes. To this end, we use successively the changes of variables $y = \Phi_{\Delta t}(x)$ and $z = Sy$ (which both have Jacobian 1) to write

$$\begin{aligned}
\int_{\mathcal{E}} r_{\Delta t}(x)\varphi(\Psi_{\Delta t}(x))\,\mu(dx) &= \int_{\mathcal{E}} r_{\Delta t}(x)\varphi(\Psi_{\Delta t}(x))\frac{\mathrm{e}^{-\beta H(x)}}{Z_\mu}\,dx \\
&= \int_{\mathcal{E}} r_{\Delta t}(\Phi_{\Delta t}^{-1}(y))\varphi(S(y))\frac{\mathrm{e}^{-\beta(H\circ\Phi_{\Delta t}^{-1})(y)}}{Z_\mu}\,dy \\
&= \int_{\mathcal{E}} r_{\Delta t}\left[(\Phi_{\Delta t}^{-1}\circ S)(z)\right]\varphi(z)\frac{\mathrm{e}^{-\beta(H\circ\Phi_{\Delta t}^{-1}\circ S)(z)}}{Z_\mu}\,dz \\
&= \int_{\mathcal{E}} r_{\Delta t}\left[\Psi_{\Delta t}(z)\right]\varphi(z)\frac{\mathrm{e}^{-\beta(H\circ\Psi_{\Delta t})(z)}}{Z_\mu}\,dz,
\end{aligned}$$

where we used that $\Phi_{\Delta t}^{-1} \circ S = \Psi_{\Delta t}^{-1} = \Psi_{\Delta t}$ in the last step. A simple computation shows that

$$r_{\Delta t}(\Psi_{\Delta t}(x))\mathrm{e}^{-\beta(H\circ\Psi_{\Delta t})(x)} = \min\left(\mathrm{e}^{-\beta H(x)}, \mathrm{e}^{-\beta(H\circ\Psi_{\Delta t})(x)}\right) = r_{\Delta t}(x)\mathrm{e}^{-\beta H(x)},$$

which leads to the desired conclusion. □

In fact, the Markov chain induced by Algorithm 6.1 enjoys better reversibility properties, as made precise in [178, Section 2.1.4] and [181, Section 2.2.4]. A building block is provided by the following statement.

Exercise 6.2. *Prove that the transition kernel is reversible by mimicking the proof of Lemma 3.1.*

6.3 Variance reduction

As already mentioned in (6.11), the variance of trajectory averages computed with discretizations of SDEs are consistent with the variance of trajectory averages computed with the continuous dynamics they approximate. In this section we discuss standard ways to reduce this variance in order to decrease the statistical error in the estimated averages (6.6).

A first important distinction should be made between target-oriented variance reduction, which corresponds to reducing the asymptotic variance σ_φ^2 defined in (6.10) for a given observable φ; and a general purpose reduction, for which the aim is to decrease

$$\sup_{\varphi\in L^2(\pi)} \frac{\sigma_\varphi^2}{\|\varphi\|_{L^2(\pi)^2}} = \sup_{\|\varphi\|_{L^2(\pi)}\leqslant 1} 2\int_{\mathcal{X}} \Pi\varphi(-\mathcal{L}^{-1}\Pi\varphi)\,d\pi. \tag{6.38}$$

We choose $\varphi \in L^2(\pi)$ for simplicity, but the same question may be raised for specific subsets of $L^2(\pi)$.

For Markov chains or Markov processes, the fact that the variance is large is due to the fact that the correlation time of the dynamics is large (see the discussion after (4.21)), which itself is due to the metastability of the process. The idea is therefore to modify the dynamics in order to remove, or at least reduce the metastability, while still being able to reconstruct canonical averages.

We present in this section standard variance reduction techniques for Markov processes. These techniques are extensions of methods used for i.i.d. sequences, for which reviews are for instance provided in [43] and [242, Chapter 5]. The most famous techniques are antithetic variables, stratification, control variate methods and importance sampling. We present flavours of the latter three approaches in this section.

harmoniser avec premiere partie livre

6.3.1 Stratification

Stratification is a way of decomposing a difficult sampling problem into several easier ones. Ideally, the phase space should be decomposed into the collection of all metastable states, corresponding to local minima of the potential energy function, and these regions should be independently sampled. The local averages in each region should then be reweighted according to the canonical weight of the region itself. This method is therefore a general purpose variance reduction technique.

There are two major ways to make this idea practical, depending on whether the considered regions overlap.

(1) When there is some overlap between the regions, bridge sampling methods such as MBAR [252] can be used. The method is based on several works in statistics [101, 192, 154, 262].
(2) Non-overlapping regions can also be constructed as the level sets of some real-valued function of the configuration of the system. In this case, the sampling is performed by constraining the dynamics on the iso-surfaces corresponding to various values of the level-set function, and varying the values of the constraint in order to sample the full phase space. This method is known as thermodynamic integration, with a reconstruction performed by computing the free energy; see Section 7.2.1, as well as [178, Chapter 3] and references therein.

6.3.2 Control variate

The control variate method is a classical technique for variance reduction, although it is not so often used in molecular simulation. Consider the case when thermodynamic averages are estimated by ergodic averages of a stochastic dynamics with generator $\mathcal{L}$. Recall that we denote the invariant measure by π and the configuration of the system by $x \in \mathcal{X}$, so that thermodynamic averages read $\mathbb{E}_\pi(\varphi)$.

Let us first explain the general principle of control variates on a simple example. Consider a given observable φ, and introduce an observable ϕ such that $\mathbb{E}_\pi(\phi) = 0$. Then,

$$\mathbb{E}_\pi(\varphi) = \mathbb{E}_\pi(\varphi - \phi).$$

The idea now is to choose ϕ such that $\mathrm{Var}_\pi(\varphi - \phi)$ is much smaller than $\mathrm{Var}_\pi(\varphi)$. Of course, the optimal choice is $\phi = \varphi - \mathbb{E}_\pi(\varphi)$, in which case $\mathrm{Var}_\pi(\varphi - \phi) = 0$. Note however that the optimal control variate depends on the quantity of interest, $\mathbb{E}_\pi(\varphi)$, which is not available.

A systematic way of constructing admissible control variates (*i.e.*, functions with average 0 with respect to π) is to choose them in the image of the generator $\mathcal{L}$. Indeed, the invariance of the measure π, formulated as (compare with (4.8))

$$\int_{\mathcal{X}} \mathcal{L}\varphi \, d\pi = 0,$$

leads to the following equality: for any C^∞ and compactly supported test function Φ,

$$\mathbb{E}_\pi(\varphi) = \mathbb{E}_\pi(\varphi - \mathcal{L}\Phi) = \int_{\mathcal{X}} (\varphi - \mathcal{L}\Phi) \, d\pi. \tag{6.39}$$

The optimal choice corresponds to Φ solution of the Poisson equation

$$\mathcal{L}\Phi = \varphi - \mathbb{E}_\pi(\varphi). \tag{6.40}$$

The solvability of this equation is ensured by results such as Corollaries 4.1 and 4.2, depending on the properties of the potential V and the integrability properties of the observable φ. By construction, the estimator based on (6.39)-(6.40), namely

$$\frac{1}{t} \int_0^t (\varphi(x_s) - \mathcal{L}\Phi(x_s)) \, ds,$$

has a variance equal to 0 since $\varphi(x) - \mathcal{L}\Phi(x) = \mathbb{E}_\pi(\varphi)$ for any value of $x \in \mathcal{X}$. Such approaches were first suggested for Markov chains in the computational statistics literature [8, 124], with more recent contributions such as [200, 64, 201, 208, 25]. There are also related propositions in the statistical physics literature [16], where they are known as the 'zero-variance principle'. The approach can in fact be extended to any operator which leaves π invariant, such as $\partial^*_{x_i}$, which already appears in Stein's test for approximate normality [256] and also in works on control variates for MCMC schemes in the computational statistics literature [208, 25].

In practice, it is generally impossible to solve the Poisson equation (6.40) exactly. However, it is possible to approximate the ideal function Φ in (6.40) on a basis of trial functions, given by the image of linear and quadratic functions under $\partial^*_{x_i}$ or $\mathcal{L}$ (see respectively [25] and [201]), or the image of kernel functions in [208]. Alternatively, it is also possible to obtain a control variate as the solution of an approximate Poisson equation, as done in [239].

6.3.3 Importance sampling

The basic idea of importance sampling is to change the measure which is sampled into a measure which is easier to sample. In the context of molecular simulation, this is most commonly done by changing the potential energy function V in the dynamics to a modified potential $V + \widetilde{V}$. The modified overdamped Langevin dynamics associated with the potential $V + \widetilde{V}$, namely

$$dq_t = -\nabla\left(V + \widetilde{V}\right)(q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t, \tag{6.41}$$

is then ergodic for the modified probability measure $\nu_{\widetilde{V}} = Z_{\widetilde{V}}^{-1}\,\mathrm{e}^{-\beta\widetilde{V}}\nu$. Likewise, the modified Langevin dynamics

$$\begin{cases} d\widetilde{q}_t = M^{-1}\widetilde{p}_t\,dt, \\ d\widetilde{p}_t = -\nabla\left(V + \widetilde{V}\right)(\widetilde{q}_t)\,dt - \gamma\,M^{-1}\widetilde{p}_t\,dt + \sqrt{\dfrac{2\gamma}{\beta}}\,dW_t \end{cases}$$

is ergodic for the modified canonical probability measure $\mu_{\widetilde{V}} = Z_{\widetilde{V}}^{-1}\,\mathrm{e}^{-\beta\widetilde{V}}\mu$. The fundamental observation to retrieve averages with respect to ν or μ with realizations of the modified dynamics is that

$$\int_{\mathcal{D}} \varphi(q)\,\nu(dq) = \int_{\mathcal{E}} \varphi(q)\,\mu(dq\,dp) = \frac{\displaystyle\int_{\mathcal{D}} \varphi\,\mathrm{e}^{\beta\widetilde{V}}\,d\nu_{\widetilde{V}}}{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{\beta\widetilde{V}}\,d\nu_{\widetilde{V}}} = \frac{\displaystyle\int_{\mathcal{E}} \varphi\,\mathrm{e}^{\beta\widetilde{V}}\,d\mu_{\widetilde{V}}}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{\beta\widetilde{V}}\,d\mu_{\widetilde{V}}}. \tag{6.42}$$

Therefore, the following estimator is considered:

$$\widehat{\varphi}_t^{\widetilde{V}} = \frac{\displaystyle\int_0^t \varphi(\widetilde{q}_s)\,\mathrm{e}^{\beta\widetilde{V}(\widetilde{q}_s)}\,ds}{\displaystyle\int_0^t \mathrm{e}^{\beta\widetilde{V}(\widetilde{q}_s)}\,ds}. \tag{6.43}$$

After discretization in time, the estimator $\widehat{\varphi}_t^{\widetilde{V}}$ is approximated by

$$\widehat{\varphi}_{N_{\mathrm{iter}},\Delta t}^{\widetilde{V}} = \frac{\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \varphi(\widetilde{q}^n)\,\mathrm{e}^{\beta\widetilde{V}(\widetilde{q}^n)}}{\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{\beta\widetilde{V}(\widetilde{q}^n)}},$$

where $\widetilde{q}^n$ is an approximation of $\widetilde{q}_{n\Delta t}$.

In order for importance sampling to be efficient, the weights $\mathrm{e}^{\beta\widetilde{V}(q^n)}$ should not be too degenerate. This can be quantified in various ways, for instance through the so-called efficiency factor

$$\frac{\displaystyle\left(\sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{\beta\widetilde{V}(q^n)}\right)^2}{\displaystyle N_{\mathrm{iter}} \sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{2\beta\widetilde{V}(q^n)}} \in [0,1].$$

The fact that this number is indeed between 0 and 1 can be seen via the Cauchy–Schwarz inequality. The efficiency factor counts the fraction of significant values on average. It should be as close as possible to 1, which is indeed the case if the weights are of similar magnitudes. In the statistics literature, the efficiency factor corresponds to the effective sample size of [153] divided by the number of sampled values.

When the observable φ under consideration is fixed (target-oriented variance reduction), it is possible to optimize the importance sampling procedure in order to minimize the variance of the estimator. We illustrate this fact for samples $\widetilde{q}^n$ independently and identically distributed from a measure with density $\mathrm{e}^{-\beta(V(q)+\widetilde{V}(q))}$, whose normalization constant fortunately does not need to be known. Consider the estimator

$$\widehat{\varphi}^{\mathrm{iid},\widetilde{V}}_{N_{\mathrm{iter}}} = \frac{\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \varphi(\widetilde{q}^n)\, \mathrm{e}^{\beta \widetilde{V}(\widetilde{q}^n)}}{\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{\beta \widetilde{V}(\widetilde{q}^n)}}, \quad \widetilde{q}^n \sim \nu_{\widetilde{V}} \ \text{ i.i.d.}$$

A simple computation based on the equality[1] $\nu_{\widetilde{V}}/\nu = \mathrm{e}^{-\beta\widetilde{V}}\, Z_0/Z_{\widetilde{V}}$ shows that

$$\sqrt{N_{\mathrm{iter}}}(\widehat{\varphi}^{\mathrm{iid},\widetilde{V}}_{N_{\mathrm{iter}}} - \mathbb{E}_\nu(\varphi)) = \frac{\sqrt{N_{\mathrm{iter}}}\left(\dfrac{1}{N_{\mathrm{iter}}}\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} [\varphi(\widetilde{q}^n) - \mathbb{E}_\nu(\varphi)] \dfrac{\nu}{\nu_{\widetilde{V}}}(\widetilde{q}^n)\right)}{\dfrac{1}{N_{\mathrm{iter}}}\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \dfrac{\nu}{\nu_{\widetilde{V}}}(\widetilde{q}^n)}.$$

By the law of large numbers, the denominator almost surely converges to 1 as $N_{\mathrm{iter}} \to +\infty$, while, by the central limit theorem, the numerator converges in law to a Gaussian distribution with variance

$$\sigma^2_{\widetilde{V}}(\varphi) = \int_{\mathcal{D}} \frac{(\Pi\varphi)^2 \nu^2}{\nu_{\widetilde{V}}},$$

where we introduced $\Pi\varphi = \varphi - \mathbb{E}_\nu(\varphi)$. By Slutsky's theorem, the random variable

$$\sqrt{N_{\mathrm{iter}}}\big(\widehat{\varphi}^{\mathrm{iid},\widetilde{V}}_{N_{\mathrm{iter}}} - \mathbb{E}_\nu(\varphi)\big)$$

therefore converges in law to a Gaussian distribution with variance $\sigma^2_{\widetilde{V}}(\varphi)$. The Cauchy–Schwarz inequality on $L^2(\nu_{\widetilde{V}})$ now shows that

$$\sigma^2_{\widetilde{V}}(\varphi) \geqslant \left(\int_{\mathcal{D}} \frac{|\Pi\varphi|\nu}{\nu_{\widetilde{V}}}\, \nu_{\widetilde{V}}\right)^2 = \left(\int_{\mathcal{D}} |\Pi\varphi|\, d\nu\right)^2,$$

with equality if and only if $|\Pi\varphi|\nu/\nu_{\widetilde{V}} \propto 1$. The optimal biased measure for i.i.d. sampling is thus

$$\nu_{\widetilde{V}}(dq) = \frac{|\Pi\varphi(q)|\, \nu(dq)}{\int_{\mathcal{D}} |\Pi\varphi| \mathrm{d}\nu}$$

which formally corresponds to the potential

$$\widetilde{V}(q) = -\frac{1}{\beta} \log |\Pi\varphi(q)|.$$

The latter expression is singular at configurations q such that $\Pi\varphi(q) = 0$. More importantly, the expression of $\widetilde{V}$ depends on $\mathbb{E}_\nu(\varphi)$, and is therefore not available as such.

Remark 6.4. *Such importance sampling approaches can be extended to averages over the path space, and the optimal bias can also be approximated in this context. See [180, Section 6.2] and references therein.*

Let us finally discuss general purpose variance reduction in the context of importance sampling. In view of the definition (6.38), a reduction of the variance for any observable φ amounts to a decrease of the operator norm of the *symmetric* part of $\mathcal{L}^{-1}$. Note indeed that only the symmetric part of of $\mathcal{L}^{-1}$ matters in the right-hand side of (6.38). For overdamped Langevin dynamics, the generator is self-adjoint: $\mathcal{L} = \mathcal{L}^*$ when these operators are considered on $L^2(\nu)$. General variance

[1] With some abuse of notation, we denote the measures $\nu_{\widetilde{V}}(dq)$ and their densities by the same symbol. The ratio $\nu_{\widetilde{V}}/\nu$ is the Radon–Nikodym derivative of $\nu_{\widetilde{V}}$ with respect to ν.

reduction therefore amounts to an increase of the spectral gap of the operator by the Rayleigh–Ritz principle. This can be done by choosing $\widetilde{V}$ to erase local minima in V which degrade the Poincaré/LSI constants (see Section 4.3.2). Good choices of $\widetilde{V}$ to overcome such metastability issues are based on the free energy associated with a suitable reaction coordinate [178]; see Section 7.1.3. When the generator $\mathcal{L}$ is not self-adjoint, there are *a priori* no simple relationships between the symmetric and antisymmetric parts of $\mathcal{L}$ and its inverse. Some results can however be obtained for specific dynamics, such as overdamped Langevin dynamics perturbed by a divergence free non reversible drift, see [75, 230].

Complements

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Uniform estimates on $P_{\Delta t}$ in the overdamped case

We state below a minorization condition stronger than is needed for Assumption 3.1, but which will prove useful later on in Section 8.4. We name it a "uniform minorization condition" since, in contrast to the above computations, the lower bound η and the probability measure λ do not depend on the time step Δt provided it is sufficiently small. To obtain such a condition, we have to consider evolutions over fixed physical times $T \simeq n\Delta t > 0$, which amounts to iterating the elementary evolution $P_{\Delta t}$ over $\lceil T/\Delta t \rceil$ time steps (where $\lceil x \rceil$ denotes the smallest integer larger than x).

Lemma 6.3 (uniform minorization condition). *Consider the evolution operator $P_{\Delta t}$ associated with the Euler–Maruyama discretization (6.25) on the position space $\mathcal{D} = (L\mathbb{T})^D$, and a given integration time $T > 0$. There exist $\Delta t^*, \eta > 0$ and a probability measure λ such that, for any bounded, measurable non-negative function f, for any $\Delta t \in (0, \Delta t^*]$ and for any $q \in \mathcal{D}$,*

$$(P_{\Delta t}^{\lceil T/\Delta t \rceil} f)(q) \geqslant \eta \int_{\mathcal{D}} f \, d\lambda.$$

Such estimates were obtained in [35] in unbounded spaces $\mathcal{D}$ for a class of Metropolis–Hastings schemes whose proposition kernel is (6.25). See also [91, 92] for related results on bounded spaces, as well as [169, 224] for discretizations of Langevin dynamics. The proof of Lemma 6.3 shows that the measure λ has a positive density with respect to the Lebesgue measure. Application of Theorem 3.1, together with an argument similar to that used to obtain (4.53) from the decay at multiples of a given time, gives the following exponential convergence.

Corollary 6.1 (ergodicity of Euler–Maruyama for compact spaces). *There exists $\Delta t^* > 0$ such that, for any $\Delta t \in (0, \Delta t^*]$, the Markov chain associated with $P_{\Delta t}$ has a unique invariant probability measure $\nu_{\Delta t}$. This measure admits a density with respect to the Lebesgue measure. Moreover, there exist $C, \kappa > 0$ such that, for all functions $f \in B^\infty(\mathcal{D})$,*

$$\forall n \in \mathbb{N}, \qquad \left\| P_{\Delta t}^n f - \int_{\mathcal{D}} f \, d\nu_{\Delta t} \right\|_{B^\infty} \leqslant C \, \mathrm{e}^{-\kappa n \Delta t} \, \|f\|_{B^\infty}. \tag{6.44}$$

The fact $\nu_{\Delta t}$ admits a density with respect to the Lebesgue measure dq follows from the minorization condition stated in Lemma 6.3, which ensures that the Markov chain is irreducible with respect to Lebesgue measure. The proof of Corollary 6.1 relies on the following result (given on a general state space with a general Lyapunov function) for the choice $W = 1$.

Lemma 6.4. *Consider a Lyapunov function $\mathscr{W} : \mathcal{X} \to [1, +\infty)$ and assume that there exists $N \geqslant 1$ and $K, \lambda > 0$ such that*

$$\forall m \in \mathbb{N}, \qquad \left\| P^{Nm} \right\|_{\mathcal{B}\left(B^\infty_{\mathscr{W},0}\right)} \leqslant K \mathrm{e}^{-\lambda m},$$

where π is the unique invariant measure of P^N and

$$B^\infty_{\mathscr{W},0} = \left\{ \varphi \in B^\infty_{\mathscr{W}}(\mathcal{X}) \, \middle| \, \int_{\mathcal{X}} \varphi \, d\pi = 0 \right\}.$$

Then, the following estimate holds at any time:

$$\forall n \in \mathbb{N}, \qquad \|P^n\|_{\mathcal{B}\left(B^\infty_{\mathscr{W},0}\right)} \leqslant \left(K \, \mathrm{e}^{\lambda} \sup_{0 \leqslant k \leqslant N-1} \left\| \frac{P^k \mathscr{W}}{\mathscr{W}} \right\|_{B^\infty} \right) \mathrm{e}^{-\lambda n / N}$$

Note that this result in particular shows that π is the unique invariant measure of P. A sufficient condition for

$$\sup_{k\geqslant 0}\left\|\frac{P^k\mathscr{W}}{\mathscr{W}}\right\|_{B^\infty} < +\infty$$

is that $P\mathscr{W} \leqslant a\mathscr{W} + b$ with $0 \leqslant a < 1$, *i.e.* a Lyapunov condition holds over one step. In this case, the supremum is smaller than $a + b/(1-a)$ since

$$0 \leqslant P^k\mathscr{W} \leqslant P^{k-1}(a\mathscr{W}+b) \leqslant \ldots \leqslant a^k\mathscr{W} + b(1+\cdots+a^{k-1}) \leqslant a^k\mathscr{W} + \frac{b}{1-a}.$$

When applied to discretization of SDEs, one typically has $1-a = \mathrm{O}(\Delta t)$ and $b = \mathrm{O}(\Delta t)$, so that the supremum is finite.

Proof. For a general index $n \in \mathbb{N}$, we write

$$n = m_n N + \widetilde{n}, \qquad 0 \leqslant \widetilde{n} \leqslant N-1.$$

We next use $|f| \leqslant \|f\|_{B^\infty_{\mathscr{W}}}\mathscr{W}$, so that $|P^k f| \leqslant \|f\|_{B^\infty_{\mathscr{W}}}P^k\mathscr{W}$, and finally

$$\|P^k f\|_{B^\infty_{\mathscr{W}}} \leqslant \|f\|_{B^\infty_{\mathscr{W}}}\left\|\frac{P^k\mathscr{W}}{\mathscr{W}}\right\|_{B^\infty}.$$

This shows that

$$\|P^k\|_{\mathcal{B}(B^\infty_{\mathscr{W},0})} \leqslant \left\|\frac{P^k\mathscr{W}}{\mathscr{W}}\right\|_{B^\infty}.$$

Therefore,

$$\|P^n\|_{\mathcal{B}(B^\infty_{\mathscr{W},0})} \leqslant \left\|(P^N)^{m_n}\right\|_{\mathcal{B}(B^\infty_{\mathscr{W},0})}\left\|P^{\tilde{n}}\right\|_{\mathcal{B}(B^\infty_{\mathscr{W},0})} \leqslant K\mathrm{e}^{-\lambda m_n}\sup_{0\leqslant k\leqslant N-1}\left\|\frac{P^k\mathscr{W}}{\mathscr{W}}\right\|_{B^\infty},$$

which gives the expected result since $m_n \geqslant n/N - 1$. □

Part III

Beyond static averages

7

Computation of free energy differences

This lecture is an introduction to the computation of free energy differences, see [178] for an extensive mathematical treatment. Free energy is a central concept in thermodynamics and in modern studies on biochemical and physical systems. In many applications, the important quantity is actually the *free energy difference* between various macroscopic states of the system, rather than the free energy itself. Free energy differences allow to quantify the relative likelihood of different states. A related but more numerical motivation is to use the free energy to devise algorithms which overcome sampling barriers. These ideas are discussed in Section 7.1. We next review in Section 7.2 the main (classes of) methods to compute free energy differences. We finally focus in Section 7.3 on the mathematical analysis of one of these methods, for which we prove the longtime convergence of a nonlinear Fokker–Planck equation.

7.1 Definition of the free energy

After a brief definition of absolute free energies in Section 7.1.1, we turn the definition of free energy differences in Section 7.1.2. One motivation to computing free energy profiles is to use the free energy as an importance sampling function, to improve the quality of the sampling, as discussed in Section 7.1.3.

7.1.1 Absolute free energy

We restrict ourselves in this lecture to the canonical ensemble, though most of the concepts and numerical methods considered can be extended to other thermodynamic ensembles (see Section 1.3.4). The *absolute free energy* of a system is defined as

$$F = -\frac{1}{\beta} \ln Z_\mu, \tag{7.1}$$

where Z_μ is the partition function

$$Z_\mu = \int_{\mathcal{E}} \mathrm{e}^{-\beta H(q,p)}\, dq\, dp. \tag{7.2}$$

Since the potential energy function V (hence the Hamiltonian H) is defined only up to an additive constant when empirical potential functions are used, so is the absolute free energy. However, this has no consequence on free energy differences, see Section 7.1.2 below. The motivation for (7.1) comes from an analogy with macroscopic thermodynamics, see for instance the discussion in [178, Section 1.3.1.2].

Remark 7.1. *The free energy* (7.1) *is called the Helmholtz free energy. Similar free energies can be considered for other thermodynamic ensembles. They are also logarithms of the partition functions multiplied by a factor* $-\beta^{-1}$*. When the isobaric-isothermal ensemble (NPT) is considered, the associated free energy is called the Gibbs free energy.*

For separable Hamiltonians (1.3), the partition function can be rewritten as

$$Z_\mu = Z_\nu \left(\frac{2\pi}{\beta}\right)^{3N/2} \prod_{i=1}^{N} m_i^{3/2}, \qquad Z_\nu = \int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\, dq,$$

and the only difficulty is the computation of the configurational partition function Z_ν. This partition function cannot be computed as such in general. It however has a simple expression for some specific systems, such as the ideal gas, or solids at low temperature (resorting to the phonon spectrum, *i.e.* assuming that the potential energy can be approximated by a sum of harmonic interactions), see [97, 233].

7.1.2 Relative free energies

As mentioned above, the quantity of interest in many applications is not the absolute free energy, but the *free energy differences* between various states. Typical examples studied by computer simulations include the solvation free energy (which is the free energy difference between a molecule *in vacuo* and its counterpart surrounded by solvent molecules), and the binding free energy of two molecules (this free energy difference determines whether a new drug can have an efficient action on a given protein for example). See [55] for other relevant examples in chemistry and biophysics.

In this section, we describe more precisely what we mean by states, and how a transition between two states can be defined. As already hinted at in the introduction to this section, two cases should be considered: alchemical transitions and transitions indexed by a reaction coordinate.

Alchemical transitions

The so-called *alchemical case* considers transitions indexed by an external parameter λ, independent of the microscopic phase space configuration (q, p). Typical examples are the intensity of an applied magnetic field for a spin system, or the constants used in the empirical force fields (such as the energy ε or the length σ in the Lennard-Jones potential (1.6)). See for instance [55, Section 2.8] for more examples. The name "alchemical" refers to the fact that the nature of the particles at hand can be modified in the computer simulation by changing the parameters of the potential describing the molecular interactions.

For a given value of λ, the system is described by a Hamiltonian H_λ. A state is then the collection of all possible microscopic configurations $\mathcal{E}$, distributed according to the canonical measure

$$\mu_\lambda(dq\, dp) = \frac{1}{Z_\lambda} \mathrm{e}^{-\beta H_\lambda(q,p)}\, dq\, dp, \qquad Z_\lambda = \int_{\mathcal{D}} \mathrm{e}^{-\beta H_\lambda(q,p)}\, dq\, dp. \tag{7.3}$$

An alchemical transition transforms the state $\lambda = 0$ into the state $\lambda = 1$. The corresponding free energy difference is

$$F(1) - F(0) = -\frac{1}{\beta} \ln \left(\frac{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H_1(q,p)}\, dq\, dp}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H_0(q,p)}\, dq\, dp} \right). \tag{7.4}$$

It is often the case that H_λ depends on λ only through the potential energy V_λ. In this case, the free energy difference simplifies as

$$F(1) - F(0) = -\frac{1}{\beta} \ln \left(\frac{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{-\beta V_1(q)}\, dq}{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{-\beta V_0(q)}\, dq} \right). \tag{7.5}$$

Transitions indexed by a reaction coordinate

In the reaction coordinate case, the Hamiltonian of the system is kept fixed. A state is a measure on a submanifold of the phase space. These submanifolds are the level sets of some function, the so-called *reaction coordinate*,

$$\xi : \mathcal{D} \to \mathcal{M} \subset \mathbb{R}^m,$$

with $m \leqslant D$. Examples of such functions are dihedral angles, or distances between two molecular subgroups. To ξ is associated a foliation of the phase space into submanifolds $\Sigma(z) = \{q \in \mathcal{D} \mid \xi(q) = z\}$, so that

$$\mathcal{D} = \bigcup_{z \in \mathcal{M}} \Sigma(z).$$

The free energy difference is related to the relative likelihoods of marginal distributions with respect to ξ. For the canonical measure (1.18), the marginal distribution is by definition

$$\mu^\xi(dz) = \left(\frac{1}{Z_\mu} \int_{\Sigma(z) \times \mathbb{R}^D} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)-z}(dq)\, dp \right) dz.$$

It is the image of the measure μ by ξ. The measure $\delta_{\xi(q)-z}(dq)$ is defined as in (1.14) and (1.15) through the relation $\delta_{\xi(q)-z}(dq)\, dz = dq$, see [178, Section 3.2.1.1] for further precision. In particular, it can be written as

$$\delta_{\xi(q)-z}(dq) = \frac{\sigma_{\Sigma(z)}(dq)}{|\nabla \xi(q)|}, \tag{7.6}$$

where $\sigma_{\Sigma(z)}(dq)$ is the area measure induced by the Lebesgue measure on the manifold $\Sigma(z)$ when $\mathcal{D}$ is equipped with the standard Euclidean scalar product. The free energy is then defined as the log-density of the marginal distribution:

$$\mathrm{e}^{-\beta F(z)}\, dz = \mu^\xi(dz).$$

Thus, $\exp(-\beta[F(1) - F(0)])$ can be interpreted as the relative likelihood of states in $\Sigma(1)$ compared to states in $\Sigma(0)$. More explicitly,

$$F(z) = -\beta^{-1} \ln \left(\frac{1}{Z_\mu} \int_{\Sigma(z) \times \mathbb{R}^{3N}} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)-z}(dq)\, dp \right). \tag{7.7}$$

The free energy can therefore also be seen as some effective potential associated with ξ. The function $z \mapsto F(z)$ is called *potential of mean force*. This terminology is motivated by the fact that $F'(z)$, called the *mean force*, is some average force exerted on the system when the reaction coordinate is kept constant, see [178, Section 3.2.2] for further precision.

The free energy difference between the state $\Sigma(0)$ and the state $\Sigma(1)$ is finally defined as

$$F(1) - F(0) = -\beta^{-1} \ln \left(\frac{\displaystyle\int_{\Sigma(1)\times\mathbb{R}^D} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)-1}(dq)\, dp}{\displaystyle\int_{\Sigma(0)\times\mathbb{R}^D} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)}(dq)\, dp} \right). \tag{7.8}$$

For separable Hamiltonians, (1.3), the free energy difference can be rewritten as

$$F(1) - F(0) = -\beta^{-1} \ln \left(\frac{\displaystyle\int_{\Sigma(1)} \mathrm{e}^{-\beta V(q)}\, \delta_{\xi(q)-1}(dq)}{\displaystyle\int_{\Sigma(0)} \mathrm{e}^{-\beta V(q)}\, \delta_{\xi(q)}(dq)} \right). \tag{7.9}$$

Notice that when $|\nabla\xi|$ is constant, the free energy difference $F(1) - F(0)$ only depends upon ξ through $\Sigma(1)$ and $\Sigma(0)$ in view of (7.6).

Remark 7.2 (Choice of the reaction coordinate). *For a given foliation of the configurational space, the free energy difference depends in general on the choice of the reaction coordinate indexing this foliation. Indeed, consider another reaction coordinate $\widetilde{\xi}$, defining the same level sets, with in particular*

$$\widetilde{\Sigma}(0) = \Big\{ q \;\Big|\; \widetilde{\xi}(q) = 0 \Big\} = \big\{ q \mid \xi(q) = 0 \big\} = \Sigma(0), \tag{7.10}$$

and a similar relation for $z = 1$. For instance, $\widetilde{\xi} = f(\xi)$ with any one-to-one increasing function $f : [0,1] \to [0,1]$ has the same level sets as ξ, and satisfies (7.10).

In general, the associated free energy differences $F(1) - F(0)$ and $\widetilde{F}(1) - \widetilde{F}(0)$ are different. Indeed, the surface measure $\sigma_{\Sigma(0)}(dq)$ is somehow intrinsic (it depends only on the submanifold $\Sigma(0) = \widetilde{\Sigma}(0)$ and on the ambient scalar product), while the measure $\delta_{\xi(q)-z}(dq)$ depends on the gradients of the reaction coordinates through the factors $|\nabla\xi(q)|^{-1}$, see the right-hand side of (7.6). *It is therefore a modelling choice to decide which reaction coordinate to use, in particular when comparing results of numerical simulations to experimental measurements. Of course, there are no such issues in the alchemical case.*

Remark 7.3 (Relation with the alchemical setting). *Alchemical transitions can be considered as a special case of transitions indexed by a reaction coordinate, upon introducing the extended variable $Q = (\lambda, q)$ and the reaction coordinate $\xi(Q) = \lambda$. In this case, the geometry of the submanifolds is very simple since $|\nabla\xi(Q)| = 1$. The level sets are $\Sigma(\lambda) = \{\lambda\} \times \mathcal{D}$, and the measure $\delta_{\xi(Q)-\lambda}(dQ)$ in the extended space is the Lebesgue measure dq on $\mathcal{D}$.*

Besides, the reaction coordinate case is sometimes considered as a limiting case of the alchemical case, using the family of Hamiltonians

$$H^\eta_\lambda(q) = V^\eta(q,\lambda) + \frac{1}{2} p^T M^{-1} p, \qquad V^\eta(q,\lambda) = V(q) + \frac{1}{2\eta}\Big(\xi(q) - \lambda\Big)^2,$$

and letting $\eta \to +\infty$, a procedure justified by the consistency result provided by Exercise 7.1.

Exercise 7.1. *Prove that*

$$\frac{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{-\beta V^\eta_\lambda(q,z)}\, dq}{\displaystyle\int_{\mathcal{M}}\int_{\mathcal{D}} \mathrm{e}^{-\beta V^\eta}} \xrightarrow[\eta\to+\infty]{} \frac{\mathrm{e}^{-\beta F(z)}}{\displaystyle\int_{\mathcal{M}} \mathrm{e}^{-\beta F}},$$

and deduce that the alchemical free energy associated with H^η_λ converges to the free energy associated with the reaction coordinate ξ (see [178, Lemma 5.3]).

7.1.3 Free energy and metastability

As discussed in Section 6.3, standard molecular simulation techniques such as thos often experience difficulties in sampling metastable potentials. Recall that potentials are called metastable when the corresponding canonical measure has several regions of high probability separated by low-probability regions. Typical numerical methods spend a lot of time in one given metastable basin, and only rarely escape it to visit another basin. These escapes are rare but fast events. The notion of metastability may be formalized and quantified in several ways, for instance through the LSI or Poincaré constants (see the discussion in Section 4.3.3). We give below two paradigmatic examples of metastable potentials, and interpret the origin of metastability from the point of view of free energy profiles.

We motivate in this section the interest of free energy methods for the sampling of metastable potentials, using importance sampling as described in Section 6.3.3. Such methods can be used provided the low- and high-probability regions of the systems are the level sets of some function $\xi(q)$, which is still called a reaction coordinate. Alternatively, $\xi(q)$ can be seen as some slowly evolving degrees of freedom encoding some coarse-grained information on the system. The free energy associated with ξ may then be used as a biasing potential to favor transitions from one metastable basin to another. Of course the reliability of the method crucially depends on the choice of the reaction coordinate. This is a very important problem in practice, unfortunately rather ill-posed.

A simple example of metastable dynamics

Consider the potential energy

$$V(x,y) = \frac{1}{6}\Big[4(1-x^2-y^2)^2 + 2(x^2-2)^2 + ((x+y)^2-1)^2 + ((x-y)^2-1)^2\Big], \tag{7.11}$$

and a single particle $q = (x,y) \in \mathbb{R}^2$ evolving according to the overdamped Langevin dynamics:

$$dq_t = -\nabla V(q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t.$$

Figure 7.1 presents the level sets of the potential (7.11) and a typical trajectory obtained by a Euler–Maruyama discretization. The dynamics projected in the y variable is irrelevant, whereas the time evolution of the x variable shows that it is a "slow" variable. If the average position $\mathbb{E}_\nu(x)$ is computed as a time-average along a trajectory, the convergence is very slow (compared to the convergence of the average $\mathbb{E}_\nu(y)$ for instance). This suggests to choose $\xi(x,y) = x$.

For later purposes, we compute the free energy profile for the reaction coordinate $\xi(x,y) = x$:

$$F(x_2) - F(x_1) = -\frac{1}{\beta}\ln\left(\frac{\psi^\xi(x_2)}{\psi^\xi(x_1)}\right), \tag{7.12}$$

where the marginals ψ^ξ of the equilibrium canonical distribution are

$$\psi^\xi(x) = \int_{\mathbb{R}} \mathrm{e}^{-\beta V(x,y)}\,dy.$$

This profile is illustrated in Figure 7.2, together with

$$F'(x) = \frac{\displaystyle\int_{\mathbb{R}} \partial_x V(x,y)\,\mathrm{e}^{-\beta V(x,y)}\,dy}{\displaystyle\int_{\mathbb{R}} \mathrm{e}^{-\beta V(x,y)}\,dy}.$$

Notice that F' is the opposite of the averaged force experienced in the direction of the reaction coordinate (the so-called mean force). There is a high free energy barrier at $x = 0$, which corresponds to a small value of $\psi^\xi(x)$. This barrier is at the origin of the metastable behavior since it separates two regions of high probability.

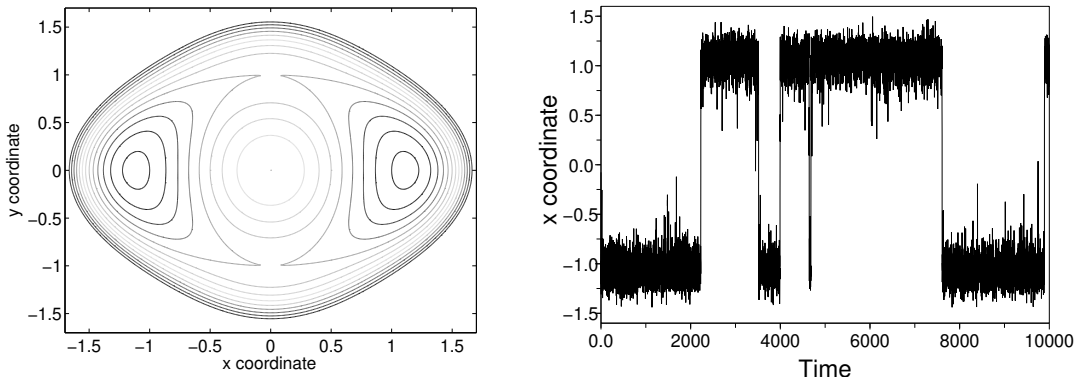


Fig. 7.1. Left: Level sets of the potential (7.11). Right: Projected trajectory in the x variable for $\Delta t = 0.01$, $\beta = 6$.

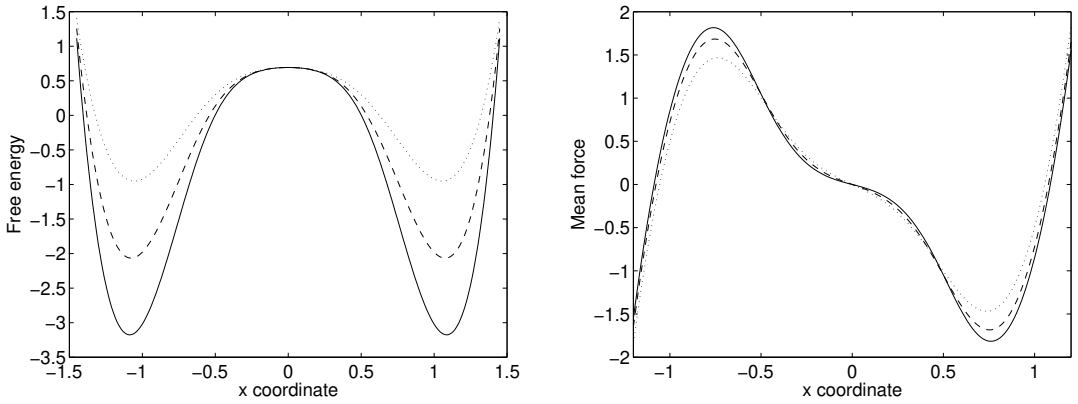


Fig. 7.2. Left: Potential of mean force for the potential plotted in Figure 7.1, using the x coordinate as a reaction coordinate. From top to bottom: $\beta = 2$ (dotted line), $\beta = 3$ (dashed line), $\beta = 4$ (solid line). Right: Associated mean forces.

Entropic and energetic barriers

Free energy barriers can have two origins, related to either energetic or entropic bottlenecks. We give below two toy examples of purely energetic and purely entropic barriers. Of course, in general, both components are mixed, and it is not so obvious to decide whether the metastability of the dynamics rather has an energetic or an entropic origin (except in some limiting temperature regime, see the discussion at the end of this section).

Purely energetic barrier.

Consider $q = (q_1, \ldots, q_D) \in \mathbb{R}^D$, $p \in \mathbb{R}^D$, and

$$H(q,p) = W(q_1) + V(q_2, \ldots, q_D) + \frac{1}{2} p^T M^{-1} p, \tag{7.13}$$

where W is a one-dimensional double-well potential $W(q_1) = h(q_1^2 - 1)^2$ with h large enough. Then, choosing the first coordinate q_1 as a reaction coordinate: $\xi(q) = q_1$, it holds (up to a multiplicative constant which does not depend on z):

$$\mathrm{e}^{-\beta F(z)} = \int_{\mathbb{R}^{2D-1}} \mathrm{e}^{-\beta H(z, q_2, \ldots, q_D, p_1, \ldots, p_D)} \, dq_2 \ldots dq_D \, dp_1 \ldots dp_D,$$

so that

$$F(z_2) - F(z_1) = W(z_2) - W(z_1).$$

In this case, it is clear that free energy barriers are purely of energetic origin.

Purely entropic barrier.

Entropic barriers are often encountered in complex systems with many degrees of freedom. In this case, the system typically has enough energy to overcome the energetic barriers it can encounter, but has not, somehow, got its energy concentrated in the right modes or directions. It is expected that entropic barriers increase with the dimensionality of the system (think of a random walk in a high-dimensional space).

A toy model of an entropic barrier is the potential presented in Figure 7.3. The potential is zero inside the curve, and $+\infty$ outside, so that the system is confined in the bone-shaped region. Here, $q = (x, y) \in \mathcal{D} = \{q \in \mathbb{R}^2 \mid V(q) = 0\}$. Denote by d the width of the tunnel between the two

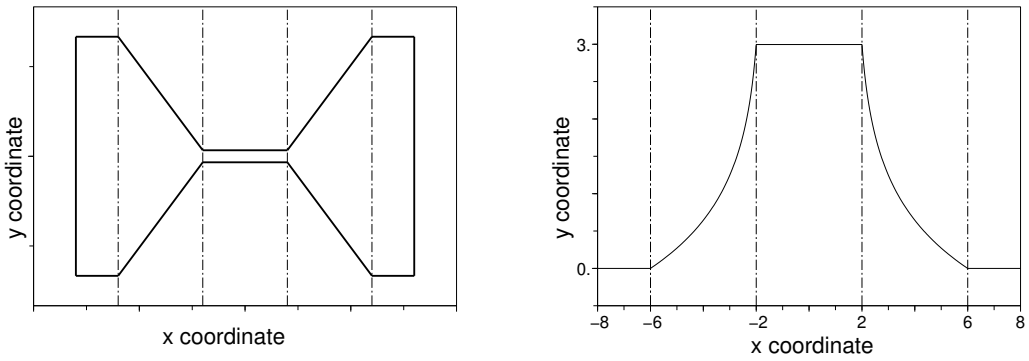


Fig. 7.3. Left: Potential for which entropic barriers have to be overcome, in the case $L_1 = 2$, $L_2 = 4$ and $L_3 = 2$. The potential is 0 in the region enclosed by the curve, and $+\infty$ outside. Right: Associated free energy profile when the x coordinate is the reaction coordinate ($\beta = 1$).

metastable regions, by $2L_1$ its length, by L_2 the length of the transition region, and by L_3 the length of the initial and final rectangular domains, which are of heights Δ. We choose $\xi(q) = x$ as the reaction coordinate. Then,

$$F(x) = \begin{cases} -\beta^{-1} \ln d & \text{when } |x| \leqslant L_1, \\ -\beta^{-1} \ln \left(d + \dfrac{\Delta - \delta}{L_2} (|x| - L_1) \right) & \text{when } L_1 \leqslant |x| \leqslant L_1 + L_2, \\ -\beta^{-1} \ln \Delta & \text{when } L_1 + L_2 \leqslant |x| \leqslant L_1 + L_2 + L_3. \end{cases} \tag{7.14}$$

There is a free energy barrier in the tunnel region, arising from the contraction of the phase space volume: Less configurations are accessible, although the energy has not changed. This barrier has no energy component in it since the average energy for a fixed value of the reaction coordinate is zero.

Figure 7.4 presents a typical trajectory in the case $L_1 = L_3 = 2$, $L_2 = \Delta = 4$, $\delta = 0.2$, for a Metropolis random walk with proposal moves

$$\widetilde{q}^{n+1} = q^n + \sqrt{\frac{2\tau}{\beta}}\, G^n,$$

where $(G^n)_{n \geqslant 0}$ are independent and identically distributed centered Gaussian random variables of identity covariance. This simply amounts here to setting $q^{n+1} = \tilde{q}^{n+1}$ when $\tilde{q}^{n+1} \in \mathcal{D}$, and $q^{n+1} = q^n$ otherwise. The simulation results show that the x coordinate only significantly varies on long timescales, which is a typical signature of metastability.

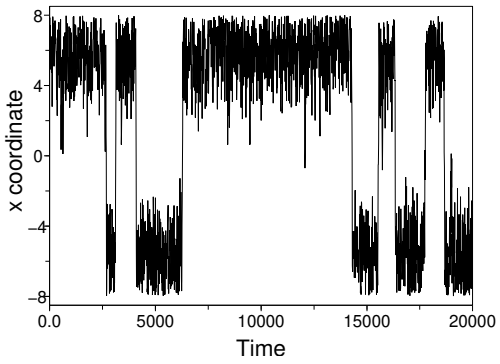


Fig. 7.4. Typical trajectory of the variable x for the potential presented in Figure 7.3, when a Metropolis dynamics is used, for the parameters $\tau = 0.1$ and $\beta = 1$. The time variable is defined as the number of iterations times the typical time τ.

Temperature dependence of the free energy barrier.

The temperature dependence of the free energy barrier is a good indicator of the nature of the bottleneck. Indeed, in the case of a purely energetic barrier (7.13), the ratio of the marginal distributions

$$\mathrm{e}^{-\beta(F(z_1)-F(z_0))} = \mathrm{e}^{-\beta(W(z_1)-W(z_0))}$$

varies exponentially as a function of β, whereas, for the example (7.14) of purely entropic barrier, this ratio does not depend on β. In general, it is expected that free energy barriers at low temperatures (*i.e.* in the limit $\beta \to +\infty$) are mostly of energetic nature, in accordance with large deviation principles [96]. On the other hand, at high temperatures (in the limit $\beta \to 0$),

$$F(z_1) - F(z_0) = -\frac{1}{\beta} \ln \left(\frac{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\, \delta_{\xi(q)-z_1}(dq)}{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\, \delta_{\xi(q)-z_0}(dq)} \right) \simeq -\frac{1}{\beta} \ln \left(\frac{\displaystyle\int_{\mathcal{D}} \delta_{\xi(q)-z_1}(dq)}{\displaystyle\int_{\mathcal{D}} \delta_{\xi(q)-z_0}(dq)} \right),$$

provided the integrals

$$I(z) = \int_{\mathcal{D}} \delta_{\xi(q)-z}(dq)$$

are finite for z_0 and z_1. In this case the free energy difference is controlled at first order by the entropic contribution. Indeed, $I(z)$ measures the accessible phase space for the constraint $\xi(q) = z$, and some entropy can be defined from this volume according to Boltzmann's definition of the entropy as the logarithm of a density of states.

Free energy biased sampling

We make precise here how to use the free energy to bias the dynamics, by considering the modified potential $V(q) - F(\xi(q))$. Notice that the free energy associated to the reaction coordinate ξ for this modified potential is constant:

$$-\frac{1}{\beta} \ln \int_{\Sigma(z)} \mathrm{e}^{-\beta(V-F\circ\xi)(q)}\, \delta_{\xi(q)-z}(dq) = \frac{1}{\beta} \ln Z_\mu.$$

The above formula is a consequence of the definition (7.7) of the free energy $F(z)$, using also the equality $F(\xi(q)) = F(z)$ on $\Sigma(z)$. The marginal law of $Z^{-1}\, \mathrm{e}^{-\beta(V-F\circ\xi)(q)}\, dq$ along ξ is therefore the uniform law.

If ξ completely describes the metastability of the potential V as in the previous examples, the modified potential $V - F \circ \xi$ is no longer metastable. An efficient importance sampling method can then be obtained, especially when F does not vary too much. We now numerically illustrate this strategy.

Application to the two-dimensional double-well potential.

Consider the system described by the potential (7.11). Figure 7.5 presents the new potential

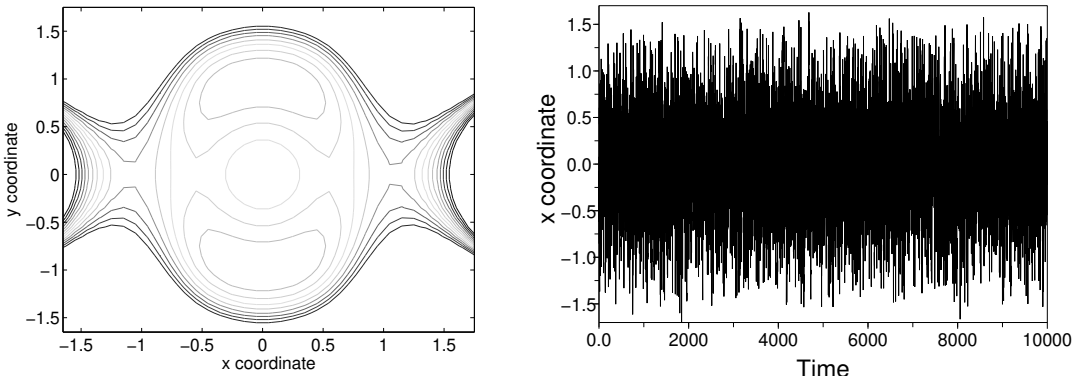


Fig. 7.5. Left: Modified potential $V - F \circ \xi$. Right: Projected trajectory in the x variable for $\Delta t = 0.01$, $\beta = 6$ for the dynamics associated with the modified potential.

$V - F \circ \xi$ (where the free energy bias, computed with standard quadrature rules, has been applied for $|x| \leqslant 1.7$) and a typical trajectory of the overdamped Langevin dynamics for the potential $V - F \circ \xi$, projected on the x coordinate. The comparison with Figure 7.1 shows that the transitions from the region $x < 0$ to the region $x > 0$ are now sufficiently frequent in order to attain good sampling accuracies.

Application to the entropic barrier problem.

Figure 7.6 presents the results for a Metropolis random-walk dynamics biased by the free energy (7.14) in the case of the potential presented in Figure 7.3. As in the previous case, the metastability is removed, and many transitions are observed from one well to the other (compare with Figure 7.4). The effect of the free energy bias is to increase the likelihood of regions close to the transition zone, so that many more crossings are attempted.

7.2 Numerical methods to compute free energy differences

We present in this section the key ideas behind the methods currently available to compute free energy differences. Some of these techniques are suited both for alchemical transitions and transitions indexed by a reaction coordinate, but not all of them. According to the classification proposed in [178], the currently available techniques fall within the following four classes:

(i) The first technique, dating back to [148], is *thermodynamic integration*, which mimics the quasi-static evolution of a system as a succession of equilibrium samplings (this amounts to an infinitely slow switching between the initial and final states). In practice, it allows to compute free energy differences by integrating the derivative of the free energy, which happens to be a canonical average for a fixed value of the reaction coordinate or alchemical parameter. This technique can be used both for alchemical transitions and transitions indexed by reaction coordinates;

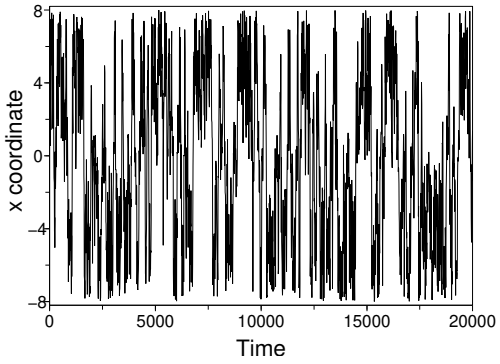


Fig. 7.6. Typical trajectory for the potential exhibiting an entropic barrier when the dynamics is biased by the analytically-known free energy. The numerical parameters are the same as for Figure 7.4.

(ii) The second one is based on straightforward sampling methods. In the alchemical case, the *free energy perturbation method*, introduced in [282], recasts free energy differences as usual canonical averages. In the reaction coordinate case, usual sampling methods can also be employed, relying on histogram methods (see [178, Section 2.5]);
(iii) A more recent class of methods relies on dynamics with an imposed schedule for the reaction coordinate or the alchemical parameter. These techniques therefore use *nonequilibrium dynamics*. Equilibrium properties can however be recovered from the nonequilibrium trajectories with a suitable exponential reweighting, see [143, 142]. This technique can handle both alchemical transitions and transitions indexed by reaction coordinates. It also has many similarities with free-energy perturbation since the corresponding free-energy estimators have the same mathematical structure (exponential averages);
(iv) Finally, *adaptive biasing dynamics* may be used in the reaction coordinate case. The switching schedule is not imposed *a priori*, but a biasing term in the dynamics forces the transition by penalizing the regions which have already been visited. This biasing term can be a biasing force as for the *Adaptive Biasing Force* technique of [58], or a biasing potential as for the Wang-Landau method [279, 278], *nonequilibrium metadynamics* [138] or Self-Healing Umbrella Sampling [188].

We refer to Figure 7.7 for a schematic comparison of the computational methods in the reaction coordinate case. We next give a flavor of these approaches, in the simple setting where $\mathcal{D} = \mathscr{D}^D$ (with $\mathscr{D} = \mathbb{R}$ or $\mathbb{T}$),

$$\xi(q) = q_1, \qquad \Sigma(z) = \mathscr{D}^{D-1},$$

in order to make the presentation more transparent and limit the technicalities related to the geometry of the submanifolds associated with the level sets of ξ (see [178] for an extensive treatment of these aspects). Note that, in view of Remark 7.3, formulas in the alchemical setting are obtained by a straightforward modification of the equations below.

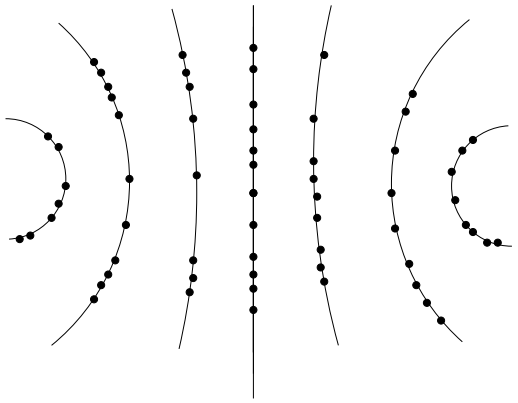
7.2.1 Thermodynamic integration

Thermodynamic integration consists in remarking that

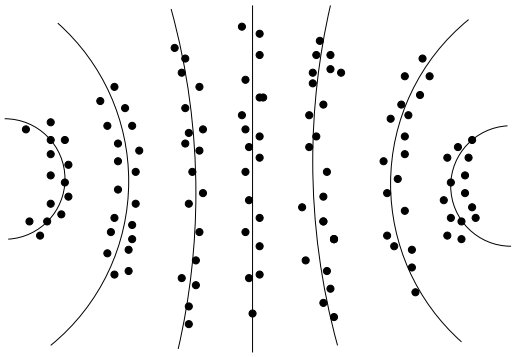
$$F(z_2) - F(z_1) = \int_{z_1}^{z_2} F'(s)\, ds, \tag{7.15}$$

and that the derivative

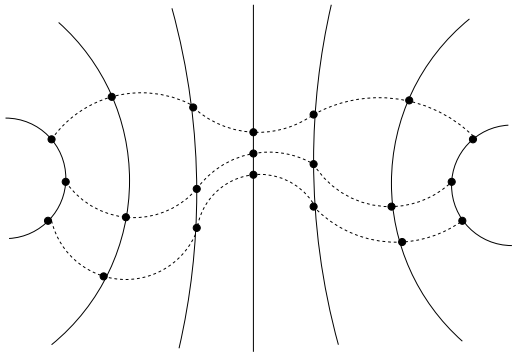
$$F'(z) = \frac{\displaystyle\int_{\mathscr{D}^{D-1}} \partial_{q_1} V(z, q_2, \ldots, q_D)\, \mathrm{e}^{-\beta V(z,q_2,\ldots,q_D)}\, dq_2 \ldots dq_D}{\displaystyle\int_{\mathscr{D}^{D-1}} \mathrm{e}^{-\beta V(z,q_2,\ldots,q_D)}\, dq_2 \ldots dq_D}$$



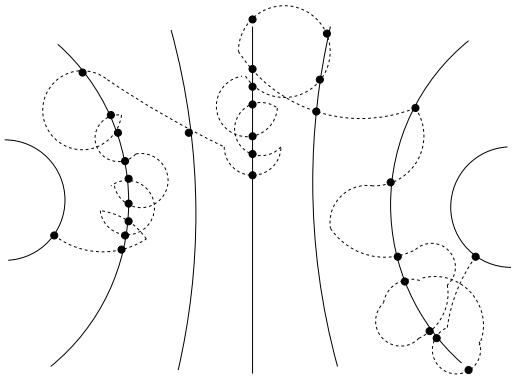
(a) Thermodynamic integration: a projected dynamics is used to sample each "slice" of the phase space.



(b) Histogram method: sample points around the level sets are generated.



(c) Nonequilibrium dynamics: the switching is imposed *a priori* and is the same for all trajectories.



(d) Adaptive dynamics: the system is forced to leave regions where the sampling is sufficient.

Fig. 7.7. Cartoon comparison of the different techniques to compute free energy differences in the reaction coordinate case.

is the canonical average of $\partial_{q_1} V(z,\cdot)$ with respect to the canonical measure in the remaining variables $(q_2,\dots,q_D)$:

$$\nu_z(dq_2\dots dq_D) = Z_z^{-1}\,\mathrm{e}^{-\beta V(z,q_2,\dots,q_D)}\,dq_2\dots dq_D. \tag{7.16}$$

In practice, $F'(s_i)$ is computed using classical sampling techniques targetting the measure ν_{s_i} for a sequence of values $s_i \in \mathscr{D}$. The integral on the right-hand side of (7.15) is then integrated numerically to obtain the free energy difference profile. The extension to transitions indexed by a reaction coordinate is presented in [178, Chapter 3].

7.2.2 Methods based on straightforward sampling

Free energy perturbation.

Free energy perturbation is a technique which is restricted to the computation of free energy differences in the alchemical case (see however Remark 7.3 for an extension of the alchemical setting to the reaction coordinate case). It consists in rewriting the free energy difference as

$$F(z_2) - F(z_1) = -\frac{1}{\beta}\ln \int_{\mathscr{D}^{D-1}} \mathrm{e}^{-\beta[V(z_2,\cdot)-V(z_1,\cdot)]} d\nu_{z_1},$$

where ν_z is defined in (7.16). An approximation of $F(z_2) - F(z_1)$ is then obtained by generating configurations $(q_2^n, \dots, q_D^n)$ distributed according to ν_{z_1} and computing the empirical average

$$\frac{1}{N_{\text{iter}}} \sum_{n=1}^{N_{\text{iter}}} \mathrm{e}^{-\beta[V(z_1,q_2^n,\dots,q_D^n) - V(z_2,q_2^n,\dots,q_D^n)]}.$$

However, the initial and the final distributions ν_{z_2} and ν_{z_1} often hardly overlap. Intermediate steps should then be considered, or some importance sampling strategy should be used to improve the numerical accuracy, see the presentation in [178, Section 2.4.1]. It is also possible to resort to bridge sampling [26]. In this case, the free energy difference $F(z_2) - F(z_1)$ is estimated using sample points from ν_{z_2} and ν_{z_1}, see [178, Section 2.4.2].

Histogram methods.

A naive algorithm to compute approximate free energy differences would be to sample configurations using a simple dynamics ergodic with respect to the canonical measure, and to compute approximations of the marginal law in the reaction coordinate. More precisely, this can be done in practice by discretizing the values of the reaction coordinate into small intervals, and approximating the free energy by computing the canonical average of the indicator function of these intervals in the limit when the interval width Δz goes to 0. Defining

$$\chi_{z,\Delta z}(q) = \frac{1}{\Delta z} \mathbf{1}_{|\xi(q)-z| \leqslant \Delta z/2},$$

it holds

$$\begin{aligned} -\frac{1}{\beta} \ln \mathbb{E}_\mu(\chi_{z,\Delta z}) &= -\frac{1}{\beta} \ln \left(\frac{1}{Z_\mu} \int_{\mathcal{E}} \frac{\mathbf{1}_{|\xi(q)-z| \leqslant \Delta z/2}}{\Delta z} \, \mathrm{e}^{-\beta H(q,p)} \, dq \, dp \right) \\ &\xrightarrow[\Delta z \to 0]{} F(z) = -\frac{1}{\beta} \ln \left(\frac{1}{Z_\mu} \int_{\mathcal{E}} \mathrm{e}^{-\beta H(q,p)} \, \delta_{\xi(q)-z}(dq) \, dp \right). \end{aligned} \tag{7.17}$$

However, the metastable features of the dynamics used for sampling usually prevent such a simple strategy from being efficient, see Section 7.1.3. The idea of histogram methods is to sample configurations centered on some level set $\Sigma(z)$, typically by sampling canonical measures associated with modified potentials

$$V(q) + \frac{1}{2\eta} \Big(\xi(q) - z \Big)^2,$$

where $\eta > 0$ is a small parameter, and to construct a global sample for the canonical measure $\mu(dq\, dp)$ by concatenating the sample points with some appropriate weighting factor; see [178, Section 2.5] for further precision. Once this global sample is obtained, an approximation of the free energy is obtained with (7.17) (for Δz small enough).

7.2.3 Nonequilibrium dynamics

Free energy differences $F(z_2) - F(z_1)$ can be expressed as a nonlinear average over nonequilibrium trajectories, using the so-called Jarzynski equality [143, 142]. This identity can easily be obtained for a system governed by Hamiltonian dynamics, with initial conditions at equilibrium (according to the canonical measure) and subjected to a switching schedule

$$\mathscr{Z} : [0,T] \to [z_1, z_2], \qquad \mathscr{Z}(0) = z_1, \qquad \mathscr{Z}(T) = z_2.$$

We first derive the identity, and then indicate how to extend it to stochastic dynamics using the Feynman–Kac formula. We consider in any case initial conditions at time 0 distributed according to the probability measure μ_{z_1}, where

$$\mu_z(dq_2 \dots dq_D \, dp_2 \dots dp_D) = Z_z^{-1} \mathrm{e}^{-\beta H_z(q_2,\dots,q_D,p_2,\dots,p_D)} \, dq_2 \dots dq_D \, dp_2 \dots dp_D,$$

with

$$H_z(q_2,\dots,q_D,p_2,\dots,p_D) = V(z,q_2,\dots,q_D) + \sum_{i=2}^{D} \frac{p_i^2}{2m},$$

where we considered for simplicity that $M = m\mathrm{Id}_D$.

When the switching is performed with Hamiltonian dynamics, the configurations are evolved according to the following non-autonomous ordinary differential equation for $0 \leqslant t \leqslant T$ (compare with (2.6)):

$$\begin{cases} \dfrac{dq_i}{dt}(t) = \dfrac{p_i(t)}{m}, \\ \dfrac{dp_i}{dt}(t) = -\partial_{q_i} V(\mathscr{Z}(t), q_2(t), \dots, q_D(t)), \end{cases} \qquad 2 \leqslant i \leqslant D. \tag{7.18}$$

Defining by $\phi^{\mathscr{Z}}$ the flow associated with this dynamics, the work performed on the system starting from some initial conditions $(q_2^0,\dots,q_D^0,p_2^0,\dots,p_D^0)$ is defined as

$$\begin{aligned} \mathcal{W}\left(q_2^0,\dots,q_D^0,p_2^0,\dots,p_D^0\right) &= \int_0^T \partial_{q_1} V(\mathscr{Z}(t), q_2(t),\dots,q_D(t))\, \dot{\mathscr{Z}}(t)\, dt \\ &= \left(H_{z_2} \circ \phi_T^{\mathscr{Z}} - H_{z_1}\right)\left(q_2^0,\dots,q_D^0,p_2^0,\dots,p_D^0\right), \end{aligned} \tag{7.19}$$

where we computed the time derivative of $t \mapsto H_{\mathscr{Z}(t)}(q_2(t),\dots,q_D(t),p_2(t),\dots,p_D(t))$ to obtain the last equality. Then,

$$\begin{aligned} &\int_{\mathcal{E}} \mathrm{e}^{-\beta \mathcal{W}(q_2,\dots,q_D,p_2,\dots,p_D)}\, \mu_{z_1}(dq_2\dots dq_D\, dp_2\dots dp_D) \\ &\qquad = Z_{z_1}^{-1} \int_{\mathcal{E}} \mathrm{e}^{-\beta\left(H_{z_2}\circ\phi_T^{\mathscr{Z}}\right)(q_2,\dots,q_D,p_2,\dots,p_D)}\, dq_2\dots dq_D\, dp_2\dots dp_D. \end{aligned}$$

Since $\phi_T^{\mathscr{Z}}$ defines a change of variables of Jacobian 1, the above equality can be restated as

$$\mathbb{E}_{\mu_{z_1}}\left(\mathrm{e}^{-\beta\mathcal{W}}\right) = \frac{Z_{z_2}}{Z_{z_1}} = \mathrm{e}^{-\beta(F(z_2)-F(z_1))}, \tag{7.20}$$

where the expectation is taken with respect to initial conditions distributed according to μ_{z_1}. This formula is called the Jarzynski identity. It shows that one can recover an equilibrium quantity, namely the free energy difference $F(\mathscr{Z}(T)) - F(\mathscr{Z}(0)) = F(z_2) - F(z_1)$, from non-equilibrium (time-inhomogeneous) dynamics started at equilibrium.

As hinted at above, it is possible to extend the identity (7.20) to situations where the dynamics is stochastic, for instance when (7.18) is replaced by the following Langevin dynamics,

$$\begin{cases} dq_{i,t} = \dfrac{p_{i,t}}{m}\, dt, \\ dp_{i,t} = -\partial_{q_i} V(\mathscr{Z}(t), q_{2,t},\dots,q_{D,t})\, dt - \gamma \dfrac{p_{i,t}}{m}\, dt + \sqrt{\dfrac{2\gamma}{\beta}}\, dW_{i,t}, \end{cases} \qquad 2 \leqslant i \leqslant D,$$

or the following overdamped Langevin dynamics:

$$dq_{i,t} = -\partial_{q_i} V(\mathscr{Z}(t), q_{2,t},\dots,q_{D,t})\, dt + \sqrt{\frac{2}{\beta}}\, dW_{i,t}, \qquad 2 \leqslant i \leqslant D. \tag{7.21}$$

In the latter case, initial conditions are distributed according to the probability measure ν_{z_1}, where ν_z denotes the marginal distribution in the variables $(q_2,\dots,d_D)$ of μ_z. For both cases, the work is still defined as (7.19). For overdamped Langevin dynamics, the work at time t is therefore

$$\mathcal{W}_t\left(q_{2,0},\dots,q_{D,0}\right) = \int_0^t \partial_{q_1} V(\mathscr{Z}(s), q_{2,s},\dots,q_{D,s})\, \dot{\mathscr{Z}}(s)\, ds.$$

Proposition 7.1. *Consider a schedule $\mathscr{Z} \in C^1([0,T])$, and assume that $(q_{2,t},\dots,q_{D,t})_{0\leqslant t\leqslant T}$ satisfies* (7.21) *with initial conditions distributed according to the probability measure $\nu_{\mathscr{Z}(0)}$. Then, for any time $t \in [0,T]$,*

$$\mathbb{E}\left[\mathrm{e}^{-\beta \mathcal{W}_t}\right] = \mathrm{e}^{-\beta[F(\mathscr{Z}(t))-F(\mathscr{Z}(0))]}. \tag{7.22}$$

Proof. The proof is based on a Feynman–Kac formula. For a fixed time $t \in (0,T]$, let us consider a C^∞ solution $v : [0,t] \times \mathscr{D}^{D-1} \to \mathbb{R}$ to the backward-in-time partial differential equation

$$\begin{aligned} \partial_s v(s,x) &= -\mathcal{L}_s v(s,x) + \beta \partial_{q_1} V(\mathscr{Z}(s),x)\dot{\mathscr{Z}}(s) v(s,x) \quad \text{for } (s,x) \in [0,t]\times \mathscr{D}^{D-1}, \\ v(t,x) &= f(x) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{for } x \in \mathscr{D}^{D-1}, \end{aligned}$$

where $\mathcal{L}_s = -\nabla V(\mathscr{Z}(s),\cdot)\cdot\nabla + \beta^{-1}\Delta$ is the infinitesimal generator of (7.21), which acts on functions of $(q_2,\dots,q_D)$. This is a standard parabolic equation which admits a unique C^∞ solution under standard regularity assumptions on the coefficients, the domain $\mathscr{D}$ and the function f. The Feynman–Kac formula in this context is given by

$$v(s,x) = \mathbb{E}^{s,x}\left(f(q_{2,t},\dots,q_{D,t})\,\mathrm{e}^{-\beta(\mathcal{W}_t-\mathcal{W}_s)}\right), \tag{7.23}$$

where the superscript s,x indicates that one considers the solution to (7.21) for $t \geqslant s$ with initial condition $(q_{2,s},\dots,q_{D,s}) = x$. To prove this equality, we use Itô calculus over the time interval $[s,t]$ to write

$$v(t,q_{2,t},\dots,q_{D,t}) \exp\left(-\beta\int_s^t \partial_{q_1} V(\mathscr{Z}(\theta),q_{2,\theta},\dots,q_{D,\theta})\dot{\mathscr{Z}}(\theta)\,d\theta\right) = v(t,q_{2,s},\dots,q_{D,s}) + \mathscr{M}_{s,t},$$

with the martingale

$$\mathscr{M}_{s,t} = \sqrt{\frac{2}{\beta}}\int_s^t \exp\left(-\beta\int_s^r \partial_{q_1} V(\mathscr{Z}(\theta),q_{2,\theta},\dots,q_{D,\theta})\dot{\mathscr{Z}}(\theta)\,d\theta\right)\nabla v(r,q_{2,r},\dots,q_{D,r})\cdot dW_r,$$

where we have used the partial differential equation satisfied by v to cancel the bounded variation part in the Itô formula. Equation (7.23) then immediately follows by taking the expectation $\mathbb{E}^{s,x}$.

Now, it is easy to check that for any $s \in [0,t]$,

$$\begin{aligned} \frac{d}{ds}\left(\int_{\mathscr{D}^{D-1}} v(s,x)\,\mathrm{e}^{-\beta V(\mathscr{Z}(s),x)}\,dx\right) &= \int_{\mathscr{D}^{D-1}}\left[\partial_s v(s,x) - \beta\partial_{q_1}V(\mathscr{Z}(s),x)\dot{\mathscr{Z}}(s)v(s,x)\right]\mathrm{e}^{-\beta V(\mathscr{Z}(s),x)}\,dx \\ &= -\int_{\mathscr{D}^{D-1}} \mathcal{L}_s v(s,x)\,\mathrm{e}^{-\beta V(\mathscr{Z}(s),x)}\,dx = 0, \end{aligned}$$

where the last equality is a consequence of the invariance of the canonical measure (see (4.8) for overdamped Langevin dynamics at s fixed). Therefore,

$$\int_{\mathscr{D}^{D-1}} v(t,x)\,\mathrm{e}^{-\beta V(\mathscr{Z}(t),x)}\,dx = \int_{\mathscr{D}^{D-1}} v(0,x)\,\mathrm{e}^{-\beta V(\mathscr{Z}(0),x)}\,dx.$$

Using (7.23), this equality can be rewritten as

$$\frac{Z_{\mathscr{Z}(t)}}{Z_{z_1}}\int_{\mathscr{D}^{D-1}} f(x)\frac{\mathrm{e}^{-\beta V(\mathscr{Z}(t),x)}}{Z_{\mathscr{Z}(t)}}dx = \int_{\mathscr{D}^{D-1}} \mathbb{E}^{0,x}[f(q_{2,t},\dots,q_{D,t})\exp(-\beta\mathcal{W}_t)]\frac{\mathrm{e}^{-\beta V(\mathscr{Z}(0),x)}}{Z_{z_1}}\,dx.$$

Taking $f = 1$, the left-hand side is $\mathrm{e}^{-\beta[F(\mathscr{Z}(t))-F(\mathscr{Z}(0))]}$, while, by a conditioning argument on initial conditions, the right-hand side is equal to $\mathbb{E}(\exp(-\beta\mathcal{W}_t))$, where the weight $\mathcal{W}_t$ is computed using the solution to (7.21) with initial conditions distributed according to the probability measure $\nu_{\mathscr{Z}(0)}$. This concludes the proof of (7.22). □

There are many extensions to this identities such as (7.22), in particular generalization to other dynamics (including discrete-time evolutions) and to reaction coordinates with a nonlinear structure, and to combinations of forward-in-time and backward-in-time schedules (leading to the Jarzynski–Crooks identity); see [178, Chapter 4]. In view of the equality (7.20), it is also already clear that the lowest values of the work dominate the nonlinear average (7.20), and the distribution of weights $\mathrm{e}^{-\beta \mathcal{W}}$ is often degenerate in practice. This prevents in general an accurate numerical computation of (7.20), and raises issues very similar to the ones encountered with free-energy perturbation. Refined strategies are therefore needed to use nonequilibrium methods in practice (see [178, Chapters 4 and 6]). The Jarzynski identity is mainly useful for extracting free energy differences from experimental measurements, by performing many non-equilibrium externally driven experiments between two states of interest [134].

7.2.4 Adaptive dynamics

Adaptive dynamics may be seen as some adaptive importance sampling strategy, with a biasing potential at time t function of the reaction coordinate. The biasing potential converges in the longtime limit to the free energy by construction of the dynamics. To illustrate this strategy, we consider the case of the Adaptive Biasing Force (ABF) method [58, 125] in the simple example when the reaction coordinate $\xi(q) = q_1$ has values in $\mathbb{T}$, while the remaining coordinates $(q_2, \ldots, q_D)$ belong to $\mathbb{R}^{D-1}$.

Let us assume that we know the free energy F associated with ξ. Then, the overdamped Langevin dynamics associated with the modified potential $V - F \circ \xi$ reads

$$\begin{cases} \displaystyle dq_t = -\Big(\nabla V(q_t) - F'(q_{1,t})\, e_1\Big) dt + \sqrt{\frac{2}{\beta}}\, dW_t, \\ \displaystyle F'(z) = \mathbb{E}_\nu\Big(\partial_{q_1} V(q) \,\Big|\, \xi(q) = z\Big) = \frac{\displaystyle\int_{\mathbb{R}^{D-1}} \partial_{q_1} V(z, q_2, \ldots, q_D)\, \mathrm{e}^{-\beta V(z, q_2, \ldots, q_D)}\, dq_2 \ldots dq_D}{\displaystyle\int_{\mathbb{R}^{D-1}} \mathrm{e}^{-\beta V(z, q_2, \ldots, q_D)}\, dq_2 \ldots dq_D}, \end{cases} \tag{7.24}$$

where $e_1 = (1, 0, \ldots, 0)^T$ is the unit vector in the q_1 direction, and ν is the canonical measure (4.2). Denote by

$$\widetilde{\nu}(dq) = \widetilde{Z}^{-1} \mathrm{e}^{-\beta[V(q) - F(q_1)]}\, dq$$

the stationary measure of the process (7.24). The equilibrium mean force $F'(z)$ can actually be rewritten as a canonical average with respect to $\widetilde{\nu}$, conditionally on $q_1 = z$:

$$F'(z) = \mathbb{E}_\nu\Big(\partial_{q_1} V(q) \,\Big|\, \xi(q) = z\Big) = \mathbb{E}_{\widetilde{\nu}}\Big(\partial_{q_1} V(q) \,\Big|\, \xi(q) = z\Big). \tag{7.25}$$

Indeed, the bias $F(\xi(q))$ is constant when $\xi(q)$ is kept constant. Therefore, conditional averages with respect to $\widetilde{\nu}$ for $\xi(q) = z$ fixed are equal to conditional averages with respect to the canonical measure (4.2) since the factor $\mathrm{e}^{-\beta F(\xi(q))}$ cancels out in the numerator and denominator of the conditional average.

Now, of course, F is not known in practice. In view of (7.24)-(7.25), it seems natural to replace, in the dynamics (7.24), the conditional expectation with respect to the stationary measure in the expression of the equilibrium mean force, by the conditional expectation with respect to the current law of q_t:

$$\begin{cases} \displaystyle dq_t = -\Big(\nabla V(q_t) - F_t'(q_{1,t})\, e_1\Big) dt + \sqrt{\frac{2}{\beta}}\, dW_t, \\ \displaystyle F_t'(z) = \mathbb{E}\Big(\partial_{q_1} V(q_t) \,\Big|\, \xi(q_t) = z\Big). \end{cases} \tag{7.26}$$

Notice that the biasing potential F_t now explicitly depends on the time variable. Denoting by $\psi_t(q)\, dq$ the law of q_t at time t (intuitively, the distribution of configurations obtained by

simulating an infinite number of replicas interacting only through the common bias they are constructing), the biasing force $F'(z)$ can be rewritten in a form closer to the expression in (7.24):

$$F_t'(z) = \frac{\displaystyle\int_{\mathbb{R}^{D-1}} \partial_{q_1} V(z, q_2, \ldots, q_D)\, \psi_t(z, q_2, \ldots, q_D)\, dq_2 \ldots dq_D}{\displaystyle\int_{\mathbb{R}^{D-1}} \psi_t(z, q_2, \ldots, q_D)\, dq_2 \ldots dq_D}.$$

We now motivate why the adaptive dynamics (7.26) may be relevant. The distribution of the variable $\xi(q_t) = q_{1,t}$ is given by the marginal law with density

$$\psi_t^\xi(z) = \int_{\mathbb{R}^{D-1}} \psi_t(z, q_2, \ldots, q_D)\, dq_2 \ldots dq_D.$$

A simple computation (see (7.34) below) shows that

$$\partial_t \psi_t^\xi(z) = \frac{1}{\beta} \partial_z^2 \psi_t^\xi(z).$$

The above diffusion equation implies that ψ_t^ξ converges (exponentially fast) to the uniform distribution on $\mathbb{T}$. Therefore, the metastable features associated with ξ are suppressed. Heuristically, the simple diffusion equation in the direction q_1 is not too surprising since the biasing force F_t' aims precisely at counteracting in average the force experienced by the system in the direction q_1.

Besides, the dynamics (7.26) in the variables $q_2, \ldots, q_D$ (at fixed z) is an overdamped Langevin dynamics associated with the potential $V(z, q_2, \ldots, q_D)$. Assuming that the dynamics is at equilibrium conditionnally on the z variable, the distribution of the variable $q_2, \ldots, q_D$ at fixed z is the following conditional canonical distribution:

$$\frac{\psi_t(z, q_2, \ldots, q_D)}{\psi_t^\xi(z)}\, dq_2 \ldots dq_D = Z_z^{-1}\, \mathrm{e}^{-\beta V(z, q_2, \ldots, q_D)}\, dq_2 \ldots dq_D.$$

Recall also that the marginal law ψ_t^ξ converges to the uniform law. On the other hand, $\widetilde{\nu}(dq)$ is the unique probability measure whose marginal distribution in the ξ variable is the uniform law, while the conditional distributions at fixed values of ξ are equal to the canonical conditional distributions. This motivates the convergence of $\psi_t(q)\, dq$ towards $\widetilde{\nu}(dq)$, and therefore the convergence of F_t towards F.

The above presentation naturally suggests a parallel implementation of the dynamics through many replicas constructing a shared biasing potential. This plain parallel implementation can be enhanced through some selection process on the replicas (see [178, Chapter 6]). There exist also adaptive dynamics where the biasing potential F_t is updated, in contrast to the method presented here where the derivative of the biasing potential is updated (see [178, Section 5.1]).

7.3 Convergence of adaptive methods to compute free energies

In this section we present a typical example where the use of PDE techniques, and more precisely entropy estimates and logarithmic Sobolev inequalities (see Section 4.3.3), appear to be very useful for understanding the efficiency of a numerical method, namely the adaptive biasing force (ABF) method. For pedagogical purposes, the convergence result is presented in an even simpler setting than the one considered in Section 7.2.4, namely $D = 2$, and $(q_1, q_2) = (x, y) \in \mathbb{T} \times \mathbb{R}$ (which simply means that $V : (x, y) \in \mathbb{R}^2 \mapsto V(x, y) \in \mathbb{R}$ is 1-periodic in the x-variable). Extensions are discussed at the end of this section.

7.3.1 The theoretical setting and the convergence result

In the simple setting considered here, the free energy biased dynamics (7.24) further reduces to

$$\begin{cases} dx_t = -\partial_x V(x_t, y_t)dt + F'(x_t)dt + \sqrt{2\beta^{-1}}dW_t^x, \\ dy_t = -\partial_y V(x_t, y_t)dt + \sqrt{2\beta^{-1}}dW_t^y, \\ F'(x) = \mathbb{E}_\nu(\partial_x V(q) \,|\, \xi(q) = x), \end{cases}$$

while the ABF dynamics (7.26) reads

$$\begin{cases} dx_t = -\partial_x V(x_t, y_t)dt + F_t'(x_t)dt + \sqrt{2\beta^{-1}}dW_t^x, \\ dy_t = -\partial_y V(x_t, y_t)dt + \sqrt{2\beta^{-1}}dW_t^y, \\ F_t'(x) = \mathbb{E}(\partial_x V(x_t, y_t)|x_t = x). \end{cases} \tag{7.27}$$

The key idea of the approach is that if the system were immediately at equilibrium with respect to the biased potential $V(x, y) - F_t(x)$, then F_t' would be equal to F' in view of (7.25). But the updating strategy is dynamic: F_t always keeps on changing and it is therefore not obvious how the system behaves in the transient phase of the dynamics (7.27). The objective of the mathematical analysis is to prove that F_t' indeed converges to F', and that, in addition, this convergence typically occurs on much smaller time scales than the convergence to equilibrium for the original simple overdamped Langevin dynamics:

$$dq_t = -\nabla V(q_t)dt + \sqrt{2\beta^{-1}}dW_t. \tag{7.28}$$

In order to study the rate of convergence to equilibrium, we will actually analyse the long-time behaviour of the density[1] $\psi(t, x, y)$ of the process (x_t, y_t) solution to (7.27), namely the Fokker–Planck equation associated with (7.27):

$$\partial_t \psi = \partial_x[(\partial_x V - F_t')\psi] + \beta^{-1}\partial_{x,x}\psi + \partial_y[(\partial_y V)\psi] + \beta^{-1}\partial_{y,y}\psi, \qquad (x, y) \in \mathbb{T} \times \mathbb{R}, \tag{7.29}$$

with

$$\forall x \in \mathbb{T}, \qquad F_t'(x) = \frac{\displaystyle\int_{\mathbb{R}} \partial_x V(x, y)\psi(t, x, y)dy}{\displaystyle\int_{\mathbb{R}} \psi(t, x, y)dy}. \tag{7.30}$$

Equation (7.30) is obtained using the fact that, for fixed time t and $x \in \mathbb{T}$, $\psi(t, x, y)dy / \int_{\mathbb{R}} \psi(t, x, y)dy$ is indeed the conditional law at time t of (x_t, y_t) given that $x_t = x$. In the following, we denote by ψ^ξ the marginal of ψ along ξ (*i.e.* the density of x_t):

$$\psi^\xi(t, x) = \int_{\mathbb{R}} \psi(t, x, y)\, dy.$$

In contrast to the Fokker–Planck equation for simple overdamped Langevin dynamics (7.28), *i.e.*,

$$\partial_t \phi = \mathrm{div}(\nabla V \phi) + \beta^{-1}\Delta\phi$$

(see (4.6)), the Fokker–Planck equation (7.29)-(7.30) is a *non-linear* parabolic equation. The non-linearity comes from the conditional expectation which appears in the drift term of the stochastic differential equation (7.27). Nonetheless, the following result is obtained as consequence of the more general convergence results provided in [177].

[1] The fact that the process (x_t, y_t) admits a density comes from the fact that the Brownian terms in (7.27) imply a smoothing effect on the law of the process.

Theorem 7.1 (Convergence of ABF). *Consider the ABF dynamics* (7.27) *on the domain* $\mathbb{T}\times\mathbb{R}$, *and assume that there exists* $\rho > 0$ *such that*

$$\text{all the conditional measures } \nu(dq|\xi(q)=x) \text{ satisfy LSI}(\rho), \tag{7.31}$$

and that the smooth potential V *is such that*

$$\|\partial_{x,y} V\|_{B^\infty(\mathbb{T}\times\mathbb{R})} < \infty. \tag{7.32}$$

Assume moreover (without loss of generality) that $\rho \neq 4\pi^2$, *and that* $\psi^\xi(0,\cdot)$ *is a positive function such that*[2]

$$\int_{\mathbb{T}} |\partial_x \ln(\psi^\xi(0,\cdot))|^2 \psi^\xi(0,\cdot) < +\infty.$$

Then there exists a positive constant C *such that*

$$\forall t \geqslant 0, \qquad \sqrt{\int_{\mathbb{T}} |F_t' - F'|^2} \leqslant C \mathrm{e}^{-\beta^{-1}\min(\rho,4\pi^2)t}. \tag{7.33}$$

In our specific context, note that the conditional measure $\nu(dq|\xi(q)=x)$ is simply the measure

$$\frac{\mathrm{e}^{-\beta V(x,y)}\,dy}{\int_{\mathbb{R}} \mathrm{e}^{-\beta V(x,y)}\,dy}.$$

Notice in addition that if $\rho = 4\pi^2$ in (7.31), one can use this result by replacing ρ by any $\tilde\rho < \rho$, so that (7.33) holds in this case for any $\tilde\rho < 4\pi^2$. Finally, we will show below (see (7.34)) that ψ^ξ satisfies the simple heat equation on $\mathbb{T}$, so that the assumptions on $\psi^\xi(0,\cdot)$ are not too stringent: if they are not satisfied by $\psi^\xi(0,\cdot)$, one simply has to consider the problem on the time interval $[t_0,+\infty)$ with initial condition $\psi^\xi(t_0,\cdot)$, for a positive time t_0.

Theorem 7.1 deserves various comments. This result first shows that the free energy F_t indeed converges to F (up to an irrelevant additive constant) at exponential rate $\beta^{-1}\min(\rho,4\pi^2)$. As will be more clear below, the limiting parameter here is ρ, the term $4\pi^2$ being only related to the rate of convergence to equilibrium of a simple diffusion on the torus $\mathbb{T}$. Further, we will actually show that the law of (x_t,y_t) (and not only F_t) converges to its equilibrium value at this rate (see (7.48) and the discussion below). This rate of convergence for ABF has to be compared with (4.44), which shows that the original simple overdamped Langevin dynamics (7.28) converges to equilibrium with rate $\beta^{-1}R$, where R is the logarithmic Sobolev constant of the measure ν. In summary, by using ABF, R has been replaced by ρ: the logarithmic Sobolev inequality constant of the measure ν has been replaced by the logarithmic Sobolev inequality constant of the measures $\nu(dq\,|\,\xi(q)=x)$. If $\xi(q)=x$ is indeed a good index of the metastable features of the original dynamics, it is typically expected that $\rho \gg R$. This inequality is actually a way to quantify the somewhat vague ideas that a good reaction coordinate ξ should be such that "the metastability of the process $(q_t)_{t\geqslant 0}$ is along ξ" or that "the directions orthogonal to ξ are fast variables", so that equilibrium is quickly reached along those directions. For example, in the two-dimensional examples of Figure 7.1 , the logarithmic Sobolev constant of the measure ν is typically very small, while, for a fixed value of $\xi(x,y)=x$, the conditional measures $\nu(dq\,|\,\xi(q)=x)$ are gentle unimodal measures with much larger associated logarithmic Sobolev constants. Unfortunately, logarithmic Sobolev constants are very delicate to evaluate, and it thus seems very difficult to turn this measure of the quality of ξ into a numerical procedure to construct good reaction coordinates. This result should thus be seen as a way to understand theoretically the conditions under which an ABF strategy will be efficient, the measure of efficiency being the rate of convergence to equilibrium.

[2] The quantity $\int_{\mathbb{T}} |\partial_x \ln(\psi^\xi(0,\cdot))|^2 \psi^\xi(0,\cdot)$ is simply $\mathcal{I}(\psi^\xi(0,\cdot)|\psi^\xi_\infty)$, where $\psi^\xi_\infty = 1$ is the long-time limit of $\psi^\xi(t,\cdot)$ and $\mathcal{I}$ the Fisher information (see (7.37)).

7.3.2 Proof of Theorem 7.1

The proof of convergence is based on two ingredients: (i) the observation that $\psi^\xi(t,x)$ (which, we recall, is the density at time t of x_t) satisfies the simple diffusion equation

$$\partial_t \psi^\xi = \beta^{-1} \partial_{x,x} \psi^\xi \text{ on } \mathbb{T}, \tag{7.34}$$

which is again a manifestation of the fact that, by using ABF, the potential V is "flattened" along the reaction coordinate ξ; (ii) entropy estimates in the vein of those explained in Section 4.3.3, and a two-scale decomposition of the entropy in the spirit of [210, 111, 172]. Let us now present these ideas in detail.

The first ingredient of the proof is based on a simple computation, which consists in looking at the evolution of the marginal of ψ along ξ, namely,

$$\psi^\xi(t,x) = \int_{\mathbb{R}} \psi(t,x,y) dy. \tag{7.35}$$

By direct integration in y of (7.29)-(7.30), we obtain

$$\partial_t \psi^\xi(t,x) = \partial_x \left(\int_{\mathbb{R}} \partial_x V(x,y) \psi(t,x,y)\, dy - F_t'(x) \psi^\xi(t,x) \right) + \beta^{-1} \partial_{x,x} \psi^\xi(t,x),$$

which yields (7.34) since

$$\int_{\mathbb{R}} \partial_x V(x,y) \psi(t,x,y) dy - F_t'(x) \psi^\xi(t,x) = 0,$$

by the definition of $F_t'(x)$. This means that the law of x_t satisfies a simple heat equation on $\mathbb{T}$, as for a simple Brownian motion on the torus.[3] This explains the interest of the ABF method: along ξ, the time marginal of the process evolves as if the potential V was perfectly flat. The convergence to equilibrium of $\psi^\xi(t,x)$ is thus very easy to analyse, and in particular we have the following convergence in terms of Fisher information, which will be useful later (see [177, Lemma 5.29] for a proof).

Lemma 7.1 (Convergence of ψ^ξ). *Let φ be the solution of the heat equation on the torus $\mathbb{T}$:*

$$\partial_t \varphi = \beta^{-1} \partial_{x,x} \varphi, \tag{7.36}$$

with initial condition $\varphi(0,\cdot)$ such that

$$\int_{\mathbb{T}} \varphi(0,\cdot) = 1, \qquad \varphi(0,\cdot) \geqslant 0, \qquad \mathcal{I}(\varphi(0,\cdot)|\varphi_\infty) < +\infty,$$

where $\varphi_\infty \equiv 1$ is the long-time limit of φ. Then,

$$\forall t \geqslant 0, \qquad \mathcal{I}(\varphi(t,\cdot) \mid \varphi_\infty) \leqslant \mathcal{I}(\varphi(0,\cdot) \mid \varphi_\infty)\, \mathrm{e}^{-\beta^{-1} 8\pi^2 t}. \tag{7.37}$$

We recall that

$$\mathcal{I}(\varphi(t,\cdot) \mid \varphi_\infty) = \int_{\mathbb{T}} \left| \partial_x \ln \left(\frac{\varphi(t,x)}{\varphi_\infty(x)} \right) \right|^2 \varphi(t,x) dx$$

is the Fisher information of $\varphi(t,x)dx$ with respect to $\varphi_\infty(x)dx$ (see (4.40)). The rate of convergence to equilibrium for $\psi(t,x,y)$ is limited by the rate of convergence to equilibrium for $\psi^\xi(t,y)$. This explains why there is a $4\pi^2$ appearing in the right-hand side of (7.33). The value $4\pi^2$ is simply the first non-zero eigenvalue of the Laplacian on the torus $\mathbb{T}$, which determines the rate of convergence to equilibrium for the heat equation (7.36) on $\mathbb{T}$.

[3] The reader should not be confused here: this does not mean that the law of the process $(x_t)_{t\geqslant 0}$ (on $\mathcal{C}(\mathbb{R}_+, \mathbb{T})$) is the same as the law of the process $(W_t)_{t\geqslant 0}$. Only the time marginals agree.

To understand the convergence to equilibrium, it now remains to understand the convergence of the conditional measures $\psi(t,x,y)\,dy/\psi^\xi(t,x)$. We will use entropy techniques to study the long-time behaviour, as in Section 4.3.3. Here comes the second ingredient of the proof, namely a decomposition of the entropy in terms of marginal and conditional measures, very much inspired by [210, 111]. Let us explain this decomposition. We denote by ψ_∞ the expected long-time limit of $\psi(t,x,y)$, defined by

$$\psi_\infty(x,y) = Z^{-1}\mathrm{e}^{-\beta[V(x,y)-F(x)]}, \qquad Z = \int_{\mathbb{T}^2} \mathrm{e}^{-\beta(V-F\circ\xi)}. \tag{7.38}$$

The marginal of ψ_∞ along ξ is

$$\psi_\infty^\xi(x) = Z^{-1}\int_{\mathbb{R}} \mathrm{e}^{-\beta[V(x,y)-F(x)]}\,dy = 1,$$

and the conditional measure of $\psi_\infty(x,y)\,dx\,dy$ given $\xi(x,y)=x$ is

$$\frac{\psi_\infty(x,y)dy}{\int_{\mathbb{R}}\psi_\infty(x,y)dy} = \nu(\cdot\,|\,\xi(q)=x).$$

Likewise, as explained above, the marginal of ψ along ξ is given by (7.35) and the conditional measure of $\psi(t,x,y)\,dx\,dy$ given that $\xi(x,y)=x$ is $\psi(t,x,y)\,dy/\psi^\xi(t,x)$. Let us now introduce the *total entropy* (see (4.39))

$$E(t) = \mathcal{H}(\psi(t,\cdot)\,|\,\psi_\infty),$$

the *macroscopic entropy* (namely the relative entropy of the marginal laws)

$$E_{\mathrm{M}}(t) = \mathcal{H}(\psi^\xi(t,\cdot)\,|\,\psi_\infty^\xi),$$

and the *microscopic entropy*

$$E_{\mathrm{m}}(t) = \int_{\mathbb{T}} e_{\mathrm{m}}(t,x)\psi^\xi(t,x)\,dx, \tag{7.39}$$

where $e_{\mathrm{m}}(t,x)$ is the relative entropy associated with the conditional measures:

$$e_{\mathrm{m}}(t,x) = \mathcal{H}\left(\frac{\psi(t,x,y)\,dy}{\psi^\xi(t,x)}\,\middle|\,\frac{\psi_\infty(x,y)\,dy}{\psi_\infty^\xi(x)}\right). \tag{7.40}$$

It is straightforward to check the following relation.

Lemma 7.2 (Extensivity of entropy). *For any $t\geqslant 0$, it holds $E(t) = E_{\mathrm{M}}(t) + E_{\mathrm{m}}(t)$.*

In order to measure the convergence of $\psi(t,\cdot)$ to ψ_∞, we study the rate of convergence to zero of E. We already know that $E_{\mathrm{M}}(t)$ converges exponentially fast to zero, *i.e.*,

$$\forall t\geqslant 0, \qquad E_{\mathrm{M}}(t) \leqslant E_{\mathrm{M}}(0)\mathrm{e}^{-8\beta^{-1}\pi^2 t}, \tag{7.41}$$

since the logarithmic Sobolev constant of the uniform law on $\mathbb{T}$ is $4\pi^2$ (see for example [20, Proposition 5.7.5]) and it is therefore sufficient to understand the convergence of $E_{\mathrm{m}}(t)$ to zero. The convergence (7.41) can also be seen as a consequence of Lemma 7.1 since

$$E_{\mathrm{M}}(t) = \mathcal{H}\left(\psi^\xi(t,\cdot)\,\middle|\,\psi_\infty^\xi\right) = \frac{1}{\beta}\int_t^\infty \mathcal{I}\left(\psi^\xi(t,\cdot)\,\middle|\,\psi_\infty^\xi\right)dt \leqslant \frac{1}{8\pi^2}\mathcal{I}\left(\psi^\xi(t,\cdot)\,\middle|\,\psi_\infty^\xi\right) = -\frac{\beta}{8\pi^2}\frac{dE_{\mathrm{M}}}{dt}(t).$$

The proof is then conducted as follows. Starting from Lemma 7.2, we have[4]

[4] Here and in the following, even though ψ_∞^ξ is simply the constant function equal to 1 in our setting, we keep the notation ψ_∞^ξ in the various expressions we obtain in order to emphasize the homogeneity of the resulting formulas, which remain the same for more general functions ξ and more general settings.

$$\frac{dE_{\rm m}}{dt} = \frac{dE}{dt} - \frac{dE_{\rm M}}{dt} = -\beta^{-1}\int_{\mathbb{T}}\int_{\mathbb{R}} \left|\nabla \ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2 \psi + \int_{\mathbb{T}}\int_{\mathbb{R}} (F_t' - F')\partial_x \ln\left(\frac{\psi}{\psi_\infty}\right)\psi + \beta^{-1}\int_{\mathbb{T}} \left|\partial_x \ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right)\right|^2 \psi^\xi, \tag{7.42}$$

which is easily obtained after some integration by parts, using the fact that ψ satisfies the following equation, which is equivalent to (7.29):

$$\partial_t \psi = \beta^{-1}\mathrm{div}\left(\psi_\infty \nabla\left(\frac{\psi}{\psi_\infty}\right)\right) + \partial_x((F' - F_t')\psi).$$

We next rely on a very useful formula for $F_t' - F'$.

Lemma 7.3. *For all $t \geqslant 0$, it holds*

$$\beta(F_t' - F') = \int_{\mathbb{R}} \partial_x \ln\left(\frac{\psi}{\psi_\infty}\right)\frac{\psi}{\psi^\xi}\,dy - \partial_x \ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right). \tag{7.43}$$

Proof. A simple computation gives (using the fact that $\psi_\infty^\xi = 1$)

$$\begin{aligned}\int_{\mathbb{R}} \partial_x \ln\left(\frac{\psi}{\psi_\infty}\right)\frac{\psi}{\psi^\xi}\,dy - \partial_x \ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right) &= \int_{\mathbb{R}} \partial_x\left(\ln\psi\right)\frac{\psi}{\psi^\xi}\,dy - \int_{\mathbb{R}} \partial_x \ln\psi_\infty \frac{\psi}{\psi^\xi}\,dy - \partial_x\left(\ln\psi^\xi\right)\\ &= \int_{\mathbb{R}} \frac{\partial_x\psi}{\psi^\xi}\,dy + \beta\int_{\mathbb{R}} \partial_x(V-F)\frac{\psi}{\psi^\xi}\,dy - \partial_x\left(\ln\psi^\xi\right)\\ &= \beta(F_t' - F'),\end{aligned}$$

where we used in the last line

$$\partial_x\left(\ln\psi^\xi\right) = \frac{1}{\psi^\xi}\partial_x\left(\int_{\mathbb{R}}\psi\,dy\right) = \int_{\mathbb{R}}\frac{\partial_x\psi}{\psi^\xi}\,dy.$$

This gives the claimed result. □

By using (7.43) in (7.42), we obtain

$$\begin{aligned}\frac{dE_{\rm m}}{dt} = &-\beta^{-1}\int_{\mathbb{T}}\int_{\mathbb{R}}\left|\partial_y \ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2\psi\\ &- \beta^{-1}\int_{\mathbb{T}}\int_{\mathbb{R}}\left|\partial_x \ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2\psi + \beta^{-1}\int_{\mathbb{T}}\left(\int_{\mathbb{R}}\partial_x\ln\left(\frac{\psi}{\psi_\infty}\right)\psi\,dy\right)^2\frac{1}{\psi^\xi}\,dx\\ &- \beta^{-1}\int_{\mathbb{T}}\int_{\mathbb{R}}\partial_x\ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right)\partial_x\ln\left(\frac{\psi}{\psi_\infty}\right)\psi + \beta^{-1}\int_{\mathbb{T}}\left|\partial_x\ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right)\right|^2\psi^\xi.\end{aligned}$$

Note that by the Cauchy–Schwarz inequality, the term on the second line above is non-positive. Therefore, again using (7.43),

$$\frac{dE_{\rm m}}{dt} \leqslant -\beta^{-1}\int_{\mathbb{T}}\int_{\mathbb{R}}\left|\partial_y\ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2\psi - \int_{\mathbb{T}}\partial_x\ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right)\psi^\xi(F_t' - F'). \tag{7.44}$$

Besides, using the assumption (7.31), we know that for any positive time t, and for any $x \in \mathbb{T}$,

$$\mathcal{H}\left(\frac{\psi(t,x,\cdot)}{\psi^\xi(t,x)}\middle|\frac{\psi_\infty(x,\cdot)}{\psi_\infty^\xi(x)}\right) \leqslant \frac{1}{2\rho}\mathcal{I}\left(\frac{\psi(t,x,\cdot)}{\psi^\xi(t,x)}\middle|\frac{\psi_\infty(x,\cdot)}{\psi_\infty^\xi(x)}\right),$$

which is given more explicitly by

$$e_{\mathrm{m}}(t,x) \leqslant \frac{1}{2\rho}\int_{\mathbb{R}} \left|\partial_y \ln\left(\frac{\psi/\psi^\xi}{\psi_\infty/\psi_\infty^\xi}\right)\right|^2 \frac{\psi}{\psi^\xi}\,dy = \frac{1}{2\rho}\int_{\mathbb{R}} \left|\partial_y \ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2 \frac{\psi}{\psi^\xi}\,dy,$$

since ψ^ξ and ψ_∞^ξ do not depend on y. Therefore,

$$E_{\mathrm{m}}(t) = \int_{\mathbb{T}} e_{\mathrm{m}}(t,x)\psi^\xi(t,x)\,dx \leqslant \frac{1}{2\rho}\int_{\mathbb{T}}\int_{\mathbb{R}} \left|\partial_y \ln\left(\frac{\psi}{\psi_\infty}\right)\right|^2 \psi.$$

By using this in (7.44), we thus obtain

$$\frac{dE_{\mathrm{m}}}{dt} \leqslant -2\beta^{-1}\rho E_{\mathrm{m}} - \int_{\mathbb{T}} \partial_x \ln\left(\frac{\psi^\xi}{\psi_\infty^\xi}\right)\psi^\xi(F_t' - F'). \tag{7.45}$$

To continue, we now need an upper bound on $F_t' - F'$ in terms of the difference between the two conditional measures. It seems natural that such an estimate holds since

$$F_t'(x) - F'(x) = \int_{\mathbb{R}} \partial_x V(x,y)\frac{\psi(t,x,y)\,dy}{\psi^\xi(t,x)} - \int_{\mathbb{R}} \partial_x V(x,y)\frac{\psi_\infty(x,y)\,dy}{\psi_\infty^\xi(x)}$$

is the "distance" (in some sense) of the averages of the same function $\partial_x V$ with respect to the two conditional measures $\psi(t,x,y)\,dy/\psi^\xi(t,x)$ and $\psi_\infty(x,y)\,dy/\psi_\infty^\xi(x)$. It is the purpose of the next lemma (which is probably the most technical part of the proof) to obtain such an estimate, the "distance" being measured in terms of relative entropy.

Lemma 7.4. *Suppose that assumptions* (7.31) *and* (7.32) *are satisfied. Then, for all* $t \geqslant 0$ *and for all* $x \in \mathbb{T}$,

$$|F_t'(x) - F'(x)| \leqslant \|\partial_{x,y} V\|_{B^\infty}\sqrt{\frac{2}{\rho}e_{\mathrm{m}}(t,x)}, \tag{7.46}$$

where e_{m} *is defined in* (7.40).

Proof. The proof uses the Talagrand inequality, which relates the Wasserstein distance and the relative entropy between two probability measures. Let us first recall the Wasserstein distance and the Talagrand inequality.

Let us introduce the set of coupling measures $\Pi(\nu_{t,x},\nu_{\infty,x})$, where, for ease of notation, we let $\nu_{t,x}(dy) = \psi(t,x,y)\,dy/\psi^\xi(t,x)$ and $\nu_{\infty,x}(dy) = \psi_\infty(x,y)\,dy/\psi_\infty^\xi(x)$, respectively, denote the conditional measures of $\psi(t,x,y)\,dx\,dy$ and $\psi_\infty(x,y)\,dx\,dy$ given that $\xi(x,y) = x$. By definition of $\Pi(\nu_{t,x},\nu_{\infty,x})$, the measures $\pi \in \Pi(\nu_{t,x},\nu_{\infty,x})$ are probability measures over $\mathbb{R}\times\mathbb{R}$ such that, for any C^∞ and compactly supported test function $\varphi : \mathbb{R} \to \mathbb{R}$,

$$\int_{\mathbb{R}\times\mathbb{R}} \varphi(y_1)\pi(dy_1\,dy_2) = \int_{\mathbb{R}} \varphi(y_1)\nu_{t,x}(dy_1)$$

and

$$\int_{\mathbb{R}\times\mathbb{R}} \varphi(y_2)\pi(dy_1\,dy_2) = \int_{\mathbb{R}} \varphi(y_2)\nu_{\infty,x}(dy_2).$$

In other words, the marginal of $\pi \in \Pi(\nu_{t,x},\nu_{\infty,x})$ on the first (resp. the second) variable is $\nu_{t,x}$ (resp. $\nu_{\infty,x}$). We next define the Wasserstein distance between two probability measures π_1 and π_2 on $\mathbb{R}^d$:

$$\mathcal{W}(\pi_1,\pi_2) = \sqrt{\inf_{\pi\in\Pi(\pi_1,\pi_2)}\int_{\mathbb{R}\times\mathbb{R}} |y_1 - y_2|^2\,\pi(dy_1\,dy_2)}.$$

The Wasserstein distance $\mathcal{W}(\nu_{t,x},\nu_{\infty,x})$ between $\nu_{t,x}$ and $\nu_{\infty,x}$ appears very naturally when estimating the difference $F_t' - F'$. Indeed, for any coupling measure $\pi \in \Pi(\nu_{t,x},\nu_{\infty,x})$, we have

$$
\begin{aligned}
|F_t'(x) - F'(x)| &= \left| \int_{\mathbb{R}\times\mathbb{R}} (\partial_x V(x,y) - \partial_x V(x,y'))\, \pi(dy\, dy') \right| \\
&\leqslant \|\partial_{x,y} V\|_{B^\infty} \int_{\mathbb{R}\times\mathbb{R}} |y - y'|\, \pi(dy\, dy') \\
&\leqslant \|\partial_{x,y} V\|_{B^\infty} \sqrt{\int_{\mathbb{R}\times\mathbb{R}} |y - y'|^2\, \pi(dy\, dy')}.
\end{aligned}
$$

so that, by taking the infimum over all $\pi \in \Pi(\nu_{t,x}, \nu_{\infty,x})$,

$$
|F_t'(x) - F'(x)| \leqslant \|\partial_{x,y} V\|_{B^\infty} W(\nu_{t,x}, \nu_{\infty,x}). \tag{7.47}
$$

This is where the assumption (7.32) is needed.

Now, in (7.45), it is not the Wasserstein distance between $\nu_{t,x}$ and $\nu_{\infty,x}$ which appears, but the relative entropy (7.40). The Talagrand inequality is exactly what we need since it relates the Wasserstein distance to the relative entropy between two measures. More precisely, we use following result, proved in a more general setting in [33, 211].

Lemma 7.5 (Talagrand inequality). *Let π_2 be a probability measure on $\mathbb{R}^d$ which satisfies LSI(ρ). Then, for all probability measures π_1 on $\mathbb{R}^d$,*

$$
\mathcal{W}(\pi_1, \pi_2) \leqslant \sqrt{\frac{2}{\rho}} \mathcal{H}(\pi_1 | \pi_2).
$$

Using this result and assumption (7.31), which exactly states that $\nu_{\infty,x} = \nu(dq \,|\, \xi(q) = x)$ satisfies LSI(ρ), we thus have

$$
\forall t \geqslant 0, \qquad \mathcal{W}(\nu_{t,x}, \nu_{\infty,x}) \leqslant \sqrt{\frac{2}{\rho}} \mathcal{H}(\nu_{t,x} \,|\, \nu_{\infty,x}) = \sqrt{\frac{2}{\rho}} e_{\mathrm{m}}(t,x).
$$

Combining this inequality with (7.47) leads to (7.46), which concludes the proof of Lemma 7.4. □

Using (7.46) in (7.45), we obtain, using a Cauchy–Schwarz inequality,

$$
\begin{aligned}
\frac{dE_{\mathrm{m}}}{dt} &\leqslant -2\beta^{-1}\rho E_{\mathrm{m}} + \sqrt{\int_{\mathbb{T}} \psi^\xi |F_t' - F'|^2} \sqrt{\int_{\mathbb{T}} \left| \partial_x \ln\left(\frac{\psi^\xi}{\psi^\xi_\infty} \right) \right|^2 \psi^\xi} \\
&\leqslant -2\beta^{-1}\rho E_{\mathrm{m}} + \|\partial_{x,y} V\|_{B^\infty} \sqrt{\frac{2}{\rho} E_{\mathrm{m}} \mathcal{I}(\psi^\xi \,|\, \psi^\xi_\infty)}.
\end{aligned}
$$

By dividing by $2\sqrt{E_{\mathrm{m}}}$ and using the estimate (7.37) on $\mathcal{I}(\psi^\xi \,|\, \psi^\xi_\infty)$, we thus obtain

$$
\frac{d\sqrt{E_{\mathrm{m}}}}{dt} \leqslant -\beta^{-1}\rho \sqrt{E_{\mathrm{m}}} + \|\partial_{x,y} V\|_{B^\infty} \sqrt{\frac{1}{2\rho} \mathcal{I}(\psi^\xi(0,\cdot) \,|\, \psi^\xi_\infty)} \mathrm{e}^{-4\beta^{-1}\pi^2 t}.
$$

Using the fact that $\rho \neq 4\pi^2$, a Gronwall lemma[5] then easily shows that there exists a constant C such that, for all $t \geqslant 0$,

$$
\sqrt{E_{\mathrm{m}}(t)} \leqslant C \mathrm{e}^{-\beta^{-1} \min(\rho, 4\pi^2) t}. \tag{7.48}
$$

From this result, the extensivity of the entropy provided by Lemma 7.2, and the convergence of the marginals in x given by (7.41), one immediately deduces that $\sqrt{E(t)}$ (and thus $\|\psi(t,\cdot) - \psi_\infty\|_{L^1(\mathbb{T}\times\mathbb{R})}$ by the Csiszár–Kullback inequality (4.42)) converges exponentially fast to zero with rate $\beta^{-1} \min(\rho, 4\pi^2)$.

[5] If $\rho = 4\pi^2$, then one obtains an upper bound of the form $(C_1 + C_2 t)\mathrm{e}^{-4\beta^{-1}\pi^2 t}$.

To deduce from these results the convergence (7.33) of $\|F_t' - F'\|_{L^2(\mathbb{T})}$ exponentially fast with the same rate, one simply uses the fact that

$$\sqrt{\int_{\mathbb{T}} |F_t' - F'|^2} \leqslant C \sqrt{\int_{\mathbb{T}} |F_t' - F'|^2 \psi^\xi} \leqslant C \sqrt{E_{\mathrm{m}}(t)}.$$

The first inequality is a consequence of the fact that $\psi^\xi(0,\cdot)$ is assumed to be positive and ψ^ξ satisfies the heat equation on $\mathbb{T}$, so that ψ^ξ is bounded from below by a positive constant. The second inequality is a consequence of (7.46). This concludes the proof of Theorem 7.1.

7.3.3 Extensions and related works

Let us make a few comments on the specific setting in which we presented the convergence result of Theorem 7.1. First, we assumed that the x-variable lives in the torus in order for ξ to be with values in a compact domain, so that the free energy biased Boltzmann–Gibbs measure with density $\mathrm{e}^{-\beta(V-F\circ\xi)}$ can be normalized. The fact that $\int \mathrm{e}^{-\beta(V-F\circ\xi)} < \infty$ is necessary for the dynamics to actually have a stationary state. In practice, if ξ does not take values in a compact domain, the classical technique is to apply the bias only over a compact domain, by using a restraining potential $\mathcal{W} \circ \xi$ (see [177, 6] for more details). Second, we assumed that ξ is a linear function of q. Let us consider the case of more general reaction coordinates $\xi : \mathbb{R}^d \to \mathbb{R}$ (we consider one-dimensional ξ for simplicity). For general reaction coordinates, one in fact has to slightly modify the ABF dynamics (7.27) by terms which depend on $|\nabla\xi|$ in order to recover the results of Theorem 7.1 (see [177, Equation (10)]). These modifications are only necessary for theoretical purposes: they are not used by practitioners. However, from a theoretical viewpoint, without these additional terms, only a weaker result can be proved (see [177, Section 2.3]).

Further, Assumption (7.31) can be somewhat weakened. One can for instance consider the situation when two channels link metastable states, so that the assumption (7.31) is only satisfied on some bounded sub-interval of the range of ξ. In this situation, it can be shown [174] that, provided the free energy profiles do not differ too much in each channel, then a similar convergence result can be obtained. Let us also mention that the convergence of a variant of the ABF method, where the biasing force is projected onto a gradient field has been established in [6]. Such a projection makes sense since the expected limit, the mean force, is indeed a gradient.

8

Computation of transport coefficients

We discuss in lecture chapter how to compute transport coefficients such as the mobility, the thermal conductivity or the shear viscosity. At the macroscopic level, transport coefficients relate an external forcing acting on the system (electric field, temperature gradient, velocity field, etc) to an average response expressed through some steady-state flux (of charged particles, energy, momentum, etc). At the microscopic level, this is modelled by systems in a stationary state, evolving according to perturbations of equilibrium dynamics.

It is observed that, in general, the response of the system, as encoded by the steady-state average of the physical observable of interest (such as the velocity, the energy flux, etc), is proportional to the magnitude of the forcing for small values of the forcing. This corresponds to the so-called linear response regime. By definition, transport coefficients are the proportionality constants relating the response to the forcing. It turns out that this linear response constant can in fact be rewritten as some integrated correlation function for an equilibrium dynamics, a celebrated equality known as the Green–Kubo formula.

We start by giving some examples of nonequilibrium dynamics in Section 8.1, before presenting non-equilibrium dynamics from a more general perspective in Section 8.2, with some emphasis on perturbations of equilibrium dynamics such as (8.1) or (8.2). We next show in Section 8.3 how first-order changes in average properties with respect to some forcing parameter can be computed, and

how these quantities are related to transport coefficients. Error estimates on the computation of transport coefficients are provided in Section 8.4. Finally, we discuss variance reduction techniques in Section 8.5.

8.1 Examples of nonequilibrium dynamics

In order to fix ideas, we describe below some dynamics which are considered to be out of equilibrium (although this notion will be made clear only later on, in Section 8.2). We consider two paradigmatic situations: cases when the drift of equilibrium dynamics is perturbed by a non-gradient force (see Section 8.1.1), and cases when the magnitude of the fluctuation terms are modified (see Section 8.1.2).

8.1.1 Non-gradient drifts

A simple example of Langevin dynamics perturbed by a non-gradient force is provided by the addition of a constant force term for dynamics in a periodic domain:

$$\begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = \left(-\nabla V(q_t) + \eta F\right) dt - \gamma M^{-1} p_t \, dt + \sqrt{\dfrac{2\gamma}{\beta}} \, dW_t, \end{cases} \tag{8.1}$$

where $(q_t, p_t) \in \mathcal{E} = \mathbb{T}^D \times \mathbb{R}^D$, $F \in \mathbb{R}^D$ with $|F| = 1$ a given direction, and V a C^∞ periodic potential. The parameter $\eta \in \mathbb{R}$ determines the strength of the external forcing. A non-zero velocity in the direction F is expected in the steady-state due to the external force F. Let us already emphasize that F does not derive from the gradient of a periodic function: it indeed holds that $F = -\nabla W_F(q)$ with $W_F(q) = -F^T q$, but the function W_F is not periodic. It is precisely because the perturbation is not of gradient type that some particle flux can appear in the steady-state.

Some qualitative properties of the steady-state of the system (provided it exists, which will be shown in Section 8.1) can be stated by computing the average with respect to the steady-state of quantities of the form $\mathcal{L}_\eta \Phi$ for various obsevables Φ (where $\mathcal{L}_\eta$ denotes the generator of the dynamics). It is possible for instance to show that the average velocity v_η in the system is such that $v_\eta \cdot F \geqslant 0$; see for instance [137, Section 2.2].

It is of course possible to consider forcings F which genuinely depend on the position q, for instance to compute shear viscosities using the sinusoidal transverse force method [268, 145] (which corresponds, in a two-dimensional setting, to a force oriented in one direction, but depending on the component of the position of the particle in the other direction), and possibly on time as well [144].

8.1.2 Dynamics with modified fluctuation terms

Another class of perturbation is obtained by modifying the fluctuation magnitude. For Langevin dynamics, one possible choice is

$$\begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = -\nabla V(q_t) \, dt - \gamma M^{-1} p_t \, dt + \sqrt{2\gamma T_\eta(q)} \, dW_t, \end{cases} \tag{8.2}$$

where the temperature $T_\eta : \mathcal{D} \to \mathbb{R}_+$ is a non-negative C^∞ function, of the form

$$T_\eta(q) = T_{\rm ref} + \eta \widetilde{T}(q)$$

for some C^∞ function $\widetilde{T}$ and a given reference temperature $T_{\rm ref} > 0$. In order for T_η to remain non-negative, the parameter η should be taken sufficiently small. Typically, $\widetilde{T}$ is constant and positive

on a subdomain $\mathcal{D}_+ \subset \mathcal{D}$, and constant and negative on another subdomain $\mathcal{D}_- \subset \mathcal{D}$, with some C^∞ transition between $\mathcal{D}_+$ and $\mathcal{D}_-$. Some energy flux is expected from the "hot" part $\mathcal{D}_+$ of the system to the "cold" one $\mathcal{D}_-$.

The model (8.2) we consider here for pedagogical purposes is a simplification of more realistic models of thermal transport such as heat transport in one dimensional chains. For a chain of N atoms of equal masses 1, whose positions and momenta are respectively denoted by $q = (q_1, \dots, q_N)$ and $p = (p_1, \dots, p_N)$, possible equations of motion read

$$\begin{cases} dq_i = p_i\, dt, \\ dp_i = \Big(v'(q_{i+1} - q_i) - v'(q_i - q_{i-1})\Big)dt, \qquad i \neq 1, N, \\ dp_1 = \Big(v'(q_2 - q_1) - v'(q_1)\Big)dt - \gamma p_1\, dt + \sqrt{2\gamma T_{\mathrm{L}}}\, dW_t^1, \\ dp_N = -v'(q_N - q_{N-1})\, dt - \gamma p_N\, dt + \sqrt{2\gamma T_{\mathrm{R}}}\, dW_t^N, \end{cases} \tag{8.3}$$

where W_t^1 and W_t^N are independent standard one-dimensional Brownian motions, and v is a smooth interaction potential. This evolution corresponds to a Hamiltonian dynamics in the bulk part of the system (that is, for $i \in \{2, \dots, N-1\}$), with associated Hamiltonian

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2} + V(q), \qquad V(q) = v(q_1) + \sum_{i=1}^{N-1} v(q_{i+1} - q_i), \tag{8.4}$$

and superimposed Ornstein-Uhlenbeck processes on the momenta at the two ends of the chain in order to impose temperatures $T_{\mathrm{L}}, T_{\mathrm{R}}$ at the boundaries. We choose here to attach the chain to a wall on the left by setting $q_0 = 0$ and $p_0 = 0$ at all times, while the right end is free. Attaching the chain on one side is important to remove the translation invariance of the whole system. Other boundary conditions are possible, for instance fixed positions at both ends or periodic boundary conditions (with thermostats at sites $1 \equiv N+1$ and $N/2$ in this case). It is also possible to consider more general interactions among the particles in the system, in particular next-nearest neighbor potentials and pinning potentials; and to superimpose other stochastic mechanisms such as momenta flip, momenta exchanges, Ornstein-Uhlenbeck processes at each site [209], etc. See the review articles [34, 183, 68, 140] for a more in-depth discussion of microscopic models of thermal transport, with some emphasis on low (one-) dimensional systems.

8.1.3 Some remarks

The two dynamics (8.1) and (8.2) reduce to the standard Langevin dynamics (5.1) when $\eta = 0$. Most of our analysis is illustrated with the dynamics (8.1), but we will occasionally refer to the dynamics (8.2) as well.

As discussed more precisely in Section 8.2, dynamics such as (8.1) and (8.2) model nonequilibrium systems since they are non reversible: the law of forward trajectories is different from the law of backward trajectories. From a physical point of view, the arrow of time can be read off the trajectories. We do not make a distinction here between non-reversible and nonequilibrium systems, although such a distinction is sometimes made in the physical literature (see for instance [29] and references therein).

Finally, let us make precise the aim of this chapter, namely the computation of transport coefficients. For (8.1), the velocity of the particle in the direction of F at stationary state is proportional to η, and the proportionality constant is called the mobility. For (8.2), the energy flux in the stationary state is proportional to η, and the proportionality constant is called the thermal conductivity. In actual physical systems such as (8.3), the parameter η is the temperature difference $T_{\mathrm{L}} - T_{\mathrm{R}}$. We chose not to discuss examples related to the computation of shear viscosities, since the methods to do so are more elaborate; see the reviews in [267, 85, 269, 268].

8.2 Definition of non-equilibrium dynamics

We provide in this section a more general perspective on non-equilibrium dynamics, by first defining what we mean by non-equilibrium dynamics in Section 8.2.1. We next discuss some properties of their invariant probability measures in Section 8.2.2, and finally give an overview of computational techniques to compute transport coefficients in Section 8.2.3.

8.2.1 Abstract characterization of non-equilibrium dynamics

As in Section 6.1, we consider a general stochastic dynamics with values in some space $\mathcal{X}$:

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t.$$

For overdamped Langevin dynamics, $x = q$ and $\mathcal{X} = \mathcal{D}$, while $x = (q,p)$ and $\mathcal{X} = \mathcal{E}$ for Langevin dynamics. We assume in the sequel that the dynamics admits a unique invariant probability measure $\pi(dx)$. This can be proved using the tools from Section 3.3.1 for instance, as done for overdamped Langevin dynamics in Section 5.4.1 and for Langevin dynamics in Section 4.3.4 since the derivations made there can be straightforwardly extended to situations when the drift is not gradient (see for instance the discussion after Theorem 4.5).

From a mathematical viewpoint, equilibrium dynamics are characterized by the self-adjointness of the generator $\mathcal{L}$ on the weighted Hilbert space $L^2(\pi)$: For any smooth functions φ, ϕ with compact supports,

$$\int_{\mathcal{X}} (\mathcal{L}\varphi)\phi\,d\pi = \int_{\mathcal{X}} \varphi(\mathcal{L}\phi)\,d\pi. \tag{8.5}$$

This expresses the reversibility of the dynamics with respect to the invariant measure of the process. A more probabilistic reformulation of the reversibility is the following: when $x_0 \sim \pi$, the law of the forward paths $(x_s)_{0\leqslant s\leqslant t}$ is the same as the law of the backward paths $(x_{t-s})_{0\leqslant s\leqslant t}$ (note that $x_t \sim \pi$ by the invariance of π). Therefore, the arrow of time cannot be read off the trajectories.

In some cases, the reversibility property holds only up to a one-to-one transformation preserving the invariant measure. For example, for Langevin dynamics, reversibility is valid only upon momentum reversal $S(q,p) = (q,-p)$ as a consequence of (5.9):

$$\int_{\mathcal{X}} (\mathcal{L}\varphi)\phi\,d\pi = \int_{\mathcal{X}} (\varphi\circ S)(\mathcal{L}(\phi\circ S))\,d\pi;$$

see [178, Section 2.2.3.1]. At the level of trajectories, this means that the law of the forward paths $(q_s,p_s)_{0\leqslant s\leqslant t}$ is the same as the law of the paths $(q_{t-s},-p_{t-s})_{0\leqslant s\leqslant t}$.

We define here non-equilibrium dynamics to be stochastic evolutions for which reversibility properties such as (8.5) no longer hold true. The non-reversibility can be quantified by the entropy production, for which fluctuation theorems hold [99, 160, 162].

8.2.2 Invariant measures

An important property of non-equilibrium systems is that their invariant measures are in general not analytically known, in contrast to equilibrium dynamics. In addition, the invariant measure depends non trivially on the details of the dynamics due to long-range correlations which are generically present in non-equilibrium systems (see for instance [65]).

Let us make the latter statement precise for overdamped Langevin dynamics on the compact configuration space $\mathbb{T} = \mathbb{R}/\mathbb{Z}$, for a C^∞ periodic potential V and $\beta = 1$. For the reversible dynamics

$$dq_t = -V'(q_t)\,dt + \sqrt{2}\,dW_t, \tag{8.6}$$

the unique invariant probability measure is $Z^{-1}\mathrm{e}^{-V(q)}\,dq$, which depends only on the value of V at the configuration q of interest (apart from a global normalization constant). For the perturbed dynamics

$$dq_t = (-V'(q_t) + F)\,dt + \sqrt{2}\,dW_t, \tag{8.7}$$

where $F \in \mathbb{R}$ is a constant force, it can be shown that there exists a unique invariant probability measure $\psi_F(q)\,dq$, with density

$$\psi_F(q) = Z_F^{-1} \int_0^1 \mathrm{e}^{V(q+y)-V(q)-Fy}\,dy, \tag{8.8}$$

where Z_F is chosen such that $\int_0^1 \psi_F = 1$. It is clear from the expression of the invariant measure that, when $F \neq 0$, the invariant measure depends on the values of V everywhere. Similar expressions are obtained for overdamped Langevin dynamics with multiplicative noise (4.9), as made precise in the following result (see [92, Appendix]).

Lemma 8.1. *Consider two smooth functions $V : \mathbb{T} \to \mathbb{R}_+$ and $A : \mathbb{T} \to \mathbb{R}$, a forcing $F \in \mathbb{R}$, and the stochastic dynamics*

$$dq_t = \left(-A(q_t)V'(q_t) + \frac{1}{\beta}A'(q_t) + F\right)dt + \sqrt{\frac{2A(q_t)}{\beta}}\,dW_t.$$

When $\min_{\mathbb{T}} A > 0$, the dynamics admits a unique invariant probability measure with a smooth density ψ_F with respect to the Lebesgue measure, which explicitly reads

$$\psi_F(q) = \frac{1}{Z_F}\mathrm{e}^{-\beta V(q)} \int_0^1 \frac{\mathrm{e}^{\beta V(q+y)-Fy}}{A(q+y)}\,dy,$$

where Z_F is a normalization constant ensuring that ψ_F integrates to 1 over $\mathbb{T}$.

Proof. Since the configuration space is compact, the existence and uniqueness of a probability measure follows for instance from the minorization condition of Section 4.3.4 . The fact that it has a smooth density is provided by regularity results for the stationary Fokker–Planck equation. To obtain the expression of ψ_F, we generalize the computations of [227, Section 2.5] (see also the references quoted in this work), written for constant diffusion coefficients A. The first step is write the Fokker–Planck equation as

$$\frac{d}{dq}\left(A(q)\left[(\beta V' - F)\psi_F + \frac{d\psi_F}{dq}\right]\right) = 0.$$

Therefore, there exists a constant $a \in \mathbb{R}$ such that $(\beta V' - F)\psi_F + \psi_F' = a/A(q)$, so that

$$\frac{d}{dq}\left[\psi_F(q)\mathrm{e}^{\beta V(q)-Fq}\right] = \frac{a\mathrm{e}^{\beta V(q)-Fq}}{A(q)}.$$

By integrating this equality from q to $q+1$ and using the periodicity of the function ψ_F, we obtain

$$\psi_F(q)\mathrm{e}^{\beta V(q)-Fq}\left(\mathrm{e}^{-F} - 1\right) = a\int_q^{q+1} \frac{\mathrm{e}^{\beta V(Q)-FQ}}{A(Q)}\,dQ = a\int_0^1 \frac{\mathrm{e}^{\beta V(q+y)-F(q+y)}}{A(q+y)}\,dy.$$

This leads to the claimed result by adjusting a in order for ψ_F to have integral 1 over the unit torus. □

Let us also show that the dynamics (8.7) is a non-equilibrium dynamics by checking that its generator is not reversible on $L^2(\psi_F)$. Since we do not need the precise expression of the invariant measure, we generalize the dynamics in arbitrary dimension, and consider $\mathcal{D} = \mathbb{T}^D$. We first rewrite ψ_F in exponential form as

$$\psi_F(q) = \mathrm{e}^{-U_F(q)},$$

and introduce a stochastic dynamics with a general drift $b(q)$:

$$dq_t = b(q_t)\,dt + \sqrt{2}\,dW_t. \tag{8.9}$$

The generator $\mathcal{L}_b$ of this generalized dynamics reads

$$\mathcal{L}_b = b \cdot \nabla + \Delta = -\nabla^* \nabla + (b + \nabla U_F)^T \nabla.$$

A simple computation shows that

$$\mathcal{L}_b^* = -\nabla^* \nabla - (b + \nabla U_F)^T \nabla + u_F, \qquad u_F = (b + \nabla U_F)^T \nabla U_F - \operatorname{div}(b + \nabla U_F).$$

When $b(q) = -\nabla V(q) + F$, reversibility holds if and only if

$$F + \nabla(U_F - V) = 0.$$

This condition cannot be satisfied since F does not derive from the gradient of a periodic function. More generally, the above computation shows that dynamics such as (8.9) are reversible if and only if the drift is the gradient of a potential energy function.

8.2.3 Computation of transport coefficients

A transport coefficient ρ relates the magnitude of the response of the system in its steady state (an average current) to the magnitude of the external forcing. We present a specific example in Section 8.3; see in particular (8.13). For the paradigmatic dynamics (8.1) and (8.2), the magnitude of the external forcing is η.

Before embarking on a more detailed analysis, it is useful to classify the current methods for computing transport coefficients, as reviewed in [85] and [269] for instance, into three main classes.

(i) *Equilibrium techniques* based on Green–Kubo formulas, which are integrated correlation functions of the general form

$$\rho = \int_0^{+\infty} \mathbb{E}_\pi(\varphi(x_t)\phi(x_0))\,dt,$$

where φ, ϕ are two observables whose expressions depend on the physical context at hand, and where the expectation denotes an average with respect to all initial conditions distributed according to the invariant probability measure π for the reference dynamics $(x_t)_{t \geqslant 0}$, and for all realizations of this dynamics.

(ii) *Transient methods*, where the system is initially locally perturbed, and the relaxation of this perturbation is monitored as a function of time. The comparison with some assumed macroscopic evolution equation (for instance the heat equation for thermal transport) allows us to identify the physical parameters of the macroscopic evolution (such as the thermal conductivity). See [133], for example, for an application of this technique.

(iii) *Non-equilibrium steady-state techniques*, where a forcing is permanently applied to the system. The latter methods can be decomposed into two subcategories: boundary-driven techniques, where the external forcing is imposed only in boundary regions (think of (8.2) with a perturbation $\widetilde{T}$ localized in two subdomains $\mathcal{D}_-, \mathcal{D}_+$), and bulk-driven dynamics, where the perturbation is experienced everywhere in the system (think of (8.1)). In both cases a flux is measured, and the transport coefficient is obtained as the average flux divided by the magnitude η of the external forcing. The expression of the flux function is again defined by analogy with macroscopic laws.

Bulk dynamics are often numerically more efficient since the forcing is applied globally to the system, and therefore the steady state can be reached more rapidly. Further, it is in general impossible to prove the existence and uniqueness of an invariant probability measure for boundary-driven dynamics, except in very simple geometries such as one-dimensional atom chains, or for stochastic lattice gases.

It should be emphasized that the definition of transport coefficients is based on an analogy with macroscopic evolution equations, which are (a system of) partial differential equations. This is clear for transient and steady-state dynamics. It is in fact also the case for equilibrium methods, since the expression of the transport coefficient as some integrated correlation function is, up to algebraic manipulations, a straightforward consequence of linear response results for steady-state non-equilibrium dynamics (see for instance (8.24) below for the specific case treated in Section 8.3).

Note that, in the simplest cases, it is in fact possible to rigorously derive the macroscopic evolution equations from microscopic dynamics. The corresponding system of PDEs is known as the hydrodynamic limit, see for instance [147] for a pedagogical introduction.

8.3 Linear response for non-equilibrium dynamics

In this section we sketch the derivation of the expression of transport coefficients, in the paradigmatic case of the mobility, which is computed with the dynamics (8.1) on the configuration space $\mathcal{E} = \mathbb{T}^D \times \mathbb{R}^D$. We denote by $\mathcal{L}_\eta = \mathcal{L}_0 + \eta\widetilde{\mathcal{L}}$ the generator, where $\widetilde{\mathcal{L}} = F \cdot \nabla_p$, and $\mathcal{L}_0$ is given in (5.7):

$$\mathcal{L}_0 = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p + \gamma \left(-p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p \right).$$

We start by discussing in Section 8.3.1 the existence and uniqueness of an invariant probability measure for the model dynamics (8.1). We next make precise in Section 8.3.2 the observables under consideration for the response of the system, and then provide a more explicit expression of the density of the invariant probability measure as a series expansion in η, when this parameter is sufficiently small, which allows to rigorously define the linear response of currents of interest in Section 8.3.3. The coefficient of linear response is by definition the transport coefficient of interest. As explained in Section 8.3.4, this coefficient can be reformulated as an integrated correlation function. We conclude this section by a discussion on how to extend the results obtained for the model dynamics (8.1) to other dynamics, including (8.2), for which the perturbation $\widetilde{\mathcal{L}}$ of $\mathcal{L}_0$ is not small from the point of view of spectral theory (see Section 8.3.5).

8.3.1 Existence and uniqueness of the invariant measure

By a simple extension of the results of Section 5.4.1, the dynamics (8.1) admits a unique invariant probability measure. Upon introducing the Lyapunov functions $\mathscr{W}_n(q,p) = 1 + |p|^n$ for $n \geqslant 2$, it is in fact possible to formulate the following convergence result, where some uniformity in the parameter η holds (see [169] and [144] for related results).

Proposition 8.1. *Consider $\eta_* > 0$. For any $\eta \in [-\eta_*, \eta_*]$, the dynamics (8.1) admits a unique invariant probability measure with a C^∞ density $\psi_\eta(q,p)$ with respect to the Lebesgue measure. Moreover, for any $n \geqslant 2$, there exist $C_n, \lambda_n > 0$ (depending on η_*) such that, for any $\eta \in [-\eta_*, \eta_*]$ and for any $\varphi \in L^\infty_{\mathscr{W}_n}(\mathcal{E})$,*

$$\forall t \geqslant 0, \qquad \left\| \mathrm{e}^{t\mathcal{L}_\eta} \varphi - \int_{\mathcal{E}} \varphi \psi_\eta \right\|_{L^\infty_{\mathscr{W}_n}} \leqslant C_n \mathrm{e}^{-\lambda_n t} \left\| \varphi \right\|_{L^\infty_{\mathscr{W}_n}}.$$

The existence and uniqueness of the invariant probability measure is proved by showing that the minorization condition and the Lyapunov condition can be stated uniformly with respect to the parameter $\eta \in \mathbb{R}$, as long as this parameter remains in a compact set. This can be obtained by a straightforward modifications of the arguments used in the proof of Theorem 4.5. For the absolute continuity and the smoothness of the density, we rely on the stationary Fokker–Planck equation

$$\mathcal{L}_\eta^\dagger \psi_\eta = 0, \quad \int_{\mathcal{E}} \psi_\eta = 1,$$

where, we recall, $\mathcal{L}_\eta^\dagger$ denotes the adjoint of $\mathcal{L}_\eta$ on the flat space $L^2(\mathcal{E})$. The smoothness of ψ_η is then a consequence of the hypoellipticiy of $\mathcal{L}_\eta^\dagger$ (see Section 5.5.1). For notational consistency, we set

$$\psi_0(q,p) = Z^{-1}\,\mathrm{e}^{-\beta H(q,p)}.$$

Note also that, as corollary of Proposition 8.1, it is possible to define $\mathcal{L}_\eta^{-1}$ as a bounded operator on the subspaces

$$B^\infty_{\mathscr{W}_n,\eta}(\mathcal{E}) = \left\{\varphi \in B^\infty_{\mathscr{W}_n}(\mathcal{E}) \,\middle|\, \int_{\mathcal{E}} \varphi\,\psi_\eta = 0\right\}.$$

Remark 8.1. *The scheme of proof of Proposition 8.1 can be employed for other dynamics which are not too degenerate, such as* (8.2)*. For very degenerate dynamics such as* (8.3)*, the controllability argument and the Lyapunov condition may be much more difficult to prove; and the law of the dynamics may even not be exponentially converging to its stationary state. More precisely, the existence and uniqueness of a smooth invariant probability measure for the dynamics* (8.3) *can be proved under appropriate assumptions on the interaction potential v, such as some (super)quadratic growth at infinity. Such results are based either on methods from spectral theory [82, 79] (in which case some additional pinning potential of the form $u(q_i)$, with u growing sufficiently fast at infinity, is required at each site), or on probabilistic techniques [81, 231, 232, 51]. In all cases, it is shown that the generator of the dynamics has a compact resolvent in an appropriate Hilbert space. When $T_\mathrm{L} = T_\mathrm{R} = T$, this invariant probability measure is the Gibbs measure at inverse temperature $\beta^{-1} = k_\mathrm{B}T$. When $T_\mathrm{L} \neq T_\mathrm{R}$, there is in general no simple expression of the invariant measure. Note that there are also situations such as the one studied in [117] where the existence of an invariant probability measure is not known. The main obstruction is the lack of a spectral gap in the spectrum of the generator.*

Let us conclude this section by proving that averages over a realization of (8.1) almost surely converge to averages with respect the stationary measure, namely: For a given observable $\varphi \in L^1(\psi_\eta)$, and any $(q_0,p_0) \in \mathcal{E}$,

$$\frac{1}{t}\int_0^t \varphi(q_s,p_s) \xrightarrow[t\to+\infty]{} \int_{\mathcal{E}} \varphi\,\psi_\eta \qquad \text{a.s.} \tag{8.10}$$

We follow the same strategy as in Section 5.3 and apply the results by [149]. The difference is however that we do not know a priori that the density ψ_η is positive, so that Lemma 4.1 cannot be applied as such. In order to guarantee the positivity of ψ_η, a sufficient condition is that the transition kernel $p_\eta(t,x,x')$ (with $x=(q,p)$ the configuration of the system) has a positive density for all $t>0$. Indeed, by invariance of ψ_η, it holds, for any $x' \in \mathcal{E}$,

double check, complete, confirm discussion

$$\psi_\eta(x') = \int_{\mathcal{E}} p_\eta(t,x,x')\psi_\eta(x)\,dx. \tag{8.11}$$

When $p_\eta(t,x,x') > 0$ for all $t>0$, the right hand side cannot be equal to 0 (otherwise ψ_η would vanish everywhere and would not integrate to 1), and so $\psi_\eta(x') > 0$ for all $x' \in \mathcal{E}$. There are various results ensuring the positivity of the transition density, for instance [197, Section 3.3.6.1], which is based on techniques from Malliavin calculus. In fact, for the above argument to work, it suffices that, for any final condition x', the transition density $x \mapsto p_\eta(t,x,x')$ is positive on an open set (when this is the case, the fact that $\psi_\eta(x') = 0$ implies by (8.11) that ψ_η vanishes on an open set, which comes in contradiction with open set irreducibility). The local positivity of $x \mapsto p_\eta(t,x,x')$ can in turn be obtained from lower bounds on the transition density, following for instance the approach of [152], as made precise for Langevin dynamics in [176].

voir aussi argument W. Zhang JMP20 dans sa reponse...

8.3.2 Observables of interest

It is expected, from a physical viewpoint, that, for the dynamics (8.1), the application of a non-zero constant force in a given direction induces a non-zero velocity in this direction. At the macroscopic

level, the mobility is the proportionality constant between the observed average velocity and the force F. To rigorously define the mobility for the microscopic dynamics (8.1) under consideration, we consider the observable

$$R(q,p) = F^T M^{-1} p. \tag{8.12}$$

The response of interest is the steady-state average $\mathbb{E}_\eta(R)$, where $\mathbb{E}_\eta$ is the expectation with respect to the invariant measure of the non-equilibrium dynamics (8.1). Note that $\mathbb{E}_0(R) = 0$. This allows us to define the mobility in the direction F as the ratio of the average projected velocity R divided by η, in the limit of small forcings (provided this limit exists), *i.e.*,

$$\rho_F = \lim_{\eta\to 0} \frac{\mathbb{E}_\eta(R) - \mathbb{E}_0(R)}{\eta} = \lim_{\eta\to 0} \frac{\mathbb{E}_\eta(R)}{\eta}. \tag{8.13}$$

This is the definition of the mobility based on the linear response of non-equilibrium dynamics.

For thermal transport as described by (8.3), a current of energy is expected from the hot to the cold reservoirs. This can be proved by computing the entropy production in the system [81, 28]. The thermal conductivity is defined as the energy flux divided by the temperature difference (see (8.30) below). The relevant physical response of the system is the total energy current J across the system

$$J(q,p) = \sum_{i=1}^{N-1} j_{i+1,i}(q,p), \qquad j_{i+1,i}(q,p) = -v'(q_{i+1}-q_i)\frac{p_i + p_{i+1}}{2}, \tag{8.14}$$

which is the sum of the local currents $j_{i,i-1}$ expressing the local conservation of the energy. The expression of these currents is motivated as follows. Consider an index $i = 2, \dots, N-1$. The energy ε_i at the i-th site is the sum of the kinetic energy and half of the interaction energies with the neighboring sites:

$$\varepsilon_i(q,p) = \frac{p_i^2}{2} + \frac{1}{2}\Big(v(q_{i+1}-q_i) + v(q_i - q_{i-1})\Big), \tag{8.15}$$

with appropriate modifications at the boundaries:

$$\varepsilon_1(q,p) = \frac{p_1^2}{2} + v(q_1) + \frac{1}{2}v(q_2-q_1), \qquad \varepsilon_N(q,p) = \frac{p_N^2}{2} + \frac{1}{2}v(q_N - q_{N-1}).$$

A simple computation shows that the variation of the local energy in the bulk ($2 \leqslant i \leqslant N-1$) is given by the following conservation law:

$$d\varepsilon_i = \Big(j_{i,i-1} - j_{i+1,i}\Big)dt.$$

The quantities $j_{i,i-1}$ can therefore be interpreted as energy fluxes from the site $i-1$ to the site i.

8.3.3 Linear response of the invariant measure

In order to ensure that the limit (8.13) is well defined, and eventually to rewrite ρ_F as some integrated correlation function, we need to characterize, to first order in η, the modification of the density $\psi_\eta(q,p)$ of the invariant measure of the dynamics (8.1) with respect to the reference canonical measure. It is convenient to this end to work on the Hilbert space $L^2(\psi_0)$. We also introduce the projection operator

$$\Pi_0 f = f - \int_{\mathcal{E}} f\,\psi_0,$$

and the Hilbert space $L^2_0(\psi_0) = \Pi_0 L^2(\psi_0)$. Recall also the notation $\mathcal{A}^*$ for the adjoint of a given operator $\mathcal{A}$ on $L^2(\psi_0)$ (see (5.8)).

Theorem 8.1 (power expansion of the invariant measure). *Consider the dynamics* (8.1) *with generator* $\mathcal{L}_\eta = \mathcal{L}_0 + \eta\widetilde{\mathcal{L}}$, *where* $\mathcal{L}_0$ *is given in* (5.7) *and* $\widetilde{\mathcal{L}} = F \cdot \nabla_p$. *Let* r *be the spectral radius of the bounded operator* $(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^* \in \mathcal{B}(L_0^2(\psi_0))$*:*

$$r = \lim_{n\to+\infty} \left\| \left[\left(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0 \right)^* \right]^n \right\|^{1/n}.$$

Then, for $|\eta| < r^{-1}$, *the unique invariant measure can be written as* $\psi_\eta = f_\eta\psi_0$, *where* $f_\eta \in L^2(\psi_0)$ *admits the following expansion in powers of* η*:*

$$f_\eta = \left(1 + \eta(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^*\right)^{-1}\mathbf{1} = \left(1 + \sum_{n=1}^{+\infty}(-\eta)^n[(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^*]^n\right)\mathbf{1}. \tag{8.16}$$

The linear term in η in the expression of f_η is denoted by

$$\mathfrak{f}_1 = -(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^*\mathbf{1} = -\left(\mathcal{L}_0^{-1}\right)^*\widetilde{\mathcal{L}}^*\mathbf{1}. \tag{8.17}$$

Note that we can omit the projector Π_0 in the second equality since $\widetilde{\mathcal{L}}^*\mathbf{1} = \beta F^T M^{-1} p$ is in $L_0^2(\psi_0)$. As will become clear in the proof of Theorem 8.1, this result can actually be proven for other dynamics than (8.1). This will be made precise in Section 8.3.5. As a corollary of Theorem (8.1), we immediately get a formula for the transport coefficient ρ_F defined by (8.13), using the fact that $\int_{\mathcal{E}} R\psi_0 = 0$:

$$\rho_F = \lim_{\eta\to 0}\frac{\int_{\mathcal{E}} Rf_\eta\psi_0}{\eta} = \int_{\mathcal{E}} R\mathfrak{f}_1\psi_0. \tag{8.18}$$

Note that the measure $f_\eta\psi_0$ is a probability measure. In particular, the normalization constant for ψ_η does not depend on η. This is due to the fact that $f_\eta - \mathbf{1} \in L_0^2(\psi_0)$, so that

$$\int_{\mathcal{E}} \psi_\eta = \int_{\mathcal{E}} \psi_0 = 1.$$

It can also be shown by a direct computation that $f_\eta \geqslant 0$, see Remark 8.2 below.

Before writing the rigorous proof of Theorem 8.1, we present formal computations motivating the objects introduced in the statement of the theorem. The main idea is to assume that one can write $\psi_\eta = f_\eta\psi_0$, with $f_\eta = \mathbf{1} + \eta\mathfrak{f}_1 + \eta^2\mathfrak{f}_2 + \dots$. The stationary Fokker–Planck equation then reads

$$\left(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}}\right)^* f_\eta = \left(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}}\right)^* \left(\mathbf{1} + \eta\mathfrak{f}_1 + \eta^2\mathfrak{f}_2 + \dots\right) = 0,$$

which suggests that

$$\mathcal{L}_0^*\mathfrak{f}_1 + \widetilde{\mathcal{L}}^*\mathbf{1} = 0,$$

and similar equations for higher order terms. This leads indeed to $\mathfrak{f}_{n+1} = (-\mathcal{L}_0^*)^{-1}\widetilde{\mathcal{L}}^*\mathfrak{f}_n$, and hence to (8.16). The strategy of the proof is to show that the functions $\mathfrak{f}_n$ are well defined, construct f_η, and check that this function satisfies the stationary Fokker–Planck equation which characterizes the invariant measure. It finally remains to make sure that $f_\eta\psi_0$ is indeed a probability measure; in particular, f_η should be nonnegative.

Proof. Let us first show that $(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^*$ is a bounded operator on $L_0^2(\psi_0)$. To this end, we show that its adjoint $\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$ is bounded from $L_0^2(\psi_0)$ to $L^2(\psi_0)$. For C^∞ and compactly supported functions φ,

$$\frac{\gamma}{\beta}\|\nabla_p\varphi\|_{L^2(\psi_0)}^2 = -\langle\mathcal{L}_0\varphi,\varphi\rangle_{L^2(\psi_0)} \leqslant \|\mathcal{L}_0\varphi\|_{L^2(\psi_0)}\|\varphi\|_{L^2(\psi_0)},$$

so that

$$\left\|\widetilde{\mathcal{L}}\varphi\right\|_{L^2(\psi_0)}^2 \leqslant \|\nabla_p\varphi\|_{L^2(\psi_0)}^2 \leqslant \frac{\beta}{\gamma}\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)}\|\varphi\|_{L^2(\psi_0)}.$$

Since $\mathcal{L}_0$ is invertible on $L_0^2(\psi_0)$ by Theorems 5.3 or 5.5, it follows that, for any $\varphi \in L_0^2(\psi_0)$,

$$\left\| \widetilde{\mathcal{L}} \mathcal{L}_0^{-1} \varphi \right\|_{L^2(\psi_0)}^2 \leqslant \frac{\beta}{\gamma} \|\varphi\|_{L^2(\psi_0)} \|\mathcal{L}_0^{-1} \varphi\|_{L^2(\psi_0)}.$$

The operator $\widetilde{\mathcal{L}} \mathcal{L}_0^{-1}$ is therefore bounded from $L_0^2(\psi_0)$ to $L^2(\psi_0)$, with operator norm bounded from above by $\beta \|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L_0^2(\psi_0))}/\gamma$. It follows that the operator $\Pi_0 \widetilde{\mathcal{L}} \mathcal{L}_0^{-1}$ is bounded on $L_0^2(\psi_0)$, so that its adjoint $(\widetilde{\mathcal{L}} \mathcal{L}_0^{-1})^* \Pi_0$ is also bounded on $L_0^2(\psi_0)$. In fact, $(\widetilde{\mathcal{L}} \mathcal{L}_0^{-1})^* \Pi_0 = (\widetilde{\mathcal{L}} \mathcal{L}_0^{-1})^*$ on $L_0^2(\psi_0)$, which proves that $(\widetilde{\mathcal{L}} \mathcal{L}_0^{-1})^*$ is bounded on $L_0^2(\psi_0)$ with operator norm bounded from above by $\sqrt{\beta \|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L_0^2(\psi_0))}/\gamma}$. As a consequence, the spectral radius r satisfies $r \leqslant \sqrt{\beta \|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L_0^2(\psi_0))}/\gamma}$.

It is then easy to check that (8.16) is a convergent series in $L^2(\psi_0)$ when $|\eta| r < 1$ since the series

$$\sum_{n=1}^{+\infty} (-\eta)^n [(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^*]^n$$

converges in $\mathcal{B}(L_0^2(\psi_0))$. Therefore, the function f_η defined by (8.16) is well defined in $L^2(\psi_0)$. We denote henceforth $\widetilde{\psi}_\eta = f_\eta \psi_0$. Note that $\int_{\mathcal{E}} \widetilde{\psi}_\eta = 1$ since $f_\eta - \mathbf{1} \in L_0^2(\psi_0)$.

Our aim is to prove that $\psi_\eta = \widetilde{\psi}_\eta$. To this end, we consider the following characterization of the invariant probability measure: for any C^∞ and compactly supported function φ,

$$\forall t \geqslant 0, \qquad \int_{\mathcal{E}} (\mathrm{e}^{t\mathcal{L}_\eta} \varphi) \psi_\eta = \int_{\mathcal{E}} \varphi \, \psi_\eta. \tag{8.19}$$

The same equality holds with ψ_η replaced by $\widetilde{\psi}_\eta$. Indeed, a straightforward computation shows that, by definition of f_η,

$$\mathcal{L}_\eta^* f_\eta = \mathcal{L}_0^* \left(1 + \eta (\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^* \right) f_\eta = \mathcal{L}_0^* \mathbf{1} = 0. \tag{8.20}$$

Therefore, $\mathrm{e}^{t\mathcal{L}_\eta^*} f_\eta = f_\eta$ for all $t \geqslant 0$. The measure $\widetilde{\psi}_\eta = f_\eta \psi_0$ is therefore such that, for all $\varphi \in L^2(\psi_0)$ and all $t \geqslant 0$,

$$\int_{\mathcal{E}} (\mathrm{e}^{t\mathcal{L}_\eta} \varphi) \widetilde{\psi}_\eta = \int_{\mathcal{E}} \varphi \, (\mathrm{e}^{t\mathcal{L}_\eta^*} f_\eta) \psi_0 = \int_{\mathcal{E}} \varphi \, f_\eta \psi_0 = \int_{\mathcal{E}} \varphi \, \widetilde{\psi}_\eta.$$

This equality can be extended to bounded, measurable functions φ.

It is however not possible to conclude at this stage that $\psi_\eta = \widetilde{\psi}_\eta$ since (8.19) characterizes invariant probability measures; whereas it is not clear that $\widetilde{\psi}_\eta$ is a probability measure (the non-negativity of the density is not guaranteed; see however Remark 8.2 below, which provides an alternative way to conclude the proof presented here). To prove the non-negativity, we rely on the ergodicity of the continuous dynamics: for any bounded measurable function φ and any initial condition $(q_0, p_0) \in \mathcal{E}$, it holds by (8.10)

$$\mathbb{E}^{(q_0,p_0)} \left(\frac{1}{t} \int_0^t \varphi(q_s, p_s) \right) = \frac{1}{t} \int_0^t (\mathrm{e}^{s\mathcal{L}_\eta} \varphi)(q_0, p_0) \, ds \xrightarrow[t \to +\infty]{} \int_{\mathcal{E}} \varphi \, \psi_\eta,$$

so that, by integration over $\mathcal{E}$ with respect to $\widetilde{\psi}_\eta$, and using Fubini's theorem to justify the first equality and the dominated convergence theorem for the limit,

$$\frac{1}{t} \int_0^t \left(\int_{\mathcal{E}} (\mathrm{e}^{s\mathcal{L}_\eta} \varphi) \, \widetilde{\psi}_\eta \right) ds = \int_{\mathcal{E}} \left(\frac{1}{t} \int_0^t \mathrm{e}^{s\mathcal{L}_\eta} \varphi \, ds \right) \widetilde{\psi}_\eta \xrightarrow[t \to +\infty]{} \int_{\mathcal{E}} \varphi \, \psi_\eta.$$

Since, for any $t > 0$,

$$\frac{1}{t} \int_0^t \left(\int_{\mathcal{E}} (\mathrm{e}^{s\mathcal{L}_\eta} \varphi) \, \widetilde{\psi}_\eta \right) ds = \int_{\mathcal{E}} \varphi \, \widetilde{\psi}_\eta,$$

we conclude that

$$\int_{\mathcal{E}} \varphi \, \widetilde{\psi}_\eta = \int_{\mathcal{E}} \varphi \, \psi_\eta.$$

This shows that $\widetilde{\psi}_\eta = \psi_\eta$. In particular, $\widetilde{\psi}_\eta \geqslant 0$.

Remark 8.2 (Positivity of the invariant measure). *It is possible to directly prove the positivity of the invariant density $f_\eta \psi_0$ by introducing the following Poisson equation:*

$$\mathcal{L}_\eta \Phi_\eta = \mathbf{1}_{\{f_\eta \leqslant 0\}} - \int_{\mathcal{E}} \mathbf{1}_{\{f_\eta \leqslant 0\}} \, \psi_\eta, \quad \int_{\mathcal{E}} \Phi_\eta \, \psi_\eta = 0, \tag{8.21}$$

where f_η is defined by (8.16)*. This equation is well posed since $\mathcal{L}_\eta$ is invertible on weighted B^∞ spaces of functions with average 0 with respect to ψ_η (see the discussion after Proposition 8.1). Now, by* (8.20)*,*

$$\int_{\mathcal{E}} (\mathcal{L}_\eta \Phi_\eta) f_\eta \, \psi_0 = \int_{\mathcal{E}} \Phi_\eta \left(\mathcal{L}_\eta^* f_\eta \right) \psi_0 = 0. \tag{8.22}$$

On the other hand, by definition of Φ_η,

$$\begin{aligned} \int_{\mathcal{E}} (\mathcal{L}_\eta \Phi_\eta) f_\eta \psi_0 &= \int_{\mathcal{E}} \mathbf{1}_{\{f_\eta \leqslant 0\}} f_\eta \, \psi_0 - \left(\int_{\mathcal{E}} \mathbf{1}_{\{f_\eta \leqslant 0\}} \, \psi_\eta \right) \int_{\mathcal{E}} f_\eta \psi_0 \\ &= \int_{\mathcal{E}} \mathbf{1}_{\{f_\eta \leqslant 0\}} f_\eta \, \psi_0 - \int_{\mathcal{E}} \mathbf{1}_{\{f_\eta \leqslant 0\}} \, \psi_\eta. \end{aligned}$$

The first integral on the right-hand side of the previous equality is non-positive, while the second one is non-negative; hence the quantity on the right-hand side is non-positive. Since the right-hand side is equal to 0 by (8.22)*, each term must be 0. This allows us to conclude that $f_\eta \geqslant 0$ almost everywhere (using the first integral, since ψ_0 has a positive density with respect to the Lebesgue measure).*

8.3.4 Reformulating the linear response as an integrated correlation

A very useful corollary of (8.17)–(8.18) is the following reformulation of the linear response definition (8.13) of the transport coefficient through the celebrated Green–Kubo formula. To state it, we introduce the conjugated response function, formally defined as $S = \widetilde{\mathcal{L}}^* \mathbf{1}$. Its expression is found in practice by integrations by parts, as follows: for all C^∞ and compactly supported function φ,

$$\int_{\mathcal{E}} \widetilde{\mathcal{L}} \varphi \, \psi_0 = \int_{\mathcal{E}} \varphi \, S \, \psi_0. \tag{8.23}$$

Note that the expression of S is determined by the applied perturbation $\widetilde{\mathcal{L}}$, and not by the response function R chosen in (8.13). For the non-equilibrium Langevin dynamics (8.1), a simple computation shows that

$$S(q,p) = \beta R(q,p) = \beta F^T M^{-1} p.$$

Note that it can be directly checked that $S \in L^2_0(\psi_0)$. In fact, (8.23) with the choice $\varphi = \mathbf{1}$ shows that S automatically has average 0 with respect to ψ_0 as soon as $\widetilde{\mathcal{L}} \mathbf{1} = 0$.

Proposition 8.2 (Green–Kubo formula). *Consider the non-equilibrium Langevin dynamics* (8.1) *and the definition* (8.23) *of the conjugate function. For any $R \in L^2_0(\psi_0)$,*

$$\lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_0^{+\infty} \mathbb{E}_0(R(q_t,p_t) S(q_0,p_0)) \, dt, \tag{8.24}$$

where the expectation $\mathbb{E}_\eta$ is with respect to the invariant measure $\psi_\eta(q,p)\, dq\, dp$ of the non-equilibrium dynamics (8.1)*, while the expectation $\mathbb{E}_0$ on the right-hand side is taken over all initial conditions distributed according to the canonical measure $\psi_0(q,p)\, dq\, dp$, and over all realizations of the reference equilibrium dynamics with generator $\mathcal{L}_0$.*

The Green-Kubo formula thus shows that a non-equilibrium property (namely the transport coefficient $\rho_F = \lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta}$ in the left-hand side of (8.24)) can be obtained using simulations at equilibrium, namely for $\eta = 0$ (see the right-hand side in (8.24)). This result can easily be generalized to other dynamics as soon as the perturbation $\widetilde{\mathcal{L}}$ is such that $S \in L^2(\psi_0)$ and the linear response result (8.17) holds (see Section 8.3.5 for possible assumptions on $\widetilde{\mathcal{L}}$).

Proof. In view of (8.13), (8.17) and (8.18), as well as the equality

$$-\mathcal{L}_0^{-1} = \int_0^{+\infty} \mathrm{e}^{t\mathcal{L}_0}\, dt$$

as operators on $L^2_0(\psi_0)$ (as given by Theorem 5.5), we can write, for $R \in L^2_0(\psi_0)$,

$$\lim_{\eta\to 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_{\mathcal{E}} R\, \mathfrak{f}_1\, \psi_0 = -\int_{\mathcal{E}} \left(\mathcal{L}_0^{-1} R\right) \left(\widetilde{\mathcal{L}}^* \mathbf{1}\right) \psi_0 = \int_0^{+\infty} \mathbb{E}_0(R(q_t,p_t) S(q_0,p_0))\, dt,$$

which gives the claimed result.

Definition of the mobility

Let us rewrite equation (8.24) more precisely in the context of (8.1). The mobility ρ_F in the direction F, defined in (8.13), is equal to β times the integrated velocity autocorrelation:

$$\rho_F = \lim_{\eta\to 0} \frac{\mathbb{E}_\eta(F\cdot M^{-1}p)}{\eta} = \beta \int_0^{+\infty} \mathbb{E}_0\left[(F\cdot M^{-1}p_t)(F\cdot M^{-1}p_0)\right] dt. \tag{8.25}$$

In fact, a simple computation also allows to relate the mobility defined by the linear response of a nonequilibrium dynamics, to the self-diffusion coefficient, which is an equilibrium property. The latter quantity is defined by the so-called Einstein formula

$$D_F = \lim_{T\to+\infty} \frac{\mathbb{E}_0\Big(F\cdot(Q_T - Q_0)\Big)^2}{2T},$$

where

$$Q_t - Q_0 = \int_0^t M^{-1}p_s\, ds \in \mathbb{R}^D$$

is the unperiodized displacement, and where, as in (8.25), the expectation is over all initial conditions distributed according to $\psi_0(q,p)\, dq\, dp$, and over all realizations of the reference equilibrium dynamics (with generator $\mathcal{L}_0$ defined in (5.7)).

Remark 8.3. *It is in fact possible to prove that the diffusively rescaled process $\varepsilon F^T(Q_{t/\varepsilon^2} - Q_0)$ weakly converges on finite time intervals to an effective Brownian motion with covariance D_F in the limit $\varepsilon \to 0$, see [212, 236].*

The relation between the mobility and the self-diffusion coefficient is

$$\rho_F = \beta D_F.$$

This equality is based on the identity (obtained similarly to (4.18))

$$\mathbb{E}_0\Big(F\cdot(Q_T - Q_0)\Big)^2 = 2T \int_0^T \mathbb{E}_0\Big((F\cdot M^{-1}p_t)(F\cdot M^{-1}p_0)\Big)\left(1 - \frac{t}{T}\right) dt.$$

An application of the dominated convergence theorem gives the conclusion when the autocorrelation function is integrable, using the expression (8.25) of the mobility ρ_F. This is the case when $\left|\mathbb{E}_0\Big((F\cdot M^{-1}p_t)(F\cdot M^{-1}p_0)\Big)\right| \leqslant K\mathrm{e}^{-\lambda t}$, see Section 5.4 for techniques to prove such inequalities, for instance Theorem 5.5.

8.3.5 Generalization to other dynamics

It is of course possible to extend linear response results and Green–Kubo formulae to other dynamics than (8.1), either by generalizing the assumptions ensuring that Theorem 8.1 and Proposition 8.2 hold (as we do below), or by working with different set of assumptions as in [17].

An inspection of the proof of Theorem 8.1 shows that the result can be generalized to other perturbations, and in fact to other reference equilibrium dynamics $(x_t^\eta)_{t\geqslant 0}$ with generator $\mathcal{L}_\eta = \mathcal{L}_0 + \eta\widetilde{\mathcal{L}}$, under the following conditions.

(1) *Existence of a unique invariant measure.* For any $\eta \in \mathbb{R}$, the perturbed dynamics admits a unique invariant measure with C^∞ density $\psi_\eta(x)$ with respect to the Lebesgue measure dx on $\mathcal{X}$. Such statements are proved relying on the results of Sections 3.3.1 and 5.3.1 (for the regularity).

(2) *Ergodicity of the perturbed dynamics.* The perturbed dynamics is ergodic in the following sense: for any bounded measurable function φ and almost all initial condition x_0,

$$\frac{1}{t}\int_0^t \varphi(x_s)\,ds \xrightarrow[t\to+\infty]{} \int_{\mathcal{X}} \varphi\,\psi_\eta \quad \text{almost surely.}$$

See Sections 4.2.1 and 5.3 for techniques to obtain such convergence results. Alternatively, as discussed in Remark 8.2, the ergodicity condition can be replaced by solvability conditions for the Poisson equation (8.21).

(3) *Properties of the equilibrium dynamics.* $\mathrm{Ker}(\mathcal{L}_0^*) = \mathbf{1}$ and $\mathcal{L}_0^*$ is invertible on $L_0^2(\psi_0)$. See Proposition 4.2 for overdamped Langevin dynamics, and Theorems 5.3 and 5.5 for Langevin dynamics.

(4) *Properties of the perturbation.* $\mathrm{Ran}(\widetilde{\mathcal{L}}^*) \subset L_0^2(\psi_0)$ and $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is bounded on $L_0^2(\psi_0)$. As discussed after (8.23), the function $\widetilde{\mathcal{L}}^*\varphi$ has average 0 with respect to ψ_0 when $\widetilde{\mathcal{L}}\mathbf{1} = 0$ since

$$\int_{\mathcal{X}} \widetilde{\mathcal{L}}^*\varphi\,\psi_0 = \int_{\mathcal{X}} \varphi\,\widetilde{\mathcal{L}}\mathbf{1}\,\psi_0 = 0.$$

The last condition, namely that $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is bounded on $L_0^2(\psi_0)$, expresses the fact that the perturbation $\widetilde{\mathcal{L}}$ is sufficiently small. A typical way of proving that $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is bounded on $L_0^2(\psi_0)$ is, as at the beginning of the proof of Theorem 8.1, to show that $\widetilde{\mathcal{L}}$ is $\mathcal{L}_0$-bounded, namely that there exist $a, b > 0$ such that, for all C^∞ and compactly supported functions φ,

$$\left\|\widetilde{\mathcal{L}}\varphi\right\|_{L^2(\psi_0)} \leqslant a\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)} + b\|\varphi\|_{L^2(\psi_0)}. \tag{8.26}$$

Then, for all $\varphi \in L_0^2(\psi_0)$,

$$\left\|\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}\varphi\right\|_{L^2(\psi_0)} \leqslant a\|\varphi\|_{L^2(\psi_0)} + b\left\|\mathcal{L}_0^{-1}\varphi\right\|_{L^2(\psi_0)},$$

so that $\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$, and its adjoint, are bounded operators on $L_0^2(\psi_0)$ with operator norm bounded by $a + b\|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L_0^2(\psi_0))}$.

Stronger perturbations

There are situations for which the condition (8.26) is not satisfied, or may be difficult to prove. This is the case for instance for generalizations of the dynamics (8.2), for which the perturbation operator $\widetilde{\mathcal{L}}$ involves second derivatives of the momenta p. More precisely, consider the dynamics (8.3) with $T_\mathrm{L} = T + \Delta T$ and $T_\mathrm{R} = T - \Delta T$, and set $\eta = 2\Delta T$. The reference equilibrium dynamics is the Langevin dynamics (8.3) with the two thermostats at the boundaries at the same temperature T. Its generator reads

$$\mathcal{L}_0 = \sum_{i=1}^{N} p_i \partial_{q_i} - (\partial_{q_i} V)\, \partial_{p_i} - \gamma\Big(p_1 \partial_{p_1} + p_N \partial_{p_N}\Big) + \gamma T\Big(\partial_{p_1}^2 + \partial_{p_N}^2\Big), \tag{8.27}$$

and the invariant probability measure has a density $\psi_0(q,p) = Z^{-1}\mathrm{e}^{-H(q,p)/T}$, where H is given by (8.4). The generator of the perturbation is

$$\widetilde{\mathcal{L}} = \gamma(\partial_{p_1}^2 - \partial_{p_N}^2). \tag{8.28}$$

In this case, it is not clear whether it is possible to write an expansion of the invariant measure as a power series in η. Nonetheless, linear response results on average properties can still be stated by following the same strategy as in the proof of Theorem 6.1. We assume to this end that Assumption 6.1 is satisfied for $\mathcal{A}_1 = \mathcal{L}_0$ and $\mathcal{A}_1 = \mathcal{L}_0^*$. First, introduce $\mathfrak{f}_1$ such that

$$\int_{\mathcal{X}} \Big[(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}})\varphi\Big]\,(1+\eta\mathfrak{f}_1)\psi_0 = \mathrm{O}(\eta^2).$$

A simple computation shows that $\mathfrak{f}_1$ is formally given by (8.17). In fact, $\mathfrak{f}_1 = -(\mathcal{L}_0^*)^{-1} S$ where S is defined in (8.23). We next replace φ by $Q_\eta\varphi$ where Q_η is the approximate inverse

$$Q_\eta = \Pi_0 \mathcal{L}_0^{-1} \Pi_0 - \eta \Pi_0 \mathcal{L}_0^{-1} \Pi_0 \widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0.$$

The operator Q_η is a well-defined operator acting on C^∞ functions with zero average with respect to ψ_0. By computations similar to the ones performed in the last part of the proof of Theorem 6.1, it can therefore be shown that, under moment conditions on the invariant measure (*i.e.*, ψ_η integrates all the scale functions appearing in Definition 6.1),

$$\int_{\mathcal{X}} \varphi\, \psi_\eta = \int_{\mathcal{X}} \varphi\, \psi_0 + \eta \int_{\mathcal{X}} \varphi\, \mathfrak{f}_1\, \psi_0 + \eta^2 r_{\varphi,\eta}, \tag{8.29}$$

where $|r_{\varphi,\eta}| \leqslant K$ for $|\eta|$ sufficiently small.

Definition of the thermal conductivity

Assume that there exists a unique invariant probability measure for the dynamics (8.3) (see Remark 8.1), and denote by $\mathbb{E}_{\Delta T}$ the associated expectation. The thermal conductivity is then defined by the linear response of the energy current:

$$\kappa = \lim_{\Delta T \to 0} \frac{\mathbb{E}_{\Delta T}(J)}{\Delta T} = \beta^2 \gamma \int_0^{+\infty} \int_{\mathcal{E}} \left(\mathrm{e}^{t\mathcal{L}_0} J\right) (p_1^2 - p_N^2)\psi_0 \, dt, \tag{8.30}$$

since the conjugate response $S = \widetilde{\mathcal{L}}^* \mathbf{1} = \gamma\beta^2(p_1^2 - p_N^2)$ in view of (8.23) and (8.28). Some (non trivial) manipulations allow to rewrite the above correlation in terms of the energy current autocorrelation (see for instance [158, 28]):

$$\kappa = 2\beta^2 \int_0^{+\infty} \mathbb{E}_0\Big(j_{i+1,i}(q_t,p_t) J(q_0,p_0)\Big)\, dt = \frac{2\beta^2}{N-1} \int_0^{+\infty} \mathbb{E}_0\Big(J(q_t,p_t) J(q_0,p_0)\Big)\, dt, \tag{8.31}$$

where the equalities hold for any $i = 1, \ldots, N-1$, and the currents are defined in (8.14).

Exercise 8.1. *Prove* (8.31) *by first taking adjoints in the last integral of* (8.30) *and resorting to a time reversal argument, and then using the following identity obtained from Itô calculus to compute the time integral of the current:*

$$d\left(\sum_{j=1}^{i} \varepsilon_j - \sum_{j=i+1}^{N} \varepsilon_j\right) = \Big(-2j_{i+1,i} - \gamma(p_1^2 - p_N^2)\Big)dt + dM_{t,i},$$

where $M_{t,i}$ are martingales.

8.4 Error estimates on the computation of transport coefficients

The results of the previous section show that there are two main ways to compute transport coefficients, either by discretizing the integrated correlation function based on the Green–Kubo formula (8.24), or by approximating the derivative of equilibrium averages with respect to the magnitude of the external forcing as in (8.13). In this section we provide, for both approaches, error estimates for these methods, starting with Green–Kubo formulas in Section 8.4.1, and then turning to linear response methods in Section 8.4.2.

8.4.1 Green–Kubo formulae

We first provide error estimates on linear responses computed using Green–Kubo formulae such as (8.24). We state the result on a general space $\mathcal{X}$ for a dynamics

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t, \tag{8.32}$$

with generator $\mathcal{L}$ (instead of the notation $\mathcal{L}_0$ used in Section 8.3). We assume that this dynamics admits a unique invariant probability measure π.

In order to approximate integrated correlation functions as the ones appearing on the right hand side of (8.24), two numerical parameters have to be introduced:

(i) a finite integration time τ to truncate the time integral;
(ii) a timestep Δt and a numerical scheme to approximate the continuous dynamics (see Lecture 6).

We successively discuss the approximation incurred by both parameters, adding a discussion on the statistical error when quantifying the bias arising from the truncation in time. As in Lecture 6, it turns out that statistical errors can be understood to first order in Δt at the level of the continuous dynamics, so that we discuss this issue before quantifying the timestep bias.

Truncation error and statistical error

From a numerical viewpoint, a first task is to truncate time integrals such as the ones appearing on the right hand side of (8.24) as

$$\rho_\tau = \int_0^\tau \mathbb{E}_0\left[R(x_t)S(x_0)\right]dt = \int_{\mathcal{X}} \left[\int_0^\tau \mathrm{e}^{t\mathcal{L}}R\,dt\right] S\,d\pi. \tag{8.33}$$

The reference integrated correlation function is denoted by ρ. Assuming that there exist $K \geqslant 1$ and $\lambda > 0$ such that (see Proposition 4.2 for overdamped Langevin dynamics and Theorem 5.5 for Langevin dynamics)

$$\left\|\mathrm{e}^{t\mathcal{L}}\right\|_{\mathcal{B}(L^2_0(\pi))} \leqslant K\mathrm{e}^{-\lambda t},$$

and that $R, S \in L^2_0(\pi)$, a simple computation shows that

$$|\rho - \rho_\tau| \leqslant \|R\|_{L^2(\pi)}\|S\|_{L^2(\pi)}\frac{K}{\lambda}\mathrm{e}^{-\lambda\tau}.$$

The bias due to the time truncation is therefore exponentially decreasing, although it may be difficult in practice to accurately estimate the exponential convergence rate.

The formula (8.33) naturally suggests the following Monte Carlo estimator for ρ_τ, based on N_{real} independent realizations $(x_t^m)_{0\leqslant t\leqslant\tau}$ of the dynamics (8.32) starting from i.i.d. initial conditions x_0^m and driven by independent Brownian motions W_t^m (with $1 \leqslant m \leqslant N_{\mathrm{real}}$):

$$\widehat{\rho}_\tau = \frac{1}{N_{\mathrm{real}}}\sum_{m=1}^{N_{\mathrm{real}}}\int_0^\tau R(x_t^m)S(x_0^m)\,dt.$$

work in progress here, to discuss

Formally, by Itô calculus,

$$\int_0^\tau R(x_t^m)\,dt = M_\tau^m + \Phi(x_0^m) - \Phi(x_\tau^m), \qquad M_\tau^m = \int_0^\tau \nabla\Phi(x_t^m)^T\sigma(x_t^m)\,dW_t^m,$$

where Φ satisfies the Poisson equation $-\mathcal{L}\Phi = R$. Sufficient conditions for the latter equation to be well posed and to admit smooth solutions are provided in Lectures 4 and 5. Typically,

$$\mathrm{Var}\left[\frac{1}{N_{\mathrm{real}}}\sum_{m=1}^{N_{\mathrm{real}}}(\Phi(x_0^m)-\Phi(x_t^m))S(x_0^m)\right] \sim \frac{1}{N_{\mathrm{real}}},$$

while

$$\mathrm{Var}\left[\frac{1}{N_{\mathrm{real}}}\sum_{m=1}^{N_{\mathrm{real}}} M_\tau^m S(x_0^m)\right] = \frac{\mathbb{E}_0(S^2)}{N_{\mathrm{real}}}\int_0^\tau \mathbb{E}_0\left(\left|\sigma^T(x_t)\nabla\Phi(x_t)\right|^2\right)dt \sim \frac{\tau}{N_{\mathrm{real}}},$$

see [222] for precise statements and an extension of the analysis performed here for continuous dynamics to the case when the dynamics is discretized in time. The main output of this analysis is that the variance of Green–Kubo estimators $\widehat{\rho}_\tau$ diverges as the truncation time increases. The mean-square error associated with $\widehat{\rho}_\tau - \rho$ is of the form

$$\frac{a}{\lambda}\mathrm{e}^{-\lambda\tau} + \frac{b\tau}{N_{\mathrm{real}}},$$

the optimal time to minimize this error being (when $a > b/N_{\mathrm{real}}$)

$$\tau = \frac{1}{\lambda}\log\left(\frac{a}{b}N_{\mathrm{real}}\right).$$

For this choice of optimal time, an error of order $\log(N_{\mathrm{real}})/N_{\mathrm{real}}$ is achieved for a computational cost of order $N_{\mathrm{real}}\tau \sim N_{\mathrm{real}}\log N_{\mathrm{real}}$.

Time-step bias

We discuss the time step bias arising in Green–Kubo formulas from the discretization of the continuous dynamics (8.32). This was first studied for Langevin dynamics in [169], and then abstracted in [180, Theorem 5.6]. Recall also that results on the timestep bias allow to make precise the statements in Section 6.1.3 relating the asymptotic variance of the continuous dynamics and its discretization.

As in Sections 6.1 and 6.2.4, we denote by $P_{\Delta t}$ the transition operator of the underlying Markov chain induced by the discretization scheme, and denote by $\pi_{\Delta t}$ the invariant measure of the numerical scheme (as in ??). We also introduce the projection operator

reference to change

$$\Pi_{\Delta t}\varphi = \varphi - \int_{\mathcal{X}} \varphi\,d\pi_{\Delta t},$$

as well as

$$B^\infty_{\mathscr{W}_s,\Delta t}(\mathcal{X}) = \Pi_{\Delta t}B^\infty_{\mathscr{W}_s}(\mathcal{X}) = \left\{\varphi \in B^\infty_{\mathscr{W}_s}(\mathcal{X}) \;\middle|\; \int_{\mathcal{X}} \varphi\,d\pi_{\Delta t} = 0\right\}.$$

The range of $\Pi_{\Delta t}$ is contained in the set of functions with average zero with respect to the invariant measure $\pi_{\Delta t}$ of the numerical scheme.

The error estimate is formulated for smooth functions in the sense of Definition 6.1. We still suppose that Assumption 6.1 holds with $\mathcal{A}_1 = \mathcal{L}$ (*i.e.*, the space $\mathcal{S}$ introduced in Definition 6.1 is dense in $L^2(\pi)$ and the operator $\mathcal{L}^{-1} : \mathcal{S}_0 \to \mathcal{S}_0$ is well defined, where $\mathcal{S}_0$ is defined in (6.13)).

Theorem 8.2 (Error estimates for Green–Kubo formulas). *Consider a numerical method with an invariant measure $\pi_{\Delta t}$ which integrates any scale function $\mathscr{W}_n$ introduced in Definition 6.1. Assume that there exists an integer $\alpha \geqslant 1$, such that, for any observable $\varphi \in \mathcal{S}$ there is $K, \Delta t^* > 0$ for which the following conditions hold:*

(1) Error on the invariant measure:

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \, d\pi + \Delta t^{\alpha} r_{\varphi,\Delta t}, \tag{8.34}$$

with $|r_{\varphi,\Delta t}| \leqslant K$ *for* $0 < \Delta t \leqslant \Delta t^*$.

(2) Expansion of $P_{\Delta t}$*:*

$$-\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\varphi = \mathcal{L}\varphi + \Delta t S_1 \varphi + \cdots + \Delta t^{\alpha-1} S_{\alpha-1}\varphi + \Delta t^{\alpha} \widetilde{R}_{\alpha,\Delta t}\varphi, \tag{8.35}$$

where the operators $S_1, \ldots, S_{\alpha-1}, \widetilde{R}_{\alpha,\Delta t}$ *(which are defined independently of* φ*) are well defined on* $\mathcal{S}$ *with values in* $\mathcal{S}$*; and there exists* $s_0 \in \mathbb{N}$ *(depending on* α *and* φ*) such that* $\|\widetilde{R}_{\alpha,\Delta t}\varphi\|_{B^{\infty}_{\mathscr{W}_{s_0}}} \leqslant K$ *for* $0 < \Delta t \leqslant \Delta t^*$.

Moreover, we assume that

(3) Uniform-in-Δt *exponential convergence of* $P_{\Delta t}$*. For any* $s \geqslant 0$*, there exist* $C_s, \lambda_s > 0$ *such that, for all* $0 < \Delta t \leqslant \Delta t^*$*,*

$$\forall n \in \mathbb{N}, \qquad \|P^n_{\Delta t}\|_{\mathcal{B}(B^{\infty}_{\mathscr{W}_s,\Delta t})} \leqslant C_s \, \mathrm{e}^{-\lambda_s n \Delta t}. \tag{8.36}$$

Then, the integrated correlation of two observables $\phi, \varphi \in \mathcal{S}_0$ *can be approximated by a Riemann sum up to an error of order* Δt^{α}*: there exists* $C > 0$ *such that*

$$\int_0^{+\infty} \mathbb{E}_{\pi}\left[\phi(x_t)\varphi(x_0)\right] dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\pi_{\Delta t}}\left[\widetilde{\phi}_{\Delta t,\alpha}(x^n)\varphi(x^0)\right] + \Delta t^{\alpha} r^{\phi,\varphi}_{\Delta t}, \tag{8.37}$$

with $|r^{\phi,\varphi}_{\Delta t}| \leqslant C$ *for* $0 < \Delta t \leqslant \Delta t^*$*. In this expression, the expectation* $\mathbb{E}_{\pi}$ *is over all initial conditions* $(q_0, p_0) \sim \pi$ *and over all realizations of the continuous dynamics with generator* $\mathcal{L}$*, while the expectation* $\mathbb{E}_{\pi_{\Delta t}}$ *is over all initial conditions* $(q_0, p_0) \sim \pi_{\Delta t}$ *and over all realizations of the Markov chain induced by* $P_{\Delta t}$*. Moreover, the modified observable* $\widetilde{\phi}_{\Delta t,\alpha} \in \mathcal{S}$ *is defined as* $\widetilde{\phi}_{\Delta t,\alpha} = \Pi_{\Delta t}\phi_{\Delta t,\alpha}$ *with*

$$\phi_{\Delta t,\alpha} = (\mathrm{Id} + \Delta t \, S_1\mathcal{L}^{-1} + \cdots + \Delta t^{\alpha-1} S_{\alpha-1}\mathcal{L}^{-1})\phi. \tag{8.38}$$

This result deserves several comments, both on the three main assumptions (8.34), (8.35) and (8.36), as well as on the error estimate (8.37) itself. The proof is presented after this discussion.

Let us start by discussing the assumptions of Theorem 8.2. Equation (8.34) can be proved by following the general strategy presented in Theorem 6.1. Note that the remainder term in (8.34) can vanish, for example when a Metropolis procedure is superimposed on the numerical scheme. In this case, α is determined by (8.35). Condition (8.35) has already been encountered when proving error estimates on the invariant measure (see (6.12)). On the other hand, proving the uniform-in-Δt convergence (8.36) requires more work. The typical way to proceed is to obtain (i) uniform-in-Δt Lyapunov conditions (see [169, Lemma 2.7] for Langevin dynamics on compact position spaces), which is usually not too difficult when weakly consistent discretization schemes are considered; and (ii) uniform-in-Δt minorization conditions. Such estimates can be obtained from the results of [22], by comparing discrete dynamics with continuous ones [35], or by careful computations allowing to write the evolution over short times as a perturbation of a driftless stochastic dynamics [76].

work in progress

Let us now comment on the error estimate (8.37). First, the result shows that the error is of order Δt^{α}, upon modifying the observable ϕ as $\widetilde{\phi}_{\Delta t,\alpha}$. Therefore, a first limitation to the reduction of the error in Green–Kubo formulae arises from the error on the invariant measure itself. However, in practice, especially when α is large, the error is actually determined by the approximation of the corrected observable $\widetilde{\phi}_{\Delta t,\alpha}$. When the operators S_k are powers of $\mathcal{L}$, the correction terms $S_k\mathcal{L}^{-1}$ in (8.38) can be easily computed. Let us denote by k_0 the last index for which $S_k\mathcal{L}^{-1}\phi$ can be evaluated. For example (see the discussion after (6.12)), if the discretization method is of weak

order k_0, then $S_k = \mathcal{L}^k/k!$ for all $k = 1, \dots, k_0$, so that $S_k \mathcal{L}^{-1}\phi$ is easy to evaluate up to $k = k_0$. If $k_0 < \alpha$, the error estimate which can be used in practice is

$$\int_0^{+\infty} \mathbb{E}_\pi \left[\phi(x_t)\varphi(x_0)\right] dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\pi_{\Delta t}} \left[\widetilde{\phi}_{\Delta t,k_0}(x^n)\varphi(x^0)\right] + \Delta t^{k_0+1} r_{\Delta t}^{\phi,\varphi}.$$

However, even if $\phi_{\Delta t,k_0}$ can be actually evaluated, it still remains to approximate $\widetilde{\phi}_{\Delta t,k_0} = \Pi_{\Delta t}\phi_{\Delta t,k_0}$, typically by approximating the average of $\phi_{\Delta t,k_0}$ with respect to $\pi_{\Delta t}$ by trajectory averages.

Let us again emphasize a very interesting application of Theorem 8.2: the approximation of the variance of discretizations of SDEs. This allows to prove formulas such as (6.9), and/or to modify quadature rules in the integral in time of the correlation in order to lower the bias (see Remark 8.5 below).

Remark 8.4 (Error estimates for Metropolis–Hastings dynamics). *For discretizations of the continuous dynamics stabilized by a Metropolis-Hastings procedure, as MALA for overdamped Langevin, the invariant measure of the numerical scheme is exact by construction. However, since the quantity $S_1\mathcal{L}^{-1}\phi$ cannot be evaluated in general, the resulting approximation of the integrated correlation is based on $\widetilde{\phi}_{\Delta t,0} = \Pi_{\Delta t}\phi$, which leads to an approximation of order Δt of the Green–Kubo integral. An error estimate of order $\Delta t^{3/2}$ can nevertheless be obtained by modifying the Metropolis–Hastings proposal. It is even possible to obtain errors of order Δt^2 by modifying the Metropolis acceptance rule. See [91] and [92] for further precisions.*

Let us now present the proof of Theorem 8.2.

Proof. Fix two observables $\varphi, \phi \in \mathcal{S}_0$. Note that

$$\int_0^{+\infty} \mathbb{E}_\pi \left[\phi(x_t)\varphi(x_0)\right] dt = \int_{\mathcal{X}} (-\mathcal{L}^{-1}\phi)\varphi \, d\pi.$$

In order to introduce the correlation functions of the numerical scheme, we would like, in view of (8.35), to replace the measure π by $\pi_{\Delta t}$ and the operator $-\mathcal{L}^{-1}$ by

$$\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right)^{-1} = \Delta t \sum_{n=0}^{+\infty} P_{\Delta t}^n.$$

However this is not possible as such for two reasons. First, as indicated in (8.36), the above sum is only convergent when the operators under consideration are restricted to subspaces of functions with average 0 with respect to $\pi_{\Delta t}$. We therefore need to introduce the projections operators $\Pi_{\Delta t}$ to restrict $\mathcal{L}^{-1}$ to the range of $\Pi_{\Delta t}$. Second, it is not possible to directly consider the inverse of the right-hand side of (8.35), so we will introduce $(\mathrm{Id} - P_{\Delta t})^{-1}(\mathrm{Id} - P_{\Delta t})$ instead in order to retrieve some operator $\mathcal{L}$ at dominant order in Δt in order to cancel the inverse operator $\mathcal{L}^{-1}$.

Let us first introduce the projection operators $\Pi_{\Delta t}$ and the invariant measure $\pi_{\Delta t}$ of the numerical scheme, using the fact that $-\mathcal{L}^{-1}\phi$ has zero average with respect to π:

$$\begin{aligned}
\int_{\mathcal{X}} (-\mathcal{L}^{-1}\phi)\varphi \, d\pi &= \int_{\mathcal{X}} (-\mathcal{L}^{-1}\phi)\Pi_{\Delta t}\varphi \, d\pi \\
&= \int_{\mathcal{X}} (-\mathcal{L}^{-1}\phi)\Pi_{\Delta t}\varphi \, d\pi_{\Delta t} + \Delta t^\alpha \widetilde{r}_{\varphi\mathcal{L}^{-1}\phi,\Delta t}, \\
&= \int_{\mathcal{X}} \Pi_{\Delta t}(-\mathcal{L}^{-1}\phi)\Pi_{\Delta t}\varphi \, d\pi_{\Delta t} + \Delta t^\alpha \widetilde{r}_{\varphi\mathcal{L}^{-1}\phi,\Delta t}, \qquad (8.39)
\end{aligned}$$

where $|\widetilde{r}_{\varphi\mathcal{L}^{-1}\phi,\Delta t}| \leqslant K/2$ for $0 < \Delta t \leqslant \Delta t^*$ by (8.34) (possibly upon increasing the value of K and decreasing Δt^*).

The next step is to approximate $\Pi_{\Delta t}(-\mathcal{L}^{-1}\phi)$ in terms of powers of $P_{\Delta t}$. We use the fact that $\Pi_{\Delta t}P_{\Delta t} = P_{\Delta t}\Pi_{\Delta t}$, and that

$$\Pi_{\Delta t} = \Pi_{\Delta t}\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)^{-1}\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right) = \Pi_{\Delta t}\left(\Delta t\sum_{n=0}^{+\infty}P_{\Delta t}^n\right)\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right).$$

Note that the above sum is convergent in $\mathcal{B}(B^\infty_{\mathscr{W}_s,\Delta t})$ in view of (8.36). Relying on (8.35),

$$\begin{aligned}
-\Pi_{\Delta t}\mathcal{L}^{-1}\phi &= -\Pi_{\Delta t}\left(\Delta t\sum_{n=0}^{+\infty}P_{\Delta t}^n\right)\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)\mathcal{L}^{-1}\phi \\
&= \Delta t\left(\sum_{n=0}^{+\infty}P_{\Delta t}^n\right)\Pi_{\Delta t}\left(\mathcal{L}+\cdots+\Delta t^{\alpha-1}S_{\alpha-1}+\Delta t^\alpha\widetilde{R}_{\alpha,\Delta t}\right)\mathcal{L}^{-1}\phi, \\
&= \Delta t\sum_{n=0}^{+\infty}P_{\Delta t}^n\widetilde{\phi}_{\Delta t,\alpha}+\Delta t^\alpha\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)^{-1}\Pi_{\Delta t}\widetilde{R}_{\alpha,\Delta t}\mathcal{L}^{-1}\phi.
\end{aligned}$$

Note that the sums on the right-hand side is well defined in view of the decay estimates (8.36). Plugging the above equality in (8.39) leads to

$$\begin{aligned}
\int_{\mathcal{X}}(-\mathcal{L}^{-1}\phi)\varphi\,d\pi &= \Delta t\sum_{n=0}^{+\infty}\int_{\mathcal{X}}P_{\Delta t}^n\widetilde{\phi}_{\Delta t,\alpha}(\Pi_{\Delta t}\varphi)\,d\pi_{\Delta t} \\
&\quad+\Delta t^\alpha\int_{\mathcal{X}}\left[\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)^{-1}\Pi_{\Delta t}\widetilde{R}_{\alpha,\Delta t}\mathcal{L}^{-1}\phi\right]\Pi_{\Delta t}\varphi\,d\pi_{\Delta t}+\Delta t^\alpha\widetilde{r}_{\varphi\mathcal{L}^{-1}\phi,\Delta t}.
\end{aligned}$$

To conclude the proof, we use the fact that, for a given smooth function f and upon increasing K and decreasing Δt^*, there exist an integer s and a constant $\widetilde{K}>0$ (depending on f) such that $\|\widetilde{R}_{\alpha,\Delta t}f\|_{B^\infty_{\mathscr{W}_s}}\leqslant\widetilde{K}$ for any $0<\Delta t\leqslant\Delta t^*$. In addition, the following resolvent bound is directly obtained from (8.36):

$$\left\|\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)^{-1}\right\|_{\mathcal{B}(B^\infty_{\mathscr{W}_s,\Delta t})}\leqslant\frac{C_s}{\lambda_s}.$$

Finally, $\pi_{\Delta t}$ integrates all scale functions $\mathscr{W}_n$ by assumption. Therefore, upon increasing the value of K, the following inequality holds for any $0<\Delta t\leqslant\Delta t^*$:

$$\left|\int_{\mathcal{X}}\left[\left(\frac{\mathrm{Id}-P_{\Delta t}}{\Delta t}\right)^{-1}\Pi_{\Delta t}\widetilde{R}_{\alpha,\Delta t}\mathcal{L}^{-1}\phi\right]\Pi_{\Delta t}\varphi\,d\pi_{\Delta t}\right|\leqslant\frac{K}{2}.$$

Since

$$\sum_{n=0}^{+\infty}\int_{\mathcal{X}}P_{\Delta t}^n\widetilde{\phi}_{\Delta t,\alpha}(\Pi_{\Delta t}\varphi)\,d\pi_{\Delta t}=\sum_{n=0}^{+\infty}\int_{\mathcal{X}}\left(P_{\Delta t}^n\widetilde{\phi}_{\Delta t,\alpha}\right)\varphi\,d\pi_{\Delta t}=\sum_{n=0}^{+\infty}\mathbb{E}_{\pi_{\Delta t}}\left[\widetilde{\phi}_{\Delta t,\alpha}(x^n)\varphi(x^0)\right],$$

equation (8.37) finally follows.

Remark 8.5 (Green–Kubo formulae for second-order schemes). *In the particular case when $\alpha=2$ in* (8.34)*, which is very relevant in practice (*e.g. *for second-order splittings of Langevin dynamics, or Geometric Langevin algorithms discussed in Section 6.2.4), it is possible to not modify the observable ϕ when S_1 is proportional to $\mathcal{L}^2$, by appropriately changing the quadrature rule. For schemes of weak order 2, for which $S_1=\mathcal{L}^2/2$, this amounts to discretizing the time integral with a trapezoidal rule instead of a Riemann sum. See [169, Corollary 2.20] and [92, Theorem 6] for further details.*

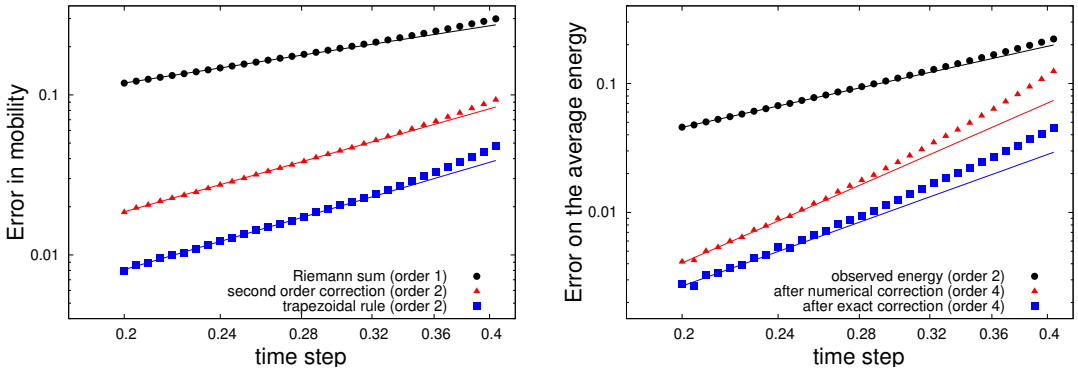


Fig. 8.1. (a) Error in the mobility as a function of the time step Δt when the integrated velocity autocorrelation function is computed using a Riemann sum or with the corrected formula (8.37) in the case $\alpha = 2$. The result from computing the integral using the trapezoidal rule is also shown. (b) Error in the computed average of total energy, with the correction term computed using the same step size by a discretization of (6.24) with the discrete Green–Kubo formula (8.37). Averages obtained with a reference correction computed more accurately at a smaller time step in a separate simulation are labelled as the 'exact correction'. In both cases, 'order α' means that the error scales as $C\Delta t^{\alpha}$.

To illustrate Theorem 8.2, we consider a simple two-dimensional system with position $q = (x, y) \in \mathcal{M} = (2\pi\mathbb{T})^2$, a potential energy function $V(q) = 2\cos(2x)+\cos(y)$, an inverse temperature $\beta = 1$, a friction $\gamma = 1$ and an identity mass matrix. Figure 8.1 displays simulation results obtained for the scheme associated with $P_{\Delta t}^{\gamma C, B, A, B, \gamma C}$ (see the discussion after (6.31) and [169] for the full expression of the numerical scheme) when approximating the mobility

$$\rho = \beta \int_0^{+\infty} \mathbb{E}_\mu(p_t \cdot p_0)\, dt.$$

For this second-order scheme, an approximation of the time integral based on a simple Riemann sum leads to errors of order Δt, while a second-order convergence is obtained upon modifying the observables according to (8.38) or using a trapezoidal rule. In addition, we show how to improve the computation of the average value of the Hamiltonian $H(q, p) = V(q) + |p|^2/2$ based on an estimation of the correction term (6.24) reformulated as some integrated correlation function. In the case of the total energy, the corresponding correction is proportional to the mobility ρ. As predicted by theoretical results similar to Theorem 6.1, errors in average properties can be reduced from Δt^2 to Δt^3 when the correction term is properly estimated; in fact, the errors can be shown to reduced to order Δt^4 (see [169, Theorem 2.16]).

8.4.2 Linear response approaches

In this part, we discuss how to approximate a transport coefficient by estimating numerically the derivative of steady state averages with respect to the forcing parameter, as given by (8.13) or the left hand side of (8.24). This requires expansions of the invariant measures of numerical approximations of non-equilibrium dynamics with respect to two small parameters: the magnitude η of the forcing and the time step Δt. To be more concrete, we illustrate the approach on the computation of the mobility with the perturbed Langevin dynamics (8.1). As in Section 8.4.1, we first discuss the statistical error at the level of the continuous dynamics, as well as the bias arising from the use of finite forcings magnitudes. We then present numerical schemes for the dynamics and state error estimates on the computation of average properties and linear responses, which allow to make precise the bias on transport coefficients due to the time discretization (following the presentation of [169, Section 3], to which we refer for further details).

Finite magnitude bias and statistical error

From a numerical viewpoint, the limit $\eta \to 0$ of the ratio in (8.13) is approximated by a finite difference using some finite value $\eta_\star > 0$:

$$\rho_{F,\eta_\star} = \frac{\mathbb{E}_{\eta_\star}(R)}{\eta_\star}. \tag{8.40}$$

In view of the expansion (8.16) (or more generally (8.29)), there exists $K > 0$ such that

$$|\rho_F - \rho_{F,\eta_\star}| \leqslant K\eta_\star,$$

so that the bias is of order one in η.

The formula (8.40) naturally suggests the following estimator ρ_F, based on longtime averages of the perturbed Langevin dynamics (8.1):

$$\widehat{\rho}_{F,\eta_\star} = \frac{1}{\eta_\star t}\int_0^t R(q_s,p_s)\,ds,$$

which converges almost surely to $\mathbb{E}_{\eta_\star}(R)/\eta_\star$ as $t \to +\infty$ by (8.10). The asymptotic variance associated with the time average $\eta_\star\widehat{\rho}_{F,\eta_\star}$ is (by manipulations similar to the ones leading to (8.29))

$$\sigma^2_{F,\eta_\star} = 2\int_{\mathcal{E}}\left[-\left(\mathcal{L}_0 + \eta_\star\widetilde{\mathcal{L}}\right)^{-1}\Pi_{\eta_\star}R\right]\Pi_{\eta_\star}R\,\psi_\eta = \sigma^2_{F,0} + \mathrm{O}(\eta_*).$$

Overall, the mean square error associated with the estimator $\widehat{\rho}_{F,\eta_\star}$ of ρ_F is therefore at dominant order of the form

$$a\eta_\star^2 + \frac{\sigma^2_{F,0}}{\eta_\star^2 t}.$$

In particular, the integration time t should be taken of order $\eta_\star^{-2}$ in order for the statistical error not to be too large. Since $\eta_\star$ should on the other hand be chosen small enough in order to limit the bias arising from the nonlinear response, this means that integration times should be quite long. More precisely, if one sets a tolerance $\varepsilon^2 > 0$ for the mean square error, then $\eta_\star \sim \varepsilon$ and $t \sim \varepsilon^{-4}$. The balance between the bias and the possibly huge statistical error is a challenge in linear response approaches.

Remark 8.6. *In practice, quite large forcings have to be used in order to measure the reponse of the system – in fact, the forcings are orders of magnitude larger than experimental forcings. To give an example, consider the computation of thermal transport in carbon nanotubes, for which temperature differences of 40-100K over distances of 1 μm are considered [48, 245]. Such temperature differences are needed to induce a sufficiently large response of the material that can emerge out of the statistical noise in a reasonable simulation time (integration times of the order of nanoseconds in physical times; for systems of 5 μm in [48], this corresponds to 5 days of computation on a cluster of 120 cores). However, when converting to macroscopic units, one realizes that these temperature gradients are absolutely enormous since they correspond to a temperature variation of the order of $4 \times 10^7 - 10^8$ K over a distance of 1m! It is remarkable that linear response still holds at the microscopic level with such high gradients...*

Timestep bias

To integrate (8.1), we consider splitting schemes which reduce to the schemes presented in Section 6.2.4 when $\eta = 0$. Recall that $\mathcal{L}_0 = A + B + \gamma C$, where the elementary operators A, B, C are introduced in (6.30):

$$A = pM^{-1}\nabla_q, \qquad B = -\nabla V(q)^T\nabla_p, \qquad C = -p^TM^{-1}\nabla_p + \frac{1}{\beta}\Delta_p.$$

Since the aim is to decompose the evolution generated by $\mathcal{L}_\eta = \mathcal{L}_0 + \eta\widetilde{\mathcal{L}}$ into analytically integrable parts, there are two principal options: either replace B by

$$B_\eta = B + \eta\widetilde{\mathcal{L}}$$

or replace γC by $\gamma C + \eta\widetilde{\mathcal{L}}$. However, the schemes built on the latter option do not perform correctly in the overdamped limit, since their invariant measures are not consistent with the invariant measures of non-equilibrium overdamped Langevin dynamics, *i.e.*,

$$dq_t = (-\nabla V(q_t) + \eta F)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t. \tag{8.41}$$

The latter dynamics is obtained from (8.1) in the limit $\gamma \to +\infty$ upon rescaling the time as γt. To illustrate this point, consider for instance the first-order splitting scheme associated with the evolution operator

$$P_{\Delta t}^{A,B,\gamma C+\eta\widetilde{\mathcal{L}}} = \mathrm{e}^{\Delta t\, A}\,\mathrm{e}^{\Delta t\, B}\,\mathrm{e}^{\Delta t(\gamma C+\eta\widetilde{\mathcal{L}})},$$

i.e.,

$$\begin{aligned}
q^{n+1} &= q^n + \Delta t\, M^{-1} p^n,\\
\widetilde{p}^{n+1} &= p^n - \Delta t\, \nabla V(q^{n+1}),\\
p^{n+1} &= \alpha_{\Delta t}\widetilde{p}^{n+1} + \frac{1-\alpha_{\Delta t}}{\gamma}\,\eta F + \sqrt{\frac{1-\alpha_{\Delta t}^2}{\beta}M}\,G^n,
\end{aligned}$$

where $\alpha_{\Delta t} = \exp(-\gamma M^{-1}\Delta t)$ is defined after (6.31), and (G^n) is a sequence of i.i.d. Gaussian random vectors with identity covariance. When $M = \mathrm{Id}$ and $\gamma \to +\infty$, a standard Euler–Maruyama discretization of the *equilibrium* overdamped Langevin dynamics (*i.e.* $\eta = 0$) is obtained; whereas we would like to obtain a consistent discretization of non-equilibrium overdamped Langevin dynamics (8.41). This suggests that numerical methods based on the integration of $\gamma C + \eta\widetilde{\mathcal{L}}$ will not estimate correctly the mobility for large γ.

We therefore prefer to consider schemes obtained by replacing B with $B + \eta\widetilde{\mathcal{L}}$, such as the first-order splitting

$$P_{\Delta t}^{A,B+\eta\widetilde{\mathcal{L}},\gamma C} = \mathrm{e}^{\Delta t\, A}\,\mathrm{e}^{\Delta t(B+\eta\widetilde{\mathcal{L}})}\,\mathrm{e}^{\gamma\Delta t\, C}, \tag{8.42}$$

or the second-order splitting

$$P_{\Delta t}^{\gamma C,B+\eta\widetilde{\mathcal{L}},A,B+\eta\widetilde{\mathcal{L}},\gamma C} = \mathrm{e}^{\gamma\Delta t\, C/2}\,\mathrm{e}^{\Delta t(B+\eta\widetilde{\mathcal{L}})/2}\,\mathrm{e}^{\Delta t\, A}\,\mathrm{e}^{\Delta t(B+\eta\widetilde{\mathcal{L}})/2}\,\mathrm{e}^{\gamma\Delta t\, C/2}. \tag{8.43}$$

For example, the numerical scheme associated with $P_{\Delta t}^{A,B+\eta\widetilde{\mathcal{L}},\gamma C}$,

$$\begin{aligned}
q^{n+1} &= q^n + \Delta t\, M^{-1} p^n,\\
\widetilde{p}^{n+1} &= p^n + \Delta t(-\nabla V(q^{n+1}) + \eta F),\\
p^{n+1} &= \alpha_{\Delta t}\widetilde{p}^{n+1} + \sqrt{\frac{1-\alpha_{\Delta t}^2}{\beta}M}\,G^n,
\end{aligned}$$

when $M = \mathrm{Id}$ and in the limit as $\gamma \to +\infty$, is a consistent discretization of non-equilibrium Langevin dynamics (8.41). Henceforth we let $P_{\eta,\Delta t}$ denote the evolution operator associated with one of these schemes for a fixed value of the friction γ (see Remark 8.7 for a discussion on the limiting regime $\gamma \to +\infty$).

It can be shown that there exists a unique invariant measure $\mu_{\eta,\Delta t}$ for the Markov chains induced by $P_{\eta,\Delta t}$ as done in Sections 6.2.3 and 6.2.4. The crucial point is that the gradient structure of the force term is never used explicitly in the proofs of the Lyapunov and minorization conditions. The following result provides error estimates for the invariant measure of splitting schemes such as (8.42) and (8.43) (see [169, Theorem 3.4]). The proof follows the same lines as the proof of Theorem 6.1, except that expansions are performed with respect to the two small parameters Δt and η.

Theorem 8.3 (Error estimates on the invariant measure for $\eta \neq 0$). *Set $\alpha = 1$ for first order splitting schemes such as (8.42) and $\alpha = 2$ for second order splitting schemes such as (8.43). Then there exist functions $f_{\alpha,0}, f_{\alpha,1} \in \mathcal{S}_0$ such that, for any smooth function $\varphi \in \mathcal{S}$, there is $\Delta t^*, \eta^*, K > 0$ (depending on φ) for which, for all $\eta \in [-\eta^*, \eta^*]$ and $\Delta t \in (0, \Delta t^*]$,*

$$\int_{\mathcal{E}} \varphi \, d\mu_{\eta,\Delta t} = \int_{\mathcal{E}} \varphi(1 + \eta f_{0,1} + \Delta t^\alpha f_{\alpha,0} + \eta \Delta t^\alpha f_{\alpha,1}) \, d\mu + r_{\varphi,\eta,\Delta t}, \tag{8.44}$$

where $f_{0,1}$ is the unique solution of the Poisson equation

$$\mathcal{L}_0^* f_{0,1} = -\widetilde{\mathcal{L}}^* \mathbf{1} = -\beta F^T M^{-1} p,$$

and

$$|r_{\varphi,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{\alpha+1}), \quad \frac{|r_{\varphi,\eta,\Delta t} - r_{\varphi,0,\Delta t}|}{\eta} \leqslant K(\eta + \Delta t^{\alpha+1}).$$

Let us now comment on (8.44). In this formula, the function $f_{0,1}$ encodes the linear response of the invariant measure when the perturbation is turned on for the continuous dynamics (see (8.17)), while $f_{\alpha,0}$ accounts at leading order for the perturbation induced by the use of finite time steps. As shown below in Corollary 8.1, the errors on transport coefficients are determined at leading order by the cross-term of order $\eta \Delta t^\alpha$, which involves the correction function $f_{\alpha,1}$. Note that the remainder term $r_{\varphi,\eta,\Delta t}$ now collects higher-order terms both as powers of the time step Δt and the non-equilibrium parameter η. The estimates we obtain on the remainder, however, allow us to take the linear response limit $\eta \to 0$, as made precise by the following error estimate on the transport coefficient (which is an immediate consequence of Theorem 8.3). In order to state the result, we introduce the reference linear response for an observable $\varphi \in \mathcal{S}$, namely

$$\mathscr{R}_{\varphi,0} = \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} \varphi \, d\mu_\eta - \int_{\mathcal{E}} \varphi \, d\mu \right),$$

and its numerical approximation,

$$\mathscr{R}_{\varphi,\Delta t} = \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} \varphi \, d\mu_{\eta,\Delta t} - \int_{\mathcal{E}} \varphi \, d\mu_{0,\Delta t} \right). \tag{8.45}$$

It is often the case that the observable φ of interest has a vanishing average with respect to μ, as for the function $\widetilde{\mathcal{L}}^* \mathbf{1} = \beta F^T M^{-1} p$ used to compute the mobility in (8.13). Even in such cases, φ generically has a non-zero average with respect to the invariant measure $\mu_{0,\Delta t}$ of the numerical scheme associated with a discretization of the equilibrium dynamics, so that it is indeed important to subtract the average obtained with $\eta = 0$ in (8.45).

Corollary 8.1 (error estimates on linear responses). *Under the assumptions of Theorem 8.3, and for any $\varphi \in \mathcal{S}$, there exist $\Delta t^* > 0$ and a constant $K > 0$ such that*

$$\mathscr{R}_{\varphi,\Delta t} = \mathscr{R}_{\varphi,0} + \Delta t^\alpha \int_{\mathcal{E}} \varphi \, f_{\alpha,1} \, d\mu + \Delta t^{\alpha+1} r_{\varphi,\Delta t},$$

with $|r_{\varphi,\Delta t}| \leqslant K$ when $0 < \Delta t \leqslant \Delta t^*$.

Note that, in contrast with the error estimates provided by the Green–Kubo formulas, the error is of order Δt^α without any need to modify the observable. This makes the linear response approach more attractive than Green–Kubo techniques when α is large and the correction function (8.38) is difficult to compute.

As an application, we obtain the following estimate on the numerically computed mobility:

$$\begin{aligned} \rho_{F,\Delta t} &= \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\eta,\Delta t}(dq\, dp) - \int_{\mathcal{E}} F^T M^{-1} p \, \mu_{0,\Delta t}(dq\, dp) \right) \\ &= \rho_F + \Delta t^\alpha \int_{\mathcal{E}} F^T M^{-1} p \, f_{\alpha,1} \, d\mu + \Delta t^{\alpha+1} r_{\Delta t}, \end{aligned} \tag{8.46}$$

where ρ_F is defined in (8.13). This error estimate is illustrated in Figures 8.2 and 8.3 for the same system as in Figure 8.1. More precisely, we check in Figure 8.2 that, for a given time step Δt, the average velocity in the direction F is indeed linear with respect to η for η sufficiently small. The corresponding slope gives an estimate of $\rho_{F,\Delta t}$. These estimates are then reported as a function of Δt in Figure 8.3. They extrapolate to the same value at $\Delta t = 0$, with errors of order Δt for first-order splitting schemes, and Δt^2 for second-order splitting schemes, as expected from Corollary 8.1.

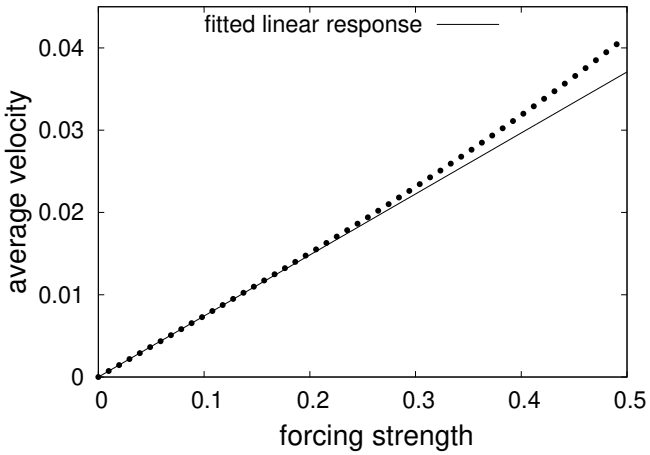


Fig. 8.2. Linear response of the numerical approximation of the average velocity $\mathbb{E}_\eta(F^T M^{-1} p)$ as a function of η for the scheme associated with $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$, for $\Delta t = 0.01$ and $\gamma = 1$. A linear fit on the first ten values gives a slope of $\rho_{F,\Delta t} \simeq 0.07416$.

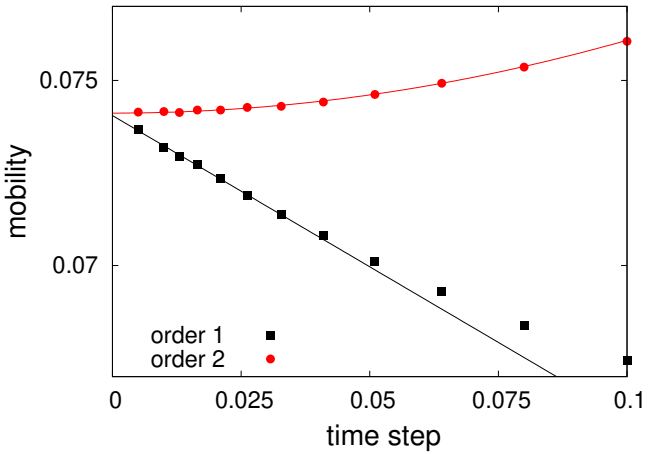


Fig. 8.3. Estimated mobility $\rho_{F,\Delta t}$ for the first-order scheme $P_{\Delta t}^{A, B_\eta, \gamma C}$ and second-order scheme $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$ as a function of the timestep Δt, for $\gamma = 1$. The fits give $\rho_{F,\Delta t} \simeq 0.0740 + 0.0817 \Delta t$ and $\rho_{F,\Delta t} \simeq 0.0741 + 0.197 \Delta t^2$, respectively.

Remark 8.7 (overdamped limits). *As explained in [169, Section 3.4], it is possible to study the overdamped limit $\gamma \to +\infty$ in the above results, and in particular to obtain error estimates on the invariant measure and on the linear response which hold uniformly for $\gamma \geqslant 1$.*

8.5 Variance reduction for non-equilibrium systems

One of the difficulties with the computation of average properties of non-equilibrium systems is that standard variance reduction techniques, such as those described in Section 6.3, cannot be used as such, as we illustrate below. We believe that finding appropriate variance reduction techniques for non-reversible dynamics is a challenging and interesting open problem.

what should be kept here? Work in progress everywhere, somehow...

add CLR?

8.5.1 Importance sampling

If the drift term $-\nabla V$ of equilibrium (overdamped) Langevin dynamics is modified to $-\nabla(V+\widetilde{V})$, the changes in the invariant probability measure can be explicitly written down: this measure now reads $\widetilde{Z}^{-1}\mathrm{e}^{-\beta(V+\widetilde{V})(q)}dq$. On the other hand, consider non-equilibrium dynamics

$$dq_t = b(q_t)\,dt + \sqrt{2}\,dW_t,$$

with invariant measure $\psi_\infty(q)\,dq$, perturbed by a gradient term, such as

$$dq_t = (b(q_t) + \nabla A(q_t))\,dt + \sqrt{2}\,dW_t.$$

We let $\psi_\infty^A(q)\,dq$ denote the invariant measure of this process, assuming it exists. In general, $\psi_\infty^A(q)\,dq$ is different from $Z^{-1}\psi_\infty(q)\mathrm{e}^{A(q)}\,dq$ (consider for instance the simple example (8.7), for which the unique invariant probability measure is the uniform measure on $\mathcal{D} = \mathbb{T}$ when $V = 0$, which transforms into (8.8) when $V \neq 0$). The expression of ψ_∞^A is not known, and generally has no simple relationship with the expression of ψ_∞. It is therefore unclear how to use importance sampling strategies for non-equilibrium systems.

8.5.2 Stratification

For equilibrium systems, it is easy to construct constrained dynamics to sample the restriction of the invariant measure of the unconstrained dynamics to some submanifold. This is the principle of thermodynamic integration for example (**REF**). The invariant measure of constrained non-equilibrium dynamics may, on the other hand, have no relationship whatsoever with the invariant measure of the unconstrained non-equilibrium dynamics. Let us illustrate this point with a simple example. Consider the dynamics

$$\begin{aligned} dq_{1,t} &= \partial_{q_2}U(q_{1,t},q_{2,t}) + \sqrt{2}\,dW_{1,t},\\ dq_{2,t} &= -\partial_{q_1}U(q_{1,t},q_{2,t}) + \sqrt{2}\,dW_{2,t}, \end{aligned}$$

on the state space $\mathbb{T}^2$, for a given C^∞ periodic function U. A simple computation shows that $\psi_\infty = \mathbf{1}_{\mathbb{T}^2}$ is an invariant probability measure. Besides, this is the unique invariant probability measure since the process is irreducible. Consider now the constraint $\xi(q) = 0$ for the choice $\xi(q) = q_2$. On the one hand, the restriction of ψ_∞ to the space $\{q \in \mathbb{T}^2 \mid \xi(q) = 0\} = \mathbb{T}\times\{0\}$ is $\overline{\psi}_\infty(q_1) = \mathbf{1}_{\mathbb{T}}$. On the other hand, the process constrained using a constraining force in the direction of $\nabla\xi$ reads

$$dq_{1,t} = f(q_{1,t})\,dt + \sqrt{2}\,dW_{1,t}, \quad f(q_1) = \partial_{q_2}U(q_1,0).$$

In general, the invariant measure for this process is different from $\mathbf{1}_{\mathbb{T}}$. Indeed, introduce

$$F = \int_0^1 f, \quad V(q_1) = -\int_0^{q_1}(f(s)-F)\,ds.$$

Note that V is a periodic function ($V(0) = V(1) = 0$) and that $f(q_1) = -V'(q_1)$. The computations performed in Section 8.2 show that the unique invariant probability measure of the constrained process is

$$\psi_\infty(q_1) = Z^{-1}\int_0^1 \mathrm{e}^{V(q_1+y)-V(q_1)-Fy}\,dy,$$

which is different from $\mathbf{1}_{\mathbb{T}}$ in general.

8.5.3 Control variate method

This method has been applied to non-equilibrium systems, but only for stochastic dynamics, for which the coupling between two configurations driven by the same random noise is strong – for example one-dimensional lattice gas systems [108]. The general idea of the control variate method in this context is to simulate a system at equilibrium and a system subjected to a small external forcing, and to monitor the difference between the flux of interest in the non-equilibrium system, and the flux in the equilibrium one (which, up to statistical errors, should vanish). When the coupling is sufficiently strong, the variance of the difference of the fluxes is much smaller than the variance of the flux of the non-equilibrium system alone. On the other hand, this approach is very difficult to use in systems where the coupling is too weak, such as perturbations of Hamiltonian dynamics, or overdamped Langevin dynamics in regions where the Hessian of the potential is not positive definite. With some care, it is however possible to estimate finite time correlation functions, as done by [56].

An interesting question is: Is there a way to modify the dynamics in order to increase its coupling properties, while keeping fixed the value of the linear response of the observable of interest? This is, to the best of our knowledge, an open problem.

Remark 8.8 (adding non-reversible drifts). *Non-reversible dynamics can also be obtained by perturbing reversible dynamics with a non-gradient force, which is divergence-free with respect to the equilibrium measure, however, and hence does not modify the invariant measure under consideration. At variance with the situations discussed above, where the non-reversible drift in the dynamics is fixed by the physical problem at hand (the computation of a given transport coefficient, induced for instance by the constant force ηF in* (8.1)*) and the non-equilibrium steady-state is unknown, here the non-equilibrium steady-state is fixed and equal to the equilibrium measure of the reversible dynamics under consideration. Moreover, the non-reversible drift is* chosen *by the user in order to accelerate the sampling procedure. For overdamped Langevin dynamics, there are several results confirming that the addition of non-gradient but divergence-free drifts improves the sampling, measured either in terms of convergence of the law of the process to the invariant distribution or in terms of asymptotic variance of observables of interest. In fact, both criteria are related to spectral gap estimates. For further precision we refer to [135, 136, 175, 229] for example.*

8.5.4 Artificial dynamics

Transport coefficients can be computed by specifying both a perturbation (described by its generator $\widetilde{\mathcal{L}}_1$) and an appropriate response function R. Once these two quantities are provided, the transport coefficient is obtained by (8.13) or (8.24). In general, the expressions of $\widetilde{\mathcal{L}}_1$ and R are motivated by an analogy with experimental setups.

Now, the perturbation $\widetilde{\mathcal{L}}$ actually enters only through the function $S = \widetilde{\mathcal{L}}^* \mathbf{1}$. There is therefore some freedom in choosing a perturbation different from the physically relevant one, while ensuring that the linear response is correct since $\widetilde{\mathcal{L}}^* \mathbf{1}$ is preserved. This is the basis of the "synthetic NEMD" algorithms (with the terminology of [85]), in which non physical perturbations are considered. The interest of these non physical perturbations is that they may have better numerical properties than the standard, physically motivated perturbations: the average linear responses are the same, but the variance of the observables may be different, or the sizes of the transient regime before the steady state is reached may be different.

Two synthetic dynamics can be proposed for thermal transport in one dimensional chains. They perturb the reference dynamics (Hamiltonian dynamics with Langevin thermostats at the same temperature at the boundaries) by nongradient forcing terms, instead of modifying the temperatures at the boundaries. These dynamics are bulk driven (the forcing is felt directly at every site in the chain).

(i) In [84, 185, 86, 164] a non-gradient perturbation $-\xi\Big(v'(q_{i+1} - q_i) + v'(q_i - q_{i-1})\Big)$ is applied at site i, with appropriate modifications at the boundaries:

$$\begin{cases} dq_i = p_i\,dt, \\ dp_i = \Big((1-\xi)v'(q_{i+1}-q_i) - (1+\xi)v'(q_i-q_{i-1})\Big)dt, \qquad i \neq 1, N, \\ dp_1 = \Big((1-\xi)v'(q_2-q_1) - v'(q_1)\Big)dt - \gamma p_1\,dt + \sqrt{2\gamma T}\,dW_t^1, \\ dp_N = -(1+\xi)v'(q_N-q_{N-1})\,dt - \gamma p_N\,dt + \sqrt{2\gamma T}\,dW_t^N, \end{cases}$$

The generator of the perturbation of the reference dynamics with generator (8.27) reads

$$\widetilde{\mathcal{L}} = -v'(q_2-q_1)\partial_{p_1} - \sum_{i=2}^{N-1}\Big(v'(q_{i+1}-q_i) + v'(q_i-q_{i-1})\Big)\partial_{p_i} - v'(q_N-q_{N-1})\,\partial_{p_N},$$

so that $\widetilde{\mathcal{L}}^* = -\widetilde{\mathcal{L}} - 2\beta J$.

(ii) Hamiltonian perturbations can also be employed. In this case, the dynamics is the Hamiltonian dynamics associated with the Hamiltonian $H_0 + \xi H_1$ with

$$H_1(q,p) = \sum_{i=1}^{N} i\varepsilon_i(q,p),$$

where ε_i is defined in (8.15), and the two end sites are still coupled to Langevin thermostats at the same temperature T. The generator of the perturbation is

$$\widetilde{\mathcal{L}} = \nabla_p H_1 \cdot \nabla_q - \nabla_q H_1 \cdot \nabla_p,$$

so that $\widetilde{\mathcal{L}}^* = -\widetilde{\mathcal{L}} - \beta J$.

In both cases, $S = \widetilde{\mathcal{L}}^*\mathbf{1} = -c\beta J$ for some constant $c > 0$, so that the linear response of J allows to recover the thermal conductivity, up to a known multiplicative constant (in view of the general result (8.24) and of the definition (8.31) of the thermal conductivity).

9

Sampling metastable dynamics

The aim of this lecture is to describe the statistics of stochastic processes which remain trapped for a very long time in a subdomain $\mathcal{S}$ of the state space – a so-called metastable state for the dynamics (see Section 9.1). A particular focus is placed on the description of the exit from $\mathcal{S}$ when this exit occurs after a very long time. Part of the question will of course be to quantify what is meant by "long time" in this context. As we argue in Section 9.2, this is useful from a theoretical viewpoint to justify the use of Markov state models in discrete state spaces to model the evolution of the system (the proof of one of the main results of Section 9.2 is postponed to Section 9.3, in the simple case of overdamped Langevin dynamics). The description of exit events is also useful from a numerical viewpoint to devise efficient sampling techniques of the exit event, using in particular the so-called accelerated molecular dynamics which have been proposed by A.F. Voter and his co-workers [276, 277, 254, 217]; see the discussion in Section 9.4.

FAIRE DES FIGURES

9.1 Efficiently simulating efficiently metastable dynamics

The dynamics we consider in this lecture are the Langevin dynamics (5.5) and its overdamped limit (4.1), which both model the evolution of a molecular system at fixed temperature. In the following, we denote by $X_t = (q_t, p_t)$ or $X_t = q_t$ the Markov process associated with the dynamics (5.5) or (4.1).

In most situations of practical interest in statistical physics, the two dynamics (5.5) and (4.1) have a metastable behavior. As already explained in Section 7.1.3, this means that the dynamics typically remain trapped in some regions, called metastable states, for very long periods of times; and only very occasionally hop from one metastable state to another one. This makes sense from a physical viewpoint since these dynamics are supposed to model the actual evolution of molecular systems. Indeed, on the one hand, the typical timescale of oscillations within a metastable state is of the order of 1 femtosecond, namely $10^{-15}s$ (see Section 1.1.1), which is also the typical size of the timestep used to discretize the dynamics (5.5) (see the discussion around (2.35)). On

the other hand, the metastable states typically correspond to macroscopic configurations of the molecular system, such as the conformations of a protein, the positions of a defect in a crystal, etc.; and transitions between these configurations indeed occur over timescales much larger than 1 femtosecond – ranging from microseconds to minutes, or even hours or more for some complicated biological processes or rare physical processes (as those occuring for radiation damage).

In order to have in mind a schematic representation of a metastable process, we refer to Figures 7.1 and 7.4, which present two realizations of low-dimensional metastable trajectories. In both cases, when plotting the x-coordinate as a function of time, one observes a metastable signal: the x-coordinate of the stochastic process remains in the vicinity of one negative value for a long time before going to the vicinity of one positive value for a long time, and so forth. Let us emphasize again that the two situations represented on Figures 7.1 and 7.4 are different in nature: in the former, metastability comes from an energetic barrier (to leave an energy well, the stochastic process has to climb the energy surface up to a saddle point) whereas in the latter, metastability comes from an entropic barrier (to leave the entropic trap, the stochastic process has to find a narrow escape). In practice, metastability comes from a combination of energetic and entropic effects.

Exercise 9.1. *Discuss how the mean exit time depends on the temperature for energetic barriers (the situation encountered in Figure 7.1) and for entropic barriers (situation of Figure 7.4).*

The way we discuss and numerically address metastability in this lecture differs in two ways from what has been done through the study of Poincaré constants as in Section 4.3 or the scaling of free energy differences in Section 7.1.3:

- we are interested here in the actual dynamics of the stochastic processes (5.5) and (4.1): we would like for example to sample the exit time and exit point from a metastable state, or the list of visited metastable states along the trajectories, with the correct distribution (these are indeed random objects). This is in contrast with Lecture 7 where the only quantities of interest are so-called thermodynamic quantities – *i.e.* averages with respect to the Boltzmann-Gibbs measure, which is the stationary state of (5.5) and (4.1)), for which techniques such as biasing (importance sampling) or conditioning (stratification) can be used. To obtain the correct dynamics, one needs to sample trajectories, not only conformations of the molecular system, and this is of course much more demanding.
- we adopt a local point of view, focusing on metastable states rather than maintaining a global point of view such as the one in Section 4.3 where we discuss the metastability of a whole dynamics, quantified by constants in functional inequalities (Poincaré inequalities or logarithmic Sobolev inequalities) involving integrals over the whole configuration space. Here, we study on the contrary the metastability of a state for a given dynamics, and concentrate on the efficient sampling of the exit from this state.

9.2 Metastable exit events and the quasi-stationary distribution

Consider a domain (*i.e.* a connected open set) $\mathcal{O} \subset \mathbb{R}^D$ defined in position space. The associated state is $\mathcal{S} = \mathcal{O} \times \mathbb{R}^D$ for Langevin dynamics, and $\mathcal{S} = \mathcal{O}$ for overdamped Langevin dynamics. The *exit event* from $\mathcal{S}$ is given by the couple of random variables

$$(\tau_{\mathcal{S}}, X_{\tau_{\mathcal{S}}}),$$

where

$$\tau_{\mathcal{S}} = \inf\{t > 0,\, q_t \notin \mathcal{O}\} = \inf\{t > 0,\, X_t \notin \mathcal{S}\}\,.$$

If $\mathcal{S}$ is a metastable state, the process X_t starting in $\mathcal{S}$ remains trapped for a very long time before exiting. In such a situation, it is thus computationally very expensive to sample the exit event from $\mathcal{S}$.

We first introduce in Section 9.2.1 the notion of quasi-stationary distribution (QSD), which is a very useful concept to describe the exit event from a metastable state; and then state a result giving the existence, uniqueness and convergence to the QSD for Langevin and overdamped Langevin dynamics (the proof for the overdamped Langevin dynamics (4.1) is postponed to Section 9.3). We next discuss interesting properties of metastable exit events in Section 9.2.2. These properties allow to construct a reduced dynamics, as done in Section 9.2.3.

9.2.1 Quasi-stationary distribution

When the process X_t remains trapped for a very long time in a state $\mathcal{S}$, it seems natural that it reaches some kind of local equilibrium within the state before exiting. This is where the notion of quasi-stationary distribution is useful. To state the definition, recall that the vector space $B^\infty(\mathcal{S})$ is the Banach space of bounded measurable functions on $\mathcal{S}$ (see Section 3.3).

Definition 9.1. *A probability measure $\nu_{\mathcal{S}}$ on $\mathcal{S}$ is called a* quasi-stationary distribution *(QSD) for the Markov process $(X_t)_{t\geqslant 0}$ if and only if*

$$X_0 \sim \nu_{\mathcal{S}} \quad \Longrightarrow \quad \forall t > 0,\ \forall \varphi \in B^\infty(\mathcal{S}), \qquad \mathbb{E}\left(\varphi(X_t) \,|\, \tau_{\mathcal{S}} > t\right) = \int_{\mathcal{S}} \varphi \, d\nu_{\mathcal{S}}.$$

In words, $\nu_{\mathcal{S}}$ is a quasi-stationary distribution for the Markov process $(X_t)_{t\geqslant 0}$ if, starting from $\nu_{\mathcal{S}}$, the stochastic process at time $t > 0$ conditionally to stay in $\mathcal{S}$ up to time t is still distributed according to $\nu_{\mathcal{S}}$. If one takes $\mathcal{O} = \mathbb{R}^D$, a quasi-stationary distribution is thus nothing but a stationary state for the Markov process. When $\mathcal{O} \subset \mathbb{R}^D$, a quasi-stationary distribution describes some kind of "local equilibrium within $\mathcal{S}$". It is therefore very natural to raise for the QSD the same questions as those which have been studied previously in these lecture notes concerning the stationary state of a Markov process: existence, uniqueness, longtime convergence, etc. The main result of this section answers these questions.

Theorem 9.1. *Assume that $\mathcal{O}$ is a bounded smooth domain of $\mathbb{R}^D$, and consider the Markov process $(X_t)_{t\geqslant 0}$ following either the Langevin* (5.5) *or the overdamped Langevin dynamics* (4.1)*. Then, there exists a unique QSD $\nu_{\mathcal{S}}$ in $\mathcal{S}$. Moreover, for any $X_0 \in \mathcal{S}$,*

$$\lim_{t\to\infty} \mathbb{E}(\varphi(X_t) \,|\, \tau_{\mathcal{S}} > t) = \int_{\mathcal{S}} \varphi \, d\nu_{\mathcal{S}}. \tag{9.1}$$

This result shows that the QSD is indeed the correct probability distribution to describe the stationary state of the Markov process $(X_t)_{t\geqslant 0}$ when it remains trapped for a very long time in $\mathcal{S}$. Section 9.3 is devoted to the proof of this result for the overdamped Langevin dynamics (4.1). Proofs for Langevin dynamics are much more involved; see the very recent results [176, 182]. Let us also mention at this point the very thorough introduction [57] on QSDs and their properties.

We conclude this section with an important remark from a modelling viewpoint. In all what follows, we are able to precisely describe and efficiently sample the exit event only when the limit (9.1) is reached before the exit from $\mathcal{S}$. This may of course depend on the initial condition in $\mathcal{S}$, or on the realization of the stochastic process. This is why we use the notion of *metastable exit* in the following, to denote an exit which occurs after the local equilibrium (namely, the QSD) has been reached within the state. A *metastable state* is then a region such that, for most of the entries within this region, the exit from it is metastable. Of course, all these notions require some tolerances (*e.g.* to measure the distance to the limit in (9.1) in some norm) to make them quantitative. It is actually one aim of the mathematical analysis to give some precise and measurable notions of such a metastable behavior.

9.2.2 Properties of the metastable exit event

A fundamental property of the exit event, when the exit is metastable, is the following one.

Theorem 9.2. *Assume that X_0 is distributed according to the QSD $\nu_{\mathcal{S}}$ in $\mathcal{S}$. Then,*

- *the first exit time $\tau_{\mathcal{S}}$ is exponentially distributed;*
- *the first exit time $\tau_{\mathcal{S}}$ is independent of the exit point $X_{\tau_{\mathcal{S}}}$.*

Proof. Consider two positive real numbers s, t. From Theorem 9.1 and the Markov property, if $X_0 \sim \nu_{\mathcal{S}}$, then the law of $(X_{s+t})_{t \geqslant 0}$ conditionally to $\tau_{\mathcal{S}} > s$ is the same as $(X_t)_{t \geqslant 0}$. Therefore,

$$\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s + t) = \mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s + t \,|\, \tau_{\mathcal{S}} > s)\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s) = \mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > t)\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s),$$

which shows that $\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s) = \exp(\lambda s)$ for some $\lambda > 0$, and so, $\tau_{\mathcal{S}}$ follows an exponential distribution. Likewise, using the same reasoning, for any measurable set $A \subset \partial\mathcal{S}$ and any $s > 0$,

$$\mathbb{P}^{\nu_{\mathcal{S}}}(X_{\tau_{\mathcal{S}}} \in A, \tau_{\mathcal{S}} > s) = \mathbb{P}^{\nu_{\mathcal{S}}}(X_{\tau_{\mathcal{S}}} \in A \,|\, \tau_{\mathcal{S}} > s)\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s) = \mathbb{P}^{\nu_{\mathcal{S}}}(X_{\tau_{\mathcal{S}}} \in A)\mathbb{P}^{\nu_{\mathcal{S}}}(\tau_{\mathcal{S}} > s),$$

which proves that $\tau_{\mathcal{S}}$ and $X_{\tau_{\mathcal{S}}}$ are independent. □

Theorem 9.2 shows that if the process has been trapped in the state $\mathcal{S}$ for a sufficiently long time so that one can assume it is distributed according to $\nu_{\mathcal{S}}$ (see the convergence property (9.1)), then the exit event satisfies the two very specific properties stated in Theorem 9.2.

9.2.3 Metastable exit events and kinetic Monte Carlo dynamics

We now use the result of Theorem 9.2 to draw a connection between the Markov dynamics on continuous state spaces, namely (5.5) and (4.1), and discrete state space Markov dynamics (Markov chains) which are also used in statistical physics to model the evolution of a molecular system. We assume to this end that the full configurational space $\mathbb{R}^D$ is partitioned into a list of domains $(\mathcal{O}_i)_{i \geqslant 1}$ (with associated states $(\mathcal{S}_i)_{i \geqslant 1}$):

$$\mathbb{R}^D = \bigcup_{i \geqslant 1} \overline{\mathcal{O}_i}, \qquad \mathcal{O}_i \cap \mathcal{O}_j = \emptyset \text{ if } i \neq j.$$

The aim is to describe the so-called state-to-state dynamics $(\mathcal{I}_t)_{t \geqslant 0}$ defined by:

$$\forall t \geqslant 0, \qquad X_t \in \mathcal{S}_{\mathcal{I}_t}.$$

The wriggles within the metastable states are indeed typically not interesting: to get the important features of the dynamics over large timescales, only the state-to-state dynamics matter. This state-to-state dynamics is encoded by the pure jump process $(\mathcal{I}_t)_{t \geqslant 0}$, which has values in a discrete space.

When the process enters a state, say $\mathcal{S}_1$ without loss of generality, there are then two possible situations:

- Either the process $(X_t)_{t \geqslant 0}$ quickly leaves $\mathcal{S}_1$, in which case the simulation of the time spent in $\mathcal{S}_1$ and of the next visited state can be done easily by simply following the dynamics of $(X_t)_{t \geqslant 0}$;
- Or the process $(X_t)_{t \geqslant 0}$ remains trapped for a long time in $\mathcal{S}_1$, in which case the simulation of the exit event following the dynamics of $(X_t)_{t \geqslant 0}$ becomes computationally very expensive. However, in such a case, one can assume that, after some convergence time, X_t is distributed according to the QSD $\nu_{\mathcal{S}_1}$, and this can be used to theoretically characterize the exit event (using a Markov chain, see below) or efficiently simulate it (as explained in Section 9.4).

Indeed, in the latter case, we know from Theorem 9.2 that the exit time is exponentially distributed and independent of the exit point, and this implies that the state-to-state dynamics $(\mathcal{I}_t)_{t \geqslant 0}$ behaves statistically as a continuous-time Markov chain. In order to mathematically formalize this idea, we introduce the following rates for a dynamics starting in $\mathcal{S}_1$:

$$\forall i \geqslant 1, \qquad k_{1,i} = \mathbb{E}^{\nu_{\mathcal{S}_1}}(\tau_{\mathcal{S}_1})\mathbb{P}^{\nu_{\mathcal{S}_1}}(X_{\tau_{\mathcal{S}_1}} \in \partial\mathcal{S}_i). \tag{9.2}$$

Note that $k_{1,i} = 0$ if $\partial\mathcal{S}_1 \cap \partial\mathcal{S}_i = \emptyset$, or more generally if $\mathbb{P}^{\nu_{\mathcal{S}_1}}(X_{\tau_{\mathcal{S}_1}} \in \partial\mathcal{S}_i) = 0$. All the states i such that $k_{1,i} \neq 0$ are called the neighbouring states of state 1. One can check that the exit

event (exit time and next visited state) for the continuous-time Markov chain with the rates (9.2) is statistically exactly the same exit event as for the original process $(X_t)_{t\geqslant 0}$. Indeed, for the continuous-time Markov chain starting from the state 1 and jumping to state i with rate $k_{1,i}$ given by (9.2),

- the residence time in state 1 is exponentially distributed with parameter $\sum_{i\neq 1} k_{1,i} = \mathbb{E}^{\nu_{\mathcal{S}_1}}(\tau_{\mathcal{S}_1})$, and has therefore exactly the same law as $\tau_{\mathcal{S}_1}$ when $X_0 \sim \nu_{\mathcal{S}_1}$;
- the next visited state is a random variable independent of the residence time, and which takes the value i_0 with probability

$$\frac{k_{1,i_0}}{\sum_{i\neq 1} k_{1,i}} = \mathbb{P}^{\nu_{\mathcal{S}_1}}(X_{\tau_{\mathcal{S}_1}} \in \partial\mathcal{S}_{i_0}).$$

  Again, this is thus statistically consistent with the law of $X_{\tau_{\mathcal{S}_1}}$ when $X_0 \sim \nu_{\mathcal{S}_1}$.

The exit event of the continuous-time Markov chain with rates (9.2) is thus exactly the same as the exit event for the process $(X_t)_{t\geqslant 0}$ starting from the QSD.

The model which consists in partitioning the configurational space into states, and introducing rates $k_{i,j}$ for transitions form state $\mathcal{S}_i$ to state $\mathcal{S}_j$ is called a *Markov state model* or *kinetic Monte Carlo* (kMC) dynamics. From a mathematical point of view, this is nothing but a continuous-time Markov chain with values in $\{1, 2, \ldots\}$ and infinitesimal generator encoded by

$$\forall (i,j) \in \{1,2,\ldots\} \times \{1,2,\ldots\}, \qquad K_{i,j} = \begin{cases} k_{i,j} \text{ if } i \neq j, \\ -\displaystyle\sum_{j\neq i} k_{i,j} \text{ if } i = j. \end{cases}$$

What we have shown above is that a natural parameterization of the kMC model is given by the formula $k_{i,j} = \mathbb{E}^{\nu_{\mathcal{S}_i}}(\tau_{\mathcal{S}_i})\mathbb{P}^{\nu_{\mathcal{S}_i}}(X_{\tau_{\mathcal{S}_i}} \in \partial\mathcal{S}_j)$. With such a parameterization, when the exit from a state is metastable, the exit even simulated with the kMC model is statistically exactly the same as what is obtained using the original dynamics (5.5)–(4.1). Compared to the latter, the interest of a kMC model from a numerical viewpoint is that one can easily sample dynamics over very long timescales, since one does not simulate the details of the dynamics within the states. However, replacing the original dynamics by the kMC model introduces a bias, since the kMC model is only correct for metastable exits. We discuss in Section 9.4 how to use such a kMC model to accelerate the sampling of the original dynamics but with a control of this bias, using a kind of predictor-corrector scheme (the kMC model being the predictor, and the original dynamics being the corrector).

Remark 9.1. *In a small temperature regime for the dynamics* (5.5) *and* (4.1)*, it is natural to define the states as the basins of attraction of the local minima of the potential function V for the steepest descent dynamics $\dot{x} = -\nabla V(x)$, and one can use harmonic approximations to estimates the rates $k_{i,j}$ by some Eyring–Kramers formulas. In this regime, the metastability is energetic in nature. We refer to [69] and references therein for more details.*

Exercise 9.2. *Assume that a list of non-intersecting metastable domains $(\mathcal{O}_i)_{i\geqslant 1}$ is given, but that this list does not make up a partition. Consider the dynamics $(\mathcal{I}_t)_{t\geqslant 0}$ given by the last visited state:*

$$\forall t > 0, \qquad X_{\sigma(t)} \in \mathcal{O}_{\mathcal{I}_t}, \qquad \sigma(t) = \sup\left\{ s \in [0,t],\ X_s \in \bigcup_{i\geqslant 1} \mathcal{O}_i \right\}.$$

Discuss the Markovianity of this process using the notion of QSD.

9.3 A proof of Theorem 9.1 for the overdamped Langevin dynamics

We give in this section a proof of Theorem 9.1 for the overdamped Langevin dynamics (4.1), for which the proof is much simpler than for the Langevin dynamics (5.5). In all this section, we

therefore assume that $X_t = q_t$ satisfies (4.1) and $\mathcal{S} = \mathcal{O}$ is a bounded smooth domain of $\mathbb{R}^D$. We also simply denote by $\tau_{\mathcal{O}} = \tau_{\mathcal{S}}$ the exit time in order to simplify the notation. Recall that the infinitesimal generator of the process reads

$$\mathcal{L} = -\nabla V \cdot \nabla + \frac{1}{\beta}\Delta,$$

while its ajoint on $L^2(\mathbb{R}^D)$ is

$$\mathcal{L}^\dagger = \operatorname{div}(\nabla V \cdot) + \frac{1}{\beta}\Delta.$$

9.3.1 Existence of a quasi-stationary distribution

Add reference

The cornerstone of the analysis is the following Feynman–Kac formula for the absorbed process.

Proposition 9.1. *Consider two smooth functions v_0 and φ, and a smooth solution $v(t,x)$ to the following problem:*

$$\begin{cases} \partial_t v(t,x) = \mathcal{L} v(t,x) & \text{for } t \geqslant 0, x \in \mathcal{O}, \\ v(t,x) = \varphi(x) & \text{for } t \geqslant 0, x \in \partial\mathcal{O}, \\ v(0,x) = v_0(x) & \text{for } x \in \mathcal{O}. \end{cases}$$

Then, for all $t \geqslant 0$ and $x \in \overline{\mathcal{O}}$,

$$v(t,x) = \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x \leqslant t}\, \varphi\left(X^x_{\tau_{\mathcal{O}}^x}\right)\right] + \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x > t}\, v_0(X_t^x)\right],$$

where X_t^x is the process following the overdamped Langevin dynamics (4.1) starting at x at time 0, and $\tau_{\mathcal{O}}^x$ is the corresponding first exit time from $\mathcal{O}$.

Proof. Fix a time $t > 0$ and consider $u(s,x) = v(t-s,x)$, which satisfies

$$\begin{cases} \partial_s u + \mathcal{L} u = 0 & \text{for } s \in [0,t], x \in \mathcal{O}, \\ u(s,x) = \varphi(x) & \text{for } s \in [0,t], x \in \partial\mathcal{O}, \\ u(t,x) = v_0(x) & \text{for } x \in \mathcal{O}. \end{cases}$$

Using Itô calculus, it holds, for any $s \in [0, t \wedge \tau_{\mathcal{O}}^x]$,

$$\begin{aligned} u(s, X_s^x) &= u(0,x) + \int_0^s (\partial_s u + \mathcal{L} u)(r, X_r^x)\, dr + \sqrt{2\beta^{-1}} \int_0^s \nabla u(r, X_r^x)\, dW_r \\ &= u(0,x) + M_s, \end{aligned}$$

where $M_s = \sqrt{2\beta^{-1}} \int_0^s \nabla u(r, X_r^x)\, dW_r$ is a stochastic integral. Since u is assumed to be smooth, and $(X_r^x)_{r \geqslant 0}$ lives in the bounded domain $\mathcal{O}$ up to time $t \wedge \tau_{\mathcal{O}}^x$, the function $r \in [0,t] \mapsto \nabla u(r, X_r^x) 1_{r \leqslant \tau_{\mathcal{O}}^x}$ belongs to $M^2([0,t])$, so that $\mathbb{E}\left(\int_0^{t \wedge \tau_{\mathcal{O}}^x} \nabla u(r, X_r^x)\, dW_r\right) = 0$. Therefore,

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$$\begin{aligned} v(t,x) = u(0,x) &= \mathbb{E}\left[u\left(t \wedge \tau_{\mathcal{O}}^x, X^x_{t \wedge \tau_{\mathcal{O}}^x}\right)\right] \\ &= \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x \leqslant t}\, u\left(\tau_{\mathcal{O}}^x, X^x_{\tau_{\mathcal{O}}^x}\right)\right] + \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x > t}\, u(t, X_t^x)\right] \\ &= \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x \leqslant t}\, \varphi\left(X^x_{\tau_{\mathcal{O}}^x}\right)\right] + \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x > t}\, v_0(X_t^x)\right], \end{aligned}$$

which concludes the proof. □

Exercise 9.3. *Consider an initial distribution $\mu_0(dx) = p_0(x)\, dx$ on $\mathcal{O}$, and define, for all $t > 0$, the law $p(t,x)\, dx$ of the so-called absorbed Markov process $(X_t 1_{\tau_{\mathcal{O}} > t})_{t \geqslant 0}$ by*

$$\forall \varphi \in B^\infty(\mathcal{O}), \qquad \mathbb{E}\left[\varphi(X_t) 1_{\tau_{\mathcal{O}} > t}\right] = \int_{\mathcal{O}} \varphi(x) p(t,x)\, dx.$$

Prove that p satisfies

$$\begin{cases} \partial_t p(t,x) = \mathcal{L}^\dagger p(t,x) & \text{for } t \geqslant 0, x \in \mathcal{O}, \\ p(t,x) = 0 & \text{for } t \geqslant 0, x \in \partial\mathcal{O}, \\ p(0,x) = p_0(x) & \text{for } x \in \mathcal{O}. \end{cases} \tag{9.3}$$

Verify that $\dfrac{d}{dt}\left(\displaystyle\int_{\mathcal{O}} p(t,x)\,dx\right) \leqslant 0.$

Recall that the unique invariant probability measure for the dynamics $X_t = q_t$ following (4.1) is $\nu(dq) = Z_\nu^{-1}\exp(-\beta V(q))\,dq$ introduced in (4.2). In the following, we denote by $L^2_\nu(\mathcal{O})$ the Hilbert space of functions from $\mathcal{O}$ to $\mathbb{R}$ which are square integrable with respect to ν, equipped with the scalar product:

passage a ν au lieu de μ dans cette section

$$\langle \varphi, \phi \rangle_{L^2_\nu(\mathcal{O})} = \int_{\mathcal{O}} \varphi\phi\,d\nu. \tag{9.4}$$

Note that $L^2_\nu(\mathcal{O}) = L^2(\mathcal{O})$ since $\mathcal{O}$ is bounded and V is smooth.

The quasi-stationary distribution is related to spectral properties of the generator $\mathcal{L}$ supplemented with zero Dirichlet boundary conditions on $\partial\mathcal{O}$. The following result summarizes the important spectral properties we need. To state it, we denote by $H^1_0(\mathcal{O})$ the closure of the space of smooth functions with compact support in $\mathcal{O}$ for the H^1 norm.

Proposition 9.2. *The operator $\mathcal{L}$ supplemented with zero Dirichlet boundary conditions on $\partial\mathcal{O}$, with domain $H^2(\mathcal{O}) \cap H^1_0(\mathcal{O})$, is a self-adjoint operator on $L^2_\nu(\mathcal{O})$, with compact resolvent. It has a discrete spectrum, with negative eigenvalues (counted with multiplicity)*

$$0 > -\lambda_1 > -\lambda_2 \geqslant \ldots \geqslant -\lambda_n \geqslant \ldots \tag{9.5}$$

and associated (normalized) eigenfunctions

$$(u_1, u_2, \ldots, u_n, \ldots), \qquad \int_{\mathcal{O}} |u_n|^2\,d\nu = 1.$$

The first negative eigenvalue $-\lambda_1$ is non-degenerate, and the associated eigenfunction u_1 has a constant sign on $\mathcal{O}$.

Proof. The results follow from standard arguments, for which we refer for instance to [103, Theorem 5.5 and Section 8.12] for more details. It was shown in Section 4.1.1 that the dynamics (4.1) is reversible with respect to ν. Recall in particular (4.7), which states that, for all smooth and compactly supported functions $\varphi, \phi : \mathbb{R}^D \to \mathbb{R}$,

$$\int_{\mathbb{R}^D} \varphi\,\mathcal{L}\phi\,d\nu = \int_{\mathbb{R}^D} (\mathcal{L}\varphi)\phi\,d\nu = -\frac{1}{\beta}\int_{\mathbb{R}^D} \nabla\varphi^T\nabla\phi\,d\nu.$$

This, in turn, implies that the dynamics restricted to $\mathcal{O}$ is reversible with respect to ν restricted to $\mathcal{O}$, namely: for all smooth functions $\varphi, \phi : \mathcal{O} \to \mathbb{R}$ with compact support in $\mathcal{O}$,

$$\int_{\mathcal{O}} \varphi\,\mathcal{L}\phi\,d\nu = \int_{\mathcal{O}} (\mathcal{L}\varphi)\phi\,d\nu = -\frac{1}{\beta}\int_{\mathcal{O}} \nabla\varphi^T\nabla\phi\,d\nu. \tag{9.6}$$

Thus, the operator $\mathcal{L}$ with Dirichlet boundary conditions on $\partial\mathcal{O}$ is negative-definite and symmetric with respect to the scalar product (9.4). Since V is assumed to be smooth, a standard reasoning based for instance on the Lax–Milgram lemma shows that the inverse of the operator $\mathcal{L}$ is bounded from $L^2_\nu(\mathcal{O})$ to $H^1_0(\mathcal{O})$, and hence compact on $L^2_\nu(\mathcal{O})$ (since the injection from $H^1_0(\mathcal{O})$ to $L^2_\nu(\mathcal{O})$ is compact). The inverse of $\mathcal{L}$ thus has a discrete spectrum. Since, the operator $\mathcal{L}$ is negative-definite and symmetric, the eigenvalues are real and negative. Note indeed that the kernel of $\mathcal{L}$ is reduced to 0, so that $\lambda_1 > 0$ in (9.5). Using the variational characterization of the first eigenvalue:

$$\lambda_1 = \inf_{\varphi \in H_0^1(\mathcal{O})} \frac{\beta^{-1} \int_{\mathcal{O}} |\nabla \varphi|^2 \, d\nu}{\int_{\mathcal{O}} \varphi^2 \, d\nu}, \tag{9.7}$$

it follows by a standard argument (if u_1 is a minimizer, then $|u_1|$ is also a minimizer) that we may always assume that u_1 is a signed, say nonnegative, function. Using the Harnack inequality, it is again standard to show u_1 does not vanish on $\mathcal{O}$. We therefore have that

$$u_1 > 0 \text{ on } \mathcal{O},$$

while u_1 vanishes on $\partial\mathcal{O}$. This in turn implies that λ_1 is non-degenerate (hence $\lambda_2 > \lambda_1$ in (9.5)).

Indeed, if u is another eigenfunction associated with λ_1, then, using the same arguments as above (namely, $|u|$ is also an eigenfunction, which cannot vanish by the Harnack inequality), it necessarily has a sign, either positive or negative on $\mathcal{O}$. This however means that it cannot be orthogonal to u_1, which proves that $\mathrm{Ker}(\mathcal{L} - \lambda_1)$ has dimension 1. □

Exercise 9.4. *Show that any eigenfunction associated with an eigenvalue $\lambda \neq \lambda_1$ necessarily takes positive and negative values. The eigenfunction u_1 is thus the only signed eigenfunction.*

Let us now introduce the probability measure

$$d\nu_{\mathcal{O}} = \frac{1_{\mathcal{O}} \, u_1 \, d\nu}{\int_{\mathcal{O}} u_1 \, d\nu}, \tag{9.8}$$

which is in fact a QSD, as made precise in the following result.

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Proposition 9.3. *The measure $\nu_{\mathcal{O}}$ defined by (9.8) is a QSD. In addition, $\nu_{\mathcal{O}}$ is an eigenfunction associated with the eigenvalue $-\lambda_1$ for the Fokker-Planck operator $\mathcal{L}^\dagger$ with homogeneous Dirichlet (also known as absorbing) boundary conditions. More precisely, if we denote by*

$$w = \frac{d\nu_{\mathcal{O}}}{dx} = \frac{u_1 \, \mathrm{e}^{-\beta V}}{\int_{\mathcal{O}} u_1 \, \mathrm{e}^{-\beta V}}$$

the density of $\nu_{\mathcal{O}}$ with respect to the Lebesgue measure, it holds

$$\begin{cases} \mathcal{L}^\dagger w = -\lambda_1 w & \text{on } \mathcal{O}, \\ w = 0 & \text{on } \partial\mathcal{O}. \end{cases} \tag{9.9}$$

The eigenvalue $-\lambda_1$ is the first eigenvalue of $\mathcal{L}^\dagger$, and it is non-degenerate.

Proof. To prove that $\nu_{\mathcal{O}}$ is a QSD (see Definition 9.1), it is sufficient to prove that, for any smooth function φ vanishing on $\partial\mathcal{O}$,

$$\int_{\mathcal{O}} \mathbb{E}\left[\varphi(X_t^x) \, 1_{\tau_{\mathcal{O}}^x > t}\right] \, \nu_{\mathcal{O}}(dx) = \int_{\mathcal{O}} \varphi(x) \, \nu_{\mathcal{O}}(dx) \int_{\mathcal{O}} \mathbb{P}\left(\tau_{\mathcal{O}}^x > t\right) \, \nu_{\mathcal{O}}(dx). \tag{9.10}$$

Denote by $v(t,x) = \mathbb{E}\left[\varphi(X_t^x) \, 1_{\tau_{\mathcal{O}}^x > t}\right]$ and $\overline{v}(t,x) = \mathbb{P}\left(\tau_{\mathcal{O}}^x > t\right)$. It follows from Proposition 9.1 that

$$\begin{cases} \partial_t v = \mathcal{L} v & \text{for } t \geqslant 0, x \in \mathcal{O}, \\ v(t,x) = 0 & \text{for } t \geqslant 0, x \in \partial\mathcal{O}, \\ v(0,x) = \varphi(x) & \text{for } x \in \mathcal{O}, \end{cases}$$

and $\overline{v}$ satisfies the same equation with initial condition $\overline{v}(0,x) = 1$. Therefore, using the definition (9.8) of $\nu_{\mathcal{O}}$ and the symmetry (9.6) of the operator $\mathcal{L}$,

$$\begin{aligned}\frac{d}{dt}\left(\int_{\mathcal{O}} \mathbb{E}\left[\varphi(X_t^x)\,1_{\tau_{\mathcal{O}}^x>t}\right]\,\nu_{\mathcal{O}}(dx)\right) &= \left(\int_{\mathcal{O}} u_1\,d\nu\right)^{-1}\frac{d}{dt}\left(\int_{\mathcal{O}} v(t,x)u_1(x)\,\nu(dx)\right)\\ &= \left(\int_{\mathcal{O}} u_1\,d\nu\right)^{-1}\int_{\mathcal{O}} \mathcal{L}v(t,x)u_1(x)\,\nu(dx)\\ &= \left(\int_{\mathcal{O}} u_1\,d\nu\right)^{-1}\int_{\mathcal{O}} v(t,x)\mathcal{L}u_1(x)\,\nu(dx)\\ &= -\lambda_1\left(\int_{\mathcal{O}} u_1\,d\nu\right)^{-1}\int_{\mathcal{O}} v(t,x)u_1(x)\,\nu(dx)\\ &= -\lambda_1\int_{\mathcal{O}} \mathbb{E}\left[\varphi(X_t^x)\,1_{\tau_{\mathcal{O}}^x>t}\right]\nu_{\mathcal{O}}(dx).\end{aligned}$$

This implies that

$$\int_{\mathcal{O}} \mathbb{E}\left[\varphi(X_t^x)\,1_{\tau_{\mathcal{O}}^x>t}\right]\nu_{\mathcal{O}}(dx) = \mathrm{e}^{-\lambda_1 t}\int_{\mathcal{O}}\varphi\,d\nu_{\mathcal{O}}.$$

A similar equality is obtained for $\overline{v}$ by replacing φ by 1, which yields (9.10).

The relation between the spectrum of the operator $\mathcal{L}$ with Dirichlet boundary conditions on $\partial\mathcal{O}$, seen as on operator on $L^2_\nu(\mathcal{O})$, and the operator $\mathcal{L}^\dagger$ with absorbing boundary conditions, follows the from variational equality satisfied by the eigenfunctions u_k:

$$\forall\varphi\in H_0^1(\mathcal{O})\cap H^2(\mathcal{O}),\qquad -\int_{\mathcal{O}} u_k\mathcal{L}\varphi\,d\nu = \frac{1}{\beta}\int_{\mathcal{O}}\nabla u_k^T\nabla\varphi\,d\nu = \lambda_k\int_{\mathcal{O}} u_k\varphi\,d\nu.$$

This equality shows that $(-\lambda_k, u_k\mathrm{e}^{-\beta V})$ is an eigenvalue/eigenfunction couple for $\mathcal{L}^\dagger$ if and only if $(-\lambda_k, u_k)$ is an eigenvalue/eigenfunction couple for $\mathcal{L}$. □

Remark 9.2. *The assumption that $\mathcal{O}$ is connected and bounded is important to ensure the uniqueness of the QSD. Indeed if $\mathcal{O}$ is bounded but not connected, there exists a QSD in each of the connected components of $\mathcal{O}$, and any convex combination of these QSDs is also QSD. In addition, if $\mathcal{O}$ is connected but unbounded, it is expected that the process admits many QSDs, see for example [57, Example 6.31] which considers the Ornstein–Uhlenbeck process in dimension 1 and $\mathcal{O} = (0, +\infty)$.*

Exercise 9.5. *Prove that if X_0 is distributed according to the QSD $\nu_{\mathcal{O}}$, then the parameter of the exponential random variable $\tau_{\mathcal{O}}$ is λ_1. What is the law of $X_{\tau_{\mathcal{O}}}$?*

9.3.2 Longtime convergence to the quasi-stationary distribution

We again consider $X_t = q_t$ solution to (4.1) with initial condition $X_0 \in \mathcal{O}$, where $\mathcal{O}$ is a bounded domain of $\mathbb{R}^D$. We denote by ν_0 the (arbitrary) distribution of X_0. We can then state the following convergence result.

Proposition 9.4. *Assume that the initial arbitrary distribution ν_0 of X_0 admits a Radon–Nikodym derivative $\dfrac{d\nu_0}{d\nu}$ with respect to the invariant measure ν of the dynamics X_t, such that*

$$\left\|\frac{d\nu_0}{d\nu}\right\|^2_{L^2_\nu(\mathcal{O})} = \int_{\mathcal{O}}\left(\frac{d\nu_0}{d\nu}\right)^2 d\nu < \infty. \tag{9.11}$$

Then, there exists $C\in\mathbb{R}_+$ (which depend on ν_0) such that

$$\forall\varphi\in B^\infty(\mathcal{O}),\quad \forall t\geqslant\frac{C}{\lambda_2-\lambda_1},\qquad \left|\mathbb{E}\left[\varphi(X_t)|\tau_{\mathcal{O}}>t\right] - \int_{\mathcal{O}}\varphi\,d\nu_{\mathcal{O}}\right| \leqslant C\|\varphi\|_\infty\mathrm{e}^{-(\lambda_2-\lambda_1)t}, \tag{9.12}$$

where $-\lambda_2 < -\lambda_1 < 0$ are the first two eigenvalues of the operator $\mathcal{L}$ on the weighted space $L^2_\nu(\mathcal{O})$.

Proof. Fix $\varphi \in B^\infty(\mathcal{O})$, and define

$$\left| \mathbb{E}\left[\varphi(X_t) | \tau_{\mathcal{O}} > t\right] - \int_{\mathcal{O}} \varphi \, d\nu_{\mathcal{O}} \right|.$$

Notice that

$$\mathbb{E}\left[\varphi(X_t) | \tau_{\mathcal{O}} > t\right] = \frac{\displaystyle\int_{\mathcal{O}} v(t,x)\, \nu_0(dx)}{\displaystyle\int_{\mathcal{O}} \overline{v}(t,x)\, \nu_0(dx)}, \tag{9.13}$$

with $v(t,x) = \mathbb{E}\left[\varphi(X_t^x) 1_{\tau_{\mathcal{O}}^x > t}\right]$ and $\overline{v}(t,x) = \mathbb{E}\left[1_{\tau_{\mathcal{O}}^x > t}\right] = \mathbb{P}(\tau_{\mathcal{O}}^x > t)$. Proposition 9.1 implies that

$$\begin{cases} \partial_t v = \mathcal{L} v & \text{for } t \geqslant 0, x \in \mathcal{O}, \\ v(t,x) = 0 & \text{for } t \geqslant 0, x \in \partial\mathcal{O}, \\ v(0,x) = \varphi(x) & \text{for } x \in \mathcal{O}, \end{cases}$$

and $\overline{v}$ satisfies the same equation with initial condition $\overline{v}(0,x) = 1$.

From the spectral decomposition of the operator $\mathcal{L}$ provided by Proposition 9.2, and recalling the notation 9.4, we obtain the following expressions for v and $\overline{v}$:

$$v(t,x) = \sum_{k \geqslant 1} \mathrm{e}^{-\lambda_k t} \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} u_k(x), \qquad \overline{v}(t,x) = \sum_{k \geqslant 1} \mathrm{e}^{-\lambda_k t} \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} u_k(x).$$

Therefore, using the definition (9.8) of the QSD $\nu_{\mathcal{O}}$ and (9.13),

$$\begin{aligned} \mathbb{E}\left[\varphi(X_t) | \tau_{\mathcal{O}} > t\right] &= \frac{\displaystyle\sum_{k \geqslant 1} \mathrm{e}^{-\lambda_k t} \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0}{\displaystyle\sum_{k \geqslant 1} \mathrm{e}^{-\lambda_k t} \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0} \\ &= \frac{\langle 1, u_1 \rangle_{L^2_\nu(\mathcal{O})} \displaystyle\int_{\mathcal{O}} \varphi \, d\nu_{\mathcal{O}} \int_{\mathcal{O}} u_1 \, d\nu_0 + \sum_{k \geqslant 2} \mathrm{e}^{-(\lambda_k - \lambda_1)t} \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0}{\langle 1, u_1 \rangle_{L^2_\nu(\mathcal{O})} \displaystyle\int_{\mathcal{O}} u_1 \, d\nu_0 + \sum_{k \geqslant 2} \mathrm{e}^{-(\lambda_k - \lambda_1)t} \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0}, \end{aligned}$$

where $\int_{\mathcal{O}} u_1 d\nu_0 > 0$ and $\int_{\mathcal{O}} u_1 \, d\nu > 0$ since $u_1 > 0$. Then,

$$\begin{aligned} e(t) &= \left| \frac{\displaystyle\sum_{k \geqslant 2} \mathrm{e}^{-(\lambda_k - \lambda_1)t} \left(\langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} - \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} \varphi \, d\nu_{\mathcal{O}} \right) \int_{\mathcal{O}} u_k \, d\nu_0}{\langle 1, u_1 \rangle_{L^2_\nu(\mathcal{O})} \displaystyle\int_{\mathcal{O}} u_1 \, d\nu_0 + \sum_{k \geqslant 2} \mathrm{e}^{-(\lambda_k - \lambda_1)t} \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0} \right| \\ &\leqslant \mathrm{e}^{-(\lambda_2 - \lambda_1)t} \frac{\displaystyle\sum_{k \geqslant 2} \left| \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0 \right| + \left| \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0 \right| \int_{\mathcal{O}} |\varphi| \, d\nu_{\mathcal{O}}}{\left| \langle 1, u_1 \rangle_{L^2_\nu(\mathcal{O})} \displaystyle\int_{\mathcal{O}} u_1 \, d\nu_0 + \sum_{k \geqslant 2} \mathrm{e}^{-(\lambda_k - \lambda_1)t} \langle 1, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0 \right|}. \end{aligned} \tag{9.14}$$

Let us start by providing upper bounds for the numerator in the latter inequality. Since $(u_k)_{k \geqslant 1}$ is an orthonormal basis of $L^2_\nu(\mathcal{O})$,

$$\begin{aligned} \sum_{k \geqslant 2} \left| \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} \int_{\mathcal{O}} u_k \, d\nu_0 \right| &= \sum_{k \geqslant 2} \left| \langle \varphi, u_k \rangle_{L^2_\nu(\mathcal{O})} \left\langle u_k, \frac{d\nu_0}{d\nu} \right\rangle_{L^2_\nu(\mathcal{O})} \right| \leqslant \|\varphi\|_{L^2_\nu(\mathcal{O})} \left\| \frac{d\nu_0}{d\nu} \right\|_{L^2_\nu(\mathcal{O})} \\ &\leqslant \sqrt{\nu(\mathcal{O})} \|\varphi\|_\infty \left\| \frac{d\nu_0}{d\nu} \right\|_{L^2_\nu(\mathcal{O})}, \end{aligned} \tag{9.15}$$

and, by similar manipulations,

$$\sum_{k\geqslant 2}\left|\langle 1,u_k\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_k\,d\nu_0\right|\int_{\mathcal{O}}|\varphi|\,d\nu_{\mathcal{O}}\leqslant\sqrt{\nu(\mathcal{O})}\|\varphi\|_\infty\left\|\frac{d\nu_0}{d\nu}\right\|_{L^2_\nu(\mathcal{O})}. \tag{9.16}$$

For the lower bound on the denominator of (9.14), we likewise write

$$\begin{aligned}\left|\sum_{k\geqslant 2}\mathrm{e}^{-(\lambda_k-\lambda_1)t}\langle 1,u_k\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_k\,d\nu_0\right|&\leqslant\mathrm{e}^{-(\lambda_2-\lambda_1)t}\sum_{k\geqslant 2}\left|\langle 1,u_k\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_k\,d\nu_0\right|\\&\leqslant\mathrm{e}^{-(\lambda_2-\lambda_1)t}\left\|\frac{d\nu_0}{d\nu}\right\|_{L^2_\nu(\mathcal{O})}.\end{aligned}$$

This implies that there exists $C\in\mathbb{R}_+$ (independent of φ) such that, for any $t\geqslant C/(\lambda_2-\lambda_1)$,

$$\langle 1,u_1\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_1\,d\nu_0+\sum_{k\geqslant 2}\mathrm{e}^{-(\lambda_k-\lambda_1)t}\langle 1,u_k\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_k\,d\nu_0\geqslant\frac{1}{2}\langle 1,u_1\rangle_{L^2_\nu(\mathcal{O})}\int_{\mathcal{O}}u_1\,d\nu_0>0.$$

Inserting respectively the inequalities (9.15)–(9.16) and the above inequality in the numerator and denominator of (9.14) leads to the desired conclusion. □

Remark 9.3. *It can actually be shown that the constant C in (9.12) is uniform with respect to the initial condition ν_0; see for example [107, Theorem 3]. This requires to study the spectrum of the operator $\mathcal{L}$ in appropriate Banach spaces, instead of the Hilbert space $L^2_\nu(\mathcal{O})$, which makes the analysis more involved.*

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Note that the assumption (9.11) on the initial condition ν_0 is not restrictive. Indeed, for the conditioned diffusion process, the time evolution of the density is regularizing. Even if (9.11) is not satisfied at initial time, this condition will be satisfied for the law of the process evolved for a positive time $t_0>0$. This allows to plug in the exponential convergence estimate (9.12) after this time t_0. The regularization part is made precise in the following lemma, stated for $t_0=1$ for simplicity of notation.

Lemma 9.1. *Consider an initial condition ν_0 on $\mathcal{O}$. Then, at time $t=1$, the law ν_1 of X_1 conditioned on $\tau_{\mathcal{O}}>1$ has a bounded density with respect to the Lebesgue measure. Moreover,*

$$\forall\varphi\in B^\infty(\mathcal{O}),\quad\forall t>1,\qquad\mathbb{E}\left[\varphi(X_t)|\tau_{\mathcal{O}}>t\right]=\mathbb{E}\left[\varphi(X_t^{\nu_1})|\tau_{\mathcal{O}}^{\nu_1}>t-1\right], \tag{9.17}$$

where $X_t^{\nu_1}$ denotes the solution to (4.1) with initial condition ν_1, and associated exit time $\tau_{\mathcal{O}}^{\nu_1}$. As a consequence,

$$\lim_{t\to\infty}\mathbb{E}\left[\varphi(X_t)|\tau_{\mathcal{O}}>t\right]=\int_{\mathcal{O}}\varphi\,d\nu_{\mathcal{O}}. \tag{9.18}$$

Note that the condition (9.17) is similar to a semigroup property, not obvious here since the evolution is nonlinear due to the renormalization of the total mass in order to define a probability measure (see for instance (9.19) in the proof below). In fact, the proof shows that the convergence (9.18) happens at an exponential rate.

Proof. The measure ν_1 is a probability measure on $\mathcal{O}$ and is defined by the equality

$$\forall\varphi\in B^\infty(\mathcal{O}),\qquad\int_{\mathcal{O}}\varphi\,d\nu_1=\mathbb{E}\left[\varphi(X_1)|\tau_{\mathcal{O}}>1\right].$$

Now,

$$\mathbb{E}\left[\varphi(X_1)|\tau_{\mathcal{O}}>1\right]=\frac{\mathbb{E}\left[\varphi(X_1)1_{\tau_{\mathcal{O}}>1}\right]}{\mathbb{P}(\tau_{\mathcal{O}}>1)}=\frac{\displaystyle\int_{\mathcal{O}}\varphi(x)p(1,x)\,dx}{\displaystyle\int_{\mathcal{O}}p(1,x)\,dx}, \tag{9.19}$$

where p satisfies (9.3). From standard regularity results on parabolic equations [87, Chapter 6], we know that p belongs to $C^\infty((0,+\infty),\overline{\mathcal{O}})$. This implies in particular that

$$\frac{d\nu_1}{dx} = \frac{p(1,\cdot)}{\displaystyle\int_{\mathcal{O}} p(1,y)\,dy}$$

and that the integrability condition (9.11) is satisfied by ν_1.

Let us next prove (9.17). Fix $t > 1$ and $\varphi \in B^\infty(\mathcal{O})$. Then,

$$\mathbb{E}\left[\varphi(X_t)1_{\tau_{\mathcal{O}}>t}\right] = \mathbb{E}\left[\varphi(X_t)1_{\tau_{\mathcal{O}}>t}|\tau_{\mathcal{O}}>1\right]\mathbb{P}(\tau_{\mathcal{O}}>1) = \mathbb{E}\left[\varphi(X_t^{\nu_1})1_{\tau_{\mathcal{O}}^{\nu_1}>t-1}\right]\mathbb{P}(\tau_{\mathcal{O}}>1),$$

where we used the Markov property for the absorbed Markov process $(X_t 1_{\tau_{\mathcal{O}}>t})_{t\geqslant 0}$. By applying this equality to $\varphi = 1$, we similarly obtain

$$\mathbb{P}(\tau_{\mathcal{O}} > t) = \mathbb{P}\left(\tau_{\mathcal{O}}^{\nu_1} > t-1\right)\mathbb{P}(\tau_{\mathcal{O}}>1).$$

Therefore,

$$\begin{aligned}\mathbb{E}\left[\varphi(X_t)|\tau_{\mathcal{O}}>t\right] &= \frac{\mathbb{E}\left[\varphi(X_t)1_{\tau_{\mathcal{O}}>t}\right]}{\mathbb{P}(\tau_{\mathcal{O}}>t)} = \frac{\mathbb{E}\left[\varphi(X_t^{\nu_1})1_{\tau_{\mathcal{O}}^{\nu_1}>t-1}\right]\mathbb{P}(\tau_{\mathcal{O}}>1)}{\mathbb{P}\left(\tau_{\mathcal{O}}^{\nu_1}>t-1\right)\mathbb{P}(\tau_{\mathcal{O}}>1)}\\ &= \mathbb{E}\left[\varphi(X_t^{\nu_1})|\tau_{\mathcal{O}}^{\nu_1}>t-1\right].\end{aligned}$$

The limit (9.18) then follows from Proposition 9.4 by sending $t\to\infty$ in the latter equality. □

Lemma 9.1 implies that, whatever the initial condition ν_0 on $\mathcal{O}$, the process $(X_t)_{t\geqslant 0}$ conditioned to stay in $\mathcal{O}$ converges in the longtime limit to the QSD $\nu_{\mathcal{O}}$ introduced in (9.8). This yields therefore the following corollary, which concludes the proof of Theorem 9.1 for the overdamped Langevin dynamics.

Corollary 9.1. *The overdamped Langevin dynamics* (4.1) *admits a unique QSD in the bounded domain* $\mathcal{O}$.

Exercise 9.6. *Prove that, under the assumptions of Proposition 9.4, the following inequality holds for any bounded measurable function* $\varphi : \mathbb{R}_+ \times \mathcal{O} \to \mathbb{R}$*:*

$$\left|\mathbb{E}\left[\varphi\left(\tau_{\mathcal{O}}-t, X_{\tau_{\mathcal{O}}}\right)|\tau_{\mathcal{O}}>t\right] - \mathbb{E}^{\nu_{\mathcal{O}}}\left[\varphi\left(\tau_{\mathcal{O}}, X_{\tau_{\mathcal{O}}}\right)\right]\right| \leqslant C\|\varphi\|_\infty \mathrm{e}^{-(\lambda_2-\lambda_1)t}.$$

To this end, check first that $\mathbb{E}\left[\varphi(\tau_{\mathcal{O}}-t, X_{\tau_{\mathcal{O}}})|\tau_{\mathcal{O}}>t\right] = \mathbb{E}\left[\phi(X_t)|\tau_{\mathcal{O}}>t\right]$ *where* $\phi(x) = \mathbb{E}\left[\varphi(\tau_{\mathcal{O}}^x, X_{\tau_{\mathcal{O}}}^x)\right]$.

Exercise 9.7. *This exercise is a follow-up of Exercise 9.3. Consider an initial condition* $\nu_0(dx) = q_0(x)\,dx$ *on* $\mathcal{O}$*. Define, for any* $t>0$*, the law* $q(t,x)\,dx$ *of* X_t *conditioned to* $\tau_{\mathcal{O}} > t$ *as*

$$\forall \varphi \in B^\infty(\mathcal{O}), \qquad \mathbb{E}\left[\varphi(X_t)|\tau_{\mathcal{O}}>t\right] = \int_{\mathcal{O}} \varphi(x) q(t,x)\,dx.$$

Prove that q *satisfies the following nonlinear system of equations:*

$$\begin{cases} \partial_t q(t,x) = \mathcal{L}^\dagger q(t,x) - \left(\displaystyle\int_{\partial\mathcal{O}} \partial_n q(t,\cdot) d\sigma_{\partial\mathcal{O}}\right) q(t,x) & \text{for } t\geqslant 0, x\in\mathcal{O},\\ q(t,x) = 0 & \text{for } t\geqslant 0, x\in\partial\mathcal{O},\\ q(0,x) = q_0(x) & \text{for } x\in\mathcal{O}, \end{cases} \tag{9.20}$$

where $\partial_n q = \mathbf{n}^T\nabla q$ *denotes the normal derivative (*$\mathbf{n}$ *being the outward normal unit vector to* $\mathcal{O}$*) and* $\sigma_{\partial\mathcal{O}}$ *is the Lebesgue measure on* $\partial\mathcal{O}$.

Remark 9.4. *As mentioned above, similar results (existence and uniqueness of the QSD, and convergence to the QSD) can be proven for the Langevin dynamics, see [176, 182]. The main additional difficulties is that in this case, the infinitesimal generator is not elliptic but hypoelliptic, and the state* $\mathcal{S} = \mathcal{O}\times\mathbb{R}^D$ *is not bounded. It is however possible to prove some compactness on the semi-group associated with the absorbed diffusion process, which yields the spectral properties needed to get the results, using in particular the Krein-Rutman theorem [62] to prove the existence, sign and non-degeneracy of the principal eigenfunction.*

9.4 From theory to numerics

As explained in Section 9.1, the simulation of the process $(X_t)_{t\geqslant 0}$ following the Langevin dynamics (5.5) or the overdamped Langevin dynamics (4.1) is computationally expensive if there are metastable states where the process remains trapped. In the previous section, we have shown that in such a situation, one has a precise characterization of the exit event out of a metastable state where the process remains trapped for a sufficiently long time. The aim of this section is to show how this information can be leveraged to devise efficient numerical methods to sample the exit event, and thus to efficiently simulate the original dynamics.

Such algorithms follow two steps:

- First, when the process $(X_t)_{t\geqslant 0}$ enters a state $\mathcal{S}$, one has to estimate the time $T_{\rm corr}$ it takes for the process trapped in $\mathcal{S}$ to reach the QSD $\nu_{\mathcal{S}}$ (see Equation (9.1) in Theorem 9.1). Notice that $T_{\rm corr}$, known as the decorrelation time, a priori depends on the initial condition in $\mathcal{S}$.
- Second, if the process does not exit before this time $T_{\rm corr}$, one would like to use the understanding we gained on the exit event (see Theorem 9.2) in order to build an efficient algorithm to sample the exit event (exit time and exit point).

These two steps are successively investigated in Sections 9.4.1 and 9.4.2.

9.4.1 Estimation of the decorrelation time

We discuss here how to estimate in practice the time $t = T_{\rm corr}$ it takes to reach the limit $\nu_{\mathcal{S}}$, up to some error, for the distribution of X_t conditioned to $\tau_{\mathcal{S}} > t$. From a theoretical viewpoint, we know that this convergence time is related to a spectral gap for the infinitesimal generator of the absorbed process (see for example (9.12) for the overdamped Langevin dynamics), but this cannot be used in practice since this spectral gap is very difficult to estimate.

One way to estimate this convergence is to first get a sample which approximates the law of X_t conditioned to $\tau_{\mathcal{S}} > t$, and then to test the stationarity of this sample (namely the fact that the law of this sample does not depend on t).

Let us first consider how to get a sample which approximates the law of X_t conditioned to $\tau_{\mathcal{S}} > t$. A natural rejection algorithm is to consider N processes following the original dynamics, and to kill a process as soon as it leaves the state $\mathcal{S}$. The problem with this algorithm is that the dynamics we consider here almost surely leave the state $\mathcal{S}$ in finite time, so that no sample at all remains in the longtime limit. A simple idea to fix this issue and keep a fixed number of samples is to duplicate one of the remaining trajectories each time a trajectory leaves the state. This is the so-called Fleming–Viot particle system [93], which we now describe. Consider i.i.d. initial conditions X_0^k ($k \in \{1, \dots, N\}$) distributed according to some initial condition μ_0. The process is then the following:

(1) Integrate N realizations of the original dynamics, driven by independent Brownian motions, until one of them, say X_t^1, exits;
(2) Kill the process that exits;
(3) With uniform probability $1/(N-1)$, randomly choose one of the survivors $(X_t^2, \dots, X_t^N)$, say X_t^2;
(4) Branch X_t^2, with one copy persisting as X_t^2, and the other becoming the new X_t^1 (and thus evolving in the future independently from X_t^2).

Notice that the Fleming–Viot particle process can be implemented in parallel, with each replica X_t^k evolving on distinct CPUs.

In order to mathematically analyze this algorithm, define the associated empirical distribution

$$\mu_{t,N} = \frac{1}{N} \sum_{k=1}^{N} \delta_{X_t^k}. \tag{9.21}$$

It is expected that (see [191, 275] for some results in that direction), for any measurable set $A \subset \mathcal{S}$,

$$\lim_{N\to\infty} \mu_{t,N}(A) = \mathbb{P}(X_t \in A \,|\, \tau_{\mathcal{S}} > t). \tag{9.22}$$

This is a so-called propagation of chaos result [259]. From (9.1) and (9.22), we infer in particular that

$$\lim_{t\to\infty} \lim_{N\to\infty} \mu_{t,N}(A) = \nu_{\mathcal{S}}(A).$$

The idea is then to quantify the convergence to $\nu_{\mathcal{S}}$ of the process X_t conditioned to $\tau_{\mathcal{S}} > t$ by considering, for a fixed N, the convergence of the Fleming–Viot particle system to its stationary state.

In order to test the stationarity of the Fleming–Viot particle system, one can use for example a criterium which compares an average over the replicas at a given time, with an average over the replicas and over time. When the two coincide (up to some fixed error threshold), the system is considered at stationarity. This requires to choose observables to average out, and also a threshold value to compare the two averages. This is the principle of the so-called Gelman–Rubin convergence diagnostic [100].

Combining these two techniques (Fleming–Viot particle process and Gelman–Rubin convergence diagnostic) yields a practical way to estimate T_{corr}, for a given initial condition μ_0 in $\mathcal{S}$. For more details, see [31, 122].

9.4.2 The parallel replica algorithm

Once the convergence to the QSD within a state $\mathcal{S}$ has been reached before the exit from this state, various algorithms can be used to efficiently sample the exit event. Let us present one such example: the parallel replica algorithm [277, 218]. Its principle is based on the following corollary of Theorem 9.2.

Corollary 9.2. *Consider N i.i.d. initial conditions X_0^k (for $k \in \{1,\dots,N\}$), distributed according to the QSD $\nu_{\mathcal{S}}$ in $\mathcal{S}$. Let each of the replicas $(X_t^k)_{t\geqslant 0}$ evolve according to the original dynamics (either Langevin (5.5) or overdamped Langevin (4.1)), driven by independent Brownian motions. Denote by $\tau_{\mathcal{S}}^k$ the exit time from $\mathcal{S}$ for the k-th replica $(X_t^k)_{t\geqslant 0}$, and by K_0 the index of the first replica which exits $\mathcal{S}$:*

$$K_0 = \operatorname*{argmin}_{1\leqslant k\leqslant N} \tau_{\mathcal{S}}^k.$$

Then, the law of $\left(N\tau_{\mathcal{S}}^{K_0}, X_{\tau_{\mathcal{S}}^{K_0}}^{K_0}\right)$ is the same as the law of $(\tau_{\mathcal{S}}^1, X_{\tau_{\mathcal{S}}^1}^1)$.

Note that the statement of the law on the exit time simply corresponds to the fact that the minimum of N independent exponential laws with mean θ is still an exponential law, but with mean $N\theta$.

Proof. From Theorem 9.2, we know that that $(\tau_{\mathcal{S}}^k)_{1\leqslant k\leqslant N}$ are N i.i.d. exponential random variables, and that $\tau_{\mathcal{S}}^k$ is independent from $X_{\tau_{\mathcal{S}}^k}^k$ for all $1 \leqslant k \leqslant N$. Denote by λ the parameter of the exponential law. Then, for any $t > 0$ and any measurable set $A \subset \partial\mathcal{S}$,

$$\begin{aligned}
\mathbb{P}\left(X_{\tau_{\mathcal{S}}^{K_0}}^{K_0} \in A,\ N\tau_{\mathcal{S}}^{K_0} > t\right) &= \sum_{k=1}^N \mathbb{P}\left(X_{\tau_{\mathcal{S}}^{K_0}}^{K_0} \in A,\ N\tau_{\mathcal{S}}^{K_0} > t,\ K_0 = k\right) \\
&= \sum_{k=1}^N \mathbb{E}\left(1_{X_{\tau_{\mathcal{S}}^k}^k \in A} 1_{\tau_{\mathcal{S}}^k > t/N} \prod_{\ell\neq k} 1_{\tau_{\mathcal{S}}^\ell > \tau_{\mathcal{S}}^k}\right) \\
&= \sum_{k=1}^N \mathbb{E}\left(1_{X_{\tau_{\mathcal{S}}^k}^k \in A} 1_{\tau_{\mathcal{S}}^k > t/N}\, \mathrm{e}^{-(N-1)\lambda\tau_{\mathcal{S}}^k}\right),
\end{aligned}$$

where we used a conditioning by $(X_t^k)_{t\geqslant 0}$ in the last step. By the independence of $\tau_{\mathcal{S}}^k$ and $X_{\tau_{\mathcal{S}}^k}^k$,

$$\begin{aligned}\mathbb{P}\left(X^{K_0}_{\tau^{K_0}_{\mathcal{S}}} \in A,\ N\tau^{K_0}_{\mathcal{S}} > t\right) &= N\mathbb{P}\left(X^1_{\tau^k_{\mathcal{S}}} \in A\right)\mathbb{E}\left(1_{\tau^1_{\mathcal{S}}>t/N}\,\mathrm{e}^{-(N-1)\lambda\tau^1_{\mathcal{S}}}\right)\\ &= N\mathbb{P}\left(X^1_{\tau^k_{\mathcal{S}}} \in A\right)\int_{t/N}^{\infty}\mathrm{e}^{-(N-1)\lambda s}\,\lambda\mathrm{e}^{-\lambda s}\,ds\\ &= \mathbb{P}\left(X^1_{\tau^k_{\mathcal{S}}} \in A\right)\mathrm{e}^{-\lambda t}\\ &= \mathbb{P}\left(X^1_{\tau^k_{\mathcal{S}}} \in A\right)\mathbb{P}\left(\tau^1_{\mathcal{S}} > t\right).\end{aligned}$$

This shows indeed that $\left(N\tau^{K_0}_{\mathcal{S}}, X^{K_0}_{\tau^{K_0}_{\mathcal{S}}}\right)$ has the same the law as $(\tau^1_{\mathcal{S}}, X^1_{\tau^1_{\mathcal{S}}})$. □

This corollary allows to check that the following generalized Parallel Replica algorithm [277, 31] yields a statistically consistent state-to-state dynamics:

(1) Run a reference walker, using the original dynamics.
(2) Each time the reference walker enters a state, start a Fleming–Viot particle process (with N replicas simulated in parallel) with the entering point as initial condition.
(3) If the reference walker exits before the Fleming–Viot particle process reaches stationarity, go back to Step (1); else go to the parallel step (Step (3)).
(4) Parallel step: Starting from the end points of the Fleming–Viot particle process (approximately i.i.d. with law the QSD), run independent trajectories and consider the first exit event. Multiply the first exit time by N and go back to Step (1), using the first exit point as an initial condition to continue the trajectory.

Recall that the time at which the Fleming–Viot particle process becomes stationary is determined using the Gelman–Rubin convergence diagnostic. As explained in Corollary 9.2, the parallel step yields a consistent exit time and exit point if the initial conditions of the N walkers are i.i.d. with law the QSD. Notice that in the parallel step, the N walkers are simulated in parallel, which means that, in terms of wall-clock time, it only takes the time to generate the first exit among the N walkers.

Consistency of the algorithm.

There are two main sources of bias in the algorithm, at the end of Step (3) and the beginning of Step (4).

- *Convergence to the QSD*: One considers that the Fleming–Viot process has reached stationarity when the Gelman–Rubin convergence diagnostic is satisfied, and that this corresponds to the time to reach the QSD. There are two parameters to control this: first, the number of replicas in the Fleming–Viot process (the larger, the better); and second, the threshold and observables used in the Gelman–Rubin statistics (the more observables and the tighter the threshold, the better).
- *Independence between the replicas in the Fleming–Viot particle process*: Both the Gelman–Rubin convergence diagnostic and the consistency of the parallel step (see Corollary 9.2) require that the replicas in the Fleming–Viot particle process are i.i.d. with law the law of X_t conditioned to $\tau_{\mathcal{S}} > t$. We already discussed in the first item the fact that the convergence to the conditioned distribution requires N to be large. In addition to this, the particles are strictly speaking not independent, because some correlations are induced by the branching in the Fleming–Viot particle process. Let us make two remarks concerning this point. First, if the state $\mathcal{S}$ is indeed metastable, very few particles actually leave the state, and the correlations are thus weak in practice. Second, it is in principle possible to reduce these correlations by using a Fleming–Viot particle process with $M \gg N$ particles, and only considering the first N walkers (the propagation of chaos result indeed shows that these N walkers become independent in the large M limit, see [259, Proposition 2.2 on page 177]).

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Let us stress that it would be interesting to obtain quantitative measures of these biases. It is observed that they are negligible for practical cases of interest and well-chosen states $\mathcal{S}$. We refer for example to [31, 122] for a discussion of the values of the parameters to control the convergence, and for some numerical illustrations of the accuracy and efficiency of this algorithm.

Interest of the algorithm.

There are various reasons why the algorithm has a practical interest:

- During Step (4) (parallel step), the sampling of the exit event is done in a wall clock time which is N times smaller than the wall clock time which would have been necessary using only 1 walker. This is because, as shown by Corollary 9.2, the first exit time among the replicas is N times smaller than the first exit time of one of them. This is the main interest of this algorithm: it gives a way to *parallelize time*, which is a very difficult task in general because of the sequential nature of the time evolution of dynamics. Moreover, the parallel efficiency (scalability) is very good: in the parallel step, using N CPUs in parallel divides the wall-clock time to sample the exit event by N.
- The algorithm is very versatile: it can be applied for any Markov process as soon as one can proves the existence of a QSD in the chosen states. Notice that the states can be very general (in particular, the metastability of the states can be of energetic or entropic nature, and it is not required that the states make up a partition).
- The time to reach the QSD is estimated on-the-fly at each time the process enters a state: it depends on the state and on the initial condition within the state. It is observed in practice that this time actually depends a lot on the initial condition [122].

Let us emphasize that this technique is very recent, and that many refinements and variants are still under study, see for example [11, 217, 218].

Remark 9.5 (Other methods to accelerate the dynamics). *As mentioned in Remark 9.1, in a small temperature regime and for states which are defined as energetic wells, there are very good approximations of the rates which parameterize the exit event. In this regime, it is then possible to use other algorithms which rely on this additional information, and can be even more efficient than Parallel Replica; see for example the hyperdynamics [276] or the temperature accelerated dynamics [254]. We refer to [173] for more details and references.*

Remark 9.6 (On the choice of the states). *The efficiency of the Parallel Replica algorithm crucially depends on the choice of the states: the maximal efficiency is obtained when a very small amount of time is spent outside the states, and when for most of the visits to the states, the QSD is reached before the reference walker leaves the state. In practice, as already mentioned in Remark 9.1, one can use the basins of attraction of the local minima of V for the steepest descent dynamics $\dot{x} = -\nabla V(x)$ to define the states. This seems indeed appropriate for application in material sciences [218]. For biological applications, states can be determined using collective variables and free energy wells, see for example [122]. For a discussion on the choice of the states, we also refer to [173, Section 4.5].*

References

[1] A. Abdulle, G. Vilmart, et K. C. Zygalakis, Long time accuracy of Lie–Trotter splitting methods for Langevin dynamics, *SIAM J. Numer. Anal.* **53** (2015) 1–16.

[2] F. Achleitner, A. Arnold, et D. Stürzer, Large-time behavior in non-symmetric Fokker-Planck equations, *Riv. Math. Univ. Parma* **6**(1) (2015) 1–68.

[3] E. Akhmatskaya et S. Reich, The targetted shadowing hybrid Monte Carlo (TSHMC method), In *New Algorithms for Macromolecular Simulation* (Springer, 2005), pp. 141–153.

[4] B. J. Alder et W. T. Wainwright, Molecular dynamics by electronic computers, In *Proc. of the Int. Symp. on Statistical Mechanical Theory of Transport Processes (Brussels, 1956)*, I. Prigogine, Ed. (Interscience, Wiley, 1956), pp. 97–131.

[5] M. P. Allen et D. J. Tildesley, *Computer Simulation of Liquids*, 2nd ed. (Oxford University Press, Inc., 2017).

[6] H. Alrachid et T. Lelièvre, Long-time convergence of an adaptive biasing force method: Variance reduction by Helmholtz projection, *SMAI J. Comput. Math.* **1** (2015) 55–82.

[7] L. Ambrosio, N. Fusco, et D. Pallara, *Functions of Bounded Variation and Free Discontinuity Problems* (Oxford Science Publications, 2000).

[8] S. Andradóttir, D. P. Heyman, et T. J. Ott, Variance reduction through smoothing and control variates for Markov chain simulations, *ACM T. Model. Comput. S.* **3**(3) (1993) 167–189.

[9] C. Andrieu, A. Durmus, N. Nüsken, et J. Roussel, Hypocoercivity of piecewise deterministic Markov process-Monte Carlo, *arXiv preprint* **1808.08592** (2018).

[10] C. Ané, S. Blachère, D. Chafaï, P. Fougères, I. Gentil, F. Malrieu, C. Roberto, et G. Scheffer, *Sur les inégalités de Sobolev logarithmiques* (Société Mathématique de France, 2000). In French.

[11] D. Aristoff, T. Lelièvre, et G. Simpson, The parallel replica method for simulating long trajectories of markov chains, *Appl. Math. Res. Express* **2** (2014) 332–352.

[12] S. Armstrong et J.-C. Mourrat, Variational methods for the kinetic Fokker-Planck equation, *arXiv preprint* **1902.04037** (2019).

[13] A. Arnold, E. Carlen, et Q. Ju, Large-time behavior of non-symmetric Fokker-Planck type equations, *Commun. Stoch. Anal.* **2**(1) (2008) 153–175.

[14] A. Arnold, P. Markowich, G. Toscani, et A. Unterreiter, On convex Sobolev inequalities and the rate of convergence to equilibrium for Fokker-Planck type equations, *Comm. Part. Diff. Eq.* **26** (2001) 43–100.

[15] V. I. Arnol'd, *Mathematical Methods of Classical Mechanics*, volume 60 of *Graduate Texts in Mathematics* (Springer-Verlag, 1989).

[16] R. Assaraf et M. Caffarel, Zero-variance principle for Monte Carlo algorithms, *Phys. Rev. Lett.* **83** (1999) 4682–4685.

[17] R. Assaraf, B. Jourdain, T. Lelièvre, et R. Roux, Computation of sensitivities for the invariant measure of a parameter dependent diffusion, *Stoch. Partial Differ. Equ. Anal. Comput.* **6**(2) (2018) 125–183.

[18] D. Bakry, F. Barthe, P. Cattiaux, et A. Guillin, A simple proof of the Poincaré inequality for a large class of probability measures including the log-concave case, *Elect. Comm. in Probab.* **13** (2008) 60–66.

[19] D. Bakry et M. Emery, Diffusions hypercontractives, In *Séminaire de Probabilités XIX*, volume 1123 of *Lecture Notes in Mathematics* (Springer Verlag, 1985), pp. 177–206.

[20] D. Bakry, I. Gentil, et M. Ledoux, *Analysis and Geometry of Markov Diffusion Operators* (Springer, 2014).

[21] R. Balian, *From Microphysics to Macrophysics. Methods and Applications of Statistical Physics*, volume I - II (Springer, 2007).

[22] V. Bally et D. Talay, The law of the Euler scheme for stochastic differential equations. I. Convergence rate of the distribution function, *Probability Theory and Related Fields* **104**(1) (1996) 43–60.

[23] J. A. Barker, Monte Carlo calculations of the radial distribution functions for a proton-electron plasma, *Aust. J. Phys.* **18** (1965) 119–133.

[24] M. I. Baskes, Modified embedded-atom potentials for cubic materials and impurities, *Phys. Rev. B* **46**(5) (1992) 2727–2742.

[25] D. Belomestny, L. Iosipoi, E. Moulines, A. Naumov, et S. Samsonov, Variance reduction for Markov chains with application to MCMC, *Stat. Comput.* **30**(4) (2020) 973–997.

[26] C. H. Bennett, Efficient estimation of free energy differences from Monte-Carlo data, *J. Comput. Phys.* **22** (1976) 245–268.

[27] E. Bernard, M. Fathi, A. Levitt, et G. Stoltz, Hypocoercivity with Schur complements, *arXiv preprint* **2003.00726** (2020).

[28] C. Bernardin et S. Olla. Nonequilibrium macroscopic dynamics of chains of anharmonic oscillators. `http://www.ceremade.dauphine.fr/~olla/springs`.

[29] L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio, et C. Landim, Macroscopic fluctuation theory, *Rev. Mod. Phys.* **87**(2) (2015) 593–636.

[30] R.N. Bhattacharya, On the functional Central Limit theorem and the law of the iterated logarithm for Markov processes, *Z. Wahrscheinlichkeit.* **60**(2) (1982) 185–201.

[31] A. Binder, G. Simpson, et T. Lelièvre, A Generalized Parallel Replica dynamics,, *J. Comput. Phys.* **284** (2015) 595–616.

[32] G. Blower et F. Bolley, Concentration of measure on product spaces with applications to Markov processes, *Studia Math.* **175** (2006) 47–72.

[33] S. Bobkov et F. Götze, Exponential integrability and transportation cost related to logarithmic Sobolev inequalities, *J. Funct. Anal.* **163**(1) (1999) 1–28.

[34] F. Bonetto, J. L. Lebowitz, et L. Rey-Bellet, Fourier's law: a challenge for theorists, In *Mathematical Physics 2000*, A. Fokas, A. Grigoryan, T. Kibble, and B. Zegarlinsky, Eds. (Imperial College Press, 2000), pp. 128–151.

[35] N. Bou-Rabee et M. Hairer, Nonasymptotic mixing of the MALA algorithm, *IMA J. Numer. Anal.* **33** (2013) 80–110.

[36] N. Bou-Rabee et H. Owhadi, Long-run accuracy of variational integrators in the stochastic context, *SIAM J. Numer. Anal.* **48** (2010) 278–297.

[37] N. Bou-Rabee et J. M. Sanz-Serna, Geometric integrators and the Hamiltonian Monte Carlo method, *Acta Numerica* **27** (2018) 113–206.

[38] N. Bou-Rabee et E. Vanden-Eijnden, Pathwise accuracy and ergodicity of metropolized integrators for SDEs, *Commun. Pure Appl. Math.* **63**(5) (2009) 655–696.

[39] N. Bou-Rabee et E. Vanden-Eijnden, A patch that imparts unconditional stability to explicit integrators for Langevin-like equations, *J. Comput. Phys.* **231** (2012) 2565–2580.

[40] E. Bouin, F. Hoffmann, et C. Mouhot, Exponential decay to equilibrium for a fiber lay-down process on a moving conveyor belt, *SIAM J. Math. Anal.* **49**(4) (2017) 3233–3251.

[41] A. Brünger, C. B. Brooks, et M. Karplus, Stochastic boundary conditions for molecular dynamics simulations of ST2 water, *Chem. Phys. Lett.* **105** (1984) 495–500.

[42] G. Bussi et M. Parrinello, Accurate sampling using Langevin dynamics, *Phys. Rev. E* **75** (2007) 056707.

[43] R. E. Caflisch, Monte Carlo and quasi-Monte Carlo methods, *Acta Numerica* **7** (1998) 1–49.

[44] E. Cancès, F. Castella, P. Chartier, E. Faou, C. Le Bris, F. Legoll, et G. Turinici, High-order averaging schemes with error bounds for thermodynamical properties calculations by molecular dynamics simulations, *J. Chem. Phys.* **121**(21) (2004) 10346–10355.

[45] E. Cancès, F. Castella, P. Chartier, E. Faou, C. Le Bris, F. Legoll, et G. Turinici, Long-time averaging for integrable Hamiltonian dynamics, *Numer. Math.* **100**(2) (2005) 211–232.

[46] E. Cancès, M. Defranceschi, W. Kutzelnigg, C. Le Bris, et Y. Maday, Computational quantum chemistry: A primer, In *Handbook of Numerical Analysis (Special volume on computational chemistry)*, P. G. Ciarlet and C. Le Bris, Eds., volume X (Elsevier, 2003), pp. 3–270.

[47] E. Cancès, F. Legoll, et G. Stoltz, Theoretical and numerical comparison of sampling methods for molecular dynamics, *Math. Model. Numer. Anal.* **41**(2) (2007) 351–390.

[48] A. Cao et J. Qu, Size dependent thermal conductivity of single-walled carbon nanotubes, *J. Appl. Phys.* **112**(1) (2012) 013503.

[49] Y. Cao, J. Lu, et L. Wang, On explicit L^2-convergence rate estimate for underdamped Langevin dynamics, *arXiv preprint* **1908.04746** (2019).

[50] R. Car et M. Parrinello, Unified approach for molecular dynamics and density-functional theory, *Phys. Rev. Lett.* **55**(22) (1985) 2471–2474.

[51] P. Carmona, Existence and uniqueness of an invariant measure for a chain of oscillators in contact with two heat baths: Some examples, *Stoch. Proc. Appl.* **117**(8) (2007) 1076–1092.

[52] P. Cattiaux, Long time behavior of Markov processes, *ESAIM Proc.* **44** (2014) 110–128.

[53] P. Cattiaux, A. Guillin, P. Monmarché, et C. Zhang, Entropic multipliers method for Langevin diffusion and weighted log Sobolev inequalities, *J. Funct. Anal.* **277**(11) (2019).

[54] D. Chafaï, From Boltzmann to random matrices and beyond, *arXiv preprint* **1405.1003** (2015).

[55] C. Chipot et A. Pohorille, Eds., *Free Energy Calculations*, volume 86 of *Springer Series in Chemical Physics* (Springer, 2007).

[56] G. Ciccotti et G. Jacucci, Direct computation of dynamical response by molecular-dynamics - mobility of a charged Lennard–Jones particle, *Phys. Rev. Lett.* **35** (1975) 789–792.

[57] P. Collet, S. Martínez, et J. San Martín, *Quasi-Stationary Distributions* (Springer, 2013).

[58] E. Darve et A. Porohille, Calculating free energy using average forces, *J. Chem. Phys.* **115** (2001) 9169–9183.

[59] R. Dautray et J.-L. Lions, *Mathematical Analysis and Numerical Methods for Science and Technology, Volume 3. Spectral Theory and Applications* (Springer, 1990).

[60] R. Dautray et J.-L. Lions, *Mathematical Analysis and Numerical Methods for Science and Technology. Evolution Problems I*, volume 5 (Springer, 2000).

[61] A. Debussche et E. Faou, Weak backward error analysis for SDEs, *SIAM J. Numer. Anal.* **50**(3) (2012) 1735–1752.

[62] K. Deimling, *Nonlinear Functional Analysis* (Springer-Verlag, Berlin, 1985).

[63] G. Deligiannidis, D. Paulin, et A. Doucet, Randomized Hamiltonian Monte Carlo as scaling limit of the Bouncy Particle Sampler and dimension-free convergence rates, *Annals of Applied Probability* (2020).

[64] P. Dellaportas et I. Kontoyiannis, Control variates for estimation based on reversible Markov chain Monte Carlo samplers, *J. R. Stat. Soc. Series B Stat. Methodol.* **74**(1) (2012) 133–161.

[65] B. Derrida, J. L. Lebowitz, et E. R. Speer, Large deviation of the density profile in the steady state of the open symmetric simple exclusion process, *J. Stat. Phys.* **107**(3/4) (2002) 599–634.

[66] L. Desvillettes et C. Villani, On the trend to global equilibrium in spatially inhomogeneous entropy-dissipating systems: The linear Fokker-Planck equation, *Comm. Pure Appl. Math.* **54**(1) (2001) 1–42.
[67] J.-D. Deuschel et D. W. Stroock, *Large deviations*, volume 137 of *Pure and Applied Mathematics* (Academic Press Inc., 1989).
[68] A. Dhar, Heat transport in low-dimensional systems, *Adv. Phys.* **57** (2008) 457–537.
[69] G. Di Gesù, T. Lelièvre, D. Le Peutrec, et B. Nectoux, Jump markov models and transition state theory: The quasi-stationary distribution approach, *Faraday discussions* **195** (2017) 469–495.
[70] J. Dolbeault, A. Klar, C. Mouhot, et C. Schmeiser, Exponential rate of convergence to equilibrium for a model describing fiber lay-down processes, *Appl. Math. Res. eXpress* **2013**(2) (2013) 165–175.
[71] J. Dolbeault, C. Mouhot, et C. Schmeiser, Hypocoercivity for kinetic equations with linear relaxation terms, *C. R. Math. Acad. Sci. Paris* **347**(9-10) (2009) 511–516.
[72] J. Dolbeault, C. Mouhot, et C. Schmeiser, Hypocoercivity for linear kinetic equations conserving mass, *Trans. AMS* **367** (2015) 3807–3828.
[73] R. Douc, G. Fort, et A. Guillin, Subgeometric rates of convergence of f-ergodic strong Markov processes, *Stoch. Proc. Appl.* **119** (2009) 897–923.
[74] S. Duane, A. D. Kennedy, B. J. Pendleton, et D. Roweth, Hybrid Monte-Carlo, *Phys. Lett. B* **195**(2) (1987) 216–222.
[75] A.B. Duncan, T. Lelièvre, et G.A. Pavliotis, Variance reduction using nonreversible Langevin samplers, *J. Stat. Phys.* **163**(3) (2016) 457–491.
[76] A. Durmus, A. Enfroy, et G. Stoltz, *in preparation* (2021).
[77] A. Durmus, E. Moulines, et E. Saksman, Irreducibility and geometric ergodicity of Hamiltonian Monte Carlo, *Ann. Statist.* **48**(6) (2020) 3545–3564.
[78] A. Eberle, A. Guillin, et R. Zimmer, Coupling and quantitative contraction rates for Langevin dynamics, *Ann. Probab.* **47**(4) (2019) 1982–2010.
[79] J.-P. Eckmann et M. Hairer, Non-equilibrium statistical mechanics of strongly anharmonic chains of oscillators, *Commun. Math. Phys.* **212** (2000) 105–164.
[80] J.-P. Eckmann et M. Hairer, Spectral properties of hypoelliptic operators, *Commun. Math. Phys.* **235** (2003) 233–253.
[81] J.-P. Eckmann, C.-A. Pillet, et L. Rey-Bellet, Entropy production in nonlinear, thermally driven Hamiltonian systems, *J. Stat. Phys.* **95**(3/4) (1999) 305–331.
[82] J.-P. Eckmann, C.-A. Pillet, et L. Rey-Bellet, Non-equilibrium statistical mechanics of anharmonic chains coupled to two heat baths at different temperatures, *Commun. Math. Phys.* **201** (1999) 657–697.
[83] S. N. Ethier et T. G. Kurtz, *Markov processes*, Probability and Mathematical Statistics (John Wiley & Sons Inc., 1986).
[84] D. J. Evans, Homogeneous NEMD algorithm for thermal conductivity. Application of noncanonical linear response theory, *Phys. Lett. A* **91**(9) (1982) 457 – 460.
[85] D. J. Evans et G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008).
[86] F. Zhang D. J. Isbister D. J. Evans, Nonequilibrium molecular dynamics simulations of heat flow in one-dimensional lattices, *Phys. Rev. E* **61** (2000) 3541–3546.
[87] L. C. Evans, *Partial Differential Equations*, second ed., volume 19 of *Graduate Studies in Mathematics* (American Mathematical Society, Providence, RI, 2010).
[88] L. C. Evans et R. F. Gariepy, *Measure Theory and Fine Properties of Functions*, Studies in Advanced Mathematics (CRC Press, 1992).
[89] E. Faou, Nosé-Hoover dynamics in a shaker, *J. Chem. Phys.* **124** (2006) 184104.
[90] E. Faou et T. Lelièvre, Conservative stochastic differential equations: Mathematical and numerical analysis, *Math. Comput.* **78** (2009) 2047–2074.
[91] M. Fathi, A.-A. Homman, et G. Stoltz, Error analysis of the transport properties of Metropolized schemes, *ESAIM Proc.* **48** (2015) 341–363.

[92] M. Fathi et G. Stoltz, Improving dynamical properties of stabilized discretizations of overdamped Langevin dynamics, *Numer. Math.* **136**(2) (2017) 545–602.
[93] P.A. Ferrari et N. Maric, Quasi-stationary distributions and Fleming-Viot processes in countable spaces, *Electron. J. Probab.* **12**(24) (2007) 684–702.
[94] J. M. Flegal et G. L. Jones, Batch means and spectral variance estimators in Markov chain Monte Carlo, *Ann. Statist.* **38**(2) (2010).
[95] M. Freidlin et M. Weber, Random perturbations of nonlinear oscillators, *Ann. Probab.* **26**(3) (1998) 925–967.
[96] M. I. Freidlin et A. D. Wentzell, *Random Perturbations of Dynamical Systems* (Springer, 1998).
[97] D. Frenkel et B. Smit, *Understanding Molecular Simulation, From Algorithms to Applications*, 2nd ed. (Academic Press, 2002).
[98] A. Friedman, *Stochastic Differential Equations and Applications*, volume 1 (Academic, 1975).
[99] G. Gallavotti et E. G. D. Cohen, Dynamical ensembles in stationary states, *J. Stat. Phys.* **80** (1995).
[100] A. Gelman et D.B. Rubin, Inference from iterative simulation using multiple sequences, *Stat. Sci.* **7**(4) (1992) 457–472.
[101] C. J. Geyer. Estimating normalizing constants and reweighting mixtures in Markov chain Monte Carlo. Tech. Rep. 565, School of Statistics, University of Minnesota, 1994.
[102] B. Gidas, Metropolis-type Monte Carlo simulation algorithms and simulated annealing, In *Topics in contemporary probability and its applications*, Probab. Stochastics Ser. (CRC, Boca Raton, FL, 1995), pp. 159–232.
[103] D. Gilbarg et N.S. Trudinger, *Elliptic Partial Differential Equations of Second Order*, Classics in Mathematics (Springer-Verlag, Berlin, 2001).
[104] M. B. Giles, Multilevel Monte Carlo path simulation, *Operations Research* **56**(3) (2008) 607–617.
[105] M. B. Giles, Multilevel Monte Carlo methods, *Acta Numerica* **24** (2015) 259–328.
[106] P. Gkeka, G. Stoltz, A. Barati Farimani, Z. Belkacemi, M. Ceriotti, J. D. Chodera, A. R. Dinner, A. L. Ferguson, J.-B. Maillet, H. Minoux, C. Peter, F. Pietrucci, A. Silveira, A. Tkatchenko, Z. Trstanova, R. Wiewiora, et T. Lelièvre, Machine learning force fields and coarse-grained variables in molecular dynamics: Application to materials and biological systems, *Journal of Chemical Theory and Computation* **16**(8) (2020) 4757–4775.
[107] G. Gong, M. Qian, et Z. Zhao, Killed diffusions and their conditioning, *Probability Theory and Related Fields* **80**(1) (1988) 151–167.
[108] J. B. Goodman et K. K. Lin, Coupling control variates for Markov chain Monte Carlo, *J. Comput. Phys.* **228** (2009) 7127–7136.
[109] L. Gross, Logarithmic Sobolev inequalities, *Amer. J. Math.* **97**(4) (1975) 1061–1083.
[110] M. Grothaus et P. Stilgenbauer, Hilbert space hypocoercivity for the Langevin dynamics revisited, *Methods Funct. Anal. Topology* **22**(2) (2016) 152–168.
[111] N. Grunewald, F. Otto, C. Villani, et M. G. Westdickenberg, A two-scale approach to logarithmic Sobolev inequalities and the hydrodynamic limit, *Ann. Inst. H. Poincaré Probab. Statist.* **45**(2) (2009) 302–351.
[112] A. Guionnet et B. Zegarlinski, Lectures on logarithmic Sobolev inequalities, In *Séminaire de Probabilités XXXVI*, volume 1801 of *Lecture Notes in Mathematics* (Springer Verlag, 2003), pp. 1–134.
[113] E. Hairer, C. Lubich, et G. Wanner, Geometric numerical integration illustrated by the Störmer-Verlet method, *Acta Numerica* **12** (2003) 399–450.
[114] E. Hairer, C. Lubich, et G. Wanner, *Geometric Numerical Integration: Structure-Preserving Algorithms for Ordinary Differential Equations*, volume 31 of *Springer Series in Computational Mathematics* (Springer-Verlag, 2006).

[115] E. Hairer, S. P. Nørsett, et G. Wanner, *Solving Ordinary Differential Equations. I*, second ed., volume 8 of *Springer Series in Computational Mathematics* (Springer-Verlag, Berlin, 1993).
[116] M. Hairer, *Convergence of Markov Processes* (Lecture notes, 2016).
[117] M. Hairer et J. Mattingly, Slow energy dissipation in chains of anharmonic oscillators, *Commun. Pure Appl. Math.* **62**(8) (2009) 999–1032.
[118] M. Hairer et J. C. Mattingly, Yet another look at Harris' ergodic theorem for Markov chains, In *Seminar on Stochastic Analysis, Random Fields and Applications VI*, volume 63 of *Progr. Probab.* (Birkhäuser/Springer, 2011), pp. 109–117.
[119] M. Hairer et G. Pavliotis, From ballistic to diffusive behavior in periodic potentials, *J. Stat. Phys.* **131** (2008) 175–202.
[120] M. Hairer, A. M. Stuart, et S. J. Vollmer, Spectral gaps for a Metropolis–Hastings algorithm in infinite dimensions, *Ann. Appl. Probab.* **24**(6) (2014) 2455–2490.
[121] W. K. Hastings, Monte Carlo sampling methods using Markov chains and their applications, *Biometrika* **57** (1970) 97–109.
[122] F. Hédin et T. Lelièvre, gen. parrep: A first implementation of the Generalized Parallel Replica dynamics for the long time simulation of metastable biochemical systems, *Computer Physics Communications* **239** (2019) 311–324.
[123] B. Helffer et F. Nier, *Hypoelliptic Estimates and Spectral Theory for Fokker–Planck Operators and Witten Laplacians*, volume 1862 of *Lecture Notes in Mathematics* (Springer-Verlag, Berlin, 2005).
[124] S. G. Henderson. *Variance Reduction via an Approximating Markov Process.* PhD thesis, Stanford University, 1997.
[125] J. Hénin et C. Chipot, Overcoming free-energy barriers using unconstrained molecular dynamics simulations, *J. Chem. Phys.* **121** (2004) 2904–2914.
[126] F. Hérau, Hypocoercivity and exponential time decay for the linear inhomogeneous relaxation Boltzmann equation, *Asymptot. Anal.* **46**(3-4) (2006) 349–359.
[127] F. Hérau, Short and long time behavior of the Fokker–Planck equation in a confining potential and applications, *J. Funct. Anal.* **244**(1) (2007) 95 – 118.
[128] F. Hérau et F. Nier, Isotropic hypoellipticity and trend to equilibrium for the Fokker-Planck equation with a high-degree potential, *Arch. Ration. Mech. Anal.* **171** (2004) 151–218.
[129] R. Holley et D. Stroock, Logarithmic Sobolev inequalities and stochastic Ising models, *J. Stat. Phys.* **46**(5-6) (1987) 1159–1194.
[130] L. Hörmander, Hypoelliptic second order differential equations, *Acta Math.* **119** (1967) 147–171.
[131] L. Hörmander, *The Analysis of Linear Partial Differential Operators I–IV* (Springer, 1985).
[132] A. M. Horowitz, A generalized guided Monte Carlo algorithm, *Phys. Lett. B* **268** (1991) 247–252.
[133] R. J. Hulse, R.L. Howley, et W.V. Wilding, Transient nonequilibrium molecular dynamic simulations of thermal conductivity. I. Simple fluids, *Int. J. Thermophys.* **26**(1) (2005) 1–12.
[134] G. Hummer et A. Szabo, Free energy reconstruction from nonequilibrium single-molecule pulling experiments, *Proc. Nat. Acad. Sci.* **98** (2001) 3658–3661.
[135] C.-R. Hwang, S.-Y. Hwang-Ma, et S. J. Sheu, Accelerating Gaussian diffusions, *Ann. Appl. Probab.* **3** (1993) 897–913.
[136] C.-R. Hwang, S.-Y. Hwang-Ma, et S. J. Sheu, Accelerating diffusions, *Ann. Appl. Probab.* **15** (2005) 1433–1444.
[137] A. Iacobucci, S. Olla, et G. Stoltz, Convergence rates for nonequilibrium Langevin dynamics, *Ann. Math. Québec* **43**(1) (2019) 73–98.
[138] M. Iannuzzi, A. Laio, et M. Parrinello, Efficient exploration of reactive potential energy surfaces using Car-Parrinello molecular dynamics, *Phys. Rev. Lett.* **90**(23) (2003) 238302.

[139] K. Ichihara et H. Kunita, A classification of the second-order degenerate elliptic operators and its probabilistic characterization, *Z. Wahrscheinlichkeit* **30** (1974) 235–254.

[140] S. Iubini, S. Lepri, R. Livi, A. Politi, et P. Politi, Nonequilibrium phenomena in nonlinear lattices: From slow relaxation to anomalous transport, In *Emerging Frontiers in Nonlinear Science*, P. Kevrekidis, J. Cuevas-Maraver, and S. A., Eds., volume 32 of *Nonlinear Systems and Complexity* (Springer, Cham, 2020), pp. 185–203.

[141] J. A. Izaguirre et S. S. Hampton, Shadow hybrid Monte Carlo: An efficient propagator in phase space of macromolecules, *J. Chem. Phys.* **200** (2004) 581–604.

[142] C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach, *Phys. Rev. E* **56**(5) (1997) 5018–5035.

[143] C. Jarzynski, Nonequilibrium equality for free energy differences, *Phys. Rev. Lett.* **78**(14) (1997) 2690–2693.

[144] R. Joubaud, G. Pavliotis, et G. Stoltz, Langevin dynamics with space-time periodic nonequilibrium forcing, *J. Stat. Phys.* **158**(1) (2015) 1–36.

[145] R. Joubaud et G. Stoltz, Nonequilibrium shear viscosity computations with Langevin dynamics, *Multiscale Model. Sim.* **10** (2012) 191–216.

[146] J. Jung, W. Nishima, M. Daniels, G. Bascom, C. Kobayashi, A. Adedoyin, M. Wall, A. Lappala, D. Phillips, W. Fischer, C.-S. Tung, T. Schlick, Y. Sugita, et K. Y. Sanbonmatsu, Scaling molecular dynamics beyond 100,000 processor cores for large-scale biophysical simulations, *J. Comput. Chem.* **40**(21) (2019) 1919–1930.

[147] C. Kipnis et C. Landim, *Scaling limits of interacting particle systems* (Springer-Verlag, 1999).

[148] J. G. Kirkwood, Statistical mechanics of fluid mixtures, *J. Chem. Phys.* **3**(5) (1935) 300–313.

[149] W. Kliemann, Recurrence and invariant measures for degenerate diffusions, *Ann. Probab.* **15**(2) (1987) 690–707.

[150] P. E. Kloeden et E. Platen, *Numerical Solution of Stochastic Differential Equations*, volume 23 of *Applications of Mathematics* (Springer, 1992).

[151] T. Komorowski, C. Landim, et S. Olla, *Fluctuations in Markov processes: Time symmetry and martingale approximation*, volume 345 of *Grundlehren der Mathematischen Wissenschaften [Fundamental Principles of Mathematical Sciences]* (Springer, 2012).

[152] V. Konakov, S. Menozzi, et S. Molchanov, Explicit parametrix and local limit theorems for some degenerate diffusion processes, *Ann. Inst. Henri Poincaré Probab. Stat.* **46**(4) (2010) 908—923.

[153] A. Kong, J. S. Liu, et W. H. Wong, Sequential imputation and Bayesian missing data problems, *J. Amer. Statist. Assoc.* **89** (1994) 278–288.

[154] A. Kong, P. McCullagh, X. L. Meng, D. Nicolae, et Z. Tan, A theory of statistical models for Monte-Carlo integration, *J. Roy. Stat. Soc. B* **65**(3) (2003) 585–618.

[155] M. Kopec, Weak backward error analysis for Langevin process, *BIT Numerical Mathematics* **55**(4) (2015) 1057–1103.

[156] M. Kopec, Weak backward error analysis for overdamped langevin processes, *IMA J. Numer. Anal.* **35**(2) (2015) 583–614.

[157] S. M. Kozlov, Effective diffusion for the Fokker-Planck equation, *Math. Notes* **45**(5-6) (1989) 360–368.

[158] A. Kundu, A. Dhar, et O. Narayan, The Green-Kubo formula for heat conduction in open systems, *J. Stat. Mech. - Theory E.* (2009) L03001.

[159] R. Kupferman, A. M. Stuart, J. R. Terry, et P. F. Tupper, Long-term behaviour of large mechanical systems with random initial data, *Stochastics and Dynamics* **2**(4) (2002) 1–30.

[160] J. Kurchan, Fluctuation theorem for stochastic dynamics, *J. Phys. A* **31** (1998) 3719–3729.

[161] D. Lamberton et G. Pagès, Recursive computation of the invariant distribution of a diffusion, *Bernoulli* **8**(3) (2002) 367–405.

[162] J. L. Lebowitz et H. Spohn, A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics, *J. Stat. Phys.* **95** (1999) 333–365.

[163] M. Ledoux, Logarithmic Sobolev inequalities for unbounded spin systems revisited, In *Séminaire de Probabilités XXXV*, volume 1755 of *Lecture Notes in Mathematics* (Springer Verlag, 2001), pp. 167–194.

[164] R. Lefevere, On the local space-time structure of non-equilibrium steady states, *J. Stat. Mech.* (2007) P01004.

[165] B. Leimkuhler et C. Matthews, Rational construction of stochastic numerical methods for molecular sampling, *Appl. Math. Res. Express* (2013) 34–56.

[166] B. Leimkuhler et C. Matthews, Robust and efficient configurational molecular sampling via Langevin dynamics, *J. Chem. Phys.* **138** (2013) 174102.

[167] B. Leimkuhler et C. Matthews, *Molecular Dynamics: With Deterministic and Stochastic Numerical Methods* (Springer, 2015).

[168] B. Leimkuhler et C. Matthews, Efficient molecular dynamics using geodesic integration and solvent-solute splitting, *P. Roy. Soc. A* **472** (2016) 20160138.

[169] B. Leimkuhler, Ch. Matthews, et G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *IMA J. Numer. Anal.* **36**(1) (2016) 13–79.

[170] B. J. Leimkuhler et S. Reich, *Simulating Hamiltonian Dynamics*, volume 14 of *Cambridge Monographs on Applied and Computational Mathematics* (Cambridge University Press, 2005).

[171] B. J. Leimkuhler et R. D. Skeel, Symplectic numerical integrators in constrained Hamiltonian systems, *J. Comput. Phys.* **112**(1) (1994) 117–125.

[172] T. Lelièvre, A general two-scale criteria for logarithmic Sobolev inequalities, *J. Funct. Anal.* **256**(7) (2009) 2211–2221.

[173] T. Lelièvre, Mathematical foundations of accelerated molecular dynamics methods, In *Handbook of Materials Modeling: Methods: Theory and Modeling*, W. Andreoni and S. Yip, Eds. (Springer, Cham, 2020), pp. 773–803.

[174] T. Lelièvre et K. Minoukadeh, Long-time convergence of an adaptive biasing force method: The bi-channel case, *Arch. Rational Mech. Anal.* **202** (2011) 1–34.

[175] T. Lelièvre, F. Nier, et G. A. Pavliotis, Optimal non-reversible linear drift for the convergence to equilibrium of a diffusion, *J. Statist. Phys.* **152** (2013) 237–274.

[176] T. Lelièvre, M. Ramil, et J. Reygner, A probabilistic study of the kinetic Fokker–Planck equation in cylindrical domains, *arXiv preprint* **2010.10157** (2020).

[177] T. Lelièvre, M. Rousset, et G. Stoltz, Long-time convergence of an Adaptive Biasing Force method, *Nonlinearity* **21** (2008) 1155–1181.

[178] T. Lelièvre, M. Rousset, et G. Stoltz, *Free-energy Computations: A Mathematical Perspective* (Imperial College Press, 2010).

[179] T. Lelièvre, M. Rousset, et G. Stoltz, Langevin dynamics with constraints and computation of free energy differences, *Math. Comput.* **81** (2012) 2071–2125.

[180] T. Lelièvre et G. Stoltz, Partial differential equations and stochastic methods in molecular dynamics, *Acta Numerica* **25** (2016) 681–880.

[181] T. Lelièvre, G. Stoltz, et W. Zhang, Multiple projection MCMC algorithms on submanifolds, *arXiv preprint* **02515267** (2020).

[182] T. Lelièvre, M. Ramil, et J. Reygner, Quasi-stationary distribution for the Langevin process in cylindrical domains, part I: Existence, uniqueness and long-time convergence, *arXiv preprint* **2101.11999** (2021).

[183] S. Lepri, R. Livi, et A. Politi, Thermal conduction in classical low-dimensional lattices, *Phys. Rep.* **377** (2003) 1–80.

[184] S. Livingstone, M. Betancourt, S. Byrne, et M. Girolami, On the geometric ergodicity of Hamiltonian Monte Carlo, *Bernoulli* **25**(4A) (2019) 3109–3138.

[185] A. Maeda et T. Munakata, Lattice thermal conductivity via homogeneous nonequilibrium molecular dynamics, *Phys. Rev. E* **52** (1995) 234–239.

[186] E. Marinari et G. Parisi, Simulated tempering - a new Monte-Carlo scheme, *Europhys. Lett.* **19**(6) (1992) 451–458.

[187] P. A. Markowich et C. Villani, On the trend to equilibrium for the Fokker-Planck equation: An interplay between physics and functional analysis, *Mat. Contemp.* **19** (2000) 1–29.

[188] S. Marsili, A. Barducci, R. Chelli, P. Procacci, et V. Schettino, Self-healing Umbrella Sampling: A non-equilibrium approach for quantitative free energy calculations, *J. Phys. Chem. B* **110**(29) (2006) 14011–14013.

[189] J. C. Mattingly, A. M. Stuart, et D. J. Higham, Ergodicity for SDEs and approximations: locally Lipschitz vector fields and degenerate noise, *Stoch. Proc. Appl.* **101**(2) (2002) 185–232.

[190] S. Melchionna, Design of quasisymplectic propagators for Langevin dynamics, *J. Chem. Phys.* **127** (2007) 044108.

[191] S. Méléard et D. Villemonais, Quasi-stationary distributions and population processes, *Probability Surveys* **9** (2012) 340–410.

[192] X.-L. Meng et W. H. Wong, Simulating ratios of normalizing constants via a simple identity: A theoretical exploration, *Stat. Sinica* **6** (1996) 831–860.

[193] G. Menz et A. Schlichting, Poincaré and logarithmic Sobolev inequalities by decomposition of the energy landscape, *Ann. Probab.* **42**(5) (2014) 1809–1884.

[194] G. Metafune, D. Pallara, et E. Priola, Spectrum of Ornstein-Uhlenbeck operators in L^p spaces with respect to invariant measures, *J. Funct. Anal.* **196**(1) (2002) 40–60.

[195] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, et E. Teller, Equations of state calculations by fast computing machines, *J. Chem. Phys.* **21**(6) (1953) 1087–1091.

[196] S. P. Meyn et R. L. Tweedie, *Markov Chains and Stochastic Stability*, Communications and Control Engineering Series (Springer, 1993).

[197] D. Michel et É. Pardoux, An introduction to Malliavin calculus and some of its applications, In *Recent Advances in Stochastic Calculus (College Park, MD, 1987)*, Progr. Automat. Info. Systems (Springer, New York, 1990), pp. 65–104.

[198] G. N. Milstein et M. V. Tretyakov, *Stochastic Numerics for Mathematical Physics*, Scientific Computation (Springer, 2004).

[199] R. A. Minlos, *Introduction to Mathematical Statistical Physics*, volume 19 of *University Lecture Series* (American Mathematical Society, 2000).

[200] A. Mira et D. J. Sargent, A new strategy for speeding Markov chain Monte Carlo algorithms, *Stat. Methods Appt.* **12**(1) (2003) 49–60.

[201] A. Mira, R. Solgi, et D. Imparato, Zero variance Markov chain Monte Carlo for Bayesian estimators, *Stat. Comput.* **23**(5) (2013) 653–662.

[202] P. Monmarché, Piecewise deterministic simulated annealing, *ALEA Lat. Am. J. Probab. Math. Stat.* **13**(1) (2016) 357–398.

[203] R. M. Neal, MCMC using Hamiltonian dynamics, In *Handbook of Markov chain Monte Carlo*, Chapman & Hall/CRC Handb. Mod. Stat. Methods (CRC Press, Boca Raton, FL, 2011), pp. 113–162.

[204] E. Nelson, *Dynamical Theories of Brownian Motion* (Princeton University Press, Princeton, N.J., 1967).

[205] G. Nelson, O. Buzko, A. Bassett, P. Spilman, K. Niazi, S. Rabizadeh, et P. Soon-Shiong, Millisecond-scale molecular dynamics simulation of spike RBD structure reveals evolutionary adaption of SARS-CoV-2 to stably bind ACE2, *bioRxiv* (2020).

[206] A. M. N. Niklasson, C. J. Tymczak, et M. Challacombe, Time-reversible Born-Oppenheimer molecular dynamics, *Phys. Rev. Lett.* **97** (2006) 123001.

[207] E. Nummelin, *General Irreducible Markov Chains and Nonnegative Operators* (Cambridge University Press, 1984).

[208] C. J. Oates, M. Girolami, et N. Chopin, Control functionals for Monte Carlo integration, *J. R. Stat. Soc. Ser. B. Stat. Methodol.* **79**(3) (2017) 695–718.

[209] S. Olla et V. Letizia, Non-equilibrium isothermal transformations in a temperature gradient from a microscopic dynamics, *Ann. Probab.* **45**(6A) (2017) 3987–4018.

[210] F. Otto et M. G. Reznikoff, A new criterion for the logarithmic Sobolev inequality, *J. Funct. Anal.* **243** (2007) 121–157.
[211] F. Otto et C. Villani, Generalization of an inequality by Talagrand and links with the logarithmic Sobolev inequality, *J. Funct. Anal.* **173**(2) (2000) 361–400.
[212] G. Papanicolaou et S. R. S. Varadhan, Ornstein-Uhlenbeck process in a random potential, *Commun. Math. Phys.* **38**(06) (1985) 819–834.
[213] E. Pardoux et A. Yu. Veretennikov, On the Poisson equation and diffusion approximation III, *Ann. Probab.* **33**(3) (2005) 1111–1133.
[214] G. A. Pavliotis, *Stochastic Processes and Applications*, volume 60 of *Texts in Applied Mathematics* (Springer, New York, 2014).
[215] G. A. Pavliotis, G. Stoltz, et U. Vaes, Scaling limits for the generalized Langevin equation, *J. Nonlinear Sci.* **31** (2021) 8.
[216] A. Pazy, *Semigroups of Linear Operators and Applications to Partial Differential Equations*, volume 44 of *Applied Mathematical Sciences* (Springer, New York, 1983).
[217] D. Perez, E.D. Cubuk, A. Waterland, E. Kaxiras, et A.F. Voter, Long-time dynamics through parallel trajectory splicing, *Journal of Chemical Theory and Computation* **12**(1) (2015) 18–28.
[218] D. Perez, B.P. Uberuaga, et A.F. Voter, The parallel replica dynamics method - coming of age, *Computational Materials Science* **100** (2015) 90–103.
[219] P. Peskun, Optimum Monte Carlo sampling using Markov chains, *Biometrika* **60** (1973) 607–612.
[220] E. A. J. F. Peters et G. de With, Rejection-free Monte-carlo sampling for general potentials, *Phys. Rev. E* **85** (2012) 026703.
[221] E. Platen, An introduction to numerical methods for stochastic differential equations, *Acta Numerica* **8** (1999) 197–246.
[222] P. Plechac, G. Stoltz, et T. Wang, *in preparation* (2021).
[223] D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, 2nd ed. (Cambridge University Press, 2004).
[224] S. Redon, G. Stoltz, et Z. Trstanova, Error analysis of modified Langevin dynamics, *J. Stat. Phys.* **164**(4) (2016) 735–771.
[225] M. Reed et B. Simon, *Methods of Modern Mathematical Physics. I. Functional Analysis* (Academic Press, 1975).
[226] M. Reed et B. Simon, *Methods of Modern Mathematical Physics. Analysis of Operators*, volume IV (Academic Press, 1978).
[227] P. Reimann, Brownian motors: noisy transport far from equilibrium, *Phys. Rep.* **61** (2002) 57–265.
[228] L. Rey-Bellet, Ergodic properties of Markov processes, In *Open Quantum Systems II*, S. Attal, A. Joye, and C.-A. Pillet, Eds., volume 1881 of *Lecture Notes in Mathematics* (Springer, 2006), pp. 1–39.
[229] L. Rey-Bellet et K. Spiliopoulos, Irreversible Langevin samplers and variance reduction: A large deviations approach, *Nonlinearity* **28** (2015) 2081–2103.
[230] L. Rey-Bellet et K. Spiliopoulos, Improving the convergence of reversible samplers, *J. Stat. Phys.* **164**(3) (2016) 472–494.
[231] L. Rey-Bellet et L. E. Thomas, Exponential convergence to non-equilibrium stationary states in classical statistical mechanics, *Commun. Math. Phys.* **225** (2002) 305–329.
[232] L. Rey-Bellet et L. E. Thomas, Fluctuations of the entropy production in anharmonic chains, *Ann. Henri Poincaré* **3** (2002) 483–502.
[233] J. M. Rickman et R. LeSar, Free-energy calculations in materials research, *Ann. Rev. Mater. Res.* **32** (2002) 195–217.
[234] G. O. Roberts, A. Gelman, et W. R. Gilks, Weak convergence and optimal scaling of random walk Metropolis algorithms, *Ann. Appl. Probab.* **7** (1997) 110–120.
[235] G. O. Roberts et J. S. Rosenthal, Optimal scaling of discrete approximations to Langevin diffusions, *J. Roy. Stat. Soc. B* **60** (1998) 255–268.

[236] H. Rodenhausen, Einstein's relation between diffusion constant and mobility for a diffusion model, *J. Stat. Phys.* **55**(5/6) (1989) 1065–1088.
[237] P. J. Rossky, J. D. Doll, et H. L. Friedman, Brownian dynamics as smart Monte Carlo simulation, *J. Chem. Phys.* **69**(10) (1978) 4628–4633.
[238] J. Roussel et G. Stoltz, Spectral methods for Langevin dynamics and associated error estimates, *M2AN* **52**(3) (2018) 1051–1083.
[239] J. Roussel et G. Stoltz, A perturbative approach to control variates in molecular dynamics, *Multiscale Model. Simul.* **17**(1) (2019) 552–591.
[240] M. Rousset, Y. Xu, et P.-A. Zitt, A weak overdamped limit theorem for Langevin processes, *ALEA Lat. Am. J. Probab. Math. Stat.* **17**(1) (2020) 1–21.
[241] G. Royer, *An Initiation to Logarithmic Sobolev Inequalities* (American Mathematical Society, 2007).
[242] R. Y. Rubinstein et D. P. Kroese, *Simulation and the Monte Carlo Method*, Wiley Series in Probability and Statistics (John Wiley & Sons, Inc., Hoboken, NJ, 2017).
[243] W. Rudin, *Real and Complex Analysis* (McGraw-Hill, 1987).
[244] J. P. Ryckaert et A. Bellemans, Molecular-dynamics of liquid alkanes, *Faraday Discuss.* **66** (1978) 95–106.
[245] K. Sääskilahti, J. Oksanen, S. Volz, et J. Tulkki, Frequency-dependent phonon mean free path in carbon nanotubes from nonequilibrium molecular dynamics, *Phys. Rev. B* **91** (2015) 115426.
[246] T. Schlick, *Molecular Modeling and Simulation* (Springer, 2002).
[247] C. Schütte, *Habilitation Thesis* (Freie Universität Berlin, 1999).
[248] T. Shardlow, Splitting for dissipative particle dynamics, *SIAM J. Sci. Comp.* **24**(4) (2003) 1267–1282.
[249] T. Shardlow et Y. B. Yan, Geometric ergodicity for dissipative particle dynamics, *Stoch. Dynam.* **6**(1) (2006) 123–154.
[250] D. E. Shaw, R. O. Dror, J. K. Salmon, J. P. Grossman, K. M. Mackenzie, J. A. Bank, C. Young, M. M. Deneroff, B. Batson, K. J. Bowers, E. Chow, M. P. Eastwood, D. J. Ierardi, J. L. Klepeis, J. S. Kuskin, R. H. Larson, K. Lindorff-Larsen, P. Maragakis, M. A. Moraes, S. Piana, Y. Shan, et B. Towles. Millisecond-Scale Molecular Dynamics Simulations on Anton. In *SC'09: Proceedings of the conference on High Performance Computing Networking, Storage and Analysis* (2009), Association for Computing Machinery.
[251] Y. Shibuta, S. Sakane, E. Miyoshi, T. Takaki, et M. Ohno, Micrometer-scale molecular dynamics simulation of microstructure formation linked with multi-phase-field simulation in same space scale, *Model. Simul. Mater. Sc.* **27**(5) (2019) 054002.
[252] M. R. Shirts et J. D. Chodera, Statistically optimal analysis of samples from multiple equilibrium states, *J. Chem. Phys.* **124**(12) (2008) 124105.
[253] R. D. Skeel et J. A. Izaguirre, An impulse integrator for Langevin dynamics, *Mol. Phys.* **100** (2002) 3885–3891.
[254] M.R. Sørensen et A.F. Voter, Temperature-accelerated dynamics for simulation of infrequent events, *J. Chem. Phys.* **112**(21) (2000) 9599–9606.
[255] B. Stamm, L. Lagardère, E. Polack, Y. Maday, et J.-P. Piquemal, A coherent derivation of the Ewald summation for arbitrary orders of multipoles: The self-terms, *J. Chem. Phys.* **149**(12) (2018) 124103.
[256] C. Stein. A bound for the error in the normal approximation to the distribution of a sum of dependent random variables. In *Proceedings of the Sixth Berkeley Symposium on Mathematical Statistics and Probability (Univ. California, Berkeley, Calif., 1970/1971), Vol. II: Probability theory* (1972), pp. 583–602.
[257] G. Stoltz et Z. Trstanova, Langevin dynamics with general kinetic energies, *Multiscale Model. Sim.* **16**(2) (2018) 777–806.
[258] D. W. Stroock, *Lectures on topics in stochastic differential equations*, volume 68 of *Tata Institute of Fundamental Research Lectures on Mathematics and Physics* (Springer, 1982).

[259] A.-S. Sznitman, Topics in propagation of chaos, In *École d'Été de Probabilités de Saint-Flour XIX—1989*, volume 1464 of *Lecture Notes in Math.* (Springer, 1991), pp. 165–251.
[260] D. Talay, Stochastic Hamiltonian dissipative systems: exponential convergence to the invariant measure, and discretization by the implicit Euler scheme, *Markov Proc. Rel. Fields* **8** (2002) 163–198.
[261] D. Talay et L. Tubaro, Expansion of the global error for numerical schemes solving stochastic differential equations, *Stoch. Proc. Appl.* **8**(4) (1990) 483–509.
[262] Z. Tan, On a likelihood approach for Monte-Carlo integration, *J. Am. Stat. Assoc.* **99**(468) (2004) 1027–1036.
[263] J. Tersoff, Modeling solid-state chemistry: Interatomic potentials for multicomponent systems, *Phys. Rev. B* **39** (1989) 5566–5568.
[264] S. Teufel, *Adiabatic Perturbation Theory in Quantum Dynamics*, volume 1821 of *Lecture Notes in Mathematics* (Springer-Verlag, Berlin, Heidelberg, New York, 2003).
[265] F. Thalmann et J. Farago, Trotter derivation of algorithms for Brownian and dissipative particle dynamics, *J. Chem. Phys.* **127** (2007) 124109.
[266] L. Tierney, Markov chains for exploring posterior distributions, *Ann. Statist.* **22**(4) (1994) 1701–1762.
[267] B. D. Todd et P. J. Daivis, Homogeneous non-quilibrium molecular dynamics simulations of viscous flow: Techniques and applications, *Mol. Sim.* **33**(3) (2007) 189–229.
[268] B. D. Todd et P. J. Daivis, *Nonequilibrium Molecular Dynamics: Theory, Algorithms and Applications* (Cambridge University Press, 2017).
[269] M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, 2010).
[270] A. C. T. van Duin, S. Dasgupta, F. Lorant, et W. A. Goddard III, ReaxFF: A reactive force field for hydrocarbons, *J. Phys. Chem. A* **105** (2001) 9396–9409.
[271] L. Verlet, Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules, *Phys. Rev.* **159** (1967) 98–103.
[272] C. Villani, A review of mathematical topics in collisional kinetic theory, In *Handbook of Mathematical Fluid Dynamics, Vol. I* (North-Holland, Amsterdam, 2002), pp. 71–305.
[273] C. Villani, *Topics in Optimal Transportation*, volume 58 of *Graduate Studies in Mathematics* (American Mathematical Society, 2003).
[274] C. Villani, Hypocoercivity, *Mem. Amer. Math. Soc.* **202**(950) (2009).
[275] D. Villemonais, General approximation method for the distribution of Markov processes conditioned not to be killed, *ESAIM Probab. Stat.* **18** (2014) 441–467.
[276] A.F. Voter, A method for accelerating the molecular dynamics simulation of infrequent events, *J. Chem. Phys.* **106**(11) (1997) 4665–4677.
[277] A.F. Voter, Parallel replica method for dynamics of infrequent events, *Phys. Rev. B* **57**(22) (1998) R13985–R13988.
[278] F. Wang et D.P. Landau, Determining the density of states for classical statistical models: A random walk algorithm to produce a flat histogram, *Phys. Rev. E* **64** (2001) 056101.
[279] F. G. Wang et D. P. Landau, Efficient, multiple-range random walk algorithm to calculate the density of states, *Phys. Rev. Lett.* **86**(10) (2001) 2050–2053.
[280] L. Wu, Large and moderate deviations and exponential convergence for stochastic damping Hamiltonian systems, *Stoch. Proc. Appl.* **91**(2) (2001) 205–238.
[281] I. Yu, T. Mori, T. Ando, R. Harada, J. Jung, Y. Sugita, et M. Feig, Biomolecular interactions modulate macromolecular structure and dynamics in atomistic model of a bacterial cytoplasm, *eLIFE* **5** (2016) e19274.
[282] R. W. Zwanzig, High-temperature equation of state by a perturbation method I. Nonpolar gases, *J. Chem. Phys.* **22**(8) (1954) 1420–1426.