Gabriel Stoltz

Introduction à la physique statistique numérique

September 11, 2020

Master AnEDP, cours de spécialité

Contents

Part IV Beyond static averages

Part I

Introduction to statistical physics

1

Introduction to statistical physics

This chapter presents the physical and mathematical framework to understand the basics of molecular simulation and computational statistical physics techniques. 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 describes physical systems 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.

1.1 Computational statistical physics: some landmarks

Before giving a detailed mathematical framework of 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 expliciting 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 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 are expressed in Å (10^{-10} m), the energies are of the order of $k_{\mathrm{B}}T \simeq 4 \times 10^{-21}$ J at room temperature, and the typical times are of the order of 10^{-15} s when the proton mass is the reference mass.

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.

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, following the dynamics of every atom would require simulating $\mathcal{N}_A$ atoms and performing $\mathrm{O}(10^{15})$ time integration 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 the complete satellite tobacco mosaic virus [59], which involved 1 million atoms over 50 ns, or the folding simulations of the Villin headpiece,[1] where a trajectory of 500 μs was integrated for 2×10^4 atoms.

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 bathtub...

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 on a conceptual level. The question is whether the estimated quantities for a system of N particles correctly approximate the macroscopic property, 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 from 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 simulation

Despite its intrinsic limitations on spatial and timescales, molecular simulation has been used and developed over the past 50 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 [124], and the first molecular dynamics simulation [3] 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

[1] See the website of the Folding@Home project: `http://folding.stanford.edu/`

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.

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?"

An example: the equation of state of Argon

Let us detail to some extent the second approach, and illustrate it with a simple but realistic example. We consider microscopic systems composed of N particles (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 $p = (p_1, \cdots, p_N) \in \mathbb{R}^{3N}$. For physical and biological systems currently studied, N is typically between 10^3 and 10^9. The vector (q, p) is called the *microscopic state* or the *configuration* of the system.

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

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

In this expression, the function A is called an *observable*. The position variable $q = (q_1, \ldots, q_N)$ belongs to $\mathcal{D}$, which is called the configuration space. The set $\mathcal{D}$ is an open subset (possibly the whole) of $\mathbb{R}^n$ with $n = 3N$, or $\mathcal{D} = \mathbb{T}^n$ (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. For the two choices mentioned above, the momentum variable $p = (p_1, \ldots, p_N)$ belongs to $\mathbb{R}^n$. The set of all possible microscopic configurations (q, p) is called the *phase space*. The probability measure μ has support on the phase space and depends on the thermodynamic ensemble used, see Section 1.2 for further precision 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 open subset of $\mathbb{R}^n$, with a potential energy function which goes sufficiently fast to ∞ on $\partial\mathcal{D}$ to prevent the dynamics from leaving the domain $\mathcal{D}$. In particular, we do not consider the case of molecular constraints (see [114, Chapter 3]).*

A statistical description through a probability measure μ is a convenient description since the whole 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 an observable is the bulk pressure P in a Lennard-Jones liquid. For particles of masses m_i, described by their positions q_i and their momenta p_i, it is given by $P = \mathbb{E}_\mu(A)$ with

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

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 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 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. The computed results are compared with experimental measurements.[2] The agreement is very good in the case of Argon. Notice also that high-pressure results, not easily obtained with experimental setups, can be computed.

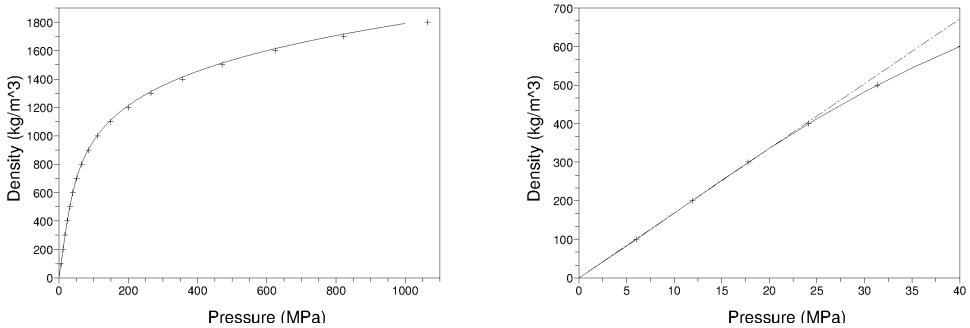

Fig. 1.1. Numerical equation of state of argon at $T = 300$ K ('+') and experimental reference curve (solid line). The picture on the right is a zoom on the low density/low pressure part of the curve, where the ideal gas regime is plotted in dash-dotted line.

Besides static equilibrium properties of the form of (1.1), we will also consider dynamical properties depending on the actual time evolution of the system (autocorrelation functions, transport coefficients such as thermal conductivity, exit times out of some region in phase space, ...).

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 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 given by the Hamiltonian

$$H(q,p) = E_{\text{kin}}(p) + V(q), \tag{1.3}$$

where the kinetic energy is

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

The matrix M is called the mass matrix. A Hamiltonian such as (1.3) is said to be *separable* since the energetic contributions of the momentum and position variables can be added independently. An instance of a non-separable Hamiltonian is the case when the mass-matrix depends on the configuration q of the system.

Most Hamiltonians encountered in applications are separable, and we will in any case restrict ourselves to separable Hamiltonians in these notes. Non-separable Hamiltonians may be considered for modelling purposes (when working with internal coordinates, for rigid body dynamics

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

for instance), or for mathematical convenience (such as the modified Hamiltonians used in the backward analysis of Hamiltonian dynamics, see the references at the end of 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). Then, we give more detail on 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 are set to 0 when the distance between two or several particles exceeds a given cut-off radii $r_{\rm cut}$. When cubic domains of length L are considered as in Figure 1.2, the domain length should be chosen so that $r_{\rm cut} < L/2$. This ensures that a particle interacts either with the primitive particle, or at most one of its periodic images;

(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 rigid body motions in this case since the potential energy is usually invariant under translations and rotations of the system;

(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 for reflections on the boundaries of the system (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.

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. Relying on the standard Born-Oppenheimer assumption, the positions q_i of the nuclei of charges Z_i are kept fixed, and the energy of the system is obtained by adding the Coulomb interaction energies between the nuclei, and the electronic ground-state energy:

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

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 $\bigwedge_{m=1}^{M} \mathrm{L}^2(\mathbb{R}^3, \mathbb{C})$ of antisymmetric functions. We omit the spin variable for notational simplicity although this variable is very important for quantitative computations. The electronic problem then reads

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

where the electronic Hamiltonian operator reads

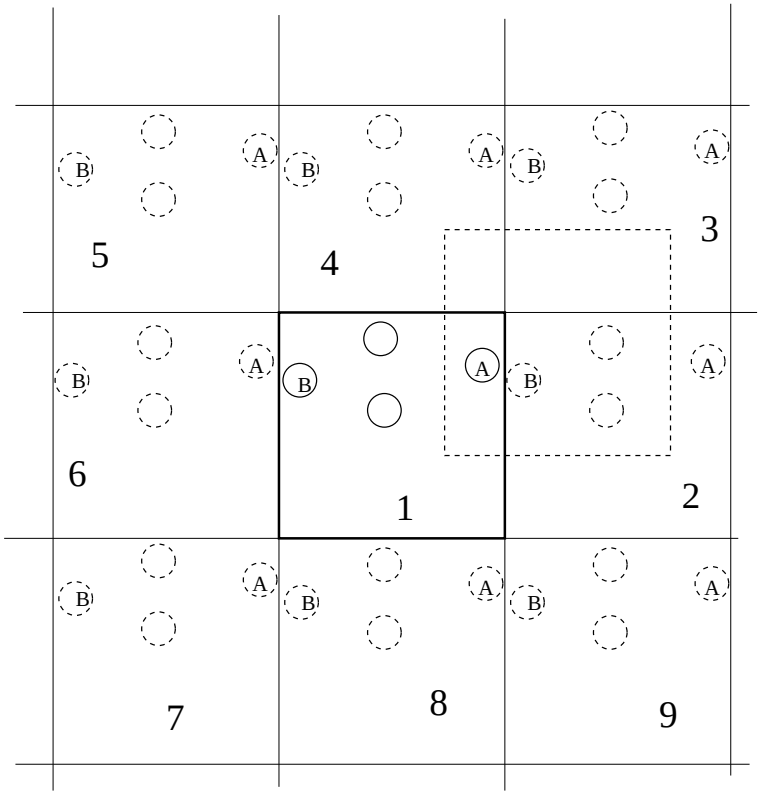

Fig. 1.2. System with periodic boundary conditions. The simulation cell is numbered "1", and the other cells are obtained by translation. The particles inside the primitive cell have interactions with particles in all the other cells.

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

We refer for instance to [31] 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 [129] or the Car-Parrinello approach [32]).

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

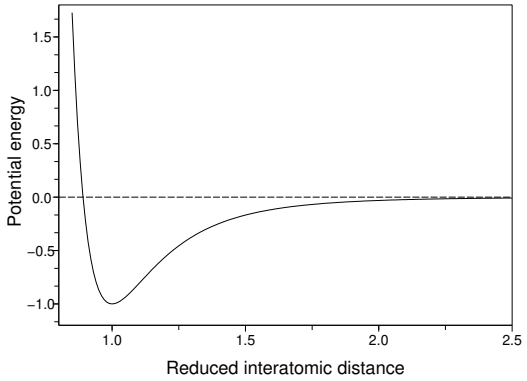

Fig. 1.3. Lennard-Jones potential (1.6) where the distance and the energy are expressed in terms of the equilibrium distance $2^{1/6}\sigma$ and the reference energy ε.

(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, $\varepsilon = 1.66 \times 10^{-21}$ 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 molecular systems contain molecules. Therefore, interaction potentials describing the existence of bonds between atoms are required. This is modelled through interactions involving several atoms. To describe these potentials, it is convenient to introduce the vector $r_{i,j} = q_j - q_i$.

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

$$\mathcal{V}_2(q_i, q_{i+1}) = \frac{k_0}{2}\left(|r_{i,i+1}| - l_{\rm eq}\right)^2,$$

where $l_{\rm eq}$ is the equilibrium length;

(2) Three atoms can interact *via* the three-body interaction potential energy

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

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;

(3) Four atoms 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

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

Local interactions have to be complemented by non-bonded interactions: van der Waals forces modelled by Lennard-Jones potentials, and Coulomb interactions, see [155] for further precision.

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 [154]). In this representation, the hydrogen atoms are not explicitly represented. 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 molecules. The solvent molecules are assumed to interact with all the other atoms through a pairwise potential $\mathcal{V}_{\mathrm{sol}}$ depending only on the relative distance. The total interaction energy then reads

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

with

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

and

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

The interactions within the molecule are

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

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

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

The parameters c_i $(i = 1, 2, 3)$ used in the united-atom model of [154] 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).

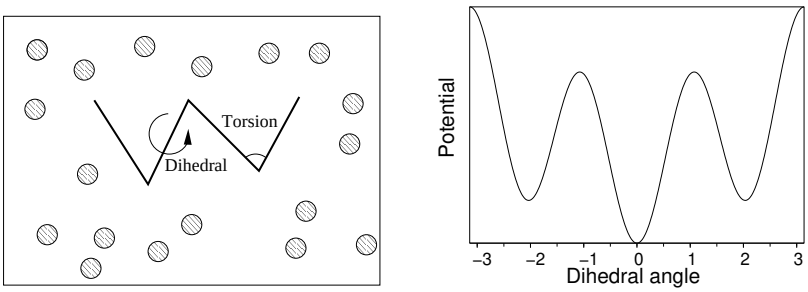

Fig. 1.4. Left: Schematic representation of a pentane molecule in a solvent (projected on a two-dimensional plane), and definition of the bond angles and dihedral angles. Right: Typical shape of the potential for the dihedral angle.

More realistic force fields.

Pairwise additive potentials such as (1.5), and two-, three- or four-body bonded interactions may however 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). Recent instances of

such potentials are the (Modified) Embedded-Atom Model potentials [17], or bond-order potentials of REBO [163] or ReaxFF [166] 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).

Non-dimensional units.

In practice, it is more convenient (and numerically more stable) to work with non-dimensional quantities. In this case, the manipulated numbers are all 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 $k_{\mathrm{B}}T$. 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:

$$t_0 = \frac{m_0^{1/2}\, l_0}{\varepsilon_0^{1/2}}. \tag{1.8}$$

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

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 A with respect to this measure, as given by (1.1):

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

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

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

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 10 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 $A(q^n, p^n)$ 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 miscropic configurations.

1.3.2 The microcanonical ensemble

The thermodynamic ensemble naturally associated with the Hamiltonian dynamics (2.1) 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:

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

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

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

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

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

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 A as

$$\int_{\mathcal{S}(E)} A(q,p)\,\delta_{H(q,p)-E}(dq\,dp) = \lim_{\Delta E\to 0}\frac{1}{\Delta E}\int_{\mathcal{N}_{\Delta E}(E)} A(q,p)\,dq\,dp. \tag{1.10}$$

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 (1.13) below, obtained with the co-area formula, and motivates the factor $|\nabla H(q,p)|^{-1}$ on the right-hand side of (1.13).

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

$$\mu_{\mathrm{mc},E}(dq\,dp) = Z_E^{-1}\,\delta_{H(q,p)-E}(dq\,dp), \tag{1.11}$$

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 (1.15) for some sufficient conditions to this end.

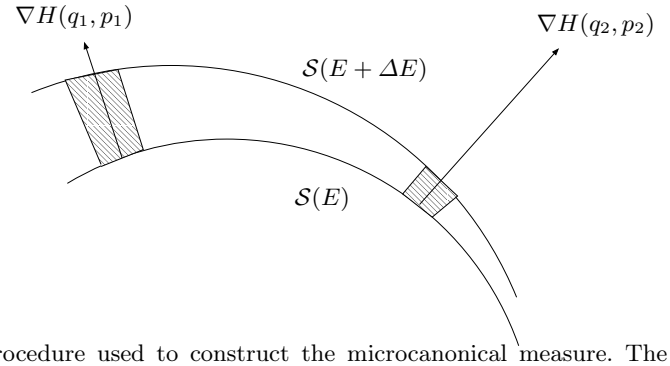

Fig. 1.5. Limiting procedure used to construct the microcanonical measure. The volume of the infinitesimal domain between $\mathcal{S}(E)$ and $\mathcal{S}(E+\Delta E)$ centered at a given point $(q,p)\in\mathcal{E}$ is proportional to $|\nabla H|^{-1}$.

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 $g:\mathbb{R}\to\mathbb{R}$,

$$\int_{\mathcal{E}} g(H(q,p))\,f(q,p)\,dq\,dp = \int_{\mathbb{R}} g(E)\int_{\mathcal{S}(E)} f(q,p)\,\delta_{H(q,p)-E}(dq\,dp)\,dE. \tag{1.12}$$

By the co-area formula (see Chapter 8), an alternative expression of the measure $\delta_{H(q,p)-E}(dq\,dp)$ is

$$\delta_{H(q,p)-E}(dq\,dp) = \frac{\sigma_{\mathcal{S}(E)}(dq\,dp)}{|\nabla H(q,p)|}, \tag{1.13}$$

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 (see Remark 8.1).

The microcanonical measure can then be rewritten as

$$\mu_{\mathrm{mc},E}(dq\,dp) = Z_E^{-1}\,\delta_{H(q,p)-E}(dq\,dp) = Z_E^{-1}\,\frac{\sigma_{\mathcal{S}(E)}(dq\,dp)}{|\nabla H(q,p)|}, \tag{1.14}$$

with

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

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. It however has a fixed temperature. 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

$$\mu(dq\,dp) = Z_\mu^{-1} \exp(-\beta H(q,p))\,dq\,dp, \tag{1.16}$$

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 (1.16) 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:

$$\nu(dq) = Z_\nu^{-1}\mathrm{e}^{-\beta V(q)}\,dq, \qquad Z_\nu = \int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\,dq, \tag{1.17}$$

and

$$\kappa(dp) = \left(\frac{\beta}{2\pi}\right)^{3N/2} \prod_{i=1}^{N} m_i^{-3/2} \exp\left(-\frac{\beta}{2} p^T M^{-1} p\right)\,dp. \tag{1.18}$$

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 are presented in Chapters 3 to 6.

Some elements on the derivation of the canonical measure

The expression (1.16) of the canonical probability measure can be obtained by maximizing the entropy under the constraint that the energy is fixed *in average*. Such a derivation is performed in [15] 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

$$\rho \geqslant 0, \qquad \int_{\mathcal{E}} \rho(q,p)\, dq\, dp = 1, \qquad \int_{\mathcal{E}} H(q,p)\rho(q,p)\, dq\, dp = E \tag{1.19}$$

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.

The statistical entropy is defined as

$$\mathfrak{S}(\rho) = -\int_{\mathcal{E}} \rho(q,p) \ln \rho(q,p)\, dq\, dp. \tag{1.20}$$

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 [15] 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 [15, 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.

The canonical measure is recovered as the solution to the following optimization problem

$$\sup\Big\{\mathfrak{S}(\rho),\ \rho \in L^1(\mathcal{E}),\ \rho \geqslant 0,\ \int_{\mathcal{E}} \rho = 1,\ \int_{\mathcal{E}} H\rho = E\Big\}. \tag{1.21}$$

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 (1.21) (normalization and average energy fixed). Since $\mathfrak{S}'(\rho) = -1 - \ln \rho$, a candidate maximizer in (1.21) 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 $\exp(1+\lambda) = Z$ 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 is indeed the unique maximizer of (1.21), as shown in [15, Section 4.2]. For the sake of completeness, we sketch the proof of this statement. Consider an arbitrary function satisfying (1.19). Using the inequality $\ln x \leqslant x - 1$ (with equality if and only if $x = 1$):

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

when ρ_1 and ρ_2 satisfy the constraints (1.19). 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 (1.19):

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

In view of the energy constraint (last condition in (1.19)),

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

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 (1.19).

1.3.4 Other thermodynamic ensembles

We saw in Section 1.3.3 that the Boltzmann-Gibbs probability measure (1.16) 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

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

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 $A_1,\dots,A_M$, 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 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:

$$\sup_{\rho\in\mathcal{S}(A_1^0,\dots,A_M^0)} \Big\{\mathfrak{S}_\lambda(\rho)\Big\}, \tag{1.22}$$

with

$$\mathcal{S}(A_1^0,\dots,A_M^0) = \left\{\rho\in L^1(\lambda)\;\middle|\;\rho\geqslant 0,\ \int_{\mathcal{E}}\rho\,d\lambda = 1,\ \int_{\mathcal{E}} A_i\rho\,d\lambda = A_i^0,\quad \forall i\in\{1,\dots,M\}\right\}.$$

The necessary condition to be satisfied by an extremum of (1.22) reads

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

Therefore,

$$\rho(q,p,x) = Z^{-1}\exp\left(\sum_{i=1}^M \alpha_i A_i(q,p,x)\right). \tag{1.23}$$

Remark 1.2 (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. There are some positive results, see [142] in the case of heat transport in one-dimensional atom chains. In general however, no explicit expression of the invariant measure is available, in contrast to formulas such as* (1.23).

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,

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

We choose a uniform measure on all possible volumes:

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

The constraints to be taken into account are $A_1 = H$ (average energy fixed), and $A_2(x,q,p) = xL^2$ (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 particles. (See for instance Chapter 3 in [127] for further precision on the construction of the reference measure for the grand-canonical ensemble.) Therefore,

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

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 $A_1 = H$ (average energy fixed) and $A_2(x,q,N) = N$ (average number of particles fixed). Applying the results of the general derivation, the grand-canonical equilibrium measure reads:

$$\rho_{\mu\mathrm{VT}}(dq\,dp\,dN) = Z_{\mu\mathrm{VT}}^{-1} \sum_{n=1}^{+\infty} \frac{\mathrm{e}^{\beta\mu n}}{n!}\,\mathrm{e}^{-\beta H_n(q,p)}\,1_{(q,p)\in\mathcal{E}_n}\,dq\,dp\,\delta_n(dN), \tag{1.24}$$

where $\beta\mu$ is the Lagrange multiplier associated with the average number constraint.[3] The parameter μ can be identified with the chemical potential.

[3] 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.

Part II

Sampling the microcanonical ensemble

2

Sampling the microcanonical ensemble

PARTOUT : CHANGER ORDRES p EN QQCHOSE QUI NE SOIT PAS DES VARIABLES DE LA DYNAMIQUE HAMILTONIENNE...

The bottom line of this chapter is the following: in order to evaluate average properties with respect to the microcanonical measure (1.11), we rely on a time-discretization of the assumed ergodic limit (2.17). Numerical schemes should therefore as a minimal requirement very well preserve the energy over very long times. Ergodicity however always remains a concern, in particular if other invariants than the energy are present.

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 discussed in Section 2.3.

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 position and momenta 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.

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

2.1.1 The Hamiltonian dynamics

For separable Hamiltonians, the evolution of isolated systems is governed by the Hamiltonian dynamics

$$\begin{cases} \dfrac{dq(t)}{dt} = \nabla_p H(q(t),p(t)) = M^{-1}p(t), \\ \dfrac{dp(t)}{dt} = -\nabla_q H(q(t),p(t)) = -\nabla V(q(t)). \end{cases} \tag{2.1}$$

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

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

The existence and uniqueness of trajectories typically follows from the Cauchy-Lipschitz theorem. A sufficient condition is that ∇H is locally Lipschitz continuous and V is bounded below. The condition that ∇H is locally Lipschitz continuous ensures the existence and uniqueness of local solutions in time; while the fact that V is bounded below implies that momenta remain bounded (since the total energy is conserved, see below), and hence positions grow at most linearly. The dynamics is therefore gloabally well posed. We will always assume in the sequel that the Cauchy problem (2.1)-(2.2) is well-posed.

We denote by ϕ_t the flow of the Hamiltonian dynamics, *i.e.* 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. 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 (2.9) 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 2.1.3 below for a proof and further comments):

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

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.

2.1.2 Equivalent reformulations

When the Hamiltonian equation (2.1) is reformulated in terms of the positions only, it reads

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

which is Newton's second law.

There are also more abstract reformulations of (2.1), which will be useful below. Introduce the first order differential operator

$$\mathcal{L}_{\mathrm{ham}} = p^T M^{-1}\nabla_q - \nabla V(q)^T \nabla_p,$$

considered for instance as an operator on $C^0(\mathcal{E})$, with domain $C^1(\mathcal{E})$. A simple computation shows that

$$\frac{d}{dt}\big[\psi(q(t),p(t))\big] = (\mathcal{L}_{\rm ham}\psi)\,(q(t),p(t)). \tag{2.5}$$

This means that $\mathcal{L}_{\rm ham}$ can be seen as the infinitesimal generator[1] of the following semigroup on $C^0(\mathcal{E})$:

$$(U(t)\psi)(q,p) = \left(\mathrm{e}^{t\mathcal{L}_{\rm ham}}\psi\right)(q,p) = \psi(\phi_t(q,p)). \tag{2.6}$$

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

Remark 2.1 (Rate of convergence of ergodic averages). *As an application of the above formalism, note that* (2.5) *can be equivalently reformulated as*

$$\frac{1}{\tau}\int_0^\tau (\mathcal{L}_{\rm ham}\psi)\,(q(t),p(t))\,dt = \frac{1}{\tau}\Big(\psi(q(\tau),p(\tau)) - \psi(q(0),p(0))\Big). \tag{2.7}$$

This shows that averages of functions in $\mathrm{Ran}(\mathcal{L}_{\rm ham})$ *converge, and that the associated error is of order* $1/T$*. The convergence rate is therefore much faster than for stochastic methods, where statistical errors typically scale as* $1/\sqrt{T}$*. It is in fact a general practical observation that deterministic methods allow to converge faster numerical results, although there is no guarantee that the limits are correct (and in some cases there are not). For Hamiltonian dynamics, the issue is that we would like to consider any observable. The above proof of convergence cannot be extended since* $\mathcal{L}_{\rm ham}^{-1}$ *is not easily defined.*

Remark 2.2 (Viriel's theorem, taken from [69]). *Consider the observable* $\psi(q,p) = p\cdot q$*, for which* $\mathcal{L}_{\rm ham}\psi(q,p) = p^T M^{-1} p - q\cdot\nabla V(q)$*. Under appropriate assumptions on the potential energy function (for instance, growth conditions on* V *ensuring that* $|\psi| \leqslant aH + b$ *for some constants* $a, b \in \mathbb{R}$*), the right-hand side of the above equality converges to 0 as* $\tau \to +\infty$*, so that, in view of* (2.7)*,*

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

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.*

The transport equation (2.5) (or equivalently the Hamiltonian equation (2.1)) 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 distributed according to some measure with density $f_0(q,p)$ with respect to the phase space Lebesgue measure $dq\,dp$, and that each initial phase space configuration is evolved according to the dynamics (2.1). Then the configurations $\phi_t(q^0,p^0)$ at time t are distributed according to a measure with density $f(t,q,p)$, whose evolution is governed by the following partial differential equation (called the Liouville equation):

$$\partial_t f = \nabla V\cdot\nabla_p f - \nabla_p H\cdot\nabla_q f = \mathcal{L}_{\rm ham}^\dagger f = -\mathcal{L}_{\rm ham} f, \qquad f(0,q,p) = f_0(q,p),$$

where $\mathcal{L}_{\rm ham}^\dagger = -\mathcal{L}_{\rm ham}$ is the adjoint of $\mathcal{L}_{\rm ham}$ on $L^2(\mathcal{E})$. This owes to the fact that (2.5) implies that, for any $\psi \in C^1(\mathcal{E})$,

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

[1] Recall that the generator $\mathcal{L}$ of a continuous semigroup $U(t)$ is characterized by the following strong limit:

$$\forall\varphi\in D(\mathcal{L}), \qquad \frac{U(t)-\mathrm{Id}}{t}\varphi \xrightarrow[t\to0]{} \mathcal{L}\varphi.$$

so that

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

An alternative derivation can be performed as follows. The configuration of the system at time t is obtained by evolving the initial conditions using the flow ϕ_t. Therefore,

$$\mathbb{E}\Big(\psi(q(t),p(t))\Big) = \int_{\mathcal{E}} \psi(\phi_t(q^0,p^0))\, f_0(q^0,p^0)\, dq^0\, dp^0 = \int_{\mathcal{E}} \psi(q,p))\, (f_0 \circ \phi_{-t})(q,p)\, dq\, dp.$$

This shows that $f(t) = f_0 \circ \phi_{-t} = \mathrm{e}^{-t\mathcal{L}_{\mathrm{ham}}} f_0$, which allows to recover the Liouville equation for initial data f_0 in an appropriate domain of $\mathcal{L}_{\mathrm{ham}}$ (for instance $f_0 \in C^1(\mathcal{E})$).

2.1.3 Properties of the Hamiltonian dynamics

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

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

$$\phi_{-t} = \phi_t^{-1}. \tag{2.8}$$

(2) *Reversibility.* Consider the momentum reversal function

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

Then, the time-reversed evolution ϕ_{-t} for $t \geqslant 0$, defined by (2.8), coincides with a forward evolution with momenta reversed (the so-called backward flow):

$$\phi_{-t} = S \circ \phi_t \circ S. \tag{2.9}$$

This statement can be proved as follows. Consider initial conditions (q_0,p_0), 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 time-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 $(\widehat{q}(t),\widehat{p}(t)) = (\phi_t \circ S)(q_0,p_0)$ both are solutions of Hamiltonian's dynamics, and start from the same initial condition $(q_0,-p_0)$; hence they are equal: $\phi_t \circ S = S \circ \phi_{-t}$. The conclusion follows by composing both sides with S and using $S^2 = \mathrm{Id}$.

(3) *Energy conservation.* The choice $\psi = H$ in the reformulation of the Hamiltonian dynamics (2.5) leads to $\dfrac{dH(q(t),p(t))}{dt} = 0$, which means that

$$H(q(t),p(t)) = H(q^0,p^0).$$

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

$$\int_{\phi_t(B)} dq\, dp = \int_B dq\, dp. \tag{2.10}$$

The volume conservation (2.10) is a consequence of the equality

$$\mathrm{Jac}\, \phi_t(q,p) = 1, \tag{2.11}$$

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

[2] In fact, as can seen from proof of Lemma 2.1, the absolute values on the determinant would not be necessary.

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

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 (2.11) relies on the fact that the Hamiltonian vector field is divergence-free:

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

The following lemma then allows us to conclude.

Lemma 2.1 ([Lemma VII.3.1 in [70]). *The flow of a differential equation $\dot{y} = f(y)$ in $\mathbb{R}^n$ is volume-preserving if and only if $\mathrm{div} f(y) = 0$ for all $y \in \mathbb{R}^n$.*

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

$$\dot{Y}(t) = A(t)Y(t), \qquad A(t) = \nabla f(\phi_t(y_0)), \tag{2.12}$$

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

$$\frac{d}{dt}\Big(\det Y\Big) = \mathrm{Tr}(A)\det Y. \tag{2.13}$$

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

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

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 $\mathrm{Tr}(A) = \mathrm{div} f$, we deduce from (2.13) that the requirement $\det Y(t) = 1$ for all $t \in \mathbb{R}$ is equivalent to $\mathrm{div}(f(\phi_t(y_0))) = 0$ for all $t \in \mathbb{R}$. The conclusion follows since y_0 is arbitrary. □

When $D = 1$, the preservation of the volume can be reformulated in a seemingly more complicated way, which however allows to characterize Hamiltonian systems (as made clear in Theorem 2.2 below).

Example 2.1 (Symplecticity of 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 oriented 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 is transformed into the parallelogram generated by Ay and Az, whose oriented volume is $(Ay)^T J(Az)$. The equality of these volumes for all possible vectors y, z is equivalent to $A^T JA = J$.

(5) *Symplecticity.* The matrix J defined by (2.3) is antisymmetric and orthogonal ($J^T = -J = J^{-1}$). In particular, $J^2 = -\mathrm{Id}$. The following property may be seen as an appropriate generalization of volume preservation, for general nonlinear mappings, and dimensions $D \geqslant 1$.

Definition 2.1. *For an open set $U \in \mathcal{E}$, a mapping $g : U \to \mathbb{R}^{2D}$ is symplectic if $\nabla g(q,p)$ satisfies*

$$\forall (q,p) \in U, \qquad (\nabla g)^T J \nabla g = J. \tag{2.14}$$

Note that the volume preservation property (2.10) is recovered as a consequence of the symplecticity property since (2.14) with $g = \phi_t$ implies that $(\det \nabla \phi_t)^2 = 1$, with the initial condition $\det \nabla \phi_0 = 1$. The symplecticity property is stronger, and can be understood as the conservation of oriented elementary parallelograms, see [109, Section 3.5] or [70, Section VI.2] for pedagogical presentations. Example 2.1 shows that symplecticity is equivalent to volume preservation in dimension 2.

It is easily shown that the flow ϕ_t is symplectic for all $t \in \mathbb{R}$ (this is a result due to Poincaré).

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 ϕ_t exists, the flow ϕ_t is a symplectic mapping.*

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,

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

where we used $J^T = -J$. This shows that $\psi(t)^T J \psi(t) = \psi(0)^T J \psi(0) = J$, which allows to conclude. □

Actually, the symplecticity of the flow is indeed a characteristic feature of Hamiltonian systems. To this end, we introduce the notion of locally Hamiltonian systems: the differential equation $\dot{y} = f(y)$ is locally Hamiltonian if for every $y_0 \in U$ there exists a neighborhood where the force field can be written as $f(y) = J\nabla H(y)$ for some function H (depending possibly on y_0).

Theorem 2.2 (Theorem VI.2.6 in [70]). *Let $f : U \to \mathbb{R}^{2D}$ be continuously differentiable. Then, the differential equation $\dot{y} = f(y)$ is locally Hamiltonian if and only if its flow ϕ_t is symplectic for all $y \in U$ and for all sufficiently small $t \in \mathbb{R}$.*

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

$$\left(\nabla \phi_t\right)^T J \nabla \phi_t = J,$$

and use (2.12) to obtain

$$Y(t)^T \left(A(t)^T J + JA(t)\right) Y(t) = 0.$$

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 $y_0 \in U$. We can then write $h(y_0) = Jf(y_0)$ as $\nabla H(y_0)$ upon introducing, for y in a neighborhood of y_0,

$$H(y) = \int_0^1 (y - y_0)^T h(y_0 + t(y - y_0))\, dt. \tag{2.15}$$

Indeed, using the symmetry property $\partial_{y_k} h_i = \partial_{y_i} h_k$, a simple computation shows that, for a component y_k $(1 \leqslant k \leqslant n)$,

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

which allows to conclude that $f = -J\nabla H$. □

2.1.4 The microcanonical measure as an ergodic limit

Practitioners often see microcanonical averages as ergodic limits over Hamiltonian trajectories. Notice first that $\mu_{\mathrm{mc},E}(dq\,dp)$ is invariant by the Hamiltonian dynamics flow ϕ_t for all energy levels E. Indeed, by the conditioning formula (1.12), and using the fact that $\operatorname{Jac} \phi_t = 1$ (see (2.11)),

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

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,

$$\int_{\mathcal{S}(E)} f(q,p)\, \delta_{H(q,p)-E}(dq\,dp) = \int_{\mathcal{S}(E)} f \circ \phi_t(q,p)\, \delta_{H(q,p)-E}(dq\,dp) \tag{2.16}$$

for all times $t \in \mathbb{R}$, which shows the claimed invariance. A more intuitive way to understand this equality is to realize that

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

by the same change of variables as above, and then to use (1.10) to obtain (2.16) in the limit $\Delta E \to 0$.

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 trajectorial averages

$$\int_{\mathcal{S}(E)} A(q,p)\, \mu_{\mathrm{mc},E}(dq\,dp) = \lim_{T \to +\infty} \frac{1}{T} \int_0^T A(\phi_t(q,p))\, dt, \tag{2.17}$$

where ϕ_t is the flow of the Hamiltonian dynamics (2.1), and the initial condition (q^0, p^0) is such that $H(q^0, p^0) = E$.

Ergodicity can be rigorously shown for completely integrable systems and their perturbations (see for instance [9]). 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

$$V(q) = \left(q^2 - 1\right)^2 . \tag{2.18}$$

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 cases 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.

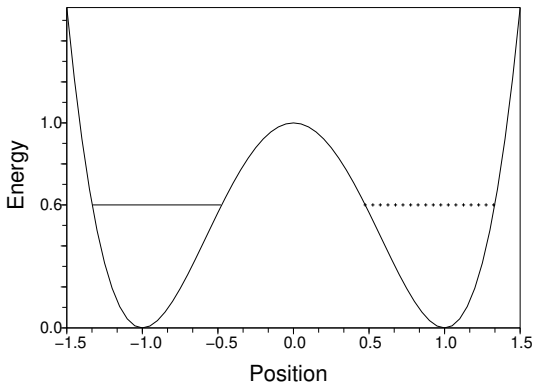

Fig. 2.1. Accessible positions in the energy surface $H(q,p) = 0.6$ for the double-well potential (2.18). If the dynamics starts in one of the connected components, it remains there.

From a numerical viewpoint, the computation of averages according to the right-hand side of (2.17) 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 (2.23). The numerical analysis of microcanonical sampling methods based on these properties (in the very particular case of completely integrable systems) can be read in [29, 30]. There exist also stochastic methods based on constrained diffusion processes to sample the microcanonical measure, see [55, 56]. 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 (2.1). 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 $\Delta t > 0$.

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:

(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 (2.17)

below). 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 devoted to Hamiltonian systems, fully taking into account the energy preservation as a basic first requirement. This requirement is more important than the scheme's order (*i.e.* the integer r 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 Δt^{r+1}), which determines the convergence rate of the numerical approximation only on finite-time intervals.

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

2.2.1 Failure of standard integration schemes

In view of (2.4), the Hamiltonian dynamics can be written as a standard ordinary differential equation (ODE). Therefore, all standard integration schemes can be used to integrate it. 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 proof of such results rely on stability properties typically obtained using a (discrete) Gronwall inequality. It should therefore be of no surprise that default integration scheme do not correctly preserve the energy over very long times. Moreover, the quest for high order schemes is not as relevant 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 [70, 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

$$H(q,p) = \frac{1}{2}\omega^2 q^2 + \frac{p^2}{2}.$$

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

$$y^{n+1} = \begin{pmatrix} q^n \\ p^n \end{pmatrix} = A_{\Delta t} y^n, \tag{2.19}$$

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

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

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 $|\lambda_{\Delta t,\pm}| = \sqrt{1+\omega^2\Delta t^2} > 1$ when $\Delta t > 0$, 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 $z_0 = P y_0$ and $\widetilde{K}_{\Delta t} = P_{\Delta t}^{-T} K P_{\Delta t}^{-1}$.

For the implicit Euler scheme, the energy exponentially decreases in time. A simple computation indeed allows to rewrite the scheme in the explicit form (2.19) (thanks to the linearity of the evolution) 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 $|\lambda_{\Delta t,\pm}| = \left(1+\omega^2\Delta t^2\right)^{-1/2} < 1$ when $\Delta t > 0$.

Let us consider one last example: the 4th order Runge-Kutta scheme, which is a default scheme for many applications in practice since it is quite precise (it has order 4, as the name indicates). The iterations read:

$$y^{n+1} = y^n + \Delta t \frac{f(Y^n) + 2f(Y^{n+1}) + 2f(Y^{n+2}) + f(Y^{n+3})}{6}. \tag{2.20}$$

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, the matrix $A_{\Delta t}$ in (2.19) reads

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

Its eigenvalues are

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

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 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 properties listes in Section 2.1.3, time reversibility for sure is not relevant since the standard integrators above satisfy this property. For instance, the numerical flow of the explicit Euler method

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

satisfies

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

The crucial property turns out to be symplecticity, although there exist some results on the longtime energy preservation of symmetric numerical methods for integrable systems (such that $\Phi_{\Delta t} \circ \Phi_{-\Delta t} = \Phi_{-\Delta t} \circ \Phi_{\Delta t} = \mathrm{Id}$; see [69, Chapter XI]).

2.2.2 Symplectic schemes

We show in this section one way to construct symplectic schemes, 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 $g, h : U \to \mathbb{R}^n$ 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 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

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

Each of the above dynamic 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

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

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

$$\begin{cases} q^{n+1} = q^n + \Delta t M^{-1}\, p^n, \\ p^{n+1} = p^n - \Delta t \nabla V(q^{n+1}). \end{cases} \tag{2.21}$$

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

$$\begin{cases} p^{n+1} = p^n - \Delta t \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t M^{-1}\, p^{n+1}. \end{cases} \tag{2.22}$$

Both schemes are explicit and of order 1, time-reversible but not symmetric.

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 [167]; 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 Section 1.3 in [69] for historical precisions). The Verlet algorithm is nowadays the standard integration scheme for Hamiltonian dynamics. It reads

$$\begin{cases} p^{n+1/2} = p^n - \dfrac{\Delta t}{2}\nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\ M^{-1}p^{n+1/2}, \\ p^{n+1} = p^{n+1/2} - \dfrac{\Delta t}{2}\nabla V(q^{n+1}). \end{cases} \tag{2.23}$$

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 (in the sense that $S \circ \Phi_{\Delta t}^{\mathrm{Verlet}} \circ S = \Phi_{-\Delta t}^{\mathrm{Verlet}}$) and symmetric (meaning $\left(\Phi_{\Delta t}^{\mathrm{Verlet}}\right)^{-1} = \Phi_{-\Delta t}^{\mathrm{Verlet}}$). It is of course symplectic by construction. It also requires only one force evaluation per timestep upon saving the forces from one timestep to the other.

Determination of the order of the Verlet scheme

The Verlet scheme can be shown to be of order 2, *i.e.*

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

where ϕ_t is the flow of the Hamiltonian dynamics). In fact, in order to make contact with manipulations useful for the numerical analysis of discretizations of stochastic differential equations (see Sections 4.4 and 5.4), we first rewrite this equality 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:

$$\begin{aligned} \left(\mathrm{e}^{tA}\psi\right)(q,p) &= \psi(\phi_t^1(q,p)) = \psi(q + tM^{-1}p, p), \\ \left(\mathrm{e}^{tB}\psi\right)(q,p) &= \psi(\phi_t^2(q,p)) = \psi(q, p - t\nabla V(q)). \end{aligned} \tag{2.24}$$

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 (2.21), and denote by $P_{\Delta t}^{A,B}$ its evolution operator:

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

The last equality is easily obtained by a direct computation based on the expressions (2.24). 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 [70, 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 2.3 (Stochastic integrators). *The above ordering of the integrators is also the correct one for stochastic evolutions. Consider for instance a numerical scheme of the form*

$$\begin{cases} q^{n+1/2} = \Phi_1(q^n, U_1^n), \\ q^{n+1} = \Phi_2(q^{n+1/2}, U_2^n), \end{cases}$$

where (U_1^n) and (U_2^n) are sequences of independent variables, the variables (U_i^n) being sampled from distributions μ_i for $i = 1, 2$. Define also the evolution operators

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

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

$$\begin{aligned} P\varphi(q) &= \mathbb{E}\Big[\varphi(q^{n+1})\Big|q^n = q\Big] = \mathbb{E}_{U_1}\left(\mathbb{E}_{U_2}\Big[\varphi\big(\Phi_2(q^{n+1/2}, U_2^n)\big)\Big]\Big|q^n = q\right) \\ &= \mathbb{E}_{U_1}\Big((P_2\varphi)(q^{n+1/2})\Big|q^n = q\Big) \\ &= P_1P_2\varphi(q). \end{aligned}$$

The order of the schemes are, from an algebraic viewpoint, most convienently obtained with the Baker-Campbell-Hausdorff (BCH) formula. For Trotter splittings,

$$\mathrm{e}^{tX}\mathrm{e}^{tY} = \mathrm{e}^{Z_t}, \qquad Z_t = t(X+Y) + \frac{t^2}{2}[X,Y] + \mathrm{O}(t^3), \tag{2.25}$$

where

$$[X,Y] = XY - YX \tag{2.26}$$

is the commutator between the operators X and Y. The equality (2.25) can be easily proved for bounded operators X, Y, in which case

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

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,

$$\begin{aligned} \mathrm{e}^{tX}\mathrm{e}^{tY} &= \left(\mathrm{Id} + tX + \frac{t^2}{2}X^2 + t^3R_{X,t}\right)\left(\mathrm{Id} + tY + \frac{t^2}{2}Y^2 + t^3R_{Y,t}\right) \\ &= \mathrm{Id} + t(X+Y) + \frac{t^2}{2}\left(X^2 + 2XY + Y^2\right) + t^3\widetilde{R}_{X,Y,t}, \end{aligned} \tag{2.27}$$

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

$$\mathrm{e}^{Z_t} = \mathrm{Id} + Z_t + \frac{Z_t^2}{2} + t^3R_{Z_t,t} = \mathrm{Id} + t(X+Y) + \frac{t^2}{2}\left((X+Y)^2 + 2\mathcal{Z}\right) + t^3\left(\widehat{R}_{X,Y,t} + t^3\widehat{R}_{X,Y,t} + R_{Z_t,t}\right).$$

Comparing this equality with (2.27) shows that

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

The higher order terms in the expansion of Z_t in powers of t can be found by induction.

Upon iterating (2.25), the following equality holds for Strang splittings:

$$\mathrm{e}^{tX/2}\mathrm{e}^{tY}\mathrm{e}^{tX/2} = \mathrm{e}^{S_t}, \qquad S_t = t(X+Y) + \frac{t^3}{12}\left(-\frac{1}{2}\big[X,[X,Y]\big] + \big[Y,[Y,X]\big]\right) + \mathrm{O}(t^5). \quad (2.28)$$

The equalities (2.25)-(2.28) can be given a rigorous meaning for bounded operators X, Y, in particular matrices (see [70, Section III.4.2]). For unbounded operators, they 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 $U_t = \mathrm{e}^{tX}$,

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

Equality holds in the strong sense for sufficiently smooth functions (such as $\bigcap_{k=1}^{n+1} D(X^k)$, 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 from spectral calculus.

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 (2.6) 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 $(\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B} - \mathrm{e}^{\Delta t(A+B)})\psi = \mathrm{O}(\Delta t^2)$ when ψ is sufficiently smooth. The choice $\psi(q,p) = (q,p)$ 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. Of course, higher-order splittings can be considered, although stability then becomes an issue since operations with negative timesteps are introduced (see [70, Section II.4]).

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 $x_\pm = \xi - 1 \pm \mathrm{i}\sqrt{\xi(2-\xi)}$ when $\xi(2-\xi) \geqslant 0$, and $x_\pm = \xi - 1 \pm \sqrt{\xi(\xi-2)}$ when $\xi(2-\xi) \leqslant 0$. The eigenvalues of $A_{\Delta t}$ therefore have modulus 1 if and only if

$$\omega\Delta t \leqslant 2. \tag{2.29}$$

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, it is easily shown that the modified energy

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

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

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

We will see below 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.

For more general potentials, 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.

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 (2.23) 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 (2.23).

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

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

the 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*

$$\dot{z} = f_{\Delta t}(z), \qquad z(0) = y^0. \tag{2.30}$$

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 $\Phi_{\Delta t}(y^0)$. In practice, only the first orders are computed, with corrections chosen such that $|z(\Delta t) - \Phi_{\Delta t}(y^0)|$ is much smaller than $|y(\Delta t) - \Phi_{\Delta t}(y^0)|$.

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

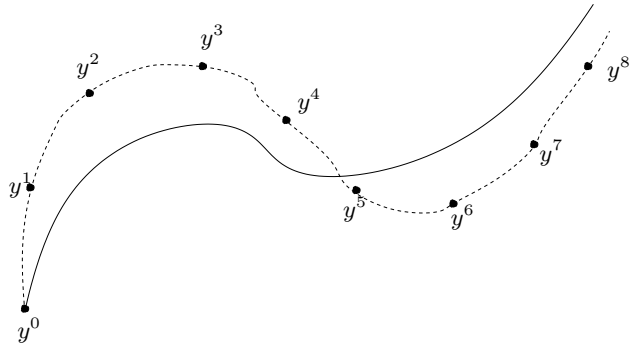

Fig. 2.2. Exact trajectory $y(t)$ (solid line) and numerical trajectory y^k (dots), interpolated by the trajectory of the modified dynamics $z(t)$ (dashed line).

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. Some 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 [69, Sections 4 and 5].

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 (2.30) is to compare the Taylor expansion of the numerical method $\Phi_{\Delta t}$ to the Taylor expansion of the solution of the modified equation $z(\Delta t)$. 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

$$\begin{aligned} z(t) &= z(0) + \Delta t\, \dot z(0) + \frac{\Delta t^2}{2} \ddot z(0) + \dots \\ &= y^0 + \Delta t [f(y^0) + \Delta t F(y^0)] + \frac{\Delta t^2}{2} f'_{\Delta t}(y^0) \dot z(0) + \dots \\ &= y^0 + \Delta t f(y^0) + \Delta t^2 \left[\frac{1}{2} f'(y^0) f(y^0) + F(y^0) \right] + \mathrm{O}(\Delta t^3). \end{aligned}$$

Now, for the explicit Euler scheme,

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

The choice $F(y) = -\frac{1}{2} f'(y) f(y)$ ensures that $\Phi^{\mathrm{EE}}_{\Delta t}(y^0) - z(\Delta t) = \mathrm{O}(\Delta t^3)$. For Hamiltonian dynamics,

$$F(y) = -\frac{1}{2}\begin{pmatrix} 0 & M^{-1} \\ -\nabla^2 V(q) & 0 \end{pmatrix}\begin{pmatrix} M^{-1}p \\ -\nabla V(q) \end{pmatrix} = \frac{1}{2}\begin{pmatrix} M^{-1}\nabla V(q) \\ \nabla^2 V(q)\cdot M^{-1}p \end{pmatrix}. \tag{2.31}$$

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 $\mathrm{div} F = 0$, which is clearly not the case for (2.31).

For the symplectic Euler scheme (2.21), 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

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

with

$$\widetilde{H}(q,p) = \frac{1}{2}p^T M^{-1}\nabla V(q). \tag{2.32}$$

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

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 [69, 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

$$\Phi_{\Delta t}(y) = y + \Delta t f(y) + \Delta t^2 D_2(y) + \Delta t^3 D_3(y) + \dots$$

with smooth vector fields D_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:

$$\Phi_{\Delta t}(y) = \varphi_{N,\Delta t}(y) + \mathrm{O}(\Delta t^{N+2}). \tag{2.33}$$

Remark 2.4. *Of course, if the numerical method is of order r (i.e. $\Phi_{\Delta t}(y) = \phi_{\Delta t}(y) + \mathrm{O}(\Delta t^{r+1})$), then the $r-1$ first order correction terms vanish: $F_1 = \dots = F_{r-1} = 0$. Note also that if the leading order term of the local trunction error is E_{r+1}:*

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

then a simple computation shows that (2.33) *holds with $N = r$ and $F_r = E_{r+1}$.*

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

$$f_{N-1,\Delta t} = J\nabla H + \Delta t J\nabla H_1 + \dots + \Delta t^{N-1} J\nabla H_{N-1}.$$

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

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

so that (2.33) implies

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

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

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

where we have used $\nabla\varphi_{N-1,\Delta t}(y) = \mathrm{Id} + \mathrm{O}(\Delta t)$ and the symplecticity of $\varphi_{N-1,\Delta t}$ in the second and third lines. The last equality shows that $J\nabla F_N(y)$ is symmetric, so that $JF_N(y) = -\nabla H_N(y)$ for some Hamiltonian H_N (see the proof of Theorem 2.2).

Longtime energy preservation

The results of the previous subsections 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 (2.15)). 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 $r \geqslant 1$, 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 $m \geqslant r+1$, there is $C_m > 0$ for which*

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

A careful proof shows that C_m depends on derivatives of H up to order m in the compact subset where the trajectory remains. The precise interpretation of this result is the following: for physical times $t \ll \Delta t^{r-m}$ which are very large when Δt is small, the dominant term in the error is $C\Delta t^r$. 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_m. Upon resorting to some optimal truncation of the series (optimizing with respect to m), 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 [70]). *Consider an analytic Hamiltonian H and a symplectic method $\Phi_{\Delta t}$ of order r. If the numerical trajectory remains in a compact subset, then there exists $h > 0$ and $\Delta t^* > 0$ such that, for $\Delta t \leqslant \Delta t^*$,*

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

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

Let us however, one last time, emphasize again that the near energy preservation is a 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 [69, 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...

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

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

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

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

Then,

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

This gives the claimed result since $\left|\widetilde{H}_m(q^n,p^n) - H(q^n,p^n)\right| \leqslant C\Delta t^r$. □

2.3 Extensions

The timestep in the Verlet method is limited by the stability requirement (2.29). 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 [110];
- 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 (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 [56].

Part III

Sampling the canonical ensemble

3

The Metropolis-Hastings algorithm

3.1 Some background material on Markov chains

We denote by $\mathcal{D}$ the configuration space, which may be either $\mathbb{R}^D$ or a compact domain. 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:

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

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

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 and continuous function),

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

Again, with some abuse of notation, we use the same notation for the evolution operator as for the kernel. When the transition kernel depends on the time index n, the chain is called time-inhomogeneous.

To study the longtime properties of a time homogeneous chain, three 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 continuous test function ϕ:
$$\int_{\mathcal{D}}\int_{\mathcal{D}} \phi(q')\,P(q, dq')\,\pi(dq) = \int_{\mathcal{D}} \phi(q)\,\pi(dq). \tag{3.1}$$
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.
- *Reversibility.* The chain P is said to be reversible with respect to π as soon as the following *detailed balance condition* is satisfied:
$$P(q, dq')\,\pi(dq) = P(q', dq)\,\pi(dq'). \tag{3.2}$$
The reversibility condition implies the stationarity of π. Indeed, a simple computation shows that, for a bounded continuous function ϕ and using (3.2),
$$\begin{aligned}\int_{\mathcal{D}}\int_{\mathcal{D}} \phi(q')\,P(q, dq')\,\pi(dq) &= \int_{\mathcal{D}}\int_{\mathcal{D}} \phi(q')\,P(q', dq)\,\pi(dq')\\ &= \int_{\mathcal{D}} \left(\int_{\mathcal{D}} P(q', dq)\right)\phi(q')\,\pi(dq')\\ &= \int_{\mathcal{D}} \phi(q')\,\pi(dq'),\end{aligned}$$
which is the stationarity condition (3.1). The detailed balance condition (3.2) 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 $(q^n, \dots, q^0)$.
- *Irreducibility.* A Markov chain is said to be irreducible with respect to some measure ρ when, for any Borel subset $S \subset \mathcal{X}$ such that $\rho(S) > 0$, and any initial condition $x^0 \in \mathcal{X}$, it holds $\mathbb{P}_{x^0}(\tau_S < +\infty) > 0$ where $\tau_S = \inf\{n \geqslant 0, x^n \in S\}$ 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
$$P^n(q, dq') = \int_{y\in\mathcal{D}} P(q, dQ)\,P^{n-1}(Q, dq'),$$
with $P^1(q, dq') := P(q, dq')$. Note that $\mathbb{P}_{x^0}(\tau_S < +\infty) > 0$ is implied by the following property: for any Borel subset $S \subset \mathcal{X}$ such that $\rho(S) > 0$ and any initial condition $x^0 \in \mathcal{X}$, there exists $n \geqslant 0$ (depending on x^0 and S) such that $P^n(x^0, S) > 0$.
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.
IL FAUT REVOIR CA, LA PROPOSITION CI DESSOUS ET LES COMMENTAIRES QUI SUIVENT...

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

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

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 $1/2$.

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 Theorem 17.1.7 in [125]):

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:*

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

Two comments are in order:

(i) we will see in Theorem 3.4 one way to prove the existence of an invariant probability measure. Some Markov chains such as the Metropolis-Hastings algorithm discussed in Section 3.2 have by construction an invariant measure which is explicitly known. Note also that π is automatically absolutely continuous with respect to the measure 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 $P(x, dy)$ is absolutely continuous with respect to the invariant probability measure π for all $x \in \mathcal{X}$, and the Markov chain is irreducible with respect to π; see [164, Corollary 1], based on [130].

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 (1.17))

$$\nu(dq) = Z^{-1} \mathrm{e}^{-\beta V(q)}\, dq. \tag{3.4}$$

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 [124], and relied on symmetric proposals in the configuration space, meaning that

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

It was later refined in [76] in order to allow for non-symmetric propositions which can bias proposals towards higher probability regions with respect to the target distribution ν.

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 (3.2) 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 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:

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

Notice that, as mentioned above, the distribution ν has to be known only up to a multiplicative constant to perform this algorithm.

It may be worth emphasizing that, as for "direct" probabilistic methods such as the rejection method, rejected moves 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.

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, 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.

3.2.1 Mathematical properties

For a given smooth test function ϕ,

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

by taking 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

$$P(q, dq') = R(q, q')T(q, dq') + (1 - \alpha(q))\, \delta_q(dq'), \tag{3.5}$$

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 occur 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 simple computation shows that the Metropolis-Hastings transition kernel P given in (3.5) is reversible with respect to ν. Indeed, consider

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

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 (3.6) can be rewritten as

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

On the other hand, for a given test function ϕ,

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

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

Remark 3.1. *The Metropolis-Hastings algorithm relies on the acceptance ratio $A(r) = \min(1, r)$ but other functions A satisfy $A(r) = rA(1/r)$ and thus lead to a dynamics reversible with respect to ν. For instance (see [63]),*

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

with $\gamma \geqslant 1$. The Metropolis rule corresponds to $\gamma = 1$, while the Barker rule $A(r) = r/(r + 1)$ (introduced in [16]) is formally recovered for $\gamma = +\infty$. However, it can be shown that the Metropolis rule is optimal in terms of asymptotic variance (see [135]).

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.

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 [147, 148], where some optimal acceptance rates are obtained in a limiting regime. We warn the reader however that these computations do not take into account specific important features of actual models (like metastability or phase space dynamics such as the Langevin dynamics). In practice, it is always a good idea to run some preliminary small simulations to roughly determine the optimal acceptance rate.

3.2.2 Some examples of proposition transition kernels

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

$$q' = q + G, \quad G \sim \mathcal{N}(0, \sigma^2 \operatorname{Id}_D),$$

in which case the proposal probability kernel is

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

where D is the dimension of the ambient space. Of course, uniformly distributed displacements could be considered as well

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

in which case

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

Both these proposals are symmetric. The problem with such proposals is that they may not be well suited to the target probability measure (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 particles $q = (q_1, \ldots, q_N)$ in a physical space of dimension d consists in applying a random walk displacement to only one particle chosen at random. This may help to propose moves which are likely to be accepted (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

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

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.

Non-symmetric move

An instance of a non-symmetric proposal which may be useful to sample the canonical measure (3.4) is the one used in the so-called Metropolis-Adjusted Langevin Algorithm (MALA) in the statistics literature, known as Smart MC in the chemistry literature [150, 148]:

$$q' = q - \alpha \nabla V(q) + \sqrt{\frac{2\alpha}{\beta}}\, G, \quad G \sim \mathcal{N}(0, \mathrm{Id}_D).$$

The proposal is built on the time discretization (with time step $\alpha > 0$) 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. It holds

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

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

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 applied community deals with new and creative proposal kernels, using for instance "non-physical moves" where molecules are broken and other ones are linked together. Another important example is parallel tempering strategies [119], 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.

3.3 Convergence of the law

3.3.1 A general result

We present in this section a result on the exponential convergence of the evolution operator in some weighted L^∞ space [73]. Similar results are provided in [125]; see also [141] for stochastic differential equations. We give the result in a general form on an abstract configuration space $\mathcal{X}$ since this result will be used in many situations: time-discrete or time-continuous dynamics, in terms of positions or positions and momenta. 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

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

Note that these definitions imply

$$\int_{\mathcal{X}} (P\varphi)\, d\mu = \int_{\mathcal{X}} \varphi\, d(P\mu). \tag{3.7}$$

Indeed, the equality is a result of the above definitions when $\varphi = \mathbf{1}_B$ for any $B \in \mathscr{B}(\mathcal{X})$, and from that we deduce the equality for any bounded measurable functions (see for instance [153]). We make the following assumptions.

Assumption 3.2 (Lyapunov condition) *There exists a function $W : \mathcal{X} \to [0, +\infty)$ and constants $K \geqslant 0$ and $\gamma \in (0, 1)$ such that*

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

Remark 3.2. *Note that, upon replacing $\mathcal{X}$ with $\{x \in \mathcal{X} \,|\, W(x) < +\infty\}$, it can be assumed that $W(x) < +\infty$ for any $x \in \mathcal{X}$.*

This assumption implies that the dynamics returns to the region of the configuration space where the values of W are not too large. Typically, one chooses functions 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 $W \geqslant 0$ (in order to be able to divide by $1 + W$, see (3.8) below).

Assumption 3.3 (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 $\mathcal{C} = \{x \in \mathcal{X} \,|\, W(x) \leqslant R\}$ for some $R > 2K/(1-\gamma)$, where γ, K are introduced in Assumption 3.2.

This condition ensures that there is a sufficiently strong coupling of the evolution in the region where the Lyapunov function is sufficiently small. **Benjamin me signale qu'en reecrivant la preuve, il s'est rendu compte qu'on peut en fait se contenter, plutot que d'une condition de minoration $Q(x, dy) \geqslant \alpha\nu(dy)$, d'une condition type $inf_{x,x'} \min(Q(x, dy), Q(x', dy))(\mathcal{X}) \geqslant \alpha$**

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

$$\|\varphi\|_{L^\infty_W} = \left\| \frac{\varphi}{1+W} \right\|_{L^\infty} < +\infty. \tag{3.8}$$

Theorem 3.4. *Assume that Assumptions 3.2 and 3.3 hold. Then, P admits a unique invariant probability measure μ which satisfies*

$$\int_{\mathcal{X}} W \, d\mu < +\infty. \tag{3.9}$$

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

$$\forall n \in \mathbb{N}, \qquad \left\| P^n \varphi - \int_{\mathcal{X}} \varphi \, d\mu \right\|_{L^\infty_W} \leqslant C r^n \left\| \varphi - \int_{\mathcal{X}} \varphi \, d\mu \right\|_{L^\infty_W}. \tag{3.10}$$

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

$$L^\infty_{W,0}(\mathcal{X}) = \left\{ \varphi \in L^\infty_W(\mathcal{X}) \;\middle|\; \int_{\mathcal{X}} \varphi \, d\mu = 0 \right\}.$$

Then, (3.10) can be equivalently written as an inequality of bounded operators on $L^\infty_{W,0}(\mathcal{X})$:

$$\|P^n\|_{\mathcal{B}\left(L^\infty_{W,0}(\mathcal{X})\right)} \leqslant C r^n. \tag{3.11}$$

Remark 3.3. *A FAIRE : quand famille de conditions de Lyapunov avec $\gamma_n \to$ et b_n, on a une famille de taux de convergence et prefacteurs... Quel est le choix optimal en fonction de n ?*

Remark 3.4 (sub-exponential convergence rates). *It is possible to weaken the Lyapunov condition (4.47) for instance as $\mathcal{L}W \leqslant \phi(W) + b$, 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 [45] or [34] for further details.*

This result allows us to obtain bounds on the resolvent $\mathrm{Id} - P$, which will prove useful in various contexts (error estimates on time discretizations, definition of the variance of Markov chains, etc).

Corollary 3.1. *If the assumptions of Theorem 3.10 are satisfied, the bounded operator* $\mathrm{Id} - P$ *is invertible on* $L^\infty_{W,0}(\mathcal{X})$*, and*

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

Proof. The proof is very simple: note that the sum $\sum_n P^n$ is convergent in $\mathcal{B}\left(L^\infty_{W,0}(\mathcal{X})\right)$ in view of (3.11). In addition, a simple computation gives

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

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

$$(\mathrm{Id}-P)^{-1} = \sum_{n=0}^{+\infty} P^n. \tag{3.12}$$

Moreover,

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

which gives the desired bound. □

Remark 3.5. *In the subsequent chapters, we will in fact consider Lyapunov functions with values larger than 1, which correspond to* $\widetilde{W} = 1 + W$ *with the notation of this chapter. Assumption* (3.2) *should then be replaced by*

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

while the Assumption 3.3 should be checked in the set $\mathcal{C} = \{x \in \mathcal{X} \,|\, \widetilde{W}(x) \leqslant R\}$ *for some* $R > 1 + 2(\widetilde{K} - 1 + \gamma)/(1-\gamma)$*.*

Proof of Theorem 3.4

The proof of Theorem 3.4 is divided into three steps:

(1) We first introduce equivalent metrics on $L^\infty_W(\mathcal{X})$, which allow to simplify some computations.
(2) We then prove a contraction principle in this equivalent metric (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 $\|\cdot\|_{L^\infty_{aW}}$:

$$\|\varphi\|_{L^\infty_{aW}} = \left\|\frac{\varphi}{1+aW}\right\|_{L^\infty}.$$

The associated induced metric on probability measures is

$$\rho_a(\mu_1,\mu_2) = \sup_{\varphi:\|\varphi\|_{L^\infty_{aW}}\leqslant 1} \int_{\mathcal{X}} \varphi(x)\Big(\mu_1(dx) - \mu_2(dx)\Big) = \int_{\mathcal{X}} (1+aW(x))|\mu_1-\mu_2|(dx). \tag{3.13}$$

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

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

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

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

as well as the induced metric on probability measures:

$$d_a(\mu_1, \mu_2) = \sup_{\varphi : \|\varphi\|_a \leqslant 1} \int_{\mathcal{X}} \varphi(x) \Big(\mu_1(dx) - \mu_2(dx) \Big). \tag{3.14}$$

In fact, as made precise in the following proposition, the two families of equivalent norms are almost identical. The basic idea is that an element $\varphi \in L^\infty_{aW}$ can be written as $\varphi = (1 + aW)\phi$ with $\phi \in L^\infty$.

Proposition 3.2. *It holds* $\|\varphi\|_a = \inf_{c \in \mathbb{R}} \|\varphi + c\|_{L^\infty_{aW}}$. *Therefore,* $d_a(\mu_1, \mu_2) = \rho_a(\mu_1, \mu_2)$.

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

$$\frac{|\varphi(x) - \varphi(y)|}{d_a(x,y)} \leqslant \frac{|\varphi(x)| + |\varphi(y)|}{2 + aW(x) + aW(y)} \leqslant \|\varphi\|_{L^\infty_{aW}}.$$

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

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

$$c_\varphi = \inf_{x \in \mathcal{X}} \big(1 + aW(x) - \varphi(x) \big). \tag{3.15}$$

We can then prove the following facts.

- The constant c_φ is finite. Indeed, consider $y \in \mathcal{X}$ such that $W(y) < +\infty$ and $|\varphi(y)| < +\infty$ (see Remark 3.2). Then,

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

  so that

$$1 + aW(x) - \varphi(x) \geqslant -1 - aW(y) - |\varphi(y)|.$$

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

$$\varphi(x) + c_\varphi \leqslant \varphi(x) + \Big(1 + aW(x) - \varphi(x) \Big) = 1 + aW(x),$$

  while on the other,

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

In conclusion, $\|\varphi + c_\varphi\|_{L^\infty_{aW}} \leqslant 1$ for the specific choice (3.15) when $\|\varphi\|_a = 1$. By homogeneity, for general measurable functions φ,

$$\inf_{c \in \mathbb{R}} \|\varphi + c\|_{L^\infty_{aW}} \leqslant \|\varphi\|_a,$$

which allows to conclude to the equality.

The equality of the induced metrics d_a and ρ_a on the space of probability measures is easily obtained since the functions belonging to the spaces $\{\varphi : \|\varphi\|_a \leqslant 1\}$ and $\{\varphi : \|\varphi\|_{L^\infty_{aW}} \leqslant 1\}$ differ only by additive constants, which are unimportant in the integrals appearing on the right-hand sides of the definitions (3.13) and (3.14). □

Proposition 3.3. *If Assumptions 3.2 and 3.3 hold, 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 3.2 and 3.3. Note that the above inequality can be iterated to obtain $\|P^n\varphi\|_a \leqslant r^n\|\varphi\|_a$. In order to obtain the conclusion 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

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

In fact, since changing φ into $\varphi + c$ does not change the left-hand side, we can replace $\|\varphi\|_a$ with $\|\varphi\|_{L^\infty_{aW}}$ on the right-hand side. We distinguish two cases, the value of a being determined by the second condition.

(i) If $W(x)+W(y) \geqslant R$ (where R is defined in Assumption 3.3): 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 $\varphi(x) \leqslant \|\varphi\|_{L^\infty_{aW}}(1+aW(x))$, we obtain

$$\begin{aligned}
|P\varphi(x) - P\varphi(y)| &\leqslant \|\varphi\|_{L^\infty_{aW}}\big(2 + aPW(x) + aPW(y)\big)\\
&\leqslant \|\varphi\|_{L^\infty_{aW}}\big(2 + \gamma aW(x) + \gamma aW(y) + 2aK\big)\\
&\leqslant \|\varphi\|_{L^\infty_{aW}}\big(2 + \gamma_0 aW(x) + \gamma_0 aW(y)\big)\\
&\leqslant \|\varphi\|_{L^\infty_{aW}}\gamma_1\big(2 + aW(x) + aW(y)\big) = \|\varphi\|_{L^\infty_{aW}}\gamma_1 d_a(x,y).
\end{aligned}$$

The last inequality is true as soon as $2(1-\gamma_1) \leqslant a(\gamma_1 - \gamma_0)R$, which motivates the choice of γ_1.

(ii) If $W(x)+W(y) \leqslant R$: 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,

$$P\varphi(x) = (1-\alpha)\widetilde{P}\varphi(x) + \alpha\int_{\mathcal{X}} \varphi\, d\lambda, \tag{3.16}$$

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

$$\begin{aligned}
|P\varphi(x) - P\varphi(y)| &= (1-\alpha)\left|\widetilde{P}\varphi(x) - \widetilde{P}\varphi(y)\right|\\
&\leqslant (1-\alpha)\|\varphi\|_{L^\infty_{aW}}\left(2 + a\widetilde{P}W(x) + a\widetilde{P}W(y)\right)\\
&\leqslant \|\varphi\|_{L^\infty_{aW}}\left(2(1-\alpha) + aPW(x) + aPW(y)\right)\\
&\leqslant \|\varphi\|_{L^\infty_{aW}}\left(2(1-\alpha) + a\gamma[W(x)+W(y)] + 2aK\right).
\end{aligned} \tag{3.17}$$

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

$$|P\varphi(x) - P\varphi(y)| \leqslant \|\varphi\|_{L^\infty_{aW}}\gamma_2 d_a(x,y).$$

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

Remark 3.6. *As discussed in [71], it is possible to consider a more general assumption than the minorization condition stated in Assumption 3.3; namely: There exists a constant $\alpha \in (0,1)$ such that, for all $(x,y) \in \mathcal{X}^2$ with $W(x)+W(y) \leqslant R$ (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 (3.16) *that Assumption 3.3 implies the latter condition. The only part of the proof which changes is the coupling estimate* (3.17) *in item (ii), for which one proceeds as follows. Consider φ such that $\|\varphi\|_{L^\infty_{aW}} \leqslant 1$ and decompose it as $\varphi = \varphi_1 + \varphi_2$ with $|\varphi_1(z)| \leqslant 1$ and $|\varphi_2(z)| \leqslant aW(z)$ for all $z \in \mathcal{X}$. Then,*

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

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

Corollary 3.2. *If Assumptions 3.2 and 3.3 hold, there exists $r \in (0,1)$ 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 (3.7) and (3.14), it holds $d_a(P\mu_1, P\mu_2) \leqslant r\, d_a(\mu_1, \mu_2)$. 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. *Under Assumptions 3.2 and 3.3, there exits an invariant probability measure μ on $\mathcal{X}$ such that*

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

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 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.

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 W with respect to μ are deduced by integrating both sides of the Lyapunov condition with respect to μ_∞:

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

which gives the upper bound $\int_{\mathcal{X}} W\, d\mu \leqslant K/(1-\gamma)$. □

Theorem 3.4 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 $\varphi \in L^\infty_{aW}$, this implies, by definition of ρ_a,

$$\left|P^n\varphi(x_0) - \int_{\mathcal{X}} \varphi \, d\mu\right| = \left|P^n\left(\varphi - \int_{\mathcal{X}} \varphi \, d\mu\right)(x_0)\right| \leqslant \rho_a(P^n\delta_{x_0}, \mu) \left\|\varphi - \int_{\mathcal{X}} \varphi \, d\mu\right\|_{L^\infty_{aW}}$$
$$\leqslant r^n \rho_a(\delta_{x_0}, \mu) \left\|\varphi - \int_{\mathcal{X}} \varphi \, d\mu\right\|_{L^\infty_{aW}}.$$

Now, $\rho_a(\delta_{x_0}, \mu) \leqslant C(1+W(x_0))$ for some constant $C > 0$ (which depends on a) since, by definition of $L^\infty_{aW}(\mathcal{X})$,

$$\int_{\mathcal{X}} \phi(x)(\delta_{x_0}(dx) - \mu(dx)) = \phi(x_0) - \int_{\mathcal{X}} \phi \, d\mu \leqslant \|\phi\|_{L^\infty_{aW}} \left(2 + aW(x_0) + a\int_{\mathcal{X}} W \, d\mu\right)$$
$$\leqslant C\|\phi\|_{L^\infty_W}\big(1 + W(x_0)\big).$$

In conclusion,

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

which leads to (3.10).

Remark 3.7. *Note that the prefactors $C, \widetilde{C} \geqslant 1$ arise from some norm equivalence. We will encounter again such prefactors in the theory of hypocoercivity, see Sections 5.3.3 and 5.3.4.*

3.3.2 Application to the Metropolis-Hastings algorithm

A simple example to apply the above framework is the following. Consider a compact state space $\mathcal{D}$, and a symmetric proposal kernel with a density with respect to the Lebesgue measure, and 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, (3.6) implies that

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

This immediately gives the minorization condition in Assumption 3.3 with $\alpha = m\eta|\mathcal{D}|/M$ and $\lambda(dq) = |\mathcal{D}|^{-1} \, dq$. Since the space is compact, the Lypunov function can be chosen to be $W = 0$ in Assumption 3.2. We can then conclude to the exponential convergence in L^∞: there exist $C > 0$ and $r \in (0, 1)$ such that, for any $\varphi \in L^\infty(\mathcal{D})$,

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

3.4 Rate of convergence of ergodic averages

Consider a bounded observable φ. 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. In fact, this convergence result can be extended to observables $\varphi \in L^1(\nu)$. In particular, if $W \in L^1(\nu)$ and $\varphi \in L^\infty_W$, then $\varphi \in L^1(\nu)$. We can assume without loss of generality that φ has average 0 with respect to ν, by replacing φ with $\Pi\varphi$ defined as

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

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 (further discussed below). We will therefore only motivate here the expression of the asymptotic variance, using the operator bounds derived in the previous section.

Proposition 3.5. *Suppose that Assumptions 3.3 and 3.2 hold, with a Lyapunov function such that*

$$\int_{\mathcal{D}} W^2 \, d\nu < +\infty.$$

Consider $\varphi \in L^\infty_W$. Then, the asymptotic variance of the random variable $\widehat{\varphi}_N$ is given by

$$\begin{aligned} N_{\text{iter}} \lim_{N_{\text{iter}} \to +\infty} \text{Var}_\nu \left(\widehat{\varphi}_{N_{\text{iter}}} \right) &= \int_{\mathcal{D}} \Pi\varphi \left[\left(2(\text{Id} - P)^{-1} - \text{Id} \right) \Pi\varphi \right] d\nu \\ &= \mathbb{E}_\nu \left(\Pi\varphi^2 \right) + 2 \sum_{n=1}^{+\infty} \mathbb{E}_\nu \left[\Pi\varphi(q^n) \Pi\varphi(q^0) \right], \end{aligned} \tag{3.18}$$

where expectations are with respect to initial conditions $q^0 \sim \nu$ (where ν is invariant by P), and over all realizations of the Markov chain.

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

$$(\text{Id} - P)\Phi = \Pi\varphi \tag{3.19}$$

belongs to $L^2(\nu)$; see [125, Theorem 17.4.4]. If $\varphi \in L^\infty_W(\mathcal{X})$ and $W \in L^2(\pi_{\Delta t})$, one way to guarantee that $\Phi \in L^2(\pi_{\Delta t})$ is to resort to Corollary 3.1. The condition $W \in L^2(\pi_{\Delta t})$ can be proved by showing that a Lyapunov condition holds for W^2 (*i.e.* Assumption 3.2 holds with W replaced by W^2).

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

$$\mathbb{E}_\nu \left[\Pi\varphi(x^n) \Pi\varphi(x^m) \right] = \mathbb{E}_\nu \left[\Pi\varphi(x^{|n-m|}) \Pi\varphi(x^0) \right]$$

for all $n, m \geqslant 0$. Then,

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

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

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

Since, by (3.11),

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

a dominated convergence argument shows that

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

with

$$\begin{aligned}\sigma^2_{\varphi,\Delta t} &= \mathbb{E}_\nu\left[(\Pi\varphi)^2\right] + 2\sum_{n=1}^{+\infty}\mathbb{E}_\nu\left[(\Pi\varphi)(x^n)(\Pi\varphi)(x^0)\right]\\ &= \int_{\mathcal{D}}(\Pi\varphi)\left[{\rm Id} + 2\sum_{n=1}^{+\infty}P^n_{\Delta t}\right]\Pi\varphi\,{\rm d}\nu\\ &= \int_{\mathcal{D}}(\Pi\varphi)[2({\rm Id}-P_{\Delta t})^{-1} - {\rm Id}]\Pi\varphi\,{\rm d}\nu. \end{aligned} \tag{3.20}$$

where we used (3.12) in the last step. □

It is instructive at this stage to compare the asymptotic variance (3.18) 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

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

whose asymptotic variance is

$$\sigma^2_{\varphi,{\rm iid}} = \lim_{N_{\rm iter}\to+\infty} N_{\rm iter}{\rm Var}_\nu\left[\left(\widehat{\Pi\varphi}^{\rm iid}_{N_{\rm iter}}\right)^2\right] = \int_{\mathcal{D}}(\Pi\varphi)^2 d\nu.$$

We write the asymptotic variance (3.18) for time averages estimates with ergodic SDEs in terms of the reference variance $\sigma^2_{\varphi,{\rm iid}}$ as

$$\sigma^2_\varphi = N_{{\rm corr},\varphi}\sigma^2_{\varphi,{\rm iid}}, \tag{3.21}$$

and interpret $N_{{\rm corr},\varphi}$ as some number of correlation steps. What is meant by that is that the mean-square error of the estimator $\widehat{\varphi}_{N_{\rm iter}}$ asymptotically behaves as $\sigma^2_\varphi/N_{\rm iter} = \sigma^2_{\varphi,{\rm iid}}N_{{\rm corr},\varphi}/N_{\rm iter}$, so that in order to have an estimator of the same quality as the one based on $N_{\rm iter}$ i.i.d. samples, $N_{{\rm corr},\varphi}N_{\rm iter}$ steps of the Markov chain should be performed.

4

The overdamped Langevin dynamics

4.1 Description of the dynamics

4.1.1 Simple overdamped Langevin dynamics

Overdamped processes are stochastic dynamics on the system positions $q \in \mathcal{D}$ only. They are described through the simplest stochastic differential equation reversible with respect to the canonical distribution in position:

$$\nu(dq) = Z_\nu^{-1} \exp(-\beta V(q))\, dq. \tag{4.1}$$

We assume here and in the sequel that the potential energy function V is smooth. The evolution equation is given by

$$dq_t = -\nabla V(q_t)\, dt + \sqrt{\frac{2}{\beta}}\, dW_t, \tag{4.2}$$

where $t \mapsto W_t$ is a standard D-dimensional Wiener process.

Generator of the dynamics

The generator associated with (4.2) acts on functions of the variable q. For a smooth function $\phi : q \mapsto \phi(q)$,

$$\mathcal{L}\phi = \frac{1}{\beta}\Delta\phi - \nabla V \cdot \nabla\phi = \frac{\mathrm{e}^{\beta V}}{\beta}\mathrm{div}\left(\mathrm{e}^{-\beta V}\nabla\phi\right). \tag{4.3}$$

This operator can be considered as an unbounded operator for instance on the Banach space $C_0^0(\mathcal{D})$ with domain $C_0^2(\mathcal{D})$, 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 [170, Lemma A.24].

A first important property of the generator 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) since

$$\left(\mathrm{e}^{t\mathcal{L}}\varphi\right)(q) = \mathbb{E}\left[\varphi(q_t) \,|\, q_0 = q\right]. \tag{4.4}$$

To prove this equality, we start from Itô's formula: for a fixed time $t > 0$, for a C^∞ function φ with compact support, and $s \in [0, t]$, we have

$$d\left(\mathrm{e}^{(t-s)\mathcal{L}}\varphi(q_s)\right) = (-\partial_t + \mathcal{L})\left(\mathrm{e}^{(t-s)\mathcal{L}}\varphi\right)(q_s)\, ds + \sqrt{\frac{2}{\beta}}\nabla\left(\mathrm{e}^{(t-s)\mathcal{L}}\varphi\right)\cdot dW_s,$$

so that, taking expectations,

$$\mathbb{E}^q(\varphi(q_t)) - \mathrm{e}^{t\mathcal{L}}\varphi(q) = \sqrt{\frac{2}{\beta}}\mathbb{E}^q\left[\int_0^t \nabla(\mathrm{e}^{(t-s)\mathcal{L}}\varphi)\cdot dW_s\right] = 0.$$

Invariance of the canonical measure

The process (4.2) is reversible with respect to the canonical probability distribution $\nu(dq)$. From a functional analytical viewpoint, this means that the generator is self-adjoint on $L^2(\nu)$. This property follows from the following computation: for any test functions φ_1 and φ_2,

$$\int_{\mathcal{D}} \varphi_1\, \mathcal{L}(\varphi_2)\, \mathrm{e}^{-\beta V} = \frac{1}{\beta}\int_{\mathcal{D}} \varphi_1\, \mathrm{div}\left(\mathrm{e}^{-\beta V}\nabla\varphi_2\right) = -\frac{1}{\beta}\int_{\mathcal{D}} \nabla\varphi_1(q)\cdot\nabla\varphi_2(q)\, \mathrm{e}^{-\beta V(q)}\, dq,$$

which is obviously symmetric in φ_1, φ_2. In fact, we can rewrite the generator as

$$\mathcal{L} = -\frac{1}{\beta}\sum_{i=1}^{D} \partial_{q_i}^* \partial_{q_i}, \tag{4.5}$$

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 consequence of reversibility is that the canonical measure is invariant: the choice $\varphi_1 = 1$ indeed leads to

$$\int_{\mathcal{D}} \mathcal{L}\varphi\, d\nu = 0 \tag{4.6}$$

for all smooth functions φ. This characterization of the invariant measure directly follows from (4.5).

Let us also mention that the evolution of the law $\psi(t,q)$ of the process q_t is governed by the Fokker-Planck equation

$$\partial_t \psi = \mathcal{L}^\dagger \psi, \qquad \psi(0,\cdot) = \psi_0, \tag{4.7}$$

where $\mathcal{L}^\dagger$ is the adjoint of $\mathcal{L}$ on $L^2(\mathcal{D})$. To derive (4.7), we proceed as follows. For $h > 0$,

$$\frac{\mathbb{E}^q[\varphi(q_{t+h})] - \mathbb{E}^q[\varphi(q_t)]}{h} = \frac{1}{h}\int_t^{t+h} \mathbb{E}^q[(\mathcal{L}\varphi)(q_s)]\, ds,$$

which, after integration with respect to ψ_0, gives

$$\frac{1}{h}\left(\int_{\mathcal{D}} \varphi(q)\psi(t+h,q)\, dq - \int_{\mathcal{D}} \varphi(q)\psi(t,q)\, dq\right) = \frac{1}{h}\int_t^{t+h}\int_{\mathcal{D}} (\mathcal{L}\varphi)(q)\psi(s,q)\, dq\, ds.$$

This leads, in the limit $h \to 0$, to the following equation:

$$\frac{d}{dt}\left(\int_{\mathcal{D}} \varphi(q)\psi(t,q)\, dq\right) = \int_{\mathcal{D}} (\mathcal{L}\varphi)(q)\psi(t,q)\, dq,$$

which is satisfied for all test functions φ (say, C^∞ and compactly supported). This is indeed the weak formulation of (4.7). For rigorous results concerning the existence and uniqueness of a solution to (4.7) and the link with stochastic differential equations, see for example to [60].

4.1.2 Dynamics with multiplicative noise

In some situations, it is relevant to consider the case when the Brownian motion in (4.2) 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

$$dq_t = \left(-A(q_t)\nabla V(q_t) + \frac{1}{\beta}\mathrm{div}A(q_t)\right)dt + \sqrt{\frac{2}{\beta}}\, B(q_t)\, dW_t. \tag{4.8}$$

The divergence of the matrix 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 column of the matrix A. The generator of this dynamics acts on smooth functions φ as

$$\mathcal{L}\varphi = \left(-A\nabla V + \frac{1}{\beta}\mathrm{div}A\right)^T \nabla\varphi + \frac{1}{\beta}\, A : \nabla^2\varphi. \tag{4.9}$$

The invariance of the canonical measure, and in fact the reversibility of the process, follow from the following rewriting:

$$\int_{\mathcal{D}} f\, \mathcal{L}g\, d\nu = -\frac{1}{\beta}\int_{\mathcal{D}} (\nabla f)^T A \nabla g\, d\nu.$$

4.2 Convergence of ergodic averages

4.2.1 Convergence of trajectorial averages

The pathwise ergodicity of the overdamped process (4.2) is easily obtained since the process can be shown to be irreducible with respect to the Lebesgue measure and the canonical measure is by construction an invariant probability measure. In fact, a work by Kliemann immediately gives the result since the generator is elliptic [90].

Let us however, for pedagogical purposes, provide the proof of the irreducibility, which is quite simple here since the noise acts on all variables. The proof is conducted in two steps: first, a

controllability argument shows that $\mathbb{P}(q_t \in S | q_0 = q) > 0$ 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.

A simple computation shows that $\mathbb{P}(q_t \in S | q_0 = q) > 0$ for any initial condition q_0 and any open measurable set S. Indeed, consider $q^* \in S$ and the interpolated path $Q(t) = (1-t)q_0 + tq^*$, as well as the control $u(t)$ 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 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 [159, Theorem 4.20])

$$\mathbb{P}\left(\sup_{0 \leqslant t \leqslant 1} |W_t - u(t)| \leqslant \varepsilon \right) > 0.$$

The idea of the proof of this result is to first reduce 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 Brownian motion, $\mathbb{P}(q_t \in S | q_0 = q) > 0$. The precise argument relies on the Stroock-Varadhan support theorem, as reviewed in [141, Section 6] and [121, Appendix A] for instance.

To prove the irreducibility with respect to the Lebesgue measure, we first note that standard results on parabolic regularity show that the transition kernel P has a smooth density $p(t, q, q')$ (which is C^∞ in all its arguments on $(0, +\infty) \times \mathcal{D}^2$):

$$P\varphi(q) = \int_{\mathcal{D}} p(t, q, q') \varphi(q')\, dq',$$

where $p(t)$ satisfies the Fokker-Planck equations (see [141, Section 7])

$$\partial_t p(t, q, \cdot) = \mathcal{L} p(t, q, \cdot), \qquad \partial_t p(t, \cdot, q') = \mathcal{L}^\dagger p(t, \cdot, q').$$

These equations have to be understood in the sense of distributions. The second one is obtained by writing

$$\frac{d}{dt}\left(\mathrm{e}^{t\mathcal{L}} \varphi \right) = \frac{d}{dt} \left(\int_{\mathcal{D}} P_t(q, dq') \varphi(q') \right) = \int_{\mathcal{D}} P_t(q, dq') (\mathcal{L}_{q'} \varphi)(q'),$$

while the first one is obtained by duality, letting $\mathrm{e}^{t\mathcal{L}^\dagger}$ act on probability distributions. The evolution equations on the density of the transition kernel allow to show that $(t, q, q') \mapsto p(t, q, q')$ is C^∞.

This allows to prove that $p(t, q, q') > 0$ for any $q, q' \in \mathcal{D}$ and $t > 0$. Consider indeed $t > 0$ and $q, q' \in \mathcal{D}$. Then, for any open ball $B(q', r)$ of radius $r > 0$ centered on q', it holds

$$P_{t/2}(q, B(q', r)) = \int_{B(q', r)} p\left(\frac{t}{2}, q, q'' \right) dq'' > 0$$

by the previous controllability results. This already shows that $p(t/2, q, q'') > 0$ for almost all $q'' \in \mathcal{D}$. Assume next, by contradiction, that $p(t, q, q') = 0$. Then, the equality

$$p(t, q, q') = \int_{\mathcal{D}} p\left(\frac{t}{2}, q, q'' \right) p\left(\frac{t}{2}, q'', q' \right) dq''$$

shows that $p\,(t/2, q'', q') = 0$ for almost all $Q \in \mathcal{D}$. This implies that

$$\int_{\mathcal{D}} p\left(\frac{t}{2}, q'', q'\right) dq'' = 0,$$

which is in contradiction with the fact that the latter integral converges to 1 as $t \to 0$.

Defining

$$\widehat{\varphi}_t = \frac{1}{t}\int_0^t \varphi(q_s)\, ds,$$

it holds, for any initial condition $q_0 \in \mathcal{D}$,

$$\lim_{t\to+\infty} \widehat{\varphi}_t = \int_{\mathcal{D}} \varphi\, d\nu \qquad \text{a.s.}$$

A similar convergence result holds for the dynamics with multiplicative noise (4.8) provided $A \geqslant a\mathrm{Id}_D$ with $a > 0$ (in the sense of symmetric matrices).

4.2.2 Asymptotic variance

Next, convergence rates 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:

$$\Pi\varphi = \varphi - \int_{\mathcal{D}} \varphi\, d\nu. \tag{4.10}$$

The asymptotic variance of the trajectorial average formally is

$$\sigma_\varphi^2 = \lim_{t\to+\infty} t\mathbb{E}\left(\left(\widehat{\Pi\varphi}_t\right)^2\right) = 2\int_0^{+\infty} \mathbb{E}(\Pi\varphi(q_t)\Pi\varphi(q_0))\, dt = -2\left\langle \Pi\varphi, \mathcal{L}^{-1}\Pi\varphi\right\rangle_{L^2(\nu)}. \tag{4.11}$$

The proof of the latter equalities is very similar to the proof of Proposition 3.5. In fact,

$$t\mathbb{E}\left(\left(\widehat{\Pi\varphi}_t\right)^2\right) = 2\int_0^t \left(1 - \frac{s}{t}\right)\left(\mathrm{e}^{s\mathcal{L}}\Pi\varphi\right)\Pi\varphi\, d\nu\, ds.$$

As motivated in the introduction of Section 4.4, the above expression of the asymptotic variance can be seen as a continuous limit of the asymptotic variance for Markov chains associated with numerical discretizations of the dynamics (4.2).

The above computations can be made rigorous using a dominated convergence argument provided we have good decay estimates on the semigroup $\mathrm{e}^{t\mathcal{L}}$, in appropriate functional spaces E. 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. *Assume that*

$$\|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(E)} \leqslant C\mathrm{e}^{-\lambda t}. \tag{4.12}$$

Then the operator $\mathcal{L}$ is invertible on E, and it holds

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(E)} \leqslant \frac{C}{\lambda}. \tag{4.13}$$

The aim of the next section is to provide estimates such as (4.12).

Proof. Introducing

$$U = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}}\, dt,$$

a simple computation shows that, for for $\varphi \in D(\mathcal{L}) = \phi \in E | \mathcal{L}\phi \in E$,

$$\mathcal{L}U\varphi = U\mathcal{L}\varphi = -\int_0^{+\infty} \frac{d}{dt}[\mathrm{e}^{t\mathcal{L}}\varphi] = \varphi.$$

These equalities show that $\mathcal{L}$ is invertible on E, with $U = \mathcal{L}^{-1}$. From the definition of U, it follows that

$$\|U\|_{\mathcal{B}(E)} \leqslant \int_0^{+\infty} \|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(E)}\, dt \leqslant C \int_0^{+\infty} \mathrm{e}^{-\lambda t}\, dt = \frac{C}{\lambda},$$

which proves the resolvent bound (4.13).

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.

Correlation times

It is possible to discuss the definition of correlation times by mimicking the discussion at the end of Section 3.4. We write the asymptotic variance (4.11) for time averages estimates with ergodic SDEs in terms of the reference variance $\sigma^2_{\varphi,\mathrm{iid}}$ as

$$\sigma^2_\varphi = \theta_{\mathrm{corr},\varphi} \sigma^2_{\varphi,\mathrm{iid}}, \tag{4.14}$$

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. When the operator $\mathcal{L}$ is self-adjoint on $L^2(\nu)$, the norm of $\mathcal{L}^{-1}$ on $L^2_0(\nu)$ is equal to $1/\lambda_1$, λ_1 being the first non-zero eigenvalue of $-\mathcal{L}$ on $L^2(\nu)$. This provides the following upper bound for the correlation time: $\theta_{\mathrm{corr},\varphi} \leqslant 1/\lambda_1$. Equality holds when φ is an eigenvector of $-\mathcal{L}$ associated with λ_1.

Central Limit Theorems

Note that (4.11) shows that it is possible to define the asymptotic variance without any reference to the evolution semigroup $\mathrm{e}^{t\mathcal{L}}$, by directly considering

$$\sigma^2_\varphi = 2 \int_{\mathcal{X}} (-\mathcal{L}^{-1} \Pi\varphi) \Pi\varphi\, d\nu.$$

The integral on the right hand side is well defined once the solution Φ of the Poisson equation

$$-\mathcal{L}\Phi = \Pi\varphi \tag{4.15}$$

belongs to a functional space $\mathscr{E} \subset L^2(\nu)$. This is the case when $\varphi \in \mathscr{E}$ and $\mathcal{L}^{-1}$ is a bounded operator on $\mathscr{E}$. There are however more general frameworks to define solutions of Poisson equations, see for instance [134] and references therein.

In fact, it was proved by [21] that a Central Limit Theorem holds once the Poisson equation (4.15) has a solution in $L^2(\nu)$ and the initial conditions are distributed according to ν. In this case,

$$\sqrt{t}\, \widehat{\Pi\varphi}_t \xrightarrow[t\to+\infty]{\mathrm{law}} \mathcal{N}(0, \sigma^2_\varphi).$$

This result can be extended to cover the case when the initial conditions are not distributed according to the invariant measure: see also [21]. The bottom line of the proof, which we write here in the general case (4.8), is to use Itô calculus to rewrite $\sqrt{t}\widehat{\Pi\varphi}_t$ as

$$\sqrt{t}\widehat{\Pi\varphi}_t = \frac{\Phi(q_0) - \Phi(q_t)}{\sqrt{t}} + \mathcal{M}_t, \qquad \mathcal{M}_t = \frac{1}{\sqrt{t}} \int_0^t \nabla\Phi(q_s)^T \sigma(q_s) dW_s.$$

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 [94] or [50]): $\mathcal{M}_t$ converges in law to a Gaussian distribution with variance

$$\widetilde{\sigma}^2 = \lim_{t\to+\infty} \mathbb{E}\left(\frac{1}{t}\int_0^t \nabla\Phi(q_s)^T\sigma(q_s)\sigma(q_s)^T\nabla\Phi(q_s)\,ds\right).$$

By ergodicity of the dynamics,

$$\widetilde{\sigma}^2 = \int_{\mathcal{X}} \nabla\Phi^T\sigma\sigma^T\nabla\Phi\,d\nu.$$

Now, recalling the expression (4.9) for the generator, a simple computation shows that

$$\mathcal{L}(\Phi^2) - 2\Phi\mathcal{L}\Phi = \sigma\sigma^T : \nabla^2(\Phi^2) - 2\Phi\sigma\sigma^T : \nabla^2\Phi = \nabla\Phi^T\sigma\sigma^T\nabla\Phi.$$

The invariance of ν then leads to

$$\widetilde{\sigma}^2 = \int_{\mathcal{X}} \nabla\Phi^T\sigma\sigma^T\nabla\Phi\,d\nu = -2\int_{\mathcal{X}} \Phi\mathcal{L}\Phi\,d\nu = \sigma_\varphi^2,$$

which allows to conclude.

4.3 Convergence of the law

Since the canonical measure is invariant, it is therefore 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 what rate. Another question, closely related, is to prove convergence rates for the semigroup $\mathrm{e}^{t\mathcal{L}}$ (such as (4.12)), in order for the asymptotic variance to be well defined.

Before presenting several answers to this question, let us first give two reformulations of the Fokker–Planck equation (4.7). A simple computation shows that the function $g = \psi\,\mathrm{e}^{\beta V/2}$ satisfies the Schrödinger-type equation

$$\partial_t g = \frac{1}{\beta}\Delta g + Wg, \quad W = \frac{1}{2}\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right), \tag{4.16}$$

together with the normalization condition

$$\forall t \geqslant 0, \qquad \int_{\mathcal{D}} g(t)\,\mathrm{e}^{-\beta V/2} = 1.$$

In addition, the function $f = \psi\,\mathrm{e}^{\beta V}$ satisfies

$$\partial_t f = \mathcal{L}f, \qquad \int_{\mathcal{D}} f\,\mathrm{e}^{-\beta V} = 1. \tag{4.17}$$

In this last setting, the functional space to consider is 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]

$$\langle\varphi_1,\varphi_2\rangle_{L^2(\nu)} = \int_{\mathcal{D}} \varphi_1\,\varphi_2\,d\nu.$$

A simple computation shows that $\mathcal{L}$ is symmetric on $L^2(\nu)$. More precisely, in view of (4.5), for test functions φ_1,φ_2 (C^∞ and compactly supported),

$$\langle\mathcal{L}\varphi_1,\varphi_2\rangle_{L^2(\nu)} = \langle\varphi_1,\mathcal{L}\varphi_2\rangle_{L^2(\nu)} = -\frac{1}{\beta}\int_{\mathcal{D}} \nabla\varphi_1\cdot\nabla\varphi_2\,d\nu. \tag{4.18}$$

In fact, it can be proved that $\mathcal{L}$ is self-adjoint on $L^2(\nu)$, see *e.g.* [14].

[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.

4.3.1 Convergence in $L^2(\nu)$

We start by considering the Fokker-Planck equation reformulated as (4.17), for an initial condition $f_0 = \psi_0/\nu$ belonging to $L^2(\nu)$. Recall that

$$f_0 \geqslant 0, \qquad \int_{\mathcal{D}} f_0 \, d\nu = 1.$$

The simplest setting to consider is when a so-called Poincaré inequality holds; see for instance [14, Section 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

$$\|\varphi\|^2_{L^2(\nu)} \leqslant \frac{1}{R} \|\nabla\varphi\|^2_{L^2(\nu)}, \qquad \forall \varphi \in H^1(\nu) \cap L^2_0(\nu). \tag{4.19}$$

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.

The inequality (4.19) 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*

$$\|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(L^2_0(\nu))} \leqslant \mathrm{e}^{-Rt/\beta}. \tag{4.20}$$

Proof. Let us first assume that the measure ν satisfies a Poincaré inequality with constant $R > 0$. In view of (4.18),

$$-\langle \mathcal{L}\varphi, \varphi \rangle_{L^2(\nu)} = \frac{1}{\beta} \|\nabla\varphi\|^2_{L^2(\nu)} \geqslant \frac{R}{\beta} \|\varphi\|^2_{L^2(\nu)}, \qquad \forall \varphi \in L^2_0(\nu). \tag{4.21}$$

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 (4.21) also gives the exponential decrease of the semigroup on $L^2_0(\nu)$ since

$$\frac{d}{dt} \left(\frac{1}{2} \|\mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\nu)} \right) = \langle \mathrm{e}^{t\mathcal{L}}\varphi, \mathcal{L}\, \mathrm{e}^{t\mathcal{L}}\varphi \rangle_{L^2(\nu)} \leqslant -\frac{R}{\beta} \|\mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\nu)}. \tag{4.22}$$

By a Gronwall inequality, it follows that

$$\forall \varphi \in L^2_0(\nu), \qquad \|\mathrm{e}^{t\mathcal{L}}\varphi\|_{L^2_0(\nu)} \leqslant \mathrm{e}^{-Rt/\beta} \|\varphi\|_{L^2_0(\nu)}.$$

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 $t > 0$,

$$\frac{\|\mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2_0(\nu)} - \|\varphi\|^2_{L^2_0(\nu)}}{t} \leqslant \|\varphi\|^2_{L^2_0(\nu)} \, \frac{\mathrm{e}^{-2Rt/\beta} - 1}{t}.$$

We next pass to the limit $t \to 0$, using the equalities in (4.21) and (4.22):

$$-\frac{2}{\beta} \|\nabla\varphi\|^2_{L^2(\nu)} \leqslant -\frac{2R}{\beta} \|\varphi\|^2_{L^2_0(\nu)}.$$

Since $\varphi \in L^2_0(\nu)$ is arbitrary, the Poincaré inequality (4.19) follows.

Following the general argument presented at the end of Section 4.2.2, 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 (4.21).[2]

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,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^2_0(\nu))} \leqslant \frac{\beta}{R}. \tag{4.23}$$

Obtaining Poincaré inequalities

First, such inequalities are easily obtained for probability measures equivalent to the Lebesgue measure, on 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 for instance 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

$$\min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 d\rho = \int_{\mathcal{D}} (\varphi - \mathbb{E}_\rho(\varphi))^2 d\rho, \qquad \forall \varphi \in L^2(\rho).$$

The proof of this assertion is easily obtained by writing $c = \mathbb{E}_\rho(f) + \widetilde{c}$ and expanding $(f-c)^2$. Therefore,

$$\min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 d\rho \leqslant \rho_{\max} \min_{c\in\mathbb{R}} \int_{\mathcal{D}} (\varphi - c)^2 \leqslant \frac{1}{R_{\mathrm{PW}}} \rho_{\max} \int_{\mathcal{D}} |\nabla\varphi|^2 \leqslant \frac{1}{R_{\mathrm{PW}}} \frac{\rho_{\max}}{\rho_{\min}} \int_{\mathcal{D}} |\nabla\varphi|^2 d\rho,$$

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 (4.1) satisfies a Poincaré inequality when the domain $\mathcal{D}$ is bounded, 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, such an 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 [12, Corollary 1.6].

Theorem 4.1. *Consider $V \in C^2(\mathbb{R}^D)$. If there exists $a \in (0,1)$, $c > 0$ and $R \geqslant 0$ such that*

$$a\beta|\nabla V(q)|^2 - \Delta V(q) \geqslant c, \qquad \forall q \in \mathbb{R}^d \text{ such that } |q| \geqslant R, \tag{4.24}$$

then ν satisfies a Poincaré inequality.

[2] 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 (4.21) 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.

The above condition is satisfied, for instance, for potentials of the form

$$V(q) = K|q|^n + \widetilde{V}(q),$$

where $n \geqslant 1$ and $\widetilde{V}$ is C^∞ and 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 (4.24) holds.

For the sake of completeness, we provide the complete proof of a result weaker than Theorem 4.1, quoted from [170, Appendix A.19] (the proof being based on an argument by Deuschel and Stroock [40]).

Theorem 4.2. *Consider $V \in C^2(\mathbb{R}^D)$ such that*

$$\frac{\beta}{2}|\nabla V(q)|^2 - \Delta V(q) \xrightarrow[|q|\to+\infty]{} +\infty.$$

Then ν satisfies a Poincaré inequality.

Proof. Define

$$w = \frac{\beta}{2}|\nabla V|^2 - \Delta V.$$

The key observation is that, for any $h \in C^1(\mathbb{R}^D)$ with compact support,

$$\int_{\mathbb{R}^D} w\, h^2\, d\nu \leqslant \frac{2}{\beta}\int_{\mathbb{R}^D} |\nabla h|^2 d\nu. \tag{4.25}$$

This allows to control the L^2 norm of h at infinity. On the other hand, we already have a control of the L^2 norm of h on bounded domains.

Let us first derive (4.25). To this end, 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 $R > 0$ such that $w(q) \geqslant 1$ for $|q| \geqslant R$, and define

$$\varepsilon(R) = \frac{1}{\inf\limits_{|q|\geqslant R} w} \geqslant 1, \qquad w_- = \inf_{q\in\mathbb{R}^D} w(q) > -\infty.$$

Note that $\varepsilon(R) \to 0$ as $R \to +\infty$. Upon increasing R, we can assume that $\varepsilon(R) w_- \leqslant 1/2$. Now, (4.25) implies that

$$w_- \int_{|q|\leqslant R} h^2\, d\nu + \frac{1}{\varepsilon(R)}\int_{|q|\geqslant R} h^2\, d\nu \leqslant \frac{2}{\beta}\int_{\mathbb{R}^D} |\nabla h|^2 d\nu,$$

which can be rewritten as

$$\int_{|q|\geqslant R} h^2\,d\nu \leqslant \varepsilon(R)\left(\frac{2}{\beta}\int_{\mathbb{R}^D}|\nabla h|^2 d\nu - w_-\int_{|q|\leqslant R} h^2\,d\nu\right). \tag{4.26}$$

We next control the L^2 norm the bounded set $B_R = \{|q| \leqslant R\}$. The probability measure $\nu_R = Z_R^{-1}\mathbf{1}_{B_R}\,\nu$ satisfies a Poincaré inequality with constant $C_R > 0$, so that

$$\int_{B_R} h^2\,d\nu_R \leqslant C_R\int_{B_R}|\nabla h|^2\,d\nu_R + \left(\int_{B_R} h\,d\nu_R\right)^2.$$

Note that $Z_R \geqslant 1$ and $Z_R \to 1$ as $R \to +\infty$, so that, upon increasing R in order to have $Z_R \geqslant 1/2$,

$$\int_{B_R} h^2\,d\nu \leqslant C_R\int_{B_R}|\nabla h|^2\,d\nu + 2\left(\int_{B_R} h\,d\nu\right)^2. \tag{4.27}$$

Assume now that

$$\int_{\mathbb{R}^D} h\,d\nu = 0.$$

Then,

$$\left(\int_{B_R} h\,d\nu\right)^2 = \left(\int_{|q|>R} h\,d\nu\right)^2 \leqslant \nu\left(\mathbb{R}^D\backslash B_R\right)\int_{|q|>R} h^2\,d\nu \leqslant \int_{|q|>R} h^2\,d\nu.$$

We therefore obtain from (4.27) the following control on the $L^2(\nu)$ norm of h on B_R:

$$\int_{B_R} h^2\,d\nu \leqslant C_R\int_{B_R}|\nabla h|^2\,d\nu + 2\int_{|q|\geqslant R} h^2\,d\nu. \tag{4.28}$$

We finally add (4.26) multiplied by 3 and (4.28) to obtain

$$\int_{\mathbb{R}^D} h^2\,d\nu \leqslant \left(C_R + \frac{6\varepsilon(R)}{\beta}\right)\int_{\mathbb{R}^D}|\nabla h|^2\,d\nu - 3\varepsilon(R)w_-\int_{|q|\leqslant R} h^2\,d\nu.$$

In conclusion, provided $R > 0$ is sufficiently large so that $3\varepsilon(R)|w_-| < 1/2$ (a condition to be satisfied only when $w_- < 0$ in fact),

$$\int_{\mathbb{R}^D} h^2\,d\nu \leqslant \frac{1}{\min\left(1, 1 + 3\varepsilon(R)w_-\right)}\left(C_R + \frac{6\varepsilon(R)}{\beta}\right)\int_{\mathbb{R}^D}|\nabla h|^2\,d\nu,$$

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* $\min(R_1, \ldots, R_d)$.

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

$$\int_{\mathcal{D}_1} |\varphi(q_1,q_2) - \overline{\varphi}(q_2)|^2 \, \rho_1(dq_1) \leqslant \frac{1}{R_1} \int_{\mathcal{D}_1} |\nabla_{q_1}\varphi(q_1,q_2)|^2 \, \rho_1(dq_1).$$

This inequality can be rewritten as

$$\int_{\mathcal{D}_1} |\varphi(q_1,q_2)|^2 \, \rho_1(dq_1) \leqslant |\overline{\varphi}(q_2)|^2 + \frac{1}{R_1} \int_{\mathcal{D}_1} |\nabla_{q_1}\varphi(q_1,q_2)|^2 \, \rho_1(dq_1). \tag{4.29}$$

Now, since $\overline{\varphi}$ has average 0 with respect to ρ_2 because φ has average 0 with respect to ρ,

$$\begin{aligned}\int_{\mathcal{D}_2} |\overline{\varphi}(q_2)|^2 \, \rho_2(dq_2) &\leqslant \frac{1}{R_2} \int_{\mathcal{D}_2} |\nabla_{q_2}\overline{\varphi}(q_2)|^2 \, \rho_2(dq_2) \\ &\leqslant \frac{1}{R_2} \int_{\mathcal{D}} |\nabla_{q_2}\varphi(q_1,q_2)|^2 \, \rho_1(dq_1) \, \rho_2(dq_2),\end{aligned}$$

where we used a Cauchy–Schwarz inequality in the last step. An integration of (4.29) with respect to $\rho_2(dq_2)$ finally leads to

$$\begin{aligned}\int_{\mathcal{D}} |\varphi(q_1,q_2)|^2 \, \rho(dq) &\leqslant \frac{1}{R_1} \int_{\mathcal{D}} |\nabla_{q_1}\varphi(q_1,q_2)|^2 \, \rho(dq) + \frac{1}{R_2} \int_{\mathcal{D}} |\nabla_{q_2}\varphi(q_1,q_2)|^2 \, \rho(dq) \\ &\leqslant \frac{1}{\min(R_1,R_2)} \int_{\mathcal{D}} |\nabla_q \varphi|^2 \, d\rho,\end{aligned}$$

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 the logarithmic Sobolev inequality implies the Poincaré inequality.

4.3.2 Convergence in 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 [68], Ledoux [105], Arnold, Markowich, Toscani and Unterreiter [8] and in [14, Section 5]. The latter two works have a PDE approach which may help readers more accustomed to analytical frameworks. Other useful introductory references include [6, 169].

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 $\mathcal{X}$, and such that π_1 is absolutely continuous with respect to π_2 (denoted $\pi_1 \ll \pi_2$ in the following), the entropy of π_1 with respect to π_2 is*

$$\mathcal{H}(\pi_1 \mid \pi_2) = \int_{\mathcal{X}} \ln\left(\frac{d\pi_1}{d\pi_2}\right) d\pi_1. \tag{4.30}$$

The Fisher information of π_1 with respect to π_2 is

$$\mathcal{I}(\pi_1 \mid \pi_2) = \int_{\mathcal{X}} \left|\nabla \ln\left(\frac{d\pi_1}{d\pi_2}\right)\right|^2 d\pi_1. \tag{4.31}$$

Using strict convexity of $x \mapsto x \ln x$ and the fact that $x \ln x - x + 1 \geqslant 0$, it is easy to check that the entropy is non-negative. Moreover, it is zero if and only if the two probability measures are identical. This is also true for the Fisher information.

There are many possible definitions of the entropy besides the relative entropy $\mathcal{H}$ defined in (4.30). Some mathematical motivations for the use of the relative entropy $\mathcal{H}$ can be found in [120], see also [35] for a historical perspective. This particular entropy may be of interest for the following extensivity property. The relative entropy of the distribution of N 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 [168], Chapter 5). This extensivity is a consequence of the extensivity of the logarithm function involved in definition (4.30) (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 [113] 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 Lebesgue measure, can be bounded by the relative entropy. This is the Csiszár–Kullback inequality (see for example [6, 152]): introducing the total variation norm

$$\|\pi_1 - \pi_2\|_{\mathrm{TV}} = \sup_{\|\varphi\|_{L^\infty} \leqslant 1} \int_{\mathcal{X}} \varphi(d\pi_1 - d\pi_2), \tag{4.32}$$

it holds

$$\|\pi_1 - \pi_2\|_{\mathrm{TV}} \leqslant \sqrt{2\mathcal{H}(\pi_1 \mid \pi_2)}. \tag{4.33}$$

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 because it is not symmetric in its arguments).

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 (4.7). 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 $\pi_1 \ll \pi_2$,*

$$\mathcal{H}(\pi_1 \mid \pi_2) \leqslant \frac{1}{2R}\mathcal{I}(\pi_1 \mid \pi_2). \tag{4.34}$$

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 is 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 some L^2 space).

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* (4.7) *satisfies*

$$\mathcal{H}(\psi(t) \mid \nu) \leqslant \mathcal{H}(\psi_0 \mid \nu) \exp(-2\beta^{-1}Rt), \qquad \forall t \geqslant 0. \tag{4.35}$$

From the Csiszár–Kullback inequality (4.33), 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 (4.7) 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

$$\int_{\mathcal{D}} \psi(t) = 1.$$

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

$$\frac{d}{dt}(\mathcal{H}(\psi(t,\cdot) \mid \nu)) = -\frac{1}{\beta}\mathcal{I}(\psi(t,\cdot) \mid \nu). \tag{4.36}$$

Assume now that ν satisfies an LSI(R). The estimate (4.35) then directly follows from (4.36).

Assume conversely that (4.35) 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 (4.36),

$$-\frac{1}{\beta}\mathcal{I}(\psi_0 \mid \nu) \leqslant -\frac{2R}{\beta}\,\mathcal{H}(\psi_0 \mid \nu),$$

which indeed leads to (4.34).

Obtaining LSI

We now present several ways to obtain LSIs for measures of the form (4.1).

(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 an LSI with constant βR holds, as first shown in [13] (see Theorem 4.3 below).

(2) When $\psi_\infty = \prod_{i=1}^d \psi_\infty^i$ and each measure $\psi_\infty^i(q)dq$ satisfies an LSI with constant $\mathbb{R}_i$, then ψ_∞ satisfies an LSI with constant $\mathbb{R} = \min\{R_1, \ldots, R_d\}$ (see [67]). 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 [79] 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 [22]), or when all the conditional laws satisfy an LSI under some weak coupling assumption (see [132]). 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 [111].

Let us now state more precisely, and prove, two fundamental results ensuring that an LSI holds for canonical measures of the form (4.1).

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).*

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 (4.36). Introduce $f(t) = \psi(t)/\nu$ for an arbitrary initial condition $f_0 = \psi_0/\nu$. In view of (4.17), 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

$$\nabla\left(\frac{1}{2}|\nabla h|^2\right) = \nabla^2 h \cdot \nabla h, \quad delta\left(\frac{1}{2}|\nabla h|^2\right) = \nabla^2 h : \nabla^2 h + \nabla(deltah) \cdot \nabla h,$$

it follows that

$$\begin{aligned}\mathcal{L}\left(\frac{1}{2}|\nabla h|^2\right) &= \frac{1}{\beta}(\nabla^2 h : \nabla^2 h + \nabla(deltah) \cdot \nabla h) - (\nabla V)^T (\nabla^2 h) \nabla h \\ &\geqslant \nabla(\mathcal{L} h) \cdot \nabla h + (\nabla h)^T (\nabla^2 V) \nabla h \\ &\geqslant \nabla(\mathcal{L} h) \cdot \nabla h + R|\nabla h|^2,\end{aligned}$$

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:

$$\mathcal{I}(\psi(t) \mid \nu) \leqslant \mathrm{e}^{-2Rt} \mathcal{I}(\psi(0) \mid \nu). \tag{4.37}$$

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 [8]. Since the operator $-\mathcal{L}$ is self-adjoint on $L^2(\nu)$ and positive by (4.21), its spectral measure P_λ is supported by $[0, +\infty)$ (see [139] and [37] for the definition of the spectral measure). In addition, (4.21) also shows that 0 is a non-degenerate eigenvalue whose associated eigenvectors are constant functions (indeed, since ν satisfies LSI(βR), it also satisfies a Poincaré inequality with the same constant, see Proposition 4.5 below). Therefore,

$$f(t) = \mathrm{e}^{t\mathcal{L}} f_0 = P_0 f_0 + \int_{(0,+\infty)} \mathrm{e}^{-t\lambda} d\left(P_\lambda f_0\right).$$

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 (4.36) together with the decay estimate (4.37), 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.

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

$$\int_{\mathcal{D}} f d\widetilde{\nu} = 1, \tag{4.38}$$

and let $\overline{f}$ denote the average of f with respect to ν:

$$\overline{f} = \int_{\mathcal{D}} f d\nu. \tag{4.39}$$

Then

$$\begin{aligned}
\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) &= \int_{\mathcal{D}} f\ln f d\widetilde{\nu} = \int_{\mathcal{D}} \phi(f) d\widetilde{\nu} \\
&\leqslant \int_{\mathcal{D}} \left[\phi(f) - (\phi(\overline{f}) + \phi'(\overline{f})(1-\overline{f}))\right] d\widetilde{\nu} \\
&\leqslant \int_{\mathcal{D}} \left[\phi(f) - \phi(\overline{f}) + \phi'(\overline{f})(\overline{f} - f)\right] d\widetilde{\nu},
\end{aligned}$$

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 (4.38) 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:

$$\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) \leqslant \frac{1}{\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \int_{\mathcal{D}} \left[\phi(f) - \phi(\overline{f}) + \phi'(\overline{f})(\overline{f} - f)\right] d\nu = \frac{1}{\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \left(\int_{\mathcal{D}} \phi(f) d\nu - \phi(\overline{f})\right),$$

in view of (4.39). 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,

$$\mathcal{H}(f\widetilde{\nu} \mid \widetilde{\nu}) \leqslant \frac{1}{2R\widetilde{Z}}\,\mathrm{e}^{-\inf \widetilde{V}} \int_{\mathcal{D}} |\nabla(\ln f)|^2 f d\nu \leqslant \frac{1}{2R}\,\mathrm{e}^{\sup \widetilde{V} - \inf \widetilde{V}} \int_{\mathcal{D}} |\nabla(\ln f)|^2 f d\widetilde{\nu},$$

which gives the claimed statement.

LSI and metastability

The previous result gives lower bounds on the LSI constants. It suggests that the LSI constant, hence that the rate of convergence to equilibrium of the overdamped Langevin dynamics, decrease 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 [123, 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. Indeed, using the inequality

$$x \ln x - x + 1 \leqslant \frac{1}{2}(x-1)^2, \qquad \forall x \geqslant 0,$$

it holds

$$\mathcal{H}(\psi_0 \,|\, \nu) \leqslant \frac{1}{2} \left\| \frac{\psi_0}{\nu} - \mathbf{1} \right\|^2_{L^2(\nu)}.$$

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.*

Proof. The idea of the proof is that the Poincaré inequality can be seen as a linearization of the logarithmic Sobolev inequality. Start from the LSI

$$\int_{\mathcal{D}} \phi \ln \phi \, d\nu \leqslant \frac{1}{2R} \int_{\mathcal{D}} \frac{|\nabla \phi|^2}{\phi} \, d\nu,$$

where $\phi \geqslant 0$ has average 1 with respect to ν. The function ϕ can be chosen of the form $\phi = 1 + \varepsilon\varphi$ where $\varphi \in L^\infty(\mathcal{D})$ has average 0 with respect to ν. For $0 < \varepsilon \leqslant 1/(2\|\varphi\|_{L^\infty})$,

$$\int_{\mathcal{D}} (1+\varepsilon\varphi)\ln(1+\varepsilon\varphi)\, d\nu \leqslant \frac{\varepsilon^2}{2R} \int_{\mathcal{D}} \frac{|\nabla\varphi|^2}{1+\varepsilon\varphi}\, d\nu = \frac{\varepsilon^2}{2R}\left(\int_{\mathcal{D}} |\nabla\varphi|^2 \, d\nu + \mathrm{O}(\varepsilon) \right).$$

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

$$\int_{\mathcal{D}} (1+\varepsilon\varphi)\ln(1+\varepsilon\varphi)\, d\nu = \frac{\varepsilon^2}{2}\left(\int_{\mathcal{D}} \varphi^2 \, d\nu + \mathrm{O}(\varepsilon) \right).$$

The conclusion is obtained for bounded functions φ by taking the limit $\varepsilon \to 0$. The general case can finally be deduced by a density argument.

4.3.3 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 4.3.1, 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 4.3.2. We consider here the following general entropy functions.

Assumption 4.5 *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 [8, 7]. We follow the presentation in [13].

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 [13, 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 (4.8), as long as the dynamics preserves the invariant measure. This freedom was used in [7] for generalize the approach of [13].

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 4.3.2 (but consistently with the approach of Section 4.3.1), 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

$$\frac{d}{dt}\Big[e_u(f(t)\nu, \nu)\Big] = \int_{\mathcal{D}} u'(f(t))\mathcal{L}f(t)\,d\nu = -I_u(f(t)\nu, \nu), \tag{4.40}$$

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 4.6 *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 4.6 ensures that the following key coercivity property holds.

Proposition 4.6. *Under Assumption 4.6, 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 (4.40), 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 [7, 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 4.1. *Assumption 4.6 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 4.1). 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

$$2\Gamma_2(v(g),v(g))=\mathcal{L}\left[\Gamma(v(g),v(g))\right]-2\Gamma(\mathcal{L}v(g),v(g)).\tag{4.41}$$

Now, $\Gamma(v(g),v(g))=v'(g)^2\Gamma(g,g)$ so that

$$\begin{aligned}\mathcal{L}\left[\Gamma(v(g),v(g))\right]&=v'(g)^2\mathcal{L}\Gamma(g,g)+\Gamma(g,g)\mathcal{L}\left(v'(g)^2\right)+2\Gamma\left(v'(g)^2,\Gamma(g,g)\right)\\&=v'(g)^2\mathcal{L}\Gamma(g,g)+2\Gamma(g,g)\left[\Gamma\left(v'(g),v'(g)\right)+v'(g)\mathcal{L}\left(v'(g)\right)\right]+2\Gamma\left(v'(g)^2,\Gamma(g,g)\right)\\&=v'(g)^2\mathcal{L}\Gamma(g,g)+2\Gamma(g,g)\Big[v''(g)^2\Gamma\left(g,g\right)+v'(g)v''(g)\mathcal{L}g+2v'(g)v^{(3)}(g)\Gamma(g,g)\Big]\\&\quad+4v'(g)v''(g)\Gamma\left(g,\Gamma(g,g)\right).\end{aligned}$$

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 (4.41). □

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 $g=f(t)$):

$$\begin{aligned}\int_{\mathcal{D}} v'(g)\Gamma(g,g)\mathcal{L}g\,d\nu &= \int_{\mathcal{D}} \Gamma\Big(g, v'(g)\Gamma(g,g)\Big)d\nu \\ &= -\int_{\mathcal{D}} v'(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu - \int_{\mathcal{D}} v''(g)\Gamma(g,g)^2\,d\nu, \end{aligned} \tag{4.42}$$

and the following one for the second term (obtained from the definition of Γ_2):

$$\begin{aligned}\int_{\mathcal{D}} v(g)\Gamma(g,\mathcal{L}g)\,d\nu &= -\int_{\mathcal{D}} v(g)\Gamma_2(g,g)\,d\nu - \frac{1}{2}\int_{\mathcal{D}} v(g)\mathcal{L}\left[\Gamma(g,g)\right]d\nu \\ &= -\int_{\mathcal{D}} v(g)\Gamma_2(g,g)\,d\nu - \frac{1}{2}\int_{\mathcal{D}} v'(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu, \end{aligned} \tag{4.43}$$

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 4.6 to obtain some positiviy, relying on the change of unknown function based on Lemma 4.1 in order to account for the fact that factors $u^{(k)}(g)$ appear.

More precisely, consider the statement of Lemma 4.1 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 (4.5) 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 (4.42); and (4.43) for the fifth term. This gives

$$(1-m)\int_{\mathcal{D}} u''(g)\Gamma_2(g,g)\,d\nu + \left(\xi - \frac{3m}{2} + 2\xi m\right)\int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu \\ + \left(\frac{\xi^2(1-m)}{2} + m(2\xi-1)\right)\int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\,d\nu \geqslant \rho\int_{\mathcal{D}} u''(g)\Gamma(g,g)\,d\nu.$$

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

$$\int_{\mathcal{D}} u''(g)\Gamma_2(g,g)\,d\nu + \int_{\mathcal{D}} u^{(3)}(g)\Gamma\Big(g,\Gamma(g,g)\Big)d\nu \\ + \left(\frac{\xi_m^2}{2} + \frac{m(2\xi_m-1)}{1-m}\right)\int_{\mathcal{D}} u^{(4)}(g)\Gamma(g,g)^2\,d\nu \geqslant \frac{\rho}{1-m}\int_{\mathcal{D}} u''(g)\Gamma(g,g)\,d\nu.$$

Since (using $m \leqslant 1$)

$$\xi_m(1+m) = \frac{1}{1+2m}\left(1 + \frac{3m}{2} + \frac{m^2}{2}\right) \leqslant 1,$$

the prefactor in front of the last integral on the left-hand satisfies

$$\frac{\xi_m^2}{2} + \frac{m(2\xi_m-1)}{1-m} = \frac{1}{2(1-m)}\left(\xi_m^2 + m\xi_m - m\right) \leqslant \frac{1}{2}.$$

It remains to note that $u^{(4)} \geqslant 0$ by Assumption 4.5, as well as $\Gamma(g,g) \geqslant 0$, which gives the claimed result since the left-hand side of the above inequality is $R_u(g\nu,\nu)/2$. □

4.3.4 Convergence in weighted L^∞ 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 L^∞ spaces very similar to the ones obtained for Markov chains 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 also emphasize 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 L^∞ 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 $\mathrm{e}^{t\mathcal{L}^\dagger}$.

The key element in the analysis of Section 3.3.1 is the transition kernel $P(q,dq')$. A natural way to define a transition kernel for the overdamped Langevin dynamics (4.2) is the following, for a given time $t_0 > 0$: for any measurable set S,

$$P(q,S) = \mathbb{E}^q(\mathbf{1}_S(q_{t_0})). \tag{4.44}$$

Here $\mathbb{E}^q$ is the expectation over the realizations of (4.2) starting from $q_0 = q$, and $\mathbf{1}_S$ is the indicator function of the set S. The operator associated with the integral kernel (4.44) is therefore $P = \mathrm{e}^{t_0\mathcal{L}}$.

For simplicity, we consider the dynamics (4.2) 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. This is one of the main interest of weighted L^∞ estimates: they do not require structural assumptions on the type of dynamics considered. This is in sharp constrast with the analysis developed in Sections 4.3.2 and 4.3.1.

DEFINIR W AVANT THM

Theorem 4.7. *Assume that $\mathcal{D}$ is bounded or that there are $A > 0$ and $B \in \mathbb{R}$ such that*

$$q \cdot \nabla V(q) \geqslant A|q|^2 - B. \tag{4.45}$$

Then, there exist $C, \kappa > 0$ such that

$$\forall \varphi \in L^\infty_W(\mathcal{D}), \qquad \left\| \mathrm{e}^{t\mathcal{L}}\varphi - \int_{\mathcal{D}} \varphi \, d\nu \right\|_{L^\infty_W} \leqslant C\mathrm{e}^{-\kappa t}\|\varphi\|_{L^\infty_W}. \tag{4.46}$$

This condition (4.45) is satisfied for potentials $V(q)$ behaving at infinity as $|q|^k$ with $k \geqslant 2$.

Proof. We first discuss how to establish the Lyapunov condition (Assumption 3.2 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 $W = \mathbf{1}$. 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 $a > 0$ and $b \geqslant 0$, and a given Lyapunov function $W \geqslant 1$:

$$\mathcal{L}W \leqslant -aW + b. \tag{4.47}$$

This leads, by a time integration on the interval $[0, s]$ (using Itô calculus), to

$$\mathrm{e}^{s\mathcal{L}}W \leqslant \mathrm{e}^{-as}W + \frac{b}{a}(1 - \mathrm{e}^{-as}) \leqslant \mathrm{e}^{-as}W + \frac{b}{a}. \tag{4.48}$$

In particular, for $s = t_0$, we obtain

$$PW \leqslant \mathrm{e}^{-at_0}W + \frac{b}{a}, \tag{4.49}$$

which is the condition of Assumption 3.2 with $\alpha = \mathrm{e}^{-at_0} \in (0, 1)$ and $R = b/a \geqslant 0$. We therefore choose W in order for (4.47) to be satisfied. For overdamped Langevin dynamics in unbounded spaces, a typical choice is $W_n(q) = |q|^n$ for $n \geqslant 2$. In this case,

$$\mathcal{L}W_n(q) = n\left(-\nabla V(q) \cdot q + \frac{D + n - 2}{\beta}\right)|q|^{n-2}.$$

With (4.45), the Lyapunov condition (4.47) indeed holds since

$$\mathcal{L}W_n(q) \leqslant -AnW_n(q) + \frac{n(D + n - 2)}{\beta}|q|^{n-2} + Bn,$$

so that

$$\lim_{|q|\to+\infty} \frac{\mathcal{L}W_n(q)}{W_n(q)} \leqslant -An.$$

Then there exist $b_n \geqslant 0$ such that

$$\mathcal{L}W_n \leqslant -\frac{An}{2}\, W_n + b_n.$$

The minorization condition is a direct consequence of the controllability property and the smoothness of the density of the transition kernel. Note first that this condition can be rewritten as: for any Borel set $S \subset \mathcal{X}$,

$$P(x, S) = \int_S p_{t_0}(x, y)\, dy \geqslant \eta\lambda(S).$$

Next, $p(t_0, q, q') > 0$ for any $q, q' \in \mathcal{D}$. The minorization condition on compact spaces (Assumption 3.3 in Section 3.3.1) then easily follows from the continuity of the density of the transition

kernel: for any compact subdomain $\mathscr{C} \subset \mathcal{D}$, there exists $\alpha_{\mathscr{C}} > 0$ such that $p(t, q, q') \geqslant \alpha_{\mathscr{C}}$ when $(q, q') \in \mathscr{C}^2$, so that

$$P(q, dq') \geqslant \eta\, \lambda(dq'), \qquad \lambda(dq') = \frac{\mathbf{1}_{\mathscr{C}}(q')}{|\mathscr{C}|}\, dq', \qquad \eta = |\mathscr{C}|\alpha_{\mathscr{C}}.$$

At this stage, we have discussed how to obtain Assumptions 3.2 and 3.3. This already implies the decay estimates (3.10) by Theorem 3.4. 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 $t = nt_0 + \theta$ with $\theta \in [0, t_0)$. Then, for any $\varphi \in L^\infty_{W,0}(\mathcal{D})$ we obtain

$$\|\mathrm{e}^{t\mathcal{L}}\varphi\|_{L^\infty_W} \leqslant Cr^n \|\mathrm{e}^{\theta\mathcal{L}}\varphi\|_{L^\infty_W} \leqslant Cr^n \sup_{0 \leqslant s \leqslant t_0} \|\mathrm{e}^{s\mathcal{L}}\varphi\|_{L^\infty_W}. \tag{4.50}$$

Now, the inequality

$$\forall q \in \mathcal{D}, \qquad |\varphi(q)| \leqslant \|\varphi\|_{L^\infty_W} W(q),$$

leads to

$$\|\mathrm{e}^{s\mathcal{L}}\varphi\|_{L^\infty_W} \leqslant \|\varphi\|_{L^\infty_W} \left\| \frac{\mathrm{e}^{s\mathcal{L}} W}{W} \right\|_{L^\infty}.$$

In view of the inequality (4.48), it holds, for any $s \geqslant 0$,

$$\left\| \frac{\mathrm{e}^{s\mathcal{L}} W}{W} \right\|_{L^\infty} \leqslant \mathrm{e}^{-as} + \frac{b}{a} \left\| \frac{1}{W} \right\|_{L^\infty} \leqslant 1 + \frac{b}{a}.$$

Upon introducing $\kappa = -\log(r)/t_0 > 0$, (4.50) implies

$$\|\mathrm{e}^{t\mathcal{L}}\varphi\|_{L^\infty_W} \leqslant C \left(1 + \frac{b}{a}\right) \mathrm{e}^{-\kappa n t_0} \|\varphi\|_{L^\infty_W} \leqslant \widetilde{C} \mathrm{e}^{-\kappa t} \|\varphi\|_{L^\infty_W},$$

with

$$\widetilde{C} = C \left(1 + \frac{b}{a}\right) \mathrm{e}^{\kappa t_0}.$$

This leads indeed to (4.46). □

Remark 4.1 (Compactness of the evolution operator). *As made precise in [141, Theorem 8.9], the evolution operator $\mathrm{e}^{t_0\mathcal{L}}$ can be shown to be compact when the constant a in (4.47) 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 $n > 1$.

Remark 4.2 (sub-exponential convergence rates). *It is possible to weaken the Lyapunov condition (4.47) for instance as $\mathcal{L}W \leqslant \phi(W) + b$, 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 [45, 34] for further details.*

The exponential convergence result (4.46) leads to the following bounds on the resolvent.

Corollary 4.2. *Consider one of the following situations: the position space is compact, in which case $W = \mathbf{1}$; or that (4.45) holds, in which case $W(q) = 1 + |q|^n$ for some $n \geqslant 2$. Then the operator $\mathcal{L}$ is invertible on $L^\infty_{W,0}(\mathcal{X})$, and the following equality holds in $\mathcal{B}(L^\infty_{W,0})$:*

$$\mathcal{L}^{-1} = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}}\, dt.$$

Moreover,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(L^\infty_{W,0})} \leqslant \frac{C}{\kappa}, \tag{4.51}$$

where C and κ are the same constants as in Theorem 4.7.

Although it is possible to keep track of the values of the various constants until (4.46), the final rate of convergence in weighted L^∞ spaces is often not very sharp. The difficult point is in general to obtain a good control on the constant η in the minorization condition of Assumption 3.3.

4.4 Time discretization

In practice, continuous dynamics such as (4.2) are discretized in time using a numerical scheme. We present in this section elements on discretizations of SDEs more general than (4.2), and come back to this specific type of dynamics in Section 4.4.5 (and next for Langevin dynamics in Section 5.4). More precisely, the continous dynamics to be discretized reads

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t. \tag{4.52}$$

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

$$x^{n+1} = x^n + b(x^n)\,\Delta t + \sigma(x^n)\sqrt{\Delta t}\,G^n, \tag{4.53}$$

where G^n is a sequence of i.i.d. Gaussian random variables with covariance matrix Id_D. We denote in the sequel the evolution operator (also called transition operator) associated with a general one-step numerical scheme as

$$P_{\Delta t}\varphi(x) = \mathbb{E}(\varphi(x^{n+1}) \mid x^n = x). \tag{4.54}$$

It is the discrete equivalent of the semigroup $\mathrm{e}^{\Delta t\mathcal{L}}$. 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 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. As discussed below, these erros can be decomposed, for sufficiently long times, into (i) a systematic part, related to errors on the invariant measure due to the time discretization; and (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.

4.4.1 Standard numerical analysis of SDEs

There are many good review articles and textbooks on the numerical analysis of SDEs, such as [91, 137, 126]. 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 $\Delta t \in (0, \Delta t^*]$,

$$\sup_{0 \leqslant n \leqslant T/\Delta t} |\mathbb{E}[\varphi(x^n)] - \mathbb{E}[\varphi(x_{n\Delta t})]| \leqslant C\Delta t^\alpha.$$

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 [126, 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 should 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 $p \in \mathbb{N}$ for which $\|r_{\varphi,\Delta t}/(1+|x|^p)\|_{L^\infty} \leqslant K$ for Δt sufficiently small.

(2) *Strong error estimates in L^p-norm for $p \geqslant 1$.* 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 $0 \leqslant \Delta t \leqslant \Delta t^*$,

$$\sup_{0 \leqslant n \leqslant T/\Delta t} (\mathbb{E}|x^n - x_{n\Delta t}|^p)^{1/p} \leqslant C\Delta t^\alpha.$$

In this case the Gaussian increments used in a numerical scheme such as (4.53) must be induced by the Brownian motion for the continuous dynamics (4.52), *i.e.*,

$$G^n = \frac{W_{(n+1)\Delta t} - W_{n\Delta t}}{\sqrt{\Delta t}}.$$

Typically, the constant C is obtained via some (discrete) Gronwall estimate, as in the standard numerical analysis of ordinary differential equations, and hence increases exponentially with time.

As an example, let us mention that, when the functions b and σ in (4.52) are globally Lipschitz, the weak and strong errors of the Euler–Maruyama scheme (4.53) 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 [102] or multilevel Monte Carlo methods [64, 65].

4.4.2 Convergence of time averages

The above error estimates 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:

$$\widehat{\varphi}_{N_{\mathrm{iter}},\Delta t} = \frac{1}{N_{\mathrm{iter}}} \sum_{n=0}^{N_{\mathrm{iter}}-1} \varphi(x^n). \tag{4.55}$$

Existence and uniquess of an invariant probability measure

A first issue is to prove that 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 typical obstruction is the presence of non-globally Lipschitz drifts which induce a transient behaviour of the Markov chain. A typical case is reported in [121, Section 6.3] for $b(x) = -x^3$ and $\sigma(x) = 1$. Then, the Euler–Maruyama scheme reads

$$x^{n+1} = x^n - \Delta t\,(x^n)^3 + \sqrt{\Delta t}\,G^n.$$

It can be shown that

$$\mathbb{P}\left(|x^n| \geqslant \frac{2^n}{\sqrt{\Delta t}}\ \forall n \geqslant 1\right) = \alpha > 0.$$

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 $\varphi(x) = 1_{|x|>R}$. There exists N_{iter} such that

$$\frac{1}{N_{\mathrm{iter}}} \sum_{n=1}^{N_{\mathrm{iter}}} \varphi(x^n)$$

is larger than $1/2$ with probability α; while, on the other hand, this quantity converges almost surely to $\mathbb{E}_{\mu_{\Delta t}}(\varphi) \leqslant 1/4$. 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 3.4. Proving that a minorization condition holds on any compact set (see Assumption 3.3) is usually not too difficult, thanks to the presence of Gaussian increments; see for instance Lemma 4.2 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.

Some assumptions on the drift, on the other hand, are usually required to state a Lyapunov condition such as Assumption 3.2: see [121]. 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 3.4).

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 (4.53) when σ has full rank d at each point $x \in \mathcal{X}$ since

$$G^1 = \sigma(x^0)^{-1} \left(\frac{x^1 - x^0 - \Delta t\, b(x^0)}{\sqrt{\Delta t}} \right) := \mathcal{G}_{x^0}(x^1),$$

so that

$$P(x^0, S) = \mathbb{P}\left(G^1 \in \mathcal{G}_{x_0}^{-1}(S)\right) > 0.$$

When σ is degenerate, several iterates may be necessary; see for instance [25] where it is proved that $P^2(x^0, S) > 0$ 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.

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 3.4, it can easily be shown that the asymptotic variance is well defined when $x^0 \sim \pi_{\Delta t}$, provided $W \in L^2(\pi_{\Delta t})$ and $\varphi \in L^\infty_W(\mathcal{X})$. The discussion follows the same lines the presentation in Section 3.4, upon replacing ν by $\pi_{\Delta t}$ 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 $W \in L^2(\pi_{\Delta t})$ is check whether the assumptions of Theorem 3.4 are satisfied for the Lyapunov function W^2 instead of W, so that the integrability condition follows from (3.9). In practice, it is often convenient to establish minorization conditions on arbitrary compact sets, and to obtain Lyapunov conditions for the family of functions $W_n(x) = 1 + |x|^n$ (for integers $n \geqslant n_0$ sufficiently large). Note that $W_n^2 = W_{2n} + 2(W_n - 1)$, so that the $L^2(\pi_{\Delta t})$ integrability of W_n follows as soon as Lyapunov estimates hold for 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 presented at the end leading to (3.21),

$$\sigma^2_{\varphi,\Delta t} = N_{\mathrm{corr},\Delta t,\varphi} \sigma^2_{\varphi,\mathrm{iid},\Delta t}, \quad \text{where} \quad \sigma^2_{\varphi,\mathrm{iid},\Delta t} = \int_{\mathcal{X}} (\Pi_{\Delta t}\varphi)^2 \, d\pi_{\Delta t}.$$

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.

4.4.3 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 (4.55), for a given one step discretization of the continuous dynamics (4.52) ergodic with respect to π. We decompose the error as the sum of two contributions:

$$\widehat{\varphi}_{N_{\rm iter},\Delta t} - \mathbb{E}_\pi(\varphi) = \Big(\widehat{\varphi}_{N_{\rm iter},\Delta t} - \mathbb{E}_{\pi_{\Delta t}}(\varphi)\Big) + \Big(\mathbb{E}_{\pi_{\Delta t}}(\varphi) - \mathbb{E}_\pi(\varphi)\Big). \tag{4.56}$$

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.

(1) According to the Central Limit Theorem for Markov chains (which holds when the Poisson equation (3.19) 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 (3.20). 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 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

$$\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\varphi = -\mathcal{L}\varphi + \mathrm{O}(\Delta t),$$

In addition, the variance $\sigma^2_{\varphi,\Delta t}$ can be rewritten as

$$\Delta t \, \sigma^2_{\varphi,\Delta t} = 2\int_{\mathcal{X}} (\Pi_{\Delta t}\varphi)\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right)^{-1} \Pi_{\Delta t}\varphi \, d\pi_{\Delta t} + \mathrm{O}(\Delta t).$$

In view of the expression σ^2_φ of the asymptotic variance of the continuous dynamics, namely (the proof being the same as for (4.11))

$$\sigma^2_\varphi = 2\int_{\mathcal{X}} (\Pi\varphi)\left(-\mathcal{L}\Pi\varphi\right)^{-1} d\pi, \tag{4.57}$$

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:

$$\Delta t \, \sigma^2_{\varphi,\Delta t} \xrightarrow[\Delta t \to 0]{} \sigma^2_\varphi. \tag{4.58}$$

A rigorous proof of this convergence is provided by Theorem 7.2. In fact, it typically holds that $\theta_{\rm corr} = N_{{\rm corr},\Delta t}\Delta t + \mathrm{O}(\Delta t)$.

The interpretation of (4.58) 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 direct study of the variances of the continuous processes, such as (4.11), rather than their discrete counterparts, which we therefore do in Section 4.5.

(2) The second term in (4.56) 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 $h_{\Delta t} = 1 + \mathrm{O}(\Delta t^p)$ for some integer p. In fact, it is often possible to make precise the leading term in the bias as follows (see Theorem 4.9 below):

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \, d\pi + \Delta t^p \int_{\mathcal{X}} \varphi f \, d\pi + \mathrm{O}(\Delta t^{p+1})$$

for some function f to be made precise. As made clear in Theorem 4.9, $p \geqslant \alpha$, 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 $p \geqslant \alpha + 1$.

An important remark is that the bias becomes noticeable only for sufficiently long integration times $T = N_{\mathrm{iter}}\Delta t$, namely when $\sigma_\varphi/\sqrt{T} \sim \Delta t^p$. More precisely,

$$N_{\mathrm{iter}} \sim \frac{\sigma_\varphi^2}{\Delta t^{2p+1}}.$$

This motivates the fact 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.

4.4.4 Analysis of the bias: general strategy

We present in this section how to analyse the bias (second term on the right-hand side of (4.56)). Assume that the continuous dynamics, with generator $\mathcal{L}$, admits a unique invariant measure π. Consider next a given numerical scheme, described in terms of its discrete evolution operator $P_{\Delta t}$ defined in (4.54), 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 p, the evolution operator can be expanded as

$$P_{\Delta t}\varphi = \varphi + \Delta t \, \mathcal{A}_1\varphi + \Delta t^2 \mathcal{A}_2\varphi + \cdots + \Delta t^{p+1}\mathcal{A}_{p+1}\varphi + \Delta t^{p+2} r_{\varphi,\Delta t}, \tag{4.59}$$

for some remainder term $r_{\varphi,\Delta t}$ (which depends on p, 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 p when $\mathcal{A}_k = \mathcal{L}^k/k!$ for $1 \leqslant k \leqslant p$. 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 p, but the invariant measure may nonetheless be correct up to error terms of order Δt^{p+1}. Moreover, as made precise in Theorem 4.9, 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 (4.59). We introduce to this end the following set of C^∞ functions.

Definition 4.4 (smooth functions). *Consider scale functions $W_n : \mathcal{X} \to [1, +\infty)$ such that*

$$\forall n \geqslant 0, \qquad W_n \leqslant W_{n+1}.$$

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 $\partial^k\varphi \in L^\infty_{W_m}(\mathcal{X})$.

In the simple case when $\mathcal{X}$ is bounded, it is possible to choose $W_n = \mathbf{1}$ for all $n \geqslant 0$, in which case $\mathcal{S} = C^\infty(\mathcal{X})$. For unbounded spaces, a typical choice is $W_n(x) = 1 + |x|^n$. 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

$$\mathcal{S}_0 = \Pi\mathcal{S} = \left\{ \varphi \in \mathcal{S} \;\middle|\; \int_{\mathcal{X}} \varphi \, d\pi = 0 \right\}, \tag{4.60}$$

where Π is defined in (4.10). 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 4.8 (stability of smooth functions by inverse operators) *The space $\mathcal{S}$ is dense in $L^2(\pi)$ (in particular $W_n \in L^2(\pi)$ 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 4.9 (error estimates on the invariant measure). *Suppose that Assumption 4.8 is satisfied, and that an expansion such as (4.59) holds for any $\varphi \in \mathcal{S}$ and a given $p \in \mathbb{N}$, 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 p) such that*

$$\forall \Delta t \leqslant \Delta t^*, \qquad \|r_{\varphi,\Delta t}\|_{L^\infty_{W_m}} \leqslant K.$$

Assume in addition that the operators $\mathcal{A}_k$ leave $\mathcal{S}$ invariant for any $k \geqslant 1$, that

$$\forall k \in \{1, \dots, p\}, \quad \forall \varphi \in \mathcal{S}, \qquad \int_{\mathcal{X}} \mathcal{A}_k \varphi \, d\pi = 0, \tag{4.61}$$

and that $g_{p+1} = \mathcal{A}_{p+1}^* \mathbf{1} \in \mathcal{S}_0$. Finally, assume that the numerical scheme admits an invariant measure $\pi_{\Delta t}$ which integrates all scale functions:

$$\forall n \geqslant 0, \qquad \int_{\mathcal{X}} W_n \, d\pi_{\Delta t} < +\infty.$$

Then, there exists $L > 0$ such that, for any $\Delta t \in (0, \Delta t^*]$,

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \, d\pi + \Delta t^p \int_{\mathcal{X}} \varphi f_{p+1} \, d\pi + \Delta t^{p+1} R_{\varphi,\Delta t}, \tag{4.62}$$

with $|R_{\varphi,\Delta t}| \leqslant L$ and where

$$f_{p+1} = -\left(\mathcal{A}_1^*\right)^{-1} g_{p+1} \in \mathcal{S}_0. \tag{4.63}$$

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 (4.52) are C^∞. Moreover, in order to obtain the expression of $g_{p+1} = \mathcal{A}_{p+1}^* \mathbf{1}$, it is convenient to resort to integrations by parts to determine the function g_{p+1} such that, for any test function $\varphi \in \mathcal{S}$,

$$\int_{\mathcal{X}} \mathcal{A}_{p+1} \varphi \, d\pi = \int_{\mathcal{X}} g_{p+1} \varphi \, d\pi. \tag{4.64}$$

It can usually be checked by direct inspection that $g_{p+1} \in \mathcal{S}$. In addition, by considering $\varphi = \mathbf{1}$ in (4.64), it follows that g_{p+1} automatically has average 0 with respect to π when $\mathcal{A}_{p+1}\mathbf{1} = 0$, 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 (4.61). 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 4.9 is as follows. First, averages with respect to $\pi_{\Delta t}$ are correct up to errors of order Δt^p. 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 (4.75) below). Let us finally mention that it is possible to obtain bounds on $R_{\varphi,\Delta t}$ in terms of weighted L^∞ norms of φ and a given number of its derivatives when more precise estimates for $\mathcal{L}^{-1}$ are available.

Proof. The proof is obtained by a generalization of the proof of [108, Theorem 2.13]. A similar result is provided in [1]. Note first that, since f_{p+1} has average 0 with respect to π, it is sufficient to establish (4.62) 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 (4.62) for functions $\varphi \in (P_{\Delta t} - \mathrm{Id})\mathcal{S}$. This step motivates the expression for the correction function f_{p+1}. Consider $\phi \in \mathcal{S}$. The invariance of $\pi_{\Delta t}$ by the discretized dynamics implies that

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \phi \right] d\pi_{\Delta t} = 0. \tag{4.65}$$

On the other hand, (4.59) and (4.61) give

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \phi \right] d\pi = \Delta t^p \int_{\mathcal{X}} \mathcal{A}_{p+1}\phi \, d\pi + \Delta t^{p+1} \int_{\mathcal{X}} r_{\phi,\Delta t} \, d\pi,$$

and, 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

$$\begin{aligned} &\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \phi \right] (1 + \Delta t^p f) \, d\pi \\ &\quad = \Delta t^p \int_{\mathcal{X}} (\mathcal{A}_{p+1}\phi + (\mathcal{A}_1\phi) f) \, d\pi \\ &\qquad + \Delta t^{p+1} \int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t} - \mathrm{Id} - \Delta t \, \mathcal{A}_1}{\Delta t^2} \phi \right] f \right) d\pi. \end{aligned}$$

The second term on the right-hand side of the previous equality is indeed of order Δt^{p+1} since the integrand of the corresponding integral is bounded in some weighted L^∞ 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

$$\int_{\mathcal{X}} (\mathcal{A}_{p+1}\phi + (\mathcal{A}_1\phi) f) \, d\pi = \int_{\mathcal{X}} (g_{p+1} + \mathcal{A}_1^* f) \phi \, d\pi.$$

This suggests choosing $f = f_{p+1} = -(\mathcal{A}_1^*)^{-1} g_{p+1}$, which is well defined by our assumptions on $\mathcal{A}_1$ since $g_{p+1} \in \mathcal{S}_0$. With this choice,

$$\begin{aligned} &\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \phi \right] (1 + \Delta t^p f_{p+1}) \, d\pi \\ &\quad = \Delta t^{p+1} \int_{\mathcal{X}} \left(r_{\phi,\Delta t} + \left[\frac{P_{\Delta t} - \mathrm{Id} - \Delta t \, \mathcal{A}_1}{\Delta t^2} \phi \right] f_{p+1} \right) d\pi. \end{aligned} \tag{4.66}$$

so that (4.62) holds for $\varphi = (\mathrm{Id} - P_{\Delta t})\phi / \Delta t$.

The second step of the proof is to extend (4.62) 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 (4.10). The equality (4.65) implies, for $\phi\in\mathcal{S}_0$ (so that $\Pi\phi=\phi$),

$$\int_{\mathcal{X}}\left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right]d\pi_{\Delta t} = -\frac{1}{\Delta t}\int_{\mathcal{X}}(P_{\Delta t}\phi)\,d\pi, \tag{4.67}$$

while, using the fact that f_{p+1} is of average 0 with respect to π, (4.66) leads to

$$\begin{aligned}\int_{\mathcal{X}}\left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right](1+\Delta t^p f_{p+1})\,d\pi &= -\frac{1}{\Delta t}\int_{\mathcal{X}}(P_{\Delta t}\phi)\,d\pi\\ &+\Delta t^{p+1}\int_{\mathcal{X}}\left(r_{\phi,\Delta t}+\left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right]f_{p+1}\right)d\pi.\end{aligned} \tag{4.68}$$

This shows that, for any $\phi\in\mathcal{S}_0$,

$$\begin{aligned}\int_{\mathcal{X}}\left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right]d\pi_{\Delta t} &= \int_{\mathcal{X}}\left[\Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi\phi\right](1+\Delta t^p f_{p+1})\,d\pi\\ &-\Delta t^{p+1}\int_{\mathcal{X}}\left(r_{\phi,\Delta t}+\left[\frac{P_{\Delta t}-\mathrm{Id}-\Delta t\,\mathcal{A}_1}{\Delta t^2}\phi\right]f_{p+1}\right)d\pi.\end{aligned}$$

We next consider an approximate inverse operator $Q_{\Delta t}$ which leaves $\mathcal{S}_0$ invariant, and is such that

$$\forall\varphi\in\mathcal{S}_0,\qquad \Pi\left(\frac{P_{\Delta t}-\mathrm{Id}}{\Delta t}\right)\Pi Q_{\Delta t}\varphi = \varphi+\Delta t^{p+1}\widetilde{r}_{\varphi,\Delta t}. \tag{4.69}$$

with $\|\widetilde{r}_{\varphi,\Delta t}\|_{L^\infty_{W^m_\pi}}$ 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 $B=\Pi\mathcal{A}_2\Pi+\cdots+\Delta t^{p-1}\Pi\mathcal{A}_{p+1}\Pi$. 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 7.1). Introducing $\widetilde{\mathcal{A}}_k=\Pi\mathcal{A}_k\Pi$ for notational simplicity, we consider

$$\widetilde{Q}_{\Delta t}=\widetilde{\mathcal{A}}_1^{-1}\sum_{n=0}^{p}(-1)^n\Delta t^n\,(B\widetilde{\mathcal{A}}_1^{-1})^n.$$

We next remove operators with powers of Δt larger than or equal to $p+1$ (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 p. Finally, the so-constructed operator,

$$\begin{aligned}Q_{\Delta t} = \widetilde{\mathcal{A}}_1^{-1}&-\Delta t\widetilde{\mathcal{A}}_1^{-1}\widetilde{\mathcal{A}}_2\widetilde{\mathcal{A}}_1^{-1}+\Delta t^2(\widetilde{\mathcal{A}}_1^{-1}\widetilde{\mathcal{A}}_2\widetilde{\mathcal{A}}_1^{-1}\widetilde{\mathcal{A}}_2\widetilde{\mathcal{A}}_1^{-1}-\widetilde{\mathcal{A}}_1^{-1}\widetilde{\mathcal{A}}_3\widetilde{\mathcal{A}}_1^{-1})\\ &+\Delta t^3\mathcal{Q}_3+\cdots+\Delta t^p\mathcal{Q}_p,\end{aligned}$$

is a well defined operator which leaves $\mathcal{S}_0$ invariant (since its action is given by the application of at most p 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 (4.69) 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 (4.62) for functions in $\mathcal{S}_0$.

We next illustrate the strategy presented here on overdamped Langevin and Langevin dynamics. We postpone a numerical illustration of the results of Theorem 4.9 to Figure 7.1 in Section 7.4. Indeed, as explained in Section 4.4.6, 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 7.4.1.

4.4.5 Application to overdamped Langevin dynamics

For overdamped Langevin dynamics, we consider for simplicity the case of a simple Euler–Maruyama discretization of a dynamics defined on the compact position space $\mathcal{D} = (L\mathbb{T})^D$:

$$q^{n+1} = q^n - \Delta t\, \nabla V(q^n) + \sqrt{\frac{2\Delta t}{\beta}}\, G^n. \tag{4.70}$$

The results below can be easily generalized to other discretization schemes. On the other hand, an extension to unbounded position spaces is not trivial (see [98]), although several results can be stated in a weaker form than the results given below.

The first task is to find an expansion of the transition operator $P_{\Delta t}$ defined in (4.54) in powers of Δt, see (4.59). We next apply Theorem 4.9 with $p = 1$. There are three types of assumptions to be checked:

(1) assumptions on the generator $\mathcal{L} = \mathcal{A}_1$ of the continuous dynamics;

(2) assumptions on the operator $\mathcal{A}_2$, whose action is given by (4.73);

(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

$$\begin{aligned}\varphi(q+\delta) = \varphi(q) + \delta^T\nabla\varphi(q) + \frac{1}{2}\delta^T\nabla^2\varphi(q)\delta + \frac{1}{6}D^3\varphi(q) : \delta^{\otimes 3} + \frac{1}{24}D^4\varphi(q) : \delta^{\otimes 4} + \frac{1}{120}D^5\varphi(q) : \delta^{\otimes 5} \\ + \frac{1}{120}\int_0^1 (1-\theta)^5 D^6\varphi(q+\theta\delta) : \delta^{\otimes 6}\, d\theta,\end{aligned}$$

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 **INASS DIT :** $\frac{1}{\beta}D^3\varphi(q) : \big(G^{\otimes 2} \otimes \nabla V(q)\big)$**...**

$$\begin{aligned}\varphi\left(\Phi_{\Delta t}(q,G)\right) &= \varphi(q) + \sqrt{\frac{2\Delta t}{\beta}} G^T \nabla\varphi(q) + \Delta t \left(\frac{1}{\beta} G^T \left(\nabla^2\varphi(q)\right) G - \nabla V(q)^T \nabla\varphi(q)\right) \\ &+ \Delta t^{3/2} \left(\frac{\sqrt{2}}{3\beta^{3/2}} D^3\varphi(q) : G^{\otimes 3} - \sqrt{\frac{2}{\beta}} G^T \nabla^2\varphi(q) \nabla V(q)\right) \\ &+ \Delta t^2 \left(\frac{1}{6\beta^2} D^4\varphi(q) : G^{\otimes 4} - \frac{1}{2\beta} D^3\varphi(q) : \left(G^{\otimes 2} \otimes \nabla V(q)\right) + \frac{1}{2} \nabla V(q)^T \nabla^2\varphi(q) \nabla V(q)\right) \\ &+ \Delta t^{5/2} \xi_{5/2}(q,G) + \Delta t^3 \widetilde{\xi}_{\Delta t}(q,G).\end{aligned}$$

Note that we have an expansion with fractional powers of Δt. However, the terms corresponding to non-integer powers of Δt (such as $\xi_{5/2}(q,\xi)$) contain an odd number of occurences of G, so that their expectations with respect to G vanish. Since $P_{\Delta t}\varphi(q) = \mathbb{E}_G\left[\varphi\left(\Phi_{\Delta t}(q,G)\right)\right]$, a simple computation shows that

$$P_{\Delta t}\varphi = \varphi + \Delta t\, \mathcal{L}\varphi + \Delta t^2 \mathcal{A}_2 \varphi + \Delta t^3 r_{\varphi,\Delta t} \tag{4.71}$$

where

$$\mathcal{A}_2 = \frac{1}{2}\left(\frac{1}{\beta^2}\Delta^2 - \frac{1}{\beta}\nabla V(q)^T \nabla(\Delta\varphi) + \nabla V(q)^T \nabla^2\varphi(q) \nabla V(q)\right),$$

and $r_{\varphi,\Delta t}(q) = \mathbb{E}_G\left[\widetilde{\xi}_{\Delta t}(q,G)\right]$ is such that $\|r_{\varphi,\Delta t}\|_{L^\infty} \leqslant K$ for Δt sufficiently small. It can be checked that $\mathcal{A}_2 \neq \frac{1}{2}\mathcal{L}^2$. Indeed,

$$\mathcal{L}^2\varphi = \frac{1}{\beta^2}\Delta^2\varphi - \frac{2}{\beta}\nabla^2 V : \nabla^2\varphi - \frac{2}{\beta}\nabla V \cdot \nabla(\Delta\varphi) - \frac{1}{\beta}\nabla(\Delta V)\cdot\nabla\varphi + (\nabla V)^T(\nabla^2\varphi)\nabla V + (\nabla V)^T(\nabla^2 V)\nabla\varphi, \tag{4.72}$$

so that

$$\mathcal{A}_2 = \frac{1}{2}\left(\mathcal{L}^2 + \mathcal{R}_2\right), \tag{4.73}$$

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 4.4, $W_n(q) = \mathbf{1}$ for all $n \geqslant 0$ when $\mathcal{D}$ is bounded, so that $\mathcal{S} = C^\infty(\mathcal{D})$. Standard results of elliptic regularity 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 $W_n(q) = 1 + |q|^n$, and the proof of this stability result are much move involved (see [98]).

Expression of the correction function

It can now be easily checked that g_2 is well defined and belongs to $\mathcal{S}$ (recall that, as discussed after Theorem 4.9, it automatically has average 0 with respect to π). To obtain the precise expression for g_2, we use integration by parts to compute

$$\begin{aligned}\int_{\mathcal{D}} \mathcal{R}_2\varphi\, d\nu &= -\frac{1}{\beta}\int_{\mathcal{D}} \nabla\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right)\cdot\nabla\varphi\, d\nu \\ &= \int_{\mathcal{D}} \mathcal{L}\left(\Delta V - \frac{\beta}{2}|\nabla V|^2\right)\varphi\, d\nu.\end{aligned}$$

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 (4.63):

$$f_2 = -\frac{1}{2} \left(\Delta V - \frac{\beta}{2} |\nabla V|^2 - \frac{a_{\beta,V}}{2} \right),$$

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 is of 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 3.4. The Lyapunov condition of Assumption 3.2 is trivially satisfied since the position space is compact. Therefore, the only property to prove is the minorization condition of Assumption 3.3. Since the space is bounded, it readily follows from (4.70) that, for any Borel subset $S \subset \mathcal{D}$,

$$\begin{aligned}
\mathbb{P}(q^1 \in S | q^0 = q) &\geqslant \mathbb{P} \left(\sqrt{\frac{2\Delta t}{\beta}} G^1 \in S - q + \Delta t \nabla V(q) \right) \\
&\geqslant \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{L^\infty}} \mathbb{P} \left(\sqrt{\frac{2\Delta t}{\beta}} G^1 \in S - \mathcal{Q} \right) \\
&= \left(\frac{\beta}{4\pi \Delta t} \right)^{d/2} \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{L^\infty}} \int_{S - \mathcal{Q}} \exp \left(-\frac{\beta |g|^2}{4\Delta t} \right) dg,
\end{aligned}$$

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

$$\widetilde{\lambda}_{\Delta t}(S) = \inf_{|\mathcal{Q}| \leqslant |\mathcal{D}| + \|\nabla V\|_{L^\infty}} \int_{S - \mathcal{Q}} \exp \left(-\frac{\beta |g|^2}{4\Delta t} \right) dg,$$

normalizing it as $\lambda_{\Delta t}(S) = \widetilde{\lambda}_{\Delta t}(S) / \widetilde{\lambda}_{\Delta t}(\mathcal{D})$, and introducing $\eta_{\Delta t} = (4\pi \Delta t / \beta)^{-d/2} \widetilde{\lambda}_{\Delta t}(\mathcal{D})$.

We state below a minorization condition stronger than is needed for Assumption 3.2, but which will prove useful later on in Section 7.4. 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 4.2 (uniform minorization condition). *Consider the evolution operator $P_{\Delta t}$ associated with the Euler–Maruyama discretization* (4.70) *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 [24] in unbounded spaces $\mathcal{D}$ for a class of Metropolis–Hastings schemes whose proposition kernel is (4.70). See also [57, 58] for related results on bounded spaces, as well as [108, 138] for discretizations of Langevin dynamics.

Proof. It is sufficient to prove the result for indicator functions of Borel sets $S \subset \mathcal{D}$. We therefore aim to prove that

$$\mathbb{P}(q^{\lceil T/\Delta t\rceil} \in S \mid q^0 = q) \geqslant \eta\, \lambda(S),$$

for a probability measure λ and a constant $\eta > 0$. The idea of the proof is to explicitly rewrite q^n as a perturbation of the reference evolution corresponding to $\nabla V = 0$. Since we consider C^∞ potentials and the position space is compact, the perturbation can be uniformly controlled. More precisely, an immediate induction argument based on (4.70) gives

$$q^n = q^0 + \mathcal{G}^n + \mathcal{F}^n,$$

with

$$\mathcal{G}^n = \sqrt{\frac{2\Delta t}{\beta}} \sum_{k=0}^{n-1} G^k, \quad \mathcal{F}^n = -\Delta t \sum_{k=0}^{n-1} \nabla V(q^k).$$

Let us now fix $n = \lceil T/\Delta t\rceil$ (so that $T \leqslant n\Delta t \leqslant T + \Delta t$). Then $|\mathcal{F}^n| \leqslant \|\nabla V\|_{L^\infty}(T + \Delta t)$, while $\mathcal{G}^n$ is a Gaussian random variable with covariance matrix $2n\Delta t\beta^{-1}\,\mathrm{Id}_D$. Therefore,

$$\begin{aligned}\mathbb{P}(q^n \in S \mid q^0 = q) &\geqslant \mathbb{P}(\mathcal{G}^n \in S - q - \mathcal{F}^n)\\ &= \left(\frac{\beta}{2\pi n\Delta t}\right)^{D/2} \int_{S-q-\mathcal{F}^n} \exp\left(-\frac{\beta|g|^2}{2n\Delta t}\right) dg.\end{aligned}$$

In the latter expression and below, we assume that the random variable $\mathcal{G}^n$ has values in $\mathbb{R}^D$ rather than $\mathcal{D}$, and regard $S - q - \mathcal{F}^n$ as a subset of $\mathbb{R}^D$ rather than $\mathcal{D}$. This amounts to neglecting the periodic images, and henceforth reduces the probability on the right-hand side of the above inequality. This is not a problem, however, since we seek a lower bound. Now, for Δt sufficiently small, we have $T/2 \leqslant n\Delta t \leqslant 2T$, so

$$\left(\frac{1}{n\Delta t}\right)^{D/2} \int_{S-q-\mathcal{F}^n} \exp\left(-\frac{\beta|g|^2}{2n\Delta t}\right) dg \geqslant \left(\frac{1}{2T}\right)^{D/2} \int_{S-q-\mathcal{F}^n} \exp\left(-\frac{\beta|g|^2}{T}\right) dg.$$

Since the state space is compact, there exists $R > 0$ such that $|q + \mathcal{F}^n| \leqslant R$ for any $q \in \mathcal{D}$. The conclusion then easily follows by defining the probability measure λ as: for all $S \subset \mathcal{D}$,

$$\lambda(S) = Z_R^{-1} \inf_{|Q|\leqslant R} \int_{S+Q} \exp\left(-\frac{\beta|g|^2}{T}\right) dg,$$

A CHANGER EN CE QUI SUIT, ICI ET PARTOUT... et dire que erreur dans articles...

$$\lambda(S) = Z_R^{-1} \int_S \left[\inf_{|Q|\leqslant R} \exp\left(-\frac{\beta|g+Q|^2}{T}\right)\right] dg,$$

and setting the constant η to the value $\eta = Z_R(4\pi T/\beta)^{-D/2}$.

The proof of Lemma 4.2 shows that the measure λ has a positive density with respect to the Lebesgue measure. Application of Theorem 3.4, together with an argument similar to that used to obtain (4.46) from the decay at multiples of a given time, gives the following exponential convergence.

Corollary 4.3 (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 $f \in L^\infty(\mathcal{D})$,*

$$\forall n \in \mathbb{N}, \qquad \left\| P_{\Delta t}^n f - \int_{\mathcal{D}} f\, d\nu_{\Delta t} \right\|_{L^\infty} \leqslant C\, \mathrm{e}^{-\kappa n\Delta t}\, \|f\|_{L^\infty}. \tag{4.74}$$

The fact $\nu_{\Delta t}$ admits a density with respect to the Lebesgue measure dq follows from the minorization condition stated in Lemma 4.2, which ensures that the Markov chain is irreducible with respect to Lebesgue measure. The proof of Corollary 4.3 relies on the following result (given on a general state space with a general Lyapunov function) for the choice $W = 1$.

Lemma 4.3. *Consider a Lyapunov function $W : \mathcal{X} \to [1, +\infty)$ and assume that there exists $N \geqslant 1$ and $K, \lambda > 0$ such that*

$$\forall m \in \mathbb{N}, \qquad \left\|P^{Nm}\right\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \leqslant K \mathrm{e}^{-\lambda m},$$

where π is the unique invariant measure of P^N and

$$L^\infty_{W,0} = \left\{ \varphi \in L^\infty_W(\mathcal{X}) \, \middle| \, \int_{\mathcal{X}} \varphi \, d\pi = 0 \right\}.$$

Then, the following estimate holds at any time:

$$\forall n \in \mathbb{N}, \qquad \|P^n\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \leqslant \left(K \, \mathrm{e}^{\lambda} \sup_{0 \leqslant k \leqslant N-1} \left\| \frac{P^k W}{W} \right\|_{L^\infty} \right) \mathrm{e}^{-\lambda n / N}$$

Note that this result in particular shows that π is the unique invariant measure of P. A sufficient condition for

$$\sup_{k \geqslant 0} \left\| \frac{P^k W}{W} \right\|_{L^\infty} < +\infty$$

is that $PW \leqslant aW + b$ with $0 \leqslant a < 1$, *i.e.* a Lyapunov condition holds over one step. In this case, the supremum is of order $1/(1-a)$. 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 $|f| \leqslant \|f\|_{L^\infty_W} W$, so that $|P^k f| \leqslant \|f\|_{L^\infty_W} P^k W$, and finally

$$\|P^k f\|_{L^\infty_W} \leqslant \|f\|_{L^\infty_W} \left\| \frac{P^k W}{W} \right\|_{L^\infty}.$$

This shows that

$$\|P^k\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \leqslant \left\| \frac{P^k W}{W} \right\|_{L^\infty}.$$

Therefore,

$$\|P^n\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \leqslant \left\|(P^N)^{m_n}\right\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \left\|P^{\tilde{n}}\right\|_{\mathcal{B}\left(L^\infty_{W,0}\right)} \leqslant K \mathrm{e}^{-\lambda m_n} \sup_{0 \leqslant k \leqslant N-1} \left\| \frac{P^k W}{W} \right\|_{L^\infty},$$

which gives the expected result since $m_n \geqslant n/N - 1$. □

Remark 4.3. *The minorization condition obtained for discretizations of SDEs on unbounded spaces may not be 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 [98].*

4.4.6 Removing the systematic error

The estimate (4.62) 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

$$\int_{\mathcal{X}} \varphi \, d\pi_{\Delta t} - \int_{\mathcal{X}} \varphi \, d\pi = \Delta t^p \int_{\mathcal{X}} \varphi f_{p+1} \, d\pi + \mathrm{O}(\Delta t^{p+1}).$$

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 [161], 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 (4.63) for f_{p+1} leads to

$$\begin{aligned} \int_{\mathcal{X}} \varphi f_{p+1} \, d\pi &= \int_{\mathcal{X}} \Pi\varphi f_{p+1} \, d\pi = -\int_{\mathcal{X}} (\mathcal{L}^{-1}\Pi\varphi) g_{p+1} \, d\pi \\ &= \int_0^{+\infty} \int_{\mathcal{X}} \left(\mathrm{e}^{t\mathcal{L}}\Pi\varphi\right) g_{p+1} \, d\pi \; dt \\ &= \int_0^{+\infty} \mathbb{E}_\pi[\varphi(x_t) g_{p+1}(x_0)] \, dt, \end{aligned} \tag{4.75}$$

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_{p+1} is usually not too difficult to obtain once the expansion (4.59) has been worked out, see the discussion after (4.64). The integrated correlation on the right-hand side is then approximated as described in Section 7.4.1 (see Theorem 7.2). This strategy has been tested on a simple case in [108]: see Figure 7.1.

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 [150, 148]. 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 4.4.2.

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 [114, Section 2.2.3.2] for a precise discussion.

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 [147, 148]). 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 [87, 2] 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 [58].
(ii) Evolve only subparts of the system as advocated by [26].

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 [26, 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 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 Chapter 7), the invariant measure of the continuous dynamics is not known.

4.5 Variance reduction

As already mentioned in (4.58), 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 (4.55).

A first important distinction should be made between target-oriented variance reduction, which corresponds to reducing the asymptotic variance σ_φ^2 defined in (4.57) for a given observable φ; and a general purpose reduction, for which the aim is to decrease

$$\sup_{\varphi \in L^2(\pi)} \frac{\sigma_\varphi^2}{\|\varphi\|_{L^2(\pi)^2}} = \sup_{\|\varphi\|_{L^2(\pi)} \leqslant 1} 2 \int_{\mathcal{X}} \Pi\varphi(-\mathcal{L}^{-1}\Pi\varphi)\, d\pi. \tag{4.76}$$

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 (4.14)), 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 a review is provided in [28]. 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.

4.5.1 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 [158] can be used. The method is based on several works in statistics [62, 122, 96, 162].

(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 [114, Chapter 3] and references therein.

4.5.2 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 (4.6))

$$\int_{\mathcal{X}} \mathcal{L}\varphi \, d\pi = 0,$$

leads to the following equality: for any C^∞ and compactly supported test function Φ,

$$\mathbb{E}_\pi(\varphi) = \mathbb{E}_\pi(\varphi - \mathcal{L}\Phi) = \int_{\mathcal{X}} (\varphi - \mathcal{L}\Phi) \, d\pi. \tag{4.77}$$

The optimal choice corresponds to Φ solution of the Poisson equation

$$\mathcal{L}\Phi = \varphi - \mathbb{E}_\pi(\varphi). \tag{4.78}$$

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 (4.77)-(4.78), 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 [5, 77] but have also been proposed in the statistical physics literature [10], where they are known as the 'zero-variance principle'.

In practice, it is generally impossible to solve the Poisson equation (4.78) exactly. However, it is possible to approximate the ideal function Φ in (4.78) on a basis of K trial functions $\Phi_1, \ldots, \Phi_K$. This amounts to optimizing the coefficients $a = (a_1, \ldots, a_K) \in \mathbb{R}^K$ such that the variance of the estimator

$$\widehat{\varphi}_t(a_1, \ldots, a_K) = \frac{1}{t} \int_0^t \phi_{a_1,\ldots,a_K}(x_s) \, ds, \quad \phi_{a_1,\ldots,a_K} = \varphi - \sum_{k=1}^K a_k \mathcal{L}\Phi_k$$

is minimal.

4.5.3 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 $V + \widetilde{V}$. Some alternative strategies however exist, see for instance [138], where the kinetic energy function is modified for Langevin dynamics. The modified overdamped Langevin dynamics associated with the potential $V + \widetilde{V}$, namely

$$dq_t = -\nabla(V + \widetilde{V})(q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t, \tag{4.79}$$

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

$$\begin{aligned} d\widetilde{q}_t &= M^{-1}\widetilde{p}_t\,dt, \\ d\widetilde{p}_t &= -\nabla(V + \widetilde{V})(\widetilde{q}_t)\,dt - \gamma\,M^{-1}\widetilde{p}_t\,dt + \sqrt{\frac{2\gamma}{\beta}}\,dW_t \end{aligned}$$

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

$$\int_{\mathcal{D}} \varphi(q)\,\nu(dq) = \int_{\mathcal{E}} \varphi(q)\,\mu(dq\,dp) = \frac{\displaystyle\int_{\mathcal{D}} \varphi\,\mathrm{e}^{\beta\widetilde{V}}\,d\nu_{\widetilde{V}}}{\displaystyle\int_{\mathcal{D}} \mathrm{e}^{\beta\widetilde{V}}\,d\nu_{\widetilde{V}}} = \frac{\displaystyle\int_{\mathcal{E}} \varphi\,\mathrm{e}^{\beta\widetilde{V}}\,d\mu_{\widetilde{V}}}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{\beta\widetilde{V}}\,d\mu_{\widetilde{V}}}. \tag{4.80}$$

Therefore, the following estimator is considered:

$$\widehat{\varphi}_t^{\widetilde{V}} = \frac{\displaystyle\int_0^t \varphi(\widetilde{q}_s)\,\mathrm{e}^{\beta\widetilde{V}(\widetilde{q}_s)}\,ds}{\displaystyle\int_0^t \mathrm{e}^{\beta\widetilde{V}(\widetilde{q}_s)}\,ds}. \tag{4.81}$$

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

$$\frac{\Big(\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{\beta\widetilde{V}(q^n)}\Big)^2}{N_{\mathrm{iter}}\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \mathrm{e}^{2\beta\widetilde{V}(q^n)}} \in [0,1].$$

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 [95] 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[3] $\nu_{\widetilde{V}}/\nu = \mathrm{e}^{-\beta\widetilde{V}}\, Z_0/Z_{\widetilde{V}}$ shows that

$$\sqrt{N_{\mathrm{iter}}}(\widehat{\varphi}^{\mathrm{iid},\widetilde{V}}_{N_{\mathrm{iter}}} - \mathbb{E}_\nu(\varphi)) = \frac{\sqrt{N_{\mathrm{iter}}}\big[\frac{1}{N_{\mathrm{iter}}}\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} [\varphi(\widetilde{q}^n) - \mathbb{E}_\nu(\varphi)]\frac{\nu}{\nu_{\widetilde{V}}}(\widetilde{q}^n)\big]}{\frac{1}{N_{\mathrm{iter}}}\displaystyle\sum_{n=0}^{N_{\mathrm{iter}}} \frac{\nu}{\nu_{\widetilde{V}}}(\widetilde{q}^n)}.$$

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.

[3] 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.

Remark 4.4. *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 [116, 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 (4.76), 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 (4.76). For overdamped Langevin dynamics, the generator is self-adjoint: $\mathcal{L} = \mathcal{L}^*$ when these operators are considered on $L^2(\nu)$. General variance 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 4.3.1). Good choices of $\widetilde{V}$ to overcome such metastability issues are based on the free energy associated with a suitable reaction coordinate [114]. 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 [46, 144].

5

The Langevin dynamics

5.1 Description of the dynamics

The Langevin dynamics reads, for a general Hamiltonian,

$$\begin{cases} dq_t = \nabla_p H(q_t, p_t)\, dt, \\ dp_t = -\nabla_q H(q_t, p_t)\, dt - \gamma(q_t)\nabla_p H(q_t, p_t)\, dt + \sigma(q_t)\, dW_t, \end{cases} \tag{5.1}$$

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. For separable Hamiltonians, 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

$$\mu(dq\, dp) = Z_\mu^{-1} \exp(-\beta H(q,p))\, dq\, dp \tag{5.3}$$

at the correct temperature is sampled:

$$\sigma\sigma^T = \frac{2\gamma}{\beta}. \tag{5.4}$$

Notice that γ is therefore 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.

5.1.1 Generator

The generator of the Langevin dynamics reads

$$\mathcal{L} = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p + \gamma \left(-p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p \right) = \mathcal{L}_{\text{ham}} - \frac{\gamma}{\beta} \sum_{i=1}^{D} \partial_{p_i}^* \partial_{p_i}, \tag{5.5}$$

where adjoints are considered on $L^2(\mu)$. By this, we mean that, for any C^∞ and compactly supported functions φ, ϕ,

$$\int_{\mathcal{E}} (\mathcal{L}\varphi)\phi \, d\mu = \int_{\mathcal{E}} \varphi(\mathcal{L}^*\phi) \, d\mu. \tag{5.6}$$

To motivate the second equality in (5.5), we note that, for smooth test functions φ, ψ with compact support,

$$\begin{aligned} \int_{\mathcal{E}} (\partial_{p_i}\varphi) \, \psi \, d\mu &= -\frac{1}{Z_\mu} \int_{\mathcal{E}} \varphi \left[\partial_{p_i} \left(\psi \, \mathrm{e}^{-\beta p^T M^{-1} p/2} \right) \right] \mathrm{e}^{-\beta V} \, dq \, dp \\ &= -\int_{\mathcal{E}} \varphi \left[\partial_{p_i}\psi - \beta \left(M^{-1} p \right)_i \psi \right] d\mu, \end{aligned}$$

which shows that $\partial_{p_i}^* = -\partial_{p_i} + \beta \left(M^{-1} p \right)_i$.

Note that the second equality in (5.5) shows an important structural property of Langevin generators: they are the sum of an antisymmetric Hamiltonian part, and a symmetric dissipation operator which is however degenerate. In particular,

$$\mathcal{L}^* = -\mathcal{L}_{\text{ham}} - \frac{\gamma}{\beta} \sum_{i=1}^{D} \partial_{p_i}^* \partial_{p_i}. \tag{5.7}$$

In fact, we can determine the kernel of the generator considered as an operator on $L^2(\mu)$ (or the kernel of its ajoint) in view of its specific structure.

Proposition 5.1 (Proposition 15 in [170]). *Consider an operator*

$$\mathcal{A} = A_0 + \sum_{j=1}^{J} A_j^* A_j$$

on a Hilbert space $\mathcal{H}$, with $A_0^* = -A_0$. Then,

$$\operatorname{Ker} \mathcal{A} \subset \bigcap_{n \geqslant 0} \bigcap_{1 \leqslant j \leqslant J} \operatorname{Ker} C_{n,j},$$

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 $\varphi \in \operatorname{Ker} \mathcal{A}$,

$$\langle \varphi, \mathcal{A}\varphi \rangle = \sum_{j=1}^{J} \left\| A_j \varphi \right\|_{\mathcal{H}}^2,$$

so that $\varphi \in \operatorname{Ker} A_j$ for any $j = 1, \dots, J$. Next, $\mathcal{A}\varphi = A_0\varphi = 0$, which implies $\varphi \in \operatorname{Ker} A_0$.

We then proceed by induction and assume that $\varphi \in \operatorname{Ker} C_{0,j} \cap \cdots \cap \operatorname{Ker} C_{n,j}$ 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. □

For the Langevin dynamics, A_j is proportional to ∂_{p_j} while $A_0 = \mathcal{L}_{\mathrm{ham}}$. 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),

$$C_{1,j} = [A_j, A_0] = \frac{1}{m_j}\partial_{q_j}.$$

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,

$$\operatorname{Ker} \mathcal{L} = \mathbb{C}\mathbf{1}.$$

Similarly, $\operatorname{Ker} \mathcal{L}^* = \mathbb{C}\mathbf{1}$.

5.1.2 Invariance and uniqueness 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 $(2\pi/\beta)^{-D/2}\det(M)^{-1/2}\mathrm{e}^{-\beta p^T M^{-1} p/2}\, dp = Z(q)^{-1}\mathrm{e}^{-\beta H(q,p)}\, dp$. In fact, this forces the invariant measure to be of canonical form. However, we postpone the discussion on the uniqueness of the invariant measure and the ergodicity of the dynamics to Section 5.2.

The invariance of μ can be reformulated as follows: for any smooth test function φ,

$$\int_{\mathcal{E}} \mathcal{L}\varphi \, d\mu = 0,$$

or equivalently $\mathcal{L}^*\mathbf{1} = 0$. The result immediately follows from (5.7).

Remark 5.1. *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. Although time-reversibility properties depend on the Hamiltonian at hand, the stationarity of the canonical distribution still holds for* (5.1) *when considering a general Hamiltonian function (*e.g. *no longer separable).*

5.1.3 Relationship with overdamped Langevin dynamics

Overdamped Langevin dynamics 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 [114, Section 2.2.4] and Section 5.5 below.

5.2 Convergence of ergodic averages

Consider, for a given observable φ, the following trajectorial average:

$$\widehat{\varphi}_t = \frac{1}{t}\int_0^t \varphi(q_s, p_s)\, ds.$$

To prove the almost-sure convergence of $\widehat{\varphi}_t$ to $\mathbb{E}_\mu(\varphi)$, it is possible to use the results by Kliemann [90], which state that, for any initial condition $q_0 \in \mathcal{D}$,

$$\lim_{t\to+\infty} \widehat{A}_t = \int_{\mathcal{E}} A\, d\mu \qquad \text{a.s.}$$

under the following conditions: (i) there exists an invariant probability measure with a positive density with respect to the Lebesgue measure; (ii) the generator of the process is hypoelliptic (see Theorem 5.1 below). The first condition is immediately seen to be satisfied, so that the proof of convergence of ergodic averages reduces to checking whether the generator is hypoelliptic.

Remark 5.2. *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 $\mathcal{L} = \partial_x$ is hypoelliptic (although somewhat trivial of course). Ergodic 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.*

Alternatively, it is possible to provide a more constructive proof by showing that (i) the process (q_t, p_t) is irreducible with respect to the Lebesgue measure, and (ii) the canonical measure μ is an invariant probability measure. The proof of the irreductibility is not trivial since the noise acts only in the momentum variable. The proof is conducted in two steps: first, a controllability argument shows that $\mathbb{P}((q_t, p_t) \in E | (q_0, p_0) = (q, p)) > 0$ when $t > 0$ and E is open; second, this property is extended to general measurable ensembles using the continuity of the transition kernel (which again relies on hypoellipticity).

The proof of the controllability is performed as for the overdamped Langevin dynamics. Consider (q_*, p_*) in the interior of E, fix a time $t_0 > 0$ and introduce a polynomial interpolation $Q(t)$ on $[0, t_0]$ such that $Q(0) = q$, $\dot{Q}(0) = M^{-1}p$ as well as $Q(t_0) = q_*$, $\dot{Q}(t_0) = M^{-1}p_*$. It is then possible to construct a control $u(t)$ such that $u(0) = 0$ and

$$M\ddot{Q}(t) = -\nabla V(Q(t)) - \gamma \dot{Q}(t) + \sqrt{\frac{2\gamma}{\beta}}\, \dot{u}(t).$$

More precisely,

$$\begin{aligned} u(t) &= \sqrt{\frac{\beta}{2\gamma}} \int_0^t M\ddot{Q}(s) + \nabla V(Q(s)) + \gamma \dot{Q}(s)\, ds \\ &= \sqrt{\frac{\beta}{2\gamma}} \left(M\dot{Q}(t) - p + \gamma(Q(t) - q) + \int_0^t \nabla V(Q(s))\, ds \right). \end{aligned}$$

By continuity of the solutions of the SDE with respect to the realizations of the Brownian motion, we can conclude that $\mathbb{P}((q_{t_0}, p_{t_0}) \in E | (q_0, p_0) = (q, p)) > 0$ (see [121, Lemma 3.4] for details).

To obtain the regularity of the transition density $p(t, (q, p), (q', p'))$, we apply Hörmander's theorem [80, 81], which involves the commutator between two operators defined in (2.26).

Theorem 5.1. *Consider C^∞ vector fields on the d-dimensional space $\mathcal{Y}$*

$$A_j = \sum_{i=1}^{D} A_{j,i}(x)\partial_{y_i},$$

and introduce the operator

$$\mathcal{A} = A_0 + \sum_{j=1}^{J} A_j^\dagger A_j,$$

where $A_j^\dagger$ is the (formal) adjoint of X_j on $L^2(\mathcal{Y})$. Assume that the Lie algebra spanned by

$$\{X_j\}_{j=0,\dots,J}, \{[X_j, X_k]\}_{j,k=0,\dots,J}, \{[[X_j, X_k], X_l]\}_{j,k,l=0,\dots,J}, \dots$$

has maximal rank d at every point $y \in \mathcal{Y}$. Then $\mathcal{A}$ is hypoelliptic, namely there exists $\varepsilon > 0$ such that $\mathcal{A}f \in H^s_{\mathrm{loc}}$ implies $f \in H^{s+\varepsilon}_{\mathrm{loc}}$.

In particular, solutions f of the equation $\mathcal{A}f = 0$ are C^∞.

Corollary 5.1. *For the Langevin dynamics, with generator* (5.5)*, the operators $\mathcal{L}$, $\mathcal{L}^\dagger$, $\partial_t - \mathcal{L}$ and $\partial_t - \mathcal{L}^\dagger$ are hypoelliptic.* **MODIFY HERE TO ALLOW FOR CONSTANT TERMS IN HORMANDER, NEEDED TO TREAT $\mathcal{L}^\dagger$.** *Therefore, the densities $p(t,(q,p),(q',p'))$ of the transition kernel P_t, 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 the Lie algebra based on $-\partial_t + \mathcal{L}$ is of dimension $2D+1$ at each microstate (q,p) and for any time t, the proofs being similar for the other operators. We apply Theorem 5.1 with $J = D$, $\mathcal{Y} = \mathbb{R} \times \mathcal{E}$,

$$A_j = \sqrt{\frac{\gamma}{\beta}}\partial_{p_j},$$

and

$$A_0 = -\partial_t + p^T M^{-1}\nabla_q - \nabla V^T \nabla_q - \gamma p^T M^{-1}\nabla_p,$$

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

$$[A_j, A_0] = \frac{1}{m_j}\sqrt{\frac{\gamma}{\beta}}\left(\partial_{q_j} - \gamma\partial_{p_j}\right),$$

we immediately deduce that the Lie algebra spanned by $\{A_j\}_{j=1,\dots,p}$, $\{[A_j, A_k]\}_{j,k=1,\dots,J}$ has rank $2D$ and spans all derivatives in q and p. Adding A_0, the derivative in time is recovered. This allows to conclude. □

As for overdamped Langevin dynamics, it can be shown that the asymptotic variance of the random variable $\widehat{A}_t$ reads

$$\lim_{t\to+\infty} t\mathbb{E}\left(\left(\widehat{\Pi_0 A_t}\right)^2\right) = 2\int_0^{+\infty} \mathbb{E}(\Pi_0 A(q_t)\Pi_0 A(q_0))\,dt = -2\left\langle \Pi_0 A, \mathcal{L}^{-1}\Pi_0 A\right\rangle_{L^2(\mu)},$$

where

$$\Pi_0 A = A - \int_{\mathcal{E}} A\,d\mu.$$

The above computation can be made rigorous provided appropriate decay estimates on the semigroup $\mathrm{e}^{t\mathcal{L}}$ are available. This is the content of the next section.

Remark 5.3 (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. Consider for example the following situation (adapted from [86, Section 5]). We 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*

$$\mathcal{L} = A_0 - \frac{1}{2}A_1^\dagger A_1, \qquad A_0 = \cos(\pi x)\left[1 - \frac{\pi}{2}\sin(\pi x)\right]\frac{d}{dx}, \qquad A_1 = \sin(\pi x)\frac{d}{dx}.$$

Note that the Lie algebra spanned by A_1 *and*

$$[A_0, A_1] = \pi\left(1 - \frac{\pi^2}{2}\sin(\pi x)^2\right)\frac{d}{dx}$$

has full rank at every point, so that $\mathcal{L}$ *is 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 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

$$\partial_t \psi = \mathcal{L}^\dagger \psi, \tag{5.8}$$

with $\mathcal{L}^\dagger$ the adjoint on $L^2(\mathcal{E})$ of the generator $\mathcal{L}$ defined in (5.5). Let us first highlight the main difficulty encountered in the study of the generator $\mathcal{L}$ and its adjoint, namely the fact that dissipation appears only in the momentum variable. Some dissipation can be transfered 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.

In all this section, we assume that the masse matrix M is diagonal and define $m_- = \min_{i=1,\dots,D} m_i$ as well as $m_+ = \max_{i=1,\dots,D} m_i$.

5.3.1 Convergence in weighted L^∞ spaces

We consider the same setting as for overdamped Langevin dynamics (see Section 4.3.4). We prove in this section the following convergence result.

Theorem 5.2. *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*

$$q^T M^{-1} \nabla V(q) \geqslant A V(q) + B q^T M^{-1} q + C. \tag{5.9}$$

Then, there exist $C, \kappa > 0$ *such that*

$$\forall \varphi \in L^\infty_W(\mathcal{D}), \qquad \left\| \mathrm{e}^{t\mathcal{L}}\varphi - \int_{\mathcal{D}} \varphi \, d\nu \right\|_{L^\infty_W} \leqslant C\mathrm{e}^{-\kappa t}\|\varphi\|_{L^\infty_W}.$$

The condition (5.9) is satisfied for potentials growing at infinity like $|q|^{2m}$ (with $m \geqslant 1$).

In order to prove this result, we rely on the same strategy as for the proof of Theorem 4.7. The minorization condition is a direct consequence of the controllability and the smoothness of the

density of the transition kernel. We therefore only need to check the Lyapunov condition. Therefore, the proof boils down to proving that Lyapunov conditions hold. 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. 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 [121]). The precise result is the following.

Lemma 5.1. *For compact position spaces $\mathcal{D}$, consider the Lyapunov functions*

$$W_n(q,p) = 1 + |p|^n$$

for $n \geqslant 1$. When the position space is not compact, assume that $V \geqslant V_- > -\infty$ and (5.9) holds, and introduce

$$W_n(q,p) = \left(1 + H(q,p) - V_- + \frac{\gamma}{2} p^T M^{-1} q + \frac{\gamma^2}{4} q^T M^{-1} q\right)^n.$$

Then for, any $n \geqslant 1$, it holds $W_n(q,p) \geqslant 1$ and $W_n(q,p) \to +\infty$ 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

$$\mathcal{L} W_n \leqslant -n a W_n + b_n. \tag{5.10}$$

Note that the Lyapunov function for unbounded position spaces has a component $p^T M^{-1} q$ which allows us to retrieve some dissipation in the q-direction from the dissipation in the momenta. This feature is reminiscent of the cross-derivative used in the scalar product introduced for the proof of hypocoercivity in Section 5.3.3 (see the terms proportional to b in (5.14)).

Proof. Let us start with compact position spaces. Since

$$\Delta\left(|p|^n\right) = n \mathrm{div}\left(p|p|^{n-2}\right) = n(n-2+D)|p|^{n-2},$$

we find (with m_+ defined in (5.23))

$$\begin{aligned}
\mathcal{L} W_n(q,p) &= -n|p|^{n-2} \nabla V(q)^T p + \gamma n \left(-p^T M^{-1} p + \frac{D+n-2}{\beta}\right) |p|^{n-2} \\
&\leqslant -\frac{\gamma n}{m_+} |p|^n + n \|\nabla V\|_{L^\infty} |p|^{n-1} + \frac{\gamma n (n+D-2)}{\beta} |p|^{n-2},
\end{aligned}$$

Therefore,

$$\lim_{|p| \to +\infty} \frac{\mathcal{L} W_n(q,p)}{W_n(q,p)} \leqslant -\frac{\gamma n}{m_+}.$$

The inequality (5.10) then holds with $a = \gamma/(2m_+)$.

Consider now the case of position spaces which are not compact. We first consider the case $n = 1$. A simple computation shows that

$$\begin{aligned}
\mathcal{L} W_1(q,p) &= \gamma \left(-p^T M^{-2} p + \frac{\mathrm{Tr}(M)}{\beta}\right) + \frac{\gamma}{2}\left(p^T M^{-2} p - q^T M^{-1} \nabla V(q) - \gamma p^T M^{-2} q\right) + \frac{\gamma^2}{2} p^T M^{-2} q \\
&= -\frac{\gamma}{2}\left(p^T M^{-2} p + q^T M^{-1} \nabla V(q)\right) + \frac{\gamma \mathrm{Tr}(M)}{\beta}.
\end{aligned}$$

On the other hand, a Cauchy-Schwarz inequality shows that

$$\begin{aligned}
W_1(q,p) &\leqslant 1 + \frac{1}{2}\left(1 + \frac{\gamma}{2}\right) p^T M^{-1} p + V(q) + \frac{\gamma(1+\gamma)}{4} q^T M^{-1} q \\
&\leqslant 1 + \frac{1}{2m_-}\left(1 + \frac{\gamma}{2}\right) p^T M^{-2} p + \max\left(\frac{1}{A}, \frac{\gamma(1+\gamma)}{4B}\right)\left[q^T M^{-1} \nabla V(q) - C\right].
\end{aligned}$$

There exist therefore $a_1 > 0$ and $b_1 \in \mathbb{R}$ such that $\mathcal{L}W_1 \leqslant -a_1 W_1 + b_1$. For the general case $n \geqslant 2$, we note that

$$\mathcal{L} = \mathcal{T}_1 + \frac{\gamma}{\beta}\Delta_p,$$

where $\mathcal{T}_1$ is a first order differential operator, so that

$$\begin{aligned}
\mathcal{L}W_n &= n(\mathcal{T}_1 W_1)W_{n-1} + \frac{n\gamma}{\beta}\Big((\Delta_p W_1)W_1^{n-1} + (n-1)|\nabla_p W_1|^2 W_1^{n-2}\Big) \\
&= n(\mathcal{L}W_1)W_1^{n-1} + \frac{n(n-1)\gamma}{\beta}|\nabla_p W_1|^2 W_1^{n-2} \\
&\leqslant n\left(-a_1 W_1 + b_1\right) W_1^{n-1} + \frac{n(n-1)\gamma}{\beta}\left(p + \frac{\gamma}{2}q\right)^T M^{-2}\left(p + \frac{\gamma}{2}q\right) W_1^{n-2} \\
&\leqslant n\left[-a_1 W_n + b_1 W_1^{n-1} + \frac{2(n-1)\gamma}{\beta m_-}\left(p^T M^{-1} p + \frac{\gamma^2}{4} q^T M^{-1} q\right)^T W_1^{n-2}\right].
\end{aligned}$$

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 $\eta = 3/2$,

$$W_1(q,p) \geqslant 1 + \frac{1}{4} p^T M^{-1} p + \frac{\gamma^2}{12} q^T M^{-1} q. \tag{5.11}$$

Then,

$$\mathcal{L}W_n \leqslant n\left[-a_1 W_n + b_1 W_1^{n-1} + \frac{8(n-1)\gamma}{\beta m_-}\left(W_1 - 1 - V_-\right) W_1^{n-2}\right].$$

Since $W_1(q,p) \to +\infty$ as $|(q,p)| \to +\infty$ in view of (5.11), we deduce that

$$\lim_{|(q,p)|\to+\infty} \frac{\mathcal{L}W_n(q,p)}{W_n(q,p)} \leqslant -n a_1 < 0.$$

This shows that (5.10) holds and concludes the proof. □

5.3.2 Lack of coercivity in $L^2(\mu)$ with canonical scalar product

It turns out to be convenient to rewrite the generator as

$$\mathcal{L} = \mathcal{L}_{\rm ham} - \frac{\gamma}{\beta}\sum_{i=1}^{D} \partial_{p_i}^* \partial_{p_i},$$

where

$$\mathcal{L}_{\rm ham} = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p$$

is the generator of the Hamiltonian part of the dynamics and $\partial_{p_i}^* = \beta(M^{-1}p)_i - \partial_{p_i}$. This decomposition highlights an important structural property of Langevin generators: they are the sum of a Hamiltonian part, and a symmetric dissipation operator which is degenerate, however, since it acts only on the momenta. A simple computation shows that the Hamiltonian part is antisymmetric on $L^2(\mu)$, so that the adjoint of $\mathcal{L}$ on $L^2(\mu)$ reads

$$\mathcal{L}^* = -\mathcal{L}_{\rm ham} - \frac{\gamma}{\beta}\sum_{i=1}^{D} \partial_{p_i}^* \partial_{p_i}.$$

The Fokker–Planck equation (5.8) can be reformulated in terms of this operator, upon writing $\psi(t) = f(t)\,\mu$, as

$$\partial_t f = \mathcal{L}^* f, \tag{5.12}$$

where the initial condition $f(0) = f_0 = \psi_0/\mu$ satisfies

$$f_0 \geqslant 0, \quad \int_{\mathcal{E}} f_0 \mathrm{d}\mu = 1.$$

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 5.3.3 below.

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 5.3) 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 (5.12).

Note also that solutions to the Fokker–Planck equation (5.12) 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 Langevin generator $\mathcal{L}$ defined in (5.5) however 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,

$$-\langle \mathcal{L}\varphi, \varphi \rangle_{L^2(\mu)} = \frac{1}{\beta} \|\nabla_p \varphi\|^2_{L^2(\mu)}, \tag{5.13}$$

which should be compared to (4.21) 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 motivates the name for the technique, in view of the analogy with hypoellipticity, which allows, through some commutator identities, to state results for non-elliptic operators that are similar to regularity results obtained for elliptic operators.

5.3.3 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).

The idea of using mixed derivatives was already present in the computations performed in [160, Section 3], and was later generalized in [170]. A careful application of the general hypocoercivity framework to Langevin dynamics can be read in [74], where some emphasis is laid on the limiting regime $\gamma \to 0$; see also [108] for the regime $\gamma \to +\infty$.

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:

$$\langle\langle u, v\rangle\rangle = \langle u, v\rangle + a\langle \nabla_p u, \nabla_p v\rangle - b\langle \nabla_p u, \nabla_q v\rangle - b\langle \nabla_q u, \nabla_p v\rangle + c\langle \nabla_q u, \nabla_q v\rangle, \tag{5.14}$$

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

$$a, c > 0, \quad \text{and} \quad ac - b^2 > 0. \tag{5.15}$$

Lemma 5.2. *Assume that* (5.15) *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

$$\alpha = \frac{1}{2}\left(a + c - \sqrt{(a-c)^2 + 4b^2}\right) = \frac{2(ac - b^2)}{a + c + \sqrt{(a-c)^2 + 4b^2}} > 0. \tag{5.16}$$

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 5.3 (hypocoercivity). *Fix* $\gamma > 0$*, and assume either that the domain* $\mathcal{D}$ *is bounded, or that there exists* $\rho > 0$ *such that*

$$\forall q \in \mathcal{D}, \qquad |\nabla^2 V(q)| \leqslant \rho(1 + |\nabla V(q)|), \tag{5.17}$$

when $\mathcal{D}$ *is not bounded. Then there exist* $a, b, c \in \mathbb{R}$ *satisfying* (5.15) *and* $K > 0$ *such that, for any* $\varphi \in H^1(\mu) \cap L^2_0(\mu)$ *and any* $t \geqslant 0$*,*

$$\frac{d}{dt}\left[\langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle\right] \leqslant -K\left(\|\nabla_p \mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\mu)} + \|\nabla_q \mathrm{e}^{t\mathcal{L}}\varphi\|^2_{L^2(\mu)}\right). \tag{5.18}$$

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* $t \geqslant 0$*,*

$$\forall \varphi \in H^1(\mu) \cap L^2_0(\mu), \qquad \langle\langle \mathrm{e}^{t\mathcal{L}}\varphi,\, \mathrm{e}^{t\mathcal{L}}\varphi\rangle\rangle \leqslant \mathrm{e}^{-2\kappa t}\langle\langle \varphi, \varphi\rangle\rangle. \tag{5.19}$$

As a consequence, there exists $C \geqslant 1$ *such that*

$$\forall t \geqslant 0, \qquad \|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(H^1(\mu) \cap L^2_0(\mu))} \leqslant C\, \mathrm{e}^{-\kappa t}. \tag{5.20}$$

In the last inequality, $H^1(\mu)$ is endowed with the canonical scalar product. The operator bound (5.20) is obtained from (5.19) 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 5.2. 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 5.3, 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,

$$\|\mathcal{L}^{-1}\|_{\mathcal{B}(H^1(\mu)\cap L^2_0(\mu))} \leqslant \frac{C}{\kappa}, \tag{5.21}$$

where C and κ are the same constants as in (5.20).

Let us now present the proof of Theorem 5.3.

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 (5.15) 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 (5.18) 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 (5.13)).

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:

$$\begin{aligned}
[\partial_{p_i}, \mathcal{L}]\varphi &= \left[\partial_{p_i}, \frac{p_i}{m_i}\partial_{q_i}\right]\varphi - \frac{\gamma}{\beta}\left[\partial_{p_i}, \partial^*_{p_i}\partial_{p_i}\right]\varphi = \frac{1}{m_i}\left(\partial_{q_i} - \gamma\partial_{p_i}\right)\varphi, \\
[\partial_{q_i}, \mathcal{L}]\varphi &= -[\partial_{q_i}, \nabla V^T \nabla_p]\varphi = -\nabla\left(\partial_{q_i} V\right)^T \nabla_p \varphi.
\end{aligned} \tag{5.22}$$

First,

$$\langle \varphi, \mathcal{L}\varphi\rangle = -\frac{\gamma}{\beta}\|\nabla_p \varphi\|^2_{L^2(\mu)}.$$

Now, using (5.22),

$$\begin{aligned}
\langle \partial_{p_i}\varphi, \partial_{p_i}\mathcal{L}\varphi\rangle &= \langle \partial_{p_i}\varphi, \mathcal{L}\partial_{p_i}\varphi\rangle + \frac{1}{m_i}\langle \partial_{p_i}\varphi, \left(\partial_{q_i} - \gamma\partial_{p_i}\right)\varphi\rangle \\
&= -\frac{\gamma}{\beta}\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\|\partial_{p_i}\varphi\|^2_{L^2(\mu)} + \frac{1}{m_i}\langle \partial_{p_i}\varphi, \partial_{q_i}\varphi\rangle.
\end{aligned}$$

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,

$$\begin{aligned}\langle \partial_{p_i}\varphi, \partial_{q_i}\mathcal{L}\varphi\rangle &= \langle \partial_{p_i}\varphi, \mathcal{L}\partial_{q_i}\varphi\rangle - \left\langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi\right\rangle \\ &= \langle \partial_{p_i}\varphi, \mathcal{L}_{\rm ham}\partial_{q_i}\varphi\rangle - \frac{\gamma}{\beta}\left\langle \nabla_p\left(\partial_{p_i}\varphi\right), \nabla_p\left(\partial_{q_i}\varphi\right)\right\rangle - \left\langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi\right\rangle.\end{aligned}$$

Finally, the last term provides some dissipation in q since

$$\begin{aligned}\langle \partial_{q_i}\varphi, \partial_{p_i}\mathcal{L}\varphi\rangle &= \langle \partial_{q_i}\varphi, \mathcal{L}\partial_{p_i}\varphi\rangle + \frac{1}{m_i}\left\langle \partial_{q_i}\varphi, \left(\partial_{q_i} - \gamma\partial_{p_i}\right)\varphi\right\rangle \\ &= \langle \partial_{q_i}\varphi, \mathcal{L}_{\rm ham}\partial_{p_i}\varphi\rangle - \frac{\gamma}{\beta}\left\langle \nabla_p(\partial_{q_i}\varphi), \nabla_p(\partial_{p_i}\varphi)\right\rangle + \frac{1}{m_i}\|\partial_{q_i}\varphi\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\left\langle \partial_{q_i}\varphi, \partial_{p_i}\varphi\right\rangle.\end{aligned}$$

Note that

$$\langle \partial_{p_i}\varphi, \mathcal{L}_{\rm ham}\partial_{q_i}\varphi\rangle = \langle \partial_{p_i}\varphi, \mathcal{L}_{\rm ham}\partial_{q_i}\varphi\rangle + \langle \mathcal{L}_{\rm ham}\partial_{q_i}\varphi, \partial_{p_i}\varphi\rangle = \langle \partial_{p_i}\varphi, \mathcal{L}_{\rm ham}\partial_{q_i}\varphi\rangle - \langle \partial_{q_i}\varphi, \mathcal{L}_{\rm ham}\partial_{p_i}\varphi\rangle.$$

which implies that

$$\langle \partial_{p_i}\varphi, \mathcal{L}_{\rm ham}\partial_{q_i}\varphi\rangle + \langle \partial_{q_i}\varphi, \mathcal{L}_{\rm ham}\partial_{p_i}\varphi\rangle = 0,$$

Gathering all terms, we obtain Some straightforward computations then show that

$$\begin{aligned}\langle\langle \varphi, \mathcal{L}\varphi\rangle\rangle &= -\frac{\gamma}{\beta}\|\nabla_p\varphi\|^2_{L^2(\mu)} \\ &+ a\sum_{i=1}^D\left(-\frac{\gamma}{\beta}\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\|\partial_{p_i}\varphi\|^2_{L^2(\mu)} + \frac{1}{m_i}\langle \partial_{p_i}\varphi, \partial_{q_i}\varphi\rangle\right) \\ &+ c\sum_{i=1}^D\left(-\frac{\gamma}{\beta}\|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)} - \langle \partial_{q_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi\rangle\right) \\ &- b\sum_{i=1}^D\left(-\frac{\gamma}{\beta}\langle \nabla_p(\partial_{p_i}\varphi), \nabla_p(\partial_{q_i}\varphi)\rangle - \langle \partial_{p_i}\varphi, \nabla(\partial_{q_i}V)^T\nabla_p\varphi\rangle\right) \\ &- b\sum_{i=1}^D\left(-\frac{\gamma}{\beta}\langle \nabla_p(\partial_{q_i}\varphi), \nabla_p(\partial_{p_i}\varphi)\rangle + \frac{1}{m_i}\|\partial_{q_i}\varphi\|^2_{L^2(\mu)} - \frac{\gamma}{m_i}\langle \partial_{q_i}\varphi, \partial_{p_i}\varphi\rangle\right).\end{aligned}$$

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.[1] 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

$$\begin{aligned}\langle\langle \varphi, \mathcal{L}\varphi\rangle\rangle \leqslant &-\gamma\left(\frac{1}{\beta} + \frac{a}{m_+}\right)\|\nabla_p\varphi\|^2_{L^2(\mu)} - \frac{b}{m_+}\|\nabla_q\varphi\|^2_{L^2(\mu)} \\ &+ \frac{a+b\gamma}{m_-}\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)} \\ &- \frac{a\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} - \frac{c\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)} \\ &+ \frac{2b\gamma}{\beta}\sum_{i=1}^D\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)} \\ &+ \langle (b\nabla_p - c\nabla_q)\varphi, (\nabla^2 V)\nabla_p\varphi\rangle,\end{aligned}$$

where

$$m_+ = \max(m_1, \ldots, m_d), \qquad m_- = \min(m_1, \ldots, m_d). \tag{5.23}$$

Condition (5.15) shows that (by a computation similar to the one performed in the proof of Lemma 5.2)

[1] When working with $\mathcal{L}^*$ instead of $\mathcal{L}$, the parameter b should be negative.

$$a\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} + c\|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)} - 2b\|\nabla_p(\partial_{p_i}\varphi)\|_{L^2(\mu)}\|\nabla_p(\partial_{q_i}\varphi)\|_{L^2(\mu)}$$
$$\geqslant \alpha(\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} + \|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)}), \tag{5.24}$$

with $\alpha > 0$ defined in (5.16). Therefore, the upper bound on $\langle\langle\varphi, \mathcal{L}\varphi\rangle\rangle$ simplifies as

$$\begin{aligned}\langle\langle\varphi, \mathcal{L}\varphi\rangle\rangle \leqslant &-\gamma\left(\frac{1}{\beta} + \frac{a}{m_+}\right)\|\nabla_p\varphi\|^2_{L^2(\mu)} - \frac{b}{m_+}\|\nabla_q\varphi\|^2_{L^2(\mu)} \\ &+ \frac{a+b\gamma}{m_-}\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)} \\ &- \frac{\alpha\gamma}{\beta}\sum_{i=1}^{d}(\|\nabla_p(\partial_{p_i}\varphi)\|^2_{L^2(\mu)} + \|\nabla_p(\partial_{q_i}\varphi)\|^2_{L^2(\mu)}) \\ &+ \langle(b\nabla_p - c\nabla_q)\varphi, (\nabla^2 V)\nabla_p\varphi\rangle.\end{aligned} \tag{5.25}$$

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

$$\begin{aligned}|\langle(b\nabla_p - c\nabla_q)\varphi, (\nabla^2 V)\nabla_p\varphi\rangle| &\leqslant C_V\|\nabla_p\varphi\|_{L^2(\mu)}\|(b\nabla_p - c\nabla_q)\varphi\|_{L^2(\mu)} \\ &\leqslant bC_V\|\nabla_p\varphi\|^2_{L^2(\mu)} + cC_V\|\nabla_p\varphi\|_{L^2(\mu)}\|\nabla_q\varphi\|_{L^2(\mu)}.\end{aligned}$$

(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 (5.17) holds (see [170, 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 $-\frac{\alpha\gamma}{\beta}\|\partial_{p_j}\partial_{q_i}\varphi\|^2_{L^2(\mu)}$ in (5.25).

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 (5.15), the values of a, b, c should be such that

$$4AB > C^2, \tag{5.26}$$

in order for $\mathcal{M}$ to be positive definite. If this is the case, (5.18) follows. The condition (5.26) is satisfied for instance when

$$a = c = \varepsilon, \qquad b = \varepsilon^{1+\delta}, \qquad \delta \in (0,1), \tag{5.27}$$

for $\varepsilon > 0$ sufficiently small. Note also that this choice is compatible with (5.15) as soon as $\varepsilon < 1$.

Let us now discuss how to obtain (5.19) from (5.18), 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, $X^T S X \geqslant \langle\langle \varphi, \varphi \rangle\rangle$ 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 $X^T \mathcal{M} X \geqslant \kappa X^T S X$. 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 (5.15). This concludes the proof of (5.19). □

Remark 5.4 (Degenerate scalar product). *The standard hypocoercive approach relies on estimates in $H^1(\mu)$, obtained under the non-degeneracy condition* (5.15)*. However, in the situation when $\nabla^2 V$ 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 [85] for the complete argument.*

One interest of the hypocoercive approach is that the constants κ and C in (5.20) 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 5.3.3 for the limits where $\gamma \to 0$ and $\gamma \to +\infty$, and in Remark 5.5 for the small temperature limit.

Remark 5.5 (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 $V = V_{\mathrm{convex}} + \widetilde{V}$. In this decomposition, the potential is separated into a strongly convex part V_{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 [170, Theorem A.8] or [74, Section 6.1], and are based on the idea of F. Hérau [78]. We follow the latter approach, which is more straightforward, although the so-obtained results are not as strong as the results presented in [170].

Theorem 5.4 (hypoelliptic regularization). *Assume that $\nabla^2 V \in L^\infty(\mathcal{D})$ or that* (5.17) *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 5.3, 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 5.4, as presented in [74].

Proof. As at the end of the proof of Theorem 5.3, 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

$$N_\varphi(t) = \frac{1}{2}\left[\|\varphi(t)\|^2_{L^2(\mu)} + c_1 t\|\nabla_p\varphi(t)\|^2_{L^2(\mu)} - c_2 t^2\langle\nabla_q\varphi(t),\nabla_p\varphi(t)\rangle_{L^2(\mu)} + c_3 t^3\|\nabla_q\varphi(t)\|^2_{L^2(\mu)}\right], \tag{5.28}$$

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 (5.14) 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 5.6 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 5.3, we obtain

$$\begin{aligned}\frac{dN_\varphi(t)}{dt} &= -\left(\frac{\gamma}{\beta} - \frac{c_1}{2}\right)\|\nabla_p\varphi(t)\|^2_{L^2(\mu)}\\ &\quad - c_1 t\sum_{i=1}^D\left[\frac{\gamma}{\beta}\|\nabla_p(\partial_{p_i}\varphi(t))\|^2_{L^2(\mu)} + \frac{\gamma}{m_i}\|\partial_{p_i}\varphi(t)\|^2_{L^2(\mu)}\right]\\ &\quad + \sum_{i=1}^D\left[t\left(\frac{c_1}{m_i} - c_2\right) + \frac{\gamma c_2 t^2}{2m_i}\right]\langle\partial_{p_i}\varphi(t),\partial_{q_i}\varphi(t)\rangle\\ &\quad + \frac{c_2 t^2}{2}\sum_{i=1}^D\frac{2\gamma}{\beta}\langle\nabla_p(\partial_{p_i}\varphi(t)),\nabla_p(\partial_{q_i}\varphi(t))\rangle + \langle\partial_{p_i}\varphi(t),\nabla(\partial_{q_i}V)^T\nabla_p\varphi(t)\rangle\\ &\quad + t^2\sum_{i=1}^D\left(\frac{3c_3}{2} - \frac{c_2}{m_i}\right)\|\partial_{q_i}\varphi(t)\|^2_{L^2(\mu)}\\ &\quad - c_3 t^3\sum_{i=1}^D\left[\frac{\gamma}{\beta}\|\nabla_p(\partial_{q_i}\varphi(t))\|^2_{L^2(\mu)} + \langle\partial_{q_i}\varphi(t),\nabla(\partial_{q_i}V)^T\nabla_p\varphi(t)\rangle\right].\end{aligned} \tag{5.29}$$

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

$$c_1, c_3 \geqslant 0, \qquad 4c_1 c_3 > c_2^2. \tag{5.30}$$

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 (5.30) and $c_2/m_+ - 3c_3/2 > 0$. For instance, $c_1 = \varepsilon$, $c_2 = \overline{c}_2\varepsilon$ and $c_3 = \overline{c}_3\varepsilon$, with $\overline{c}_2, \overline{c}_3$ sufficiently small so that $\overline{c}_2 > 3m_+\overline{c_3}/2$ and $4\overline{c}_3 \geqslant \overline{c}_2^2$. 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 5.6. *Let us now motivate more precisely the definition* (5.28)*. As discussed after this equation, the choice* (5.28) *corresponds to the scalar product* (5.14) *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* (5.29)*, 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 5.3 are obtained for a given value of γ. 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 $\gamma \to +\infty$.

Hypocoercivity allows to quantify the degradation of the convergence rate. Let κ_γ denote the exponential decay rate given by Theorem 5.3 for a given value of γ. By tracking the dependency of all estimates on γ in the proofs of Theorems 5.3 and 5.4, it is possible to show the following result.

Proposition 5.2. *Under the same assumptions as for Theorem 5.3, 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,

$$\left\|\mathcal{L}^{-1}\right\|_{\mathcal{B}\left(L^2_0(\mu)\right)} \leqslant \frac{\overline{C}}{\overline{\kappa}}\max\left(\gamma, \frac{1}{\gamma}\right). \tag{5.31}$$

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 [74] 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 5.2 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 [74, 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 $\gamma\mathcal{L}_{\rm ovd}$ (see [108, Theorem 2.5] and Theorem 5.10 in Section 5.5.1 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 5.2). 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 (5.14) of order 1 since the condition (5.26) 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 $0 < \gamma \leqslant 1$,

$$\left\langle\left\langle \mathrm{e}^{t\mathcal{L}}\varphi, \mathrm{e}^{t\mathcal{L}}\varphi\right\rangle\right\rangle_\gamma \leqslant \mathrm{e}^{-2\gamma\overline{\kappa}t}\left\langle\langle\varphi,\varphi\rangle\right\rangle_\gamma, \tag{5.32}$$

  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 (5.28). 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 (5.26) 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 (5.28). 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 5.2. □

Remark 5.7. *A result similar to Proposition 5.2 cannot be stated in a $H^1(\mu)$ setting since the constant C appearing in* (5.20) *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 5.4 (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 [38].

We rely to this end on (5.32) 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 [75, 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 $\|P_t\|_{\mathcal{B}(L^2_0(\mu))} \leqslant 1$.

Hypocoercivity in the entropic sense

Here we show how the computations performed in $H^1(\mu)$ can be modified to prove the decay of some logarithmic entropy, similar to the one used for LSIs. The interest of this approach is that initial conditions in a larger functional spaces can be considered. The general strategy is presented in [170, Section 6]. These computations can be simplified for Langevin-type dynamics; see [131, Appendix D].

We state here convergence results for the function $f(t)$, which is the Radon–Nikodym derivative of the law $\psi(t)$ of the process at time t with respect to the density of the invariant measure μ. Starting from $f_0 \geqslant 0$ with $\int_{\mathcal{E}} f_0 \mathrm{d}\mu = 1$, the function $f(t)$ therefore evolves according to the Fokker–Planck equation (5.12), *i.e.*, $f(t) = \mathrm{e}^{t\mathcal{L}^*}f_0$. It is expected that $f(t)$ converges to the constant function $\mathbf{1}$.

To quantify the convergence rate, we introduce the entropy functional

$$\mathscr{E}(f) = \int_{\mathcal{E}} f \, \ln f \, d\mu + \int_{\mathcal{E}} \frac{\nabla f^T S \nabla f}{f} \, d\mu,$$

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 [170, Remark 29] for a context where a dependence on the position q may be useful). Finally, note that $\mathscr{E}(\mathbf{1}) = 0$, so that the entropy is expected to converge to 0 as $t \to +\infty$.

Proposition 5.3. *Assume that $\nabla^2 V$ is in $L^\infty(\mathcal{D})$. Then there exist a nonnegative symmetric matrix $S \in \mathbb{R}^{2d \times 2d}$ and $\alpha > 0$ such that*

$$\forall t \geqslant 0, \qquad \frac{d}{dt}[\mathscr{E}(f(t))] \leqslant -\alpha \int_{\mathcal{E}} \frac{|\nabla f(t)|^2}{f(t)} \, d\mu. \tag{5.33}$$

If in addition $\nu(dq)$ satisfies a logarithmic Sobolev inequality, then there exists $\kappa > 0$ such that

$$\forall t \geqslant 0, \qquad \frac{d}{dt}[\mathscr{E}(f(t))] \leqslant -\kappa \, \mathscr{E}(f(t)). \tag{5.34}$$

In particular, $0 \leqslant \mathscr{E}(f(t)) \leqslant \mathscr{E}(f_0) \, \mathrm{e}^{-\kappa t}$ for any $t \geqslant 0$.

Notice that we do not require the matrix S to be definite for the result to hold.

Proof. One of the main ideas in the proof is to rewrite the time derivative of the second term in the expression of $\mathscr{E}$ as a sum of terms similar to the ones appearing in the proof of Theorem 5.3. To this end, consider $g(t) = \sqrt{f(t)}$, so that

$$\int_{\mathcal{E}} \frac{\nabla f(t)^T S \nabla f(t)}{f(t)} d\mu = 4 \int_{\mathcal{E}} \nabla g(t)^T S \nabla g(t) \, d\mu. \tag{5.35}$$

In order to determine the time evolution of this quantity, we first write the time evolution for $g(t)$. Simple computations show that

$$\partial_t g(t) = \frac{\partial_t f(t)}{2\sqrt{f(t)}} = \frac{\mathcal{L}^* f(t)}{2g(t)}, \quad \Delta_p g(t) = \frac{\Delta_p f(t)}{2\sqrt{f(t)}} - \frac{|\nabla_p f(t)|^2}{4f(t)^{3/2}} = \frac{\Delta_p f(t)}{2g(t)} - \frac{|\nabla_p g(t)|^2}{g(t)},$$

so that

$$\partial_t g(t) = \mathcal{L}^* g(t) + \frac{\gamma}{\beta} \frac{|\nabla_p g(t)|^2}{g(t)}.$$

We next compute the time derivatives of the various terms in $\mathscr{E}(f(t))$, relying on the reformulation (5.35). This leads to expressions very similar to those encountered in the proof of Theorem 5.3. First,

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} f(t) \, \ln f(t) \, d\mu\right) &= \int_{\mathcal{E}} (1 + \ln f(t)) \mathcal{L}^* f(t) \, d\mu \\
&= \int_{\mathcal{E}} \mathcal{L}_{\mathrm{ham}} (1 + \ln f(t)) f(t) \, d\mu - \frac{\gamma}{\beta} \int_{\mathcal{E}} \nabla_p f(t) \cdot \nabla_p (\ln f(t)) \, d\mu \\
&= \int_{\mathcal{E}} \mathcal{L}_{\mathrm{ham}} f(t) \, d\mu - \frac{\gamma}{\beta} \int_{\mathcal{E}} \frac{|\nabla_p f(t)|^2}{f(t)} \, d\mu = -\frac{4\gamma}{\beta} \int_{\mathcal{E}} |\nabla_p g(t)|^2 \, d\mu,
\end{aligned}$$

in view of the invariance of μ by $\mathcal{L}_{\mathrm{ham}}$. Next,

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} |\partial_{p_i} g(t)|^2 \, d\mu\right) &= 2\int_{\mathcal{E}} \partial_{p_i} g(t)\, \partial_{p_i}(\mathcal{L}^* g(t))\, d\mu + \frac{2\gamma}{\beta}\int_{\mathcal{E}} \partial_{p_i} g(t)\, \partial_{p_i}\left(\frac{|\nabla_p g(t)|^2}{g(t)}\right) d\mu \\
&= 2\int_{\mathcal{E}} \partial_{p_i} g(t)\, \mathcal{L}^*(\partial_{p_i} g(t)) d\mu - \frac{2}{m_i}\int_{\mathcal{E}} \partial_{p_i} g(t)\, (\partial_{q_i} + \gamma\partial_{p_i}) g(t)\, d\mu \\
&\quad + \frac{2\gamma}{\beta}\int_{\mathcal{E}} \partial_{p_i} g(t)\left(\frac{2\nabla_p(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)} - \frac{|\nabla_p g(t)|^2}{g(t)^2}\partial_{p_i} g(t)\right) d\mu \\
&= -\frac{2}{m_i}\int_{\mathcal{E}} \partial_{p_i} g(t)\, (\partial_{q_i} + \gamma\partial_{p_i}) g(t)\, d\mu \\
&\quad - \frac{2\gamma}{\beta}\int_{\mathcal{E}} |\nabla_p \partial_{p_i} g(t)|^2 - 2\nabla_p(\partial_{p_i} g(t)) \cdot \frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)} + \frac{|\nabla_p g(t)|^2 (\partial_{p_i} g(t))^2}{g(t)^2}\, d\mu,
\end{aligned}$$

where we have used

$$\begin{aligned}
&\int_{\mathcal{E}} \partial_{p_i} g(t)\, \mathcal{L}^*(\partial_{p_i} g(t))\, d\mu \\
&\qquad = -\int_{\mathcal{E}} \partial_{p_i} g(t)\, \mathcal{L}_{\mathrm{ham}}(\partial_{p_i} g(t)) d\mu - \frac{2\gamma}{\beta}\sum_{j=1}^{D}\int_{\mathcal{E}} \partial_{p_i} g(t)\, \partial^*_{p_j}\partial_{p_j}(\partial_{p_i} g(t))\, d\mu,
\end{aligned}$$

and the first integral on the right-hand side vanishes since $\mathcal{L}_{\mathrm{ham}}$ is antisymmetric. Therefore,

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{\mathcal{E}} |\partial_{p_i} g(t)|^2 \, d\mu\right) \\
&\quad = -\frac{2}{m_i}\int_{\mathcal{E}} \partial_{p_i} g(t)\, (\partial_{q_i} + \gamma\partial_{p_i}) g(t)\, d\mu - \frac{2\gamma}{\beta}\int_{\mathcal{E}} \left|\nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)}\right|^2 d\mu.
\end{aligned}$$

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

$$\begin{aligned}
\frac{d}{dt}\left(\int_{\mathcal{E}} \partial_{p_i} g(t)\, \partial_{q_i} g(t)\, d\mu\right) &= \int_{\mathcal{E}} \partial_{p_i} g(t)\, (\nabla\partial_{q_i} V)\cdot\nabla_p g(t)\, d\mu \\
&\quad - \frac{1}{m_i}\int_{\mathcal{E}} \partial_{q_i} g(t)\, (\partial_{q_i} + \gamma\partial_{p_i}) g(t)\, d\mu \\
&\quad - \frac{2\gamma}{\beta}\int_{\mathcal{E}} \left(\nabla_p \partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t))\nabla_p g(t)}{g(t)}\right)\cdot\left(\nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t))\nabla_p g(t)}{g(t)}\right) d\mu.
\end{aligned}$$

Considering

$$S = \begin{pmatrix} a\,\mathrm{Id}_D & b\,\mathrm{Id}_D \\ b\,\mathrm{Id}_D & c\,\mathrm{Id}_D \end{pmatrix}$$

it follows that

$$
\begin{aligned}
\frac{d}{dt}(\mathscr{E}(f(t))) &= -\frac{4\gamma}{\beta}\int_{\mathcal{E}} |\nabla_p g(t)|^2 \, d\mu \\
&+ 8a \sum_{i=1}^{D} \int_{\mathcal{E}} \partial_{q_i} g(t) \, (\nabla \partial_{q_i} V) \cdot \nabla_p g(t) \, d\mu \\
&- 8b \sum_{i=1}^{D} \left(- \int_{\mathcal{E}} \partial_{p_i} g(t) \, (\nabla \partial_{q_i} V) \cdot \nabla_p g(t) d\mu + \frac{1}{m_i} \int_{\mathcal{E}} \partial_{q_i} g(t) \, (\partial_{q_i} + \gamma \partial_{p_i}) g(t) \, d\mu \right) \\
&- \frac{8c}{m_i} \sum_{i=1}^{D} \int_{\mathcal{E}} \partial_{p_i} g(t) \, (\partial_{q_i} + \gamma \partial_{p_i}) g(t) \, d\mu \\
&- \frac{8\gamma a}{\beta} \sum_{i=1}^{D} \int_{\mathcal{E}} \left| \nabla_p \partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t)) \nabla_p g(t)}{g(t)} \right|^2 \, d\mu \\
&- \frac{16\gamma b}{\beta} \sum_{i=1}^{D} \int_{\mathcal{E}} \left(\nabla_p \partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t)) \nabla_p g(t)}{g(t)} \right) \cdot \left(\nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t)) \nabla_p g(t)}{g(t)} \right) \, d\mu \\
&- \frac{8\gamma c}{\beta} \sum_{i=1}^{D} \int_{\mathcal{E}} \left| \nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t)) \nabla_p g(t)}{g(t)} \right|^2 \, d\mu.
\end{aligned}
$$

Note that the sum of the last three terms in the above equality can be bounded from above by

$$
-\frac{8\gamma}{\beta} \sum_{i=1}^{d} (a X_i^2 - 2b X_i Y_i + c Y_i^2), \tag{5.36}
$$

with

$$
X_i = \left\| \nabla_p \partial_{q_i} g(t) - \frac{(\partial_{q_i} g(t)) \nabla_p g(t)}{g(t)} \right\|_{L^2(\mu)}, \quad Y_i = \left\| \nabla_p \partial_{p_i} g(t) - \frac{(\partial_{p_i} g(t)) \nabla_p g(t)}{g(t)} \right\|_{L^2(\mu)}.
$$

We assume in the following

$$
ac - b^2 \geqslant 0,
$$

which ensures that the matrix S is nonnegative and that (5.36) is non-positive. Then, recalling the definition (5.23) for m_+ and m_-,

$$
\begin{aligned}
\frac{d}{dt}(\mathscr{E}(f(t))) \leqslant & -4\gamma \left(\frac{1}{\beta} + \frac{2c}{m_+} \right) \|\nabla_p g(t)\|^2_{L^2(\mu)} - \frac{8b}{m_+} \|\nabla_q g(t)\|^2_{L^2(\mu)} \\
& + 8 \sum_{i=1}^{D} \int_{\mathcal{E}} (a \partial_{q_i} g(t) + b \partial_{p_i} g(t)) \, (\nabla \partial_{q_i} V) \cdot \nabla_p g(t) \, d\mu \\
& - 8(\gamma b + c) \sum_{i=1}^{D} \frac{1}{m_i} \int_{\mathcal{E}} \partial_{q_i} g(t) \, \partial_{p_i} g(t) \, d\mu.
\end{aligned}
$$

Since $\nabla^2 V$ is assumed to be bounded and

$$
\|\nabla_p g(t)\|^2_{L^2(\mu)} + \|\nabla_q g(t)\|^2_{L^2(\mu)} = \frac{1}{4} \int_{\mathcal{E}} \frac{|\nabla f(t)|^2}{f(t)} \, d\mu,
$$

the inequality (5.33) follows by choosing appropriate values for the coefficients a, b, c in S. For instance, $a = b = c = \varepsilon > 0$ with $\varepsilon > 0$ sufficiently small.

To deduce (5.34), we note that, by tensorization of LSI, there exists $R > 0$ such that, for any C^∞ function $h \geqslant 0$ satisfying

$$
\int_{\mathcal{E}} h \, d\mu = 1,
$$

the following inequality holds:

$$\int_{\mathcal{E}} h \ln h \, d\mu \leqslant \frac{1}{2R} \int_{\mathcal{E}} \frac{|\nabla_p h|^2 + |\nabla_q h|^2}{h} \, d\mu.$$

In addition,

$$\int_{\mathcal{E}} \frac{(\nabla h)^T S \nabla h}{h} \, d\mu \leqslant \lambda_S \int_{\mathcal{E}} \frac{|\nabla h|^2}{h} \, d\mu,$$

where λ_S is the largest eigenvalue of S. Combining these two estimates, we obtain the existence of $\kappa > 0$ such that

$$\frac{d}{dt}(\mathscr{E}(f(t))) \leqslant -\kappa \left(\int_{\mathcal{E}} f(t) \ln f(t) d\mu + \int_{\mathcal{E}} \frac{(\nabla f(t))^T S \nabla f(t)}{f(t)} \, d\mu \right) = -\kappa \mathscr{E}(f(t)),$$

which is indeed (5.34). The exponential decay follows by a Gronwall inequality. □

Here again, the final constant κ can be made quite explicit in terms of the various parameters in the model (LSI constant R, bounds on $\nabla^2 V$, etc).

5.3.4 Hypocoercivity in a $L^2(\mu)$ setting

We present in this section a way to directly prove the exponential decay of the semigroup $\mathrm{e}^{t\mathcal{L}}$ in $L^2(\mu)$, instead of first proving a decay in $H^1(\mu)$ and then relying on hypoelliptic regularization (the proof for $\mathrm{e}^{t\mathcal{L}^*}$ being identical up to a few sign changes). This approach also turns out to be more robust to perturbations, since it can be used for nonequilibrium systems in a perturbative framework [27, 85] or for spectral discretization of the Langevin dynamics [151]. It also allows to quantify more easily the convergence rate in terms of the parameters of the dynamics [42].

We need the following assumptions on the potential energy function.

Assumption 5.5 *The potential V is smooth, and the marginal measure ν satisfies a Poincaré inequality with constant $C_\nu > 0$: for any function of the positions $\varphi \in H^1(\nu)$,*

$$\left\| \varphi - \int_{\mathcal{D}} \varphi \, d\nu \right\|^2_{L^2(\nu)} \leqslant \frac{1}{C_\nu} \|\nabla_q \varphi\|^2_{L^2(\nu)}. \tag{5.37}$$

Moreover, there exist $c_1 > 0$, $c_2 \in [0, 1)$ and $c_3 > 0$ such that V satisfies

$$\Delta V \leqslant c_1 + \frac{\beta c_2}{2} |\nabla V|^2, \quad |\nabla^2 V| \leqslant c_3 \left(1 + |\nabla V|\right). \tag{5.38}$$

Note that the second condition does not necessarily imply the Poincaré inequality (it does not imply (4.24) because of the sign of c_1; a typical example is a potential behaving as $\sqrt{|q|}$ at infinity, which satisfies (5.38) but not (4.24)). The precise convergence result is then the following [43, 44].

Theorem 5.6 (Hypocoercivity in $L^2(\mu)$). *Suppose that Assumption 5.5 holds. Then there exist $C > 0$ 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 initial datum $\varphi \in L^2_0(\mu)$,*

$$\forall t \geqslant 0, \qquad \left\| \mathrm{e}^{t\mathcal{L}} \varphi \right\| \leqslant C \mathrm{e}^{-\lambda_\gamma t} \|\varphi\|. \tag{5.39}$$

Moreover, the convergence rate is of order $\min(\gamma, \gamma^{-1})$: there exists $\overline{\lambda} > 0$ such that

$$\lambda_\gamma \geqslant \overline{\lambda} \min(\gamma, \gamma^{-1}).$$

Remark 5.8. *Theorem 5.6 admits a dual version in terms of probability measures. Consider an initial condition $\psi_0 \in L^2(\mu)$, which represents the density with respect to μ of a probability measure $f_0 = \psi_0 \mu$. In particular,*

$$\psi_0 \geqslant 0, \qquad \int_{\mathcal{E}} \psi_0 \, d\mu = 1.$$

Then the time-evolved probability measure $f_t = \psi_t \mu$ with $\psi_t = \mathrm{e}^{t\mathcal{L}^*} \psi_0$ converges exponentially fast to μ in the following sense:

$$\forall t \geqslant 0, \qquad \|\psi_t - \mathbf{1}\| \leqslant C \mathrm{e}^{-\lambda_\gamma t} \|\psi_0\|. \tag{5.40}$$

Let us first highligh some elements of the proof of Theorem 5.6. In order to formulate the result more rigorously, we introduce the core $\mathscr{C}$ composed of all C^∞ functions with compact support. The first key element in the proof is to use an entropy functional which is equivalent to the $L^2(\mu)$ squared norm. To define this functional, the generator $\mathcal{L}$ is decomposed into a symmetric part (corresponding to the fluctuation/dissipation) and an anti-symmetric part (corresponding to Hamiltonian transport):

$$\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}}, \qquad \text{with} \qquad \begin{cases} \mathcal{L}_{\mathrm{ham}} = \left(\frac{p}{m}\right)^\top \nabla_q - \nabla V^\top \nabla_p, \\ \mathcal{L}_{\mathrm{FD}} = -\left(\frac{p}{m}\right)^\top \nabla_p + \frac{1}{\beta} \Delta_p. \end{cases} \tag{5.41}$$

IN THE SEQUEL: WRONG NOTATION ∇_q FOR ∇_p AT VARIOUS PLACES... With this notation, $\mathcal{L}_{\mathrm{ham}}^* = -\mathcal{L}_{\mathrm{ham}}$ while $\mathcal{L}_{\mathrm{FD}}^* = \mathcal{L}_{\mathrm{FD}}$. In fact, since

$$\nabla_p^* = -\nabla_p^\top + \beta \frac{p^\top}{m}, \qquad \nabla_q^* = -\nabla_q^\top + \beta \nabla V^\top,$$

the two parts of the generator $\mathcal{L}$ can be reformulated as

$$\mathcal{L}_{\mathrm{FD}} = -\frac{1}{\beta} \nabla_q^* \nabla_q, \qquad \mathcal{L}_{\mathrm{ham}} = \frac{1}{\beta} \left(\nabla_q^* \nabla_q - \nabla_q^* \nabla_q \right). \tag{5.42}$$

We also need the orthogonal projector in $L^2_0(\mu)$ on the subspace of functions depending only on positions:

$$\forall \varphi \in L^2(\mu), \qquad (\Pi_p \varphi)(q) = \int_{\mathbb{R}^D} \varphi(q,p) \, \kappa(dp). \tag{5.43}$$

Definition 5.1 (Entropy functional). *Fix $\varepsilon \in (-1,1)$. For any function $\varphi \in \mathscr{C}$,*

$$\mathcal{H}[\varphi] = \frac{1}{2} \|\varphi\|^2 - \varepsilon \langle A\varphi, \varphi \rangle, \qquad A = \left(1 + (\mathcal{L}_{\mathrm{ham}} \Pi_p)^* (\mathcal{L}_{\mathrm{ham}} \Pi_p)\right)^{-1} (\mathcal{L}_{\mathrm{ham}} \Pi_p)^*. \tag{5.44}$$

A more explicit expression of the operator A is provided in (5.55). Since this operator is used in the sequel to state some conditions required for the error estimates, we gather some of its properties in the following lemma.

Lemma 5.3. *It holds $A = \Pi_p A (1 - \Pi_p)$. Moreover, for any $\varphi \in L^2(\mu)$,*

$$\|A\varphi\| \leqslant \frac{1}{2} \|(1 - \Pi_p)\varphi\|, \qquad \|\mathcal{L}_{\mathrm{ham}} A \varphi\| \leqslant \|(1 - \Pi_p)\varphi\|.$$

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 $-1 < \varepsilon < 1$:

$$\frac{1-\varepsilon}{2} \|\varphi\|^2 \leqslant \mathcal{H}[\varphi] \leqslant \frac{1+\varepsilon}{2} \|\varphi\|^2. \tag{5.45}$$

The second key element is a coercivity property enjoyed by the time-derivative of the entropy functional. Denoting by $\langle\langle \cdot, \cdot \rangle\rangle$ the scalar product associated by polarization with $\mathcal{H}$, the following result can be proved.

Proposition 5.4. *There exists $\overline{\varepsilon} \in (0,1)$ and $\overline{\lambda} > 0$, such that, by considering $\varepsilon = \overline{\varepsilon}\min(\gamma, \gamma^{-1})$ in* (5.44)*,*

$$\forall \varphi \in \mathscr{C} \cap L^2_0(\mu), \qquad \mathscr{D}[\varphi] := \langle\langle -\mathcal{L}\varphi, \varphi\rangle\rangle \geqslant \widetilde{\lambda}_\gamma \|\varphi\|^2, \tag{5.46}$$

with $\widetilde{\lambda}_\gamma \geqslant \overline{\lambda}\min(\gamma, \gamma^{-1})$.

This coercivity property 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 (5.39) follows by the norm equivalence of $\sqrt{\mathcal{H}}$ and $\|\cdot\|$.

Proof of Theorem 5.6

We now provide a proof of Theorem 5.6, as presented in [43, 44]. We start with the proofs of the technical results presented above.

Proof (Proof of Lemma 5.3). Consider $\varphi \in \mathscr{C}$. A simple computation shows that

$$\mathcal{L}_{\mathrm{ham}} \Pi_p = \frac{1}{\beta} \nabla_q \nabla_q^* \Pi_p = \left(\frac{p}{m}\right)^\top \nabla_q \Pi_p, \tag{5.47}$$

which immediately implies that $\mathcal{L}_{\mathrm{ham}}\Pi_p\varphi$ has average 0 with respect to $\kappa(dp)$ for any $q \in \mathcal{D}$. Therefore, $\Pi_p \mathcal{L}_{\mathrm{ham}} \Pi_p = 0$, which implies $A = A(1 - \Pi_p)$.

By definition of the operator A, it also holds

$$A\varphi + (\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p)A\varphi = (\mathcal{L}_{\mathrm{ham}}\Pi_p)^*\varphi.$$

This identity immediately implies that $\Pi_p A = A$. Taking the scalar product with $A\varphi$, we obtain, using $\mathcal{L}_{\mathrm{ham}} A = \mathcal{L}_{\mathrm{ham}}\Pi_p A = (1 - \Pi_p)\mathcal{L}_{\mathrm{ham}} A$:

$$\begin{aligned} \|A\varphi\|^2 + \|\mathcal{L}_{\mathrm{ham}} A\varphi\|^2 &= \langle \mathcal{L}_{\mathrm{ham}} A\varphi, \varphi\rangle = \langle \mathcal{L}_{\mathrm{ham}} A\varphi, (1-\Pi_p)\varphi\rangle \\ &\leqslant \|(1-\Pi_p)\varphi\|\, \|\mathcal{L}_{\mathrm{ham}} A\varphi\| \\ &\leqslant \frac{1}{4}\|(1-\Pi_p)\varphi\|^2 + \|\mathcal{L}_{\mathrm{ham}} A\varphi\|^2. \end{aligned} \tag{5.48}$$

The last inequality gives $\|A\varphi\| \leqslant \|(1-\Pi)\varphi\|/2$, while the second one implies that $\|\mathcal{L}_{\mathrm{ham}} A\varphi\| \leqslant \|(1-\Pi_p)\varphi\|$. The conclusion is finally obtained by density of $\mathscr{C}$ in $L^2(\mu)$.

The key element to prove Proposition 5.4 are the following coercivity estimates, respectively called "microscopic" and "macroscopic" coercivity in [43, 44].

Proposition 5.5 (Coercivity properties). *The operators $\mathcal{L}_{\mathrm{FD}}$ and $\mathcal{L}_{\mathrm{ham}}\Pi_p$ satisfy the following coercivity properties:*

$$\forall \varphi \in \mathscr{C}, \qquad -\langle \mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle \geqslant \frac{1}{m}\|(1-\Pi_p)\varphi\|^2, \tag{5.49}$$

$$\forall \varphi \in \mathscr{C} \cap L^2_0(\mu), \qquad \|\mathcal{L}_{\mathrm{ham}}\Pi_p\varphi\|^2 \geqslant \frac{DC_\nu}{\beta m}\|\Pi_p\varphi\|^2, \tag{5.50}$$

where C_ν is defined in (5.37)*. As a corollary, the following inequality holds in the sense of symmetric operators on $L^2_0(\mu)$:*

$$A\mathcal{L}_{\mathrm{ham}}\Pi_p \geqslant \lambda_{\mathrm{ham}}\Pi_p, \qquad \lambda_{\mathrm{ham}} = 1 - \left(1 + \frac{DC_\nu}{\beta m}\right)^{-1} > 0. \tag{5.51}$$

Proof. The inequality (5.49) directly results from a Poincaré inequality for the Gaussian measure κ (see [18]), the position q being seen as a parameter. Indeed, for a given $\varphi \in \mathscr{C}$,

$$\forall q \in \mathcal{D}, \qquad \int_{\mathbb{R}^D} |\nabla_q \varphi(q,p)|^2 \, \kappa(dp) \geqslant \frac{\beta}{m}\int_{\mathbb{R}^D} |(1-\Pi_p)\varphi(q,p)|^2 \, \kappa(dp) \tag{5.52}$$

Integrating against ν and noting that $-\langle \mathcal{L}_{\mathrm{FD}}\varphi, \varphi\rangle = \beta^{-1}\|\nabla_q \varphi\|^2$ leads to the desired inequality.

To prove (5.50), we use (5.47), which leads to

$$\|\mathcal{L}_{\mathrm{ham}}\Pi_p\varphi\|^2_{L^2(\mu)} \leqslant \|\nabla_q \Pi_p\varphi\|^2_{L^2(\nu)} \left\|\frac{1}{m}p\right\|^2_{L^2(\kappa)} = \frac{D}{\beta m}\|\nabla_q \Pi_p\varphi\|^2_{L^2(\nu)}. \tag{5.53}$$

The conclusion then follows from the Poincaré inequality (5.37), since, for $\varphi \in \mathscr{C} \cap L^2_0(\mu)$, the function $\Pi_p\varphi$ has average 0 with respect to ν (namely, $\mathbb{E}_\nu[\Pi_p\varphi] = \mathbb{E}_\mu[\varphi] = 0$).

The macroscopic coercivity (5.50) allows to write $(\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p) \geqslant \frac{DC_\nu}{\beta m}\Pi_p$ in the sense of symmetric operators on $L^2_0(\mu)$. Moreover,

$$A\mathcal{L}_{\mathrm{ham}}\Pi_p = \left[1 + (\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p)\right]^{-1}(\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p).$$

Since $(\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p)$ is self-adjoint and the function $x \mapsto x/(1+x) = 1 - 1/(1+x)$ is increasing, the inequality (5.51) follows by spectral calculus.

Another technical argument is the boundedness of certain operators, which appear in the proof of Proposition 5.4.

Lemma 5.4. *For any $\ell \in \mathbb{N}^*$, $i \in \{1, 2, \dots, D\}$ and $\varphi \in L^2(\mu)$,*

$$\|\Pi_p \partial_{p_i}^\ell \varphi\|_{L^2(\nu)} \leqslant \sqrt{\left(\frac{\beta}{m}\right)^\ell \ell!}\, \|(1-\Pi_p)\varphi\|.$$

In particular, $\left\|\Pi_p \partial_{p_i}^\ell\right\| = \left\|\left(\partial_{p_i}^*\right)^\ell \Pi_p\right\| \leqslant \sqrt{\beta^\ell \ell!}$.

Proof. Fix $\varphi \in \mathscr{C}$. For $q \in \mathcal{D}$,

$$\left(\Pi_p \partial_{p_i}^n \varphi\right)(q) = \int_{\mathbb{R}^D} \left(\partial_{p_i}^n (1-\Pi_p)\varphi\right)(q,p)\,\kappa(dp) = \int_{\mathbb{R}^D} (1-\Pi_p)\varphi(q,p)\,(\partial_{p_i}^*)^n \mathbf{1}\,\kappa(dp).$$

Denoting by $H_\ell(p_i) = (m/\beta)^{\ell/2}\ell!^{-1/2}(\partial_{p_i}^*)^\ell \mathbf{1}$ the Hermite polynomials in the variable p_i (which, we recall, are such that $\|H_\ell\|_{L^2(\kappa)} = 1$), a Cauchy–Schwarz inequality shows that

$$\begin{aligned}
\|\Pi_p \partial_{p_i}^\ell \varphi\|^2_{L^2(\nu)} &\leqslant \int_{\mathcal{D}} \left(\int_{\mathbb{R}^D} |(1-\Pi_p)\varphi(q,p)| \left|\sqrt{\left(\frac{\beta}{m}\right)^\ell \ell!} H_\ell(p_i)\right| \kappa(dp)\right)^2 \nu(dq) \\
&\leqslant \left(\frac{\beta}{m}\right)^\ell \ell! \int_{\mathcal{D}} \|(1-\Pi_p)\varphi(q,\cdot)\|^2_{L^2(\kappa)} \|H_\ell\|^2_{L^2(\kappa)} \nu(dq) = \left(\frac{\beta}{m}\right)^\ell \ell! \|(1-\Pi_p)\varphi\|^2,
\end{aligned}$$

which gives the claimed result.

Proposition 5.6 (Boundedness of auxiliary operators). *There exist $R_{\mathrm{ham}} > 0$ such that*

$$\forall \varphi \in \mathscr{C}, \qquad \begin{cases} \|A\mathcal{L}_{\mathrm{ham}}(1-\Pi_p)\varphi\| \leqslant R_{\mathrm{ham}}\|(1-\Pi_p)\varphi\|, \\ \|A\mathcal{L}_{\mathrm{FD}}\varphi\| \leqslant \dfrac{1}{2m}\|(1-\Pi_p)\varphi\|. \end{cases} \tag{5.54}$$

Proof. 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 ∇_q, ∇_q^* and Π_p). Moreover the relations $\partial_{p_i}\Pi_p = 0$, $\Pi_p\partial_{p_i}^* = 0$ and $\Pi_p\partial_{p_i}\partial_{p_j}^* = \partial_{p_i}\partial_{p_j}^*\Pi_p = \frac{\beta}{m}\Pi_p\delta_{ij}$ allow to simplify the action of $(\mathcal{L}_{\mathrm{ham}}\Pi_p)^*(\mathcal{L}_{\mathrm{ham}}\Pi_p)$ as follows:

$$(\mathcal{L}_{\rm ham}\Pi_p)^*(\mathcal{L}_{\rm ham}\Pi_p) = -\frac{1}{\beta^2}\Pi_p(\nabla_q^*\nabla_q - \nabla_q^*\nabla_q)(\nabla_q^*\nabla_q - \nabla_q^*\nabla_q)\Pi_p$$
$$= \frac{1}{\beta^2}\Pi_p(\nabla_q^*\nabla_q)(\nabla_q^*\nabla_q)\Pi_p = \frac{1}{\beta m}\nabla_q^*\nabla_q\Pi_p.$$

The operator A can therefore be reformulated as

$$A = \frac{1}{\beta}\left(1 + \frac{1}{\beta m}\nabla_q^*\nabla_q\right)^{-1}\nabla_q^*\Pi_p\nabla_q. \tag{5.55}$$

To obtain bounds on the operator $A\mathcal{L}_{\rm ham}(1-\Pi_p)$, we next consider its adjoint:

$$-(1-\Pi_p)\mathcal{L}_{\rm ham}A^* = -\frac{1}{\beta^2}(1-\Pi_p)\left(\nabla_q^*\nabla_q - \nabla_q^*\nabla_q\right)\nabla_q^*\nabla_q\Pi_p\left(1 + \frac{1}{\beta m}\nabla_q^*\nabla_q\right)^{-1}$$
$$= -\frac{1}{\beta^2}(1-\Pi_p)\left(\nabla_q^*\nabla_q\nabla_q^*\nabla_q - \frac{\beta}{m}\nabla_q^*\nabla_q\right)\Pi_p\left(1 + \frac{1}{\beta m}\nabla_q^*\nabla_q\right)^{-1}$$
$$= -\frac{1}{\beta^2}(1-\Pi_p)\nabla_q^*\nabla_q\nabla_q^*\nabla_q\Pi_p\left(1 + \frac{1}{\beta m}\nabla_q^*\nabla_q\right)^{-1},$$

where we used $(1-\Pi_p)\nabla_q^*\nabla_q\Pi_p = 0$ in the last line. Moreover, the operator

$$\nabla_q^*\nabla_q\nabla_q^*\nabla_q\Pi_p = \sum_{i,j=1}^{D}\partial_{p_i}^*\partial_{p_j}^*\Pi_p\partial_{q_i}\partial_{q_j}$$

is bounded from $H^2(\nu)$ to $L^2(\mu)$ according to Lemma 5.4. Moreover, as proved in [44], Assumption 5.5 ensures that the operator $\Pi_p\left(1 + \frac{1}{\beta m}\nabla_q^*\nabla_q\right)^{-1}$ is bounded from $L^2(\mu)$ to $H^2(\nu)$. In conclusion, $-(1-\Pi_p)\mathcal{L}_{\rm ham}A^*$ is bounded on $L^2(\mu)$.

The boundedness of the operator $A\mathcal{L}_{\rm FD}$ comes from the fact that

$$\Pi_p\mathcal{L}_{\rm ham}\mathcal{L}_{\rm FD} = -\frac{1}{\beta^2}\Pi_p\left(\nabla_q^*\nabla_q - \nabla_q^*\nabla_q\right)\nabla_q^*\nabla_q = \frac{1}{\beta^2}\Pi_p\nabla_q^*\nabla_q\nabla_q^*\nabla_q$$
$$= \frac{1}{\beta m}\Pi_p\nabla_q^*\nabla_q = -\frac{1}{m}\Pi_p\mathcal{L}_{\rm ham}.$$

In conclusion, $A\mathcal{L}_{\rm FD} = -A/m$, **PLUS SIMPLE : calculer action de $\mathcal{L}_{\rm FD}\mathcal{L}_{\rm ham}\Pi$ et passer aux adjoints...** which gives the claimed result with Lemma 5.3.

We can now proceed with the proof of Proposition 5.4.

Proof (Proof of Proposition 5.4). Note first that, for a given $\varphi \in \mathscr{C}$, the entropy dissipation $\mathscr{D}[\varphi]$ can be explicitly written as

$$\mathscr{D}[\varphi] = \langle -\gamma\mathcal{L}_{\rm FD}\varphi, \varphi\rangle + \varepsilon\langle A\mathcal{L}_{\rm ham}\Pi_p\varphi, \varphi\rangle + \varepsilon\langle A\mathcal{L}_{\rm ham}(1-\Pi_p)\varphi, \varphi\rangle$$
$$- \varepsilon\langle \mathcal{L}_{\rm ham}A\varphi, \varphi\rangle + \varepsilon\gamma\langle A\mathcal{L}_{\rm FD}\varphi, \varphi\rangle, \tag{5.56}$$

since $\mathcal{L}_{\rm FD}A = \mathcal{L}_{\rm FD}\Pi_p A = 0$. Using respectively the properties (5.49), (5.51), (5.54) and Lemma 5.3, it follows

$$\mathscr{D}[\varphi] \geqslant \frac{\gamma}{m}\|(1-\Pi_p)\varphi\|^2 + \varepsilon\lambda_{\rm ham}\|\Pi_p\varphi\|^2 - \varepsilon\left(R_{\rm ham} + \frac{\gamma}{2m}\right)\|(1-\Pi_p)\varphi\|\,\|\Pi_p\varphi\|$$
$$- \varepsilon\langle \mathcal{L}_{\rm ham}A\varphi, \varphi\rangle. \tag{5.57}$$

Since, by Lemma 5.3,

$$\langle \mathcal{L}_{\rm ham}A\varphi, \varphi\rangle = \langle (1-\Pi_p)\mathcal{L}_{\rm ham}\Pi_p A(1-\Pi_p)\varphi, \varphi\rangle \leqslant \|(1-\Pi_p)\varphi\|^2,$$

it holds $\mathscr{D}[\varphi] \geqslant X^\top S X$, where

$$X = \begin{pmatrix} \|\Pi_p \varphi\| \\ \|(1-\Pi_p)\varphi\| \end{pmatrix}, \qquad S = \begin{pmatrix} S_{--} & S_{-+}/2 \\ S_{-+}/2 & S_{++} \end{pmatrix},$$

with

$$S_{--} = \varepsilon \lambda_{\mathrm{ham}}, \qquad S_{-+} = -\varepsilon \left(R_{\mathrm{ham}} + \frac{\gamma}{2m} \right), \qquad S_{++} = \frac{\gamma}{m} - \varepsilon.$$

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

$$\varepsilon = \overline{\varepsilon} \min(\gamma, \gamma^{-1}). \tag{5.58}$$

It is then easy to check that there exists $\overline{\varepsilon} > 0$ sufficiently small such that $\Lambda(\gamma, \overline{\varepsilon} \min(\gamma, \gamma^{-1})) > 0$ for all $\gamma > 0$. Moreover, it can be proved that $\Lambda(\gamma, \overline{\varepsilon} \min(\gamma, \gamma^{-1}))/\gamma$ converges to a positive value as $\gamma \to 0$, while $\gamma \Lambda(\gamma, \overline{\varepsilon} \min(\gamma, \gamma^{-1}))$ converges to a positive value as $\gamma \to +\infty$. This gives the claimed result with $\widetilde{\lambda}_\gamma = \Lambda(\gamma, \overline{\varepsilon} \min(\gamma, \gamma^{-1}))$.

The proof of Theorem 5.6 is now easy to obtain. 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,

$$\mathscr{H}'(t) = -\mathscr{D}[\varphi(t)] \leqslant -\widetilde{\lambda}_\gamma \|\varphi(t)\|^2.$$

Using the norm equivalence (5.45) and the choice (5.58) 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,

$$\mathscr{H}(t) \leqslant \mathscr{H}(0) \exp\left(-\frac{2\widetilde{\lambda}_\gamma}{1 + \overline{\varepsilon} \min(\gamma, \gamma^{-1})} t \right).$$

Using again the norm equivalence (5.45), it follows that

$$\|\varphi(t)\|^2 \leqslant \frac{1 + \overline{\varepsilon}}{1 - \overline{\varepsilon}} \, \mathrm{e}^{-2\lambda_\gamma t} \|\varphi(0)\|^2,$$

with the decay rate

$$\lambda_\gamma = \frac{\widetilde{\lambda}_\gamma}{1 + \overline{\varepsilon} \min(\gamma, \gamma^{-1})}.$$

The desired estimate finally follows by density of $\mathrm{Dom}(\mathcal{L})$ in $L^2(\mu)$.

5.4 Time discretization

We focus on splitting schemes, as studied in [25, 107, 108], and therefore restrict the presentation to dynamics in compact position spaces. The extension of the results presented below to unbounded position spaces requires some non-trivial extensions, the most important one being the ergodicity of the numerical schemes. We work on the core $\mathcal{S}$ introduced in Definition 4.4, considering the Lyapunov functions $W_n(q,p) = 1 + |p|^{2n}$.

5.4.1 Description of the numerical schemes

In order to describe more conveniently splitting schemes, it is useful to introduce the elementary dynamics with generators

$$A = M^{-1}p \cdot \nabla_q, \qquad B = -\nabla V(q) \cdot \nabla_p, \qquad C = -M^{-1}p \cdot \nabla_p + \frac{1}{\beta}\Delta_p. \tag{5.59}$$

The generator $\mathcal{L}_\gamma$ for equilibrium Langevin dynamics (5.1), defined on the core $\mathcal{S}$, is the sum of the generators of the elementary dynamics:

$$\mathcal{L}_\gamma = A + B + \gamma C,$$

where $\mathcal{L}_{\rm ham} = A + B$ is the generator associated with the Hamiltonian part of the dynamics.

First-order splitting schemes

First-order schemes are obtained by a Lie-Trotter splitting of the elementary evolutions generated by $A, B, \gamma C$. The motivation for this splitting is that all elementary evolutions are analytically integrable (see the expressions of the associated semigroups in (5.80) below). 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

$$\begin{cases} \widetilde{p}^{n+1} = p^n - \Delta t\, \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\, M^{-1}\widetilde{p}^{n+1}, \\ p^{n+1} = \alpha_{\Delta t}\widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}^2}{\beta}}\, M\, G^n, \end{cases} \tag{5.60}$$

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 5.9. *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. This is discussed in [115, 114].*

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:

$$\left(P_{\Delta t}^{A,B,\gamma C}\right)^n = T_{\Delta t}\left(P_{\Delta t}^{\gamma C,A,B}\right)^{n-1} U_{\gamma,\Delta t}, \qquad U_{\gamma,\Delta t} = \mathrm{e}^{\gamma \Delta t C}, \qquad T_{\Delta t} = \mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B}. \tag{5.61}$$

It is therefore not surprising that the invariant measures of the schemes with operators composed in the same order have very similar properties, as made precise in Theorem 5.8, relying on Lemma 5.7.

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 Section 5.5).

Geometric Langevin Algorithms

In fact, as already proved in [25] (see also Corollary 5.4 below), 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:

$$\begin{aligned} P_{\Delta t}^{\gamma C,A,B,A} &= \mathrm{e}^{\gamma \Delta t C}\mathrm{e}^{\Delta t A/2}\mathrm{e}^{\Delta t B}\mathrm{e}^{\Delta t A/2}, \qquad & P_{\Delta t}^{\gamma C,B,A,B} &= \mathrm{e}^{\gamma \Delta t C}\mathrm{e}^{\Delta t B/2}\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B/2}, \\ P_{\Delta t}^{A,B,A,\gamma C} &= \mathrm{e}^{\Delta t A/2}\mathrm{e}^{\Delta t B}\mathrm{e}^{\Delta t A/2}\mathrm{e}^{\gamma \Delta t C}, \qquad & P_{\Delta t}^{B,A,B,\gamma C} &= \mathrm{e}^{\Delta t B/2}\mathrm{e}^{\Delta t A}\mathrm{e}^{\Delta t B/2}\mathrm{e}^{\gamma \Delta t C}. \end{aligned} \tag{5.62}$$

5.4.2 Ergodicity of numerical schemes

We obtain convergence estimates uniformly in the time step Δt, following the results presented in Section 3.3.1 and using Lemma 4.3. The uniformity with respect to the timestep is necessary to obtain the resolvent bound (5.67), which is a fundamental ingredients in the proofs of error estimates.

Lemma 5.5 (Uniform Lyapunov condition). *For any $s^* \in \mathbb{N}^*$, there exist $\Delta t^* > 0$ and $C_a, C_b > 0$ such that, for any $1 \leqslant s \leqslant s^*$ and $0 < \Delta t \leqslant \Delta t^*$,*

$$P_{\Delta t} W_s \leqslant \mathrm{e}^{-C_a \Delta t} W_s + C_b \Delta t. \tag{5.63}$$

In particular, for any $T > 0$,

$$P_{\Delta t}^{\lceil T/\Delta t \rceil} W_s \leqslant \exp(-C_a T) W_s + \frac{C_b \Delta t}{1 - \mathrm{e}^{-C_a \Delta t}}. \tag{5.64}$$

Lemma 5.6 (Uniform minorization condition). *Consider $T > 0$ sufficiently large, and fix any $p_{\max} > 0$. There exist $\Delta t^*, \alpha > 0$ and a probability measure π such that, for any bounded, measurable non-negative function f, and any $0 < \Delta t \leqslant \Delta t^*$,*

$$\inf_{|p| \leqslant p_{\max}} \left(P_{\Delta t}^{\lceil T/\Delta t \rceil} f \right)(q,p) \geqslant \alpha \int_{\mathcal{E}} f(q,p)\, \pi(dq\, dp).$$

The uniform minorization condition can formally be rewritten as

$$\forall (q_0,p_0) \in \mathcal{D} \times B(0, p_{\max}), \qquad P_{\Delta t}\Big((q_0,p_0), dq\, dp\Big) \geqslant \alpha \pi(dq\, dp).$$

We present a direct proof of Lemma 5.6 below. Extending this result to unbounded position spaces is much more difficult in general, see for instance the recent works [92, 93] and [24] where non-degeneracy of the noise is assumed.

Let us now precisely state the ergodicity result.

Proposition 5.7 (Ergodicity of numerical schemes). *Fix $s^* \geqslant 1$. For any $0 < \gamma < +\infty$, there exists $\Delta t^* > 0$ such that, for any $0 < \Delta t \leqslant \Delta t^*$, the Markov chain associated with $P_{\Delta t}$ has a unique invariant probability measure $\mu_{\gamma,\Delta t}$, which admits a density with respect to the Lebesgue measure $dq\,dp$, and has finite moments: There exists $R > 0$ such that, for any $1 \leqslant s \leqslant s^*$,*

$$\int_{\mathcal{E}} W_s \, d\mu_{\gamma,\Delta t} \leqslant R < +\infty, \tag{5.65}$$

uniformly in the timestep Δt. There also exist $\lambda, K > 0$ (depending on s^* and γ but not on Δt) such that

$$\|P_{\Delta t}^n\|_{\mathcal{B}(L^\infty_{W_s,\Delta t})} \leqslant K\,\mathrm{e}^{-\lambda n \Delta t}, \tag{5.66}$$

on the Banach space

$$L^\infty_{W_s,\Delta t} = \left\{ \psi \in L^\infty_{W_s} \;\middle|\; \int_{\mathcal{E}} \psi \, d\mu_{\gamma,\Delta t} = 0 \right\}.$$

Let us again emphasize that, compared to the results of [121, 160, 25], the only new estimate is the uniform-in-Δt decay rate in (5.66) as obtained in [24] for Metropolis schemes. Recall also that the convergence rates we obtain of course depend on the friction parameter γ.

Corollary 5.3. *For any $s^* \in \mathbb{N}^*$, there exist $\Delta t^* > 0$ and $R > 0$ such that, for all $0 \leqslant s \leqslant s^*$, a uniform resolvent bound holds: for any $0 < \Delta t \leqslant \Delta t^*$,*

$$\left\| \left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \right\|_{\mathcal{B}(L^\infty_{W_s,\Delta t})} \leqslant R. \tag{5.67}$$

We now give the proofs of the above results.

Proof (of Lemma 5.5). We write the proof for the scheme associated with the evolution operator $P_{\Delta t}^{B,A,\gamma C}$, starting by the case $s = 1$, before turning to the general case $s \geqslant 2$. The proofs for other schemes are very similar, and we therefore skip them.

The numerical scheme corresponding to $P_{\Delta t}^{B,A,\gamma C}$ is (5.60). We introduce $m \in (0, +\infty)$ such that $m \leqslant M \leqslant m^{-1}$ (in the sense of symmetric matrices). A simple computation shows that

$$\begin{aligned}
\mathbb{E}\left[\left(p^{n+1}\right)^2 \,\middle|\, \mathcal{F}_n \right] &= \left(p^n - \Delta t \nabla V(q^n)\right)^T \alpha_{\Delta t}^2 \left(p^n - \Delta t \nabla V(q^n)\right) + \frac{1}{\beta} \mathrm{Tr}\left[\left(1 - \alpha_{\Delta t}^2\right) M^2 \right] \\
&\leqslant \mathrm{e}^{-2m\gamma\Delta t} \left(p^n\right)^2 + 2\Delta t \left\|\nabla V\right\|_{L^\infty} |p^n| + \Delta t^2 \left\|\nabla V\right\|_{L^\infty}^2 + \frac{1 - \mathrm{e}^{-2\gamma\Delta t/m}}{\beta m^2} \\
&\leqslant \left(\mathrm{e}^{-2m\gamma\Delta t} + \varepsilon \Delta t\right) \left(p^n\right)^2 + \Delta t \left(\frac{1}{\varepsilon} + \Delta t\right) \left\|\nabla V\right\|_{L^\infty}^2 + \frac{1 - \mathrm{e}^{-2\gamma\Delta t/m}}{\beta m^2}.
\end{aligned}$$

We choose for instance $\varepsilon = m\gamma$, in which case

$$0 \leqslant \mathrm{e}^{-2m\gamma\Delta t} + \varepsilon \Delta t \leqslant \exp\left(-C_a \Delta t\right), \qquad C_a = \frac{m\gamma}{2},$$

and

$$0 \leqslant \Delta t \left(\frac{1}{\varepsilon} + \Delta t\right) \left\|\nabla V\right\|_{L^\infty}^2 + \frac{1 - \mathrm{e}^{-2\gamma\Delta t/m}}{\beta m^2} \leqslant \widetilde{C}_b \Delta t, \qquad \widetilde{C}_b = \frac{2}{m\gamma} \left\|\nabla V\right\|_{L^\infty}^2 + \frac{4\gamma}{\beta m^3},$$

for Δt sufficiently small. Finally, since $W_2(q,p) = 1 + |p|^2$,

$$\mathbb{E}\left[W_2\left(q^{n+1}, p^{n+1}\right) \,\middle|\, \mathcal{F}_n \right] \leqslant \mathrm{e}^{-C_a\Delta t} W_2\left(q^n, p^n\right) + 1 - \mathrm{e}^{-C_a\Delta t} + \widetilde{C}_b \Delta t \leqslant \mathrm{e}^{-C_a\Delta t} W_2\left(q^n, p^n\right) + C_b \Delta t,$$

for Δt sufficiently small. This gives (5.63). To obtain (5.64), we iterate the bound (5.63):

$$P_{\Delta t}^n W_s \leqslant \mathrm{e}^{-C_a\, n\Delta t} W_s + C_b \Delta t \left(1 + \mathrm{e}^{-C_a \Delta t} + \cdots + \mathrm{e}^{-C_a\,(n-1)\Delta t}\right) \leqslant \mathrm{e}^{-C_a\, n\Delta t} W_s + \frac{C_b \Delta t}{1 - \mathrm{e}^{-C_a \Delta t}}.$$

The computations are similar for a general power $s \geqslant 2$. We write $p^{n+1} = \alpha_{\Delta t} p^n + \delta_{\Delta t}$ with $\delta_{\Delta t} = -\alpha_{\Delta t} \Delta t \nabla V(q^n) + \sqrt{\beta^{-1}(1-\alpha_{\Delta t}^2) M}\, G^n$. Note that $\delta_{\Delta t}$ is of order $\Delta t^{1/2}$ because of the random term. We work componentwise, using the assumption that M is diagonal, so that, denoting by m_i the mass of the ith degree of freedom,

$$\begin{aligned}
\left(p_i^{n+1}\right)^{2s} &= \left(\mathrm{e}^{-\gamma \Delta t/m_i} p_i^n + \delta_{i,\Delta t}\right)^{2s} \\
&= \mathrm{e}^{-2s\gamma\Delta t/m_i} \left(p_i^n\right)^{2s} + 2s\, \mathrm{e}^{-(2s-1)\gamma\Delta t/m_i} \left(p_i^n\right)^{2s-1} \delta_{i,\Delta t} \\
&\quad + s(2s-1) \mathrm{e}^{-2(s-1)\gamma\Delta t/m_i} \left(p_i^n\right)^{2(s-1)} \delta_{i,\Delta t}^2 + \dots
\end{aligned}$$

Taking expectations,

$$\begin{aligned}
\mathbb{E}\left[\left(p_i^{n+1}\right)^{2s} \,\middle|\, \mathcal{F}_n \right] &= \mathrm{e}^{-2s\gamma\Delta t/m_i} \left(p_i^n\right)^{2s} - 2s\, \Delta t\, \mathrm{e}^{-2s\gamma\Delta t/m_i} \left(p_i^n\right)^{2s-1} \partial_{q_i} V(q^n) \\
&\quad + s(2s-1) \mathrm{e}^{-2(s-1)\gamma\Delta t/m_i} \left(p_i^n\right)^{2(s-1)} \left(\Delta t^2 \mathrm{e}^{-2\gamma\Delta t/m_i} \partial_{q_i} V(q^n) + \frac{(1 - \mathrm{e}^{-2\gamma\Delta t/m_i}) m_i}{\beta} \right) \\
&\quad + \Delta t^2 r_{s,\Delta t,i}(q^n) \left(1 + \left(p^n\right)^{2s-3}\right),
\end{aligned}$$

where the remainder $r_{s,\Delta t}(q^n)$ is uniformly bounded as $\Delta t \to 0$. Distinguishing between $|p_i| \geqslant 1/\varepsilon$ and $|p_i| \leqslant 1/\varepsilon$, we have

$$|p_i|^{2s-m} \leqslant \varepsilon^m (p_i)^{2s} + \frac{1}{\varepsilon^{2s-m}},$$

from which we obtain

$$\mathbb{E}\left[\left(p_i^{n+1}\right)^{2s} \,\middle|\, \mathcal{F}_n \right] \leqslant \widehat{a}_{\Delta t,\varepsilon,i} \left(p_i^n\right)^{2s} + \widehat{b}_{\Delta t,\varepsilon,i},$$

with

$$\begin{aligned}
\widehat{a}_{\Delta t,\varepsilon,i} &= \mathrm{e}^{-2s\gamma\Delta t/m_i} + 2s\varepsilon\Delta t \|\partial_{q_i} V\|_{L^\infty} \\
&\quad + s(2s-1)\varepsilon^2 \left(\Delta t^2 \|\partial_{q_i} V\|_{L^\infty} + \frac{(1 - \mathrm{e}^{-2\gamma\Delta t/m_i}) m_i}{\beta} \right) + \varepsilon^3 \Delta t^2 \|r_{s,\Delta t,i}\|_{L^\infty},
\end{aligned}$$

and

$$\begin{aligned}
\widehat{b}_{\Delta t,\varepsilon,i} &= \frac{2s}{\varepsilon} \Delta t \|\partial_{q_i} V\|_{L^\infty} \\
&\quad + \frac{s(2s-1)}{\varepsilon^2} \left(\Delta t^2 \|\partial_{q_i} V\|_{L^\infty} + \frac{(1 - \mathrm{e}^{-2\gamma\Delta t/m_i}) m_i}{\beta} \right) + \Delta t^2 \left(1 + \frac{1}{\varepsilon^3}\right) \|r_{s,\Delta t,i}\|_{L^\infty}.
\end{aligned}$$

The proof is then concluded as in the case $s = 1$ by choosing ε sufficiently small (independently of Δt). □

Proof (of Lemma 5.6). It is sufficient to prove the result for indicator functions of Borel sets $A = A_q \times A_p \subset \mathcal{E}$, where $A_q \subset \mathcal{D}$ while $A_p \subset \mathbb{R}^D$ (see [153]). We therefore aim at proving

$$\mathbb{P}\left((q^n, p^n) \in A \,\middle|\, |p^0| \leqslant p_{\max} \right) \geqslant \alpha\, \pi(A),$$

for a well chosen probability measure π and a constant $\alpha > 0$. The idea of the proof is to explicitly rewrite q^n and p^n as perturbations of the reference evolution corresponding to $\nabla V = 0$ and $(q^0, p^0) = (0, 0)$. Since we consider smooth potentials and the position space is compact, the perturbation can be uniformly controlled when the initial momenta are within a compact set.

We write the proof for the scheme associated with the evolution operator $P_{\Delta t}^{B,A,\gamma C}$, as in the proof of Lemma 5.5. A simple computation shows that, for $n \geqslant 1$,

$$q^n = q^0 + \Delta t M^{-1}\left(p^{n-1} + \cdots + p^0\right) - \Delta t^2 M^{-1}\Big(\nabla V(q^{n-1}) + \cdots + \nabla V(q^0)\Big),$$

and

$$p^n = \alpha_{\Delta t}^n\, p^0 - \Delta t\, \alpha_{\Delta t}\left(\nabla V(q^{n-1}) + \alpha_{\Delta t}\nabla V(q^{n-2}) + \cdots + \alpha_{\Delta t}^{n-1}\nabla V(q^0)\right) + \sqrt{\frac{1-\alpha_{\Delta t}^2}{\beta}M}\left(G^{n-1} + \alpha_{\Delta t}G^{n-2} + \cdots + \alpha_{\Delta t}^{n-1}G^0\right).$$

Denote by $\mathcal{G}^n$ the centered Gaussian random variable

$$\mathcal{G}^n = \sqrt{\frac{1-\alpha_{\Delta t}^2}{\beta}M}\left(G^{n-1} + \alpha_{\Delta t}G^{n-2} + \cdots + \alpha_{\Delta t}^{n-1}G^0\right).$$

Introduce also

$$\begin{aligned}
F^n &= -\alpha_{\Delta t}\left(\nabla V(q^{n-1}) + \alpha_{\Delta t}\nabla V(q^{n-2}) + \cdots + \alpha_{\Delta t}^{n-1}\nabla V(q^0)\right),\\
\mathscr{P}^n &= \alpha_{\Delta t}^n\, p^0 + \Delta t\, F^n,\\
\mathscr{Q}^n &= q^0 + \Delta t M^{-1}\left(\Delta t\sum_{m=0}^{n-1} F^m + \frac{1-\alpha_{\Delta t}^n}{1-\alpha_{\Delta t}}p^0\right) - \Delta t^2 M^{-1}\Big(\nabla V(q^{n-1}) + \cdots + \nabla V(q^0)\Big).
\end{aligned}$$

With this notation,

$$p^n = \mathscr{P}^n + \mathcal{G}^n, \qquad q^n = \mathscr{Q}^n + \widetilde{\mathcal{G}}^n,$$

where

$$\begin{aligned}
\widetilde{\mathcal{G}}^n &= \Delta t M^{-1}\sum_{m=1}^{n-1}\mathcal{G}^m\\
&= \Delta t\sqrt{\frac{1-\alpha_{\Delta t}^2}{\beta}M^{-1}}\Big(G^{n-2} + (1+\alpha_{\Delta t})G^{n-3} + \cdots + (1+\alpha_{\Delta t}+\cdots+\alpha_{\Delta t}^{n-2})G^0\Big)
\end{aligned}$$

is a centered Gaussian random variable. Now,

$$\mathbb{P}\left((q^n,p^n)\in A \;\middle|\; |p^0|\leqslant p_{\max}\right) = \mathbb{P}\left(\left(\widetilde{\mathcal{G}}^n,\mathcal{G}^n\right)\in (A_q-\mathscr{Q}^n)\times(A_p-\mathscr{P}^n)\;\middle|\; |p^0|\leqslant p_{\max}\right). \quad (5.68)$$

In fact, we consider in the sequel that the random variable $\widetilde{\mathcal{G}}^n$ has values in $\mathbb{R}^D$ rather than $\mathcal{D}$ and understand $A_q - \mathscr{Q}^n$ as a subset of $\mathbb{R}^D$ rather than $\mathcal{D}$. This amounts to neglecting the possible periodic images, and henceforth reduces the probability on the right-hand side of the above inequality. This is however not a problem since we seek a lower bound.

Note that $\Delta t\, F^n$ is uniformly bounded: using $0\leqslant\alpha_{\Delta t}\leqslant\exp(-\gamma m\Delta t)$ in the sense of symmetric, positive matrices (with $m\leqslant M\leqslant m^{-1}$),

$$|\Delta t\, F^n| \leqslant \|\nabla V\|_{L^\infty}\frac{\Delta t}{1-\exp(-\gamma m\Delta t)} \leqslant \frac{2}{m\gamma}\|\nabla V\|_{L^\infty}$$

provided Δt is sufficiently small. Therefore, there exists a constant $R>0$ (depending on $p_{\max}$) and $\Delta t^*>0$ such that, for all timesteps $0<\Delta t\leqslant\Delta t^*$ and corresponding integration steps $0\leqslant n\leqslant T/\Delta t$,

$$|\mathscr{Q}^n|\leqslant R, \qquad |\mathscr{P}^n|\leqslant R. \quad (5.69)$$

A lengthy but straightforward computation shows that the variance of the centered Gaussian vector $\left(\widetilde{\mathcal{G}}^n,\mathcal{G}^n\right)$ is

$$\mathscr{V}^n = \mathbb{E}\left[\left(\widetilde{\mathcal{G}}^n,\mathcal{G}^n\right)^T\left(\widetilde{\mathcal{G}}^n,\mathcal{G}^n\right)\right] = \begin{pmatrix}\mathscr{V}_{qq}^n & \mathscr{V}_{qp}^n\\ \mathscr{V}_{qp}^n & \mathscr{V}_{pp}^n\end{pmatrix}$$

with

$$\begin{cases} \mathscr{V}_{qq}^n = \dfrac{\Delta t\,(1-\alpha_{\Delta t}^2)}{(1-\alpha_{\Delta t})^2} M^{-1}\left((n-1)\Delta t - \dfrac{2\Delta t\,\alpha_{\Delta t}}{1-\alpha_{\Delta t}}(1-\alpha_{\Delta t}^{n-1}) + \dfrac{\Delta t\,\alpha_{\Delta t}^2}{1-\alpha_{\Delta t}^2}\left(1-\alpha_{\Delta t}^{2(n-1)}\right)\right), \\ \mathscr{V}_{qp}^n = \dfrac{\Delta t\,\alpha_{\Delta t}}{\beta(1-\alpha_{\Delta t})}\Big(1-\alpha_{\Delta t}^{n-1}(1+\alpha_{\Delta t})+\alpha_{\Delta t}^{2n-1}\Big), \\ \mathscr{V}_{pp}^n = \dfrac{M}{\beta}(1-\alpha_{\Delta t}^{2n}). \end{cases}$$

To check that this expression is appropriate, we note that it converges as $\Delta t \to 0$ with $n\Delta t \to T$ to the variance of the limiting continuous process

$$dq_t = M^{-1}p_t\,dt, \qquad dp_t = -\gamma M^{-1}p_t\,dt + \sqrt{\frac{2\gamma}{\beta}}\,dW_t,$$

starting from $(q_0, p_0) = (0,0)$, which reads

$$\mathscr{V} = \begin{pmatrix} \mathscr{V}_{qq} & \mathscr{V}_{qp} \\ \mathscr{V}_{qp} & \mathscr{V}_{pp} \end{pmatrix},$$

with

$$\begin{cases} \mathscr{V}_{qq} = \dfrac{1}{\beta\gamma}\left(2T - \dfrac{M}{\gamma}\left(3 - 4\,\alpha_T + \alpha_T^2\right)\right), \\ \mathscr{V}_{qp} = \dfrac{M}{\beta\gamma}\left(1-\alpha_T\right)^2, \\ \mathscr{V}_{pp} = \dfrac{M}{\beta}\left(1-\alpha_T^2\right). \end{cases}$$

Upon reducing $\Delta t^* > 0$, it holds $\mathscr{V}/2 \leqslant \mathscr{V}^{\lceil T/\Delta t\rceil} \leqslant 2\mathscr{V}$ for $0 < \Delta t \leqslant \Delta t^*$. In particular, $\mathscr{V}^{\lceil T/\Delta t\rceil}$ is invertible for T sufficiently large. For a set $A_q \times A_p \subset \mathbb{R}^{2D}$, it then holds that

$$\begin{aligned} \mathbb{P}\left(\left(\widetilde{\mathcal{G}}^{\lceil T/\Delta t\rceil}, \mathcal{G}^{\lceil T/\Delta t\rceil}\right) \in E\right) &= (2\pi)^{-D}\det\left(\mathscr{V}^{\lceil T/\Delta t\rceil}\right)^{-1/2} \int_{A_q\times A_p} \exp\left(-\frac{1}{2}x^T\left(\mathscr{V}^{\lceil T/\Delta t\rceil}\right)^{-1}x\right)\,dx \\ &\geqslant \pi^{-D}2^{-3D/2}\det\left(\mathscr{V}\right)^{-1/2}\int_{A_q\times A_p}\exp\left(-x^T\mathscr{V}^{-1}x\right)\,dx. \end{aligned} \tag{5.70}$$

The result follows by combining (5.68)-(5.69)-(5.70) and introducing the probability measure

$$\pi(A_q\times A_p) = Z_R^{-1}\inf_{|\mathscr{Q}|,|\mathscr{P}|\leqslant R}\int_{(A_q-\mathscr{Q})\times(A_p-\mathscr{P})}\exp\left(-x^T\mathscr{V}^{-1}x\right)\,dx,$$

as well as $\alpha = Z_R\pi^{-D}2^{-3D/2}\det\left(\mathscr{V}\right)^{-1/2}$. □

Proposition 5.7 easily follows from the arguments in Section 3.3.1. The inequality (5.66) is proved as for Corollary 4.3.

5.4.3 Error estimates on the invariant measure

In this section we study the error on the average of sufficiently smooth functions, which allows us to characterize the corrections to the invariant measure. In Theorems 5.8 and 5.9, below, we characterize all the first- and second-order splittings; the technique of proof allows us to provide a rigorous study of the error estimates in the overdamped regime (see Section 5.5.2).

We state the results for smooth functions in the sense of Definition 4.4 with $\mathcal{X} = \mathcal{E}$ and $W_n(q,p) = 1 + |p|^{2n}$. A careful analysis of the proof presented in [160], as provided by [97], gives the following stability result.

Theorem 5.7. *The space $\widetilde{\mathcal{S}}$ is stable under $\mathcal{L}^{-1}$ and $(\mathcal{L}^*)^{-1}$.*

If only the order of magnitude of the correction is of interest, and not the expression of the correction in itself, no regularity on the derivatives is required (see [25]), in contrast to situations where such corrections are explicitly considered, as in [160] for instance.

Relating invariant measures of two numerical schemes

We classified in Section 5.4.1 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 (5.61) above (see also (5.71) 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 (5.71) below). See (5.61) for a concrete example.

Lemma 5.7 (Here and elsewhere: TU lemma). *Consider two numerical schemes with associated evolution operators $P_{\Delta t}, Q_{\Delta t}$ bounded on $L^\infty(\mathcal{E})$, for which there exist bounded operators $U_{\Delta t}, T_{\Delta t}$ on $L^\infty(\mathcal{E})$ such that, for all $n \geqslant 1$,*

$$Q_{\Delta t}^n = T_{\Delta t} P_{\Delta t}^{n-1} U_{\Delta t}. \tag{5.71}$$

We also assume that both schemes are ergodic with associated invariant measures denoted respectively by $\mu_{P,\Delta t}$, $\mu_{Q,\Delta t}$: For almost all $(q,p) \in \mathcal{E}$ and $f \in L^\infty(\mathcal{E})$,

$$\lim_{n\to+\infty} P_{\Delta t}^n f(q,p) = \int_{\mathcal{E}} f \, d\mu_{P,\Delta t}, \qquad \lim_{n\to+\infty} Q_{\Delta t}^n f(q,p) = \int_{\mathcal{E}} f \, d\mu_{Q,\Delta t}. \tag{5.72}$$

Then, for all $\varphi \in L^\infty(\mathcal{E})$,

$$\int_{\mathcal{E}} \varphi \, d\mu_{Q,\Delta t} = \int_{\mathcal{E}} (U_{\Delta t}\varphi) \, d\mu_{P,\Delta t}. \tag{5.73}$$

Ergodicity results such as (5.72) are implied by conditions such as (5.66).

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 (5.72) 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 (5.73). □

Let us now show how we will use Lemma 5.7 in the sequel. Assume that a weak error estimate holds on the invariant measure $\mu_{P,\Delta t}$: there exist $\alpha \geqslant 1$ and a function $f_\alpha \in \mathcal{S}$ such that

$$\int_{\mathcal{E}} \psi \, d\mu_{P,\Delta t} = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^\alpha \int_{\mathcal{E}} \psi \, f_\alpha \, d\mu + \Delta t^{\alpha+1} r_{\psi,\alpha,\Delta t},$$

with $|r_{\psi,\alpha,\Delta t}| \leqslant K$ for Δt sufficiently small. Combining this equality and (5.73), the following expansion is obtained for $\mu_{Q,\Delta t}$:

$$\int_{\mathcal{E}} \psi \, d\mu_{Q,\Delta t} = \int_{\mathcal{E}} (U_{\Delta t}\psi) \, d\mu_{P,\Delta t} = \int_{\mathcal{E}} (U_{\Delta t}\psi) \, d\mu + \Delta t^{\alpha} \int_{\mathcal{E}} (U_{\Delta t}\psi) \, f_\alpha \, d\mu + \Delta t^{\alpha+1} r_{U_{\Delta t}\psi,\alpha,\Delta t}.$$

For an evolution operator $U_{\Delta t}$ preserving the measure μ at order $\delta \geqslant 1$, we can write

$$U_{\Delta t} = \mathrm{Id} + \Delta t \, \mathcal{A}_1 + \cdots + \Delta t^{\delta-1} \mathcal{A}_{\delta-1} + \Delta t^{\delta} \, S_\delta + \Delta t^{\delta+1} \, R_{\delta,\Delta t},$$

where all the operators on the right hand side are defined on the core $\mathcal{S}$, and the operators $\mathcal{A}_k$ preserve the measure μ:

$$\forall \varphi \in \mathcal{S}, \qquad \int_{\mathcal{E}} \mathcal{A}_k \varphi \, d\mu = 0,$$

while the operator S_δ does not. For Langevin dynamics, $\mathcal{A}_k$ typically is a composition of the operators $A+B$ and C. In addition, for a given function $\varphi \in \mathcal{S}$, the remainder $R_{\delta,\Delta t}\varphi$ is uniformly bounded for Δt sufficiently small. Three cases should then be distinguished:

(i) When $\delta \geqslant \alpha + 1$, the weak error in the invariant measure $\mu_{Q,\Delta t}$ is of the same order as for $\mu_{P,\Delta t}$ since

$$\int_{\mathcal{E}} \psi \, d\mu_Q = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^{\alpha} \int_{\mathcal{E}} \psi \, f_\alpha \, d\mu + \Delta t^{\alpha+1} \widetilde{r}_{\psi,\alpha,\delta,\Delta t}.$$

(ii) For $\delta \leqslant \alpha - 1$, the weak error in the invariant measure μ_Q arises at dominant order from the operator $U_{\Delta t}$:

$$\int_{\mathcal{E}} \psi \, d\mu_Q = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^{\delta} \int_{\mathcal{E}} \psi \, \left(S_\delta^* \mathbf{1}\right) \, d\mu + \Delta t^{\delta+1} \widetilde{r}_{\psi,\alpha,\delta,\Delta t}.$$

(iii) The interesting case corresponds to $\alpha = \delta$. In this situation,

$$\int_{\mathcal{E}} \psi \, d\mu_Q = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^{\alpha} \int_{\mathcal{E}} \psi \, \left(f_\alpha + S_\alpha^* \mathbf{1}\right) \, d\mu + \Delta t^{\alpha+1} \widetilde{r}_{\psi,\alpha,\delta,\Delta t}. \tag{5.74}$$

An increase in the order of the error on the invariant measure is obtained when the leading order correction vanishes for all admissible observables ψ, that is, if and only if $f_\alpha + S_\alpha^* \mathbf{1} = 0$.

First-order schemes

The following result characterizes at leading order the invariant measure of the schemes based on a first-order splitting (see Section 5.4.1). We first study the error estimates in the invariant measure of the schemes $P_{\Delta t}^{\gamma C,B,A}$, $P_{\Delta t}^{\gamma C,A,B}$ (which can be interpreted as GLA schemes with a symplectic Euler discretization of the Hamiltonian part, see [25]), and then deduce error estimates for the four remaining schemes introduced in Section 5.4.1 by making use of Lemma 5.7.

Theorem 5.8. *Consider any of the first order splittings presented in Section 5.4.1, and denote by $\mu_{\gamma,\Delta t}(dq\,dp)$ its invariant measure. Then there exists a function $f_{1,\gamma} \in \widetilde{\mathcal{S}}$ such that, for any function $\psi \in \mathcal{S}$,*

$$\int_{\mathcal{E}} \psi(q,p) \, \mu_{\gamma,\Delta t}(dq\,dp) = \int_{\mathcal{E}} \psi(q,p) \, \mu(dq\,dp) + \Delta t \int_{\mathcal{E}} \psi(q,p) f_{1,\gamma}(q,p) \, \mu(dq\,dp) + \Delta t^2 r_{\psi,\gamma,\Delta t}, \tag{5.75}$$

where the remainder $r_{\psi,\gamma,\Delta t}$ is uniformly bounded for Δt sufficiently small. The expressions of the correction functions $f_{1,\gamma}$ depend on the numerical scheme at hand. They are defined as the unique solutions of the following Poisson equations:

$$\begin{aligned} \mathcal{L}_\gamma^* f_1^{\gamma C,B,A} &= -\frac{1}{2}(A+B)g, \qquad g(q,p) = \beta p^T M^{-1} \nabla V(q), \\ f_1^{\gamma C,A,B} &= f_1^{A,B,\gamma C} = -f_1^{B,A,\gamma C} = -f_1^{\gamma C,B,A}, \\ f_1^{A,\gamma C,B} &= -f_1^{B,\gamma C,A} = f_1^{\gamma C,B,A} - g. \end{aligned} \tag{5.76}$$

It would in fact possible to obtain bounds on the the remainder $r_{\psi,\gamma,\Delta t}$ with respect to ψ, thanks to functional inequalities given in Appendix A of [97].

Remark 5.10. *The equations* (5.76) *could be analytically solved if, instead of the fluctuation/dissipation operator C, we were using the mass-weighted differential operator as in [107]:*

$$C_M = -p^T \nabla_p + \frac{1}{\beta} M : \nabla_p^2.$$

The corresponding generator $\mathcal{L}_{\gamma,M} = A + B + \gamma C_M$ defined on the core $\mathcal{S}$ is associated with Langevin dynamics where the friction force is proportional to the momenta rather than velocities. A simple computation shows that

$$-\frac{1}{2}(A+B)g = \mathcal{L}^*_{\gamma,M}\left(\frac{\beta}{2}V - g\right).$$

The condition (5.76) *would be replaced by $\mathcal{L}^*_{\gamma,M} f_1^{\gamma C,B,A} = -(A+B)g/2$, so that $f_1^{\gamma C,B,A} = \beta V/2 - g + c$ where c is a constant ensuring that $f_1^{\gamma C,B,A}$ has a vanishing average with respect to μ.*

Hamiltonian limit of the correction term

For first order splitting schemes, the limit of the leading order correction term in (5.75) can be studied as $\gamma \to 0$. Not surprisingly, it turns out that the leading order correction is the first term in the expansion of the modified Hamiltonian of the symplectic Euler method in powers of Δt (see (2.32)). In contrast to the more complete proof we are able to present for the overdamped limit (see Section 5.5), we were not able to study the behavior of the remainder terms $r_{\psi,\gamma,\Delta t}$ in (5.75). There is a technical obstruction to controlling these remainders from the way we prove our results since the limiting operator $\mathcal{L}_0 = A + B$ is not invertible. Let us also mention that studying the corresponding Hamiltonian limit for second order schemes turns out to be a much more difficult question (see Remark 5.11).

Proposition 5.8. *There exists a constant $K > 0$ such that, for all $0 < \gamma \leqslant 1$,*

$$\left\| f_1^{\gamma C,B,A} - \frac{\beta}{2} p^T M^{-1} \nabla V \right\|_{L^2(\mu)} \leqslant K\gamma,$$

with similar estimates for $f_1^{B,\gamma C,A}$ and $f_1^{B,A,\gamma C}$; and

$$\left\| f_1^{\gamma C,A,B} + \frac{\beta}{2} p^T M^{-1} \nabla V \right\|_{L^2(\mu)} \leqslant K\gamma,$$

with similar estimates for $f_1^{A,\gamma C,B}$ and $f_1^{A,B,\gamma C}$.

Second-order schemes

The following result characterizes at leading order the invariant measure of the schemes based on a second-order splitting (see Section 5.4.1).

Theorem 5.9. *Consider any of the second order splittings presented in Section 5.4.1, and denote by $\mu_{\gamma,\Delta t}(dq\,dp)$ its invariant measure. Then there exists a function $f_{2,\gamma} \in \widetilde{\mathcal{S}}$ such that, for any function $\psi \in \mathcal{S}$,*

$$\int_{\mathcal{E}} \psi(q,p)\,\mu_{\gamma,\Delta t}(dq\,dp) = \int_{\mathcal{E}} \psi(q,p)\,\mu(dq\,dp) + \Delta t^2 \int_{\mathcal{E}} \psi(q,p) f_{2,\gamma}(q,p)\,\mu(dq\,dp) + \Delta t^4 r_{\psi,\gamma,\Delta t}, \quad (5.77)$$

where the remainder $r_{\psi,\gamma,\Delta t}$ is uniformly bounded for Δt sufficiently small. The expressions of the correction functions $f_{2,\gamma}$ depend on the numerical scheme at hand. They are defined as the unique solutions of the following Poisson equations:

$$
\begin{aligned}
\mathcal{L}_\gamma^* f_2^{\gamma C,B,A,B,\gamma C} &= \frac{1}{12}(A+B)\left[\left(A+\frac{B}{2}\right)g\right], \qquad g(q,p) = \beta p^T M^{-1}\nabla V(q),\\
\mathcal{L}_\gamma^* f_2^{\gamma C,A,B,A,\gamma C} &= -\frac{1}{12}(A+B)\left[\left(B+\frac{A}{2}\right)g\right],\\
f_2^{A,B,\gamma C,B,A} &= f_2^{\gamma C,B,A,B,\gamma C} + \frac{1}{8}(A+B)g,\\
f_2^{B,A,\gamma C,A,B} &= f_2^{\gamma C,A,B,A,\gamma C} - \frac{1}{8}(A+B)g.
\end{aligned}
\tag{5.78}
$$

Let us emphasize that no Δt^3 correction term appears in (5.77) after the Δt^2 term. In fact, a more careful treatment would allow us to write an error expansion in terms of higher orders of Δt, with only even powers of Δt appearing.

The results from Theorem 5.9 allow us to obtain error estimates for the so-called Geometric Langevin Algorithms (GLA) introduced in [25]. Recall the somewhat surprising result that the error in the invariant measure of the GLA schemes is of order Δt^p for a discretization of order p of the Hamiltonian part, even though the weak and strong orders of the scheme are only one. The following result complements the estimate given in [25] by making precise the leading order corrections to the invariant measure of the numerical scheme with respect to the canonical measure.

Corollary 5.4 (Error estimates for GLA schemes). *Consider one of the GLA schemes defined in* (5.62)*, and denote by $\mu_{\gamma,\Delta t}(dq\,dp)$ its invariant measure. Then there exist functions $f_{2,\gamma}, f_{3,\gamma} \in \widetilde{\mathcal{S}}$ such that, for any function $\psi \in \mathcal{S}$,*

$$
\begin{aligned}
\int_{\mathcal{E}} \psi(q,p)\,\mu_{\gamma,\Delta t}(dq\,dp) = \int_{\mathcal{E}} \psi(q,p)\,\mu(dq\,dp) + \Delta t^2 \int_{\mathcal{E}} \psi(q,p) f_{2,\gamma}(q,p)\,\mu(dq\,dp)\\
+ \Delta t^3 \int_{\mathcal{E}} \psi(q,p) f_{3,\gamma}(q,p)\,\mu(dq\,dp) + \Delta t^4 r_{\psi,\gamma,\Delta t},
\end{aligned}
\tag{5.79}
$$

where the remainder $r_{\psi,\gamma,\Delta t}$ is uniformly bounded for Δt sufficiently small. The expressions of the correction functions $f_{2,\gamma}$ and $f_{3,\gamma}$ are

$$
\begin{aligned}
f_2^{\gamma C,A,B,A} &= f_2^{\gamma C,A,B,A,\gamma C}, \qquad & f_3^{\gamma C,A,B,A} &= -\frac{\gamma}{2} C f_2^{\gamma C,A,B,A},\\
f_2^{\gamma C,B,A,B} &= f_2^{\gamma C,B,A,B\gamma C}, \qquad & f_3^{\gamma C,B,A,B} &= -\frac{\gamma}{2} C f_2^{\gamma C,B,A,B}.
\end{aligned}
$$

Note that the leading order term of the error is the same as for the corresponding second order splitting schemes. The next order correction (of order Δt^3) vanishes for functions ψ depending only on the position variable q.

Proof (of Corollary 5.4). The proof relies on the results of Theorem 5.9 and the TU lemma (Lemma 5.7). More precisely, the error estimate (5.79) is established by following the same lines of proof as for second order splitting schemes (see Section 5.4.4), except that the contributions of order Δt^3 do not vanish. We then use the TU lemma by considering the GLA evolution as the reference, and express the invariant measure of second order splitting schemes in terms of the invariant measure of the GLA scheme. For instance, consider $P_{\Delta t}^{\gamma C,B,A,B}$ and $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$, in which case $U_{\Delta t} = \mathrm{e}^{\gamma \Delta t C/2}$. Then,

$$
\begin{aligned}
&\int_{\mathcal{E}} \psi\, d\mu_{\Delta t}^{\gamma C,B,A,B,\gamma C} = \int_{\mathcal{E}} (U_{\Delta t}\psi)\, d\mu_{\Delta t}^{\gamma C,B,A,B}\\
&= \int_{\mathcal{E}} U_{\Delta t}\psi\, d\mu + \Delta t^2 \int_{\mathcal{E}} (U_{\Delta t}\psi) f_2^{\gamma C,B,A,B}\, d\mu + \Delta t^3 \int_{\mathcal{E}} (U_{\Delta t}\psi) f_3^{\gamma C,B,A,B}\, d\mu + \Delta t^4 r_{\psi,\gamma,\Delta t}\\
&= \int_{\mathcal{E}} \psi\, d\mu + \Delta t^2 \int_{\mathcal{E}} \psi\, f_2^{\gamma C,B,A,B}\, d\mu + \Delta t^3 \int_{\mathcal{E}} \psi \left(f_3^{\gamma C,B,A,B} + \frac{\gamma}{2} C f_2^{\gamma C,B,A,B}\right) d\mu + \Delta t^4 \widetilde{r}_{\psi,\gamma,\Delta t},
\end{aligned}
$$

where we have used the invariance of μ by $U_{\Delta t}$. The comparison with (5.77)-(5.78) gives the desired result. □

Remark 5.11 (Hamiltonian limit of the correction functions $f_{2,\gamma}$). *Proving a result similar to Proposition 5.8 for second order splitting schemes or GLA schemes turns out to be much more difficult, although we formally expect that the limit of $f_{2,\gamma}$ as $\gamma \to 0$ is the first order correction of the modified Hamiltonian constructed by backward analysis. From* (5.78)*, it should indeed be the case that $f_2^{\gamma C,B,A,B,\gamma C}$ converges to*

$$f_2^{B,A,B} = -\frac{1}{12}\left(A + \frac{B}{2}\right) g.$$

Moreover, as we already mentioned before Proposition 5.8, we are not able to uniformly control remainder terms in the error expansion (5.77) *as $\gamma \to 0$.*

5.4.4 Elements of proof

The proof of the above results follows the lines of the general argument presented in Section 4.4.4. We therefore provide only the required additional points, namely the algebra necessary to write expansions of the evolution operators in powers of Δt, reformulations of the Poisson equations to be solved, and the proof of the Hamiltonian limit for first order schemes.

Expansion of the evolution operators

The first point is however to obtain expressions for evolution operators of the form

$$P_t = \mathrm{e}^{tA_M} \dots \mathrm{e}^{tA_1},$$

which can easily be compared to the evolution operator $\mathrm{e}^{t(A_1+\dots+A_M)}$. For the elementary generators A, B, C defined in (5.59), it is in fact possible to analytically write down the action of the associated semigroups:

$$\begin{cases} \left(\mathrm{e}^{tA}\varphi\right)(q,p) = \varphi\Big(q + tM^{-1}p, p\Big), \\ \left(\mathrm{e}^{tB}\varphi\right)(q,p) = \varphi\Big(q, p - t\nabla V(q)\Big), \\ \left(\mathrm{e}^{tC}\varphi\right)(q,p) = \displaystyle\int_{\mathbb{R}^D} \varphi\left(q, \mathrm{e}^{-\gamma M^{-1}t}p + \left(\frac{1-\mathrm{e}^{-2\gamma M^{-1}t}}{\beta}M\right)^{1/2} x\right) \frac{\mathrm{e}^{-|x|^2/2}}{(2\pi)^{D/2}}\, dx. \end{cases} \tag{5.80}$$

Coming back to the general case, the key building block for the subsequent numerical analysis is the following equality (already encountered in Section 2.2.2):

$$P_t = P_0 + t\left.\frac{dP_t}{dt}\right|_{t=0} + \frac{t^2}{2}\left.\frac{d^2P_t}{dt^2}\right|_{t=0} + \dots + \frac{t^n}{n!}\left.\frac{d^nP_t}{dt^n}\right|_{t=0} + \frac{t^{n+1}}{n!}\int_0^1 (1-\theta)^n \left.\frac{d^{n+1}P_s}{ds^{n+1}}\right|_{s=\theta t} d\theta.$$

Now,

$$\begin{aligned} \frac{dP_t}{dt} &= A_M \mathrm{e}^{tA_M} \dots \mathrm{e}^{tA_1} + \mathrm{e}^{tA_M} A_{M-1} \mathrm{e}^{tA_{M-1}} \dots \mathrm{e}^{tA_1} + \dots + \mathrm{e}^{tA_M} \dots \mathrm{e}^{tA_1} A_1 \\ &= \mathcal{T}\left[(A_1 + \dots + A_M) P_t\right] \end{aligned}$$

where $\mathcal{T}$ is a notation indicating that the operators with the smallest indices (or their associated semigroups) are farthest to the right. In fact, simple computations show that

$$\frac{d^nP_t}{dt^n} = \mathcal{T}\Big[(A_1 + \dots + A_M)^n P_t\Big].$$

Therefore, the following equality holds when applied to smooth functions:

$$P_t\varphi = \varphi + t(A_1+\cdots+A_M)\varphi + \frac{t^2}{2}\mathcal{T}\Big[(A_1+\cdots+A_M)^2\Big]\varphi + \cdots + \frac{t^n}{n!}\mathcal{T}\Big[(A_1+\cdots+A_M)^n\Big]\varphi + \frac{t^{n+1}}{n!}\int_0^1 (1-\theta)^n \mathcal{T}\Big[(A_1+\cdots+A_M)^{n+1}P_{\theta t}\Big]\varphi\, d\theta. \tag{5.81}$$

In order to rewrite the various terms in the right-hand side of (5.81) in a form more amenable to analytical computations, *i.e.*

$$\mathcal{T}\Big[(A_1+\cdots+A_M)^n\Big] = (A_1+\cdots+A_M)^n + S_n,$$

where the operator S_n involves commutators $[A_i, A_j]$, we rely on extensions of the BCH formula for two operators (provided in Section 2.2.2) obtained by composing it:

$$\mathrm{e}^{\Delta t A_3}\mathrm{e}^{\Delta t A_2}\mathrm{e}^{\Delta t A_1} = \mathrm{e}^{\Delta t \mathcal{A}}, \qquad \mathcal{A} = A_1 + A_2 + A_3 + \frac{\Delta t}{2}\Big([A_3, A_1+A_2] + [A_2, A_1]\Big) + \dots,$$

and

$$\mathrm{e}^{\Delta t A_1/2}\mathrm{e}^{\Delta t A_2/2}\mathrm{e}^{\Delta t A_3}\mathrm{e}^{\Delta t A_2/2}\mathrm{e}^{\Delta t A_1/2} = \mathrm{e}^{\Delta t \mathcal{A}}, \tag{5.82}$$

with

$$\mathcal{A} = A_1 + A_2 + A_3 + \frac{\Delta t^2}{12}\Big([A_3,[A_3,A_2]] + [A_2+A_3,[A_2+A_3,A_1]] - \frac{1}{2}[A_2,[A_2,A_3]] - \frac{1}{2}[A_1,[A_1,A_2+A_3]]\Big) + \dots$$

where we do not write down the expressions of the higher order terms Δt^{2n} (for $n \geqslant 2$). Let us insist that these formulas are only formal (since the operators appearing in the argument of the exponential on the right-hand side involve more and more derivatives), but nonetheless allow us to find the algebraic expressions of S_n upon formally expanding the exponential as

$$\mathrm{e}^{\Delta t \mathcal{A}} = \mathrm{Id} + \Delta t \mathcal{A} + \frac{\Delta t^2}{2}\mathcal{A}^2 + \dots$$

and identifying terms with the same powers of Δt in (5.81).

Expression of the correction functions

We present the computation of some correction functions, taking as an illustration (5.76). The function $f_1^{\gamma C,B,A} \in \widetilde{\mathcal{S}}$ (denoted by $f_{1,\gamma}$ above) is uniquely determined by the equation

$$\mathcal{L}_\gamma^* f_1^{\gamma C,B,A} = -\frac{1}{2}S_1^*\mathbf{1} = -\frac{1}{2}\Big([C, A+B] + [B,A]\Big)^*\mathbf{1}, \qquad \int_{\mathcal{E}} f_1^{\gamma C,B,A}\, d\mu = 0,$$

where we have used $[\mathcal{L}_\gamma^2]^*\mathbf{1} = 0$ to simplify the right-hand side. Now, $[C, A+B]^* = [C, A+B]$ since $C^* = C$ and $(A+B)^* = -(A+B)$. Therefore, $[C, A+B]^*\mathbf{1} = 0$. In addition,

$$[B,A]^*\mathbf{1} = -(A+B)^* g = (A+B)g,$$

since $A^* = -A + g$ and $B^* = -B - g$. Therefore,

$$S_1^*\mathbf{1} = (A+B)g. \tag{5.83}$$

This gives the first expression in (5.76).

Hamiltonian limit of the correction term for first-order splittings

To obtain the expressions of $f_1^{A,\gamma C,B}$ and $f_1^{B,A,\gamma C}$, we use the TU lemma, where the operators $U_{\Delta t}$ respectively read $\mathrm{e}^{\gamma \Delta t C}\mathrm{e}^{\Delta t B} = \mathrm{Id} + \Delta t(B + \gamma C) + \Delta t^2 R_{\Delta t}$ and $\mathrm{e}^{\gamma \Delta t C}$ (which preserves μ). We actually are in a situation similar to (5.74):

$$f_1^{B,A,\gamma C} = f_1^{\gamma C,B,A}, \qquad f_1^{A,\gamma C,B} = f_1^{\gamma C,B,A} + B^*\mathbf{1}.$$

The expressions for the first order corrections when the operators A and B are exchanged are obtained by noting that the sign of $S_1^*\mathbf{1}$ is changed and that $f_1^{B,\gamma C,A} = f_1^{\gamma C,A,B} + A^*\mathbf{1}$.

To obtain the Hamiltonian limit, we use a very standard strategy: first, we propose an ansatz for the correction term $f_{1,\gamma}$ as

$$f_{1,\gamma} = f_1^0 + \gamma f_1^1 + \gamma^2 f_1^2 + \dots,$$

then identify the two leading order terms in this expression, and finally use the resolvent estimate (5.31) to conclude. Note that our ansatz is not obvious since the estimate (5.31) shows that, in general, a leading order correction term of order $1/\gamma$ should be considered. It turns out however that, due to the specific structure of the right-hand side of (5.76) (namely the fact that the right-hand is at leading order in γ the image under the Hamiltonian operator of some function), such a divergent leading order term is not necessary.

Consider for instance the case when $f_{1,\gamma}$ is $f_1^{\gamma C,B,A}$. This function solves

$$\Big[-(A+B) + \gamma C\Big] f_1^{\gamma C,B,A} = -\frac{1}{2}(A+B)g, \qquad \int_{\mathcal{E}} f_1^{\gamma C,B,A}\, d\mu = 0,$$

so that we consider the ansatz $f_1^{\gamma C,B,A} = g/2 + \gamma f_1^1 + \dots$. Identifying terms with same powers of γ, we see that the correction term f_1^1 should satisfy

$$(A+B) f_1^1 = \frac{1}{2} C g = \frac{\beta}{2} p^T M^{-2} \nabla V.$$

Possible solutions are defined up to elements of the kernel of $A + B$ (which contains function of the form $\varphi \circ H$). One possible choice is to set $f_1^1 = \beta p^T M^{-2} p/4 + c_1^1$, where the constant c_1^1 is chosen in order for f_1^1 to have a vanishing average with respect to μ. Then,

$$\mathcal{L}_\gamma^* \left(f_1^{\gamma C,B,A} - \frac{g}{2} - \gamma f_1^1 \right) = \gamma^2 C f_1^1.$$

In view of (5.31), this implies that there exists a constant $K > 0$ such that

$$\left\| f_1^{\gamma C,B,A} - \frac{g}{2} - \gamma f_1^1 \right\|_{L^2(\mu)} \leqslant K\gamma,$$

for $\gamma \leqslant 1$, which gives the desired estimate on $f_1^{\gamma C,B,A}$. Similar computations give the estimate on $f_1^{\gamma C,A,B}$, while the estimates on the remaining functions are obtained from (5.76).

5.5 Overdamped limit

In this section, we denote by $\mathcal{L}_\gamma$ the resolvent of the Langevin operator in order to highlight the dependence on the friction parameter. For simplicity, we set $M = \mathrm{Id}$ in this section.

5.5.1 Limit of the continuous dynamics

Finite time limit of the stochastic processes

Let us first non-dimensionalize the Langevin equations by introducing three units:

- a unit of time t_0,
- a unit of length l_0,
- a unit of mass m_0.

Let us introduce the non-dimensional variables associated to these characteristic quantities:

$$\bar{t} = \frac{t}{t_0}, \qquad \overline{W}_{\bar{t}} = \frac{1}{\sqrt{t_0}} W_{t_0 \bar{t}},$$

$$\overline{q}_{\bar{t}} = \frac{q_t}{l_0} = \frac{q_{t_0\bar{t}}}{l_0}, \qquad \overline{p}_{\bar{t}} = \frac{p_t}{m_0 l_0 t_0^{-1}} = \frac{p_{t_0\bar{t}}}{m_0 l_0 t_0^{-1}},$$

$$\overline{V}(\overline{q}) = \beta V(q) = \beta V(l_0 \overline{q}).$$

Notice that $\overline{W}_{\bar{t}}$ is a standard $3N$-dimensional Brownian motion.

By a change of variable, the non-dimensional Langevin equation then writes:

$$\begin{cases} d\overline{q}_{\bar{t}} = m_0 m^{-1} \overline{p}_{\bar{t}}\, d\bar{t}, \\ d\overline{p}_{\bar{t}} = -m_0^{-1} l_0^{-2} \beta^{-1} t_0^2 \nabla_{\overline{q}} \overline{V}(\overline{q}_{\bar{t}})\, d\bar{t} - \gamma m^{-1} t_0 \overline{p}_{\bar{t}}\, d\bar{t} + \sqrt{2\beta^{-1}\gamma t_0^3 m_0^{-2} l_0^{-2}}\, d\overline{W}_{\bar{t}}. \end{cases}$$

Using the following non-dimensional numbers:

$$\alpha_1 = \frac{m}{m_0}, \qquad \alpha_2 = \frac{\gamma t_0}{m_0}, \qquad \alpha_3 = \frac{\beta m_0 l_0^2}{t_0^2},$$

this equation can be rewritten as

$$\begin{cases} d\overline{q}_{\bar{t}} &= \overline{v}_{\bar{t}}\, d\bar{t}, \\ \alpha_1 d\overline{v}_{\bar{t}} = -\dfrac{1}{\alpha_3} \nabla_{\overline{q}} \overline{V}(\overline{q}_{\bar{t}})\, d\bar{t} - \alpha_2 \overline{v}_{\bar{t}}\, d\bar{t} + \sqrt{2\dfrac{\alpha_2}{\alpha_3}}\, d\overline{W}_{\bar{t}}, \end{cases} \tag{5.84}$$

where we introduced the velocity $v_t = m^{-1} p_t$, which is non-dimensionalized (consistently with the previous non-dimensionalization) as $\overline{v}_{\bar{t}} = m_0 m^{-1} \overline{p}_{\bar{t}}$.

Consider now the following scaling for a small parameter $\varepsilon > 0$:

$$\frac{1}{\alpha_3} = \alpha_2 = \sqrt{\frac{\alpha_2}{\alpha_3}} = \frac{\alpha_1}{\varepsilon}. \tag{5.85}$$

The physical interpretation of this condition is discussed more precisely in Remark 5.12 below. Dropping the bar for the ease of notation, we get from (5.84):

$$\begin{cases} dq_t &= v_t\, dt, \\ \varepsilon dv_t = -\nabla V(q_t)\, dt - v_t\, dt + \sqrt{2}\, dW_t. \end{cases} \tag{5.86}$$

By noticing that the second equation can be reformulated as

$$\varepsilon dv_t = -\nabla V(q_t)\, dt - dq_t + \sqrt{2}\, dW_t,$$

it is intuitively clear that in the limit $\varepsilon \to 0$, the limiting process on positions is the overdamped Langevin process:

$$dq_t^0 = -\nabla V(q_t^0)\, dt + \sqrt{2}\, dW_t. \tag{5.87}$$

Let us now state a precise result concerning the limit $\varepsilon \to 0$.

Proposition 5.9. *Denote by $(q_t^\varepsilon, v_t^\varepsilon)$ the solution to* (5.86)*, with a given initial condition $(q_0^\varepsilon, v_0^\varepsilon) = (q_{\text{init}}, v_0)$, and assume that ∇V is a Lipschitz function. Then, the following pathwise convergence holds: for any time $t > 0$,*

$$\lim_{\varepsilon \to 0} \sup_{0 \leqslant s \leqslant t} \|q_s^\varepsilon - q_s^0\| = 0 \qquad a.s.,$$

where $(q_t^0)_{t \geqslant 0}$ is the solution to (5.87) *with the initial condition $q_0^0 = q_{\text{init}}$.*

Proof. It is easily seen from (5.86) that

$$v_t^\varepsilon = v_0 \, \mathrm{e}^{-t/\varepsilon} - \varepsilon^{-1} \int_0^t \mathrm{e}^{-(t-s)/\varepsilon} \nabla V(q_s) \, ds + \varepsilon^{-1} \sqrt{2} \int_0^t \mathrm{e}^{-(t-s)/\varepsilon} \, dW_s.$$

Thus,

$$\begin{aligned}
q_t^\varepsilon &= q_{\text{init}} + \int_0^t v_s^\varepsilon \, ds \\
&= q_{\text{init}} + \int_0^t v_0 \, \mathrm{e}^{-s/\varepsilon} \, ds - \varepsilon^{-1} \int_0^t \int_0^s \mathrm{e}^{-(s-r)/\varepsilon} \nabla V(q_r^\varepsilon) \, dr \, ds + \varepsilon^{-1} \sqrt{2} \int_0^t \int_0^s \mathrm{e}^{-(s-r)/\varepsilon} \, dW_r \, ds \\
&= q_{\text{init}} + v_0 \, \varepsilon (1 - \mathrm{e}^{-t/\varepsilon}) - \varepsilon^{-1} \int_0^t \int_r^t \mathrm{e}^{-(s-r)/\varepsilon} \, ds \nabla V(q_r^\varepsilon) \, dr + \varepsilon^{-1} \sqrt{2} \int_0^t \int_r^t \mathrm{e}^{-(s-r)/\varepsilon} \, ds \, dW_r \\
&= q_{\text{init}} + v_0 \, \varepsilon (1 - \mathrm{e}^{-t/\varepsilon}) - \int_0^t \left(1 - \mathrm{e}^{-(t-r)/\varepsilon}\right) \nabla V(q_r^\varepsilon) \, dr + \sqrt{2} \int_0^t \left(1 - \mathrm{e}^{-(t-r)/\varepsilon}\right) \, dW_r.
\end{aligned}$$

From (5.87),

$$q_t^0 = q_{\text{init}} - \int_0^t \nabla V(q_s^0) \, ds + \sqrt{2} \int_0^t dW_s$$

with the same Brownian motion, so that, finally,

$$\begin{aligned}
q_t^\varepsilon - q_t^0 = &- \int_0^t \left(1 - \mathrm{e}^{-(t-r)/\varepsilon}\right) \left(\nabla V(q_r^\varepsilon) - \nabla V(q_r^0)\right) \, dr \\
&+ v_0 \, \varepsilon (1 - \mathrm{e}^{-t/\varepsilon}) + \int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \nabla V(q_r^0) \, dr - \sqrt{2} \int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \, dW_r.
\end{aligned} \tag{5.88}$$

The first term is bounded by $kt \sup_{s \leqslant t} \left|q_s^\varepsilon - q_s^0\right|$, where k is the Lipschitz constant of ∇V. As $\varepsilon \to 0$, the second term on the right-hand side converges to zero uniformly on compact time intervals. For the third term,

$$\left| \int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \nabla V(q_r^0) \, dr \right| \leqslant \max_{0 \leqslant r \leqslant t} \|\nabla V(q_r^0)\| \, \varepsilon (1 - \mathrm{e}^{-t/\varepsilon}),$$

so that this integral also converges to zero uniformly on compact time intervals. For the last term, an integration by parts gives:

$$\int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \, dW_r = \int_0^t \frac{\mathrm{e}^{-(t-r)/\varepsilon}}{\varepsilon} \left(W_t - W_r\right) dr + W_t \, \mathrm{e}^{-t/\varepsilon}.$$

By the continuity of paths of Brownian motion (and thus uniform continuity on compact intervals), the first term also goes to zero uniformly on compact interval in time, while the second one converges to zero uniformly on compact time intervals. Thus, for a fixed time t_0,

$$\forall t \leqslant t_0, \qquad \sup_{s \leqslant t} \left|q_s^\varepsilon - q_s^0\right| \leqslant k \int_0^t \sup_{r \leqslant s} \left|q_r^\varepsilon - q_r^0\right| \, ds + r_{t_0}(\varepsilon),$$

with $r_{t_0}(\varepsilon) \to 0$ as $\varepsilon \to 0$. An application of Gronwall's lemma yields the result. □

Remark 5.12 (Physical interpretation of the scaling (5.85)). *Equation (5.85) implies that, for a given value $\varepsilon > 0$ there is actually only one free parameter among $(\alpha_1, \alpha_2, \alpha_3)$, the other two being then automatically fixed, since (5.85) is equivalent to*

$$\frac{1}{\alpha_3} = \alpha_2 = \frac{\alpha_1}{\varepsilon}.$$

(i) Overdamped limit*: This is the case when α_1 is independent of ε, namely*

$$\alpha_1 = 1, \qquad \alpha_2 = \varepsilon^{-1}, \qquad \alpha_3 = \varepsilon. \tag{5.89}$$

This can be obtained in practice by setting $\gamma = \varepsilon^{-1/2}$ and $t_0 = \varepsilon^{-1/2}$ (the other parameters being independent of ε, so that $\overline{V}$ does not depend on ε). This amounts to assuming a change of the time scaling, and a very large friction force.

(ii) Zero-mass limit*: This is the case when α_2 (or equivalently α_3) is independent of ε:*

$$\alpha_1 = \varepsilon, \quad \alpha_2 = \alpha_3 = 1. \tag{5.90}$$

This can be obtained in practice by setting $m = \varepsilon$, the other parameters being chosen independently of ε (again, $\overline{V}$ does not depend on ε).

Asymptotic expansion of the resolvent

The following result gives bounds on the resolvent of the Langevin generator in the overdamped regime, and in fact quantifies the difference between the resolvent $\mathcal{L}_\gamma^{-1}$ and the resolvent $\mathcal{L}_{\rm ovd}^{-1}$ appropriately rescaled by a factor γ (in order to take into account the time rescaling). We introduce

$$\widetilde{H}^1(\mu) = H^1(\mu) \backslash \mathrm{Ker}(\mathcal{L}_\gamma) = \left\{ u \in H^1(\mu) \;\middle|\; \int_{\mathcal{E}} u \, d\mu = 0 \right\},$$

and the projection operator

$$(\pi\varphi)(q) = \int_{\mathbb{R}^D} \varphi(q,p)\, \kappa(dp), \tag{5.91}$$

which averages functions with respect to momenta.

Theorem 5.10. *There exist two constants $c_-, c_+ > 0$ such that, for any $\gamma \geqslant 1$,*

$$c_- \gamma \leqslant \|\mathcal{L}_\gamma^{-1}\|_{\mathcal{B}(\widetilde{H}^1(\mu))} \leqslant c_+ \gamma. \tag{5.92}$$

More precisely, there exists a constant $K > 0$ such that, for any $\gamma \geqslant 1$,

$$\begin{aligned} \left\| \mathcal{L}_\gamma^{-1} - \gamma \mathcal{L}_{\rm ovd}^{-1}\pi - p^T \nabla_q \mathcal{L}_{\rm ovd}^{-1}\pi + \mathcal{L}_{\rm ovd}^{-1}\pi(A+B)C^{-1}(\mathrm{Id}-\pi) \right\|_{\mathcal{B}(\widetilde{H}^1(\mu))} &\leqslant \frac{K}{\gamma}, \\ \left\| \left(\mathcal{L}_\gamma^*\right)^{-1} - \gamma \mathcal{L}_{\rm ovd}^{-1}\pi + p^T \nabla_q \mathcal{L}_{\rm ovd}^{-1}\pi - \mathcal{L}_{\rm ovd}^{-1}\pi(A+B)C^{-1}(\mathrm{Id}-\pi) \right\|_{\mathcal{B}(\widetilde{H}^1(\mu))} &\leqslant \frac{K}{\gamma}, \end{aligned} \tag{5.93}$$

where $(C^{-1}\psi)(q,p)$ is understood as applying the operator C^{-1} to the function $\psi(q,\cdot) \in L^2(\kappa)$ for all values of $q \in \mathcal{D}$.

Note that the function $\mathcal{L}_{\rm ovd}^{-1}\pi f$ is well defined since, as f belongs to $\widetilde{H}^1(\mu)$, the function πf has a vanishing average with respect to ν. The fact that $\mathcal{L}_{\rm ovd}^{-1}\pi(A+B)C^{-1}(\mathrm{Id}-\pi)$ is bounded on $\widetilde{H}^1(\mu)$ is discussed in the proof of Theorem 5.10. An important ingredient in the proof is the following estimate, which we call uniform hypocoercivity estimate since the resolvent bound is independent of γ in contrast to (5.31).

Lemma 5.8 (Uniform hypocoercivity for large frictions). *Consider the following subspace of $H^1(\mu)$:*

$$\mathcal{H}^1_\perp = \left\{ u \in \widetilde{H}^1(\mu) \;\middle|\; \overline{u}(q) = \int_{\mathbb{R}^D} u(q,p)\,\kappa(dp) = 0 \right\}.$$

There exists a constant $K > 0$ such that, for any $\gamma \geqslant 1$,

$$\forall f \in \mathcal{H}^1_\perp, \qquad \|\mathcal{L}_\gamma^{-1} f\|_{H^1(\mu)} \leqslant K \|f\|_{H^1(\mu)}.$$

Proof (of Lemma 5.8). We show that the operator $\mathcal{L}_\gamma$ is uniformly hypocoercive for $\gamma \geqslant 1$. The aim is to obtain bounds on the inverse $\mathcal{L}_\gamma^{-1}$ extended to $\mathcal{H}^1_\perp$. To this end, we decompose $\mathcal{L}_\gamma$ for $\gamma \geqslant 1$ as

$$\mathcal{L}_\gamma = \mathcal{L}_1 + (\gamma - 1)C.$$

From the results of Section 5.3.3, there exist $\widetilde{\alpha} > 0$ and coefficients $b \ll a = c \ll 1$ satisfying (5.15) and such that, for all $u \in \mathcal{S}$,

$$-\langle\langle u, \mathcal{L}_1 u \rangle\rangle \geqslant \widetilde{\alpha}\, \langle\langle u, u \rangle\rangle .$$

It follows that there exists $\alpha > 0$ independent of γ such that

$$\alpha\, \|u\|^2_{H^1(\mu)} - (\gamma - 1)\, \langle\langle u, Cu \rangle\rangle \leqslant -\langle\langle u, \mathcal{L}_\gamma u \rangle\rangle . \tag{5.94}$$

Let us now show that

$$\forall u \in \mathcal{H}^1_\perp \cap \mathcal{S}, \qquad -\langle\langle u, Cu \rangle\rangle \geqslant 0. \tag{5.95}$$

Using the equality

$$C = -\frac{1}{\beta} \sum_{i=1}^D \partial^*_{p_i} \partial_{p_i},$$

and the commutation relations $[\partial_{p_i}, \partial^*_{p_j}] = \beta \delta_{ij}$, a simple computation shows

$$\begin{aligned}
\left\langle\left\langle u, (\partial_{p_i})^* \, \partial_{p_i} u \right\rangle\right\rangle &= (1 + \beta a) \|\partial_{p_i} u\|^2 + a \|\nabla_p \partial_{p_i} u\|^2 \\
&\quad + a \|\nabla_q \partial_{p_i} u\|^2 - 2b \langle \nabla_q \partial_{p_i} u, \nabla_p \partial_{p_i} u \rangle - \beta b \langle \partial_{q_i} u, \partial_{p_i} u \rangle \\
&\geqslant \left(1 + \beta \left(a - \frac{b}{2}\right)\right) \|\partial_{p_i} u\|^2 + (a - b)\, \|\nabla_p \partial_{p_i} u\|^2 \\
&\quad + (a - b) \|\nabla_q \partial_{p_i} u\|^2 - \frac{\beta b}{2} \|\partial_{q_i} u\|^2.
\end{aligned}$$

Now, since the Gaussian measure $\kappa(dp)$ satisfies a Poincaré inequality, there exists a constant $A > 0$ such that, for all $i = 1, \ldots, D$

$$\|\partial_{q_i} u\|^2 \leqslant A \|\nabla_p \partial_{q_i} u\|^2.$$

Note indeed that $\partial_{q_i} u$ has a vanishing average with respect to the Gaussian measure $\kappa(dp)$ because

$$\int_{\mathbb{R}^D} \partial_{q_i} u(q,p)\, \kappa(dp) = \partial_{q_i} \overline{u}(q) = 0$$

for functions $u \in \mathcal{H}^1_\perp$. Therefore,

$$\sum_{i=1}^D \|\partial_{q_i} u\|^2 \leqslant A \sum_{i,j=1}^D \|\partial_{p_j} \partial_{q_i} u\|^2 = A \sum_{j=1}^D \|\nabla_q \partial_{p_j}\|^2.$$

Summing on $i \in \{1, \ldots, D\}$, the quantity (5.95) is seen to be non-negative for an appropriate choice of constants $a \gg b \gg 1$.

From (5.94), we then deduce that there exists a constant $K > 0$ such that, for any $\gamma \geqslant 1$ and for any $u \in \mathcal{H}^1_\perp \cap \mathcal{S}$, it holds $\|u\|_{H^1(\mu)} \leqslant K \|\mathcal{L}_\gamma u\|_{H^1(\mu)}$. Taking inverses and by density of $\mathcal{H}^1_\perp \cap \mathcal{S}$ into $\mathcal{H}^1_\perp$,

$$\forall \gamma \geqslant 1, \quad \forall u \in \mathcal{H}^1_\perp, \qquad \left\|\mathcal{L}_\gamma^{-1} u\right\|_{H^1(\mu)} \leqslant K \|u\|_{H^1(\mu)},$$

which is the desired result. □

We are now in position to give the proof of Theorem 5.10.

Proof (of Theorem 5.10). We write the proof for $\mathcal{L}_\gamma^{-1}$. The estimates for $(\mathcal{L}_\gamma^*)^{-1}$ are obtained by using $\mathcal{L}_\gamma^* = \mathcal{R}\mathcal{L}_\gamma\mathcal{R}$, with the momentum reversal operator

$$(\mathcal{R}\varphi)(q,p) = \varphi(q,-p), \tag{5.96}$$

Note indeed that $\mathcal{R}C\mathcal{R} = C$, $\mathcal{R}\mathcal{L}_{\rm ovd}\mathcal{R} = \mathcal{L}_{\rm ovd}$ and $\mathcal{R}(A+B)\mathcal{R} = -(A+B)$.

The lower bound in (5.92) could be obtained directly provided V is not constant, by considering the special case

$$\mathcal{L}_\gamma\Big(p^T\nabla V + \gamma(V-v)\Big) = p^T M^{-1}\left(\nabla^2 V\right)p - |\nabla V|^2,$$

where v is a constant chosen such that $p^T\nabla V + \gamma(V-v)$ has a vanishing average with respect to μ. This example is also useful to motivate the fact that, in general, solutions of the Poisson equation $\mathcal{L}_\gamma u_\gamma = f$ have divergent parts of order γ as $\gamma \to +\infty$.

Let us now turn to the refined upper and lower bounds (5.93), which we prove using techniques from asymptotic analysis. Consider $f \in \widetilde{H}^1(\mu)$, and $u_\gamma \in \widetilde{H}^1(\mu)$ the unique solution of the following Poisson equation $\mathcal{L}_\gamma u_\gamma = f$. The above example suggests the following expansion in inverse powers of γ:

$$u_\gamma = \gamma u^{-1} + u^0 + \frac{1}{\gamma}u^1 + \dots \tag{5.97}$$

To rigorously prove this expansion, we first proceed formally, taking (5.97) as an ansatz, plugging it into $\mathcal{L}_\gamma u = f$ and identifying terms according to powers of γ. This leads to

$$\begin{aligned} Cu^{-1} &= 0,\\ (A+B)u^{-1} + Cu^0 &= 0,\\ (A+B)u^0 + Cu^1 &= f. \end{aligned}$$

The first equality implies that $u^{-1} = u^{-1}(q)$ since C satisfies a Poincaré inequality on $L^2(\kappa)$ (where κ is defined in (5.91)). The second then reduces to $Cu^0 = -M^{-1}p\cdot\nabla_q u^{-1}$, from which we deduce $u^0(q,p) = p^T\nabla u^{-1}(q) + \widetilde{u}^0(q)$. Inserting this expression in the third equality gives

$$Cu^1 = f - p^T M^{-1}\left(\nabla^2 u^{-1}\right)p - p^T M^{-1}\nabla\widetilde{u}^0 + (\nabla V)^T\nabla u^{-1}.$$

The solvability condition for this equation is that the right-hand side has a vanishing average with respect to κ, *i.e.* belongs to the kernel of π. This condition reads

$$\frac{1}{\beta}\Delta u^{-1} - (\nabla V)^T\nabla u^{-1} = \pi f,$$

so that $u^{-1} = \mathcal{L}_{\rm ovd}^{-1}\pi f$ (which is well defined since πf has a vanishing average with respect to ν). Note that the function u^{-1} is in $H^{n+2}(\nu)$ when $f \in H^n(\mu)$, so that $p^T M^{-1}(\nabla^2 u^{-1})p$ belongs to $L^2(\mu)$. The equation determining u^1 then reduces to

$$Cu^1 = (f - \pi f) - p^T M^{-1}\nabla\widetilde{u}^0 - p^T M^{-1}\left(\nabla^2 u^{-1}\right)p + \frac{1}{\beta}\Delta u^{-1}.$$

Since $C(p^T A p) = -p^T M^{-1}(A + A^T)p + 2\beta^{-1}{\rm Tr}(A)$, we can choose

$$u^1(q,p) = \left[C^{-1}(f-\pi f)\right](q,p) + \frac{1}{2}p^T(\nabla^2 u^{-1}(q))p + p^T\nabla_q\widetilde{u}^0(q).$$

Coming back to (5.97), we see that the proposed approximate solution is such that

$$\mathcal{L}_\gamma\left(u_\gamma - \gamma u^{-1} - u^0 - \frac{1}{\gamma}u^1\right) = -\frac{1}{\gamma}(A+B)u^1. \tag{5.98}$$

We now choose $\widetilde{u}^0$ such that $(A+B)u^1$ belongs to $\mathcal{H}^1_\perp$, which amounts to

$$\pi(A+B)p^T\nabla_q\widetilde{u}^0 = \mathcal{L}_{\rm ovd}\widetilde{u}^0 = -\pi(A+B)C^{-1}(f-\pi f).$$

It is easily checked that $\widetilde{u}^0 = -\mathcal{L}_{\rm ovd}^{-1}\pi(A+B)C^{-1}(f-\pi f)$ is a well defined element in $\widetilde{H}^1(\mu)$ for $f \in H^1(\mu)$: first, $C^{-1}(f-\pi f) \in \widetilde{H}^1(\mu)$, so $(A+B)C^{-1}(f-\pi f) \in L^2(\mu)$. Finally, the image under $\mathcal{L}_{\rm ovd}^{-1}\pi$ of any function in $L^2(\mu)$ is a function of average zero with respect to ν, depending only on the position variable q and belonging to $H^2(\nu)$; hence to $\widetilde{H}^1(\mu)$.

Combining (5.98) and Lemma 5.8, we see that there exists a constant $R > 0$, such that, for all $\gamma \geqslant 1$, it holds $\|u_\gamma - \gamma u^{-1} - u^0\|_{H^1(\mu)} \leqslant R\|f\|_{H^1(\mu)}/\gamma$ for the above choices of functions u^{-1}, u^0. This gives (5.93). □

5.5.2 Limit of the numerical schemes

We first study the consistency of the invariant measures of limiting numerical schemes, before stating precise convergence results for second order splitting schemes. Ultimately, we relate the overdamped limit of the correction terms obtained for finite γ to the correction obtained by directly studying the overdamped limit.

Overdamped limits of splitting schemes

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 (4.2) 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 [107])

$$\begin{aligned} q^1 &= q^0 - \frac{\Delta t^2}{4}\nabla V(q^0) + \frac{\Delta t}{2\sqrt{\beta}}(G^0+G^1), \\ q^{n+1} &= q^n - \frac{\Delta t^2}{2}\nabla V(q^n) + \frac{\Delta t}{2\sqrt{\beta}}(G^n+G^{n+1}), \quad \text{for } n>0. \end{aligned}$$

Note that (q^n) is not a Markov chain due to the correlations in the random noises.

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 5.4.1. 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 (4.2) (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 (4.2) with an effective timestep $h = \Delta t^2$ but an inverse temperature 2β rather than β.

Rigorous error estimates

The following result quantifies the errors of the invariant measure of second order splitting schemes of Langevin dynamics, for large values of γ. We restrict ourselves to the second order splittings where the Ornstein-Uhlenbeck part is either at the ends or in the middle (categories (i) and (ii) in Section 5.4.1). From a technical viewpoint, we are able here to bound remainder terms uniformly in γ by relying on the properties of the limiting operator $\mathcal{L}_{\mathrm{ovd}}^{-1}$. The result we obtain is the following.

Theorem 5.11. *Consider any of the second order splittings presented in Section 5.4.1, denote by $\mu_{\gamma,\Delta t}(dq\,dp)$ its invariant measure, and by $\nu_{\gamma,\Delta t}(dq)$ its marginal in the position variable. Then there exists a function $f_{2,\infty} = f_{2,\infty}(q) \in C^\infty(\mathcal{D})$, with average zero with respect to ν, such that, for any smooth $\psi = \psi(q) \in C^\infty(\mathcal{D})$ and $\gamma \geqslant 1$,*

$$\int_{\mathcal{D}} \psi(q)\, \nu_{\gamma,\Delta t}(dq) = \int_{\mathcal{D}} \psi\, d\nu + \Delta t^2 \int_{\mathcal{D}} \psi\, f_{2,\infty}\, d\nu + r_{\psi,\gamma,\Delta t},$$

where the remainder is of order Δt^4 up to terms exponentially small in $\gamma\Delta t$. More precisely, there exist constants $a, b \geqslant 0$ and $\kappa > 0$ (all depending on ψ) such that

$$|r_{\psi,\gamma,\Delta t}| \leqslant a\Delta t^4 + b\, \mathrm{e}^{-\kappa\gamma\Delta t}.$$

The expression of $f_{2,\infty}$ depends on the numerical scheme at hand:

$$\begin{aligned}
f_{2,\infty}^{\gamma C,B,A,B,\gamma C}(q) &= \frac{1}{8}\left(-2\Delta V + \beta|\nabla V|^2 + a_{\beta,V}\right), \qquad a_{\beta,V} = \int_{\mathcal{D}} \Delta V\, d\nu = \beta \int_{\mathcal{D}} |\nabla V|^2\, d\nu, \\
f_{2,\infty}^{A,B,\gamma C,B,A}(q) &= -\frac{1}{8}\left(\Delta V - a_{\beta,V}\right), \\
f_{2,\infty}^{\gamma C,A,B,A,\gamma C}(q) &= \frac{1}{8}\left(\Delta V - \beta|\nabla V|^2\right), \\
f_{2,\infty}^{B,A,\gamma C,A,B}(q) &= 0.
\end{aligned} \tag{5.99}$$

The real number $a_{\beta,V}$ ensures that all functions $f_{2,\infty}$ are of average zero with respect to ν. Two comments are in order. Note first that the result is stated for observables which depend only on the position variable q since the limiting case $\gamma \to +\infty$ corresponds to a dynamics on the positions only. There is anyway no restriction in stating the result using such observables since the error on the marginal in the position variables is the relevant error, momenta being trivial to sample exactly under the canonical measure. Secondly, let us emphasize that the Δt^2 correction term vanishes for the method associated with $P_{\Delta t}^{B,A,\gamma C,A,B}$ (as already noted in [107]). This means that the corresponding discretization of overdamped Langevin dynamics (formally obtained by setting $\gamma = +\infty$) has an invariant measure which is correct at second-order in the effective timestep $h = \Delta t^2/2$.

Proof. We write the proof for the evolution operator $P_{\Delta t}^{\gamma C,A,B,A,\gamma C}$ first. The proofs for the other operators are very similar, and we refer to [108]. We decompose the proof is several steps.

(i) *Reduction to a limiting operator up to exponentially small terms.*
Let us introduce the evolution operator corresponding to the standard position Verlet scheme: $P_{\mathrm{ham},\Delta t} = \mathrm{e}^{\Delta t A/2}\mathrm{e}^{\Delta t B}\mathrm{e}^{\Delta t A/2}$, so that $P_{\Delta t}^{\gamma C,A,B,A\gamma C} = \mathrm{e}^{\gamma\Delta t C/2} P_{\mathrm{ham},\Delta t}\, \mathrm{e}^{\gamma \Delta \mathrm{t} C/2}$. On the other hand, we have the following convergence result.

Lemma 5.9. *Fix $s^* \in \mathbb{N}^*$. Then, there exist $K, \alpha > 0$ such that, for any $1 \leqslant s \leqslant s^*$ and any $t \geqslant 0$,*

$$\left\| \mathrm{e}^{\gamma t C} - \pi \right\|_{\mathcal{B}(L^\infty_{W_s})} \leqslant K \mathrm{e}^{-\alpha\gamma t},$$

where π is the projection operator defined in (5.91).

Indeed, the convergence results obtained in Section 4.3.4 show that there exist $R_s, \alpha_s > 0$ such that

$$\left| \left(\mathrm{e}^{tC} f\right)(p) - \int_{\mathbb{R}^D} f(p)\,\kappa(dp) \right| \leqslant R_s \mathrm{e}^{-\alpha_s t} \|f\|_{L^\infty_{W_s}(dp)} W_s(p),$$

where the notation $L^\infty_{W_s}(dp)$ emphasizes that the supremum is taken over a function of the momentum variable only. The desired result now follows by applying the above bound to the function $\psi(q,\cdot)$ for any element $\psi \in L^\infty_{W_s}$, and taking the supremum over q.
This suggests to consider the limiting operator $P_{\infty,\Delta t} = \pi P_{\mathrm{ham},\Delta t}\pi$ and to write

$$P_{\Delta t}^{\gamma C,A,B,A,\gamma C} - P_{\infty,\Delta t} = \left(\mathrm{e}^{\gamma\Delta t C/2} - \pi\right) P_{\mathrm{ham},\Delta t}\pi + \mathrm{e}^{\gamma\Delta t C/2} P_{\mathrm{ham},\Delta t}\left(\mathrm{e}^{\gamma\Delta t C/2} - \pi\right). \quad (5.100)$$

For a given smooth function $\varphi \in \mathcal{S}$ which depends only on the position variable q,

$$\int_{\mathcal{E}} \left(\mathrm{Id} - P_{\Delta t}^{\gamma C,A,B,A,\gamma C}\right)\varphi\, d\mu_{\gamma,\Delta t} = 0 = \int_{\mathcal{E}} (\mathrm{Id} - P_{\infty,\Delta t})\varphi\, d\mu_{\gamma,\Delta t} + r^1_{\varphi,\gamma,\Delta t}, \quad (5.101)$$

with the remainder

$$r^1_{\varphi,\gamma,\Delta t} = \int_{\mathcal{E}} \left(P_{\infty,\Delta t} - P_{\Delta t}^{\gamma C,A,B,A,\gamma C}\right)\varphi\, d\mu_{\gamma,\Delta t}.$$

On the other hand,

$$\int_{\mathcal{E}} \left[\left(\mathrm{Id} - P_{\Delta t}^{\gamma C,B,A,B,\gamma C}\right)\varphi\right](1+\Delta t^2 f_{2,\infty})\, d\mu = \int_{\mathcal{E}} \left[(\mathrm{Id} - P_{\infty,\Delta t})\varphi\right](1+\Delta t^2 f_{2,\infty})\, d\mu + r^2_{\varphi,\gamma,\Delta t}, \quad (5.102)$$

with the remainder

$$r^2_{\varphi,\gamma,\Delta t} = \int_{\mathcal{E}} \left[\left(P_{\infty,\Delta t} - P_{\Delta t}^{\gamma C,B,A,B,\gamma C}\right)\varphi\right](1+\Delta t^2 f_{2,\infty})\, d\mu.$$

The idea is that the remainders $r^1_{\varphi,\gamma,\Delta t}$ and $r^2_{\varphi,\gamma,\Delta t}$ are exponentially small when the function φ is sufficiently smooth (see below for a more precise discussion, once φ has been replaced by $Q_h\psi$ with Q_h an appropriate approximate inverse). Therefore, the leading order terms in the error estimate are obtained by considering the limiting operator $P_{\infty,\Delta t}$ only.

(ii) *Error estimates for the limiting operator $P_{\infty,\Delta t}$.*
We now study the error estimates associated with $P_{\infty,\Delta t}$, following the strategy used in Section 4.4.4. We first use the results of Section 5.4.4 with $M = 3$, $A_1 = A_3 = A/2$ and $A_2 = B$ to expand $P_{\mathrm{ham},\Delta t}$ as

$$P_{\infty,\Delta t} = \pi + \Delta t\pi(A+B)\pi + \frac{\Delta t^2}{2}\pi(A+B)^2\pi + \frac{\Delta t^3}{6}\pi S_3\pi + \frac{\Delta t^4}{24}\pi S_4\pi + \frac{\Delta t^5}{120}\pi S_5\pi + \Delta t^6 \pi R_{\Delta t}\pi, \quad (5.103)$$

with $S_i = \mathcal{T}[(A_1 + A_2 + A_3)^i]$. To give more precise expressions of the operators appearing on the right-hand side of the above equality, we use the following facts:

$$\forall n \in \mathbb{N}, \qquad B^n\pi = 0, \qquad \pi A^{2n+1}\pi = 0, \quad (5.104)$$

and

$$\forall n \geqslant m+1, \qquad B^n A^m \pi = 0. \quad (5.105)$$

In addition,

$$\pi A^2 \pi = \frac{1}{\beta}\Delta_q \pi, \qquad BA\pi = -\nabla V \cdot \nabla_q \pi.$$

Using these rules in (5.103) leads to

$$\pi(A+B)\pi = 0, \qquad \pi(A+B)^2\pi = \pi(A^2 + BA)\pi = \mathcal{L}_{\mathrm{ovd}}\pi. \quad (5.106)$$

The operator S_3 is a combination of terms of the form $A^aB^bA^c$ with $a+b+c=3$ and $a,b,c\in\mathbb{N}$. In view of (5.104)-(5.105), only the terms with $c\geqslant 1$ and $b\leqslant c$ have to be considered, so that only BA^2 and ABA remain. A simple computation shows that $BA^2\pi\varphi$ and $ABA\pi\varphi$ are functions linear in p, so that $\pi BA^2\pi=\pi ABA\pi\varphi=0$. Finally, $\pi S_3\pi=0$. A similar reasoning shows that $\pi S_5\pi=0$ and that many terms appearing in the expression of S_4 also disappear.
Plugging the above results in (5.103) and introducing $h=\Delta t^2/2$,

$$P_{\infty,\Delta t}=\pi+h\pi\mathcal{L}_{\rm ovd}\pi+\frac{h^2}{6}\pi\left(A^4+\frac{3}{2}A^2BA+\frac{3}{2}ABA^2+\frac{3}{2}B^2A^2+\frac{1}{2}BA^3\right)\pi+h^3R_{\infty,\Delta t}.$$

Using

$$\begin{aligned}
\pi A^4\pi\varphi&=\frac{3}{\beta^2}\Delta_q^2\pi\varphi=3\left(\pi A^2\pi\right)^2\varphi,\\
\pi BA^3\pi\varphi&=-\frac{3}{\beta}\nabla V\cdot\nabla_q\Big(\Delta_q\pi\varphi\Big)=3\pi BA\pi A^2\pi\varphi,\\
\pi B^2A^2\pi\varphi&=2(\nabla V)^T\Big(\nabla_q^2\pi\varphi\Big)\nabla V,\\
\pi ABA^2\pi\varphi&=-\frac{2}{\beta}\left(\nabla^2V:\nabla^2\varphi+\nabla V\cdot\nabla(\Delta\varphi)\right),\\
\pi A^2BA\pi\varphi&=-\frac{1}{\beta}\left(2\nabla^2V:\nabla^2\varphi+\nabla V\cdot\nabla(\Delta\varphi)+\nabla(\Delta V)\cdot\nabla\varphi\right)=\pi A^2\pi BA\pi\varphi,
\end{aligned}\tag{5.107}$$

it follows

$$\begin{aligned}
&\left(A^4+\frac{3}{2}A^2BA+\frac{3}{2}ABA^2+\frac{3}{2}B^2A^2+\frac{1}{2}BA^3\right)\pi\varphi\\
&\quad=\frac{3}{\beta^2}\Delta_q^2\varphi-\frac{6}{\beta}\nabla^2V:\nabla^2\varphi-\frac{6}{\beta}\nabla V\cdot\nabla(\Delta\varphi)-\frac{3}{2\beta}\nabla(\Delta V)\cdot\nabla\varphi+3(\nabla V)^T(\nabla^2\varphi)\nabla V.
\end{aligned}$$

In view of the expression of $\mathcal{L}_{\rm ovd}$ given in (4.72),

$$\pi\left(A^4+\frac{3}{2}A^2BA+\frac{3}{2}ABA^2+\frac{3}{2}B^2A^2+\frac{1}{2}BA^3\right)\pi=3\left(\mathcal{L}_{\rm ovd}^2+D\right)\pi,$$

with

$$D\varphi=\frac{1}{2\beta}\nabla(\Delta V)\cdot\nabla\varphi-(\nabla V)^T(\nabla^2V)\nabla\varphi.\tag{5.108}$$

In conclusion,

$$P_{\infty,\Delta t}=\pi+h\mathcal{L}_{\rm ovd}+\frac{h^2}{2}\left(\mathcal{L}_{\rm ovd}^2+D\right)\pi+h^3R_{\infty,\Delta t}.\tag{5.109}$$

Let us emphasize that this operator acts on functions of q (we define it on $\mathcal{S}\cap\mathrm{Ker}(\pi)=C^\infty(\mathcal{D})$), that π is the identity operator for functions which are independent of p, and note that for any $\phi\in C^\infty(\mathcal{D})$,

$$\frac{\pi-P_{\infty,\Delta t}}{h}\phi=-\mathcal{L}_{\rm ovd}\phi-\frac{h}{2}\left(\mathcal{L}_{\rm ovd}^2+D\right)\phi-h^2R_{\Delta t}\phi.\tag{5.110}$$

In fact, proceeding as in Section 4.4.4, we project out averages with respect to $\nu(dq)$ in order to properly define approximate inverses. Introduce to this end the projector

$$\overline{\Pi}^\perp\phi=\phi-\int_{\mathcal{D}}\phi(q)\,\nu(dq)$$

defined on the core $C^\infty(\mathcal{D})$. The equality (5.110) then implies the following equality on $C^\infty(\mathcal{D})\cap\mathrm{Ran}(\overline{\Pi}^\perp)$:

$$\overline{\Pi}^\perp \frac{\pi - P_{\infty,\Delta t}}{h} \overline{\Pi}^\perp = -\mathcal{L}_{\rm ovd} - \frac{h}{2}\left(\mathcal{L}_{\rm ovd}^2 + \overline{\Pi}^\perp D \overline{\Pi}^\perp\right) - h^2 \overline{\Pi}^\perp R_{\Delta t} \overline{\Pi}^\perp.$$

An approximate inverse of the operator appearing on the left hand side of the above equality is thus

$$Q_h = -\mathcal{L}_{\rm ovd}^{-1} + \frac{h}{2}\left(\overline{\Pi}^\perp + \mathcal{L}_{\rm ovd}^{-1}\overline{\Pi}^\perp D \overline{\Pi}^\perp \mathcal{L}_{\rm ovd}^{-1}\right).$$

Denote by $\nu_{\infty,\Delta t}(dq)$ the invariant measure of the Markov chain generated by the limiting method $P_{\infty,\Delta t}$. Proceeding as in Section 4.4.4 by first identifying the leading order correction $f_{2,\infty}$, projecting out averages with respect to $\nu(dq)$ using $\overline{\Pi}^\perp$, and replacing $\overline{\Pi}^\perp\varphi$ by $Q_h\psi$, the equality (5.109) allows us to obtain

$$\int_{\mathcal{D}} \psi(q)\,\nu_{\infty,\Delta t}(dq) = \int_{\mathcal{D}} \psi(q)\,\nu(dq) + \Delta t^2 \int_{\mathcal{D}} \psi(q) f_{2,\infty}(q)\,\nu(dq) + \Delta t^4 \overline{r}_{\Delta t,\psi}, \tag{5.111}$$

where $f_{2,\infty}$ is the unique solution of

$$\mathcal{L}_{\rm ovd} f_{2,\infty} = -\frac{1}{4} D^*\mathbf{1}. \tag{5.112}$$

A more explicit expression can be obtained by noting that

$$D\varphi = \frac{1}{2}\nabla\left(\frac{1}{\beta}\Delta V - |\nabla V|^2\right)\cdot\nabla\varphi,$$

so that (recalling $\mathcal{L}_{\rm ovd} = -\beta^{-1}\nabla^*\nabla = -\beta^{-1}\sum_{i=1}^D \partial_{q_i}^*\partial_{q_i}$ where the formal adjoints are taken on $L^2(\nu)$)

$$\begin{aligned}\int_{\mathcal{D}} \varphi\,(D^*\mathbf{1})\,d\nu &= \int_{\mathcal{D}} D\varphi\,d\nu = \frac{1}{2}\int_{\mathcal{D}} \varphi\nabla^*\nabla\left(\frac{1}{\beta}\Delta V - |\nabla V|^2\right)d\nu \\ &= -\frac{1}{2}\int_{\mathcal{D}} \varphi\,\mathcal{L}_{\rm ovd}\left(\Delta V - \beta|\nabla V|^2\right)d\nu.\end{aligned}$$

Since $f_{2,\infty}$ should have a vanishing average with respect to μ, this proves that

$$f_{2,\infty}(q) = \frac{1}{8}\left(\Delta V - \beta|\nabla V|^2\right) + a, \tag{5.113}$$

where the constant a is adjusted to account for the constraint of vanishing average. A simple computation shows $a = 0$.

(iii) *Conclusion of the proof.*

We now come back to (5.101)-(5.102) and replace $\overline{\Pi}^\perp\varphi$ by $Q_h\psi$:

$$\int_{\mathcal{E}} \psi\,d\mu_{\gamma,\Delta t} = \int_{\mathcal{E}} \psi(1+\Delta t^2 f_{2,\infty})\,d\mu + r^1_{\psi,\gamma,\Delta t} + r^2_{\psi,\gamma,\Delta t} + \Delta t^4 \overline{r}_{\Delta t,\psi}, \tag{5.114}$$

where $\overline{r}_{\Delta t,\psi}$ is the same as in (5.111), while

$$\begin{aligned} r^1_{\psi,\gamma,\Delta t} &= \int_{\mathcal{E}} \left(P_{\infty,\Delta t} - P_{\Delta t}^{\gamma C,A,B,A,\gamma C}\right) Q_h\psi\,d\mu_{\gamma,\Delta t}, \\ r^2_{\psi,\gamma,\Delta t} &= \int_{\mathcal{E}} \left[\left(P_{\infty,\Delta t} - P_{\Delta t}^{\gamma C,B,A,B,\gamma C}\right) Q_h\psi\right](1+\Delta t^2 f_{2,\infty})\,d\mu. \end{aligned}$$

We then integrate with respect to momenta in (5.114), and bound the remainders by $K\mathrm{e}^{-\kappa\gamma\Delta t}$ in view of the decomposition (5.100) and Lemma 5.9 (the operators $P_{\rm ham,\Delta t}$ and $\mathrm{e}^{\gamma\Delta t C/2}$ being bounded on $L^\infty_{W_s}$ uniformly in Δt).

□

Overdamped limit of the correction terms

In order to relate the convergence result from Theorem 5.11 to the error estimates from Theorem 5.9, we prove that the limits of the correction functions $f_{2,\gamma}$ as $\gamma \to +\infty$ agree with the functions defined in (5.99). This can be seen as a statement regarding the permutation of the limits $\gamma \to +\infty$ and $\Delta t \to 0$ for the leading correction term. Namely, for a smooth function $\psi = \psi(q) \in C^\infty(\mathcal{D})$,

$$\begin{aligned}\lim_{\Delta t\to 0}\lim_{\gamma\to+\infty}\frac{1}{\Delta t^2}\left(\int_{\mathcal{D}}\psi\,d\nu_{\gamma,\Delta t}-\int_{\mathcal{D}}\psi\,d\nu\right) &= \lim_{\gamma\to+\infty}\lim_{\Delta t\to 0}\frac{1}{\Delta t^2}\left(\int_{\mathcal{D}}\psi\,d\nu_{\gamma,\Delta t}-\int_{\mathcal{D}}\psi\,d\nu\right)\\ &= \lim_{\gamma\to+\infty}\int_{\mathcal{D}}\psi\,(\pi f_{2,\gamma})\,d\nu\\ &= \int_{\mathcal{D}}\psi\,f_{2,\infty}\,d\nu.\end{aligned}$$

The precise result is the following:

Proposition 5.10. *There exists a constant $K > 0$ such that, for all $\gamma \geqslant 1$,*

$$\begin{aligned}\left\|f_2^{\gamma C,B,A,B,\gamma C}-\frac{1}{8}\left(-2\Delta V+\beta|\nabla V|^2+a_{\beta,V}\right)\right\|_{H^1(\mu)} &\leqslant \frac{K}{\gamma},\\ \left\|f_2^{A,B,\gamma C,B,A}-\frac{1}{8}\left(-2\Delta V+\beta p^T(\nabla^2 V)p+a_{\beta,V}\right)\right\|_{H^1(\mu)} &\leqslant \frac{K}{\gamma},\\ \left\|f_2^{\gamma C,A,B,A,\gamma C}-\frac{1}{8}\left(\Delta V-\beta|\nabla V|^2\right)\right\|_{H^1(\mu)} &\leqslant \frac{K}{\gamma},\\ \left\|f_2^{B,A,\gamma C,A,B}-\frac{1}{8}\left(\Delta V-\beta p^T(\nabla^2 V)p\right)\right\|_{H^1(\mu)} &\leqslant \frac{K}{\gamma},\end{aligned}$$

where the constant $a_{\beta,V}$ is defined in (5.99).

Note that, as expected, the averages with respect to $\kappa(dp)$ of the above limiting functions coincide with the functions $f_{2,\infty}$ given in (5.99), that is, $\pi f_{2,\gamma} = f_{2,\infty} + \mathrm{O}(\gamma^{-1})$.

Proof. Recall that we set $M = \mathrm{Id}$ for overdamped limits. We consider first $f_2^{\gamma C,B,A,B,\gamma C}$, which satisfies (5.78). Let us first compute the right-hand side. Since

$$\left[\left(A+\frac{1}{2}B\right)g\right] = \beta\left(p^T(\nabla^2 V)p-\frac{1}{2}|\nabla V|^2\right),$$

a simple computation shows that

$$\widetilde{g} = \frac{1}{12}(A+B)\left[\left(A+\frac{1}{2}B\right)g\right] = \frac{\beta}{12}\Big[(\nabla^3 V):(p\otimes p\otimes p)-3p^T(\nabla^2 V)\nabla V\Big].$$

Note that the above function has average zero with respect to κ. We then apply Theorem 5.10 to obtain

$$\left\|f_2^{\gamma C,B,A,B,\gamma C}-\mathcal{L}_{\mathrm{ovd}}^{-1}\pi(A+B)C^{-1}\widetilde{g}\right\|_{H^1(\mu)} \leqslant \frac{K}{\gamma}.$$

Since

$$C\Big[(\nabla^3 V):(p\otimes p\otimes p)\Big] = -3(\nabla^3 V):(p\otimes p\otimes p)+\frac{6}{\beta}p^T\nabla\left(\Delta V\right),$$

it is easily checked that

$$\begin{aligned}C^{-1}\widetilde{g} &= -\frac{\beta}{36}(\nabla^3 V):(p\otimes p\otimes p)-\frac{1}{6}p^T\nabla(\Delta V)+\frac{\beta}{4}p^T(\nabla^2 V)\nabla V\\ &= -\frac{\beta}{36}A^3\pi V+A\pi\left(-\frac{1}{6}(\Delta V)+\frac{\beta}{8}|\nabla V|^2\right).\end{aligned}$$

To compute $\pi(A+B)C^{-1}\widetilde{g}$, we rely on (5.106) and (5.107) and obtain

$$\begin{aligned}\pi(A+B)C^{-1}\widetilde{g} &= -\frac{1}{12}\left(\frac{1}{\beta}\Delta^2 V - \nabla V\cdot\nabla(\Delta V)\right) + \mathcal{L}_{\mathrm{ovd}}\left(-\frac{1}{6}(\Delta V) + \frac{\beta}{8}|\nabla V|^2\right)\\ &= \mathcal{L}_{\mathrm{ovd}}\left(-\frac{1}{4}\Delta V + \frac{\beta}{8}|\nabla V|^2\right).\end{aligned}$$

This allows us to conclude that the limit of $f_2^{\gamma C,B,A,B,\gamma C}$ is the argument of the operator $\mathcal{L}_{\mathrm{ovd}}$ in the previous line, up to an additive constant chosen to ensure that $f_2^{\gamma C,B,A,B,\gamma C}$ has a vanishing average with respect to μ (which turns out to be $a_{\beta,V}/8$). We deduce the limit for $f_2^{A,B,\gamma C,B,A}$ with (5.78) since $(A+B)g = p^T(\nabla^2 V)p - |\nabla V|^2$. The expressions for the limits of $f_2^{\gamma C,A,B,A\gamma C}$ and $f_2^{B,A,\gamma C,A,B}$ are obtained in a similar fashion. □

Let us also mention that the overdamped limit of the correction function $f_{1,\gamma}$ for first order splittings is not well defined. This is not surprising since the invariant measures of the corresponding numerical schemes are not consistent with ν, as discussed in the introduction of this section. For instance, combining (5.93) and the expressions of the correction functions (5.76), we see that there exists a constant $K>0$ such that

$$\left\| f_1^{\gamma C,B,A} + \frac{\gamma\beta}{2}\mathcal{L}_{\mathrm{ovd}}^{-1}\mathcal{L}_{\mathrm{ovd},M}V \right\|_{H^1(\mu)} \leqslant K, \tag{5.115}$$

where the operator

$$\mathcal{L}_{\mathrm{ovd},M} = -M^{-1}\nabla V\cdot\nabla_q + \frac{1}{\beta}M:\nabla^2,$$

defined on $\mathcal{S}$, is the generator of the overdamped Langevin dynamics with non-trivial mass matrix:

$$dq_t = -M^{-1}\nabla V(q_t)\,dt + \sqrt{\frac{2}{\beta}}M^{-1/2}\,dW_t.$$

Note that, when $M=\mathrm{Id}$, the solution can in fact be analytically computed as $f_1^{\gamma C,B,A} = -\beta(\gamma V + p^T\nabla V)/2$. In any case, (5.115) shows that $f_1^{\gamma C,B,A}$ diverges as $\gamma\to+\infty$.

6

Other dynamics sampling the canonical ensemble

We present in this chapter 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 and piecewise deterministic Markov processes.

6.1 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,

$$\begin{cases} \dot{q} = M^{-1}p, \\ \dot{p} = -\nabla V(q) - \xi p, \\ \dot{\xi} = \dfrac{1}{Q}\left(p^T M^{-1} p - \dfrac{3N}{\beta}\right) \end{cases} \tag{6.1}$$

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

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

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 (1.16).

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 [165]. 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.

6.2 Extensions of the Langevin dynamics

6.2.1 Generalized Langevin dynamics

A Mori-Zwanzig derivation is provided in [100] 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 5.3.3.

6.2.2 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.

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

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 [157]. Numerical discretizations are typically obtained by a splitting strategy [156].

6.3 An example of piecewise deterministic Markov process

We present in this section a 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 [136] but was also independently introduced in the mathematics literature [128].

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 $\mathcal{L} = \mathcal{L}_{\mathrm{j/d}} + \gamma \mathcal{L}_{\mathrm{thm}}$ with

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

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,

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

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 6.1. *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 [128].

Part IV

Beyond static averages

7

Computation of transport coefficients

A AJOUTER : UNE DISCUSSION SUR LE SHEAR ? DES ELEMENTS SUR LA DIFFUSION EFFECTIVE AVEC APPROCHE MARTINGALE ?

We discuss in this 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 strength 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 7.1 and then give a general presentation of non-equilibrium dynamics in Section 7.2, with some emphasis on perturbations of equilibrium dynamics such as (7.1) or (7.2). We next show in Section 7.3 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 7.4. Finally, we discuss variance reduction techniques in Section 7.5.

7.1 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 7.2). We consider two paradigmatic situations: cases when the drift of equilibrium dynamics is perturbed by a non-gradient force (see Section 7.1.1), and cases when the magnitude of the fluctuation terms are modified (see Section 7.1.2).

7.1.1 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:

$$\begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = (-\nabla V(q_t) + \eta F) \, dt - \gamma M^{-1} p_t \, dt + \sqrt{\dfrac{2\gamma}{\beta}} \, dW_t, \end{cases} \tag{7.1}$$

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 7.1) 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 [85, Section 2.2].

7.1.2 Dynamics with modified fluctuation terms

Another class of perturbation is obtained by modifying the fluctuation magnitude. For Langevin dynamics, one possible choice is

$$\begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = -\nabla V(q_t) \, dt - \gamma M^{-1} p_t \, dt + \sqrt{2\gamma T_\eta(q)} \, dW_t, \end{cases} \tag{7.2}$$

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 (7.2) 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

$$\begin{cases} dq_i = p_i\, dt, \\ dp_i = \Big(v'(q_{i+1} - q_i) - v'(q_i - q_{i-1})\Big) dt, \qquad i \neq 1, N, \\ dp_1 = \Big(v'(q_2 - q_1) - v'(q_1)\Big) dt - \gamma p_1\, dt + \sqrt{2\gamma T_{\mathrm{L}}}\, dW_t^1, \\ dp_N = -v'(q_N - q_{N-1})\, dt - \gamma p_N\, dt + \sqrt{2\gamma T_{\mathrm{R}}}\, dW_t^N, \end{cases} \tag{7.3}$$

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

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2} + V(q), \qquad V(q) = v(q_1) + \sum_{i=1}^{N-1} v(q_{i+1} - q_i), \tag{7.4}$$

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 [131], etc. See the review articles by [23], [117] and [41].

7.1.3 Some remarks

The two dynamics (7.1) and (7.2) reduce to the standard Langevin dynamics (5.1) when $\eta = 0$. Most of our analysis is illustrated with the dynamics (7.1), but we will occasionally refer to the dynamics (7.2) as well.

As discussed more precisely in Section 7.2, dynamics such as (7.1) and (7.2) model non-equilibrium 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 non-equilibrium systems, although such a distinction is sometimes made in the physical literature (see for instance [20] and references therein).

Finally, let us make precise the aim of this chapter, namely the computation of transport coefficients. For (7.1), 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 (7.2), 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 (7.3), the parameter η is the temperature difference $T_{\mathrm{L}} - T_{\mathrm{R}}$.

7.2 Definition of non-equilibrium dynamics

7.2.1 Abstract characterization of non-equilibrium dynamics

Consider a general stochastic dynamics

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t.$$

Recall that the existence and uniqueness of an invariant probability measure π can be proved in such a general setting with the techniques provided in Section 3.3.1 for instance. From a mathematical viewpoint, equilibrium systems are characterized by the self-adjointness of the generator $\mathcal{L}$ on the weighted Hilbert space $L^2(\pi)$:

$$\int_{\mathcal{X}} (\mathcal{L}f)\, g\, d\pi = \int_{\mathcal{X}} f\, (\mathcal{L}g)\, d\pi. \tag{7.5}$$

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

$$\int_{\mathcal{X}} (\mathcal{L}f)\, g\, d\pi = \int_{\mathcal{X}} (f\circ S)\, (\mathcal{L}(g\circ S))\, d\pi;$$

see [114, 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 (7.5) no longer hold true. The non-reversibility can be quantified by the entropy production, for which fluctuation theorems hold [61, 101, 104].

7.2.2 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 [39]). 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

$$dq_t = -V'(q_t)\,dt + \sqrt{2}\,dW_t, \tag{7.6}$$

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

$$dq_t = (-V'(q_t) + F)\,dt + \sqrt{2}\,dW_t, \tag{7.7}$$

where $F \in \mathbb{R}$ is a constant force, it can be shown that there exists a unique invariant probability measure $\psi_F(q)\,dq$. The density ψ_F satisfies the stationary Fokker–Planck equation

$$\frac{d}{dq}\left((V'-F)\psi_F + \frac{d\psi_F}{dq}\right) = 0, \tag{7.8}$$

which can be solved as (see [140, Section 2.5] and references therein)

$$\psi_F(q) = Z_F^{-1}\int_0^1 \mathrm{e}^{V(q+y)-V(q)-Fy}\,dy, \tag{7.9}$$

with Z_F 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 (4.8), see [58].

Let us also show that the dynamics (7.7) 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 $b(q)$:

$$dq_t = b(q_t)\,dt + \sqrt{2}\,dW_t. \tag{7.10}$$

The generator $\mathcal{L}_b$ of this generalized dynamics reads $\mathcal{L}_b = b \cdot \nabla + \Delta$. A simple computation shows that

$$\begin{aligned}\int_{\mathcal{D}} (\mathcal{L}_b f) g\,\psi_F = \int_{\mathcal{D}} f(\mathcal{L}_b g)\,\psi_F - 2\int_{\mathcal{D}} f[(b+\nabla U_F)\cdot\nabla g]\,\psi_F \\ + \int_{\mathcal{D}} fg[-\mathrm{div}(b) - \Delta U_F + \nabla U_F \cdot (b + \nabla U_F)]\,\psi_F.\end{aligned}$$

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 (7.10) are reversible if and only if the drift is the gradient of a potential energy function.

7.2.3 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 7.3; see in particular (7.12). For the paradigmatic dynamics (7.1) and (7.2), 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 [52] and [165] 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 [82], 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 (7.2) 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 (7.1)). 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 (7.22) below for the specific case treated in Section 7.3).

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 [89] for a pedagogical introduction.

7.3 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 (7.1). 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 (5.5):

$$\mathcal{L}_0 = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p + \gamma \left(-p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p \right).$$

7.3.1 Existence and uniqueness of the invariant measure.

The first observation is that, by a simple extension of the results of Section 5.3.1, the dynamics (7.1) admits a unique invariant probability measure. Upon introducing the Lyapunov functions $W_n(q,p) = 1 + |p|^n$ for $n \geqslant 2$, it is in fact possible to formulate the following convergence result, where some uniformity in the parameter η holds (see [108] and [88] for related results).

Proposition 7.1. *Consider $\eta_* > 0$. For any $\eta \in [-\eta_*, \eta_*]$, the dynamics (7.1) 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 $\varphi \in L^\infty_{W_n}(\mathcal{E})$,*

$$\forall t \geqslant 0, \qquad \left\| \mathrm{e}^{t\mathcal{L}_\eta} \varphi - \int_{\mathcal{E}} \varphi \psi_\eta \right\|_{L^\infty_{W_n}} \leqslant C_n \mathrm{e}^{-\lambda_n t} \left\| \varphi \right\|_{L^\infty_{W_n}}.$$

Recall that the density of the invariant measure satisfies the 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 a consequence of the hypoellipticiy of $\mathcal{L}_\eta^\dagger$ (see Section 5.3.3). For notational consistency, we set

$$\psi_0(q,p) = Z^{-1} \, \mathrm{e}^{-\beta H(q,p)}.$$

Note also that, as corollary of Proposition 7.1, it is possible to define $\mathcal{L}_\eta^{-1}$ as a bounded operator on the subspaces

$$L^\infty_{W_n,\eta}(\mathcal{E}) = \left\{ \varphi \in L^\infty_{W_n}(\mathcal{E}) \,\middle|\, \int_{\mathcal{E}} \varphi \, \psi_\eta = 0 \right\}.$$

In more complicated cases...

The existence and uniqueness of a smooth invariant probability measure for the dynamics (7.3) can be proved under appropriate assumptions on the interaction potential v. In particular, some (super)quadratic growth at infinity is required. Such results are based either on methods from spectral theory [49, 47] (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 [48, 145, 146, 33]. 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 [72] 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.

7.3.2 Linear response

Relevant observables

It is expected, from a physical viewpoint, that, for the dynamics (7.1), 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 (7.1) under consideration, we consider the observable

$$R(q,p) = F^T M^{-1} p. \tag{7.11}$$

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 (7.1). 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.*,

$$\rho_F = \lim_{\eta\to 0} \frac{\mathbb{E}_\eta(R) - \mathbb{E}_0(R)}{\eta} = \lim_{\eta\to 0} \frac{\mathbb{E}_\eta(R)}{\eta}. \tag{7.12}$$

This is the definition of the mobility based on the linear response of non-equilibrium dynamics.

For thermal transport as described by (7.3), 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 [48, 19]. The thermal conductivity is defined as the energy flux divided by the temperature difference (see (7.24) below). The relevant physical response of the system is the total energy current J across the system

$$J(q,p) = \sum_{i=1}^{N-1} j_{i+1,i}(q,p), \qquad j_{i+1,i}(q,p) = -v'(q_{i+1} - q_i)\frac{p_i + p_{i+1}}{2}, \tag{7.13}$$

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:

$$\varepsilon_i(q,p) = \frac{p_i^2}{2} + \frac{1}{2}\Big(v(q_{i+1} - q_i) + v(q_i - q_{i-1})\Big), \tag{7.14}$$

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.

Proving that linear response holds

In order to ensure that the limit (7.12) 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 (7.1) 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 (5.6)).

Theorem 7.1 (power expansion of the invariant measure). *Consider the dynamics* (7.1) *with generator* $\mathcal{L}_\eta = \mathcal{L}_0 + \eta \widetilde{\mathcal{L}}$, *where* $\mathcal{L}_0$ *is given in* (5.5) *and* $\widetilde{\mathcal{L}} = F \cdot \nabla_p$. *Let* r *be the spectral radius of the bounded operator* $(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^* \in \mathcal{B}(L^2_0(\psi_0))$*:*

$$r = \lim_{n \to +\infty} \| [(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^*]^n \|^{1/n}.$$

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*:*

$$f_\eta = \Big(1 + \eta (\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^* \Big)^{-1} \mathbf{1} = \left(1 + \sum_{n=1}^{+\infty} (-\eta)^n [(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^*]^n \right) \mathbf{1}. \tag{7.15}$$

The linear term in η in the expression of f_η is denoted by

$$\mathfrak{f}_1 = -(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^* \mathbf{1} = - \left(\mathcal{L}_0^{-1} \right)^* \widetilde{\mathcal{L}}^* \mathbf{1}. \tag{7.16}$$

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 $L^2_0(\psi_0)$. As will become clear in the proof of Theorem 7.1, this result can actually be proven for other dynamics than (7.1). This will be made precise in Section 7.3.4. As a corollary of Theorem (7.1), we immediately get a formula for the transport coefficient ρ_F defined by (7.12), using the fact that $\int_{\mathcal{E}} R \psi_0 = 0$:

$$\rho_F = \lim_{\eta \to 0} \frac{\int_{\mathcal{E}} R f_\eta \psi_0}{\eta} = \int_{\mathcal{E}} R \mathfrak{f}_1 \psi_0. \tag{7.17}$$

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 $f_\eta - \mathbf{1} \in L^2_0(\psi_0)$, 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 7.1 below.

Proof. Let us first show that $(\widetilde{\mathcal{L}} \Pi_0 \mathcal{L}_0^{-1} \Pi_0)^*$ is a bounded operator on $L^2_0(\psi_0)$. To this end, we show that its adjoint $\widetilde{\mathcal{L}} \mathcal{L}_0^{-1}$ is bounded from $L^2_0(\psi_0)$ to $L^2(\psi_0)$. For C^∞ and compactly supported functions φ,

$$\frac{\gamma}{\beta}\|\nabla_p\varphi\|^2_{L^2(\psi_0)} = -\langle\mathcal{L}_0\varphi,\varphi\rangle_{L^2(\psi_0)} \leqslant \|\mathcal{L}_0\varphi\|_{L^2(\psi_0)}\|\varphi\|_{L^2(\psi_0)},$$

so that

$$\|\widetilde{\mathcal{L}}\varphi\|^2_{L^2(\psi_0)} \leqslant \|\nabla_p\varphi\|^2_{L^2(\psi_0)} \leqslant \frac{\beta}{\gamma}\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)}\|\varphi\|_{L^2(\psi_0)}.$$

Since $\mathcal{L}_0$ is invertible on $L^2_0(\psi_0)$ by Proposition 5.2 or Theorem 5.3, it follows that, for any $\varphi \in L^2_0(\psi_0)$,

$$\|\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}\varphi\|^2_{L^2(\psi_0)} \leqslant \frac{\beta}{\gamma}\|\varphi\|_{L^2(\psi_0)}\|\mathcal{L}_0^{-1}\varphi\|_{L^2(\psi_0)}.$$

The operator $\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$ is therefore bounded from $L^2_0(\psi_0)$ to $L^2(\psi_0)$, with operator norm bounded from above by $\beta\|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L^2_0(\psi_0))}/\gamma$. It follows that the operator $\Pi_0\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$ is bounded on $L^2_0(\psi_0)$, so that its adjoint $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*\Pi_0$ is also bounded on $L^2_0(\psi_0)$. In fact, $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*\Pi_0 = (\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ on $L^2_0(\psi_0)$, which proves that $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is bounded on $L^2_0(\psi_0)$ with operator norm bounded from above by $\beta\|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L^2_0(\psi_0))}/\gamma$. As a consequence, the spectral radius r satisfies $r \leqslant \sqrt{\beta\|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L^2_0(\psi_0))}/\gamma}$.

It is then easy to check that (7.15) 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 $\mathcal{B}(L^2_0(\psi_0))$. Therefore, the function f_η defined by (7.15) 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 $f_\eta - \mathbf{1} \in L^2_0(\psi_0)$.

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,

$$\forall t \geqslant 0, \qquad \int_{\mathcal{E}}(\mathrm{e}^{t\mathcal{L}_\eta}\varphi)\psi_\eta = \int_{\mathcal{E}}\varphi\,\psi_\eta. \tag{7.18}$$

The same equality holds with ψ_η replaced by $\widetilde{\psi}_\eta$. Indeed, a straightforward computation shows that, by definition of f_η,

$$\mathcal{L}_\eta^* f_\eta = \mathcal{L}_0^*\left(1 + \eta(\widetilde{\mathcal{L}}\Pi_0\mathcal{L}_0^{-1}\Pi_0)^*\right)f_\eta = \mathcal{L}_0^*\mathbf{1} = 0.$$

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.

It is however not possible to conclude at this stage that $\psi_\eta = \widetilde{\psi}_\eta$ since (7.18) 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 7.1 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 ergodicity of the Langevin dynamics,[1]

$$\mathbb{E}^{(q_0,p_0)}\left(\frac{1}{t}\int_0^t\varphi(q_s,p_s)\right) = \frac{1}{t}\int_0^t(\mathrm{e}^{s\mathcal{L}_\eta}\varphi)(q_0,p_0)\,ds \xrightarrow[t\to+\infty]{} \int_{\mathcal{E}}\varphi\,\psi_\eta,$$

[1] The proof of the almost-sure convergence of averages over a trajectory, for all initial conditions, is obtained as in Section 5.2, in application of the results by [90]. A first step is to prove that ψ_η is positive.

so that, 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 7.1 (positivity of the invariant measure). *It is possible to prove directly the positivity of the invariant density $f_\eta\psi_0$ by introducing the following Poisson equation:*

$$\mathcal{L}_\eta \Phi_\eta = \mathbf{1}_{\{f_\eta \leqslant 0\}} - \int_{\mathcal{E}} \mathbf{1}_{\{f_\eta\leqslant 0\}}\,\psi_\eta, \quad \int_{\mathcal{E}} \Phi_\eta\,\psi_\eta = 0, \tag{7.19}$$

where f_η is defined by (7.15)*. This equation is well posed since $\mathcal{L}_\eta$ is invertible on weighted L^∞ spaces of functions with average 0 with respect to ψ_η (see the discussion after Proposition 7.1). Now, by the definition* (7.15) *of f_η,*

$$\int_{\mathcal{E}} (\mathcal{L}_\eta\Phi_\eta) f_\eta\psi_0 = 0. \tag{7.20}$$

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 (7.20)*, 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).*

7.3.3 Reformulating the linear response as an integrated correlation

A very useful corollary of (7.16)–(7.17) is the following reformulation of the linear response definition (7.12) 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,

$$\int_{\mathcal{E}} \widetilde{\mathcal{L}}\varphi\,\psi_0 = \int_{\mathcal{E}} \varphi\, S\,\psi_0. \tag{7.21}$$

Note that the expression of S is determined by the applied perturbation $\widetilde{\mathcal{L}}$, and not by the response function R chosen in (7.12). For the non-equilibrium Langevin dynamics (7.1), 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, (7.21) with the choice $\varphi = \mathbf{1}$ shows that this is indeed the case as soon as $\widetilde{\mathcal{L}}\mathbf{1} = 0$.

Proposition 7.2 (Green–Kubo formula). *Consider the non-equilibrium Langevin dynamics* (7.1) *and the definition* (7.21) *of the conjugate function. For any* $R \in L^2_0(\psi_0)$,

$$\lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_0^{+\infty} \mathbb{E}_0(R(q_t,p_t)S(q_0,p_0))\,dt, \tag{7.22}$$

where the expectation $\mathbb{E}_\eta$ *is with respect to the invariant measure* $\psi_\eta(q,p)\,dq\,dp$ *of the non-equilibrium dynamics* (7.1)*, 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 (7.22)) can be obtained using simulations at equilibrium, namely for $\eta = 0$ (see the right-hand side in (7.22)). 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 (7.16) holds (see Section 7.3.4 for possible assumptions on $\widetilde{\mathcal{L}}$).

Proof. In view of (7.12), (7.16) and (7.17), 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 Proposition 5.2 or Theorem 5.3), we can write, for $R \in L^2_0(\psi_0)$,

$$\begin{aligned}\lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta} &= \int_{\mathcal{E}} R\, \mathfrak{f}_1\, \psi_0 = -\int_{\mathcal{E}} [\mathcal{L}_0^{-1}R][\widetilde{\mathcal{L}}^* \mathbf{1}]\, \psi_0 \\ &= \int_0^{+\infty} \mathbb{E}(R(q_t,p_t)S(q_0,p_0))\,dt,\end{aligned}$$

which gives the claimed result.

Definition of the mobility

Let us rewrite equation (7.22) more precisely in the context of (7.1). The mobility ρ_F in the direction F, defined in (7.12), is equal to β times the integrated velocity autocorrelation:

$$\rho_F = \lim_{\eta \to 0} \frac{\mathbb{E}_\eta(F \cdot M^{-1}p)}{\eta} = \beta \int_0^{+\infty} \mathbb{E}_0((F \cdot M^{-1}p_t)(F \cdot M^{-1}p_0))\,dt. \tag{7.23}$$

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

$$Q_t - Q_0 = \int_0^t M^{-1}p_s\,ds$$

is the unperiodized displacement, and where, as in (7.23), 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 (5.5)).

Remark 7.2. *It is in fact possible to prove that the diffusively rescaled process* $\varepsilon F^T q_{t/\varepsilon^2}$ *weakly converges on finite time intervals to an effective Brownian motion with covariance* D_F *in the limit* $\varepsilon \to 0$*, see [133, 149].*

The relation between the mobility and the self-diffusion coefficient is

$$\rho_F = \beta D_F.$$

This equality is based on the identity

$$\mathbb{E}_0\Big(F\cdot(Q_T-Q_0)\Big)^2 = 2T\int_0^T \mathbb{E}_0\Big((F\cdot M^{-1}p_t)(F\cdot M^{-1}p_0)\Big)\left(1-\frac{t}{T}\right)dt.$$

An application of the dominated convergence theorem gives the conclusion when the autocorrelation function is integrable, using the expression (7.23) of the mobility ρ_F. This is the case when $\mathbb{E}_0\Big((F\cdot M^{-1}p_t)(F\cdot M^{-1}p_0)\Big) \leqslant K\mathrm{e}^{-\lambda t}$, see Section 5.3 for techniques to prove such inequalities.

Definition of the thermal conductivity

For the system evolving according to (7.3), the thermal conductivity is defined by the linear response of the energy current :

$$\kappa = \lim_{\Delta T\to 0}\frac{\langle J\rangle_{\Delta T}}{\Delta T} = -\beta^2\gamma\int_0^{+\infty}\int_{\mathcal{E}}\left(\mathrm{e}^{-t\mathcal{L}_0}J\right)(p_1^2-p_N^2)\psi_0\,dt. \tag{7.24}$$

Some (non trivial) manipulations allow to rewrite the above correlation in terms of the energy current autocorrelation (see for instance [99, 19]):

$$\kappa = 2\beta^2\int_0^{+\infty}\mathbb{E}\Big(j_{i+1,i}(q_t,p_t)J(q_0,p_0)\Big)\,dt = \frac{2\beta^2}{N-1}\int_0^{+\infty}\mathbb{E}\Big(J(q_t,p_t)J(q_0,p_0)\Big)\,dt, \tag{7.25}$$

where the equalities hold for any $i = 1,\dots,N-1$.

7.3.4 Generalization to other dynamics

It is of course possible to extend linear response results and Green–Kubo formulae to other dynamics than (7.1), either by generalizing the assumptions ensuring that Theorem 7.1 and Proposition 7.2 hold (as we do below), or by working with different set of assumptions as in [11].

An inspection of the proof of Theorem 7.1 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 results are proved relying on the results of Section 3.3.1.

(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 5.2 for techniques to obtain such convergence results.
Alternatively, as discussed in Remark 7.1, the ergodicity condition can be replaced by solvability conditions for the Poisson equation (7.19).

(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 Proposition 5.2 or Theorem 5.3 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 $L_0^2(\psi_0)$. Note that, as soon as $\widetilde{\mathcal{L}}\mathbf{1} = 0$, the function $\widetilde{\mathcal{L}}^*\varphi$ has average 0 with respect to ψ_0:

$$\int_{\mathcal{X}}\widetilde{\mathcal{L}}^*\varphi\,\psi_0 = \int_{\mathcal{X}}\varphi\,\widetilde{\mathcal{L}}\mathbf{1}\,\psi_0 = 0.$$

The last condition, namely that $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is bounded on $L^2_0(\psi_0)$, 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 $L^2_0(\psi_0)$ is, as at the beginning of the proof of Theorem 7.1, 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,

$$\|\widetilde{\mathcal{L}}\varphi\|_{L^2(\psi_0)} \leqslant a\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)} + b\|\varphi\|_{L^2(\psi_0)}. \tag{7.26}$$

Then, for all $\varphi \in L^2_0(\psi_0)$,

$$\|\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}\varphi\|_{L^2(\psi_0)} \leqslant a\|\varphi\|_{L^2(\psi_0)} + b\|\mathcal{L}_0^{-1}\varphi\|_{L^2(\psi_0)},$$

so that $\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$, and its adjoint, are bounded operators on $L^2_0(\psi_0)$ with operator norm bounded by $a + b\|\mathcal{L}_0^{-1}\|_{\mathcal{B}(L^2_0(\psi_0))}$.

Stronger perturbations

There are situations for which the condition (7.26) is not satisfied. This is the case for instance for generalizations of the dynamics (7.2), for which the perturbation operator $\widetilde{\mathcal{L}}$ involves second derivatives of the momenta p, whereas $\mathcal{L}_0$ may control only first order derivatives. More precisely, consider the dynamics (7.3) with $T_{\rm L} = T + \Delta T$ and $T_{\rm R} = T - \Delta T$, and set $\eta = \Delta T$. The reference equilibrium dynamics is the Langevin dynamics (7.3) with the two thermostats at the boundaries at the same temperature T. Its generator reads

$$\mathcal{L}_0 = \sum_{i=1}^{N} p_i\partial_{q_i} - (\partial_{q_i}V)\,\partial_{p_i} - \gamma\Big(p_1\partial_{p_1} + p_N\partial_{p_N}\Big) + \gamma T\Big(\partial^2_{p_1} + \partial^2_{p_N}\Big), \tag{7.27}$$

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 (7.4). The generator of the perturbation is

$$\widetilde{\mathcal{L}} = \gamma(\partial^2_{p_1} - \partial^2_{p_N}).$$

In this case, it is not 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 4.9. We assume to this end that Assumption 4.8 is satisfied for $\mathcal{A}_1 = \mathcal{L}_0$ and $\mathcal{A}_1 = \mathcal{L}_0^*$. First, introduce $\mathfrak{f}_1$ such that

$$\int_{\mathcal{X}} [(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}})\varphi](1 + \eta\mathfrak{f}_1)\psi_0 = \mathrm{O}(\eta^2).$$

A simple computation shows that $\mathfrak{f}_1$ is formally given by (7.16). In fact, $\mathfrak{f}_1 = -(\mathcal{L}_0^*)^{-1}S$ where S is defined in (7.21). 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. 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 4.4),

$$\int_{\mathcal{X}} \varphi\,\psi_\eta = \int_{\mathcal{X}} \varphi\,\psi_0 + \eta\int_{\mathcal{X}} \varphi\,\mathfrak{f}_1\,\psi_0 + \eta^2 r_{\varphi,\eta},$$

where $|r_{\varphi,\eta}| \leqslant K$ for $|\eta|$ sufficiently small.

7.4 Error estimates on the computation of transport coefficients

The results of the previous section show that there are two ways to compute transport coefficients, either by discretizing the integrated correlation function based on the Green–Kubo formula (7.22), or by approximating the derivative of equilibrium averages with respect to the magnitude of the external forcing as in (7.12). In this section we provide, for both approaches, error estimates on the bias generated by the use of finite time steps to integrate the dynamics. The results quoted here were first presented in [108].

7.4.1 Green–Kubo formulae

We first provide error estimates on linear responses computed using Green–Kubo formulae such as (7.22). We state the result on a general space $\mathcal{X}$ for a dynamics

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t,$$

with generator $\mathcal{L}$ (instead of the notation $\mathcal{L}_0$ used in Section 7.3). The precise result is formulated for smooth functions in the sense of Definition 4.4. We let π denote the reference invariant measure, and still suppose that Assumption 4.8 holds with $\mathcal{A}_1 = \mathcal{L}$ (*i.e.*, the space $\mathcal{S}$ introduced in Definition 4.4 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 (4.60)).

As in Sections 4.4 and 5.4, we consider a discretization of the continuous dynamics under consideration, with transition operator $P_{\Delta t}$, and denote by $\pi_{\Delta t}$ the invariant measure of the numerical scheme (as in Corollary 4.3 or Proposition 5.7). We also introduce the projection operator

$$\Pi_{\Delta t}\varphi = \varphi - \int_{\mathcal{X}} \varphi\, d\pi_{\Delta t},$$

as well as

$$L^\infty_{W_s,\Delta t}(\mathcal{X}) = \Pi_{\Delta t} L^\infty_{W_s}(\mathcal{X}) = \left\{ \varphi \in L^\infty_{W_s}(\mathcal{X}) \,\middle|\, \int_{\mathcal{X}} \varphi\, d\pi_{\Delta t} = 0 \right\}.$$

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.

Theorem 7.2 (error estimates for Green–Kubo). *Consider a numerical method with an invariant measure $\pi_{\Delta t}$ which integrates any scale function W_n introduced in Definition 4.4. Assume that there exists an integer $\alpha \geqslant 1$, such that, for any observable $\phi \in \mathcal{S}$ there is $K, \Delta t^* > 0$ for which the following conditions hold:*

(1) Error on the invariant measure:

$$\int_{\mathcal{X}} \phi\, d\pi_{\Delta t} = \int_{\mathcal{X}} \phi\, d\pi + \Delta t^\alpha r_{\phi,\Delta t}, \tag{7.28}$$

with $|r_{\phi,\Delta t}| \leqslant K$ for $0 < \Delta t \leqslant \Delta t^*$.

(2) Expansion of $P_{\Delta t}$:

$$-\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\phi = \mathcal{L}\phi + \Delta t S_1\phi + \cdots + \Delta t^{\alpha-1} S_{\alpha-1}\phi + \Delta t^\alpha \widetilde{R}_{\alpha,\Delta t}\phi, \tag{7.29}$$

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 $\|\widetilde{R}_{\alpha,\Delta t}\phi\|_{L^\infty_{W_{s_0}}} \leqslant K$ 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 $0 < \Delta t \leqslant \Delta t^*$,

$$\forall n \in \mathbb{N}, \qquad \|P_{\Delta t}^n\|_{\mathcal{B}(L^\infty_{W_s,\Delta t})} \leqslant C_s \, \mathrm{e}^{-\lambda_s n \Delta t}. \tag{7.30}$$

Then, the integrated correlation of two observables $\psi, \varphi \in \mathcal{S}_0$ can be approximated by a Riemann sum up to an error of order Δt^α: there exists $K > 0$ such that

$$\int_0^{+\infty} \mathbb{E}_\pi(\psi(x_t)\varphi(x_0))\, dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\pi_{\Delta t}}(\widetilde{\psi}_{\Delta t,\alpha}(x^n)\varphi(x^0)) + \Delta t^\alpha r_{\Delta t}^{\psi,\varphi}, \tag{7.31}$$

with $|r_{\Delta t}^{\psi,\varphi}| \leqslant K$ 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 $\widetilde{\psi}_{\Delta t,\alpha} \in \mathcal{S}$ is defined as $\widetilde{\psi}_{\Delta t,\alpha} = \Pi_{\Delta t}\psi_{\Delta t,\alpha}$ with

$$\psi_{\Delta t,\alpha} = (\mathrm{Id} + \Delta t\, S_1\mathcal{L}^{-1} + \cdots + \Delta t^{\alpha-1} S_{\alpha-1}\mathcal{L}^{-1})\psi. \tag{7.32}$$

This result deserves several comments, both on the three main assumptions (7.28), (7.29) and (7.30), as well as on the error estimate (7.31) itself. The proof is presented after this discussion.

Let us start by discussing the assumptions of Theorem 7.2. Equation (7.28) can be proved by following the general strategy presented in Theorem 4.9. Note that the remainder term in (7.28) can vanish, for example when a Metropolis procedure is superimposed on the numerical scheme. In this case, α is determined by (7.29). Condition (7.29) has already been encountered when proving error estimates on the invariant measure (see (4.59)). Finally, the uniform-in-Δt convergence (7.30) is given, for the Euler-Maruyama discretization of overdamped Langevin dynamics, by (4.74), which is a consequence of the uniform minorization condition of Lemma 4.2; similar results exist for certain discretization of Langevin dynamics, see [108].

Let us now comment on the error estimate (7.31). First, the result shows that the error is of order Δt^α, upon modifying the observable ψ as $\widetilde{\psi}_{\Delta t,\alpha}$. 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 $\widetilde{\psi}_{\Delta t,\alpha}$. When the operators S_k are powers of $\mathcal{L}$, the correction terms $S_k\mathcal{L}^{-1}$ in (7.32) can be easily computed. Let us denote by k_0 the last index for which $S_k\mathcal{L}^{-1}\psi$ can be evaluated. For example (see the discussion after (4.59)), if the discretization method is of weak order k_0, then $S_k = \mathcal{L}^k/k!$ for all $k = 1, \ldots, k_0$, so that $S_k\mathcal{L}^{-1}\psi$ is easy to evaluate up to $k = k_0$. If $k_0 < \alpha$, the error estimate which can be used in practice is

$$\int_0^{+\infty} \mathbb{E}_\pi(\psi(x_t)\varphi(x_0))\, dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\pi_{\Delta t}}(\widetilde{\psi}_{\Delta t,k_0}(x^n)\varphi(x^0)) + \Delta t^{k_0+1} r_{\Delta t}^{\psi,\varphi}.$$

However, even if $\psi_{\Delta t,k_0}$ can be actually evaluated, it still remains to approximate $\widetilde{\psi}_{\Delta t,k_0} = \Pi_{\Delta t}\psi_{\Delta t,k_0}$, typically by approximating the average of $\psi_{\Delta t,k_0}$ with respect to $\pi_{\Delta t}$ by trajectory averages.

Let us emphasize a very interesting application of Theorem 7.2: the approximation of the variance of discretizations of SDEs. This allows to prove formulas such as ??, and/or to modify quadature rules in the integral in time of the correlation in order to lower the bias.

Remark 7.3 (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 $S_1\mathcal{L}^{-1}\psi$ cannot be evaluated in general, the resulting approximation of the integrated*

correlation is based on $\widetilde{\psi}_{\Delta t,0} = \Pi_{\Delta t}\psi$, 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 [57] and [58] for further precisions.

Let us now present the proof of Theorem 7.2.

Proof. Fix two observables $\varphi, \psi \in \mathcal{S}_0$. Note that

$$\int_0^{+\infty} \mathbb{E}_\pi(\psi(x_t)\varphi(x_0))\,dt = \int_{\mathcal{X}} (-\mathcal{L}^{-1}\psi)\varphi\,d\pi.$$

In order to introduce the correlation functions of the numerical scheme, we would like, in view of (7.29), 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 (7.30), 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 (7.29), 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 $-\mathcal{L}^{-1}\psi$ has zero average with respect to π:

$$\begin{aligned}
\int_{\mathcal{X}} (-\mathcal{L}^{-1}\psi)\varphi\,d\pi &= \int_{\mathcal{X}} (-\mathcal{L}^{-1}\psi)\Pi_{\Delta t}\varphi\,d\pi \\
&= \int_{\mathcal{X}} (-\mathcal{L}^{-1}\psi)\Pi_{\Delta t}\varphi\,d\pi_{\Delta t} + \Delta t^\alpha \widetilde{r}_{\Delta t}^{\mathcal{L}^{-1}\psi,\varphi}, \\
&= \int_{\mathcal{X}} \Pi_{\Delta t}(-\mathcal{L}^{-1}\psi)\Pi_{\Delta t}\varphi\,d\pi_{\Delta t} + \Delta t^\alpha \widetilde{r}_{\Delta t}^{\mathcal{L}^{-1}\psi,\varphi},
\end{aligned} \tag{7.33}$$

where $|\widetilde{r}_{\Delta t}^{\mathcal{L}^{-1}\psi,\varphi}| \leqslant K/2$ for $0 < \Delta t \leqslant \Delta t^*$ by (7.28) (possibly upon increasing the value of K and decreasing Δt^*).

The next step is to approximate $\Pi_{\Delta t}(-\mathcal{L}^{-1}\psi)$ 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

$$\begin{aligned}
\Pi_{\Delta t} &= \Pi_{\Delta t}\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right)^{-1}\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right) \\
&= \Pi_{\Delta t}\left(\Delta t \sum_{n=0}^{+\infty} P_{\Delta t}^n\right)\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right).
\end{aligned}$$

Note that the above sum is convergent in $\mathcal{B}(L^\infty_{W_s,\Delta t})$ in view of (7.30). Relying on (7.29),

$$\begin{aligned}
-\Pi_{\Delta t}\mathcal{L}^{-1}\psi &= -\Pi_{\Delta t}\left(\Delta t \sum_{n=0}^{+\infty} P_{\Delta t}^n\right)\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right)\mathcal{L}^{-1}\psi \\
&= \Delta t\left(\sum_{n=0}^{+\infty} P_{\Delta t}^n\right)\Pi_{\Delta t}(\mathcal{L} + \cdots + \Delta t^{\alpha-1}S_{\alpha-1} + \Delta t^\alpha \widetilde{R}_{\alpha,\Delta t})\mathcal{L}^{-1}\psi, \\
&= \Delta t \sum_{n=0}^{+\infty} P_{\Delta t}^n \widetilde{\psi}_{\Delta t,\alpha} + \Delta t^\alpha \left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t}\right)^{-1} \Pi_{\Delta t}\widetilde{R}_{\alpha,\Delta t}\mathcal{L}^{-1}\psi.
\end{aligned}$$

Note that the sums on the right-hand side is well defined in view of the decay estimates (7.30). Plugging the above equality in (7.33) leads to

$$\int_{\mathcal{X}} (-\mathcal{L}^{-1}\psi)\varphi \, d\pi = \Delta t \sum_{n=0}^{+\infty} \int_{\mathcal{X}} P_{\Delta t}^n \widetilde{\psi}_{\Delta t,\alpha}(\Pi_{\Delta t}\varphi) \, d\pi_{\Delta t} + \Delta t^\alpha \int_{\mathcal{X}} \left(\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \Pi_{\Delta t} \widetilde{R}_{\alpha,\Delta t} \mathcal{L}^{-1}\psi \right) \Pi_{\Delta t}\varphi \, d\pi_{\Delta t} + \Delta t^\alpha \widetilde{r}_{\Delta t}^{\mathcal{L}^{-1}\psi,\varphi}.$$

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 $\|\widetilde{R}_{\alpha,\Delta t} f\|_{L^\infty_{W_s}} \leqslant \widetilde{K}$ for any $0 < \Delta t \leqslant \Delta t^*$. In addition, the following resolvent bound is directly obtained from (7.30):

$$\left\| \left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \right\|_{\mathcal{B}(L^\infty_{W_s,\Delta t})} \leqslant \frac{C_s}{\lambda_s}.$$

Finally, $\pi_{\Delta t}$ integrates all scale functions W_n by assumption. Therefore, upon increasing the value of K, the following inequality holds for any $0 < \Delta t \leqslant \Delta t^*$:

$$\left| \int_{\mathcal{X}} \left(\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \Pi_{\Delta t} \widetilde{R}_{\alpha,\Delta t} \mathcal{L}^{-1}\psi \right) \Pi_{\Delta t}\varphi \, d\pi_{\Delta t} \right| \leqslant \frac{K}{2}.$$

Since

$$\begin{aligned} \sum_{n=0}^{+\infty} \int_{\mathcal{X}} P_{\Delta t}^n \widetilde{\psi}_{\Delta t,\alpha}(\Pi_{\Delta t}\varphi) \, d\pi_{\Delta t} &= \sum_{n=0}^{+\infty} \int_{\mathcal{X}} P_{\Delta t}^n \widetilde{\psi}_{\Delta t,\alpha} \, \varphi \, d\pi_{\Delta t} \\ &= \sum_{n=0}^{+\infty} \mathbb{E}_{\pi_{\Delta t}}(\widetilde{\psi}_{\Delta t,\alpha}(x^n)\varphi(x^0)), \end{aligned}$$

equation (7.31) finally follows.

Remark 7.4 (Green–Kubo formulae for second-order schemes). *In the particular case when $\alpha = 2$ in* (7.28)*, which is very relevant in practice (*e.g. *for second-order splittings of Langevin dynamics, or Geometric Langevin algorithms discussed respectively in Sections 5.4.1 and 5.4.1), it is possible to not modify the observable ψ 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 Corollary 2.20 in [108] and Theorem 6 in [58] for further details.*

To illustrate Theorem 7.2, 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 7.1 displays simulation results obtained for the scheme associated with $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$ (see the discussion after (5.60) and [108]) 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 (7.32) 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 (4.75) 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 4.9, errors in average properties can be reduced from Δt^2 to Δt^3 when the correction term is correctly estimated; in fact, the errors can be shown to reduced to order Δt^4 (see Theorem 2.16 in [108]).

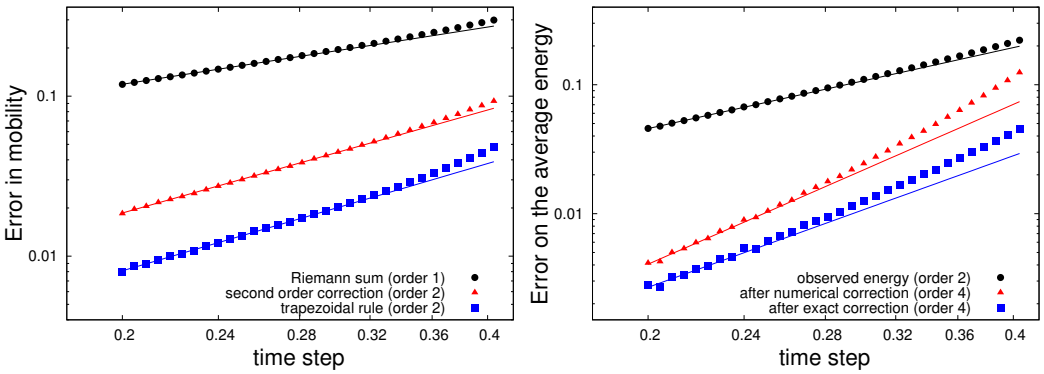

Fig. 7.1. (a) Error in the mobility as a function of the time step Δt when the integrated velocity autocorrelation function is computed using a Riemann sum or with the corrected formula (7.31) in the case $\alpha = 2$. The result from computing the integral using the trapezoidal rule is also shown. (b) Error in the computed average of total energy, with the correction term computed using the same step size by a discretization of (4.75) with the discrete Green–Kubo formula (7.31). 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 $C\Delta t^{\alpha}$.

7.4.2 Linear response approaches

In this part, we we discuss how to approximate a transport coefficient by estimating numerically the derivative of equilibrium averages with respect to the forcing parameter, see (7.12). 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 (7.1). We first present numerical schemes for this dynamics, before stating error estimates on the computation of average properties and linear responses. The discussion here follows the presentation of [108, Section 3], to which we refer for further details.

We still consider splitting schemes which reduce to the schemes presented in Section 5.4.1 when $\eta = 0$. Recall that $\mathcal{L}_0 = A + B + \gamma C$, where the elementary operators A, B, C are introduced in (5.59):

$$A = M^{-1} p \cdot \nabla_q, \quad B = -\nabla V(q) \cdot \nabla_p, \quad C = -M^{-1} p \cdot \nabla_p + \frac{1}{\beta} \Delta_p.$$

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.*,

$$dq_t = (-\nabla V(q_t) + \eta F)\, dt + \sqrt{\frac{2}{\beta}}\, dW_t. \tag{7.34}$$

The latter dynamics is obtained from (7.1) 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 (5.60), 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 (7.34). 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

$$
P_{\Delta t}^{A, B+\eta\widetilde{\mathcal{L}}, \gamma C} = \mathrm{e}^{\Delta t\, A}\, \mathrm{e}^{\Delta t (B+\eta\widetilde{\mathcal{L}})}\, \mathrm{e}^{\gamma \Delta t\, C}, \tag{7.35}
$$

or the second-order splitting

$$
P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A, B+\eta\widetilde{\mathcal{L}}, \gamma C} = \mathrm{e}^{\gamma \Delta t\, C/2}\, \mathrm{e}^{\Delta t (B+\eta\widetilde{\mathcal{L}})/2}\, \mathrm{e}^{\Delta t\, A}\, \mathrm{e}^{\Delta t (B+\eta\widetilde{\mathcal{L}})/2}\, \mathrm{e}^{\gamma \Delta t\, C/2}. \tag{7.36}
$$

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 (7.34). 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 7.5 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 $P_{\eta, \Delta t}$ by following the strategy used to prove Corollary 4.3 or Proposition 5.7. 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 (see Assumptions 3.2 and 3.3) since we rely solely on the boundedness of the force. This in fact allows us to obtain exponential convergence results similar to (3.10), see Proposition 3.3 in [108]: for any $\eta_* > 0$ and for any $s \geqslant 0$, there exist $C, \lambda, \Delta t^* > 0$ (which depend on s and η_*) such that, for all $0 < \Delta t \leqslant \Delta t^*$ and for all $\eta \in [-\eta_*, \eta_*]$,

$$
\forall n \in \mathbb{N}, \qquad \| P_{\eta, \Delta t}^n \|_{\mathcal{B}(L^\infty_{W_s, \Delta t, \eta})} \leqslant C\, \mathrm{e}^{-\lambda n \Delta t}.
$$

where

$$
L^\infty_{W_s, \Delta t, \eta}(\mathcal{E}) = \left\{ \varphi \in L^\infty_{W_s}(\mathcal{E}) \,\middle|\, \int_{\mathcal{E}} \varphi \, d\mu_{\eta, \Delta t} = 0 \right\}.
$$

Let us emphasize that we do not have any control over the convergence rate λ in terms of η^*, and it could well be that λ goes to 0 as η^* increases.

The following result provides error estimates for the invariant measure of splitting schemes such as (7.35) and (7.36) (see Theorem 3.4 in [108]). The proof follows the same lines as the proof of Theorem 4.9, except that expansions are performed with respect to the two small parameters Δt and η.

Theorem 7.3 (error estimates on the invariant measure for $\eta \neq 0$). *Set $\alpha = 1$ for first order splitting schemes such as* (7.35) *and $\alpha = 2$ for second order splitting schemes such*

as (7.36). *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* $\Delta t \in (0, \Delta t^*]$,

$$\int_{\mathcal{E}} \varphi \, d\mu_{\eta,\Delta t} = \int_{\mathcal{E}} \varphi(1 + \eta f_{0,1} + \Delta t^\alpha f_{\alpha,0} + \eta \Delta t^\alpha f_{\alpha,1}) \, d\mu + r_{\varphi,\eta,\Delta t}, \tag{7.37}$$

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 (7.37). 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 (7.16)), while $f_{\alpha,0}$ accounts at leading order for the perturbation induced by the use of finite time steps. As shown below in Corollary 7.1, 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 7.3). 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,

$$\mathscr{R}_{\varphi,\Delta t} = \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} \varphi \, d\mu_{\eta,\Delta t} - \int_{\mathcal{E}} \varphi \, d\mu_{0,\Delta t} \right). \tag{7.38}$$

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 (7.12). 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 (7.38).

Corollary 7.1 (error estimates on linear responses). *Under the assumptions of Theorem 7.3, 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 (7.32) is difficult to compute.

As an application, we obtain the following estimate on the numerically computed mobility:

$$\begin{aligned} \rho_{F,\Delta t} &= \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\eta,\Delta t}(dq\, dp) - \int_{\mathcal{E}} F^T M^{-1} p \, \mu_{0,\Delta t}(dq\, dp) \right) \\ &= \rho_F + \Delta t^\alpha \int_{\mathcal{E}} F^T M^{-1} p \, f_{\alpha,1} \, d\mu + \Delta t^{\alpha+1} r_{\Delta t}, \end{aligned} \tag{7.39}$$

where ρ_F is defined in (7.12). This error estimate is illustrated in Figures 7.2 and 7.3 for the same system as in Figure 7.1. More precisely, we check in Figure 7.2 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 7.3. 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 7.1.

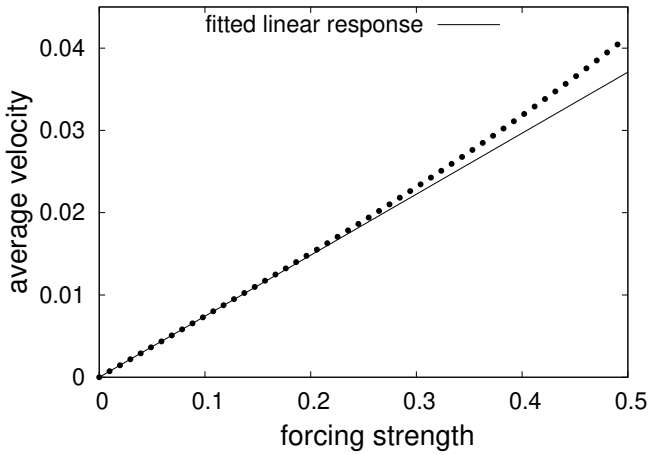

Fig. 7.2. Linear response of the numerical approximation of the average velocity $\mathbb{E}_\eta(F^T M^{-1} p)$ as a function of η for the scheme associated with $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$, for $\Delta t = 0.01$. A linear fit on the first ten values gives a slope of $\rho_{F,\Delta t} \simeq 0.07416$.

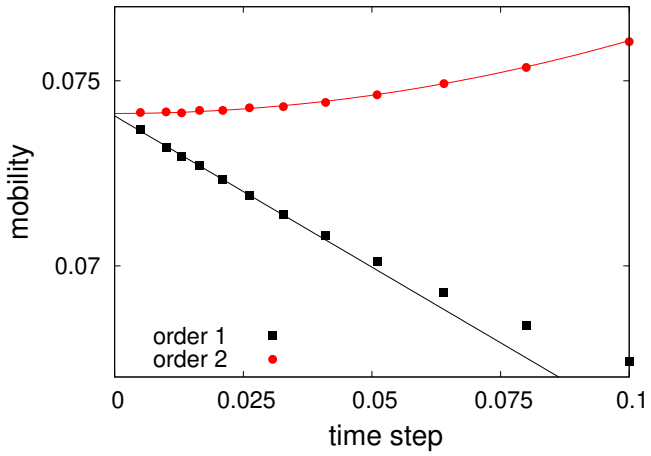

Fig. 7.3. Estimated mobility $\rho_{F,\Delta t}$ for the first-order scheme $P_{\Delta t}^{A, B_\eta, \gamma C}$ and second-order scheme $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$ as a function of the timestep Δt. The fits give $\rho_{F,\Delta t} \simeq 0.0740 + 0.0817 \Delta t$ and $\rho_{F,\Delta t} \simeq 0.0741 + 0.197 \Delta t^2$, respectively.

Remark 7.5 (overdamped limits). *As explained in [108, 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 $\gamma \geqslant 1$.*

Proof of Theorem 7.3

The proof again is along the lines of the proof written in Section 4.4.4, and we are therefore very brief, mentioning only the most important modifications to be considered.

Case $\alpha = 1$.

Let us first consider the first order scheme $P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A}$. Recalling the definition $B_\eta = B + \eta\widetilde{\mathcal{L}}$, we write

$$P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A} = \mathrm{Id} + \Delta t\,(A + B_\eta + \gamma C) + \frac{\Delta t^2}{2}\mathcal{T}\left[\Big(A + B_\eta + \gamma C\Big)^2\right] + \frac{\Delta t^3}{2} R_{\eta,\Delta t}, \tag{7.40}$$

where $\mathcal{T}$ is the ordering operator introduced in Section 5.4.4, and

$$R_{\eta,\Delta t} = \int_0^1 (1-\theta)^2\,\mathcal{T}\left[(A + B_\eta + \gamma C) P_{\theta\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A}\right]^3 d\theta.$$

All the operators appearing in the expressions above are defined on the core $\mathcal{S}$, and have values in $\mathcal{S}$. Since

$$\mathrm{e}^{\theta\Delta t B_\eta} - \mathrm{e}^{\theta\Delta t B} = \eta \int_0^1 \mathrm{e}^{\theta s B_\eta}\,\widetilde{\mathcal{L}}\,\mathrm{e}^{\theta(1-s)B}\,ds,$$

it is easy to see that the operator $R_{\eta,\Delta t}$ can be rewritten as the sum of two contributions: $R_{\eta,\Delta t} = R_{0,\Delta t} + \eta\widetilde{R}_{\eta,\Delta t}$, where, for $\psi \in \mathcal{S}$, the smooth function $\widetilde{R}_{\eta,\Delta t}\psi$ can be uniformly controlled in η for $|\eta| \leqslant 1$. Finally, the evolution operator can be rewritten as

$$P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A} = \mathrm{Id} + \Delta t\left(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}}\right) + \frac{\Delta t^2}{2}\left(\mathcal{L}_0^2 + S_1 + \eta D_1\right) + \Delta t^2 \mathscr{R}_{\eta,\Delta t}, \tag{7.41}$$

where S_1 is the correction term obtained in the case $\eta = 0$, $D_1 = (2\gamma C + B)\widetilde{\mathcal{L}} + \widetilde{\mathcal{L}}(2A + B)$, and

$$\mathscr{R}_{\eta,\Delta t} = \frac{\Delta t}{2} R_{0,\Delta t} + \frac{\eta\Delta t}{2}\widetilde{R}_{\eta,\Delta t} + \frac{\eta^2}{2}\widetilde{\mathcal{L}}^2.$$

We next compute, for $\varphi \in \mathcal{S}$ and $f_{1,1} \in \widetilde{\mathcal{S}}$ to be chosen later,

$$\begin{aligned}
&\int_{\mathcal{E}} \left[\left(\frac{\mathrm{Id} - P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A}}{\Delta t}\right)\varphi\right](1 + \Delta t f_{1,0} + \eta f_{0,1} + \eta\Delta t f_{1,1})\,d\mu \\
&= -\int_{\mathcal{E}} \left[\left(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}} + \frac{\Delta t}{2}\left(\mathcal{L}_0^2 + S_1 + \eta D_1\right) + \Delta t\mathscr{R}_{\eta,\Delta t}\right)\varphi\right](1 + \Delta t f_{1,0} + \eta f_{0,1} + \eta\Delta t f_{1,1})\,d\mu \\
&= -\eta\int_{\mathcal{E}} \left[\widetilde{\mathcal{L}}\varphi + (\mathcal{L}_0\varphi) f_{0,1}\right] d\mu - \Delta t \int_{\mathcal{E}} \left[\frac{1}{2} S_1\varphi + (\mathcal{L}_0\varphi) f_{1,0}\right] d\mu \\
&\quad - \eta\Delta t \int_{\mathcal{E}} \left[\left(\widetilde{\mathcal{L}}\varphi\right) f_{1,0} + \frac{1}{2}\left(\mathcal{L}_0^2 + S_1\right)\varphi\, f_{0,1} + (\mathcal{L}_0\varphi) f_{1,1} + \frac{1}{2} D_1\varphi\right] d\mu \\
&\quad - \eta^2 \int_{\mathcal{E}} \left(\widetilde{\mathcal{L}}\varphi\right)(f_{0,1} + \Delta t f_{1,1})\,d\mu - \frac{\Delta t^2}{2}\int_{\mathcal{E}} \left[\left(\mathcal{L}_0^2 + S_1 + \eta D_1\right)\varphi\right](f_{1,0} + \eta f_{1,1})\,d\mu \\
&\quad - \Delta t \int_{\mathcal{E}} \mathscr{R}_{\eta,\Delta t}\varphi\,(1 + \Delta t f_{1,0} + \eta f_{0,1} + \eta\Delta t f_{1,1})\,d\mu.
\end{aligned}$$

The first two terms in the last expression vanish by definition of $f_{0,1}$ and $f_{1,0}$, while the third one vanishes when the function $f_{1,1}$ is defined by the Poisson equation

$$\mathcal{L}_0^* f_{1,1} = -\widetilde{\mathcal{L}}^* f_{1,0} - \frac{1}{2}\left(\mathcal{L}_0^2 + S_1\right)^* f_{0,1} - \frac{1}{2} D_1^* \mathbf{1}. \tag{7.42}$$

It is easy to check that the right-hand side of this equation has a vanishing average with respect to μ (integrating with respect to μ and letting the adjoints of the operators act on $\mathbf{1}$). We then project (7.40) using the projection operator $\Pi^\perp$ onto functions with average 0 with respect to μ, and introduce the approximate inverse of the operator $(\mathrm{Id} - P_{\Delta t})/\Delta t$, defined on $\widetilde{\mathcal{S}}$ as

$$\begin{aligned} Q_{\eta,\Delta t} = &-\mathcal{L}_0^{-1} + \eta \mathcal{L}_0^{-1}\Pi^\perp \widetilde{\mathcal{L}} \Pi^\perp \mathcal{L}_0^{-1} + \frac{\Delta t}{2}\left[\Pi^\perp + \mathcal{L}_0^{-1}\Pi^\perp\left(S_1 + \eta D_1\right)\Pi^\perp \mathcal{L}_0^{-1}\right] \\ &- \frac{\eta \Delta t}{2}\mathcal{L}_0^{-1}\Pi^\perp \widetilde{\mathcal{L}} \Pi^\perp \mathcal{L}_0^{-1}\left(\mathcal{L}_0^2 + \Pi^\perp S_1 \Pi^\perp + \eta \Pi^\perp D_1 \Pi^\perp\right)\mathcal{L}_0^{-1} \\ &- \frac{\eta \Delta t}{2}\mathcal{L}_0^{-1}\left(\mathcal{L}_0^2 + \Pi^\perp S_1 \Pi^\perp + \eta \Pi^\perp D_1 \Pi^\perp\right)\mathcal{L}_0^{-1}\Pi^\perp \widetilde{\mathcal{L}} \Pi^\perp \mathcal{L}_0^{-1}, \end{aligned}$$

obtained by truncating the formal series expansion of the inverse operator by discarding terms associated with η^2 or Δt^2. The approximate inverse is such that

$$\Pi^\perp \left(\frac{\mathrm{Id} - P_{\Delta t}^{\gamma C, B+\eta\widetilde{\mathcal{L}}, A}}{\Delta t}\right)\Pi^\perp Q_{\eta,\Delta t} = \Pi^\perp + \eta^2 \mathcal{R}^1_{\eta,\Delta t} + \Delta t^2 \mathcal{R}^2_{\eta,\Delta t},$$

with $\mathcal{R}^2_{\eta,\Delta t} = \mathcal{R}^2_{0,\Delta t} + \eta \widetilde{\mathcal{R}}^2_{\eta,\Delta t}$. We then replace $\Pi^\perp \varphi$ by $Q_{\eta,\Delta t}\psi$ and conclude as in Section 4.4.4.

Case $\alpha = 2$.

The result for the second order splitting is obtained by appropriate modifications of the proof written above for $p = 1$, similar to the ones introduced in Section 5.4.4. We will therefore mention only the most important point, which is the following. Replacing B by B_η in the expansion of the evolution operator for equilibrium Langevin dynamics, we see that

$$\begin{aligned} \frac{\mathrm{Id} - P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}}{\Delta t} &= -\mathcal{L}_0 - \eta\widetilde{\mathcal{L}} - \frac{\Delta t}{2}(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}})^2 - \Delta t^2\left(\frac{1}{6}(\mathcal{L}_0 + \eta\widetilde{\mathcal{L}})^3 + S_2 + \eta \widetilde{S}_{2,\eta}\right) - \Delta t^3 R_{\eta,\Delta t} \\ &= -\mathcal{L}_0 - \eta\widetilde{\mathcal{L}} - \frac{\Delta t}{2}\mathcal{L}_0^2 - \frac{\eta\Delta t}{2}\left(\mathcal{L}_0\widetilde{\mathcal{L}} + \widetilde{\mathcal{L}}\mathcal{L}_0\right) - \frac{\eta^2\Delta t}{2}\widetilde{\mathcal{L}}^2 - \Delta t^2\left(\frac{1}{6}\mathcal{L}_0^3 + S_2\right) \\ &\quad - \eta\Delta t^2\left(\frac{1}{6}\left(\mathcal{L}_0^2\widetilde{\mathcal{L}} + \mathcal{L}_0\widetilde{\mathcal{L}}\mathcal{L}_0 + \widetilde{\mathcal{L}}\mathcal{L}_0^2\right) + \widetilde{S}_{2,0}\right) + \mathscr{R}_{\eta,\Delta t}, \end{aligned}$$

where $\mathscr{R}_{\eta,\Delta t}$ regroups operators of order $\Delta t^{3+\alpha}\eta^{\alpha'}$ or $\Delta t^{2+\alpha}\eta^{2+\alpha'}$ for $\alpha, \alpha' \geqslant 0$, the operator S_2 is the one obtained when $\eta = 0$, and $\widetilde{S}_{2,\eta}$ satisfies

$$\begin{aligned} 12\,\widetilde{S}_{2,\eta} = &\left[A, \left[A, \widetilde{\mathcal{L}}\right]\right] - \frac{1}{2}\left[B, \left[\widetilde{\mathcal{L}}, A\right]\right] - \frac{1}{2}\left[\widetilde{\mathcal{L}}, [B, A]\right] + \gamma\left[\widetilde{\mathcal{L}}, [A + B, C]\right] + \gamma\left[A + B, \left[\widetilde{\mathcal{L}}, C\right]\right] \\ &- \frac{\gamma^2}{2}\left[C, \left[C, \widetilde{\mathcal{L}}\right]\right] + \eta\left(\gamma\left[\widetilde{\mathcal{L}}, \left[\widetilde{\mathcal{L}}, C\right]\right] - \frac{1}{2}\left[\widetilde{\mathcal{L}}, \left[\widetilde{\mathcal{L}}, A\right]\right]\right). \end{aligned}$$

We next compute the dominant terms in

$$\int_{\mathcal{E}}\left[\left(\frac{\mathrm{Id} - P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}}{\Delta t}\right)\varphi\right]\left(1 + \Delta t^2 f_{2,0} + \eta f_{0,1} + \eta\Delta t^2 f_{2,1}\right)\, d\mu.$$

We consider only contributions of the form $\eta^\alpha \Delta t^{\alpha'}$ with $\alpha = 0, 1$ and $0 \leqslant \alpha' \leqslant 2$. The contributions in $\Delta t, \Delta t^2$ are the same as in the case $\eta = 0$ and therefore vanish. The contribution in η vanishes in view of the choice of $f_{0,1}$. For the same reason, the contribution in $\eta\Delta t$ vanishes as well:

$$-\frac{\eta\Delta t}{2}\int_{\mathcal{E}}\left(\mathcal{L}_0\widetilde{\mathcal{L}} + \widetilde{\mathcal{L}}\mathcal{L}_0\right)\varphi + \left(\mathcal{L}_0^2\varphi\right) f_{0,1}\, d\mu = -\frac{\eta\Delta t}{2}\int_{\mathcal{E}}\left(\mathcal{L}_0\varphi\right)\left(\widetilde{\mathcal{L}}^*\mathbf{1} + \mathcal{L}_0^* f_{0,1}\right) d\mu = 0.$$

The contribution in $\eta \Delta t^2$ is proportional to

$$\int_{\mathcal{E}} \left[\left(\frac{\mathcal{L}_0^2 \widetilde{\mathcal{L}} + \mathcal{L}_0 \widetilde{\mathcal{L}} \mathcal{L}_0 + \widetilde{\mathcal{L}} \mathcal{L}_0^2}{6} + \widetilde{S}_{2,0} \right) \varphi + \left(\widetilde{\mathcal{L}} \varphi \right) f_{2,0} + \left[\left(\frac{\mathcal{L}_0^3}{6} + S_2 \right) \varphi \right] f_{0,1} + \left(\mathcal{L}_0 \varphi \right) f_{2,1} \right] d\mu.$$

The requirement that this expression vanishes for all functions $\varphi \in \mathcal{S}$ characterizes the function $f_{2,1}$ (the discussion on the solvability of this equation following the same lines as the discussion on the solvability of (7.42)). The proof is then concluded as in the case $p = 1$.

7.5 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 4.5, 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.

7.5.1 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 (7.7), for which the unique invariant probability measure is the uniform measure on $\mathcal{D} = \mathbb{T}$ when $V = 0$, which transforms into (7.9) 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.

7.5.2 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 7.2 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.

7.5.3 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 [66]. 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 [36].

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 7.6 (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 (7.1)) 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 [83, 84, 112, 143] for example.*

7.5.4 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 (7.12) or (7.22). 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 [52]), 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 [51, 118, 53, 106] 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 (7.27) 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 (7.14), 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 (7.22) and of the definition (7.25) of the thermal conductivity).

8

Co-area formula

A reaction coordinate is an application defined on the configurational space

$$\xi : \mathbb{R}^n \to \mathbb{R}^m$$

(where $n = 3N$, N being the number of particles) which indexes the transformation of interest. For example, it can be a dihedral angle in a molecule, which measures the change of conformation of the molecule. It may also be a distance between two (groups of) atoms, which measures a binding energy. In any case, it is meant to be a function with value in a small dimensional space compared to the dimension of the configurational space ($m < n$). In all the following, we assume that ξ is a smooth function such that

$$\operatorname{rank}(\nabla\xi) = m \tag{8.1}$$

where $\operatorname{rank}(\nabla\xi)$ is the rank of the $n \times m$ matrix $\left(\dfrac{\partial \xi_\alpha}{\partial q_i}\right)_{i,\alpha}$. The notation convention in the following is that Latin (respectively Greek) indices vary between 1 and n (respectively m).

We define

$$\Sigma(z) = \Big\{q, \xi(q) = z\Big\}$$

is the submanifold of codimension m of $\mathbb{R}^n$ corresponding to positions q at a fixed value z of the reaction coordinate.

The co-area formula

Let us introduce the $m \times m$ Gram matrix:

$$G = (\nabla\xi)^T \nabla\xi, \tag{8.2}$$

which writes componentwise: $G_{\alpha,\beta} = \nabla\xi_\alpha \cdot \nabla\xi_\beta$. The non-degeneracy assumption (8.1) is equivalent to the fact that $\det G > 0$. We will need the following technical assumption: $\forall q \in \mathbb{R}^n$,

$$\sup_{1 \leqslant \alpha \leqslant m} \left| \sum_{\zeta=1}^{m} G^{-1}_{\alpha,\zeta}(q) \nabla\xi_\zeta(q) \right| < \infty. \tag{8.3}$$

All the results we present below may be generalized to other configuration spaces $\mathcal{D}$, see Remark 1.1. Of course, the assumptions (8.1) and (8.3) need to be checked only for $q \in \mathcal{D}$.

Two probability measures can be associated with a reference measure ν (such as the Boltzmann Gibbs measure) on the configuration space:

- The image of the measure ν by ξ (also called the marginal of ν in ξ) which is denoted by $\nu^\xi(dz)$.
- The probability measure $\nu^\xi(dq|z)$ which is the measure ν conditioned to a fixed value z of the reaction coordinate.

These two measures are defined by the following conditioning formula:

Definition 8.1 (Marginal and conditional probability measures). *The measures ν^ξ and $\nu^\xi(\cdot|z)$ are defined by: for any bounded measurable functions $f : \mathbb{R}^m \to \mathbb{R}$ and $g : \mathbb{R}^n \to \mathbb{R}$,*

$$\int_{\mathbb{R}^n} f(\xi(q))\, g(q)\, \nu(dq) = \int_{\mathbb{R}^m} f(z) \left(\int_{\Sigma(z)} g\, d\nu^\xi(\cdot|z) \right) \nu^\xi(dz). \tag{8.4}$$

Let us now introduce the conditional measure $\delta_{\xi(q)-z}(dq)$ (also called delta measure) which is defined as: for any test functions $f : \mathbb{R}^m \to \mathbb{R}$ and $g : \mathbb{R}^n \to \mathbb{R}$,

$$\int_{\mathbb{R}^n} f(\xi(q))\, g(q)\, dq = \int_{\mathbb{R}^m} f(z) \left(\int_{\Sigma(z)} g\, \delta_{\xi(q)-z}(dq) \right) dz,$$

or, in short,

$$dq = \delta_{\xi(q)-z}(dq)\, dz. \tag{8.5}$$

Alternative expressions of marginal and conditional probability measures in terms of the surface measure on $\Sigma(z)$ will be useful. To derive these expressions, a very important formula is needed, which will be used many times in the following: the co-area formula.

Lemma 8.1 (Co-area formula). *For any smooth function $f : \mathbb{R}^n \to \mathbb{R}$,*

$$\int_{\mathbb{R}^n} f(q) (\det G)^{1/2}(q)\, dq = \int_{\mathbb{R}^m} \int_{\Sigma(z)} f\, d\sigma_{\Sigma(z)}\, dz, \tag{8.6}$$

where $\sigma_{\Sigma(z)}$ denotes the surface measure on $\Sigma(z)$, namely the Lebesgue measure on $\Sigma(z)$ induced by the Lebesgue measure in the ambient Euclidean space $\mathbb{R}^n$. In the case $m = 1$, Equation (8.6) writes:

$$\int_{\mathbb{R}^n} f(q) |\nabla \xi|(q)\, dq = \int_{\mathbb{R}} \int_{\Sigma(z)} f\, d\sigma_{\Sigma(z)}\, dz. \tag{8.7}$$

In view of (8.6) and (8.5), it holds:

$$\delta_{\xi(q)-z}(dq) = (\det G)^{-1/2} d\sigma_{\Sigma(z)}. \tag{8.8}$$

A corollary of the co-area formula (8.6) is the following:

Corollary 8.1. *If a continuous random variable Q has law $\psi(q)\, dq$ in $\mathbb{R}^n$, then $\xi(Q)$ has law*

$$\left(\int_{\Sigma(z)} \psi\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)} \right) dz,$$

and the law of Q conditioned to a fixed value z of $\xi(Q)$ is

$$\frac{\psi\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)}}{\displaystyle\int_{\Sigma(z)} \psi\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)}}.$$

In particular,

$$\nu^\xi(dz) = \left(\int_{\Sigma(z)} Z_\nu^{-1} \mathrm{e}^{-\beta V}\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)} \right) dz, \tag{8.9}$$

and

$$d\nu^\xi(\cdot|z) = \frac{\mathrm{e}^{-\beta V}\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)}}{\displaystyle\int_{\Sigma(z)} \mathrm{e}^{-\beta V}\, (\det G)^{-1/2}\, d\sigma_{\Sigma(z)}}. \tag{8.10}$$

Proof. For any bounded functions f and g, using the co-area formula (8.6),

$$\begin{aligned}\mathbb{E}\Big(f(\xi(Q))\,g(Q)\Big) &= \int_{\mathbb{R}^n} f(\xi(q))\,g(q)\,\psi(q)\,dq \\ &= \int_{\mathbb{R}^m}\int_{\Sigma(z)} (f\circ\xi)\,g\,\psi\,(\det G)^{-1/2} d\sigma_{\Sigma(z)}\,dz \\ &= \int_{\mathbb{R}^m} f(z)\frac{\displaystyle\int_{\Sigma(z)} g\,\psi\,(\det G)^{-1/2} d\sigma_{\Sigma(z)}}{\displaystyle\int_{\Sigma(z)} \psi\,(\det G)^{-1/2} d\sigma_{\Sigma(z)}}\left(\int_{\Sigma(z)} \psi\,(\det G)^{-1/2} d\sigma_{\Sigma(z)}\right) dz,\end{aligned}$$

which concludes the proof in view of the definition (8.4).

Remark 8.1 (The surface measure $\sigma_{\Sigma(z)}$). *The surface measure $\sigma_{\Sigma(z)}$ on the submanifold $\Sigma(z)\subset\mathbb{R}^n$ may be defined as follows. For any open set B of $\Sigma(z)$, consider the open set (in $\mathbb{R}^n$)*

$$B^\varepsilon = \{q+\lambda n(q),\, q\in B, \lambda\in(-\varepsilon,\varepsilon)\}$$

where $n(q)$ is the unit normal to $\Sigma(z)$ at point q (for the usual Euclidean scalar product). Then $\sigma_{\Sigma(z)}(B) = \lim_{\varepsilon\to 0}\frac{|B^\varepsilon|}{2\varepsilon}$, where $|B^\varepsilon|$ here denotes the Lebesgue measure (in $\mathbb{R}^n$) of B^ε.

More rigorously, if $\varphi: U\to\mathbb{R}^n$ denotes a (local) parametrization of $\Sigma(z)$ (U is an open subset of $\mathbb{R}^{n-m}$), then, for any $B\subset\varphi(U)$, $\sigma_{\Sigma(z)}(B) = \displaystyle\int_{\varphi^{-1}(B)} \left(\det(\nabla\varphi\,\nabla\varphi^T)\right)^{1/2}(x)\,dx$, where dx denotes the Lebesgue measure in $\mathbb{R}^{n-m}$ and $(\nabla\varphi)_{i,j} = \left(\frac{\partial\varphi_j}{\partial q_i}\right)$ is the Jacobian matrix (in $\mathbb{R}^{(n-m)\times n}$) of φ.

All this holds of course under regularity assumptions on $\Sigma(z)$ ($\Sigma(z)$ should be C^1). We refer for example to Section VII.5.4 in [103].

Let us now prove Lemma 8.1.

Proof. Classical proofs of the co-area formula can be found in the reference textbooks [4, 54]. These proofs are however quite involved since they assume only Lipschitz regularity for ξ. For the sake of completeness, we give here an elementary proof in the case of a smooth ξ.

For any $q\in\mathbb{R}^n$, we introduce the matrices $\overline{A}(q)$ and $\widetilde{A}(q)$, respectively with dimensions $m\times m$ and $m\times(n-m)$ such that $(\nabla\xi)^T = \left[\overline{A}\middle|\widetilde{A}\right]$. It holds $G = (\nabla\xi)^T\nabla\xi = \overline{A}\,\overline{A}^T + \widetilde{A}\widetilde{A}^T$. Note that, using a partition of unity, it is sufficient to prove (8.6) for f with support in an open set such that $\det\overline{A}\neq 0$ (since $\mathrm{rank}(\nabla\xi)=m$). We can therefore suppose without loss of generality that the first m columns of the matrix $(\nabla\xi)^T$ are linearly independent. Let us introduce the global change of variable $\Phi(q) = (\xi(q), q_{m+1},\dots,q_n)$. We use the notation $z=\xi(q)$ and $y=(q_{m+1},\dots,q_n)$. Note that

$$(\nabla\Phi)^T = \left[\begin{array}{c|c}\overline{A} & \widetilde{A}\\ \hline 0 & \mathrm{Id}_{n-m}\end{array}\right],\ \text{and}\ (\nabla\Phi)^{-T} = \Big((\nabla\Phi)^T\Big)^{-1} = \left[\begin{array}{c|c}\overline{A}^{-1} & -\overline{A}^{-1}\widetilde{A}\\ \hline 0 & \mathrm{Id}_{n-m}\end{array}\right],$$

where Id_k denotes the $k\times k$ identity matrix. This implies that

$$\left|\mathrm{Jac}(\Phi^{-1})\right| = \left|\det\overline{A}^{-1}\right|\circ\Phi^{-1}.$$

Therefore, using the change of variable $(z,y)=\Phi(q)$ and Fubini theorem, it holds:

$$\begin{aligned}&\int_{\mathbb{R}^n} f(\det G)^{1/2} \\ &= \int_{\mathbb{R}^m}\int_{\mathbb{R}^{n-m}} \left(f\left[\det\left(\overline{A}\,\overline{A}^T + \widetilde{A}\widetilde{A}^T\right)\right]^{1/2}\left|\det\overline{A}^{-1}\right|\right)\circ\Phi^{-1}(z,y)\,dy\,dz.\end{aligned} \tag{8.11}$$

Besides, for a fixed $z\in\mathbb{R}^m$, by definition of the Lebesgue measure on $\Sigma(z)$ (see Remark 8.1) and since $y\mapsto\Phi^{-1}(z,y)$ is a (local) parametrization of $\Sigma(z)$,

$$\int f d\sigma_{\Sigma(z)} \tag{8.12}$$
$$= \int_{\mathbb{R}^{n-m}} f \circ \Phi^{-1}(z,y) \left(\det\left(\nabla\Phi^{-1}(z,.)(\nabla\Phi^{-1}(z,.))^T\right)\right)^{1/2}(y)\, dy.$$

Note that (for a fixed $z \in \mathbb{R}^m$), $\nabla\Phi^{-T}(z,.) = \left[\begin{array}{c} -\overline{A}^{-1}\widetilde{A} \\ \hline \mathrm{Id}_{n-m} \end{array}\right] \circ \Phi^{-1}(z,.)$ (the gradient being only with respect to the y variable) so that

$$\nabla\Phi^{-1}(z,.)(\nabla\Phi^{-1}(z,.))^T = \left(\mathrm{Id}_{n-m} + \widetilde{A}^T\overline{A}^{-T}\overline{A}^{-1}\widetilde{A}\right) \circ \Phi^{-1}(z,.).$$

Thus, considering (8.11) and (8.12), the proof of the co-area formula is completed provided that

$$\det\left(\overline{A}\,\overline{A}^T + \widetilde{A}\widetilde{A}^T\right)\left(\det\overline{A}^{-1}\right)^2 = \det\left(\mathrm{Id}_{n-m} + \widetilde{A}^T\overline{A}^{-T}\overline{A}^{-1}\widetilde{A}\right)$$

which is equivalent to showing

$$\det\left(\mathrm{Id}_m + BB^T\right) = \det\left(\mathrm{Id}_{n-m} + B^TB\right), \tag{8.13}$$

where B denotes the $m \times (n-m)$ matrix:

$$B = \overline{A}^{-1}\widetilde{A}.$$

The identity (8.13) is a consequence of Lemma 8.2 below, which thus concludes the proof.

Lemma 8.2. *Let $A \in \mathbb{R}^{k\times l}$ and $B \in \mathbb{R}^{l\times k}$ denote two matrices. Then*

$$\det(\mathrm{Id}_k - AB) = \det(\mathrm{Id}_l - BA).$$

Proof. The proof relies on the two identities:

$$\left[\begin{array}{c|c} \mathrm{Id}_k & A \\ \hline B & \mathrm{Id}_l \end{array}\right]\left[\begin{array}{c|c} \mathrm{Id}_k & -A \\ \hline 0 & \mathrm{Id}_l \end{array}\right] = \left[\begin{array}{c|c} \mathrm{Id}_k & 0 \\ \hline B & \mathrm{Id}_l - BA \end{array}\right] \tag{8.14}$$

and

$$\left[\begin{array}{c|c} \mathrm{Id}_k & A \\ \hline B & \mathrm{Id}_l \end{array}\right]\left[\begin{array}{c|c} \mathrm{Id}_k & 0 \\ \hline -B & \mathrm{Id}_l \end{array}\right] = \left[\begin{array}{c|c} \mathrm{Id}_k - AB & A \\ \hline 0 & \mathrm{Id}_l \end{array}\right]. \tag{8.15}$$

Now, note that the left-hand sides of (8.14) and (8.15) have the same determinant. The proof then follows on noticing that the determinant of the right-hand side of (8.14) (respectively of (8.15)) is $\det(\mathrm{Id}_l - BA)$ (respectively $\det(\mathrm{Id}_k - AB)$).

Remark 8.2 (On the notation δ). *In the mathematical literature, the notation δ_Σ (where Σ is a smooth submanifold in $\mathbb{R}^n$) is sometimes used to denote the Dirac distribution defined by: for any smooth test function ϕ,*

$$\langle \delta_\Sigma, \phi\rangle = \int_\Sigma \phi\, d\sigma_\Sigma,$$

where σ_Σ is the surface measure and $\langle\cdot,\cdot\rangle$ here denotes the distribution bracket. The factor $(\det G)^{-1/2}$ does not appear in this formula (compare with (8.8)). The Dirac distribution δ_Σ should not be confused with the notation $\delta_{\xi(q)-z}(dq)$. The Dirac distribution is typically introduced as the derivative of a characteristic function. Namely, for any smooth domain $\Omega \in \mathbb{R}^n$ with boundary $\partial\Omega = \Sigma$ and unit outward normal n, the distribution δ_Σ satisfies: for any smooth test function ϕ,

$$\langle \delta_\Sigma, \phi\cdot n\rangle = \int_\Omega \mathrm{div}(\phi),$$

which can be rewritten (in the sense of distributions):

$$\nabla 1_\Omega = -n\,\delta_\Sigma,$$

where 1_Ω denotes the characteristic function of the domain Ω.

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] E. Akhmatskaya et S. Reich, The targetted shadowing hybrid Monte Carlo (TSHMC method), In *New Algorithms for Macromolecular Simulation* (Springer, 2005), pp. 141–153.

[3] 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.

[4] L. Ambrosio, N. Fusco, et D. Pallara, *Functions of Bounded Variation and Free Discontinuity Problems* (Oxford Science Publications, 2000).

[5] 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.

[6] C. Ané, S. Blachère, D. Chafaï, P. Fougères, I. Gentil, F. Malrieu, C. Roberto, et G. Scheffer, *Sur les inÃľgalités de Sobolev logarithmiques* (Société Mathématique de France, 2000). In French.

[7] 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.

[8] 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.

[9] V. I. Arnol'd, *Mathematical Methods of Classical Mechanics*, volume 60 of *Graduate Texts in Mathematics* (Springer-Verlag, 1989).

[10] R. Assaraf et M. Caffarel, Zero-variance principle for Monte Carlo algorithms, *Phys. Rev. Lett.* **83** (1999) 4682–4685.

[11] 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.

[12] 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.

[13] D. Bakry et M. Emery, Diffusions hypercontractives, In *SÃľminaire de ProbabilitÃľs XIX*, volume 1123 of *Lecture Notes in Mathematics* (Springer Verlag, 1985), pp. 177–206.

[14] D. Bakry, I. Gentil, et M. Ledoux, *Analysis and Geometry of Markov Diffusion Operators* (Springer, 2014).

[15] R. Balian, *From Microphysics to Macrophysics. Methods and Applications of Statistical Physics*, volume I - II (Springer, 2007).

[16] J. A. Barker, Monte Carlo calculations of the radial distribution functions for a proton-electron plasma, *Aust. J. Phys.* **18** (1965) 119–133.

[17] M. I. Baskes, Modified embedded-atom potentials for cubic materials and impurities, *Phys. Rev. B* **46**(5) (1992) 2727–2742.

[18] William Beckner, A generalized PoincarÃľ inequality for Gaussian measures, *P. Am. Math. Soc.* **105**(2) (1989) 397–400.

[19] C. Bernardin et S. Olla. Nonequilibrium macroscopic dynamics of chains of anharmonic oscillators. `http://www.ceremade.dauphine.fr/~olla/springs`.

[20] L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio, et C. Landim, Macroscopic fluctuation theory, *Rev. Mod. Phys.* **87**(2) (2015) 593–636.

[21] 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.

[22] G. Blower et F. Bolley, Concentration of measure on product spaces with applications to Markov processes, *Studia Math.* **175** (2006) 47–72.

[23] 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.

[24] N. Bou-Rabee et M. Hairer, Nonasymptotic mixing of the MALA algorithm, *IMA J. Numer. Anal.* **33** (2013) 80–110.

[25] N. Bou-Rabee et H. Owhadi, Long-run accuracy of variational integrators in the stochastic context, *SIAM J. Numer. Anal.* **48** (2010) 278–297.

[26] 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.

[27] E. Bouin, F. Hoffmann, et C. Mouhot, Exponential decay to equilibrium for a fibre lay-down process on a moing conveyor belt, *arXiv preprint* **1605.04121** (2016).

[28] R. E. Caflisch, Monte Carlo and quasi-Monte Carlo methods, *Acta Numerica* **7** (1998) 1–49.

[29] 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.

[30] 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.

[31] 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.

[32] R. Car et M. Parrinello, Unified approach for molecular dynamics and density-functional theory, *Phys. Rev. Lett.* **55**(22) (1985) 2471–2474.

[33] 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.

[34] P. Cattiaux, Long time behavior of Markov processes, *ESAIM Proc.* **44** (2014) 110–128.

[35] D. Chafaï, From Boltzmann to random matrices and beyond, *arXiv preprint* **1405.1003** (2015).

[36] 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.

[37] R. Dautray et J.-L. Lions, *Mathematical Analysis and Numerical Methods for Science and Technology, Volume 3. Spectral Theory and Applications* (Springer, 1990).

[38] G. Deligiannidis, D. Paulin, et A. Doucet, Randomized Hamiltonian Monte Carlo as scaling limit of the Bouncy Particle Sampler and dimension-free convergence rates, *arXiv preprint* **1808.04299** (2018).

[39] 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.

[40] J.-D. Deuschel et D. W. Stroock, *Large deviations*, volume 137 of *Pure and Applied Mathematics* (Academic Press Inc., 1989).
[41] A. Dhar, Heat transport in low-dimensional systems, *Adv. Phys.* **57** (2008) 457–537.
[42] 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.
[43] 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.
[44] J. Dolbeault, C. Mouhot, et C. Schmeiser, Hypocoercivity for linear kinetic equations conserving mass, *Trans. AMS* **367** (2015) 3807–3828.
[45] R. Douc, G. Fort, et A. Guillin, Subgeometric rates of convergence of f-ergodic strong Markov processes, *Stoch. Proc. Appl.* **119** (2009) 897–923.
[46] A.B. Duncan, T. LeliÃĺvre, et G.A. Pavliotis, Variance reduction using nonreversible Langevin samplers, *J. Stat. Phys.* **163**(3) (2016) 457–491.
[47] J.-P. Eckmann et M. Hairer, Non-equilibrium statistical mechanics of strongly anharmonic chains of oscillators, *Commun. Math. Phys.* **212** (2000) 105–164.
[48] 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.
[49] 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.
[50] S. N. Ethier et T. G. Kurtz, *Markov processes*, Probability and Mathematical Statistics (John Wiley & Sons Inc., 1986).
[51] D. J. Evans, Homogeneous NEMD algorithm for thermal conductivity. Application of non-canonical linear response theory, *Phys. Lett. A* **91**(9) (1982) 457 – 460.
[52] D. J. Evans et G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008).
[53] 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.
[54] L. C. Evans et R. F. Gariepy, *Measure Theory and Fine Properties of Functions*, Studies in Advanced Mathematics (CRC Press, 1992).
[55] E. Faou, Nosé-Hoover dynamics in a shaker, *J. Chem. Phys.* **124** (2006) 184104.
[56] E. Faou et T. Lelièvre, Conservative stochastic differential equations: Mathematical and numerical analysis, *Math. Comput.* **78** (2009) 2047–2074.
[57] M. Fathi, A.-A. Homman, et G. Stoltz, Error analysis of the transport properties of Metropolized schemes, *ESAIM Proc.* **48** (2015) 341–363.
[58] M. Fathi et G. Stoltz, Improving dynamical properties of stabilized discretizations of overdamped Langevin dynamics, *Numer. Math.* **136**(2) (2017) 545–602.
[59] P. L. Freddolino, A. S. Arkhipov, S. B. Larson, A. McPherson, et K. Schulten, Molecular dynamics simulations of the complete satellite tobacco mosaic virus, *Structure* **14** (2006) 437–449.
[60] A. Friedman, *Stochastic Differential Equations and Applications*, volume 1 (Academic, 1975).
[61] G. Gallavotti et E. G. D. Cohen, Dynamical ensembles in stationary states, *J. Stat. Phys.* **80** (1995).
[62] C. J. Geyer. Estimating normalizing constants and reweighting mixtures in Markov chain Monte Carlo. Tech. Rep. 565, School of Statistics, University of Minnesota, 1994.
[63] 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.
[64] M. B. Giles, Multilevel Monte Carlo path simulation, *Operations Research* **56**(3) (2008) 607–617.
[65] M. B. Giles, Multilevel Monte Carlo methods, *Acta Numerica* **24** (2015) 259–328.

[66] J. B. Goodman et K. K. Lin, Coupling control variates for Markov chain Monte Carlo, *J. Comput. Phys.* **228** (2009) 7127–7136.
[67] L. Gross, Logarithmic Sobolev inequalities, *Amer. J. Math.* **97**(4) (1975) 1061–1083.
[68] A. Guionnet et B. Zegarlinski, Lectures on logarithmic Sobolev inequalities, In *SÃľminaire de ProbabilitÃľs XXXVI*, volume 1801 of *Lecture Notes in Mathematics* (Springer Verlag, 2003), pp. 1–134.
[69] E. Hairer, C. Lubich, et G. Wanner, Geometric numerical integration illustrated by the Störmer-Verlet method, *Acta Numerica* **12** (2003) 399–450.
[70] 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).
[71] M. Hairer, *Convergence of Markov Processes* (Lecture notes, 2016).
[72] M. Hairer et J. Mattingly, Slow energy dissipation in chains of anharmonic oscillators, *Commun. Pure Appl. Math.* **62**(8) (2009) 999–1032.
[73] 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.
[74] M. Hairer et G. Pavliotis, From ballistic to diffusive behavior in periodic potentials, *J. Stat. Phys.* **131** (2008) 175–202.
[75] 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.
[76] W. K. Hastings, Monte Carlo sampling methods using Markov chains and their applications, *Biometrika* **57** (1970) 97–109.
[77] S. G. Henderson. *Variance Reduction via an Approximating Markov Process.* PhD thesis, Stanford University, 1997.
[78] F. Hérau, Short and long time behavior of the FokkerâĂŞPlanck equation in a confining potential and applications, *J. Funct. Anal.* **244**(1) (2007) 95 – 118.
[79] R. Holley et D. Stroock, Logarithmic Sobolev inequalities and stochastic Ising models, *J. Stat. Phys.* **46**(5-6) (1987) 1159–1194.
[80] L. Hörmander, Hypoelliptic second order differential equations, *Acta Math.* **119** (1967) 147–171.
[81] L. Hörmander, *The Analysis of Linear Partial Differential Operators I–IV* (Springer, 1985).
[82] 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.
[83] C.-R. Hwang, S.-Y. Hwang-Ma, et S. J. Sheu, Accelerating Gaussian diffusions, *Ann. Appl. Probab.* **3** (1993) 897–913.
[84] C.-R. Hwang, S.-Y. Hwang-Ma, et S. J. Sheu, Accelerating diffusions, *Ann. Appl. Probab.* **15** (2005) 1433–1444.
[85] A. Iacobucci, S. Olla, et G. Stoltz, Convergence rates for nonequilibrium Langevin dynamics, *Ann. Math. Québec* **43**(1) (2019) 73–98.
[86] K. Ichihara et H. Kunita, A classification of the second-order degenerate elliptic operators and its probabilistic characterization, *Z. Wahrscheinlichkeit* **30** (1974) 235–254.
[87] 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.
[88] R. Joubaud, G. Pavliotis, et G. Stoltz, Langevin dynamics with space-time periodic nonequilibrium forcing, *J. Stat. Phys.* **158**(1) (2015) 1–36.
[89] C. Kipnis et C. Landim, *Scaling limits of interacting particle systems* (Springer-Verlag, 1999).
[90] W. Kliemann, Recurrence and invariant measures for degenerate diffusions, *Ann. Probab.* **15**(2) (1987) 690–707.
[91] P. E. Kloeden et E. Platen, *Numerical Solution of Stochastic Differential Equations*, volume 23 of *Applications of Mathematics* (Springer, 1992).

[92] S. A. Klokov et A. Y. Veretennikov, On mixing and convergence rates for a family of Markov processes approximating SDEs, *Random Oper. Stochastic Equations* **14**(2) (2006) 103–126.

[93] S. A. Klokov et A. Y. Veretennikov, On local mixing conditions for SDE approximations, *Theor. Probab. Appl.* **57**(1) (2013) 110–131.

[94] 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).

[95] A. Kong, J. S. Liu, et W. H. Wong, Sequential imputation and Bayesian missing data problems, *J. Amer. Statist. Assoc.* **89** (1994) 278–288.

[96] 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.

[97] M. Kopec, Weak backward error analysis for Langevin process, *BIT Numerical Mathematics* **55**(4) (2015) 1057âĂŞ1103.

[98] Marie Kopec, Weak backward error analysis for overdamped langevin processes, *IMA J. Numer. Anal.* **35**(2) (2015) 583–614.

[99] A. Kundu, A. Dhar, et O. Narayan, The Green-Kubo formula for heat conduction in open systems, *J. Stat. Mech. - Theory E.* (2009) L03001.

[100] 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.

[101] J. Kurchan, Fluctuation theorem for stochastic dynamics, *J. Phys. A* **31** (1998) 3719–3729.

[102] D. Lamberton et G. Pagès, Recursive computation of the invariant distribution of a diffusion, *Bernoulli* **8**(3) (2002) 367–405.

[103] F. Laudenbach, *Calcul différentiel et intégral* (Ecole Polytechnique, 2001). In French.

[104] 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.

[105] M. Ledoux, Logarithmic Sobolev inequalities for unbounded spin systems revisited, In *SÃľminaire de ProbabilitÃľs XXXV*, volume 1755 of *Lecture Notes in Mathematics* (Springer Verlag, 2001), pp. 167–194.

[106] R. Lefevere, On the local space-time structure of non-equilibrium steady states, *J. Stat. Mech.* (2007) P01004.

[107] B. Leimkuhler et Ch. Matthews, Rational construction of stochastic numerical methods for molecular sampling, *Appl. Math. Res. Express* (2013) 34–56.

[108] 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.

[109] B. J. Leimkuhler et S. Reich, *Simulating Hamiltonian Dynamics*, volume 14 of *Cambridge Monographs on Applied and Computational Mathematics* (Cambridge University Press, 2005).

[110] B. J. Leimkuhler et R. D. Skeel, Symplectic numerical integrators in constrained Hamiltonian systems, *J. Comput. Phys.* **112**(1) (1994) 117–125.

[111] T. Lelièvre, A general two-scale criteria for logarithmic Sobolev inequalities, *J. Funct. Anal.* **256**(7) (2009) 2211–2221.

[112] 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.

[113] T. Lelièvre, M. Rousset, et G. Stoltz, Long-time convergence of an Adaptive Biasing Force method, *Nonlinearity* **21** (2008) 1155–1181.

[114] T. Lelièvre, M. Rousset, et G. Stoltz, *Free-energy Computations: A Mathematical Perspective* (Imperial College Press, 2010).

[115] T. Lelièvre, M. Rousset, et G. Stoltz, Langevin dynamics with constraints and computation of free energy differences, *Math. Comput.* **81** (2012) 2071–2125.

[116] T. Lelièvre et G. Stoltz, Partial differential equations and stochastic methods in molecular dynamics, *Acta Numerica* **25** (2016) 681–880.

[117] S. Lepri, R. Livi, et A. Politi, Thermal conduction in classical low-dimensional lattices, *Phys. Rep.* **377** (2003) 1–80.

[118] A. Maeda et T. Munakata, Lattice thermal conductivity via homogeneous nonequilibrium molecular dynamics, *Phys. Rev. E* **52** (1995) 234–239.

[119] E. Marinari et G. Parisi, Simulated tempering - a new Monte-Carlo scheme, *Europhys. Lett.* **19**(6) (1992) 451–458.

[120] 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.

[121] 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.

[122] 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.

[123] G. Menz et A. Schlichting, Poincaré and logarithmic Sobolev inequalities by decomposition of the energy landscape, *Ann. Probab.* **42**(5) (2014) 1809–1884.

[124] 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.

[125] S. P. Meyn et R. L. Tweedie, *Markov Chains and Stochastic Stability*, Communications and Control Engineering Series (Springer, 1993).

[126] G. N. Milstein et M. V. Tretyakov, *Stochastic Numerics for Mathematical Physics*, Scientific Computation (Springer, 2004).

[127] R. A. Minlos, *Introduction to Mathematical Statistical Physics*, volume 19 of *University Lecture Series* (American Mathematical Society, 2000).

[128] P. Monmarché, Piecewise deterministic simulated annealing, *ALEA Lat. Am. J. Probab. Math. Stat.* **13**(1) (2016) 357–398.

[129] A. M. N. Niklasson, C. J. Tymczak, et M. Challacombe, Time-reversible Born-Oppenheimer molecular dynamics, *Phys. Rev. Lett.* **97** (2006) 123001.

[130] E. Nummelin, *General Irreducible Markov Chains and Nonnegative Operators* (Cambridge University Press, 1984).

[131] S. Olla et V. Letizia, Non-equilibrium isothermal transformations in a temperature gradient from a microscopic dynamics, *arXiv preprint*(1505.05002) (2015).

[132] F. Otto et M. G. Reznikoff, A new criterion for the logarithmic Sobolev inequality, *J. Funct. Anal.* **243** (2007) 121–157.

[133] G. Papanicolaou et S. R. S. Varadhan, Ornstein-Uhlenbeck process in a random potential, *Commun. Math. Phys.* **38**(06) (1985) 819–834.

[134] E. Pardoux et A. Yu. Veretennikov, On the Poisson equation and diffusion approximation III, *Ann. Probab.* **33**(3) (2005) 1111–1133.

[135] P. Peskun, Optimum Monte Carlo sampling using Markov chains, *Biometrika* **60** (1973) 607–612.

[136] E. A. J. F. Peters et G. de With, Rejection-free Monte-carlo sampling for general potentials, *Phys. Rev. E* **85** (2012) 026703.

[137] E. Platen, An introduction to numerical methods for stochastic differential equations, *Acta Numerica* **8** (1999) 197–246.

[138] S. Redon, G. Stoltz, et Z. Trstanova, Error analysis of modified Langevin dynamics, *J. Stat. Phys.* **164**(4) (2016) 735–771.

[139] M. Reed et B. Simon, *Methods of Modern Mathematical Physics. I. Functional Analysis* (Academic Press, 1975).

[140] P. Reimann, Brownian motors: noisy transport far from equilibrium, *Phys. Rep.* **61** (2002) 57–265.

[141] 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.

[142] L. Rey-Bellet, Open classical systems, *Lect. Notes Math.* **1881** (2006) 41–78.
[143] L. Rey-Bellet et K. Spiliopoulos, Irreversible Langevin samplers and variance reduction: A large deviations approach, *Nonlinearity* **28** (2015) 2081–2103.
[144] L. Rey-Bellet et K. Spiliopoulos, Improving the convergence of reversible samplers, *J. Stat. Phys.* **164**(3) (2016) 472–494.
[145] 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.
[146] L. Rey-Bellet et L. E. Thomas, Fluctuations of the entropy production in anharmonic chains, *Ann. Henri Poincaré* **3** (2002) 483–502.
[147] 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.
[148] G. O. Roberts et J. S. Rosenthal, Optimal scaling of discrete approximations to Langevin diffusions, *J. Roy. Stat. Soc. B* **60** (1998) 255–268.
[149] H. Rodenhausen, Einstein's relation between diffusion constant and mobility for a diffusion model, *J. Stat. Phys.* **55**(5/6) (1989) 1065–1088.
[150] 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.
[151] J. Roussel et G. Stoltz, Spectral methods for Langevin dynamics and associated error estimates, *M2AN* **52**(3) (2018) 1051–1083.
[152] G. Royer, *An Initiation to Logarithmic Sobolev Inequalities* (American Mathematical Society, 2007).
[153] W. Rudin, *Real and Complex Analysis* (McGraw-Hill, 1987).
[154] J. P. Ryckaert et A. Bellemans, Molecular-dynamics of liquid alkanes, *Faraday Discuss.* **66** (1978) 95–106.
[155] T. Schlick, *Molecular Modeling and Simulation* (Springer, 2002).
[156] T. Shardlow, Splitting for dissipative particle dynamics, *SIAM J. Sci. Comp.* **24**(4) (2003) 1267–1282.
[157] T. Shardlow et Y. B. Yan, Geometric ergodicity for dissipative particle dynamics, *Stoch. Dynam.* **6**(1) (2006) 123–154.
[158] M. R. Shirts et J. D. Chodera, Statistically optimal analysis of samples from multiple equilibrium states, *J. Chem. Phys.* **124**(12) (2008) 124105.
[159] 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).
[160] 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.
[161] D. Talay et L. Tubaro, Expansion of the global error for numerical schemes solving stochastic differential equations, *Stoch. Proc. Appl.* **8**(4) (1990) 94–120.
[162] Z. Tan, On a likelihood approach for Monte-Carlo integration, *J. Am. Stat. Assoc.* **99**(468) (2004) 1027–1036.
[163] J. Tersoff, Modeling solid-state chemistry: Interatomic potentials for multicomponent systems, *Phys. Rev. B* **39** (1989) 5566–5568.
[164] L. Tierney, Markov chains for exploring posterior distributions, *Ann. Statist.* **22**(4) (1994) 1701–1762.
[165] M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, 2010).
[166] 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.
[167] L. Verlet, Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules, *Phys. Rev.* **159** (1967) 98–103.
[168] 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.
[169] C. Villani, *Topics in Optimal Transportation*, volume 58 of *Graduate Studies in Mathematics* (American Mathematical Society, 2003).

[170] C. Villani, Hypocoercivity, *Mem. Amer. Math. Soc.* **202**(950) (2009).