Sorbonne Université

2021-2022

Stage de Master 2

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Titre

Projet réalisé en collaboration avec le CERMICS
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March 3, 2022

Contents

Introduction

The aim of molecular simulation

Notational conventions

We convene that the gradient of a function $\varphi : \mathbb{R}^n \mapsto \mathbb{R}$ is a column vector-valued function

$$\nabla\varphi : \mathbb{R}^n \mapsto \mathbb{R}^n := \mathbb{R}^{n\times 1}$$

Notationally,

$$\nabla = \begin{pmatrix} \partial x_1 \\ \vdots \\ \partial x_n \end{pmatrix}$$

So that the Hessian operator writes

$$\nabla^2 := \nabla\nabla^\intercal = \begin{pmatrix} \partial x_1\partial_{x_1} & \cdots & \partial x_1\partial x_n \\ \vdots & \ddots & \vdots \\ \partial x_n\partial x_1 & \cdots & \partial x_n\partial x_1 \end{pmatrix}$$

And for $f = (f_1, \cdots, f_n)^\intercal : \mathbb{R}^n \mapsto \mathbb{R}^n$

$$Jf = \begin{pmatrix} \nabla^\intercal f_1 \\ \vdots \\ \nabla^\intercal f_n \end{pmatrix} = (\nabla f^\intercal)^\intercal \qquad\qquad \operatorname{div} f = \partial_{x_1} f_1 + \cdots + \partial_{x_n} f_n = \nabla^\intercal f$$

are respectively the Jacobian and divergence of f.

Chapter 1

Classical ensembles

1.1 Hamiltonian averages

1.1.1 Classical Hamiltonian dynamics

Definition 1 (Phase space coordinates)**.** *We describe the state of a system of N particles by a tuple*

$$(q, p) \in \mathcal{M}^N \times \mathbb{R}^{dN} := \mathcal{S}$$

Where $\mathcal{M}$ is a d-dimensional manifold on which lives the coordinate variable q, and p is the momentum coordinate.
The momentum of a particle is its velocity multiplied by its mass, thus we may write

$$v = M^{-1}p$$

where M is a diagonal matrix encoding the masses of each particle, and v is the velocity coordinate. As we are interested in the evolution of systems through time, we will be interested in trajectories through the phase space $\mathcal{S}$, that is functions

$$\begin{cases} \mathbb{R}_+ \mapsto \mathcal{S} \\ t \mapsto (q_t, p_t) \end{cases}$$

Definition 2 (Hamiltonian)**.** *The Hamiltonian of a system is the function defined on $\mathcal{S}$ by*

$$H(q, p) = \frac{1}{2} p^\intercal M^{-1} p + V(q) \tag{1.1}$$

It is the total energy of the system in state (q, p), sum of its kinetic energy and potential energy

Under this description, Newton's second law admits the following reformulation, which defines Hamiltonian dynamics.

$$\begin{cases} \mathrm{d}q_t = M^{-1} p_t \mathrm{d}t = \nabla_p H(q_t, p_t)\mathrm{d}t \\ \mathrm{d}p_t = -\nabla V(q_t)\mathrm{d}t = -\nabla_q H(q_t, p_t)\mathrm{d}t \end{cases} \tag{1.2}$$

Remark 1. *Equation (1.2) concisely writes, for $X_t := (q_t, p_t)$,*

$$dX_t = J\nabla H(X_t)\, dt \tag{1.3}$$

Where

$$J = \begin{pmatrix} 0_{dN} & I_{dN} \\ -I_{dN} & 0_{dN} \end{pmatrix}$$

is the symplectic matrix. By the chain rule, we have

$$dH(X_t) = dX_t^\intercal \nabla H(X_t) = (J\nabla H(X_t))^\intercal \nabla H(X_t) dt = 0$$

This relation expresses the fact that the total energy is conserved along trajectories of the system under Hamilton's equation. Note this property is only due to the form of J, and not to the particular expression (1.1) of the classical Hamiltonian. In full generality, we may consider any dynamics of the form (1.3), where we are free to choose H, and note that the conservation property holds. However, one key property of the classical Hamiltonian is that it is a sum of two terms each involving only one of the coordinate and momentum variable. Such Hamiltonian are called separable, and we shall see that separability proves a useful property to construct numerical schemes dedicated to the integration of such dynamics.

(1.4)

1.1.2 The Lennard-Jones Model

1.1.3 Numerical integration of Hamiltonian dynamics

1.1.4 Examples of instantaneous observables

1.1.5 Shortcomings of the Hamiltonian approach

1.2 Canonical averages

1.2.1 The notion of ensemble

1.2.2 Langevin dynamics

We consider a special case of the inertial Langevin dynamics, defined by the following stochastic differential equation (SDE), where γ, β are set real constants.

$$\begin{cases} \mathrm{d}q_t = M^{-1} p_t \mathrm{d}t \\ \mathrm{d}p_t = -\nabla V(q_t)\mathrm{d}t - \gamma M^{-1} p_t \mathrm{d}t + \sqrt{\frac{2\gamma}{\beta}} \mathrm{d}W_t \end{cases} \tag{1.5}$$

Where $(W_t)_{t \geqslant 0}$ is a standard dN-dimensional Brownian motion.
This process is a combination of a Hamiltonian evolution with an additional action on the momenta which, if isolated, defines a dN-dimensional Ornstein-Uhlenbeck process.
This additional term be interpreted physically as the combination of two effects: a dissipation term which can be understood as the effect of a viscous friction force on the particles, and a fluctuation term, which corresponds to the input of kinetic energy into the system as thermal agitation induced by a surrounding heat bath at temperature $1/(k_B\beta)$.
However, the physical meaning can be forgotten thanks to the fact that, *in fine*, we only require that the canonical measure be ergodic under this dynamic: as we shall shortly see, this is indeed the case.

Remark 2. *There are several ways to generalize this process.*
One way is to consider more general, possibly non-separable, Hamiltonians, as in (1.1.1), rather than the classical Hamiltonian used above.

The other is to allow the fluctuation-dissipation term to be parametrized by coefficients γ and σ depending on the state variable, and which obey a relation ensuring ergodicity.
Hence in full generality, we could consider the following Langevin dynamic:

$$\begin{cases} dq_t = \nabla_p H(q_t, p_t)\, dt \\ dp_t = -\nabla_q H(q_t, p_t)\, dt - \gamma(q_t, p_t)\nabla_p H(q_t, p_t)\, dt + \sigma(q_t, p_t)\, dW_t \end{cases} \tag{1.6}$$

1.2.3 Properties of the Langevin dynamics

To investigate some of the properties of the dynamics, it is useful to introduce the notion of a generator for a process defined by a possibly inhomogeneous SDE.

The generator

We consider a general process defined by a SDE of the form:

$$\mathrm{d}X_t = b(t, X_t)\mathrm{d}t + \sigma(t, X_t)\mathrm{d}W_t \tag{1.7}$$

Where b is a $\mathbb{R}^n$-valued function, W is a standard d-dimensional Brownian motion and σ is a $n \times d$ matrix-valued function.
For φ a smooth bounded function, Itô's lemma allows us to compute:

$$\begin{aligned} d\varphi(t, X_t) &= \frac{\partial \varphi}{\partial t}(t, X_t)\mathrm{d}t + \nabla^\intercal \varphi(t, X_t)\mathrm{d}X_t + \frac{1}{2}\operatorname{Tr}(\nabla^{2\intercal}\varphi(t, X_t)\mathrm{d}\langle X, X\rangle_t) \\ &= \left(\frac{\partial \varphi}{\partial t} + \nabla^\intercal \varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2 \varphi \sigma\sigma^\intercal)\right)(t, X_t)\mathrm{d}t + (\nabla^\intercal \varphi \sigma)(t, X_t)\mathrm{d}W_t \end{aligned}$$

Where ∇, ∇^2 are with respect to the spatial coordinates. In other words,

$$\varphi(t, X_t) = \varphi(0, X_0) + \int_0^t \left(\frac{\partial \varphi}{\partial t} + \nabla^\intercal \varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2 \varphi \sigma\sigma^\intercal)\right)(s, X_s)\mathrm{d}s + \int_0^t \nabla^\intercal \varphi \sigma(s, X_s)\mathrm{d}W_s \tag{1.8}$$

Definition 3 (Generator of an Itô process)**.** *Let X_t be a $\mathbb{R}^n$-valued process defined by 1.7. We define its generator at time t as the operator defined by*

$$\mathcal{L}_t \varphi(x) = \left(\frac{\partial \varphi}{\partial t} + \nabla^\intercal \varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2 \varphi \sigma\sigma^\intercal)\right)(t, x) \tag{1.9}$$

In view of (1.8), we have, provided regularity conditions on σ and φ,

$$\mathbb{E}\left[\varphi(t, X_t) \middle| X_s = x\right] = x + \int_s^t \mathbb{E}[\mathcal{L}_u \varphi(X_u)]\mathrm{d}u$$

so that, at least formally,

$$\frac{\partial}{\partial t}\mathbb{E}[\varphi(t, X_t)|X_s = x] = \mathbb{E}[\mathcal{L}_t \varphi(X_t)|X_s = x] = \mathcal{L}_t \mathbb{E}[\varphi(t, X_t)|X_s = x] \tag{1.10}$$

If we define a family of evolution operators $(P_{s,t})_{s \leqslant t}$ by the formula

$$P_{s,t}\varphi(x) = \mathbb{E}[\varphi(t, X_t)|X_s = x]$$

(1.10) rewrites

$$\frac{\partial}{\partial t} P_{s,t}\varphi(x) = P_{s,t}\mathcal{L}_t\varphi(x) = \mathcal{L}_t P_{s,t}\varphi(x)$$

An important special case occurs when b, σ and φ do not depend on time. In this case the generator is a single operator $\mathcal{L}$, defined by

$$\mathcal{L}\varphi = \nabla^\intercal \varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2\varphi\sigma\sigma^\intercal)$$

The evolution operators $P_t := P_{0,t}$ ($= P_{s,s+t}$ $\forall s$ by stationarity) form a semi-group, and act on the space of smooth functions as

$$P_t\varphi(x) = \mathbb{E}[\varphi(X_t)|X_0 = x]$$

The formal derivative is given by

$$\frac{\partial}{\partial t} P_t = P_t\mathcal{L} = \mathcal{L}P_t$$

As in (1.1.1), we may write, by analogy with the finite-dimensional setting, $e^{t\mathcal{L}} := P_t$

Invariance of the canonical measure

The Langevin dynamics (1.5), when written under the form (1.7), corresponds to the case

$$b(q,p) = \begin{pmatrix} M^{-1}p \\ -\nabla V(q) - \gamma M^{-1}p \end{pmatrix},\ \sigma(q,p) = \sqrt{\frac{2\gamma}{\beta}} \begin{pmatrix} 0_{dN} & 0_{dN} \\ 0_{dN} & \mathrm{I}_{dN} \end{pmatrix}$$

Hence, applying 1.9, we obtain the generator for the dynamics

$$\mathcal{L} = \mathcal{L}_q + \mathcal{L}_p$$

where

$$\mathcal{L}_q\varphi = \nabla_q^\intercal \varphi M^{-1}p$$

$$\mathcal{L}_p\varphi = -\nabla_p^\intercal \varphi(\nabla V(q) + \gamma M^{-1}p) + \frac{\gamma}{\beta}\Delta_p$$

which we may rewrite, recognizing the generator for the Hamiltonian dynamics 1.4

$$\mathcal{L} = \mathcal{L}_H + \gamma\mathcal{L}_{\mathrm{ou}}$$

where $\mathcal{L}_{\mathrm{ou}}\varphi = -M^{-1}\nabla_p^\intercal\varphi p + \frac{1}{\beta}\Delta_p\varphi$

Lemma 1. *Let φ, ψ be smooth compactly supported functions on $\mathcal{S}$. Then*

1.2.4 Numerical integration of the Langevin dynamics

Splitting methods

Implementation

1.2.5 Illustration: the equation of state of Argon

1.2.6 The Metropolis method

Chapter 2

Transport properties

Chapter 3

Norton methods

Performance analysis