Sorbonne Université

2021-2022

Stage de Master 2

Noé Blassel

Titre

Projet réalisé en collaboration avec le CERMICS
Ecole Nationale des Ponts et Chaussées
6 et 8 avenue Blaise Pascal
Cité Descartes - Champs sur Marne
77455 Marne la Vallée Cedex 2

Tuteur : Gabriel Stoltz

March 3, 2022

Contents

1 Classical ensembles **4**
1.1 Hamiltonian averages . . . 4
1.1.1 Classical Hamiltonian dynamics . . . 4
1.1.2 The Lennard-Jones Model . . . 5
1.1.3 Numerical integration of Hamiltonian dynamics . . . 5
1.1.4 Symplecticity . . . 5
1.1.5 Symplectic Euler . . . 5
1.1.6 Examples of instantaneous observables . . . 5
1.1.7 Shortcomings of the Hamiltonian approach . . . 5
1.2 Canonical averages . . . 5
1.2.1 The notion of ensemble . . . 5
1.2.2 Langevin dynamics . . . 5
1.2.3 Properties of the Langevin dynamics . . . 7
1.2.4 Numerical integration of the Langevin dynamics . . . 9
1.2.5 Illustration: the equation of state of Argon . . . 9
1.2.6 The Metropolis method . . . 9

2 Transport properties **11**

3 Norton methods **12**

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 considering trajectories through the phase space $\mathcal{S}$, functions

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

Definition 2 (Hamiltonian)**.** *The Hamiltonian of an atomic 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

Using this description, Newton's second law has the following form, 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

$$dH(X_t) = dX_t^\intercal \nabla H(X_t) = (J\nabla H(X_t))^\intercal \nabla H(X_t) dt = 0 \tag{1.4}$$

This relation expresses the fact that the Hamiltonian map is invariant under the flow of equation (1.3). This, in turn, is the mathematical translation of the principle of conservation of energy in physics.

More generally, we may apply the chain rule to smooth functions $\varphi : \mathcal{S} \mapsto \mathbb{R}$. We obtain

$$\mathrm{d}\varphi(X_t) = \mathrm{d}X_t^\intercal \nabla \varphi(X_t) = (J\nabla H(X_t))^\intercal \nabla \varphi(X_t)\mathrm{d}t = (\nabla_p H \cdot \nabla_q - \nabla_q H \cdot \nabla_p)\varphi(X_t)\mathrm{d}t$$

This motivates the following.

Definition 3 (Generator of the Hamiltonian dynamics)**.** *We define the generator associated with the Hamiltonian dynamics to be the operator $\mathcal{L}_H$ defined on smooth functions by*

$$\mathcal{L}_H \varphi = (\nabla_p H \cdot \nabla_q - \nabla_q H \cdot \nabla_p)\varphi \tag{1.5}$$

Remark 2. *Property (1.4) is only due to the form of J, and not to the particular expression for H. Thus, we may consider any dynamics of the form (1.3), to devise a dynamical system whose orbits are restricted to the level set $H^{-1}\{H(q_0, p_0)\}$.*
Conversely, given a dynamical system, if through a change of coordinates one is able to write the system under the form (1.3), one has found a conservation law.

One key property of the classical Hamiltonian is that it is *separable*: it splits into a kinetic part involving only the momentum variable and a potential part involving only the coordinate variable. We will see when implementing numerical schemes for Hamiltonian systems that separability permits one to construct a number of schemes based on explicit splittings of the evolution operator over a timestep, which turn out to display interesting qualitative properties.

1.1.2 The Lennard-Jones Model

1.1.3 Numerical integration of Hamiltonian dynamics

1.1.4 Symplecticity

1.1.5 Symplectic Euler

Energy conservation properties

The Verlet scheme

1.1.6 Examples of instantaneous observables

1.1.7 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.

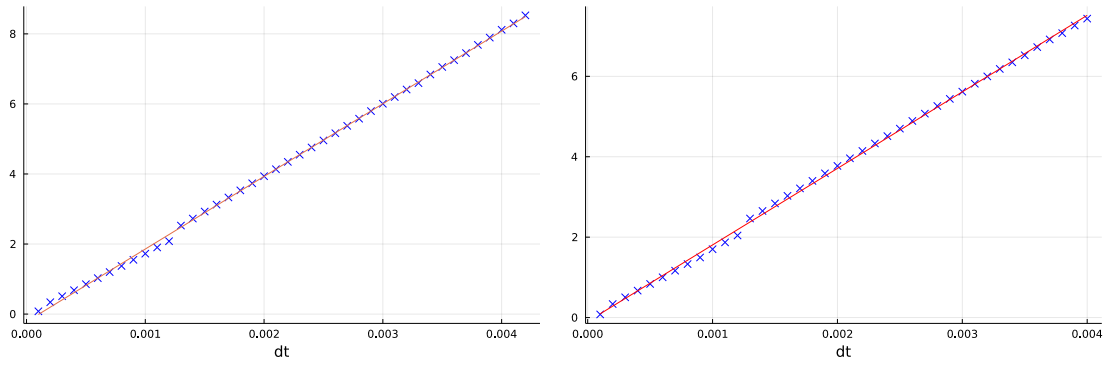

Figure 1.1: Absolute variation of the Hamiltonian $\|H - \min H\|_\infty$ as a function of the time step over 1000 iterations of the symplectic Euler schemes (A on the left and B on the right). A linear regression line is plotted in red.

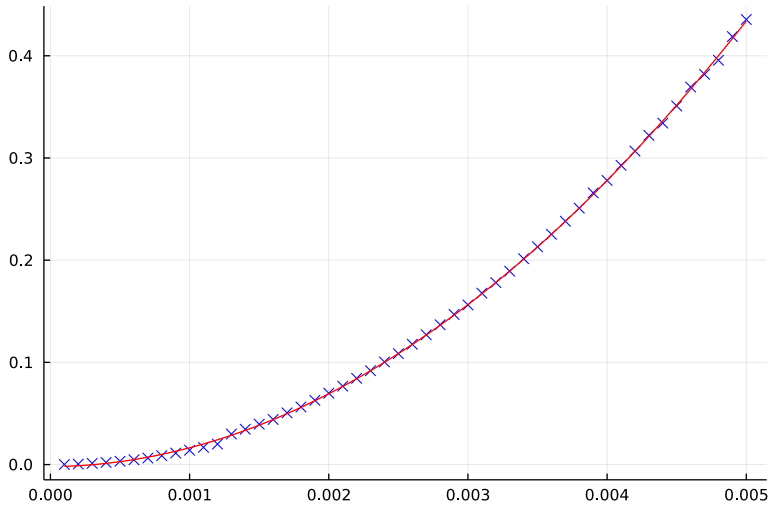

Figure 1.2: Absolute variation of the Hamiltonian as a function of the time step over 1000 iterations of the Velocity Verlet scheme. A quadratic regression curve is plotted in red.

$$\begin{cases} \mathrm{d}q_t = M^{-1}p_t\mathrm{d}t \\ \mathrm{d}p_t = -\nabla V(q_t)\mathrm{d}t - \gamma M^{-1}p_t\mathrm{d}t + \sqrt{\frac{2\gamma}{\beta}}\mathrm{d}W_t \end{cases} \tag{1.6}$$

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 3. *There are several ways to generalize this process.*
One way is to consider more general, possibly non-separable, Hamiltonians, as in (2), 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:

$$\begin{cases} dq_t = \nabla_p H(q_t,p_t)\,dt \\ dp_t = -\nabla_q H(q_t,p_t)\,dt - \gamma(q_t,p_t)\nabla_p H(q_t,p_t)\,dt + \sigma(q_t,p_t)\,dW_t \end{cases} \tag{1.7}$$

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:

$$\mathrm{d}X_t = b(t,X_t)\mathrm{d}t + \sigma(t,X_t)\mathrm{d}W_t \tag{1.8}$$

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,

$$\varphi(t,X_t) = \varphi(0,X_0) + \int_0^t \left(\frac{\partial\varphi}{\partial t} + \nabla^\intercal\varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2\varphi\sigma\sigma^\intercal)\right)(s,X_s)\mathrm{d}s + \int_0^t \nabla^\intercal\varphi\sigma(s,X_s)\mathrm{d}W_s \tag{1.9}$$

Definition 4 (Generator of an Itô process)**.** *Let X_t be a $\mathbb{R}^n$-valued process defined by 1.8. We define its generator at time t as the operator defined by*

$$\mathcal{L}_t\varphi(x) = \left(\frac{\partial\varphi}{\partial t} + \nabla^\intercal\varphi b + \frac{1}{2}\operatorname{Tr}(\nabla^2\varphi\sigma\sigma^\intercal)\right)(t,x) \tag{1.10}$$

In view of (1.9), 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,

$$\frac{\partial}{\partial t}\mathbb{E}[\varphi(t,X_t)|X_s = x] = \mathbb{E}[\mathcal{L}_t\varphi(X_t)|X_s = x] = \mathcal{L}_t\mathbb{E}[\varphi(t,X_t)|X_s = x] \tag{1.11}$$

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

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

(1.11) rewrites

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

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 (1.6), when written under the form (1.8), 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 1.10, 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 1.5

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

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

text

Splitting methods

text

Implementation

text

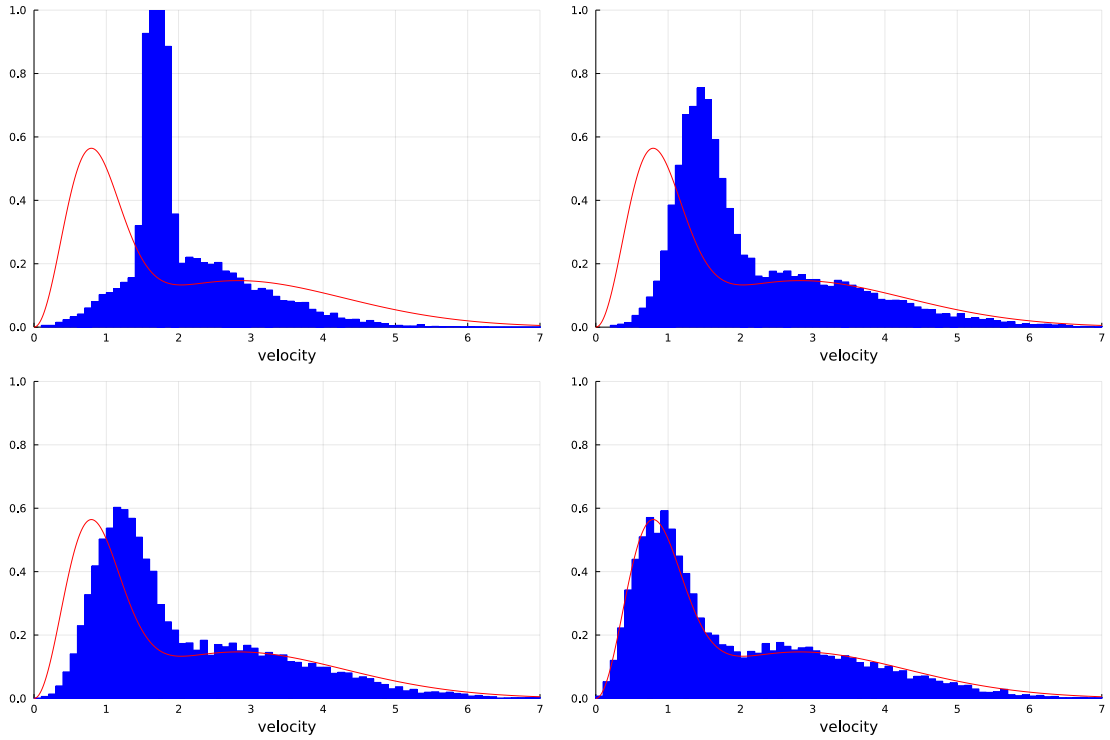

Figure 1.3: Convergence of the velocity distribution to a mixture of Maxwell-Boltzmann distributions for a mixture of two ideal gases with different atomic masses, starting from a Dirac distribution $\delta_{\sqrt{3}}$. Snapshots of the empirical distribution are shown after 20, 200, 400 and 1000 steps ($\mathrm{d}t = 5 \times 10^{-3}\tau^*, T = T^*$)

1.2.5 Illustration: the equation of state of Argon

text

1.2.6 The Metropolis method

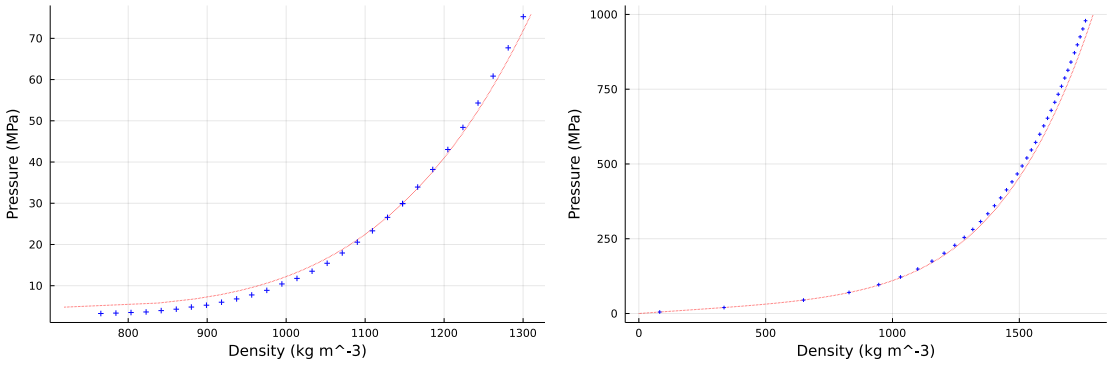

Figure 1.4: Simulated equations of state of Argon at 150 K (liquid phase) on the left and 300K (supercritical phase) on the right. Simulated data points are shown in blue, and the red dotted curve shows the results of experimental measurements.

Chapter 2

Transport properties

Chapter 3

Norton methods

Performance analysis