Long Time Integration of Molecular Dynamics at Constant Temperature with the Symplectic Euler Method

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Abstract

Simulations of particle systems at constant temperature may be used to estimate several of the system’s physical properties, and some require integration over very long time to be accurate. To achieve sufficient accuracy in finite time the choice of numerical scheme is important and we suggest to use the symplectic Euler method combined with a step in an Ornstein-Uhlenbeck process. This scheme is computationally very cheap and is often used in applications of molecular dynamics. This thesis strives to motivate the usage of the scheme due to the lack of theoretical results and comparisons to alternative methods. We conduct three numerical experiments to evaluate the scheme. The design of each experiment aims to expose weaknesses or strengths of the method. For both model problems and more realistic experiments are the results positive in favor of the method; the symplectic Euler method combined with an Ornstein-Uhlenbeck step does perform well over long times.

Keywords: the symplectic Euler method, Ornstein-Uhlenbeck process, Molecular dynamics, Long time integration, Canonical ensemble, Constant temperature.
Sammanfattning

Integration över lång tid i molekyldynamik med symplektisk Euler-metoden vid konstant temperatur


Nyckelord: symplektisk Euler, Ornstein-Uhlenbeck-process, molekyldynamik, integration över lång tid, kanonisk ensemble, konstant temperatur.
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Chapter 1

Introduction

1.1 Molecular dynamics

For several hundred years numerical values of physical observables based on equations derived from the laws of physics were only accessible for limited, special cases when it was possible to find a nice analytic solution. Then the computer was invented, and with it during the second half of the 20th century, came molecular dynamic (MD) simulations.

In 1960 a group of researchers published the results from a first realistic simulation of the damage of radiation on a crystal, followed by simulations of liquid argon 1964. The main idea from those days is the same today: take a system, simulate the smallest possible particles (even down to the atomic level) using fundamental laws of physics, and compute whatever you want to know about the system!

As processing power hugely increased over the proceeding years larger, heterogeneous, more complex and hence more interesting systems became accessible to MD. Thus did the number of applications increase. A brief introduction (with a presentation of alternatives) to MD and applications of it to biochemistry is found in [1], mentioning e.g. protein folding and ion transport through membranes. A time line relating MD methods and its performance on simulations of proteins in solvents is found in the introduction of [2]. The last example there is from 2010, when it is possible to simulate the protein bovine pancreatic trypsin inhibitor in water for periods of milliseconds. A more in-depth motivation of MD (and a good handbook) which explains the underlying physics of presented examples is [3], with applications towards e.g. phase transitions of classical many-body systems. For an introduction with a focus on the mathematical aspect, see [4]. Another interesting note on MD is that during the last years it has become possible to incorporate quantum effects in MD simulations; however, none of mentioned texts focus on this (but some do mention it).

Although, it is not only the persisting increase of processing power that makes MD more useful, but foremost the development of algorithms that save computation time and capture behavior not yet mimicked by today’s methods. That algorithms
advance further is essential if we in the future want more accurate results, or want to study larger and more complex systems over longer time periods than today.

1.2 The practical aspect of MD

This thesis considers a system which is in contact with a heat bath, some reservoir that the system may exchange energy with. If the heat bath is "infinite" so that it does not change temperature when energy is transported to and from it, the connected system will eventually settle at the heat bath's temperature. In this setting we can simulate a constant number \( N \) of particles, in a constant volume \( V \) and at constant temperature \( T \) (which is called \( NVT \)). A system with constant temperature is described by the Langevin equation which will be presented in chapter 2. It is relevant to study how realizations of this equation will be able to estimate observables, i.e. functions of the trajectory. Our interest is in studying observables that require integration over long time intervals (here the diffusion coefficient). Due to the ergodic property of the Langevin equation we hope to use the ergodic hypothesis to estimate such observables (which is what leads to integration over long time intervals); but it is not obvious that a numerical scheme will preserve the imperative ergodicity, or a realistic behavior of the system.

Different numerical methods may exhibit very different solutions depending on the problem. If the drift terms are Lipschitz continuous it is straightforward to use forward Euler, but if we restrict our experiments to less 'nice' problems (e.g. one-sided Lipschitz continuous, but not Lipschitz continuous, problems) the same method will diverge over long time integration and will therefore not be ergodic [5]. Some implicit methods, e.g. the split-step backward Euler method, are ergodic for these problems, but undesirable to use since every time step will require solving some system of equations. When particles interact with each other and the number of particles is high this can lead to huge computational work. Another solution is to use a Metropolis-Hastings adjusted stepping method, a somewhat more computationally expensive than an non-adjusted forward method. Yet, since we need a cheap method, this thesis studies the symplectic Euler method combined with a step in an Ornstein-Uhlenbeck process. The accuracy is of second order in the spatial coordinate, and of first order in the momentum coordinate.

To evaluate the performance of the symplectic Euler method we design three numerical experiments which have their own special properties that may be troublesome for the method. In the two first experiments we also compare the symplectic Euler method to split-step backward Euler and a Metropolis-adjusted forward scheme. The third experiment is a more realistic problems (a Lennard-Jones fluid) where other methods (e.g. the forward Euler method) do not perform well due to that the potential goes regularly to infinity, or are undesirable to use by being too expensive computationally (as split-step backward Euler).
1.3 Motivation of studying the symplectic Euler method over long time integration

The rationale behind this study is to encourage the usage of the symplectic Euler method for integration over long times when knowledge of the system’s trajectory through the state space is necessary. The method’s ability to conserve energy is well known, but other methods are also available. A significant problem when integrating over long time is energy drifts; even a slightest increase or decrease of energy may affect the accuracy of the estimation and therefore are symplectic methods interesting. In [6] the authors study how different thermostats can be compared (by defining an efficiency) and conclude that the so-called Nosé-Hoover-Langevin thermostat is most appropriate (compared to the Langevin thermostat, among others); however, their result is based on a Maclaurin expansion of an observable for very short time integration. Hence question remains, what methods are suitable for the long time integration case?

A Monte Carlo method would preserve the correct invariant measure, but does not simulate trajectories necessary when integrating paths dependent of time, as in determining e.g. the diffusion for long time integration. Thus the only method at hand is molecular dynamic simulation.

1.4 Problem formulations

Symplectic Euler with Langevin dynamics is regarded as a geometric ergodic method (i.e., independently of the initial state the time average converges at exponential rate to the ensemble average) which we want to confirm for some case. This is done by studying where the trajectory of a particle intersects a plane through the state space. The particle interacts with the potential

\[ V(q_1, q_2) = \frac{q_1^2}{2} + \frac{q_2^2}{\sqrt{2}} + \beta \sin(q_1 q_2). \]  

(1.1)

This experiment is referred to as Experiment 1. For the same potential we also study the estimation of the self-diffusion, a transport coefficient that requires very long time integration. This is described in more detail in section 3.1.

Experiment 2 is an SDE with a one-sided Lipschitz continuous drift term. Metropolis-Hastings adjusted methods are suitable for these types of problems. Hence it is interesting to compare self-diffusion coefficients determined by the symplectic Euler method and by a Metropolis-Hasting method. The potential here is

\[ V(q) = \frac{1}{4}(\|q\|^2 - 1)^2, \quad q = (q_1, q_2). \]  

(1.2)

The last, Experiment 3, is a test of a more realistic character. A fluid or crystal can be simulated by particles interacting through the Lennard-Jones potential. If the distance between two particles goes to zero the potential diverges, which is very
problematic for numerical methods. We set up such a system with the number of particles being 864. The system is to be in the fluid state. Here we again calculate the self-diffusion coefficient by the symplectic Euler method.

1.5 Conclusions

1.5.1 Main conclusions from numerical experiments

The main result of this study is that the symplectic Euler method combined with a step in an Ornstein-Uhlenbeck process is stable for large time steps and converges towards the invariant measure as the time of integration is increased. The fact of it being stable in combination of being computationally very cheap is an advantage compared to other methods we have tested. Also, an efficient implementation of the symplectic Euler method is easily done since the method only requires one evaluation of the force field per time step, which is the main part of the computation of most numerical methods.

The symplectic Euler method seems to be suitable for both Lipschitz and one-sided Lipschitz continuous problems. When unbounded forces are introduced in the third experiment the method requires smaller time steps to stabilize. All experiments imply that the sample deviation (of several estimations) of the diffusion coefficient depend more on the integration time than the time step. From this we can conclude that as soon as a stable time step has been reached it is important to use long enough time integration to approximate the integration over infinite time, to achieve desired accuracy.

In Experiment 1 we study more thoroughly the ergodic property of the symplectic Euler method, comparing symplectic Euler to the split-step backward Euler method. We study the distribution of where trajectories intersect a subspace of the state space. The split-step backward Euler method is known to converge even for one-sided Lipschitz continuous problems. For Experiment 1 symplectic Euler visits states of higher energy while split-step backward Euler seem to not conserve the energy correctly unless using relatively small time steps. By calculating and comparing the diffusion coefficient by the symplectic Euler method and other methods we conclude that the symplectic Euler method uses less CPU time to achieve either better or equal accuracy.

1.5.2 Critique

It is relevant to question how reference values in the first and third experiment have been estimated. It was not the initial intention to use the symplectic Euler method to calculate these, but eventually we had to do so to find any reference at all.

A weakness in this study is the absence of a thorough error analysis, due to the focus on problem formulations and time limitations of a master thesis. It would have been interesting to have studied backward error analysis [4] and apply appendix D,
1.6 ORGANIZATION OF THESIS

Statistical errors, in [3] which treats the impact of the size of the system on statistical error and autocorrelations, and how to calculate these.

1.5.3 Suggestions on future research

A general question on tuning the Langevin thermostat could be further studied: If the Langevin thermostat is used (or any other dynamic with diffusion and friction coefficients), how can the diffusion-friction $\alpha$ be optimally chosen? On the one hand, with a larger $\alpha$ less number of steps need to be taken since a trajectory faster loses its memory of where it started and thus promoting a chaotic behavior; on the other, with too large coefficient the deviation from the real value of a time dependent observable becomes too large to be neglected, and hence the estimation is less accurate. Also, with large diffusion $\alpha$ comes a greater risk of the energy not being conserved over long time. It is possible to imagine that these errors somehow depend of $\alpha$ analytically expressible, and if these relations could be found, an optimal $\alpha$ could be used.

It would be relevant to study what thermostat is more suitable for long time integration as an extension of this work and [6]. If CPU time can be reduced by choosing a better thermostat higher accuracy can be achieved faster.

1.6 Organization of thesis

This thesis is organized as follows: Chapter 1 is to introduce the reader to the thesis and present problems studied and conclusions drawn from theory and following numerical experiments. Chapter 2 treats necessary background material such as stochastic differential equations, statistical physics and ergodicity and the Langevin equation. Also, the main topic of the thesis, the symplectic Euler method combined with a step in a Ornstein-Uhlenbeck process, is presented, and a number of other numerical schemes which we will compare with each other. Along with the definitions of the methods come some comments on implementations. This is followed by Chapter 3 were new results are presented from experiments which are described in more detail. Some general programming implementations and conclusions on the results are presented.
Chapter 2

Background material

2.1 Stochastic differential equations

For a thorough review of below definitions and concepts regarding the Itô integral and stochastic differential equations we refer the reader to Øksendal [7].

2.1.1 The Wiener process

The concept of stochastic differential equations (SDEs) is imperative for studies of the Langevin equation and begins with the Wiener process $W(t) : \mathbb{R} \rightarrow \mathbb{R}$. The process $W(t)$ has the following properties:

(i) $W(0) = 0$, \hspace{2cm} (2.1)
(ii) the sample path $t \mapsto W(t)$ is almost surely continuous, \hspace{2cm} (2.2)
(iii) $W(t_2) - W(t_1) \in N(0, t_2 - t_1)$ for $t_2 > t_1$, \hspace{2cm} (2.3)
(iv) all increments $W_{t_1}, W_{t_2} - W_{t_1}, \ldots, W_{t_k} - W_{t_{k-1}}$ are independent. \hspace{2cm} (2.4)

Even though the Wiener process is absolutely continuous in every time $t$, it is nowhere differentiable.

2.1.2 The Itô integral

In the deterministic case differential equations are often designed to describe the change $\frac{\partial f}{\partial t}(t)$ for some sought variable $f(t)$ depending on the current value $f(t)$, $t$ and other parameters and functions. This is also an aim of SDEs, but to describe changes in a function $S = S(t, W(t))$ as a derivative is not possible; as previously mentioned: it is not possible to differentiate $W(t)$. To circumvent this problem we use the Itô integral $I(f(S, t), t_1, t_2)$, which for a deterministic function $f = f(S, t)$ is the following limit:
CHAPTER 2. BACKGROUND MATERIAL

Definition 2.1.1. The Itô integral

\[
\sum_{i=1}^{N} f(S(s_i), s_i)(W(s_{i+1}) - W(s_i)) \to I(f, t_1, t_2), \text{ when } \max(s_{j+1} - s_j) \to 0.
\]

(2.5)

To clarify: the sequence \( t_1 = s_1 < s_2 < \ldots < s_N = t_2 \) is a partition of \([t_1, t_2]\).

The Itô integral \( I(f, t_1, t_2) \) is the limit when the largest sub-interval \([s_i, s_{i+1})\) in the partition tends to zero; this limit is the Itô integral. To emphasize similarities to other integrals it is customary to write \( I(f, t_1, t_2) \) as

\[
\int_{t_1}^{t_2} f(Y(s), s) \, dW(s).
\]

(2.6)

Definition 2.1.1 is practical in the context in numerical analysis of SDEs [8]. Note that \( I(f(S,t), t_1, t_2) \) is a stochastic process, with random outcomes, a probability density, possibly with moments of different orders etc.; it is not in general a deterministic function with a fixed value.

2.1.3 Stochastic differential equations

With the Itô integral defined we now can formulate and find what stochastic process \( Y(t) \) that fulfills e.g.

\[
Y(t) = Y(0) + \int_{0}^{t} g(Y(s), s) \, ds + \int_{0}^{t} h(Y(s), s) \, dW(s)
\]

\( Y(0) = y_0. \) \hspace{1cm} (2.7)

A standard way to write (2.7-2.8) is

\[
dY(t) = g(Y(t), t) \, dt + h(Y(t), t) \, dW(t)
\]

\( Y(0) = y_0. \) \hspace{1cm} (2.9)

A term corresponding to \( g(Y(t), t) \) is referred to as the drift term. By dropping the integral signs we arrive at something that looks like a differential equation, which we call a stochastic differential equation.

Finding analytic solutions is hard; only few classes of SDEs have known explicit analytic solutions. An example is the Ornstein-Uhlenbeck process, which we will encounter again when introducing the Langevin equation:

\[
dY(t) = \theta(\mu - Y(t)) \, dt + \varsigma \, dW(t)
\]

\( Y(0) = Y_0 \)

(2.11)

where \( \theta > 0, \mu \in \mathbb{R}, \varsigma \in \mathbb{R} \) and \( W(t) \) is a Wiener process. This SDE has the solution

\[
Y(t) = y_0 e^{-\theta t} + \mu(1 - e^{-\theta t}) + \varsigma \int_{0}^{t} e^{\theta(s-t)} dW(s).
\]

(2.12)
2.2. THE LANGEVIN EQUATION

2.2 The Langevin Equation

Our interest in this report is to study how the symplectic Euler method estimates properties of systems described by the Langevin equation. By the Langevin equation we refer to a modification introducing randomness in the Hamiltonian dynamics. Hamiltonian dynamics describe the motion of a system of \( d \) particles by derivatives of the Hamiltonian

\[
H = H(q_1, \ldots, q_d, p_1, \ldots, p_d) \in \mathbb{R}.
\]

Throughout this report \( q_i = q_i(t) = (q_{i,1}(t), \ldots, q_{i,J}(t)) \in \mathbb{R}^J \) is a particle indexed \( i \)'s position and \( p_i = p_i(t) = (p_{i,1}(t), \ldots, p_{i,J}(t)) \in \mathbb{R}^J \) its momentum in \( J \)-dimensional space. Either \( J = 2 \) or \( J = 3 \). For ease of notation we will write that \( q = (q_1, \ldots, q_d)^T \in \mathbb{R}^{Jd} \) and \( p = (p_1, \ldots, p_d)^T \in \mathbb{R}^{Jd} \) and denote a phase point \((q, p)\) by \( x \in \mathbb{R}^n \). In this thesis \( n = 2Jd \) denotes the number of degrees of freedom. The whole phase space in which \((q, p)\) lies is \( \Gamma \overset{\text{def}}{=} \mathbb{R}^n \). To even furthermore shorten potentially long and illegible mathematical expressions we use the following operators on an arbitrary function \( f = f(q, p, t) \)

\[
\nabla_{q_i}(f) = \left( \frac{\partial f}{\partial q_{i,1}}, \ldots, \frac{\partial f}{\partial q_{i,J}} \right)^T, \\
\nabla_{p_i}(f) = \left( \frac{\partial f}{\partial p_{i,1}}, \ldots, \frac{\partial f}{\partial p_{i,J}} \right)^T, \\
\nabla_q(f) = \left( \nabla_{q_1}(f)^T, \ldots, \nabla_{q_d}(f)^T \right)^T, \\
\nabla_p(f) = \left( \nabla_{p_1}(f)^T, \ldots, \nabla_{p_d}(f)^T \right)^T, \\
\nabla^2_{p_i}(f) = \sum_{j=1}^J \frac{\partial^2 f}{\partial p_{i,j}^2}.
\]

Operators (2.13-2.16) are gradients and (2.17) the Laplace operator. The function \( H \) is the total energy of the system, so

\[
H(q, p) \overset{\text{def}}{=} \sum_{i=1}^d \frac{||p_i||^2}{2m_i} + V(q_1, \ldots, q_d),
\]

where \( m_i > 0 \) denotes the mass of the \( i \)th particle and \( V(q_1, \ldots, q_d) \in \mathbb{R} \) the potential energy of the configuration of the particles. The sum \( \sum_{i=1}^d \frac{||p_i||^2}{2m_i} \) is the total kinetic energy of the system. The relation between position and momentum is described by the Hamiltonian equations of motion

\[
\frac{\partial q}{\partial t}(t) = \nabla_p(H(q(t), p(t))), \quad \frac{\partial p}{\partial t}(t) = -\nabla_q(H(q(t), p(t))).
\]

So, if we know the function \( H(x) \) and the initial state \( x(0) \) of a system we can by the Hamiltonian equations of motion find every particle’s position and momentum
for every time. The addition to this idea by Langevin is to add a friction and a noise term to the change of each $p_i$, often illustrated as how a fluid of much smaller particles affect the motion of larger particles moving through. In thermodynamics the smaller particles are referred to as a "heat bath" and is treated as a fluid. The friction $\alpha > 0$ of the fluid acts in the opposite direction of the motion, proportional to $\left| p_i \right|$, and the noise is the resulting force of all smaller particles of the fluid colliding with the larger. The noise is described by a $Jd$-dimensional Wiener process and is proportional to $\sqrt{\alpha}$, chosen to yield convergence to the Gibbs invariant measure (see below, (2.26)). Thus we now leave the Hamiltonian equations of motion on its form of derivatives for the Langevin dynamics and a system of SDEs:

$$dq(t) = \nabla_p (H(q(t), p(t))) \, dt,$$

$$dp(t) = -\nabla_q (H(q(t), p(t))) \, dt - \alpha p(t) \, dt + \sigma \, dW(t),$$

where

$$m^{-1} = \begin{bmatrix}
\frac{1}{m_1} I_J & Z_J & \cdots & Z_J \\
Z_J & \frac{1}{m_2} I_J & \cdots & \\
\vdots & \ddots & \ddots & Z_J \\
Z_J & \cdots & Z_J & \frac{1}{m_d} I_J
\end{bmatrix} \in \mathbb{R}^{Jd \times Jd},$$

and

$$\sigma = \sqrt{2\alpha k_B T} \begin{bmatrix}
\sqrt{m_1} I_J & Z_J & \cdots & Z_J \\
Z_J & \sqrt{m_2} I_J & \cdots & \\
\vdots & \ddots & \ddots & Z_J \\
Z_J & \cdots & Z_J & \sqrt{m_d} I_J
\end{bmatrix} \in \mathbb{R}^{Jd \times Jd}. \tag{2.23}$$

Here $I_J$ is the identity matrix in $\mathbb{R}^{J \times J}$, $Z_J$ the zero matrix in $\mathbb{R}^{J \times J}$, $k_B$ is the Boltzmann constant, $T$ the temperature of the heat bath and $W(t)$ an independent $Jd$-dimensional Wiener process.

If we partially carry out the process of differentiating certain terms of the equations we get

$$dq(t) = m^{-1} p(t) \, dt$$

$$dp(t) = -\nabla_q (V(q(t))) \, dt - \alpha p(t) \, dt + \sigma \, dW(t). \tag{2.25}$$

In this SDE setting each phase point $x = (q_1, \ldots, q_d, p_1, \ldots, p_d)$ becomes a stochastic outcome in $\Gamma$, with probability densities $\rho = \rho(x, t)$. The probability densities satisfy the Fokker-Planck equation (c.f. [7], equation (8.6.35)):

$$\frac{\partial \rho}{\partial t}(x, t) = \sum_{i=1}^{d} \left[ \alpha \left( J \rho + p_i^T \nabla p_i (\rho) + m_i k_B T \nabla^2 p_i (\rho) \right) + \nabla q_i (V(q_i))^T \nabla p_i (\rho) - \frac{1}{m_i} p_i^T \nabla q_i (\rho) \right]. \tag{2.26}$$
2.3. SOME CONCEPTS FROM STATISTICAL PHYSICS AND ERGODICITY

The stationary solution of (2.26) (i.e., the time independent solution,) is called the invariant density and is denoted $\pi(x)$. The invariant measure is

$$\pi(x) = \frac{\exp\left(-\frac{H(x)}{k_B T}\right)}{\int_I \exp\left(-\frac{H(x)}{k_B T}\right) dx}.$$  \hspace{1cm} (2.27)

That (2.27) is the invariant measure is easily proven by inserting it into (2.26). However, it is not certain that the solution is unique. Since $H$ can be of many complicated forms (e.g. if the potential energy is Lennard-Jones, (3.8)), explicitly finding $\pi(x)$ is not easily done even though we have an analytic expression (the denominator of (2.27) can be very difficult to calculate) and thus we use MD (and other numerical methods) when calculating expectations of observables. The measure $\pi(x)$ is also known as the Gibbs measure, which is defined and derived from physical laws in any literature on statistical physics. The measure is characteristic for the canonical ensemble, i.e. a system with constant number of particles $N$, constant volume $V$ and constant temperature $T$. Thus by the choice of frictional term and noise term in (2.20-2.21) the invariant measure of $(q,p)$ under Langevin dynamics is the same as in the canonical ensemble. Hence the Langevin equation yields an NVT ensemble.

2.3 Some concepts from statistical physics and ergodicity

2.3.1 Temperature and thermostats

In statistical physics temperature is defined by a derivative of the logarithm of the number of accessible microstates, but in the case of molecular dynamics it is more convenient to use the result of the Equipartition theorem. The theorem states that [3]:

**Theorem 2.3.1. Equipartition theorem**

For a system with $Jd$ momentum degrees of freedom, with kinetic energy $K_i = \frac{\|p_i\|^2}{2m_i}$, $i = 1, \ldots, Jd$ associated to each degree, the following holds:

$$\mathbb{E} \left[ \sum_{i=1}^{Jd} K_i \right] = \frac{Jd}{2} k_B T.$$ \hspace{1cm} (2.28)

where the expectation is w.r.t. the invariant measure $\pi(x)$.

Our purpose is to simulate dynamics at constant temperature $T$ for a system, rather than forcing the energy to be constant for all times. By referring to the Equipartition theorem we achieve constant temperature as long as the mean kinetic energy is constant. What this means is that the kinetic energy may fluctuate, but not drift.
If a system starts in some arbitrary initial state $x_0$ and is in contact with (here immersed into) some reservoir that can absorb an infinite amount of energy without changing temperature we call the reservoir a heat bath. The system itself is a thermostat. When discussing that the system is in contact with this heat bath we speak of the larger particles moving in the heat bath. With this interpretation the notion of constant volume needs to be clarified: Actually, when we say constant volume we mean that the particles are confined in a space of constant size, which they may not escape from (assuming constant $N$).

It would be preferable to sample initial states from the invariant measure $\pi(x)$, however in reality it is not possible. Instead, the sampling can be done by realizing a trajectory from some arbitrary point. When the empirical temperature of the system is approximately the target temperature we take that as an initial point in the state space. The empirical temperature is defined similarly as temperature, but under another measure:

$$\theta = \frac{2E_t[K]}{Jdk_B}.$$  \hspace{1cm} (2.29)

The density is some $\rho(x,t)$ (that solves (2.26)) given the initial state $x_0$ and dependent of time $t$; the superscript $t$ is to emphasize the dependence and that the measure is not the invariant measure. From [6] we have the following approach of $\theta$ towards $T$ under the Langevin dynamics:

$$\theta(t) \approx T + constant \cdot e^{-\alpha Jdk_B t/C(T)}$$ \hspace{1cm} (2.30)

where $C(T)$ is the heat capacity of the system at target temperature $T$. If the time is long enough and the initial difference is small enough the empirical temperature thus approaches the thermostat temperature, and we have a good initial sample. Note that

$$constant \approx (T_0 - T).$$ \hspace{1cm} (2.31)

### 2.3.2 Averages

The following definitions are necessary when studying ergodicity:

**Definition 2.3.2. Ensemble average**

For a stochastic process $Y(t): t \mapsto y \in \Gamma$, an invariant measure $\pi(y)$ and integrable functions $f = f(Y(t))$ the ensemble average is

$$\langle f \rangle_\pi \overset{\text{def}}{=} \int_{\Gamma} f(y) \, d\pi(y).$$ \hspace{1cm} (2.32)

Note: Above in the Equipartition theorem the expectation is actually this ensemble average.

**Definition 2.3.3. Time average**

For a stochastic process $Y(t): t \mapsto y \in \Gamma$ and integrable functions $f(Y(t))$ the time average is

$$\langle f \rangle_\infty \overset{\text{def}}{=} \lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} f(Y(s)) \, ds.$$ \hspace{1cm} (2.33)
2.3. SOME CONCEPTS FROM STATISTICAL PHYSICS AND ERGODICITY

2.3.3 Ergodicity and geometric ergodicity

The concept of ergodicity is a central part of our studies of estimations of observables; here defined by the ensemble and time averages.

**Definition 2.3.4. Ergodic**

A process $Y(t)$ is ergodic if

\[ \langle f(Y(t)) \rangle_\infty = \langle f(Y(t)) \rangle_\pi. \]  

(2.34)

independently of $Y(0) \in \Gamma$, for any integrable function $f : \mathbb{R}^n \rightarrow \mathbb{R}$.

Geometric ergodicity is a property of processes for which we can appreciate the proportion of the error as subsiding exponentially:

**Definition 2.3.5. Geometric ergodicity**

A process $Y(t)$ is geometrically ergodic if

\[ \left| \mathbb{E}^t [f(Y(t)) - \langle f \rangle_\pi | Y(0) = y_0] \right| \leq C \cdot e^{-\lambda t} \]  

(2.35)

independently of $y_0 \in \Gamma$, for some constant $C$, for any integrable function $f : \mathbb{R}^n \rightarrow \mathbb{R}$.

2.3.4 Geometric ergodicity of the Langevin equation

In [9] the authors provide a Markov chain-based method for establishing geometric ergodicity for SDEs and time discretizations. For the Langevin equation the conditions become

**Condition 2.3.6.** The potential $V(q) \in C^\infty(\mathbb{R}^d, \mathbb{R})$ and satisfies

(i) $V(q) \geq 0 \quad \forall q \in \mathbb{R}^d$,

(ii) \( \exists a > 0 \text{ and } \exists \beta \in (0,1) \text{ s.t.} \)

\[ \frac{1}{2} \langle \nabla_q V(q), q \rangle \geq \beta V(q) + \alpha^2 \beta (2 - \beta) \frac{1}{8(1 - \beta)} \| q \|^2 - a. \]  

If Condition 2.3.6 holds the Langevin equation (2.20-2.21) has a unique invariant measure $\pi(x)$, and realizations of $f(q, p)$ converge in the strong sense geometrically to $\pi(f)$ for measurable functions $f$. To state this as a theorem we need to define a Lyapunov function $L_y$ by

\[ L_y(q, p) = \frac{1}{2} \| p \|^2 + V(q) + \frac{\alpha}{2} \langle p, q \rangle + \frac{\alpha^2}{4} \| q \|^2 + 1. \]  

(2.36)

From now on when we write that the dynamics of $(q, p)$ is geometrically ergodic if it satisfies the following theorem:
CHAPTER 2. BACKGROUND MATERIAL

Theorem 2.3.7. If Condition 2.3.6 holds, then the solution to (2.20-2.21) has a unique invariant measure \( \pi(x) \). If \( q(0) = q_0, p(0) = p_0 \), then \( \forall l \geq 1, \exists C = C(l) > 0, \lambda = \lambda(l) > 0 \) s.t., \( \forall f \in F_l = \{ \text{measurable } f : \mathbb{R}^n \to \mathbb{R} \text{ with } |f| \leq L_y \} \),

\[
\left| \mathbb{E}^t [f(q, p) - \langle f \rangle_\pi | q(0) = q_0, p(0) = p_0] \right| \leq C L_y(q_0, p_0)^l e^{-\lambda t}, \forall t \geq 0.
\]

A proof of this is provided in [9], section 3.

2.3.5 Geometric ergodicity of numerical methods

It is not enough that the dynamics of a particle are ergodic; if we want to simulate the particle with this property we need to make sure the numerical method we apply preserves it.

The numerical methods considered in next section fulfill the Markovian property and can be regarded as Markov chains denoted \( X_n = (q_n, p_n) \). For Markov chains we have:

Theorem 2.3.8. Geometric ergodicity of a Markov chain

Under Assumptions 2.1 and 2.2 in [9] a unique invariant measure \( \pi \) exists. Furthermore, an \( r \in (0, 1) \) and a \( \kappa \in (0, \infty) \) exist, so that for all measurable functions \( f(X_n) \):

\[
\left| \mathbb{E}^t [f(X_n) - \langle f \rangle_\pi | X_0 = (q(0), p(0))] \right| \leq \kappa r^n L_y(q(0), p(0)) \quad (2.37)
\]

\( \forall x_0 \in \Gamma \) and \( \forall \) measurable \( f : |f| \leq L_y \).

Assumptions 2.1 and 2.2 are somewhat more intricate and require several new definitions we will not use in practice, so we refer the reader to the original article [9] for more details.

2.3.6 The diffusion coefficient \( D \)

To evaluate the performance of further down specified methods we need some problem to solve. An easily calculated observable is the (self-)diffusion coefficient \( D \), given by

\[
D = \lim_{\tau' \to \infty} \frac{1}{n \tau'} \left\langle \|q(t + \tau') - q(t)\|_\pi^2 \right\rangle.
\]

An interpretation of \( D \) is how fast "an initially nonuniform concentration profile (e.g., an ink drop in water) is smoothed in the absence of flow" (from [3], 4.4.1.), see "Fick’s law". \( \langle \|q(t + \tau') - q(t)\|_\pi^2 \rangle \) is often referred to as the mean-square displacement.

For the limit (2.38) to exist there must exist some large enough \( \tau \) for which

\[
D \approx \frac{1}{n \tau} \left\langle \|q(t + \tau) - q(t)\|_\pi^2 \right\rangle \Leftrightarrow
\]

\[
\Leftrightarrow nD \tau \approx \left\langle \|q(t + \tau) - q(t)\|_\pi^2 \right\rangle. \quad (2.39)
\]
If we assume that the dynamics are ergodic, we end up with

\[ nD\tau \approx \lim_{t' \to \infty} \frac{1}{t'} \int_{t'0}^{t'} \|q(s + \tau) - q(s)\|^2 ds, \text{ for large } \tau. \]  

(2.40)

To evaluate this integral numerically we also need to approximate \( t' \to \infty \) by some large enough value.

### 2.3.7 The Lennard-Jones potential

In the third experiment we will simulate a so called Lennard-Jones fluid, and thus we need to introduce the Lennard-Jones potential, abbreviated LJ. This pair potential approximates the interaction of two particles at sites \( q_i \) and \( q_j \) by

\[
V_{ij} = V_{ij}(q_i, q_j) = 4\epsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{\|q_i - q_j\|} \right)^{12} - \left( \frac{\sigma_{LJ}}{\|q_i - q_j\|} \right)^6 \right], \text{ if } i \neq j
\]

(2.41)

where \( \epsilon_{LJ} \) is the depth of the potential and \( \sigma_{LJ} \) the distance where the potential is zero (see fig. 2.1). It is important to assume that the initial configuration of particles is separated; no particles can share the same spatial point. Two particles sharing the same position would yield an infinite potential at that point and an infinite force acting on both particles. When \( i = j \) it is natural to set \( V_{ij} = 0 \), a particle does not interact with itself.

The total potential energy \( V(q_1, \ldots, q_d) \) is given by summing the interaction between all pairs, thus

\[
V(q_1, \ldots, q_d) = \sum_{i=1}^{d} \sum_{j=1}^{d} V_{ij}.
\]

(2.42)

![Figure 2.1: Graph of (3.8) where \( r = \|q_i - q_j\| \)](image-url)
Chapter 2. Background Material

2.4 Symplectic Euler

The numerical scheme this thesis focuses on is the symplectic Euler method combined with an implicit step in an Ornstein-Uhlenbeck process, often from now on denoted by SE. The scheme applied to the Langevin equation, with time step $\Delta t$, becomes

\begin{align*}
q_{n+1} &= q_n + p_n \Delta t \\
p_{n+1} &= p_n - \nabla_q(V(q_{n+1}))\Delta t - \alpha p_{n+1} \Delta t + \sigma \Delta W_n. \tag{2.44}
\end{align*}

The terms within the box are the symplectic Euler-step, and the terms to the right of it are a backward Euler-step in an Ornstein-Uhlenbeck process (2.11) with $\mu = 0$, $\theta = \alpha$ and $\varsigma = \sigma$. The backward Euler-step could be substituted by a forward Euler-step, but we choose the former to make the following rearrangement possible:

\begin{align*}
q_{n+1} &= q_n + p_n \Delta t \\
p_{n+1} &= p_n - \nabla_q(V(q_n + p_n \Delta t))\Delta t + \sigma \Delta W_n \left/ \left(1 + \alpha \Delta t \right) \right. \tag{2.46}
\end{align*}

In both systems of equations $q_0 = q(0)$, $p_0 = p(0)$ and $\Delta W_n = (W_1((n+1)\Delta t) - W_1(n\Delta t), \ldots, W_d((n+1)\Delta t) - W_d(n\Delta t))^T$. The explicit form of the symplectic Euler method has an advantage compared to implicit methods since each step is much computationally cheaper. We also suspect that division by $1 + \alpha \Delta t$ due to the backward Euler-step will stabilize the evolution of $p_{n+1}$ for large $\alpha$. It would be interesting to further study if there is any distinct difference between using a forward or backward Euler step in the Ornstein-Uhlenbeck process.

2.5 Other numerical methods

2.5.1 Forward Euler

The forward Euler method (FE) (or Euler-Maruyama, or Explicit Euler) is

\begin{align*}
q_{n+1} &= q_n + m^{-1} p_n \Delta t \\
p_{n+1} &= p_n - \nabla_q(V(q_n)) \Delta t - \alpha p_n \Delta t + \sigma \Delta W_n. \tag{2.48}
\end{align*}

The method is stable for Lipschitz continuous terms [8], but [5] proves that for non-globally Lipschitz continuous cases the forward Euler method can diverge in both the strong and the weak sense.
2.5. OTHER NUMERICAL METHODS

2.5.2 Split-step backward Euler

The split-step backward Euler (SSBE) is

\[ q_{n+1} = q_n + \frac{m}{\alpha^2} p^\star \Delta t \]  \hspace{1cm} (2.49)
\[ p^\star = p_n - \nabla q(V(q_{n+1})) \Delta t - \alpha p^\star \Delta t \]  \hspace{1cm} (2.50)
\[ p_{n+1} = p^\star + \sigma \Delta W_n \]  \hspace{1cm} (2.51)

where \( p^\star \) is the backward Euler solution to the deterministic part of the system, an intermediate step variable. An important result (Corollary 8.2 with Theorem 2.5) presented in [9] is that SSBE is geometrically ergodic for (2.20-2.21) if Condition 2.3.6 is fulfilled and \( \nabla q(V(q)) \) is either Lipschitz continuous or one-sided Lipschitz continuous.

The biggest difference between SSBE compared to FE and SE is that each SSBE-step requires solving \( q_{n+1} \) and \( p^\star \) for an implicit system of equations. We chose to apply fix-point iteration to solve (2.49-2.50). The convergence may be slow but is ensured for small enough \( \Delta t \), with a good start guess of \( q_{n+1}, p_{n+1} \), which are \( q_n, p_n \) respectively. Our experience is that fix-point iteration need only three or four steps to acquire machine accuracy, i.e. \( 10^{-16} \). By experimenting with the parameters in Experiment 1 and setting a maximum number of iterations (\( > 100 \)) we found an upper limit for which fix-point iteration could solve a step, \( \Delta t = 0.3 \).

2.5.3 The Metropolis-corrected BBK scheme

The idea of Metropolis-corrected schemes is to combine the Monte Carlo methods ability to preserve the exact invariant measure with MD. It is believed that Metropolis-corrected schemes are more stable than non-corrected for SDEs with unbounded drift terms. In [2] the author presents how to add a Metropolis acceptance-rejection step to a Brünger-Brooks-Karplus (BBK) scheme, which first calculates a proposal move by

\[ q^\bullet = q_n + m^{-1} \left( p_n \Delta t - \nabla q(V(q_n)) \frac{\Delta t^2}{2} \right) \]  \hspace{1cm} (2.52)
\[ p^\bullet = p_n - \left( \nabla q(V(q_n)) + \nabla q(V(q^\bullet)) \right) \frac{\Delta t}{2}. \]  \hspace{1cm} (2.53)

If the calculations are carried out in the order \( q^\bullet, p^\bullet \), no system of equations need to be solved, with the benefit that a lesser number of evaluations of the force field is necessary. Thus computation time is saved compared to SSBE. This is followed by the acceptance-rejection step: if \( \xi \in U(0, 1) \) (uniformly distributed random variable, in \( [0, 1] \)) is less than the Metropolis ration

\[ \alpha_M = \alpha_M(q_n, p_n, q^\bullet, p^\bullet) = \min \left( 1, \exp \left( -\frac{1}{k_B T} (H(q^\bullet, p^\bullet) - H(q_n, p_n)) \right) \right) \]  \hspace{1cm} (2.54)
the step is accepted with probability $\alpha_M$. Otherwise the position is kept, but the momentum flipped. Note that the exponent in (2.54) is $\pi(H(Q,P))/\pi(H(q,p))$, c.f. (2.27). After this the noise is added and summarized as

\begin{align}
\tilde{q} &= \begin{cases} 
qu, & \text{if } \xi \leq \alpha_M \\
q_n, & \text{if } \xi > \alpha_M \end{cases} \quad (2.55) \\
\tilde{p} &= \begin{cases} 
pq, & \text{if } \xi \leq \alpha_M \\
-p_n, & \text{if } \xi > \alpha_M \end{cases} \quad (2.56)
\end{align}

\begin{align}
q_{n+1} &= \tilde{q} \quad (2.57) \\
p_{n+1} &= \exp(-\alpha \Delta t)\tilde{p} + \sqrt{k_B T\Delta t} \sum_{m=1}^{1/2} \exp(-2\alpha \Delta t)m^{-1/2} \Delta W_n. \quad (2.58)
\end{align}

Calculating the proposal move does take two more evaluations of the force field compared to a forward step in SE. In addition to each step, the ratio (2.54) needs to be evaluated and compared to $\xi$, which in turn must be sampled. So, for this method to be efficient the gain of convergence to the invariant measure needs to be greater than the loss of increasing computation time. By rejecting steps error is introduced so it is desirable to have a high acceptance rate, which can be controlled by $\Delta t$. 

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Chapter 3

Numerical experiments

All the following experiments are carried out in Matlab and all masses $m_i = 1$ and the Boltzmann constant $k_B = 1$ to simplify the implementations. Most algorithms were easy to program efficiently, but when it came to storing large sets of data the following structure was very useful: Positions $q_i \approx q(i\Delta t)$ up to the current time $t = n\Delta t$, back to $n\Delta t - \max(\tau) - \Delta t$ are stored in a matrix. An index keeps track on which column of the matrix that contains the latest position $q_n$. When a step is taken the oldest remaining position is replaced with the newest $q_{n+1}$. Then the index is increased by one, or if the index becomes larger than the number of columns it is reset to one. Only one column needs to be rewritten in every step but all necessary states are saved in the correct order.

3.1 Experiment 1: A corrugated potential

The first experiment we conduct is a system of one particle moving in two spatial dimensions $(q_1, q_2)$, with two momentum coordinates $(p_1, p_2)$. The particle is affected by the potential

$$V(q_1, q_2) = \frac{q_1^2}{2} + \frac{q_2^2}{\sqrt{2}} + \beta \sin(q_1 q_2)$$

(3.1)

where the $\sin(q_1 q_2)$ term couples the dimensions. Under Hamiltonian dynamics and $\beta = 2$ this systems behaves ergodically, but not when $\beta = 0.3$. Our aim with this experiment is to study the performance of SE when $\beta = 2$ and $\beta = 0.3$, by calculating the diffusion constant $D$ under Langevin dynamics. Are there any significant differences for the different cases of $\beta$? What affect does the diffusion-friction $\alpha$ have on the dynamics? Also, how does SE perform compared to some other method, known to converge to the invariant measure?

Due to the $\sin(q_1 q_2)$ term the landscape of the potential energy will be corrugated, which may introduce difficulties for the convergence to the invariant measure. When $\beta = 2$ the corrugation will be more distinct, see fig. 3.1.
3.1.1 Problem formulation

One way to study ergodicity of a system is to follow a realization of the particle and see at which states in \( \Gamma \) it passes through over long time. Here, when the particle passes through the subspace of \( \{ x \mid q_1 = 0 \} \) we note where this is in a plot of \( q_2, p_1, p_2 \). From now on we denote \( \{ x \mid q_1 = 0 \} \) by \( q_1^{hit} \). For a system in thermal equilibrium (which is reasonable to assume the trajectory will eventually be in over a long time integration), \( \pi(x) = e^{-H(x)/Z(T)} \). From this we conclude that all states \( x \) with the same total energy \( H(x) \) are equally probable. If the method being used is ergodic, then over a long time period all states should be visited, and this we should perceive in the \( q_2, p_1, p_2 \) plot.

A method which is known to be geometrically ergodic is SSBE, and thus we compare SE and SSBE. We will also vary between \( \alpha = 0 \) (the Hamiltonian case) and \( \alpha = 0.01 \) (Langevin case) to see how the noise affects the ergodic property.

After this we want to calculate the diffusion coefficient with the two methods and study their behaviors for different integration periods and time steps. The comparison is done by firstly estimating \( D \) by the first-order term in a least-square fit of data for a run with each method, followed by taking the average \( \bar{D} \) over the combination of \( t' \) and \( \Delta t \) denoting it \( \bar{D} \); secondly, by the spread of the estimations measured by \( s \), the sample deviation for all runs with same \( \Delta t \) and \( t' \) for each method:

\[
s = \sqrt{\frac{1}{m-1} \sum_{i=1}^{m} \left( \bar{D}_i - \frac{1}{m} \sum_{j=1}^{m} \bar{D}_j \right)^2}.
\]  

(3.2)

Figure 3.1: Plots of the potentials in Experiment 1 for different choices of \( \beta \). Below in the \( q_1q_2 \)-plane is a contour plot of the potential.
3.1. EXPERIMENT 1: A CORRUGATED POTENTIAL

thirdly, by the mean-square deviation $s_{ref}$ from a reference value $D_{ref}$ defined by:

$$s_{ref} = \sqrt{\frac{1}{m-1} \sum_{i=1}^{m} (D_i - D_{ref})^2}.$$  \hspace{1cm} (3.3)

3.1.2 Implementation

Since it is not possible to know exactly where in $\Gamma$ state $(q,p)$ hits the $q_1^{hit}$ plane linear interpolation is used to estimate the position $q$. After each step the previous position $q_1$ and current $q_2$ are compared relative to $q_1^{hit}$; if $q_1^{hit} \leq q_1$ or if $q_1^{hit} \geq q_2$, then the hit point $(q_1^{hit}, q_2^{hit}, p_1^{hit}, p_2^{hit})$ is estimated by

$$q_2^{hit} \approx \frac{q_2 - q_1}{q_2 - q_1^{hit}} (q_1^{hit} - q_1),$$

$$p_1^{hit} \approx \frac{p_2 - p_1}{q_2 - q_1^{hit}} (q_1^{hit} - q_1),$$

$$p_2^{hit} \approx \frac{p_2 - p_1}{q_2 - q_1^{hit}} (q_1^{hit} - q_1).$$ \hspace{1cm} (3.4)

Under Implementation for Experiment 2 we explain how initial states are sampled.

3.1.3 Results and conclusions

Hit points on the $q_1^{hit}$ plane

In fig. 3.3-3.5 the number of steps are always $10^8$ and in all but one is $\Delta t = 0.0001$. The corresponding integration time is therefore $10^4$. In one other case (see fig. 3.5) the integration is $10^8$ and $\Delta t = 10^{-5}$ to get a sharper set of hit points (when $\Delta t = 0.0001$ a clear pattern had emerged but time discretization error made it very fuzzy). Red points denote $p_1$ and blue points $p_2$. Plots to the left are undisturbed, i.e. $\alpha = 0$, and those to the right are disturbed with $\alpha = 0.01$.

If we start by studying realizations when $\beta = 2$, we see a distinct difference between SE and SSBE in the deterministic case: SE exhibits a sharply defined ellipse, while SSBE-trajectories seem to pass through the same domain but do not form the same clear geometric figure. When $\alpha = 0.01$ the figures diffuse and it becomes difficult to distinguish the plots from each other. The main conclusion is that fig. 3.2-3.3 display ergodic behavior, and the deterministic case confines the state of the particle at constant energy.

Fig. 3.4-3.5 shows that the deterministic cases are non-ergodic when $\beta = 0.3$, in view of that only a small subset of accessible states are visited, in a clear pattern. This pattern deteriorates when the diffusion-friction is introduced and a much larger set of states are accessed. The only difference for the methods is that SSBE required smaller time steps for the pattern to fully emerge when $\alpha = 0$. 

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Figure 3.2: Plot when $\beta = 2$ of hit points $p_1, p_2$ versus $q_2$ on $q_1^{hit}$, using symplectic Euler.

Figure 3.3: Plot when $\beta = 2$ of hit points $p_1$ versus $q_2$ on $q_1^{hit}$, using split-step backward Euler.

Figure 3.4: Plot when $\beta = 0.3$ of hit points $p_1$ versus $q_2$ on $q_1^{hit}$, using symplectic Euler.
3.1. EXPERIMENT 1: A CORRUGATED POTENTIAL

Figure 3.5: Plot when $\beta = 0.3$ of hit points $p_1$ versus $q_2$ on $q_1^{hit}$, using split-step backward Euler.

To study the distribution even further, it would be possible to count the number of times the trajectory passes through each square of some grid, calculate the average energy over that square and study that distribution.

The main conclusion is however positive: the symplectic Euler method does behave ergodically for the ergodic examples.
CHAPTER 3. NUMERICAL EXPERIMENTS

The diffusion coefficient

Our expectation of SSBE was that it would be stable and yield a reference solution we could use, but the estimation did not converge. Due to limitations in processing power it was not possible to choose a small enough time step and long enough integration time that would yield a $\bar{D}$ that did not change too much when $t'$ was increased or $\Delta t$ was decreased. What we instead use as a reference is longer runs of SE: For $\beta = 2$ we ran with $\Delta t = 0.1$ and $\Delta t = 0.01$ for $10^6$ units of time and noted that the differences between the $\bar{D}$s were small enough to be considered stable reference solutions. Then we did a least-square fit of the data sets of two runs of $\Delta t = 0.01$. With this $D_{ref}$ we calculated $s_{ref}$ in Table 3.1. The value of $\alpha$ was 0.01.

It is not obvious how to devote the limited CPU time. We may either choose to decrease the time step $\Delta t$ or increase the total integration time $t'$. To study this we grouped data in sets of the same number of steps. The different groups then correspond to the same processing time for each method. The conclusion we can draw from Table 3.1 and Table 3.2 is that SE performs better when the integration time is longer, $s_{ref}$ is least for the longest $t'$. Changing $\Delta t$ does not have much effect at all, e.g., for $\beta = 2$ and $t' = 10^4$, the deviations from the reference are:

<table>
<thead>
<tr>
<th>$\Delta t$</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
<th>0.0001</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{ref}$</td>
<td>0.0313</td>
<td>0.0399</td>
<td>0.0686</td>
<td>0.0657</td>
</tr>
</tbody>
</table>

If we assume that the error $\epsilon_{err}$ is proportional to $s_{ref}$, that the time discretization error is proportional to the time step $\Delta t$ and the statistical error is proportional to the reciprocal of the square root of the integration time $t'$ we can do a least-square fit of the total error to

$$\epsilon_{err} \propto s_{ref} = a_{err}(\Delta t) + b_{err}(t')^{-1/2}. \quad (3.5)$$

We do a fit for $\beta = 2$ and values $\Delta t$ and $t'$ so the total number of steps is $\leq 10^7$. For each combination we have done seven runs, see Table 3.1. The result is

$$a_{err} = 0.0076, \quad b_{err} = 4.4.$$  

Clearly the integration time is the largest factor in the total error. To achieve an error with a significant contribution from time discretization when $\Delta t = 0.1$ the integration time would need to be $t' > 3 \cdot 10^7$.

The behavior of SSBE is very different, the lowest deviation from the reference solution is when the smallest time step is used, over the longest time. It does not get as close as several combinations of $t'$ and $\Delta t$ for SE for both $\beta$. Though, what is most interesting is the $s$ column: its values are very low for large $t'$ and comparably spread out as SE for $t' = 1000$. The conclusion is that SSBE performs poorly compared to SE since the $\bar{D}$s hugely increase as $\Delta t$ is decreases and does not stabilize around some value. To emphasize this we attached a plot (fig. 3.6) of the
3.1. EXPERIMENT 1: A CORRUGATED POTENTIAL

Figure 3.6: Plot of the estimation of the integral in (2.40); blue curves are calculated by SE and green by SSBE.

estimation of the integral in (2.40) which \( D \) is proportional to. Note that in fig. 3.6 the curves settle (and oscillate around some value) for larger \( \tau \) and do not tend to infinity as (2.40) imply. This is due to that the potential is a well from which there is no escape and a particle can only move some certain distance away from where it was \( \tau \) units of time ago. Thus only points on the curves between \( 0.6 < \tau < 2.1 \) are used when interpolating the first-order function yielding \( \overline{D} \).

3.1.4 Combining results

If we return to the left plot in fig. 3.5 and use what we have learned about SSBE’s ability to not converge for larger time steps in previous section The diffusion coefficient we can conclude that both results imply that SSBE is highly inaccurate for this problem and studied time steps. Same tables and figures suggest that SE is ergodic. We can also conclude that the importance of integrating over long time should not be underestimated, as we see for SSBE and especially SE. When \( \alpha > 0 \) the non-ergodic potential \( (\beta = 0.3) \) becomes ergodic, and both methods capture this behavior, but SE does better than SSBE. Question is, why? Theorem 2.3.7 and Theorem 2.3.8’s criteria are sufficient, so it is possible that when \( \beta = 0.3 \) only one, or neither, criteria are fulfilled. The description of case \( \beta = 2 \) being more corrugated than when \( \beta = 0.3 \) has not yet explained why the former is ergodic and the latter
CHAPTER 3. NUMERICAL EXPERIMENTS

\[ \beta = 2 \]

<table>
<thead>
<tr>
<th>( t' ) / ( \Delta t ) (# runs)</th>
<th>SE</th>
<th>SSBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 0.1 (7)</td>
<td>( \bar{D} ) 0.5926 0.1480 0.1480</td>
<td>( \bar{D} ) 0.0160 0.0013 0.6188</td>
</tr>
<tr>
<td>1000 0.01 (7)</td>
<td>( \bar{D} ) 0.5630 0.0823 0.0869</td>
<td>( \bar{D} ) 0.1645 0.0259 0.4591</td>
</tr>
<tr>
<td>10000 0.1 (7)</td>
<td>( \bar{D} ) 0.6051 0.0259 0.0313</td>
<td>( \bar{D} ) 0.0158 0.0005 0.6191</td>
</tr>
<tr>
<td>1000 0.001 (7)</td>
<td>( \bar{D} ) 0.6719 0.1440 0.1696</td>
<td>( \bar{D} ) 0.5368 0.1013 0.1159</td>
</tr>
<tr>
<td>10000 0.1 (7)</td>
<td>( \bar{D} ) 0.6029 0.0190 0.0243</td>
<td>( \bar{D} ) 0.1638 0.0100 0.4592</td>
</tr>
<tr>
<td>100000 0.01 (7)</td>
<td>( \bar{D} ) 0.6257 0.1425 0.1479</td>
<td>( \bar{D} ) 0.6897 0.2133 0.2395</td>
</tr>
<tr>
<td>10000 0.001 (3)</td>
<td>( \bar{D} ) 0.6176 0.0556 0.0657</td>
<td>( \bar{D} ) 0.5764 0.0577 0.0600</td>
</tr>
</tbody>
</table>

Table 3.1: Results from calculating the diffusion coefficient for a particle in potential (3.1) when \( \beta = 2 \) with symplectic Euler (SE) and split-step backward Euler (SSBE). The reference valued used is \( D_{ref} = 0.5889 \), from a least-square fit of the data from four runs of SE when \( \Delta t = 0.01 \) and total integration time is \( 10^6 \).

<table>
<thead>
<tr>
<th>( t' ) / ( \Delta t ) (# runs)</th>
<th>SE</th>
<th>SSBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000 0.1 (7)</td>
<td>( \bar{D} ) 0.8984 0.0839 0.1098</td>
<td>( \bar{D} ) 0.0719 0.0023 0.8219</td>
</tr>
<tr>
<td>10000 0.01 (7)</td>
<td>( \bar{D} ) 0.8351 0.0789 0.0789</td>
<td>( \bar{D} ) 0.3946 0.0169 0.4735</td>
</tr>
<tr>
<td>100000 0.1 (7)</td>
<td>( \bar{D} ) 0.8565 0.0155 0.0300</td>
<td>( \bar{D} ) 0.0688 0.0004 0.8252</td>
</tr>
<tr>
<td>10000 0.001 (7)</td>
<td>( \bar{D} ) 0.8384 0.0624 0.0627</td>
<td>( \bar{D} ) 0.7524 0.0675 0.1099</td>
</tr>
<tr>
<td>100000 0.01 (7)</td>
<td>( \bar{D} ) 0.8399 0.0114 0.0137</td>
<td>( \bar{D} ) 0.3914 0.0100 0.4768</td>
</tr>
<tr>
<td>100000 0.001 (3)</td>
<td>( \bar{D} ) 0.8425 0.0900 0.0904</td>
<td>( \bar{D} ) 0.7777 0.0433 0.0801</td>
</tr>
<tr>
<td>100000 0.001 (3)</td>
<td>( \bar{D} ) 0.8416 0.0260 0.0282</td>
<td>( \bar{D} ) 0.7450 0.0260 0.1105</td>
</tr>
</tbody>
</table>

Table 3.2: Results from calculating the diffusion coefficient for a particle in potential (3.1) when \( \beta = 0.3 \) with symplectic Euler (SE) and split-step backward Euler (SSBE). The reference valued used is \( D_{ref} = 0.8328 \), from a least-square fit of the data from four runs of SE when \( \Delta t = 0.01 \) and total integration time is \( 10^6 \).
3.2 EXPERIMENT 2: ONE-SIDED LIPSCHITZ CONTINUOUS PROBLEM

is not when \( \alpha = 0 \). The deviation from the reference \( s_{\text{ref}} \) is lower for the former case, so the complication of the convergence due to corrugation seems to have been overestimated. Instead the corrugation have contributed to the convergence. The impact of introducing several local minima do lessen the long-time correlation which promotes the convergence to the invariant measure.

3.2 Experiment 2: One-sided Lipschitz continuous problem

The previous experiment was mainly used to study properties of diffusion for Langevin dynamics and ergodicity of SE for a simple, Lipschitz continuous case; although in reality most problems are not Lipschitz continuous. Therefore we now run an experiment with a potential that has only a one-sided Lipschitz continuous drift term, i.e. a potential with a gradient that is one-sided Lipschitz continuous w.r.t. \( q \). We evaluate how SE performs for this problem by calculating the diffusion coefficient \( D \). For comparison we again apply SSBE, which is suitable for the potential of this problem; hypothetically the profit of using implicit steps could be more discernible. We also apply the Metropolis-corrected Brünger-Brooks-Karplus scheme, which is claimed to be very suitable for one-sided Lipschitz continuous problems.

3.2.1 Theory and problem formulation

First we state the definition of one-sided Lipschitz continuous:

**Definition 3.2.1.** A function \( f : \mathbb{R}^m \rightarrow \mathbb{R}^m \) is one-sided Lipschitz continuous (OSL) if and only if

\[
\exists c > 0 : \langle y_2 - y_1, f(y_2) - f(y_1) \rangle \geq -c\|y_2 - y_1\|^2. \tag{3.6}
\]

The potential used here is

\[
V(q) = \frac{1}{4}(\|q\|^2 - 1)^2, \tag{3.7}
\]

where \( q \in \mathbb{R}^2 \), i.e. \( \Gamma = \mathbb{R}^4 \) (two spatial and two momenta coordinates). The potential fulfills Condition 2.3.6 and its gradient fulfills Definition 3.2.1. The frictional coefficient \( \alpha \) will be set to \( \alpha = 0.01 \) and all other coefficients \( T = k_B = m_i = 1 \).

3.2.2 Implementation

All implementations of the numerical schemes are straightforward from the definitions. The initial state is chosen by starting out in \((0, 0, 1, -1)\) and running an equilibration period. The equilibration period is to assure that the empirical temperature is correct and so that the trajectory has 'forgotten' were it started out from. Some trial-runs were done to see what integration time seemed to yield a convergence to the invariant measure for the time steps \(0.1, 0.01, 0.001\) and \(10^{-4}\). We decided to study the methods over the integration time \(10^5\). Again is \( \alpha = 0.01 \).
Table 3.3: Results from calculating the diffusion coefficient for a particle in potential (3.7) with symplectic Euler (SE), split-step backward Euler (SSBE) and Metropolized Brünger-Brooks-Karplus (M-BBK) for different $\Delta t$ and constant integration time $t' = 10^5$. The reference valued used is $D_{ref} = 0.6882$ from two runs with M-BBK when $\Delta t = 0.1$ and $t' = 10^5$, calculated as in Experiment 1.

### 3.2.3 Results and conclusions on the OSL problem

The results of the simulations are presented in Table 3.3. The first observation from the data is that both SE and M-BBK outperform SSBE for the larger time steps, even though it is only for SSBE we are certain of the geometric ergodicity. Only for very small time steps is the geometric convergence of SSBE verified numerically. If we consider our aim again, to integrate over long times, then large time steps are preferable, thus SE and M-BBK become more favorable than SSBE. The reference used is from two runs of the Metropolized scheme with $\Delta t = 0.1$ and $t' = 10^5$.

### 3.3 Experiment 3: A Lennard-Jones fluid

Up to now we have exclusively studied problems for single particle systems in different artificial potentials to test methods. Molecular dynamic simulations that approximate real world problems are often based on several or single particles in potentials related to specific experiments. Therefore we want to study how SE solves a more realistic system and estimate the diffusion coefficient for it. The potential we use now is the Lennard-Jones potential, a well-studied problem, which for low temperatures yields the FCC (face-centered cubic) crystal and at higher melts into a fluid. The number of particles we will use is $d = 864$. If the model mimics realistic
behavior of a particle system it will be possible to study several observables, e.g.
the pressure; when the temperature rises the pressure rise as well (since we have
assumed a constant volume). Also, when the temperature is changed a change in
the state of matter should be perceivable in e.g. a radial distribution plot.

3.3.1 Theory and problem formulation

In previous experiments $\Gamma = \mathbb{R}^4$ but now we will take a state space of size $\Gamma = \mathbb{R}^{5184}$,
i.e. $d = 864$ and $J = 3$, which will be very computationally difficult to solve by
e.g. implicit methods. To understand this we first re-introduce the Lennard-Jones
potential:

$$V_{ij} = \begin{cases} 4\epsilon_{LJ} \left( \frac{\sigma_{LJ}}{||q_i - q_j||} \right)^{12} - \left( \frac{\sigma_{LJ}}{||q_i - q_j||} \right)^6, & i \neq j \\ 0, & i = j. \end{cases}$$ (3.8)

It turns out this Lennard-Jones potential also is one-sided Lipschitz continuous,
and thus we in theory can apply SSBE, but due to the number of evaluations of the
force field this option is considered to be too expensive to carry out in practice.

We want to study the estimation of the diffusion $D$ for the system by SE, the
only method of interest that will be computationally possible to study thoroughly.
The system will again be an $NVT$ and the volume constitutes a cube with sides
of length $l = 8.7336$ and density 1.297 particles per unit volume. The particles are
initially placed in some shape of a crystal, displaced with a normally distributed
random vector, and the total energy is rescaled so that the initial temperature
$T_0 = 1$. This is followed by an equilibration period with $\alpha_{equl} = 5$ and left to
equilibrare for time 1.5. The particles should then form an FCC-crystal. Then the
temperature will be set to melt the crystal, here $T = 5$, with the same very high
$\alpha_{equil}$. Another equilibration period passes of length 2. At this point the system
should have reached the intended temperature and $\alpha$ is set to $\alpha = 0.01$. Depending
on the choice of $\Delta t$ another period now runs to fill up a matrix of positions at
this new equilibrium. This is followed by the long time integration of the mean-
displacement to estimate $D$. The integration time is either $t_e' = 100$ or $t_e' = 500$ and
the time step is $\Delta t = 0.001$ or $\Delta t = 0.0005$. To have a reference value we simulate
four realizations with time step $\Delta t = 0.001$ and integration time $t_e' = 1000$. The
interactions are over periodic boundaries, so that a particle is projected in identical
boxes around the actual box. Thus the particle interacts with the closest image of
each other particle in any of these (and the actual) boxes. At the same time it is
possible to keep track on how far a particle actually have traveled even if it crosses
boundaries.
3.3.2 Implementation

An important note: The main program (especially the implementations described below) is from the study material of a course at the Royal Institute of Technology, Stockholm, Sweden, written by Tomas Oppelstrup at the Department of Mathematics. The author of this thesis cannot take credit for writing the whole program, but does take responsibility for any flaws in the outcomes of the modified version used here. The author also wants to express his gratitude to Tomas Oppelstrup for letting him use the program in his research.

With a significantly increased number of particles the code implementing the method should not waste processing power on negligible interactions. Thus we introduce a cut-off, i.e. a distance $r_{\text{cut-off}}$ such that each particle interacts only with particles within $r_{\text{cut-off}}$ of it. The method is also known as truncating the pairwise interactions. The formula (3.8) then becomes

$$V_{ij} = \begin{cases} 4\epsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{\|q_i - q_j\|} \right)^{12} - \left( \frac{\sigma_{LJ}}{\|q_i - q_j\|} \right)^6 \right] + r, & \text{if } i \neq j \text{ and } \|q_i - q_j\| \leq r_{\text{cut-off}}, \\ 0, & \text{if } i = j \text{ or } \|q_i - q_j\| > r_{\text{cut-off}}. \end{cases}$$

(3.9)

where $r = 4\epsilon_{LJ} \left[ (\sigma_{LJ}/r_{\text{cut-off}})^6 - (\sigma_{LJ}/r_{\text{cut-off}})^{12} \right]$. The term $r$ is added to make the gradient of the potential field continuous. We denote for each $i$ a set of indexes $j$ fulfilling the former case of (3.9) by $K_i = \{ j : \|q_i - q_j\| \leq r_{\text{cut-off}} \}$. To keep track on which particles belong to $K_i$ and not we use a Verlet list (also known as a neighbor list). Each particle $i$ has a Verlet list listing all particles within $r_v > r_{\text{cut-off}}$. To speed up the calculation when constructing the Verlet list it is combined with a cell list; a cell list is a list of which sub-box of the system a particle is in. Using a Verlet list also requires some condition when to recalculate it, and the criterion here is when any one particle has moved more than $r_v - r_{\text{cut-off}}$ away from the position where it were when the current Verlet list was calculated. The constant $r_v$ is thus the outer radius of a spherical shell of thickness $r_v - r_{\text{cut-off}}$. See also Algorithm 1.

In this experiment $r_{\text{cut-off}} = 2.5$, $r_v = 2.75$, $\sigma_{LJ} = 1$, $\epsilon_{LJ} = 1$ and the sides of the cube are 8.7336.

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3.3. EXPERIMENT 3: A LENNARD-JONES FLUID

Algorithm 1 Pseudocode describing how a Verlet list is calculated using a cell list. C.f. appendix F in [3].

```verbatim
Initiate $q_0$; all particle $i$’s positions
$q_p = q_0$;
list = calculateNeighbors($q_0, r_v$); lists of neighbors within $r_v$ for each particle $i$
for $1 \leq n \leq N$ do
    $F$ = calculateForces($q_{n-1}$, list); calculate the force acting on each particle based on list
    $q_n$ = takeStep($q_{n-1}$, $F$); take a step with chosen method
Now test if some particle $i$ has moved further than $r_v - r_{cut-off}$ from $q_{i,p}$:
    if $\max(\|q_{i,n} - q_{i,p}\|) > r_v - r_{cut-off}$ then
        list = calculateNeighbors($q_n, r_v$);
        $q_p = q_n$;
    end if
    ...
    calculate pressure, diffusion coefficient etc.
    ...
end for
```

```verbatim
function calculateNeighbors($q, r_v$)
    $B$ = assignParticlesToBoxes($q$); take all particles positions and return which sub-box they are in
    unsortedList = calculateDistances_v($q$, $B$); use information about the distribution of particles in sub-boxes and calculate the distance between each
    list = sortList(unsortedList); sort the list, from closest to far-most
    return list;
end function
```

3.3.3 Results and conclusions

Initially we had the idea to compare the results from the simulations to previous work, but this did turn out to be too cumbersome. In retrospect, the best alternative would have been to implement the M-BBK scheme along with SE and compare as in Experiment 2.

In fig. 3.10 the radial distribution functions illustrate the phase of the fluid; in (a) a distinct structure is perceived and in (b) the structure has dissipated into a fluid-like state as intended. In Table 3.4 we again see that longer integration time yields lower sample deviation, c.f. $t' = 1000$ with other $t'$s. The deviation from the reference value when $t' = 1000$ is also much lower, albeit, the reference used is calculated by those simulations so the result is somewhat biased. But it still agrees with earlier results. Decreasing time step does not have a clear positive affect on $s_{ref}$, compare e.g. the values of the deviation from the reference when $t' = 100$ and
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<table>
<thead>
<tr>
<th>$t'$ / $\Delta t$</th>
<th># runs</th>
<th>$\bar{D}$</th>
<th>$s$</th>
<th>$s_{ref}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100   0.001  8</td>
<td>0.223435 0.0791 0.0801</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100   0.0005 8</td>
<td>0.234946 0.0870 0.0906</td>
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<td></td>
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</tr>
<tr>
<td>500   0.001  5</td>
<td>0.226143 0.0456 0.0484</td>
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</tr>
<tr>
<td>500   0.0005  5</td>
<td>0.210459 0.0303 0.0304</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000  0.001  4</td>
<td>0.211594 0.0115 0.0115</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Results from calculating the diffusion coefficient for the LJ-fluid using SE. The reference value is $D_{ref} = 0.211594$, calculated by a least-square fit of the data from four runs with SE using $\Delta t = 0.001$ and $t' = 1000$. The reference $D_{ref}$ is also in the table.

$\Delta t$ varies.

In fig. 3.9 we believe that the huge increase of the integral's value between $0 < \tau < 0.5$ is due to the particle's movement in its nearest vicinity, a phenomenon that should occur on a small time scale. Over long time the transport by diffusion dominates, which is what the curve follows when $1.5 < \tau$. The initial rapid increase is negligible when computing the diffusion coefficient since $D$ is proportional to the first-order term in a first-order fit to the integral's value at very large $\tau$.

In this experiment we did note that there is a threshold for when SE is stable, as illustrated in fig. 3.7: For too large $\Delta t$ the energy starts to drift if the temperature is e.g. $T = 5$. For a simulation this is catastrophic. The drift at $\Delta t = 0.01$ could probably be mitigated by adjusting $\alpha$, but this we did not study any further. Instead we chose smaller time steps for the experiment. For time steps $\Delta t = 0.001$ and 0.0005 the simulations kept the system at correct temperatures.
3.3. EXPERIMENT 3: A LENNARD-JONES FLUID

(a) Plot of the average (per particle) energies during a simulation when $\Delta t = 0.01$ and $T = 5$.

(b) Plot of the average (per particle) energies during a simulation when $\Delta t = 0.001$ and $T = 5$. Mean empirical temperature $\theta = 4.9919$ over the whole integration.

Figure 3.7: Plots to illustrate the energy drift when using too large time steps with SE. All axes with energy values have the same scale, not all $t$ axes does.

(a) Plot of the average (per particle) energies during a simulation when $\Delta t = 0.01$ and $T = 1$. Mean empirical temperature $\theta = 0.9991$.

(b) Plot of the average (per particle) energies during a simulation when $\Delta t = 0.001$ and $T = 1$. Mean empirical temperature $\theta = 1.0179$.

Figure 3.8: Plots of the average energy per particle. There variations of the energies are lower in the plot to the right. C.f. fig. 3.7.
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Integral of square-displacement when \( t' = 1000 \) and \( \Delta t = 0.001 \)

Figure 3.9: Plot of the estimations of the integral in (2.40) for \( t' = 1000 \) and \( \Delta t = 0.001 \).

(a) \( T = 1 \): after the equilibration period, precisely before increasing the temperature.

(b) \( T = 5 \): after the equilibration period.

Figure 3.10: Plots of the radial distribution functions at different temperatures \( T \) after equilibration.
References


