Chapter 6

Brownian Dynamics

Contents

6.1 Discretization of Time ........................................... 91
6.2 Monte Carlo Integration of Stochastic Processes ............... 93
6.3 Ito Calculus and Brownian Dynamics .......................... 95
6.4 Free Diffusion ....................................................... 96
6.5 Reflective Boundary Conditions .................................. 100

In 1827 the botanist Robert Brown examined under his microscope pollen of plants suspended in water. He observed that the pollen, about $10^{-6} m$ in diameter, performed stochastic motions of the order of $10^{-5} m$. Even though Brown could not explain the cause of this motion any continuous stochastic process like that of a pollen is now referred to as Brownian dynamics.

In this chapter we introduce a numerical technique that generates a solution of the Fokker-Planck equation (5.1) by simulating an ensemble of stochastic processes. Due to these stochastic processes one calls this numerical method Brownian dynamics as well.

We provide two derivations of the numerical method of Brownian dynamics. In the first section we transform the Fokker-Planck equation (5.1) into a multi-dimensional integral. We then explain in the second section how to evaluate this multi-dimensional integral using the Monte Carlo integration method introduced in the previous chapter. We show in the third section that this Monte Carlo integration is equivalent to simulating an ensemble of stochastic processes. The equivalence is shown by deriving the Brownian dynamics method a second time starting with the stochastic differential equation (5.2). We exemplify the idea of Brownian dynamics by applying it to a free diffusion model in the fourth section and conclude this chapter in the fifth section by showing how to incorporate boundary conditions in Brownian dynamics.

6.1 Discretization of Time

Discretization is the basis of many numerical procedures. This also holds true for Brownian dynamics. The object of discretization is the continuous time axis. A computer can not represent a continuous line or function. The infinitely many points would simply not fit into a finite digital computer nor could they be processed in a finite amount of time. Hence, one needs to approximate a continuous dimension with a finite set of points. This approximation is called discretization.
We solve the Fokker-Planck equation numerically by breaking the time axes parameterized by \( t \) into discrete points labeled by \( t_0, t_1, t_2, \ldots \). These time points do not need to be equally spaced, but they usually are to simplify the calculations.

One now has to adapt the Fokker-Planck equation (2.148) to the discretized time axis. For the sake of simplicity we consider the one-dimensional version

$$\partial_t p(x,t|x_0,t_0) = -\partial_x A(x,t) p(x,t|x_0,t_0) + \frac{1}{2} \partial^2_x B^2(x,t) p(x,t|x_0,t_0). \quad (6.1)$$

Let \( p(x,t|x_0,t_0) \) be the, yet unknown, solution of (6.1) for the initial condition \( x(t_0) = x_0 \). One finds a solution \( p(x,t|x_0,t_0) \) on a discrete sequence of times \( \{t_0,t_1,t_2,\ldots\} \) by constructing transition probabilities \( p(x_{i+1},t_{i+1}|x_i,t_i) \) from one discrete time point \( t_i \) to the next. With these transition probabilities one can reassemble the complete solution \( p(x,t|x_0,t_0) \).

We need to first disassemble the time evolution of \( p(x,t|x_0,t_0) \) into many small time increments. For this purpose we proceed as follows. To obtain a solution \( p(x_2,t_2|x_0,t_0) \) with an initial starting position at \( x(t_0) = x_0 \) one can first solve for \( p(x_1,t_1|x_0,t_0) \) which describes the solution for an intermediate state at some time \( t_1 \) prior to \( t_2 \) and after \( t_0 \). The probability distribution at time \( t_1 \) may then be taken as the initial condition for a second solution of (6.1) reaching from time \( t_1 \) to time \( t_2 \). This second solution can be assembled due to the linearity of (6.1) using \( p(x_2,t_2|x_1,t_1) \) for the initial condition \( x(t_1) = x_1 \). Summing \( p(x_2,t_2|x_1,t_1) \) over all possible initial positions \( x_1 \) in the domain \( \Omega \) weighted with the initial probability determined through \( p(x_1,t_1|x_0,t_0) \) one obtains \( p(x_2,t_2|x_0,t_0) \) and the Chapman-Kolmogorov equation

$$p(x_2,t_2|x_0,t_0) = \int_{\Omega} dx_1 p(x_2,t_2|x_1,t_1) p(x_1,t_1|x_0,t_0). \quad (6.2)$$

This is the Chapman-Kolmogorov equation encountered already above [c.f. (9.17)]. The process of dividing the evolution in the interval \([t_0,t_2]\) into consecutive evolution in the intervals \([t_0,t_1]\) and \([t_1,t_2]\) can be repeated. For this purpose one starts from (6.2), replaces variables \( x_2 \) and \( t_2 \) with \( x_3 \) and \( t_3 \), and applies (6.2) to \( p(x_3,t_3|x_1,t_1) \) while naming the intermediate state \( x_2 \) and \( t_2 \). One derives

$$p(x_3,t_3|x_0,t_0) = \int_{\Omega} dx_1 p(x_3,t_3|x_1,t_1) p(x_1,t_1|x_0,t_0)$$

$$= \int_{\Omega} dx_1 dx_2 p(x_3,t_3|x_2,t_2) p(x_2,t_2|x_1,t_1) p(x_1,t_1|x_0,t_0). \quad (6.3)$$

These steps may be repeated again. Doing so \((N-1)\) times one obtains

$$p(x_N,t_N|x_0,t_0) = \int_{\Omega} \cdots \int_{\Omega} \left( \prod_{i=1}^{N-1} dx_i p(x_{i+1},t_{i+1}|x_i,t_i) \right) p(x_1,t_1|x_0,t_0). \quad (6.4)$$

The procedure above has divided now the time evolution of \( p(x_N,t_N|x_0,t_0) \) into \( N \) steps over time intervals \([t_{i+1},t_i]\) where \( t_i, \ i = 1, 2, \ldots, N-1 \) denotes the intermediate times. We will identify below \( t \) and \( t_N \). In order to evaluate \( p(x_N,t_N|x_0,t_0) \) we need to determine the transition probabilities \( p(x_{i+1},t_{i+1}|x_i,t_i) \). The respective algorithm can exploit the possibility that one can choose the time intervals \([t_{i+1},t_i]\) very short such that certain approximations can be evoked without undue errors. In fact, for equally spaced time points \( t_i \) the length of each time segment is \( \Delta t = (t_i - t_{i-1}) = (t - t_0)/N \). One can choose \( N \) always large enough that the time period \( \Delta t \) is short enough to justify the approximations introduced below.
Let $\Delta x$ be the typical distance that a particle governed by the probability distribution $p(x, t_0 + \Delta t | x_0, t_0)$ may cover due to drift and diffusion within a time period $\Delta t$, i.e.

$$\Delta x = \left| \langle x \rangle \right| + \sqrt{\langle x^2 \rangle} \sim |A(x_0, t_0)| \Delta t + B(x_0, t_0) \sqrt{\Delta t}.$$  \hspace{1cm} (6.5)

The approximation introduced assumes that $A(x, t)$ and $B(x, t)$ are constant for each time period $[t_i, t_{i+1}]$ and spatially independent in each range $[x_i - \Delta x, x_i + \Delta x]$,

$$A(t \in [t_i, t_{i+1}], x \in [x_i - \Delta x, x_i + \Delta x]) \sim A(t_i, x_i)$$ \hspace{1cm} (6.6)

$$B(t \in [t_i, t_{i+1}], x \in [x_i - \Delta x, x_i + \Delta x]) \sim B(t_i, x_i),$$ \hspace{1cm} (6.7)

One replaces than the functions $p(x_{i+1}, t_{i+1}|x_i, t_i)$ in (6.4) by solutions of the Fokker-Planck equation (6.1) with constant coefficients $A(x, t)$ and $B(x, t)$. In case of boundary conditions at $x \to \pm \infty$ the resulting expression is, according to (4.28, 4.39)

$$p(x_{i+1}, t_{i+1}|x_i, t_i) = \frac{1}{\sqrt{2\pi B^2(x_i, t_i)(t_{i+1} - t_i)}} \exp\left(-\frac{(x_{i+1} - x_i - A(x_i, t_i)(t_{i+1} - t_i))^2}{2 B^2(x_i, t_i)(t_{i+1} - t_i)}\right).$$ \hspace{1cm} (6.8)

We will consider solutions for other boundary conditions on page 100 further below.

Employing (6.8) in the iterated form of the Chapman-Kolmogorov equation (6.4), one derives

$$p(x, t|x_0, t_0) = \int \cdots \int_{\Omega} \left(\prod_{i=1}^{N-1} dx_i\right)^{N-1} \frac{1}{\sqrt{2\pi B^2(x_i, t_i) \Delta t}} \exp\left(-\frac{(x_{i+1} - x_i - A(x_i, t_i) \Delta t)^2}{2 B^2(x_i, t_i) \Delta t}\right).$$ \hspace{1cm} (6.9)

Thus, we have solved the Fokker-Planck equation (6.1) up to an $N$-dimensional integral. This integral needs to be evaluated numerically for which purpose one applies the Monte Carlo integration method.

### 6.2 Monte Carlo Integration of Stochastic Processes

The integral on the r.h.s. of (6.4) and (6.9) is a truly high-dimensional integral. The Monte Carlo method is therefore the appropriate integration method.

Before we apply the Monte Carlo method we modify equation (6.4) slightly. The probability distribution $p(x, t|x_0, t_0)$ is not always what one wants to determine. A more feasible construct is the average $\bar{q}(t|x_0, t_0)$ of an arbitrary observable $Q$ with a sensitivity function $q(x)$ in state space $\Omega$ given by the integral

$$\bar{q}(t|x_0, t_0) = \int_{\Omega} dx \ q(x) \ p(x, t|x_0, t_0).$$ \hspace{1cm} (6.10)

Equation (6.10) is very comprehensive. Even the probability distribution $p(\tilde{x}, t|x_0, t_0)$ can be viewed as an observable $Q$, namely, for the sensitivity function $q_{\tilde{x}}(x) = \delta(x - \tilde{x})$. 

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We now apply the Monte Carlo integration method as stated in equation (5.26) to the expanded form of (6.10)

\[
\bar{q}(t|x_0, t_0) = \int_\Omega dx \ q(x) \times \prod_{i=1}^{N-1} dx_i \ p(x_{i+1}, t_{i+1}|x_i, t_i) \ p(x_1, t_1|x_0, t_0).
\]

(6.11)

One can associate \( q(x) \) with \( f(x) \) and the product of \( p(x_{i+1}, t_{i+1}|x_i, t_i) \) with \( p(x) \). The only problem now is finding a random number generator that produces random numbers \( \bar{r} \) with a distribution equivalent to the product of all \( p(x_{i+1}, t_{i+1}|x_i, t_i) \). This seems to be an impossible endeavor unless one recalls how the product of all the \( p(x_{i+1}, t_{i+1}|x_i, t_i) \) came about.

Let us start with the case \( N = 0 \). Given a random number generator that produces numbers \( \bar{r}(x_0, t_0) \) with a distribution \( p(x, t|x_0, t_0) \) the solution is

\[
\bar{q}(t|x_0, t_0) = \int_\Omega dx \ q(x) \ p(x, t|x_0, t_0) \\
\sim \frac{1}{M} \sum_{k=1}^{M} q(\bar{r}_k(x_0, t_0)).
\]

(6.12)

We denote the \( x_0 \) and \( t_0 \)-dependence of the random numbers \( \bar{r}_k(x_0, t_0) \) explicitly for later use. The reader should note that \( \bar{r}_k(x_0, t_0) \) exhibits a distribution \( p(x, t|x_0, t_0) \) around \( x_0 \).

Implementing the Chapman-Kolmogorov equation (6.2) for \( p(x, t|x_0, t_0) \) once we obtain the case \( N = 1 \) and two nested integrals.

\[
\bar{q}(t|x_0, t_0) = \int_\Omega dx \ q(x) \int_\Omega dx_1 \ p(x, t|x_1, t_1) p(x_1, t_1|x_0, t_0).
\]

(6.13)

To approximate (6.13) numerically one determines first the inner integral with the integration variable \( x_1 \). The Monte Carlo method yields

\[
\bar{q}(t|x_0, t_0) \sim \int_\Omega dx \ q(x) \frac{1}{M} \sum_{k_0=1}^{M} p(x, t|\bar{r}_{k_0}(x_0, t_0), t_1).
\]

(6.14)

In a second step one applies applies the Monte Carlo method to the outer integral, now however with a probability distribution \( p(x, t|\bar{r}_{k_0}(x_0, t_0), t_1) \) exhibiting the initial starting point \( \bar{r}_{k_1}(x_0, t_0) \).

We therefore use the random numbers \( \bar{r}_{k_1}(\bar{r}_{k_0}(x_0, t_0), t_1) \).

\[
\bar{q}(t|x_0, t_0) \sim \frac{1}{M^2} \sum_{k_1=1}^{M} \sum_{k_0=1}^{M} q(\bar{r}_{k_1}(\bar{r}_{k_0}(x_0, t_0), t_1)).
\]

(6.15)

Note the nesting of random numbers \( \bar{r}_{k_1}(\bar{r}_{k_0}(x_0, t_0), t_1) \). The Gaussian random number \( \bar{r}_{k_1}(\ldots) \) is distributed around the previous random number \( \bar{r}_{k_0}(\ldots) \) which itself is distributed around \( x_0 \).

Performing the above steps \( N \) times, thus iterating the Chapman-Kolmogorov equation (6.9), one
obtains
\[
q(t|x_0, t_0) = \int q(x) \prod_{i=1}^{N-1} p(x_{i+1}, t_{i+1}|x_i, t_i) p(x_1, t_1|x_0, t_0)
\]
\[
\sim \frac{1}{M^N} \sum_{k_0=1}^{M} \sum_{k_1=1}^{M} \cdots \sum_{k_N=1}^{M} q(\tilde{r}_{k_N}(\cdots \tilde{r}_{k_1}(\tilde{r}_{k_0}(x_0, t_0), t_1)\cdots, t_N)) ,
\tag{6.16}
\]
where the random numbers \(\tilde{r}_{k_j}(x_j, t_j)\) should exhibit the probability distributions
\[
p(\tilde{r}_{k_j}(x_j, t_j)) = p(x_{j+1}t_{j+1}|x_j, t_j) .
\tag{6.17}
\]

The iteration above simplifies the problem of finding an appropriate random number generator. We now need random numbers that simply obey (6.17). In the specific case (6.8) one can generate the appropriate random numbers \(\tilde{r}_k(x_0, t_0)\) utilizing a Gaussian number generator as described in the previous chapter. If \(\tilde{r}_k\) is a random number with the normalized Gaussian probability distribution \(\exp(-r^2/2)/\sqrt{2\pi} dr\) one obtains \(\tilde{r}_k(x_0, t_0)\) with the mapping
\[
\tilde{r}_k(x_0, t_0) = B(x_0, t_0) \sqrt{t-t_0} r_k + A(x_0, t_0) (t-t_0) + x_0 .
\tag{6.18}
\]

With the help of (5.18) one can verify
\[
p(\tilde{r}(x_0, t_0)) = \frac{1}{\sqrt{2\pi} B^2(x_0, t_0)(t-t_0)} \exp\left(-\frac{(\tilde{r}(x_0, t_0) - x_0 - A(x_0, t_0) (t-t_0))^2}{2 B^2(x_0, t_0)(t-t_0)}\right) .
\tag{6.19}
\]

Thus, we finally have all the ingredients to perform the Monte Carlo integration (6.16). However, before putting (6.16) to use we can simplify the summations. The nesting of random numbers \(\tilde{r}_{k_N}(\cdots \tilde{r}_{k_1}(\tilde{r}_{k_0}(x_0, t_0), t_1)\cdots, t_N)\) is in effect a random walk starting at \(x_0\) and proceeding with Gaussian random steps \(\tilde{r}_k\). With the summations in (6.16) one takes the average over all random walks that can be formed with a given set of \(M\) random steps \(\tilde{r}_k\) for \(i = 1, \ldots, N\). One can simplify this equation by summing over \(M^N\) independent random pathes \(\tilde{r}_{i_N}(\cdots \tilde{r}_{i_1}(\tilde{r}_{i_0}(x_0, t_0), t_1)\cdots, t_N)\) instead. Equation (6.16) becomes
\[
q(t|x_0, t_0) \sim \frac{1}{M^N} \sum_{l=1}^{M^N} q(\tilde{r}_{l_N}(\cdots \tilde{r}_{l_1}(\tilde{r}_{l_0}(x_0, t_0), t_1)\cdots, t_N)) .
\tag{6.20}
\]

## 6.3 Ito Calculus and Brownian Dynamics

Before applying Brownian dynamics in the form of equation (6.20) we want to shed light on the close relation between the Monte Carlo integration introduced above and the concept of stochastic processes as described in chapter 2.

Equation (6.20) describes the algorithm of Brownian dynamics. In essence one simulates the random walk of a given number of Brownian particles and samples their final position in state space \(\Omega\). To demonstrate this we return to chapter 2. Within the framework of Ito calculus we consider the stochastic differential equation (2.138) that corresponds to the Fokker-Planck equation (6.1)
\[
\frac{\partial}{\partial t} x(t) = A(x(t), t) + B(x(t), t) \eta(t) .
\tag{6.21}
\]
The corresponding Ito-formula (2.137) is

\[
df[x(t)] = A(x(t), t) \left( \partial_x f[x(t)] \right) dt + B(x(t), t) \left( \partial_x^2 f[x(t)] \right) d\omega(t) \\
+ \frac{1}{2} B^2(x(t), t) \left( \partial_x^2 f[x(t)] \right) dt.
\] (6.22)

Assume \( f[x(t)] = x(t) \). We thus derive for \( x(t) \)

\[
dx(t) = A(x(t), t) dt + B(x(t), t) d\omega(t). \] (6.23)

Integrating (6.23) over small time periods \( \Delta t \) for which we can assume \( A(x(t), t) \) and \( B(x(t), t) \) to be constant, we obtain the finite difference equation

\[
x(t + \Delta t) - x(t) = A(x(t), t) \Delta t + B(x(t), t) \Delta \omega,
\] (6.24)

with \( \Delta \omega \) being a random variable with the Gaussian probability distribution (2.48) for \( D = 1/2 \). Such a random variable can be generated with a normalized Gaussian random number \( r \) and the mapping \( \Delta \omega = \sqrt{\Delta t} \, r \)

\[
x(t + \Delta t) - x(t) = A(x(t), t) \Delta t + B(x(t), t) \sqrt{\Delta t} \, r.
\] (6.25)

Note, that \( x(t + \Delta t) - x(t) \) in (6.25) is the same as \( \tilde{r}(x_0, t) - x_0 \) defined in (6.18). Iterating equation (6.25) and thus numerically integrating the stochastic differential equation (6.21) according to Ito calculus, we generate a sample path \( x(t) \) starting at any given \( x(t_0) = x_0 \). Such a sample path can then be used in the Monte Carlo procedure (6.20).

### 6.4 Free Diffusion

We now test the numerical Brownian dynamics procedure outlined above. For this purpose we resort to examples that can be solved analytically.

We begin with free diffusion in an infinite domain. The Fokker Planck equation, i.e., the respectively Einstein diffusion equation, is

\[
\partial_t p(x, t | x_0, t_0) = D \partial_x^2 p(x, t | x_0, t_0).
\] (6.26)

Comparing (6.26) and (6.1) one finds the drift coefficient \( A(x, t) \) to be zero and the noise coupling coefficient \( B(x, t) = \sqrt{2D} \) to be constant in time and space. Thus, assumptions (6.6) and (6.7) are met for any time step size \( \Delta t = t_{i+1} - t_i \). Due to this fact one could choose \( \Delta t = t - t_0 \) and obtain with (6.8) the final result right away, thereby, rendering the following numerical simulation, employing a division into many short time intervals, unnecessary. Since we intend to verify the numerical approach we choose a division into \( N \) intermediate time steps nevertheless. These intermediate steps will become necessary when considering a potential and consequently a spatially dependent \( A(x, t) \) further below.

One can proceed in a straightforward manner. Starting with Gaussian random numbers \( r_k \) as generated in (5.23) one derives the required random numbers \( \tilde{r}_k(x, t) \) according to (6.18).

\[
\tilde{r}_k(x, t) = \sqrt{2D\Delta t} \, r_k + x.
\] (6.27)

These random numbers \( \tilde{r}_k(x, t) \) exhibit the probability distribution

\[
p(\tilde{r}(x, t)) = \frac{1}{\sqrt{4\pi D\Delta t}} \exp\left(-\frac{(\tilde{r}(x, t) - x)^2}{4D\Delta t}\right). \] (6.28)
as shown in (6.19). To determine the endpoint \( x(t) \) of a sample path of free diffusion one creates a chain of random numbers, i.e., a random walk,

\[
x(t = t_N) = \tilde{r}_N(\ldots \tilde{r}_1(\tilde{r}_0(x_0, t_0), t_1)\ldots , t_N)
= \sqrt{2D\Delta t} \sum_{k=1}^{N} r_k .
\]  

(6.29)

Figure 6.1 displays an ensemble of 1000 such paths, each path being \( N = 100 \) steps long. The trajectories start at \( x = 0 \) and proceed towards the rear, as indicated by the time axis. \( D = 1 \) defines the relation between temporal and spatial units. Ten paths are displayed in black to examplify the behavior of single random walks. The other 990 paths are shown as a grey background. Note the parabolic shape of the trajectory distribution in time. This property, the broadening of the standard deviation of the trajectory distribution proportional to \( \sqrt{t} \) was derived in (2.51). In the rear of the figure is a bin count of all trajectory locations at \( t = 1 \). The solid line imposed on the bar chart represents the theoretical solution according to equation (6.28) with \( \Delta t = t - t_0 \).

The paths of (6.29) can be used to determine the expectation value \( \langle q(t|x_0, t_0) \rangle \) of an observable \( Q \) at time \( t = t_N \) as described in (6.10) and (6.20). Obviously such a sampling of an observable value can only be done with a finite ensemble of trajectories. A statistical error in the result is inevitable. Hence the question: how large is the statistical error?

Assume we know the probability \( p(x, t|x_0, t_0) \). The exact expectation value \( \langle q(t|x_0, t_0) \rangle \) is then given by

\[
\langle q(t|x_0, t_0) \rangle = \int_\Omega dx \ q(x) \ p(x, t|x_0, t_0) .
\]  

(6.30)
One can rewrite (6.30) in terms of a probability distribution \( \tilde{p}(q,t|x_0,t_0) \) that does not depend on \( x \) but on the observable value \( q \).

\[
\langle q(t|x_0,t_0) \rangle = \int_{\Omega} dq \frac{\partial x(q)}{\partial q} p(x(q),t|x_0,t_0) \tilde{p}(q,t|x_0,t_0) .
\] (6.31)

With respect to \( \tilde{p}(q,t|x_0,t_0) \) we can then express the exact average (6.31) and the variance of the observable value \( q(t|x_0,t_0) \) in terms of cumulants.

\[
\langle q(t|x_0,t_0) \rangle = \langle \langle q(t|x_0,t_0) \rangle \rangle ,
\] (6.32)

\[
\langle (q(t|x_0,t_0) - \langle q(t|x_0,t_0) \rangle)^2 \rangle = \langle q^2(t|x_0,t_0) \rangle .
\] (6.33)

The variance (6.33) is the variance of single sample readings of an observable \( Q \). Equation (6.33) does not apply to an expectation value \( \bar{q}(t|x_0,t_0) \), which is the average of an ensemble of samples. Nevertheless, denoting the outcome of an \( i \)-th reading by \( q^{(i)}(t|x_0,t_0) \) one can express the expectation value according to (6.20)

\[
\bar{q}(t|x_0,t_0) = \frac{1}{M} \sum_{i=1}^{M} q^{(i)}(t|x_0,t_0) .
\] (6.34)

The second order cumulant of (6.34) renders

\[
\langle \langle q^2(t|x_0,t_0) \rangle \rangle = \langle \left( \frac{1}{M} \sum_{i=1}^{M} q^{(i)}(t|x_0,t_0) \right)^2 \rangle
\]

\[
= \frac{1}{M^2} \langle \left( \sum_{i=1}^{M} q^{(i)}(t|x_0,t_0) \right)^2 \rangle .
\] (6.35)

Since every \( q^{(i)}(t|x_0,t_0) \) stems from an independent trajectory sample one can apply (2.44) and we can write

\[
\langle \langle q^2(t|x_0,t_0) \rangle \rangle = \frac{1}{M^2} \sum_{i=1}^{M} \langle \left( q^{(i)}(t|x_0,t_0) \right)^2 \rangle .
\] (6.36)

Every sample \( q^{(i)}(t|x_0,t_0) \) should also exhibit the same variance (6.33) so that we finally obtain

\[
\langle \langle q^2(t|x_0,t_0) \rangle \rangle = \frac{1}{M^2} \sum_{i=1}^{M} \langle q^2(t|x_0,t_0) \rangle
\]

\[
= \frac{1}{M} \langle q^2(t|x_0,t_0) \rangle .
\] (6.37)

Hence, the variance of the average of \( M \) samples is about \( 1/M \) times smaller than the variance of a single sample. Consequently the standard deviation of the expectation value decreases with \( 1/\sqrt{M} \).

To finally determine the statistical error of an expectation value \( \bar{q}(t|x_0,t_0) \) given by the standard deviation \( \sqrt{\langle \langle q^2(t|x_0,t_0) \rangle \rangle} \) one has to provide a value for the cumulant \( \langle \langle q^2(t|x_0,t_0) \rangle \rangle \) in (6.37). An
estimate for the upper limit of this variance is sufficient in most cases. One can provide an estimate either with the help of some analytical approximation or by simply determining the variance of an ensemble of $\tilde{M}$ samples $q^{(i)}(t|x_0, t_0)$ according to

$$\left\langle q^2(t|x_0, t_0) \right\rangle \approx \frac{1}{\tilde{M} - 1} \sum_{i=1}^{\tilde{M}} \left( q^{(i)}(t|x_0, t_0) - \bar{q}(t|x_0, t_0) \right)^2. \tag{6.38}$$

To examplify the tools just introduced we will consider a bin count. For a bin count one measures the probability $q_{[a,b]}$ to find a trajectory end point within a given interval $[a, b]$, called bin. The sensitivity function $q(x)$ for a single bin reaching from $a$ to $b$ is $q_{[a,b]}(x) = \Theta(x - a) - \Theta(x - b)^1$. One can determine the expectation value $\bar{q}_{[a,b]}(t|x_0, t_0)$ with the help of (6.15), (6.20) and (6.29)

$$\bar{q}_{[a,b]}(t|x_0, t_0) = \int_{\Omega} dx \, q_{[a,b]}(x) \, p(x, t|x_0, t_0) \approx \frac{1}{\tilde{M}} \sum_{l=1}^{\tilde{M}} q_{[a,b]} \left( \sqrt{2D \Delta t} \sum_{k_l=1}^{N} r_{k_l} \right). \tag{6.39}$$

Performing calculation (6.39) for an array of adjacent bins one can approximate a probability density within a bin increases as the bin size decreases. Thus, one has to balance these two objectives as we will do in the following calculation. One thereby obtains an estimate for the probability density between $a$ and $b$

$$p(x \in [a, b], t|x_0, t_0) \approx \frac{\bar{q}_{[a,b]}(t|x_0, t_0)}{|b - a|}. \tag{6.40}$$

How much confidence can we have in a probability density distribution determined through (6.40)? There are two precision objectives to consider. First, one would like to have a sufficient spatial resolution. The bin size should be smaller than the spatial features of the probability distribution $p(x, t|x_0, t_0)$. This can be achieved by implementing a grid with many tiny bins; the smaller the bin, the better. This however is counteracting the second objective. The statistical error of a probability density within a bin increases as the bin size decreases. Thus, one has to balance these two objectives as we will do in the following calculation.

We will focus our attention on a bin $[a, b]$. The spatial resolution $res_s$ of a bin count based on bins like $[a, b]$ is given by the bin size in relation to the relevant diffusion domain $\Omega$

$$res_s = \frac{|a - b|}{|\Omega|}. \tag{6.41}$$

One can define a resolution of the probability density $res_p$ in a similar fashion. Let $\Delta \bar{p}_{[a,b]}(t|x_0, t_0)$ be the standard deviation of the probability density in bin $[a, b]$. One can view this standard deviation $\Delta \bar{p}_{[a,b]}(t|x_0, t_0)$ as the analog to the bin size $|a - b|$. The relation between the standard deviation $\Delta \bar{p}_{[a,b]}(t|x_0, t_0)$ and the size $|p(\Omega)|$ of the overall range of probability density values in a distribution would then define the resolution $res_p$. Hence

$$res_p = \frac{\Delta \bar{p}_{[a,b]}(t|x_0, t_0)}{|p(\Omega)|}. \tag{6.42}$$

\[^1\Theta(x)\] represents Heaviside’s step function: $\Theta(x) = 0$ for $x < 0$, and $\Theta(x) = 1$ for $x > 0$. 

Preliminary version March 28, 2000
To optimize a bin count one has to balance the resolutions \( \text{res}_s \) and \( \text{res}_p \). We thus assume
\[
\text{res}_s \approx \text{res}_p . \tag{6.43}
\]

Out of this equation we can derive the sample number \( M \) needed to achieve the desired precision goal.

The sample number \( M \) enters equation (6.43) via (6.42) and \( \Delta \bar{p}_{[a,b]}(t|x_0, t_0) \). Starting with (6.40) one can derive
\[
\Delta \bar{p}_{[a,b]}(t|x_0, t_0) = \sqrt{\frac{\left\langle p^2_{[a,b]}(t|x_0, t_0) \right\rangle}{M}}
\]
\[
= \sqrt{\frac{\left\langle q^2_{[a,b]}(t|x_0, t_0) \right\rangle}{M |a - b|^2}} . \tag{6.44}
\]

\( \left\langle q^2_{[a,b]}(t|x_0, t_0) \right\rangle \) can be approximated assuming \( \left\langle q_{[a,b]}(t|x_0, t_0) \right\rangle \) to be equal \( \bar{q}_{[a,b]}(t|x_0, t_0) \).

Inserting (6.48) back into (6.44) one obtains
\[
\Delta \hat{p}_{[a,b]}(t|x_0, t_0) = \sqrt{\frac{\bar{q}_{[a,b]}(t|x_0, t_0) \left( 1 - \bar{q}_{[a,b]}(t|x_0, t_0) \right)}{M |a - b|^2}} . \tag{6.49}
\]

Implementing (6.49) in (6.42) and (6.43) and solving for \( M \) we derive
\[
M = \bar{q}_{[a,b]}(t|x_0, t_0) \left( 1 - \bar{q}_{[a,b]}(t|x_0, t_0) \right) \left( \frac{|\Omega|}{|a - b|^2 |p(\Omega)|} \right)^2 . \tag{6.50}
\]

One can use equation (6.50) to estimate the number of particles needed in a Brownian dynamics simulation when creating probability distributions via a bin count. In Figure 6.1 we had to consider the parameters \( |\Omega| = 6 \), \( \Delta x = 0.3 \), \( |p(\Omega)| = 0.4 \) and \( \bar{q}_{[a,b]} = \Delta x \bar{p}_{[a,b]} \approx 0.04 \). With these numbers equation (6.50) renders \( M = 1067 \) which is roughly the number of trajectories used in our example. Unfortunately many interesting simulations require much larger \( M \) and thus tremendous computational resources.

### 6.5 Reflective Boundary Conditions

So far in this chapter we have considered solely Brownian dynamics with boundaries at \( x \to \pm \infty \). We now seek to account for the existence of reflective boundaries at finite positions in the diffusion domain. For the purpose of a numerical Brownian dynamics description we divide
again the evolution of the probability function into many small time intervals, assuming that the corresponding $\Delta x$ and $\Delta t$ values are small such that conditions (6.6) and (6.7) are satisfied. Furthermore we now assume, that the average spatial increment $\Delta x$ of a simulated trajectory is minute compared to the spatial geometry of the diffusion domain and its reflective boundary. In this case a stochastic trajectory will most likely encounter not more than a single boundary segment at a time. Furthermore, we approximate these boundary segments by planes, which is appropriate as long as the curvature of the boundary is small in comparison to $\Delta x$. Under all these conditions one can again provide an approximate analytical solution $p(x, t_0 + \Delta t| x_0, t_0)$ for a single simulation step. One can then use this solution to construct an adequate numerical simulation over longer time intervals.

As stated, we assume reflective boundaries governed by the boundary condition (4.24)

$$\hat{a}(x) \cdot J p(x, t|x_0, t_0) = 0, \quad x \text{ on } \partial \Omega, \quad (6.51)$$

where $\hat{a}(x)$ denotes the normalized surface vector of the planar boundary segment. One derives an analytical solution for $p(x, t|x_0, t_0)$ in the present case by emulating a mirror image of a diffusing particle behind the planar boundary segment so that the flow of particles and the flow of mirror particles through the boundary segment cancel each other to satisfy (6.51). This is established through the probability

$$p(x, t_0 + \Delta t|x_0, t_0) = \left( \frac{1}{\sqrt{2\pi} [B^T B](x_0, t_0) \Delta t} \right)^n \exp \left[ -\frac{(x - x_0 - A(x_0, t_0) \Delta t)^2}{2 [B^T B](x_0, t_0) \Delta t} \right] + \left( \frac{1}{\sqrt{2\pi} [B^T B](x_0, t_0) \Delta t} \right)^n \exp \left[ -\frac{(x - R_{\partial \Omega}[x_0] + A(x_0, t_0) \Delta t)^2}{2 [B^T B](x_0, t_0) \Delta t} \right].$$

$R_{\partial \Omega}$ denotes the operation of reflection at the boundary plane $\partial \Omega$. To perform the reflection operation $R_{\partial \Omega}$ explicitly one splits every position vector $x$ into two components, one parallel $x_\parallel$ and one orthogonal $x_\perp$ to the planar boundary $\partial \Omega$. If $b \in \partial \Omega$ one can express the operation of reflection as

$$x_\parallel \xrightarrow{R_{\partial \Omega}} x_\parallel$$

$$x_\perp \xrightarrow{R_{\partial \Omega}} 2 b_\perp - x_\perp. \quad (6.53)$$

With this notation one can write boundary condition (6.51) as

$$\left( \frac{[B^T B]}{2} \right) \partial_{x_\perp} p(x, t | x_0, t_0) \bigg|_{x \in \partial \Omega} = 0.$$

and one can easily verify that equation (6.52)

$$p(x, t|x_0, t_0) = \left( \frac{1}{\sqrt{2\pi} [B^T B](x_0, t_0) \Delta t} \right)^n \exp \left[ -\frac{(x - x_0)^2}{4 D \Delta t} \right] + \exp \left[ -\frac{(x_\parallel - x_0)^2 + (x_\perp + x_\perp - 2 b_\perp)^2}{2 [B^T B](x_0, t_0) \Delta t} \right].$$

is a solution of the diffusion equation which obeys (6.55).
The function on the r.h.s. of (6.56) describes a Wiener process which is modified, in that the
endpoint of the Gaussian distribution which reaches across the boundary $\partial \Omega$ is ‘reflected’ back into
the domain $\Omega$. The modified Wiener process is therefore defined as follows

$$x(t + \Delta t) = \begin{cases} 
  x(t) + \sqrt{2D\Delta t} r(t) & \text{, if } x(t) + \sqrt{2D\Delta t} r(t) \in \Omega \\
  R_{\partial \Omega}[x(t) + \sqrt{2D\Delta t} r(t)] & \text{, if } x(t) + \sqrt{2D\Delta t} r(t) \notin \Omega
\end{cases} \quad (6.57)$$

Whenever $x(t + \Delta t)$ reaches outside the domain $\Omega$ the actual value of the coordinate $x(t + \Delta t)$ is
readjusted according to the rules set by Eq. (6.57).