Chapter 14
Random Walk and Brownian Motion

Random walk processes are an important class of stochastic processes. They have many applications in physics, computer science, ecology, economics, and other fields. A random walk [67] *is a sequence of successive random steps. In this chapter we study Markovian* [68, 69][1] *discrete time*[2] *models. The time evolution of a system is described in terms of a N-dimensional vector* $\mathbf{r}(t)$*, which can be, for instance, the position of a molecule in a liquid or the price of a fluctuating stock. At discrete times* $t_n = n\Delta t$ *the position changes suddenly* (Fig. 14.1):

$$\mathbf{r}(t_{n+1}) = \mathbf{r}(t_n) + \Delta\mathbf{r}_n, \tag{14.1}$$

where the steps are distributed according to the probability distribution[3]

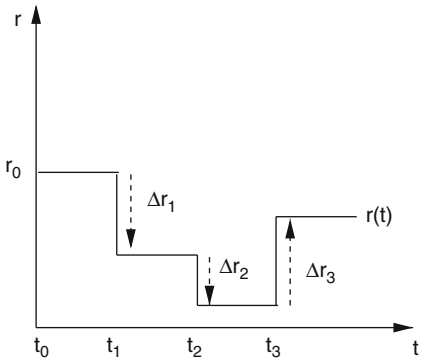

Fig. 14.1 Discrete time random walk

[1] Different steps are independent.

[2] A special case of the more general continuous time random walk with a waiting time distribution of $P(\tau) = \delta(\tau - \Delta t)$.

[3] General random walk processes are characterized by a distribution function $P(\mathbf{R}, \mathbf{R}')$. Here we consider only correlated processes for which $P(\mathbf{R}, \mathbf{R}') = P(\mathbf{R}' - \mathbf{R})$.

P.O.J. Scherer, *Computational Physics*, DOI 10.1007/978-3-642-13990-1_14,

$$P(\Delta \mathbf{r}_n = \mathbf{b}) = f(\mathbf{b}). \tag{14.2}$$

The probability of reaching the position $\mathbf{R}$ *after* $n+1$ *steps obeys the equation*

$$\begin{aligned} P_{n+1}(\mathbf{R}) &= P\left(\mathbf{r}(t_{n+1}) = \mathbf{R}\right) \\ &= \int \mathrm{d}^N \mathbf{b}\, P_n(\mathbf{R} - \mathbf{b})\, f(\mathbf{b}). \end{aligned} \tag{14.3}$$

14.1 Random Walk in One Dimension

Consider a random walk in one dimension. We apply the central limit theorem to calculate the probability distribution of the position r_n after n steps. The first two moments and the standard deviation of the step distribution are

$$\overline{b} = \int \mathrm{d}b\, b\, f(b) \quad \overline{b^2} = \int \mathrm{d}b\, b^2\, f(b) \quad \sigma_b = \sqrt{\overline{b^2} - \overline{b}^2}. \tag{14.4}$$

Hence the normalized quantity

$$\xi_i = \frac{\Delta x_i - \overline{b}}{\sigma_b} \tag{14.5}$$

is a random variable with zero average and unit standard deviation. The distribution function of the new random variable

$$\eta_n = \frac{\xi_1 + \xi_2 + \cdots + \xi_n}{\sqrt{n}} = \frac{r_n - n\overline{b}}{\sigma_b \sqrt{n}} \tag{14.6}$$

approaches a normal distribution for large n

$$f(\eta_n) \to \frac{1}{\sqrt{2\pi}} \mathrm{e}^{-\eta_n^2/2} \tag{14.7}$$

and finally from

$$f(r_n)\mathrm{d}r_n = f(\eta_n)\mathrm{d}\eta_n = f(\eta_n)\frac{\mathrm{d}r_n}{\sigma_b\sqrt{n}}$$

we have

$$f(r_n) = \frac{1}{\sqrt{2\pi n}\sigma_b} \exp\left\{-\frac{(r_n - n\overline{b})^2}{2n\sigma_b^2}\right\}. \tag{14.8}$$

The position of the walker after n steps obeys approximately a Gaussian distribution centered at $\overline{r}_n = n\overline{b}$ with a standard deviation of (Fig. 14.2)

$$\sigma_{r_n} = \sqrt{n}\sigma_b. \tag{14.9}$$

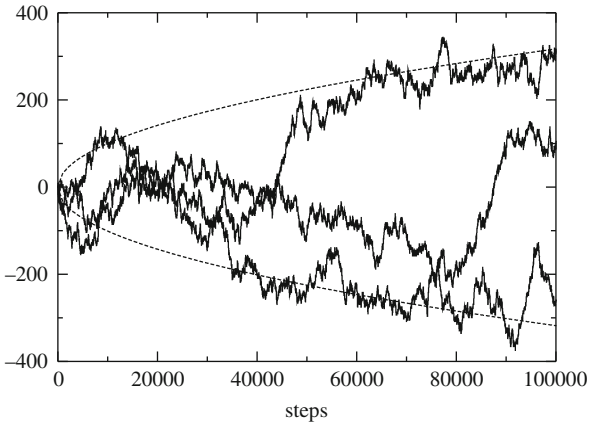

Fig. 14.2 Random walk with constant step size. The figure shows the position r_n for three different one-dimensional random walks with step size $\Delta x = \pm 1$. The *dashed curves* show the width $\pm\sigma = \pm\sqrt{n}$ of the Gaussian approximation (14.8)

14.1.1 Random Walk with Constant Step Size

In the following we consider the classical example of a one-dimensional random walk process with constant step size. At time t_n the walker takes a step of length Δx to the left with probability p or to the right with probability $q = 1 - p$ (Fig. 14.3). The corresponding step size distribution function is

$$f(b) = p\delta(b + \Delta x) + q\delta(b - \Delta x) \tag{14.10}$$

with the first two moments

$$\overline{b} = (q - p)\Delta x \quad \overline{b^2} = \Delta x^2. \tag{14.11}$$

Let the walker start at $r(t_0) = 0$. The probability $P_n(m)$ of reaching position $m\Delta x$ after n steps obeys the recursion

$$P_{n+1}(m) = pP_n(m + 1) + qP_n(m - 1) \tag{14.12}$$

which obviously leads to a binomial distribution. From the expansion of

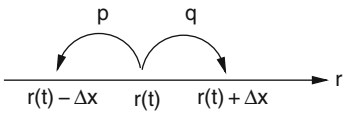

Fig. 14.3 Random walk with constant step size

$$(p+q)^n = \sum \binom{n}{m} p^m q^{n-m} \tag{14.13}$$

we see that

$$P_n(n-2m) = \binom{n}{m} p^m q^{n-m} \tag{14.14}$$

or after substitution $m' = n - 2m = -n, -n+2, \ldots n-2, n$:

$$P_n(m') = \binom{n}{(n-m')/2} p^{(n-m')/2} q^{(n+m')/2}. \tag{14.15}$$

Since the steps are uncorrelated we easily find the first two moments

$$\overline{r}_n = \sum_{i=1}^{n} \overline{\Delta x_i} = n\overline{b} = n\Delta x(q-p) \tag{14.16}$$

and

$$\overline{r_n^2} = \overline{\left(\sum_{i=1}^{n} \Delta x_i\right)^2} = \overline{\sum_{i,j=1}^{n} \Delta x_i \Delta x_j} = \sum_{i=1}^{n} \overline{(\Delta x_i)^2} = n\overline{b^2} = n\Delta x^2. \tag{14.17}$$

14.2 The Freely Jointed Chain

We consider a simple statistical model for the conformation of a biopolymer like DNA or a protein (Figs. 14.4, 14.5).

The polymer is modeled by a three-dimensional chain consisting of M units with constant bond length. The relative orientation of the segments is arbitrary. The configuration can be described by a point in a $3(M+1)$-dimensional space which is reached after M steps $\Delta\mathbf{r}_i = \mathbf{b}_i$ of a three-dimensional random walk with constant step size

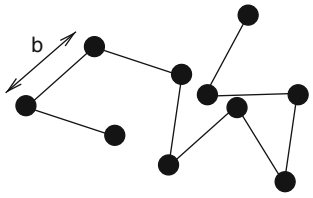

Fig. 14.4 Freely jointed chain with constant bond length b

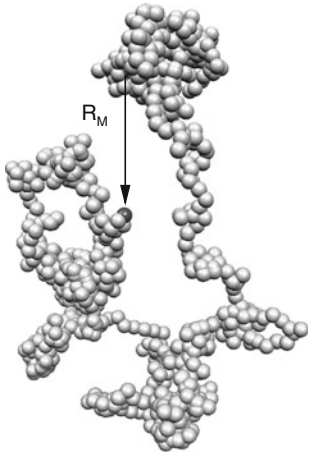

Fig. 14.5 Freely jointed chain. The figure shows a random three-dimensional structure with 1000 segments visualized as *balls* (Molekel graphics [70])

$$(\mathbf{r}_0, \mathbf{r}_1 \cdots \mathbf{r}_M) \quad \mathbf{r}_M = \mathbf{r}_0 + \sum_{i=1}^{M} \mathbf{b}_i . \tag{14.18}$$

14.2.1 Basic Statistic Properties

The M bond vectors

$$\mathbf{b}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \tag{14.19}$$

have a fixed length $|\mathbf{b}_i| = b$ and are oriented randomly. The first two moments are

$$\overline{\mathbf{b}_i} = 0 \quad \overline{\mathbf{b}_i^2} = b^2. \tag{14.20}$$

Since different units are independent

$$\overline{\mathbf{b}_i \mathbf{b}_j} = \delta_{i,j} b^2. \tag{14.21}$$

Obviously the relative position of segment j

$$\mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_0 = \sum_{i=1}^{j} \mathbf{b}_i \tag{14.22}$$

has zero mean

$$\overline{\mathbf{R}_j} = \sum_{i=1}^{j} \overline{\mathbf{b}_i} = 0 \tag{14.23}$$

and its second moment is

$$\overline{R_j^2} = \overline{\left(\sum_{i=1}^{j} \mathbf{b}_i \sum_{k=1}^{j} \mathbf{b}_k\right)} = \sum_{i,k=1}^{j} \overline{\mathbf{b}_i \mathbf{b}_k} = jb^2. \tag{14.24}$$

For the end to end distance

$$\mathbf{R}_M = \mathbf{r}_M - \mathbf{r}_0 = \sum_{i=1}^{M} \mathbf{b}_i \tag{14.25}$$

this gives

$$\overline{\mathbf{R}}_M = 0, \quad \overline{R_M^2} = Mb^2. \tag{14.26}$$

Let us apply the central limit theorem for large M. For the x-coordinate of the end to end vector we have

$$X = \sum_{i=1}^{M} \mathbf{b}_i \mathbf{e}_x = b \sum_i \cos\theta_i. \tag{14.27}$$

With the help of the averages[4]

$$\overline{\cos\theta_i} = \frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \cos\theta \, \sin\theta \mathrm{d}\theta = 0 \tag{14.28}$$

$$\overline{(\cos\theta_i)^2} = \frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \cos^2\theta \, \sin\theta \mathrm{d}\theta = \frac{1}{3} \tag{14.29}$$

we find that the scaled difference

$$\xi_i = \sqrt{3} \cos\theta_i \tag{14.30}$$

has zero mean and unit variance and therefore the sum

$$\widetilde{X} = \frac{\sqrt{3}}{b\sqrt{M}} X = \sqrt{\frac{3}{M}} \sum_{i=1}^{M} \cos\theta_i \tag{14.31}$$

converges to a normal distribution:

[4] For a one-dimensional polymer $\overline{\cos\theta_i} = 0$ and $\overline{(\cos\theta_i)^2} = 1$. In two dimensions $\overline{\cos\theta_i} = \frac{1}{\pi}\int_0^{\pi} \cos\theta \, \mathrm{d}\theta = 0$ and $\overline{(\cos\theta_i)^2} = \frac{1}{\pi}\int_0^{\pi} \cos^2\theta \, \mathrm{d}\theta = \frac{1}{2}$. To include these cases the factor 3 in the exponent of (14.34) should be replaced by the dimension d.

$$P(\widetilde{X}) = \frac{1}{\sqrt{2\pi}} \exp\left\{-\frac{\widetilde{X}^2}{2}\right\}. \tag{14.32}$$

Hence

$$P(X) = \frac{1}{\sqrt{2\pi}} \frac{\sqrt{3}}{b\sqrt{M}} \exp\left\{-\frac{3}{2Mb^2} X^2\right\} \tag{14.33}$$

and finally in three dimensions

$$\begin{aligned} P(\mathbf{R}_M) &= P(X)\, P(Y)\, P(Z) \\ &= \frac{\sqrt{27}}{b^3\sqrt{(2\pi M)^3}} \exp\left\{-\frac{3}{2Mb^2}\mathbf{R}_M^2\right\}. \end{aligned} \tag{14.34}$$

14.2.2 Gyration Tensor

For the center of mass

$$\mathbf{R}_\mathrm{c} = \frac{1}{M}\sum_{i=1}^{M} \mathbf{R}_i \tag{14.35}$$

we find

$$\overline{\mathbf{R}_\mathrm{c}} = 0 \quad \overline{R_c^2} = \frac{1}{M^2}\sum_{i,j} \overline{\mathbf{R}_i \mathbf{R}_j} \tag{14.36}$$

and since

$$\overline{\mathbf{R}_i \mathbf{R}_j} = \min(i,\, j)\, b^2 \tag{14.37}$$

we have

$$\overline{R_\mathrm{c}^2} = \frac{b^2}{M^2}\left(2\sum_{i=1}^{M} i(M-i+1) - \sum_{i=1}^{M} i\right) = \frac{b^2}{M^2}\left(\frac{M^3}{3} + \frac{M^2}{2} + \frac{M}{6}\right) \approx \frac{Mb^2}{3}. \tag{14.38}$$

The gyration radius [71] is generally defined by

$$\begin{aligned} R_\mathrm{g}^2 &= \frac{1}{M}\sum_{i=1}^{M} \overline{(\mathbf{R}_i - \mathbf{R}_\mathrm{c})^2} \\ &= \frac{1}{M}\sum_{i=1}^{M}\left(\overline{R_i^2} + \overline{R_c^2} - 2\frac{1}{M}\sum_{j=1}^{M}\overline{\mathbf{R}_i \mathbf{R}_j}\right) = \frac{1}{M}\sum_{i}(\overline{R_i^2}) - \overline{R_\mathrm{c}^2} \\ &= b^2\frac{M+1}{2} - \frac{b^2}{M^2}\left(\frac{M^3}{3} + \frac{M^2}{2} + \frac{M}{6}\right) = b^2\left(\frac{M}{6} - \frac{1}{6M}\right) \approx \frac{Mb^2}{6}. \end{aligned} \tag{14.39}$$

R_g can be also written as

$$R_g^2 = \left(\frac{1}{M} \sum_i \overline{R_i^2} - \frac{1}{M^2} \sum_{ij} \overline{\mathbf{R}_i \mathbf{R}_j} \right) = \frac{1}{2M^2} \sum_{i=1}^{M} \sum_{j=1}^{M} \overline{(\mathbf{R}_i - \mathbf{R}_j)^2} \tag{14.40}$$

and can be experimentally measured with the help of scattering phenomena. It is related to the gyration tensor which is defined as

$$\Omega_g = \frac{1}{M} \sum_i \overline{(\mathbf{R}_i - \mathbf{R}_c)(\mathbf{R}_i - \mathbf{R}_c)^t}. \tag{14.41}$$

Its trace is

$$\mathrm{tr}(\Omega_g) = R_g^2 \tag{14.42}$$

and its eigenvalues give us information about the shape of the polymer (Fig. 14.6).

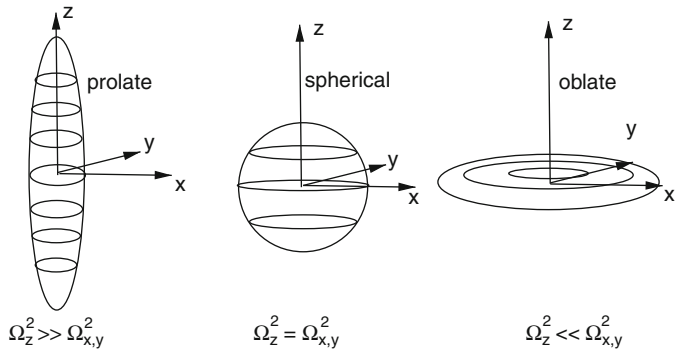

Fig. 14.6 Gyration tensor. The eigenvalues of the gyration tensor give information on the shape of the polymer. If the extension is larger (*smaller*) along one direction than in the perpendicular plane, one eigenvalue is larger (*smaller*) than the two other

14.2.3 Hookean Spring Model

Simulation of the dynamics of the freely jointed chain is complicated by the constraints which are implied by the constant chain length. Much simpler is the simulation of a model which treats the segments as Hookean springs. In the limit of a large force constant the two models give equivalent results (Fig. 14.7).

We assume that the segments are independent (self-crossing is not avoided). Then for one segment the energy contribution is

$$E_i = \frac{f}{2} \left(|\mathbf{b}_i| - b \right)^2 . \tag{14.43}$$

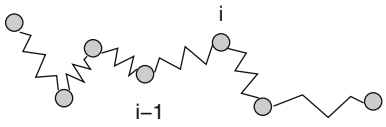

Fig. 14.7 Polymer model with Hookean springs

If the fluctuations are small (Fig. 14.8)

$$\overline{||\mathbf{b}_i| - b|} \ll b \tag{14.44}$$

then

$$\overline{|\mathbf{b}_i|} \approx b \quad \overline{\mathbf{b}_i^2} \approx b^2 \tag{14.45}$$

and the freely jointed chain model (14.34) gives the entropy as a function of the end to end vector

$$S = -k_\mathrm{B}\ \ln\left(P(\mathbf{R}_M)\right) = -k_\mathrm{B}\ \ln\left(\frac{\sqrt{27}}{b^3\sqrt{(2\pi M)^3}}\right) + \frac{3k_\mathrm{B}}{2Mb^2}{\mathbf{R}_M}^2. \tag{14.46}$$

If one end of the polymer is fixed at $\mathbf{r}_0 = 0$ and a force $\boldsymbol{\kappa}$ is applied to the other end, the free energy is given by

$$F = TS - \boldsymbol{\kappa}\mathbf{R}_M = \frac{3k_\mathrm{B}T}{2Mb^2}\mathbf{R}_M^2 - \boldsymbol{\kappa}\mathbf{R}_M + \text{const.} \tag{14.47}$$

In thermodynamic equilibrium the free energy is minimal, hence the average extension is

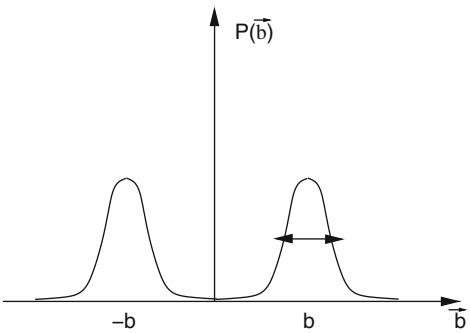

Fig. 14.8 Distribution of bond vectors. The bond vector distribution for a one-dimensional chain of springs has maxima at $\pm b$. For large force constants the width of the two peaks becomes small and the chain of springs resembles a freely jointed chain with constant bond length

$$\overline{\mathbf{R}_M} = \frac{Mb^2}{3k_\mathrm{B}T}\boldsymbol{\kappa}. \tag{14.48}$$

This linear behavior is similar to a Hookean spring with an effective force constant

$$f_\mathrm{eff} = \frac{Mb^2}{3k_\mathrm{B}T} \tag{14.49}$$

and is only valid for small forces. For large forces the freely jointed chain asymptotically reaches its maximum length of $R_{M,\max} = Mb$, whereas for the chain of springs $R_M \to M(b + \kappa/f)$.

14.3 Langevin Dynamics

A heavy particle moving in a bath of much smaller and lighter particles (for instance, atoms and molecules of the air) shows what is known as Brownian motion [72–74]. Due to collisions with the thermally moving bath particles it experiences a fluctuating force which drives the particle into a random motion. The French physicist Paul Langevin developed a model to describe this motion without including the light particles explicitly. The fluctuating force is divided into a macroscopic friction force proportional to the velocity

$$\mathbf{F}_\mathrm{fr} = -\gamma\mathbf{v} \tag{14.50}$$

and a randomly fluctuating force with zero mean and infinitely short correlation time

$$\overline{\mathbf{F}_\mathrm{rand}(t)} = 0 \quad \overline{\mathbf{F}_\mathrm{rand}(t)\mathbf{F}_\mathrm{rand}(t')} = \overline{\mathbf{F}^2_\mathrm{rand}}\delta(t - t'). \tag{14.51}$$

The equations of motion for the heavy particle are

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x} &= \mathbf{v} \\ \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v} &= -\gamma\mathbf{v} + \frac{1}{m}\mathbf{F}_{fr}(t) - \frac{1}{m}\nabla U(\mathbf{x}) \end{aligned} \tag{14.52}$$

with the macroscopic friction coefficient γ and the potential $U(\mathbf{x})$.

The behavior of the random force can be better understood if we introduce a time grid $t_{n+1} - t_n = \Delta t$ and take the limit $\Delta t \to 0$. We assume that the random force has a constant value during each interval

$$\mathbf{F}_\mathrm{rand}(t) = \mathbf{F}_n \quad t_n \le t < t_{n+1} \tag{14.53}$$

and that the values at different intervals are uncorrelated

$$\overline{\mathbf{F}_n\mathbf{F}_m} = \delta_{m,n}\overline{\mathbf{F}_n^2}. \tag{14.54}$$

The auto-correlation function then is given by

$$\overline{\mathbf{F}_{\text{rand}}(t)\mathbf{F}_{\text{rand}}(t')} = \begin{cases} 0 & \text{different intervals} \\ \overline{\mathbf{F}_n^2} & \text{same interval} \end{cases}. \tag{14.55}$$

Division by Δt gives a sequence of functions which converges to a delta function in the limit $\Delta t \to 0$:

$$\frac{1}{\Delta t}\overline{\mathbf{F}_{\text{rand}}(t)\mathbf{F}_{\text{rand}}(t')} \to \overline{\mathbf{F}_n^2}\,\delta(t-t'). \tag{14.56}$$

Hence we find

$$\overline{\mathbf{F}_n^2} = \frac{1}{\Delta t}\overline{\mathbf{F}_{\text{rand}}^2}. \tag{14.57}$$

Within a short time interval $\Delta t \to 0$ the velocity changes by

$$\mathbf{v}(t_n + \Delta t) = \mathbf{v} - \gamma\mathbf{v}\Delta t - \frac{1}{m}\nabla U(\mathbf{x})\Delta t + \frac{1}{m}\mathbf{F}_n\Delta t + \cdots \tag{14.58}$$

and taking the square gives

$$\mathbf{v}^2(t_n+\Delta t) = \mathbf{v}^2 - 2\gamma\mathbf{v}^2\Delta t - \frac{2}{m}\mathbf{v}\nabla U(\mathbf{x})\Delta t + \frac{2}{m}\mathbf{v}\mathbf{F}_n\Delta t + \frac{\mathbf{F}_n^2}{m^2}(\Delta t)^2 + \cdots. \tag{14.59}$$

Hence for the total energy

$$\begin{aligned} E(t_n + \Delta t) &= \frac{m}{2}\mathbf{v}^2(t_n + \Delta t) + U(\mathbf{x}(t_n + \Delta t)) \\ &= \frac{m}{2}\mathbf{v}^2(t_n + \Delta t) + U(\mathbf{x}) + \mathbf{v}\nabla U(\mathbf{x})\Delta t + \cdots \end{aligned} \tag{14.60}$$

we have

$$E(t_n + \Delta t) = E(t_n) - m\gamma\mathbf{v}^2\Delta t + \mathbf{v}\mathbf{F}_n\Delta t + \frac{\mathbf{F}_n^2}{2m}(\Delta t)^2 + \cdots. \tag{14.61}$$

On the average the total energy $\overline{E}$ should be constant and furthermore in d dimensions

$$\frac{m}{2}\overline{\mathbf{v}^2} = \frac{d}{2}k_{\text{B}}T. \tag{14.62}$$

Therefore we conclude

$$m\gamma\overline{\mathbf{v}^2} = \frac{\Delta t}{2m}\overline{\mathbf{F}_n^2} = \frac{1}{2m}\overline{\mathbf{F}_{\text{rand}}^2} \tag{14.63}$$

from which we obtain finally

$$\overline{\mathbf{F}_n^2} = \frac{2m\gamma d}{\Delta t} k_\mathrm{B} T. \tag{14.64}$$

Problems

Problem 14.1 Random Walk in One Dimension

This program generates random walks with (a) fixed step length $\Delta x = \pm 1$ or (b) step length equally distributed over the interval $-\sqrt{3} < \Delta x < \sqrt{3}$. It also shows the variance, which for large number of walks approaches $\sigma = \sqrt{n}$. See also Fig. 14.2.

Problem 14.2 Gyration Tensor

The program calculates random walks with M steps of length b. The bond vectors are generated from M random points $\mathbf{e}_i$ on the unit sphere as $\mathbf{b}_i = b\mathbf{e}_i$. End to end distance, center of gravity, and gyration radius are calculated and can be averaged over a large number of random structures. The gyration tensor (Sect. 14.2.2) is diagonalized and the ordered eigenvalues are averaged.

Problem 14.3 Brownian Motion in a Harmonic Potential

The program simulates a particle in a one-dimensional harmonic potential

$$U(\mathbf{x}) = \frac{f}{2}x^2 - \kappa x$$

where κ is an external force. We use the improved Euler method (11.34). First the coordinate and the velocity at midtime are estimated

$$\mathbf{x}\left(t_n + \frac{\mathrm{d}t}{2}\right) = \mathbf{x}(t_n) + \mathbf{v}(t_n)\frac{\mathrm{d}t}{2} \tag{14.65}$$

$$\mathbf{v}\left(t_n + \frac{\mathrm{d}t}{2}\right) = \mathbf{v}(t_n) - \gamma\mathbf{v}(t_n)\frac{\mathrm{d}t}{2} + \frac{\mathbf{F}_n}{m}\frac{\mathrm{d}t}{2} - \frac{f}{m}\mathbf{x}(t_n)\frac{\mathrm{d}t}{2} \tag{14.66}$$

where $\mathbf{F}_n$ is a random number obeying (14.64)

Now the values at t_{n+1} are calculated as

$$\begin{aligned}
\mathbf{x}(t_n + \mathrm{d}t) &= \mathbf{x}(t_n) + \mathbf{v}\left(t_n + \frac{\mathrm{d}t}{2}\right)\mathrm{d}t \\
\mathbf{v}(t_n + \mathrm{d}t) &= \mathbf{v}(t_n) - \gamma\mathbf{v}\left(t_n + \frac{\mathrm{d}t}{2}\right)\mathrm{d}t + \frac{\mathbf{F}_n}{m}\mathrm{d}t - \frac{f}{m}\mathbf{x}\left(t_n + \frac{\mathrm{d}t}{2}\right)\mathrm{d}t
\end{aligned} \tag{14.67}$$

Problem 14.4 Force Extension Relation

The program simulates a chain of springs (Sect. 14.2.3) with potential energy

$$U = \frac{f}{2} \sum (|\mathbf{b}_i| - b)^2 - \boldsymbol{\kappa} \mathbf{R}_M \tag{14.68}$$

The force can be varied and the extension along the force direction is averaged over a large number of time steps.