



**Figure 7.12** Example of the evolution of the true self-avoiding walk with  $g = 1$  (see (7.49)). The shaded site represents the location of the walker at time  $t$ . The number of visits to each site are given within each site, and the probability of a step to a nearest neighbor site is given below it. Note the use of periodic boundary conditions.

$C(t)$  is defined so that  $C(t = 0) = 1$  and  $C(t) = 0$  if the configurations are not correlated. Because the configurations will become uncorrelated if the time  $t$  between the configurations is sufficiently long, we expect that  $C(t) \rightarrow 0$  for  $t \gg 1$ . We expect that  $C(t) \sim e^{-t/\tau}$ ; that is,  $C(t)$  decays exponentially with a decay or correlation time  $\tau$ . Estimate  $\tau$  from a plot of  $\ln C(t)$  versus  $t$ . Another way of estimating  $\tau$  is from the integral  $\int_0^\infty dt C(t)$ , where  $C(t)$  is normalized so that  $C(0) = 1$ . (Because we determine  $C(t)$  at discrete values of  $t$ , this integral is actually a sum.) How do your two estimates of  $\tau$  compare? A more detailed discussion of the estimation of correlation times can be found in Section 15.7. ■

Another type of random walk that is less constrained than the self-avoiding random walk is the “true” self-avoiding walk. This walk describes the path of a random walker that avoids visiting a lattice site with a probability that is a function of the number of times the site has been visited already. This constraint leads to a reduced excluded volume interaction in comparison to the usual self-avoiding walk.

### Problem 7.32 The true self-avoiding walk in one dimension

In one dimension the true self-avoiding walk corresponds to a walker that can jump to one of its two nearest neighbors with a probability that depends on the number of times these neighbors have already been visited. Suppose that the walker is at site  $i$  at step  $t$ . The probability that the walker will jump to site  $i + 1$  at time  $t + 1$  is given by

$$p_{i+1} = \frac{e^{-gn_{i+1}}}{e^{-gn_{i+1}} + e^{-gn_{i-1}}}, \quad (7.49)$$

where  $n_{i\pm 1}$  is the number of times that the walker has already visited site  $i \pm 1$ . The probability of a jump to site  $i - 1$  is  $p_{i-1} = 1 - p_{i+1}$ . The parameter  $g$  ( $g > 0$ ) is a measure of the “desire” of the path to avoid itself. The first few steps of a typical true self-avoiding walk are shown in Figure 7.12. The main quantity of interest is the exponent  $\nu$ . We know that  $g = 0$  corresponds to the usual random walk with  $\nu = 1/2$ , and that the limit  $g \rightarrow \infty$  corresponds to the self-avoiding walk. What is the value of  $\nu$  for a self-avoiding walk in

one dimension? Is the value of  $\nu$  for any finite value of  $g$  different than these two limiting cases?

Write a program to do a Monte Carlo simulation of the true self-avoiding walk in one dimension. Use an array to record the number of visits to every site. At each step calculate the probability  $p$  of a jump to the right. Generate a random number  $r$  and compare it to  $p$ . If  $r \leq p$ , move the walker to the right; otherwise, move the walker to the left. Compute  $\langle \Delta x^2 \rangle$  as a function of the number of steps  $N$ , where  $x$  is the distance of the walker from the origin. Make a log-log plot of  $\langle \Delta x^2 \rangle$  versus  $N$  and estimate  $\nu$ . Can you distinguish  $\nu$  from its random walk and self-avoiding walk values? Reasonable choices of parameters are  $g = 0.1$  and  $N \sim 10^3$ . Averages over  $10^3$  trials yield qualitative results. For comparison, published results are for  $N \sim 10^4$  and for  $10^3$  trials; extended results for  $g = 2$  are given for  $N = 2 \times 10^5$  and  $10^4$  trials (see Bernasconi and Pietronero). ■

## 7.8 ■ DIFFUSION-CONTROLLED CHEMICAL REACTIONS

Imagine a system containing particles of a single species  $A$ . The particles diffuse, and when two particles “collide,” a reaction occurs such that the two combine to form an inert species which is no longer involved in the reaction. We can represent this chemical reaction as



If we ignore the spatial distribution of the particles, we can describe the kinetics by a simple rate equation:

$$\frac{dA(t)}{dt} = -kA^2(t), \quad (7.51)$$

where  $A$  is the concentration of  $A$  particles at time  $t$  and  $k$  is the rate constant. (In the chemical kinetics literature, it is traditional to use the term concentration rather than the number density.) For simplicity, we assume that all reactants are entered into the system at  $t = 0$ , and that no reactants are added later (the system is closed). It is easy to show that the solution of the first-order differential equation (7.51) is

$$A(t) = \frac{A(0)}{1 + ktA(0)}. \quad (7.52)$$

Hence,  $A(t) \sim t^{-1}$  in the limit of long times.

Another interesting case is the bimolecular reaction



If we neglect spatial fluctuations in the concentration as before (this neglect yields what is known as a mean-field approximation), we can write the corresponding rate equation as

$$\frac{dA(t)}{dt} = \frac{dB(t)}{dt} = -kA(t)B(t). \quad (7.54)$$

We also have

$$A(t) - B(t) = \text{constant}, \quad (7.55)$$