Figure 12.9: Example of the time evolution of the true self-avoiding walk with $g = 1$. 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.

move the walker to the right; otherwise move the walker to the left. Compute $\langle \Delta x_N^2 \rangle$, where x is the distance of the walker from the origin, as a function of the number of steps N. Make a log-log plot of $\langle \Delta x_N^2 \rangle$ versus N and estimate ν. Can you distinguish ν 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 give qualitative results. For comparison, published results (see Bernasconi and Pietronero) are for $N = 10^4$ and for 10^3 trials; extended results for $g = 2$ are given for $N = 2 \times 10^5$ and 10^4 trials.

12.4   Diffusion Controlled Chemical Reactions

from Gould Tobochnik - problem 12.15

Imagine a system containing particles of a single species A. The particles diffuse, and when two particles collide, a "reaction" occurs such that either one particle is annihilated or the two combine to form an inert species which is no longer involved in the reaction. In the latter case we can represent the chemical reaction as

$$A + A \to 0. \qquad \text{(inert)} \qquad (12.22)$$
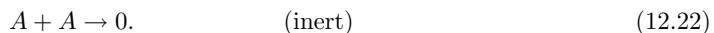
If we ignore the spatial fluctuations of the density of species A, we can describe the kinetics by a simple rate equation:

$$\frac{dA(t)}{dt} = -kA^2(t), \qquad (12.23)$$

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 (a closed system). It is easy to show that the solution of the first-order differential equation (12.23) is

$$A(t) = \frac{1}{kt + 1/A(0)}, \tag{12.24}$$

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

Another interesting case is the bimolecular reaction

$$A + B \rightarrow 0. \tag{12.25}$$

If we neglect 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

$$\frac{dA(t)}{dt} = \frac{dB(t)}{dt} = -kA(t)B(t). \tag{12.26}$$

We also have that

$$A(t) - B(t) = \text{constant}, \tag{12.27}$$

because each reaction leaves the difference between the concentration of A and B particles unchanged. For the special case of equal initial concentrations, the solution of (12.26) with (12.27) is the same as (12.24). What is the solution for the case $A(0) \neq B(0)$?

The above derivation of the time dependence of A for the kinetics of the one and two species annihilation process is straightforward, but is based on the neglect of spatial fluctuations. In the following two problems, we simulate the kinetics of these processes and test this assumption.

Problem 12.15. Diffusion controlled chemical reactions in one dimension

a. Assume that N particles do a random walk on a one-dimensional lattice of length L with periodic boundary conditions. Every particle moves once in one unit of time. It is convenient to associate an array `site(j)` which records the label of the particle, if any, at site j. Because we are interested in the long time behavior of the system when the concentration $A = N/L$ of particles is small, it is efficient to also maintain an array of particle positions, `posx` such that `site(posx(i)) = i`. For example, if particle 5 is located at site 12, then `posx(5) = 12` and `site(12) = 5`. We also need an array, `newSite`, to maintain the new positions of the walkers as they are moved one at a time. If two walkers land on the same position k, then `newSite(k) = 0`, and the value of `posx` for these two walkers to 0. After all the walkers have moved, we let `site = ewSite` for all sites, and remove all the reacting particles in `posx` that have values equal to 0. This operation can be accomplished by replacing any reacting particle in `posx` by the last particle in the array. Begin with all sites occupied, $A(t = 0) = 1$.

Make a log-log plot of the quantity $1/A(t) - 1$ versus the time t. The times should be separated by exponential intervals so that your data is equally spaced on a logarithmic plot. For example, you might include data with times equal to 2^p, with $p = 1, 2, 3, \ldots$ Does your log-log plot yield a straight line in the limit of long times? If so, calculate its slope. Is the mean-field approximation for $A(t0$ valid in one dimension? You can obtain crude results for small lattices of order $L = 100$ and times of order $t = 10^2$. To obtain results to within ten percent, you need lattices of order $L = 10^4$ and times of order $t = 2^{13}$.

b. More insight into the origin of the time dependence of $A(t)$ can be gained from the behavior of the quantity $P(r,t)$, the probability distribution of the nearest neighbor distances at time t. The nearest neighbor distance of a particle is defined as the minimum distance between the particle and all other particles. ($P(r)$ is not the same as the radial distribution function $g(r)$ considered in Section 8.8.) The distribution of these distances changes dramatically as the reaction proceeds, and this change can give information about the reaction mechanism. Place particles at random on a one-dimensional lattice and verify that the most probable nearest neighbor distance is $r = 1$ (one lattice constant) for all concentrations. (This result is true in any dimension.) Then verify that the distribution of nearest neighbor distances on a $d = 1$ lattice is given by

$$P(r, t = 0) = 2A\,e^{-2A(r-1)}. \tag{12.28}$$

Is the form (12.28) properly normalized? Start with $A(t = 0) = 0.1$ and find $P(r,t)$ for $t = 10, 100$, and 1000. Average over all particles. How does $P(r,t)$ change as the reaction proceeds? Does it retain the same form as the concentration decreases?

c. Compute the quantity $D(t)$, the number of *distinct* sites visited by an individual walker. How does the time dependence of $D(t)$ compare to the computed time dependence of $1/A(t) - 1$?

d. Write a program to simulate the $A + B = 0$ reaction. For simplicity, assume that multiple occupancy of the same site is not allowed, for example, an A particle cannot jump to a site already occupied by an A particle. The easiest procedure is to allow a walker to choose one of its nearest neighbor sites at random, but to not move the walker if the chosen site is already occupied by a particle of the same type. If the site is occupied by a walker of another type, then the pair of reacting particles is annihilated. Keep separate arrays for the A and B particles, with the value of the array denoting the label of the particle as before. An easy way to distinguish A and B walkers is to make the array element `site(k)` positive if the site is occupied by an A particle and negative if the site is occupied by a B particle. Start with equal concentrations of A and B particles and occupy the sites at random. Some of the interesting questions are similar to those that we posed in parts (a)–(c). Color code the particles and observe what happens to the relative positions of the particles.

*Problem 12.16. Reaction diffusion in two dimensions

a. Do a similar simulation as in Problem 12.15 on a two-dimensional lattice for the reaction $A+A \to 0$. In this case it is convenient to have one array for each dimension, for example, `posx` and `posy`. Set $A(t = 0) = 1$, and choose $L = 50$. Show the configuration of walkers after each Monte Carlo step per walker. Describe the geometry of the clusters of particles as the diffusion process proceeds. Are the particles uniformly distributed throughout the lattice for all times? Calculate $A(t)$ and compare your results for $1/A(t) - 1/A(0)$ to the t-dependence of $D(t)$, the number of distinct lattice sites that are visited in time t. ($D(t) \sim t/\log t$ for two dimensions.) How well do the slopes compare? Do a similar simulation with $A(t = 0) = 0.01$. What slope do you obtain in this case? What can you conclude about the initial density dependence? Is the mean-field approximation valid in this case? If time permits, do a similar simulation in three dimensions.