

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 (7.54) with (7.55) is the same as (7.52). What is the solution for the case  $A(0) \neq B(0)$ ?

This 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 assumption that the particles are distributed uniformly. In the following two problems, we simulate the kinetics of these processes and test this assumption.

### Problem 7.33 Diffusion controlled chemical reactions in one dimension

- 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. Use the array `site[j]` to record 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 `x[i]` such that `site[x[i]] = i`. For example, if particle 5 is located at site 12, then `x[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. After each walker is moved, we check to see if two walkers have landed on the same position  $k$ . If they have, we set `newSite[k] = -1` and the value of `x[i]` for these two walkers to  $-1$ . The value  $-1$  indicates that no particle exists at the site. After all the walkers have moved, we let `site = newSite` for all sites and remove all the reacting particles in `x` that have values equal to  $-1$ . This operation can be accomplished by replacing any reacting particle in `x` by the last particle in the array. Begin with all sites occupied:  $A(t = 0) = 1$ .
- Make a log-log plot of the quantity  $A(t)^{-1} - A(0)^{-1}$  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  $p = 1, 2, 3, \dots$ . Does your log-log plot yield a straight line for long times? If so, calculate its slope. Is the mean-field approximation for  $A(t)$  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 10%, you will need lattices of order  $L = 10^4$  and times of order  $t = 2^{13}$ .
- 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 that the nearest neighbor distance is  $r$  at time  $t$ . The nearest neighbor distance of a given particle is defined as the minimum distance between it and all other particles. The distribution of these distances changes dramatically as the reaction proceeds, and this change can give information about the reaction mechanism. Place the 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 one-dimensional lattice is given by

$$P(r, t = 0) = 2A e^{-2A(r-1)} \quad (\text{random distribution}). \quad (7.56)$$

Is the form (7.56) 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?

- 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  $A(t)^{-1} - 1$ ?
- Write a program to simulate the reaction  $A + B \rightarrow 0$ . 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 not to 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. One 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 (b)–(d). Color code the particles and observe what happens to the relative positions of the particles.

### \*Problem 7.34 Reaction diffusion in two dimensions

- Do a similar simulation as in Problem 7.33 on a two-dimensional lattice for the reaction  $A + A \rightarrow 0$ . In this case it is convenient to have one array for each dimension, for example, `siteX` and `siteY`, or to store the lattice as a one-dimensional array (see Section 12.2). Set  $A(t = 0) = 1$  and choose  $L = 50$ . Show the walkers after each Monte Carlo step per walker and describe their distribution as they diffuse. Are the particles uniformly distributed throughout the lattice for all times? Calculate  $A(t)$  and compare your results for  $A(t)^{-1} - A(0)^{-1}$  to the  $t$ -dependence of  $D(t)$ , the number of distinct lattice sites that are visited in time  $t$ . (In two dimensions,  $D(t) \sim t/\log t$ .) 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?
- Begin with  $A$  and  $B$  type random walkers initially segregated on the left and right halves (in the  $x$  direction) of a square lattice. The process  $A + B \rightarrow C$  exhibits a reaction front where the production of particles of type  $C$  is nonzero. Some of the quantities of interest are the time dependence of the mean position  $\langle x \rangle(t)$  and the width  $w(t)$  of the reaction front. The rules of this process are the same as in part (a) except that a particle of type  $C$  is added to a site when a reaction occurs. A particular site can be occupied by one particle of type  $A$  or type  $B$  as well as any number of particles of type  $C$ . If  $n(x, t)$  is the number of particles of type  $C$  at a distance  $x$