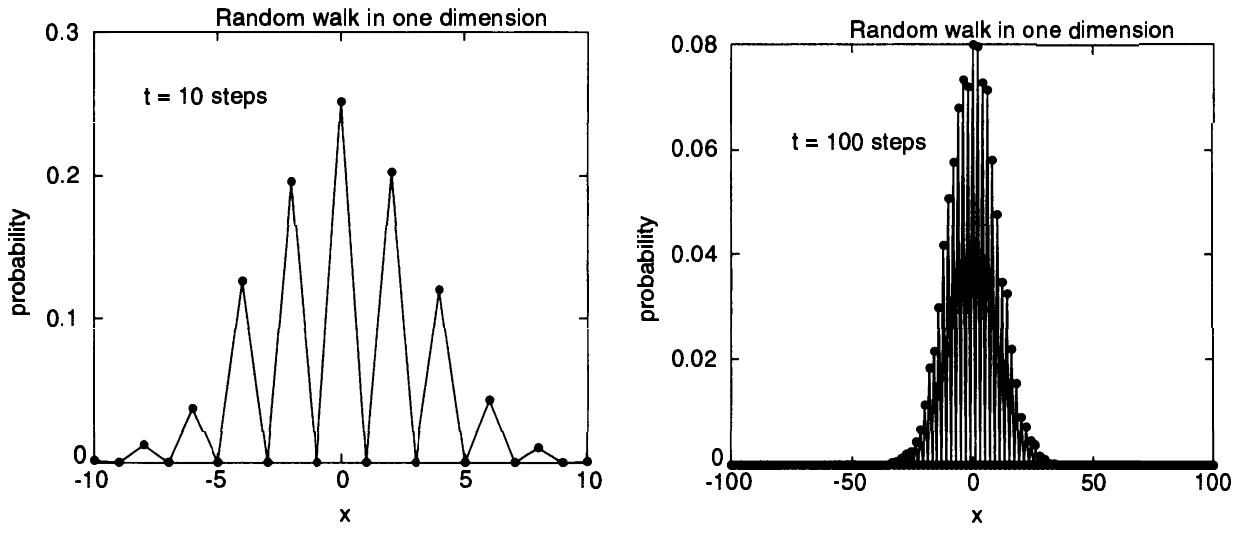

Figure 7.17: Random-walk distributions in one dimension. A large number of walkers began at the origin, and their positions after 10 (shown at left) and 100 steps (shown at right) were used to obtain the probability distribution as a function of position.

Exercises

1. Write a program to solve the finite-difference form of the diffusion equation in one dimension, (7.15). Use it to confirm that (7.16) is, indeed, a solution. To do this, begin with an initial density profile that is sharply peaked at $x = 0$, but choose the grid size such that this profile extends over at least several grid sites. Then show that at later times the density distribution satisfies (7.16).

*2. Repeat the calculation of the previous problem in either two or three dimensions (or both). Begin by deriving the finite-difference equation corresponding to (7.15), suitably generalized to the desired dimensionality. Then show that the density distribution spreads in time according to (7.16) with a half-width that grows as $t^{1/2}$.

*3. Use the program developed for the previous problem to investigate how more complicated initial-density distributions evolve with time. For example, consider an initial distribution that is a constant along the x axis and zero everywhere else. Study how this distribution spreads with time.

7.7 Diffusion, Entropy, and the Arrow of Time

We introduced the cream-in-your-coffee problem at the beginning of this chapter when we were trying to motivate an interest in random processes. Now we want to reconsider it from the point of view of nonequilibrium statistical mechanics and use it to illustrate how a system approaches equilibrium.

Our initial conditions are, again, a cup of black coffee containing a drop of cream at its center. For simplicity we consider a two-dimensional cup with an initial cream distribution as shown in Figure 7.18. The black dots, which form a square black mass at $t = 0$, are the cream molecules. For the simulation we assume that each of these molecules executes a random walk on a two-dimensional square lattice and allow multiple occupancy of a lattice site (although our results would not change qualitatively if we were to limit occupancy to only one molecule per site). At each time step we choose a molecule at random and let it take one step in its random walk. The distributions after 10^4, 10^5, and 10^6 time steps

are shown in Figures 7.18 and 7.19. As expected, the cream spreads with time in a manner that appears by eye to be diffusive (we will leave quantitative verification of this claim to the exercises). We have assumed that there are walls at $x = \pm 100$ and $y = \pm 100$, so the molecules are constrained to stay in the region shown here.

These results are equivalent to our solution of the two dimensional diffusion equation in the previous section. Here we want to carry this example one step further and discuss how it is related to the second law of thermodynamics and the manner in which systems approach equilibrium. For this it is useful to consider the entropy of the system. Roughly speaking, entropy is a measure of the amount of disorder. A perfectly ordered system has zero entropy, while a disordered one has a large entropy. Furthermore, statistical physics tells us that the entropy of a closed system will either remain the same or increase with time.

Our cream-in-your-coffee simulation illustrates these ideas very nicely. Initially, all of the cream molecules are packed tightly into a small region of the cup, so the system is highly ordered and has a small value of the entropy. As time passes the molecules spread to fill the cup and their arrangement becomes more disordered. We can make this description quantitative by calculating the entropy explicitly. To do this we recall that the statistical definition of entropy S is

$$S = -\sum_i P_i \ln P_i \,, \tag{7.18}$$

where the sum is over all possible states of the system and P_i is the probability of finding the system in state i. To apply this definition to our problem we imagine that the system is divided into a square grid, as shown in Figure 7.20. Note that this grid is *not* related to the square lattice occupied by our walkers. It is just a convenient way of partitioning space; each of these partitions is a distinct state in

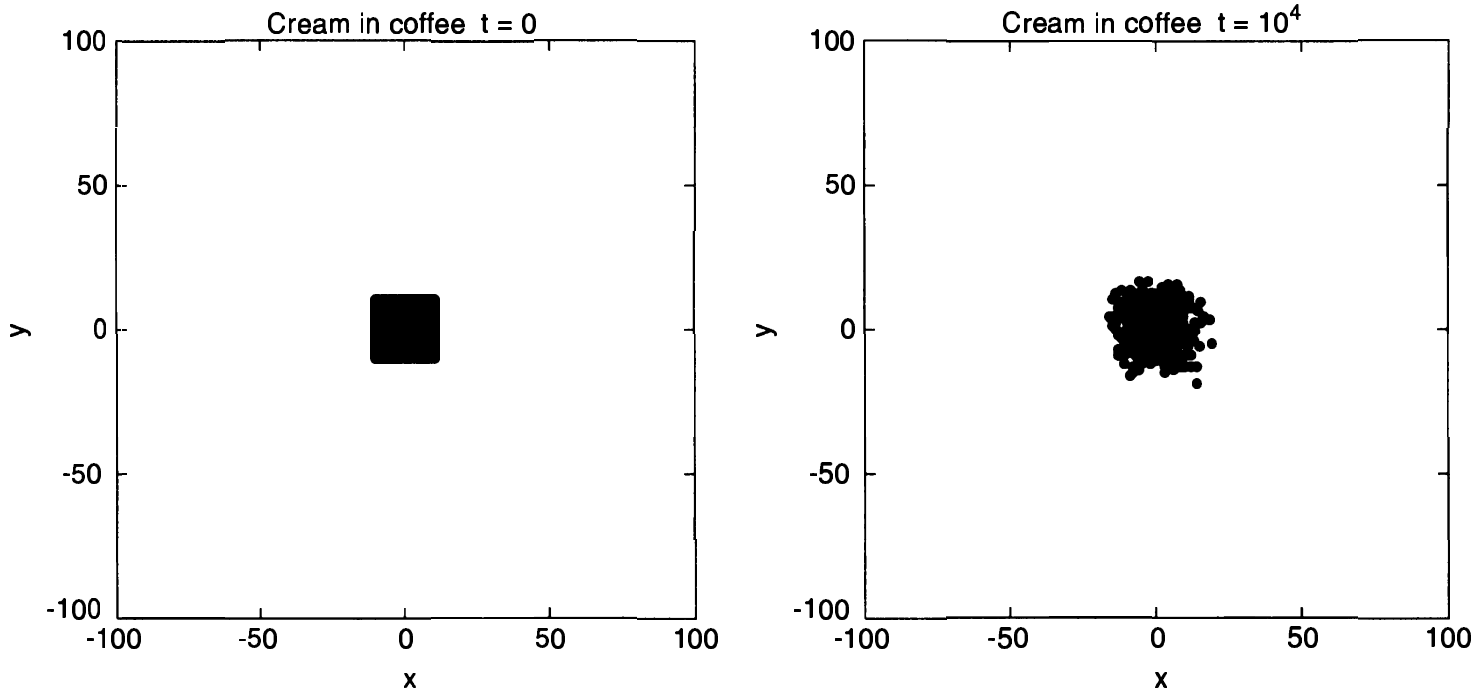

Figure 7.18: Random-walk simulation of diffusion of cream in coffee. Left: the initial ($t = 0$) cream distribution in which all of the molecules were near the center of the cup. Right: after $t = 10^4$ time steps, only a little spreading has taken place. There were 400 molecules constrained to a 200 x 200 square lattice.

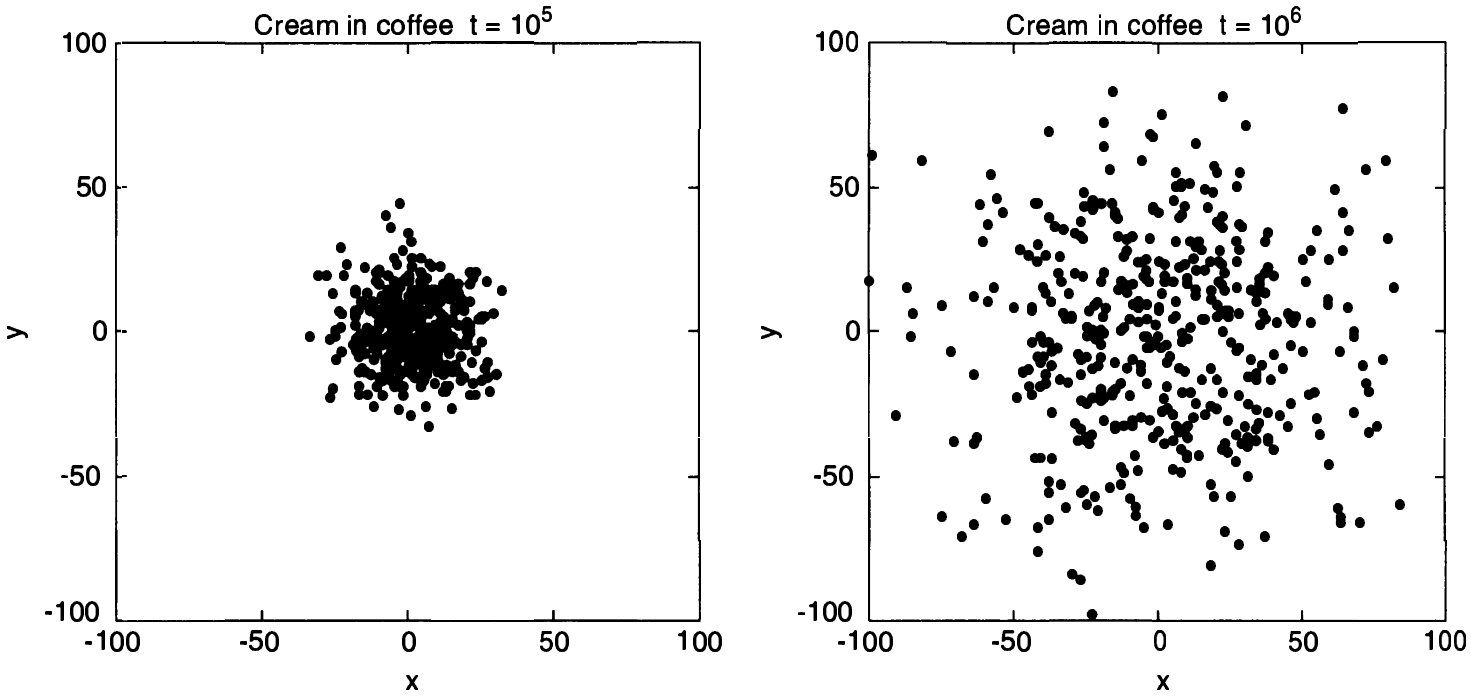

Figure 7.19: Diffusion of cream in coffee; continuation of the random-walk simulation in Figure 7.19. Left: after $t = 10^5$ time steps; right: after $t = 10^6$ time steps.

which a molecule might be found. To appreciate the meaning of (7.18) it is useful to first imagine a system containing only a single cream molecule (we'll add the others from Figures 7.18 and 7.19 in a moment). The state we label i then corresponds to the molecule being located in grid cell i, and P_i is the probability of finding the molecule in this cell at any particular time. The sum over i in (7.18) is,

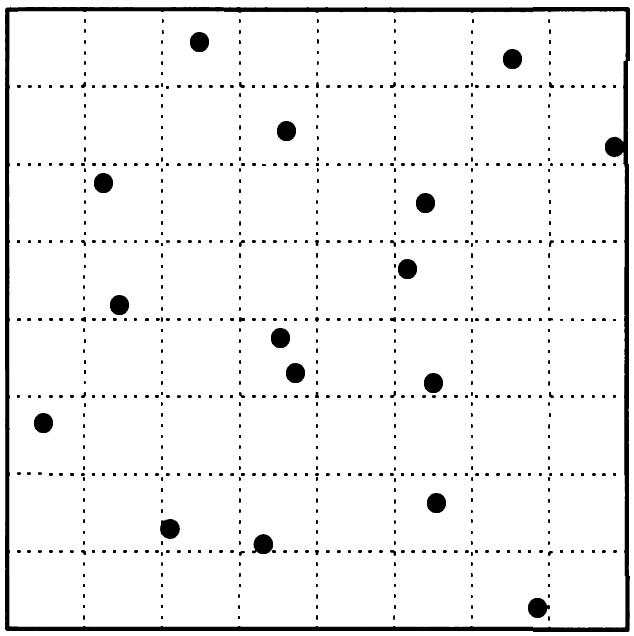

Figure 7.20: Schematic division of our coffee cup into grid cells, with a few molecules distributed throughout the cup. P_i is the probability of finding a molecule in cell i.

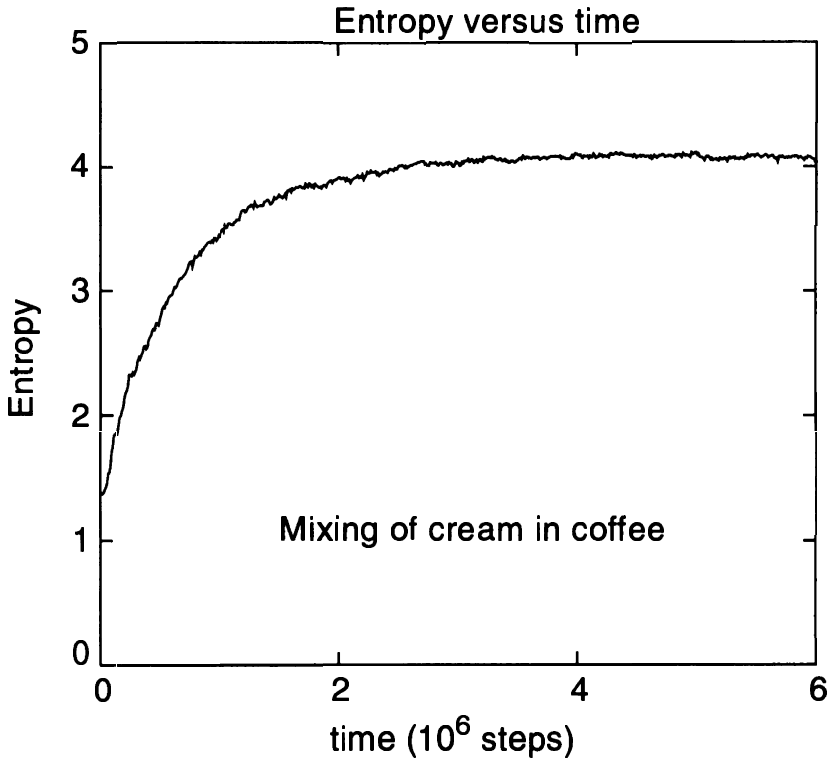

Figure 7.21: Entropy as a function of time (total number of random-walk steps) for cream mixing in coffee, calculated from the simulation that yielded the snapshots in Figures 7.18 and 7.19. The grid used to calculate the entropy had $8 \times 8 = 64$ cells.

then, a sum over all of the cells in the grid. The simulations in Figures 7.18 and 7.19 involve a large number of molecules, and we can use all of them in the computation of P_i.

We have used the molecular positions from the random-walk simulation in Figures 7.18 and 7.19 to calculate these probabilities and evaluate S, and some results are shown in Figure 7.21. The behavior is in complete accord with our intuitive definition of entropy as it applies to the cream. The system is initially in a highly ordered state, with a low value of S. As time passes, the entropy increases and eventually levels off; it approaches a constant value at long times, signaling that the system has reached equilibrium.

This illustrates how a closed system approaches equilibrium. The molecules spread to fill the available states (in this case the available space) uniformly, thereby maximizing the entropy. This tendency to maximize the entropy is not built into the microscopic equations of motion. Rather, it occurs because the system explores (or spends time in) all of the available states with equal probability. This eventually makes the probability of finding a cream molecule the same in all of the grid cells. The equilibrium condition is one in which all available states have equal probabilities.

According to the *ergodic hypothesis*, all of the available states of a system in equlibrium will be occupied with equal probabilities. This is not a result of Newton's laws or any other microscopic equations of motion. Rather, it is a *hypothesis* that plays a key role in statistical physics. While it has not been possible to derive this hypothesis from microscopic laws or principles, it has been shown to hold (rigorously) for certain systems. The difficulty with deriving the ergodic hypothesis in a completely general way can be appreciated from the snapshots of the cream in Figures 7.18 and 7.19. The picture at $t = 10^6$ shows a fairly random distribution of molecules, which contrasts greatly with the completely

ordered picture at $t = 0$. If we were to follow the system beyond $t = 10^6$, we would expect to find the randomness of this distribution to either stay the same or increase; we would certainly not expect it to decrease. However, such a decrease would not violate any microscopic laws of nature. These laws leave open the possibility that a cream distribution such as the one at $t = 10^6$ might evolve with time into a perfectly ordered arrangement like that at $t = 0$. That is, the cream could "unmix" and all flow to the center of the cup. However, this is extremely unlikely and, so far as we know, has never been observed in nature.

In the present example the ergodic behavior is a result of the rules of our random walk. The fact that each step is independent of the previous steps leads the particles to explore all parts of the cup with equal probability. However, this assumption of independence is just that, an *assumption.* We know that on a microscopic level the trajectory followed by a molecule is not independent of its prior history, but could in principle be calculated (using, for example, molecular dynamics as we will discuss in Chapter 9). So how can we explain why the ergodic hypothesis is so widely applicable? The answer to this question is not completely settled, but one attractive possibility can be seen from our work on chaotic systems. There we saw that deterministic systems can behave chaotically and exhibit an extreme sensitivity to initial conditions.[24] This sensitivity leads to essentially random behavior of systems such as the pendulum, asteroids near a Kirkwood gap, etc. It may be that this essentially random behavior is responsible for the ergodic behavior observed in nature. With this in mind, it is intriguing to reconsider the billiard problem discussed in Chapter 3. That can be viewed as a (classical) model for the motion of gas molecules in a closed container and is thus very similar to our cream-in-your-coffee problem. You may recall that except for very specially shaped containers, the motion of the billiard is chaotic. Thus it would not be surprising to find that the motions of our cream molecules are also chaotic, making the system ergodic.

Exercises

1. Calculate the entropy for the cream-in-your-coffee problem, and reproduce the results in Figure 7.21.
2. Calculate S as a function of time for the cream-in-your-coffee problem for containers with different sizes. Show that the time necessary to reach equilibrium varies as the square of the size.

*3. Perform the random-walk simulation of Figures 7.18 and 7.19 and show that the size of the drop of cream increases as $t^{1/2}$ (our familiar diffusive behavior), so long as the drop is smaller than the size of the container. Show that the behavior changes when the drop has spread so much that it uniformly fills the container. The time at which the size of the drop stops increasing should be the same as the time at which the system reaches equilibrium as determined by the entropy. Hint: A convenient measure of the size of the drop of cream is the root-mean-square distance of the particles from the origin, $\sqrt{(\sum r_i^2)/N}$.

*4. Perform the random-walk simulation of spreading cream (Figures 7.18 and 7.19), and let one of the walls of the container possess a small hole so that if a cream molecule enters the hole, it leaves the container. Calculate the number of molecules in the container as a function of time. Show that this number, which is proportional to the partial pressure of the cream molecules, varies as

[24] They are also extremely sensitive to changes in external parameters, which would also contribute to ergodicity.

$\exp(-t/\tau)$, where τ is the effective time constant for the escape. Hint: Reasonable parameter choices are a 50×50 container lattice and a hole 10 units in length along one of the edges.

5. Carry out an analysis of the entropy for the nonlinear damped pendulum studied in Chapter 3. Consider the behavior of $\theta(t)$ and divide the possible range for θ into a number of cells (try 100). Simulate the pendulum and calculate a histogram of the number of times the pendulum angle falls into a cell as a function of θ; sample $\theta(t)$ in synchrony with the drive force, as we did in calculating the Poincaré sections. Calculate the entropy using (7.18) as a function of the driving force. You should find that S is small in the periodic regime and large when the pendulum is chaotic. What is S in the period-2 and period-4 regimes?

7.8 Cluster Growth Models

We have spent a good deal of time in this chapter exploring random walks and their connection with diffusion and the approach to equilibrium. Another interesting random process which turns out to be closely related to random walks, concerns the growth of clusters, such as snowflakes and soot particles. In this section we will examine two different models of cluster growth. The first is known as the Eden model and operates according to the following rules. Consider a two dimensional lattice of points (x, y), where x and y are both integers. These are the allowed locations for the particles that will make up the cluster. We begin by placing a seed particle at the origin ($x = 0$, $y = 0$); this is our initial cluster. A cluster grows by the addition of particles to its perimeter. Our initial cluster has nearest-neighbor points on the lattice at $(\pm 1, 0)$ and $(0, \pm 1)$. We will refer to such unoccupied near-neighbor sites as the perimeter sites of the cluster. We next choose one of these perimeter sites at random and place a particle at the chosen location. The cluster now contains two particles and a correspondingly larger perimeter. This process is then repeated; a perimeter site is chosen at random, and a particle added at that location. We continue this process until a cluster of the desired size is obtained. This is the Eden model of cluster growth.

A typical Eden cluster is shown in Figure 7.22. While it is a little rough around the edges, it is basically a circular disc with a few holes. Note that as the cluster grows these holes tend to fill in, since they are treated on the same footing (they are equally likely to be occupied by the next particle) as the exterior perimeter sites.

The Eden model is sometimes referred to as a "cancer" model, because the clusters grow from within by expanding their borders. However, not all clusters grow in this manner. For example, snowflakes and soot particles grow by the addition of new particles that originate from outside the cluster.[25] This process is captured by a different cluster model, which is known as diffusion-limited aggregation, or DLA.

The growth rules for DLA clusters are as follows. We again start with a seed particle at the origin. We then release a particle at a randomly chosen location (x, y) that is some distance away from the seed and let it perform a random walk. If (or when) this walker lands on a perimeter site, it sticks there and becomes part of the cluster. This process is repeated with many walkers until a large cluster is grown. One way to motivate (or justify!) the choice of these growth rules is to consider how a large particle might be built up from smaller particles or molecules in a solution. If the cluster is located well away from any other objects, such as walls or other clusters, small particles will approach it from all

[25] More precisely, the places where new particles are added depend on processes that take place outside the cluster.