CHAPTER

15 Monte Carlo Simulations of Thermal Systems

We discuss how to simulate thermal systems using a variety of Monte Carlo methods including the traditional Metropolis algorithm. Applications to the Ising model and various particle systems are discussed and more efficient Monte Carlo algorithms are introduced.

15.1 ■ INTRODUCTION

The Monte Carlo simulation of the particles in the box problem discussed in Chapter 7 and the molecular dynamics simulations discussed in Chapter 8 have exhibited some of the important qualitative features of macroscopic systems such as the irreversible approach to equilibrium and the existence of equilibrium fluctuations in macroscopic quantities. In this chapter we apply various Monte Carlo methods to simulate the equilibrium properties of thermal systems. These applications will allow us to explore some of the important concepts of statistical mechanics.

Due in part to the impact of computer simulations, the applications of statistical mechanics have expanded from the traditional areas of dense gases, liquids, crystals, and simple models of magnetism to the study of complex materials, particle physics, and theories of the early universe. For example, the demon algorithm introduced in Section 15.3 was developed by a physicist interested in lattice gauge theories which are used to describe the interactions of fundamental particles.

15.2 ■ THE MICROCANONICAL ENSEMBLE

We first discuss an isolated system for which the number of particles N, the volume V, and the total energy E are fixed and external influences such as gravitational and magnetic fields can be ignored. The *macrostate* of the system is specified by the values of E, V, and N. At the microscopic level, there are many different ways or *configurations* in which the macrostate (E, V, N) can be realized. A particular configuration or *microstate* is accessible if its properties are consistent with the specified macrostate.

All we know about the accessible microstates is that their properties are consistent with the known physical quantities of the system. Because we have no reason to prefer one microstate over another when the system is in equilibrium, it is reasonable to postulate that the system is *equally* likely to be in any one of its accessible microstates. To make this postulate of *equal a priori probabilities* more precise, imagine an isolated system with Ω

accessible states. The probability P_s of finding the system in microstate s is

$$P_s = \begin{cases} 1/\Omega & \text{if } s \text{ is accessible} \\ 0 & \text{otherwise.} \end{cases} \tag{15.1}$$

The sum of P_s over all Ω states is equal to unity. Equation (15.1) is applicable only when the system is in equilibrium.

The averages of physical quantities can be determined in two ways. In the usual laboratory experiment, the physical quantities of interest are measured over a time interval long enough to allow the system to sample a large number of its accessible microstates. We computed such time averages in Chapter 8, where we used the method of molecular dynamics to compute the time-averaged values of quantities such as the temperature and pressure. An interpretation of the probabilities in (15.1) that is consistent with such a time average is that during a sequence of observations, P_s yields the fraction of times that a single system is found in a given microstate.

Although time averages are conceptually simple, it is convenient to imagine a collection or *ensemble* of systems that are identical mental copies characterized by the same macrostate but, in general, by different microstates. In this interpretation, the probabilities in (15.1) describe an ensemble of identical systems, and P_s is the probability that a system in the ensemble is in microstate s. An ensemble of systems specified by E, N, V is called a *microcanonical* ensemble. An advantage of ensembles is that statistical averages can be determined by sampling the states according to the desired probability distribution. Much of the power of Monte Carlo methods is that we can devise sampling methods based on a fictitious dynamics that is more efficient than the real dynamics.

Suppose that a physical quantity A has the value A_s when the system is in microstate s. Then the ensemble average of A is given by

$$\langle A \rangle = \sum_{s=1}^{\Omega} A_s P_s, \tag{15.2}$$

where P_s is given by (15.1).

To illustrate these ideas, consider a one-dimensional system of N noninteracting spins on a lattice. The spins can be in one of two possible directions which we take to be up or down. The total energy of the system is $E = -\mu B \sum_i s_i$, where each lattice site has associated with it a number $s_i = \pm 1$, where $s_i = +1$ for an up spin and $s_i = -1$ for a down spin; B is the magnetic field, and μ is the magnetic moment of a spin. A particular microstate of the system of spins is specified by the set of variables $\{s_1, s_2, \ldots, s_N\}$. In this case the macrostate of the system is specified by E and N.

In Table 15.1 we show the 16 microstates with $N = 4$. If the total energy $E = -2\mu B$, we see that there are four accessible microstates. Hence, in this case there are four systems in the ensemble each with an equal probability. The enumeration of the systems in the ensemble and their probability allows us to calculate ensemble averages for the physical quantities of interest.

Problem 15.1 A simple ensemble average

Consider a one-dimensional system of $N = 4$ noninteracting spins with total energy $E = -2\mu B$. What is the probability P_i that the ith spin is up? Does your answer depend on which spin you choose? ■