Chapter 17

Monte Carlo Simulation of the Canonical Ensemble

22 April 2002

We discuss Monte Carlo methods for simulating equilibrium systems. Applications are made to models of magnetism and simple fluids.

17.1 The Canonical Ensemble

Most physical systems are not isolated, but exchange energy with their environment. Because such systems are usually small in comparison to their environment, we assume that any change in the energy of the smaller system does not have a significant effect on the temperature of the environment. We say that the environment acts as a *heat reservoir* or *heat bath* at a fixed absolute temperature T. If a small but macroscopic system is placed in thermal contact with a heat bath, the system reaches thermal equilibrium by exchanging energy with the heat bath until the system attains the temperature of the bath.

Imagine an infinitely large number of copies of a system at fixed volume V and number of particles N in equilibrium at temperature T. In Chapter 16 we verified that P_s, the probability that the system is in microstate s with energy E_s, is given by

$$P_s = \frac{1}{Z} e^{-\beta E_s}, \text{(canonical distribution)} \tag{17.1}$$

where $\beta = 1/kT$, and Z is a normalization constant. The ensemble defined by (17.1) is known as the *canonical* ensemble. Because $\sum P_s = 1$, Z is given by

$$Z = \sum_{s=1}^{M} e^{-E_s/kT}. \tag{17.2}$$

The summation in (17.2) is over all M accessible microstates of the system. The quantity Z is known as the *partition function* of the system.

We can use (17.1) to obtain the ensemble average of the physical quantities of interest. For example, the mean energy is given by

$$\langle E \rangle = \sum_{s=1}^{M} E_s \, P_s = \frac{1}{Z} \sum_{s=1}^{M} E_s \, e^{-\beta E_s}. \tag{17.3}$$

Note that the energy fluctuates in the canonical ensemble.

17.2 The Metropolis Algorithm

How can we simulate a system of N particles confined in a volume V at a fixed temperature T? Because we can generate only a finite number m of the total number of M microstates, we might hope to obtain an estimate for the mean value of the physical quantity A by writing

$$\langle A \rangle \approx A_m = \frac{\sum_{s=1}^{m} A_s \, e^{-\beta E_s}}{\sum_{s=1}^{m} e^{-\beta E_s}}. \tag{17.4}$$

A_s is the value of the physical quantity A in microstate s. A crude Monte Carlo procedure is to generate a microstate s at random, calculate E_s, A_s, and $e^{-\beta E_s}$, and evaluate the corresponding contribution of the microstate to the sums in (17.4). However, a microstate generated in this way would likely be very improbable and hence contribute little to the sums. Instead, we use an *importance sampling* method and generate microstates according to a probability distribution function π_s.

We follow the same procedure as in Section 11.7 and rewrite (17.4) by multiplying and dividing by π_s:

$$A_m = \frac{\sum_{s=1}^{m} (A_s/\pi_s) \, e^{-\beta E_s} \, \pi_s}{\sum_{s=1}^{m} (1/\pi_s) \, e^{-\beta E_s} \, \pi_s}. \text{(no importance sampling)} \tag{17.5}$$

If we generate microstates with probability π_s, then (17.5) becomes

$$A_m = \frac{\sum_{s=1}^{m} (A_s/\pi_s) \, e^{-\beta E_s}}{\sum_{s=1}^{m} (1/\pi_s) \, e^{-\beta E_s}}. \text{(importance sampling)} \tag{17.6}$$

That is, if we average over a biased sample, we need to weight each microstate by $1/\pi_s$ to eliminate the bias. Although any form of π_s could be used, the form of (17.6) suggests that a reasonable choice of π_s is the Boltzmann probability itself, that is,

$$\pi_s = \frac{e^{-\beta E_s}}{\sum_{s=1}^{m} e^{-\beta E_s}}. \tag{17.7}$$

This choice of π_s implies that the estimate A_m of the mean value of A can be written as

$$A_m = \frac{1}{m}\sum_{s=1}^{m} A_s. \tag{17.8}$$

The choice (17.7) for π_s is due to Metropolis et al.

Although we discussed the Metropolis sampling method in Section 11.8 in the context of the numerical evaluation of integrals, it is not necessary to read Section 11.8 to understand the Metropolis algorithm in the present context. The Metropolis algorithm can be summarized in the context of the simulation of a system of spins or particles as follows:

1. Establish an initial microstate.
2. Make a random trial change in the microstate. For example, choose a spin at random and flip it. Or choose a particle at random and displace it a random distance.
3. Compute $\Delta E \equiv E_{\rm trial} - E_{\rm old}$, the change in the energy of the system due to the trial change.
4. If ΔE is less than or equal to zero, accept the new microstate and go to step 8.
5. If ΔE is positive, compute the quantity $w = e^{-\beta\Delta E}$.
6. Generate a random number r in the unit interval.
7. If $r \leq w$, accept the new microstate; otherwise retain the previous microstate.
8. Determine the value of the desired physical quantities.
9. Repeat steps (2) through (8) to obtain a sufficient number of microstates.
10. Periodically compute averages over microstates.

Steps 2 through 7 give the conditional probability that the system is in microstate $\{s_j\}$ given that it was in microstate $\{s_i\}$. These steps are equivalent to the transition probability

$$W(i \to j) = \min\left(1, e^{-\beta\Delta E}\right), \text{(Metropolis algorithm)} \tag{17.9}$$

where $\Delta E = E_j - E_i$. $W(i \to j)$ is the probability per unit time for the system to make a transition from microstate i to microstate j. Because it is necessary to evaluate only the ratio $P_j/P_i = e^{-\beta\Delta E}$, it is not necessary to normalize the probability. Note that because the microstates are generated with a probability proportional to the desired probability, all averages become arithmetic averages as in (17.8). However, because the constant of proportionally is not known, it is not possible to estimate the partition function Z in this way.

Although we choose π_s to be the Boltzmann distribution, other choices of π_s are possible and are useful in some contexts. In addition, the choice (17.9) of the transition probability is not the only one that leads to the Boltzmann distribution. It can be shown that if W satisfies the "detailed balance" condition

$$W(i \to j)\, e^{-\beta E_i} = W(j \to i)\, e^{-\beta E_j}, \text{(detailed balance)} \tag{17.10}$$

then the corresponding Monte Carlo algorithm generates a sequence of states distributed according to the Boltzmann distribution. The derivation that the Metropolis algorithm generates states with a probability proportional to the Boltzmann probability distribution after a sufficient number of steps does not add much to our physical understanding of the algorithm. Instead, in Section 17.2 we apply the algorithm to the ideal classical gas and to a classical magnet in a magnetic field, and verify that the Metropolis algorithm yields the Boltzmann distribution after a sufficient number of trial changes have been made.

We have implicitly assumed in the above discussion that the system is ergodic. Ergodicity refers to the sampling of the important microstates of a system. In a Monte Carlo simulation, the existence of ergodicity depends on the way the trial moves are made, and on the nature of the energy barriers between microstates. For example, consider a one-dimensional lattice of Ising spins with all spins up. If the spins are updated sequentially from right to left, then if one spin is flipped, all remaining flips will be accepted regardless of the temperature because the change in energy is zero. Clearly, the system is not ergodic for this implementation of the algorithm, and we would not obtain the correct thermodynamic behavior.

17.3 Verification of the Boltzmann Distribution

We first consider the application of the Metropolis algorithm to an ideal classical gas in one dimension. The energy of an ideal gas depends only on the velocity of the particles, and hence a microstate is completely described by a specification of the velocity (or momentum) of each particle. Because the velocity is a continuous variable, it is necessary to describe the accessible microstates so that they are countable, and hence we place the velocity into bins. Suppose we have $N = 10$ particles and divide the possible values of the velocity into twenty bins. Then the total number of microstates would be 20^{10}. Not only would it be difficult to label these 20^{10} states, it would take a prohibitively long time to obtain an accurate estimate of their relative probabilities, and it would be difficult to verify directly that the Metropolis algorithm yields the Boltzmann distribution. For this reason we consider a single classical particle in one dimension in equilibrium with a heat bath and adopt the less ambitious goal of verifying that the Metropolis algorithm generates the Boltzmann distribution for this system. The quantity of interest is the probability $P(v)\,dv$ that the system has a velocity between v and $v + dv$. The algorithm is implemented in `SUB metropolis` in `Program boltzmann` listed below. The array `P` stores the desired probability. We choose units such that Boltzmann's constant and the mass are unity.

```
PROGRAM boltzmann
! Metropolis algorithm for a particle in one dimension
DIM P(-100 to 100),accum(3)
CALL initial(v,E,beta,mcs,nequil,delta,nbin,delv)
FOR imcs = 1 to nequil            ! equilibrate system
    CALL metropolis(v,E,beta,delta,accept)
NEXT imcs
CALL initialize_sums(P(),accum(),accept,nbin)
FOR imcs = 1 to mcs
    CALL metropolis(v,E,beta,delta,accept)
```

```
    ! accumulate data after each trial change
    CALL data(P(),accum(),v,E,nbin,delv)
NEXT imcs
CALL output(P(),accum(),mcs,accept,nbin,delv)
END

SUB initial(v0,E0,beta,mcs,nequil,delta,nbin,delv)
    RANDOMIZE
    INPUT prompt "temperature = ": T
    LET beta = 1/T
    INPUT prompt "number of Monte Carlo steps = ": mcs
    LET nequil = int(0.1*mcs)
    INPUT prompt "initial speed = ": v0
    LET E0 = 0.5*v0*v0            ! initial kinetic energy
    INPUT prompt "maximum change in velocity = ": delta
    LET vmax = 10*sqr(T)
    LET nbin = 20                 ! number of bins
    LET delv = vmax/nbin          ! velocity interval
END SUB

SUB initialize_sums(P(),accum(),accept,nbin)
    FOR ibin = -nbin to nbin
        LET P(ibin) = 0
    NEXT ibin
    FOR i = 1 to 3
        LET accum(i) = 0
    NEXT i
    LET accept = 0
END SUB

SUB metropolis(v,E,beta,delta,accept)
    LET dv = (2*rnd - 1)*delta    ! trial velocity change
    LET vtrial = v + dv           ! trial velocity
    LET dE = 0.5*(vtrial*vtrial - v*v)      ! trial energy change
    IF dE > 0 then
       IF exp(-beta*dE) < rnd then
          EXIT SUB                ! step not accepted
       END IF
    END IF
    LET v = vtrial
    LET accept = accept + 1
    LET E = E + dE
END SUB

SUB data(P(),accum(),v,E,nbin,delv)
    LET accum(1) = accum(1) + E
```

```
    LET accum(2) = accum(2) + E*E
    LET accum(3) = accum(3) + v
    LET ibin = round(v/delv)
    LET P(ibin) = P(ibin) + 1
END SUB

SUB output(P(),accum(),mcs,accept,nbin,delv)
    LET accept = accept/mcs
    PRINT "acceptance probability ="; accept
    LET vave = accum(3)/mcs
    PRINT "mean velocity ="; vave
    LET Eave = accum(1)/mcs
    PRINT "mean energy ="; Eave
    LET E2ave = accum(2)/mcs
    LET sigma2 = E2ave - Eave*Eave
    PRINT "sigma_E = "; sqr(sigma2)
    PRINT
    PRINT " v ", "P(v)"
    PRINT
    LET v = -nbin*delv
    FOR ibin = -nbin to nbin
        IF p(ibin) > 0 then
           LET prob = p(ibin)/mcs
           PRINT v,
           PRINT using "--.###": prob
        END IF
        LET v = v + delv
    NEXT ibin
END SUB
```

Problem 17.1. The Boltzmann distribution

a. Use `Program boltzmann` to determine the form of the probability distribution that is generated by the Metropolis algorithm. Let the temperature $T = 4$, the initial velocity `v0` $= 0$, the maximum change in the particle's velocity $\delta = 4.0$, and the number of trial moves or Monte Carlo steps `mcs` $= 10000$. Compute the mean energy, the mean velocity, and the probability density $P(v)$.

b. Is $P(v)$ an increasing or decreasing function of the energy $E = \frac{1}{2}v^2$? Increase the number of Monte Carlo steps until the Boltzmann form of $P(v)$ is approximately verified. Verify that a plot of $\ln P(v)$ versus E yields a straight line with a slope equal to $-1/T$.

c. How do your results for the mean energy and the mean velocity compare with the corresponding exact values?

d. To insure that your results do not depend on the initial conditions, let `v0` $= 2$ and compute the mean energy and velocity. How do your results compare with those found in part (a)? Explain

why the computed mean particle velocity is approximately zero even though the initial particle velocities are not zero.

e. The *acceptance probability* is the fraction of trial moves that are accepted. What is the effect of changing the value of δ on the acceptance probability?

Problem 17.2. Planar spin in an external magnetic field

a. Consider a classical planar magnet with magnetic moment μ_0. The magnet can be oriented in any direction in the x-y plane, and the energy of interaction of the magnet with an external magnetic field $\mathbf{B}$ is $-\mu_0 B \cos\phi$, where ϕ is the angle between the moment and $\mathbf{B}$. What are the possible microstates of this system? Write a Monte Carlo program to sample the microstates of this system in thermal equilibrium with a heat bath at temperature T. Compute the mean energy as a function of the ratio $\beta\mu_0 B$.

b. Do an analytical calculation of the mean energy and compare the analytical and computed results for various values of $\beta\mu_0 B$.

c. Compute the probability density $P(\phi)$ and analyze its dependence on the energy.

In Problem 17.3 we consider the Monte Carlo simulation of a classical ideal gas of N particles. It is convenient to say that one "time unit" or one "Monte Carlo step per particle" (MCS) has elapsed after N particles have had one chance each on the average to change their coordinates. If the particles are chosen at random, then during one Monte Carlo step per particle, some particles might not be chosen. Of course, all particles will be chosen equally on the average. The advantage of this definition is that the time is independent of the number of particles. However, this definition of time has no obvious relation to a physical time.

Problem 17.3. Simulation of an ideal gas in one dimension

a. Modify `Program boltzmann` to simulate an ideal gas of N particles in one dimension. Assume all particles have the same initial velocity `v0` $= 10$. Let $N = 20$, $T = 10$, and `mcs` $= 200$. Choose the value of δ so that the acceptance probability is approximately 40%. What is the mean kinetic energy and mean velocity of the particles?

b. We might expect the total energy of an ideal gas to remain constant because the particles do not interact with one another and hence cannot exchange energy directly. What is the value of the initial total energy of the system in part (a)? Does the total energy remain constant? If not, explain how the energy changes.

c. What is the nature of the time dependence of the total energy starting from the initial condition in (a)? Estimate the number of Monte Carlo steps per particle necessary for the system to reach thermal equilibrium by computing a moving average of the total energy over a fixed time interval. Does this average change with time after a sufficient time has elapsed? What choice of the initial velocities allows the system to reach thermal equilibrium at temperature T as quickly as possible?

d. Compute the probability $P(E)\,dE$ for the system of N particles to have a total energy between E and $E + dE$. Do you expect $\ln P(E)$ to depend linearly on E? Plot $P(E)$ as a function of E

and describe the qualitative behavior of $P(E)$. If the plot of $\ln P(E)$ versus E does not yield a straight line, describe the qualitative features of the plot, and determine a functional form for $P(E)$.

e. Compute the mean energy for $T = 10, 20, 40, 80$, and 120 and estimate the heat capacity from its definition $C = \partial E/\partial T$.

f. Compute the mean square energy fluctuations $\langle(\Delta E)^2\rangle = \langle E^2\rangle - \langle E\rangle^2$ for $T = 10$ and $T = 40$. Compare the magnitude of the ratio $\langle(\Delta E)^2\rangle/T^2$ with the heat capacity determined in part (e).

You might have been surprised to find in Problem 17.3d that the form of $P(E)$ is a Gaussian centered about the mean energy of the system. That is, the distribution function of a *macroscopic* quantity such as the total energy is sharply peaked about its mean value. If the microstates are distributed according to the Boltzmann probability, why is the total energy distributed according to the Gaussian distribution?

17.4 The Ising Model

One of the more interesting natural phenomena in nature is magnetism. You are probably familiar with ferromagnetic materials such as iron and nickel which exhibit a spontaneous magnetization in the absence of an applied magnetic field. This nonzero magnetization occurs only if the temperature is lower than a well defined temperature known as the Curie or critical temperature T_c. For temperatures $T > T_c$, the magnetization vanishes. Hence T_c separates the disordered phase for $T > T_c$ from the ferromagnetic phase for $T < T_c$.

The origin of magnetism is quantum mechanical in nature and an area of much experimental and theoretical interest. However, the study of simple classical models of magnetism has provided much insight. The two- and three-dimensional Ising model is the most commonly studied classical model and is particularly useful in the neighborhood of the magnetic phase transition. As discussed in Chapter 16, the energy of the Ising model is given by

$$E = -J \sum_{i,j=\mathrm{nn}(i)}^{N} s_i s_j - \mu_0 B \sum_{i=1}^{N} s_i, \tag{17.11}$$

where $s = \pm 1$, J is a measure of the strength of the interaction between spins, and the first sum is over all pairs of spins that are nearest neighbors. The second term in (17.11) is the energy of interaction of the magnetic moment with an external magnetic field. Because of the neglect of the other spin components, the Ising model does not give a complete description of ferromagnetism, especially at temperatures well below T_c.

The thermal quantities of interest for the Ising model include the mean energy $\langle E\rangle$ and the heat capacity C. As we have discussed, one way to determine C at constant external magnetic field is from its definition $C = \partial\langle E\rangle/\partial T$. An alternative way of determining C is to relate it to the statistical fluctuations of the total energy in the canonical ensemble (see Appendix 17.31):

$$C = \frac{1}{kT^2}\left(\langle E^2\rangle - \langle E\rangle^2\right). \tag{17.12}$$

Another quantity of interest is the mean magnetization $\langle M \rangle$ (see (16.7)) and the corresponding thermodynamic derivative χ:

$$\chi = \lim_{H \to 0} \frac{\partial \langle M \rangle}{\partial H}, \tag{17.13}$$

where H is proportional to the external magnetic field. In the following, we will refer to H as the magnetic field. The zero field magnetic susceptibility χ is an example of a linear response function, because it measures the ability of a spin to "respond" due to a change in the external magnetic field. In analogy to the heat capacity, χ is related to the fluctuations of the magnetization (see Appendix 17.31):

$$\chi = \frac{1}{kT}\big(\langle M^2 \rangle - \langle M \rangle^2\big), \tag{17.14}$$

where $\langle M \rangle$ and $\langle M^2 \rangle$ are evaluated in zero magnetic fields. Relations (17.12) and (17.14) are examples of the general relation between linear response functions and equilibrium fluctuations.

Now that we have specified several equilibrium quantities of interest, we implement the Metropolis algorithm for the Ising model. The possible trial change is the flip of a spin, $s_i \to -s_i$. The Metropolis algorithm was stated in Section 17.2 as a method for generating states with the desired Boltzmann probability, but the flipping of single spins also can be interpreted as a reasonable approximation to the real dynamics of an anisotropic magnet whose spins are coupled to the vibrations of the lattice. The coupling leads to random spin flips, and we expect that one Monte Carlo step per spin is proportional to the average time between single spin flips observed in the laboratory. We can regard single spin flip dynamics as a time dependent process and observe the relaxation to equilibrium after a sufficiently long time. In the following, we will frequently refer to the application of the Metropolis algorithm to the Ising model as "single spin flip dynamics."

In Problem 17.4 we use the Metropolis algorithm to simulate the one-dimensional Ising model. Note that the parameters J and kT do not appear separately, but appear together in the dimensionless ratio J/kT. Unless otherwise stated, we measure temperature in units of J/k, and set $H = 0$.

Problem 17.4. One-dimensional Ising model

a. Write a Monte Carlo program to simulate the one-dimensional Ising model in equilibrium with a heat bath. (Modify `SUB changes` in `Program demon` (see Chapter 16) or see `Program ising`, listed in the following, for an example of the implementation of the Metropolis algorithm to the two-dimensional Ising model.) Use periodic boundary conditions. As a test of your program, compute the mean energy and magnetization of the lattice for $N = 20$ and $T = 1$. Draw the microscopic state (configuration) of the system after each Monte Carlo step per spin.

b. Choose $N = 20$, $T = 1$, `mcs` $= 100$, and all spins up, that is, $s_i = +1$ initially. What is the initial "temperature" of the system? Visually inspect the configuration of the system after each Monte Carlo step and estimate the time it takes for the system to reach equilibrium. Then change the initial condition so that the orientation of the spins is chosen at random. What is the initial "temperature" of the system in this case? Estimate the time it takes for the system to reach equilibrium in the same way as before.

c. Choose $N = 20$ and equilibrate the system for `mcs` ≥ 100. Let `mcs` ≥ 1000 and determine $\langle E\rangle$, $\langle E^2\rangle$, $\langle M\rangle$, and $\langle M^2\rangle$ as a function of T in the range $0.1 \leq T \leq 5$. Plot $\langle E\rangle$ as a function of T and discuss its qualitative features. Compare your computed results for $\langle E(T)\rangle$ to the exact result (for $H = 0$)

$$\langle E\rangle = -N \tanh \beta J. \tag{17.15}$$

Use the relation (17.12) to determine the T dependence of C.

d. What is the qualitative dependence of $\langle M\rangle$ on T? Use the relation (17.14) to estimate the T dependence of χ. One of the best laboratory realizations of a one-dimensional Ising ferromagnet is a chain of bichloride-bridged Fe^{2+} ions known as FeTAC (Greeney et al.). Measurements of χ yield a value of the exchange interaction J given by $J/k = 17.4\,\mathrm{K}$. (Experimental values of J are typically given in temperature units.) Use this value of J to plot your Monte Carlo results for χ versus T with T given in Kelvin. At what temperature is χ a maximum for FeTAC?

e. Is the acceptance probability an increasing or decreasing function of T? Does the Metropolis algorithm become more or less efficient as the temperature is lowered?

f. Compute the probability density $P(E)$ for a system of 50 spins at $T = 1$. Choose `mcs` ≥ 1000. Plot $\ln P(E)$ versus $(E - \langle E\rangle)^2$ and discuss its qualitative features.

We next apply the Metropolis algorithm to the two-dimensional Ising model on the square lattice. The main program is listed in the following.

```
PROGRAM ising
! Monte Carlo simulation of the Ising model on the square lattice
! using the Metropolis algorithm
DIM spin(32,32),w(-8 to 8),accum(10)
LIBRARY "csgraphics"
CALL initial(N,L,T,spin(,),mcs,nequil,w(),E,M)
FOR i = 1 to nequil          ! equilibrate system
    CALL Metropolis(N,L,spin(,),E,M,w(),accept)
NEXT i
CALL initialize(accum(),accept)
FOR pass = 1 to mcs          ! accumulate data while updating spins
    CALL Metropolis(N,L,spin(,),E,M,w(),accept)
    CALL data(E,M,accum())
NEXT pass
CALL output(T,N,mcs,accum(),accept)
END
```

In `SUB initial` we choose the initial directions of the spins, and compute the initial values of the energy and magnetization. To compute the total energy, we consider the interaction of a spin with its nearest neighbor spins to the north and the east. In this way we compute the energy of each interaction only once and avoid double counting. One of the most time consuming parts of the Metropolis algorithm is the calculation of the exponential function $e^{-\beta\Delta E}$. Because there are only a small number of possible values of $\beta\Delta E$ for the Ising model (see Fig. 16.3), we store the

small number of different probabilities for the spin flips in the array w. The values of this array are computed in SUB initial.

```
SUB initial(N,L,T,spin(,),mcs,nequil,w(),E,M)
    RANDOMIZE
    INPUT prompt "linear dimension of lattice = ": L
    LET N = L*L                    ! number of spins
    ! temperature measured in units of J/k
    INPUT prompt "temperature = ": T
    INPUT prompt "# MC steps per spin for equilibrium = ": nequil
    INPUT prompt "# MC steps per spin for data = ": mcs
    LET M = 0
    FOR y = 1 to L                 ! random initial configuration
        FOR x = 1 to L
            IF rnd < 0.5 then
               LET spin(x,y) = 1   ! spin up
            ELSE
               LET spin(x,y) = -1
            END IF
            LET M = M + spin(x,y)      ! total magnetization
        NEXT x
    NEXT y
    LET E = 0
    FOR y = 1 to L                 ! compute initial energy
        IF y = L then
           LET up = 1              ! periodic boundary conditions
        ELSE
           LET up = y + 1
        END IF
        FOR x = 1 to L
            IF x = L then
               LET right = 1
            ELSE
               LET right = x + 1
            END IF
            LET sum = spin(x,up) + spin(right,y)
            LET E = E - spin(x,y)*sum  ! total energy
        NEXT x
    NEXT y
    ! compute Boltzmann probability ratios
    FOR dE = -8 to 8 step 4
        LET w(dE) = exp(-dE/T)
    NEXT dE
END SUB
```

One way to implement the Metropolis algorithm is to determine the change in the energy ΔE

and then accept the trial flip if $\Delta E \leq 0$. If this condition is not satisfied, the second step is to generate a random number in the unit interval and compare it to $e^{-\beta \Delta E}$. Instead of this two step process, we implement the Metropolis algorithm in one step. Which method do you think is faster?

```
SUB Metropolis(N,L,spin(,),E,M,w(),accept)
    DECLARE DEF DeltaE
    ! one Monte Carlo step per spin
    FOR ispin = 1 to N
        LET x = int(L*rnd + 1)    ! random x coordinate
        LET y = int(L*rnd + 1)    ! random y coordinate
        LET dE = DeltaE(x,y,L,spin(,))      ! compute change in energy
        IF rnd <= w(dE) then
           LET spin(x,y) = -spin(x,y)  ! flip spin
           LET accept = accept + 1
           LET M = M + 2*spin(x,y)
           LET E = E + dE
        END IF
    NEXT ispin
END SUB
```

A typical laboratory system has at least 10^{18} spins. In contrast, the number of spins that can be simulated typically ranges from 10^3 to 10^9. As we have discussed in other contexts, the use of periodic boundary conditions minimizes finite size effects. However, periodic boundary conditions reduce the maximum separation between spins to one half the length of the system, and more sophisticated boundary conditions are sometimes convenient. For example, we can give the surface spins extra neighbors, whose direction is related to the mean magnetization of the microstate. We adopt the simpler periodic boundary conditions in `FUNCTION DeltaE` in which the change in energy `dE` of flipping a spin is computed.

```
FUNCTION DeltaE(x,y,L,spin(,))
    ! periodic boundary conditions
    IF x = 1 then
       LET left = spin(L,y)
    ELSE
       LET left = spin(x - 1,y)
    END IF
    IF x = L then
       LET right = spin(1,y)
    ELSE
       LET right = spin(x + 1,y)
    END IF
    IF y = 1 then
       LET down = spin(x,L)
    ELSE
       LET down = spin(x,y - 1)
    END IF
```

```
    IF y = L then
       LET up = spin(x,1)
    ELSE
       LET up = spin(x,y + 1)
    END IF
    LET DeltaE = 2*spin(x,y)*(left + right + up + down)
END DEF
```

SUB data is called from the main program and the values of the physical observables are recorded after each Monte Carlo step per spin. The optimum time for sampling various physical quantities is explored in Problem 17.6. Note that if a flip is rejected and the old configuration is retained, thermal equilibrium is not described properly unless the old configuration is included again in computing the averages. Various variables are initialized in SUB initialize.

```
SUB initialize(accum(),accept)
    ! use array to save accumulated values of magnetization and
    ! energy. Array used to make it easier to add other quantities
    FOR i = 1 to 5
        LET accum(i) = 0
    NEXT i
    LET accept = 0
END SUB

SUB data(E,M,accum())
    ! accumulate data after every Monte Carlo step per spin
    LET accum(1) = accum(1) + E
    LET accum(2) = accum(2) + E*E
    LET accum(3) = accum(3) + M
    LET accum(4) = accum(4) + M*M
    LET accum(5) = accum(5) + abs(M)
END SUB
```

At the end of a run various averages are normalized and printed in SUB output. All averages such as the mean energy and the mean magnetization are normalized by the number of spins.

```
SUB output(T,N,mcs,accum(),accept)
    LET norm = 1/(mcs*N)          ! averages per spin
    LET accept = accept*norm
    LET eave = accum(1)*norm
    LET e2ave = accum(2)*norm
    LET mave = accum(3)*norm
    LET m2ave = accum(4)*norm
    LET abs_mave = accum(5)*norm
    CLEAR
    SET BACKGROUND COLOR "black"
    SET COLOR "yellow"
```

```
    PRINT "temperature = "; T
    PRINT "acceptance probability = "; accept
    PRINT "mean energy per spin = "; eave
    PRINT "mean squared energy per spin = "; e2ave
    PRINT "mean magnetization per spin = "; mave
    PRINT "mean of absolute magnetization per spin = "; abs_mave
    PRINT "mean squared magnetization per spin = "; m2ave
END SUB
```

Achieving thermal equilibrium can account for a substantial fraction of the total run time. The most practical choice of initial conditions is a configuration from a previous run that is at a temperature close to the desired temperature. The following subroutine saves the last configuration of a run and can be included at the end of the main loop in `Program ising`.

```
SUB save_config(N,L,T,spin(,))
    INPUT prompt "name of file for last configuration = ": file$
    OPEN #2: name file$, access output, create new
    PRINT #2: T
    FOR y = 1 to L
        FOR x = 1 to L
            PRINT #2: spin(x,y)
        NEXT x
    NEXT y
    CLOSE #2
END SUB
```

A previous configuration can be used in a later run by adding a few statements to `SUB initial` to allow the user to choose a previous configuration or a random configuration. A previous configuration can be read by calling the following subroutine:

```
SUB read_config(N,L,T,spin(,))
    INPUT prompt "filename?": file$
    OPEN #1: name file$, access input
    INPUT #1: T
    FOR y = 1 to L
        FOR x = 1 to L
            INPUT #1: spin(x,y)
        NEXT x
    NEXT y
    CLOSE #1
END SUB
```

Problem 17.5. Equilibration of the two-dimensional Ising model

a. Run `Program ising` with the linear dimension of the lattice $L = 16$ and the heat bath temperature $T = 2$. Determine the time, `nequil`, needed to equilibrate the system, if the directions of the spins are initially chosen at random. Plot the values of E and M after each Monte Carlo

step per spin. Estimate how many Monte Carlo steps per spin are necessary for the system to reach equilibrium.

b. Write a subroutine that shows the spin configurations on the screen. One simple way to do so is to draw a solid square about each spin site and color code the orientation of the spins. Is the system "ordered" or "disordered" at $T = 2$ after equilibrium has been established?

c. Repeat part (a) with all spins initially up. Does the equilibration time increase or decrease?

d. Repeat parts (a)–(c) for $T = 2.5$.

Problem 17.6. Comparison with exact results

In general, a Monte Carlo simulation yields exact answers only after an infinite number of configurations have been sampled. How then can we be sure our program works correctly, and our results are statistically meaningful? One check is to ensure that our program can reproduce exact results in known limits. In the following, we test `Program ising` by considering a small system for which the mean energy and magnetization can be calculated analytically.

a. Calculate analytically the T dependence of E, M, C and χ for the two-dimensional Ising model with $L = 2$ and periodic boundary conditions. (A summary of the calculation is given in Appendix 17.31.)

b. Use `Program ising` with $L = 2$ and estimate E, M, C, and χ for $T = 0.5$ and 0.25. Use the relations (17.12) and (17.14) to compute C and χ, respectively. Compare your estimated values to the exact results found in part (a). Approximately how many Monte Carlo steps per spin are necessary to obtain E and M to within 1%? How many Monte Carlo steps per spin are necessary to obtain C and χ to within 1%?

Now that we have checked our program and obtained typical equilibrium configurations, we consider the calculation of the mean values of the physical quantities of interest. Suppose we wish to compute the mean value of the physical quantity A. In general, the calculation of A is time consuming, and we do not want to compute its value more often than necessary. For example, we would not compute A after the flip of only one spin, because the values of A in the two configurations would almost be the same. Ideally, we wish to compute A for configurations that are statistically independent. Because we do not know *a priori* the mean number of spin flips needed to obtain configurations that are statistically independent, it is a good idea to estimate this time in our preliminary calculations.

One way to estimate the time interval over which configurations are correlated is to compute the time displaced *autocorrelation* function $C_A(t)$ defined as

$$C_A(t) = \frac{\langle A(t+t_0)A(t_0)\rangle - \langle A\rangle^2}{\langle A^2\rangle - \langle A\rangle^2}. \tag{17.16}$$

$A(t)$ is the value of the quantity A at time t. The averages in (17.16) are over all possible time origins t_0 for an equilibrium system. Because the choice of the time origin is arbitrary for an equilibrium system, C_A depends only on the time difference t rather than t and t_0 separately. For sufficiently large t, $A(t)$ and $A(0)$ will become uncorrelated, and hence $\langle A(t+t_0)A(t_0)\rangle \rightarrow$

$\langle A(t+t_0)\rangle\langle A(t_0)\rangle = \langle A\rangle^2$. Hence $C_A(t) \to 0$ as $t \to \infty$. In general, $C_A(t)$ will decay exponentially with t with a decay or correlation time τ_A whose magnitude depends on the choice of the physical quantity A as well as the physical parameters of the system, for example, the temperature. Note that $C_A(t=0)$ is normalized to unity.

The time dependence of the two most common correlation functions, $C_M(t)$ and $C_E(t)$ is investigated in Problem 17.7. As an example of the calculation of $C_E(t)$, consider the equilibrium time series for E for the $L = 4$ Ising model at $T = 4$: -4, -8, 0, -8, -20, -4, 0, 0, -24, -32, -24, -24, -8, -8, -16, -12. The averages of E and E^2 over these sixteen values are $\langle E\rangle = -12$, $\langle E^2\rangle = 240$, and $\langle E^2\rangle - \langle E\rangle^2 = 96$. We wish to compute $E(t)E(0)$ for all possible choices of the time origin. For example, $E(t=4)E(0)$ is given by

$$\begin{aligned}\langle E(t=4)E(0)\rangle = \frac{1}{12}\big[&(-20\times -4)+(-4\times -8)+(0\times 0)\\ &+(0\times -8)+(-24\times -20)+(-32\times -4)\\ &+(-24\times 0)+(-24\times 0)+(-8\times -24)\\ &+(-8\times -32)+(-16\times -24)+(-12\times -24)\big].\end{aligned} \tag{17.17}$$

We averaged over the twelve possible choices of the origin for the time difference $t = 4$. Verify that $\langle E(t=4)E(0)\rangle = 460/3$ and $C_E(t=4) = 7/72$.

In the above calculation of $\langle E(t)E(0)\rangle$, we included all possible combinations of $E(t)E(0)$ for a given time series. To implement this procedure on a computer, we would need to store the time series in memory or in a data file. An alternative procedure is to save the last `nsave` values of the time series in memory and to average over fewer combinations. This procedure is implemented in `SUB correl`; the correlation functions are computed and printed in `SUB c_output`. `SUB correl` uses two arrays, `Esave` and `Msave`, to store the last `nsave` values of the energy and the magnetization at each Monte Carlo step per spin. These arrays and the arrays `Ce` and `Cm` may be initialized in a separate subroutine.

```
SUB correl(Ce(),Cm(),E,M,esave(),msave(),pass,nsave)
    ! accumulate data for time correlation functions
    ! save last nsave values of M and E
    ! index0 = array index for earliest saved time
    IF pass > nsave then
       ! compute Ce and Cm after nsave values are saved
       LET index0 = mod(pass-1,nsave) + 1
       LET index = index0
       FOR tdiff = nsave to 1 step -1
           LET Ce(tdiff) = Ce(tdiff) + E*esave(index)
           LET Cm(tdiff) = Cm(tdiff) + M*msave(index)
           LET index = index + 1
           IF index > nsave then LET index = 1
       NEXT tdiff
    END IF
    ! save latest value in array position of earliest value
    LET esave(index0) = E
    LET msave(index0) = M
```

```
END SUB

SUB c_output(N,Ce(),Cm(),accum(),mcs,nsave)
    ! compute time correlation functions
    LET ebar = accum(1)/mcs
    LET e2bar = accum(2)/mcs
    LET Ce(0) = e2bar - ebar*ebar
    LET mbar = accum(3)/mcs
    LET m2bar = accum(4)/mcs
    LET Cm(0) = m2bar - mbar*mbar
    LET norm = 1/(mcs - nsave)
    PRINT
    PRINT "t","Ce(t)","Cm(t)"
    PRINT
    FOR tdiff = 1 to nsave
        ! correlation functions defined so that C(t=0) = 1
        ! and C(infinity) = 0
        LET Ce(tdiff) = (Ce(tdiff)*norm - ebar*ebar)/Ce(0)
        LET Cm(tdiff) = (Cm(tdiff)*norm - mbar*mbar)/Cm(0)
        PRINT tdiff,Ce(tdiff),Cm(tdiff)
    NEXT tdiff
END SUB
```

Problem 17.7. Correlation times

a. Choose $L = 4$ and $T = 3$ and equilibrate the system. Then look at the time series of M and E after every Monte Carlo step per spin and estimate how often M changes sign. Does E change sign when M changes sign? How often does M change sign for $L = 8$ (and $T = 3$)? In equilibrium, positive and negative values of M are equally likely in the absence of an external magnetic field. Is your time series consistent with this equilibrium property? Why is it more meaningful to compute the time displaced correlation function of the absolute value of the magnetization rather than the magnetization itself if L is relatively small?

b. Choose $L = 16$ and $T = 1$ and equilibrate the system. Then look at the time series of M. Do you find that positive and negative values of M are equally likely? Explain your results.

c. Modify `Program ising` so that the equilibrium averaged values of $C_M(t)$ and $C_E(t)$ are computed. As a check on your program, use the time series for E given in the text to do a hand calculation of $C_E(t)$ in the way that it is computed in `SUB correl` and `SUB c_output`. Choose `nsave` $= 10$.

d. Estimate the correlation times from the energy and the magnetization correlation functions for $L = 8$, and $T = 3$, $T = 2.3$, and $T = 2$. Save the last `nsave` $= 100$ values of the magnetization and energy only after the system is equilibrated. Are the correlation times τ_M and τ_E comparable? One way to determine τ is to fit $C(t)$ to an assumed exponential form $C(t) \sim e^{-t/\tau}$. Another way is to define the integrated correlation time as

$$\tau = \sum_{t=1} C(t). \tag{17.18}$$

The sum is cut off at the first negative value of $C(t)$. Are the negative values of $C(t)$ physically meaningful? How does the behavior of $C(t)$ change if you average your results over longer runs? How do your estimates for the correlation times compare with your estimates of the relaxation time found in Problem 17.5? Why would the term "decorrelation time" be more appropriate than "correlation time?"

e. To describe the relaxation towards equilibrium as realistically as possible, we have randomly selected the spins to be flipped. However, if we are interested only in equilibrium properties, it might be possible to save computer time by selecting the spins sequentially. Determine if the correlation time is greater, smaller, or approximately the same if the spins are chosen sequentially rather than randomly. If the correlation time is greater, does it still save CPU time to choose spins sequentially? Why is it not desirable to choose spins sequentially in the one-dimensional Ising model?

Problem 17.8. Estimate of errors

How can we quantify the accuracy of our measurements, for example, the accuracy of the mean energy $\langle E\rangle$? As discussed in Chapter 11, the usual measure of the accuracy is the standard deviation of the mean. If we make n independent measurements of E, then the most probable error is given by

$$\sigma_m = \frac{\sigma}{\sqrt{n-1}}, \tag{17.19}$$

where the standard deviation σ is defined as

$$\sigma^2 = \langle E^2\rangle - \langle E\rangle^2. \tag{17.20}$$

The difficulty is that, in general, our measurements of the time series E_i are not independent, but are correlated. Hence, σ_m as given by (17.19) is an underestimate of the actual error.

How can we determine whether the measurements are independent without computing the correlation time? One way is based on the idea that the magnitude of the error should not depend on how we group the data. For example, suppose that we group every two data points to form $n/2$ new data points $E_i^{(2)}$ given by $E_i^{(g=2)} = (1/2)[E_{2i-1} + E_{2i}]$. If we replace n by $n/2$ and E by $E^{(2)}$ in (17.19) and (17.20), we would find the same value of σ_m as before provided that the original E_i are independent. If the computed σ_m is not the same, we continue this averaging process until σ_m calculated from

$$E_i^{(g)} = \frac{1}{2}[E_{2i-1}^{(g/2)} + E_{2i}^{(g/2)}] \qquad (g = 2, 4, 8, \dots) \tag{17.21}$$

is approximately the same as that calculated from $E^{(g/2)}$.

a. Use the above averaging method to estimate the errors in your measurements of $\langle E\rangle$ and $\langle M\rangle$ for the two-dimensional Ising model. Let $L = 8$, $T = 2.269$, and `mcs` ≥ 16384, and calculate averages after every Monte Carlo step per spin after the system has equilibrated. If necessary, increase the number of Monte Carlo steps for averaging. A rough measure of the correlation time is the number of terms in the time series that need to be averaged for σ_m to be approximately unchanged. What is the qualitative dependence of the correlation time on $T - T_c$?

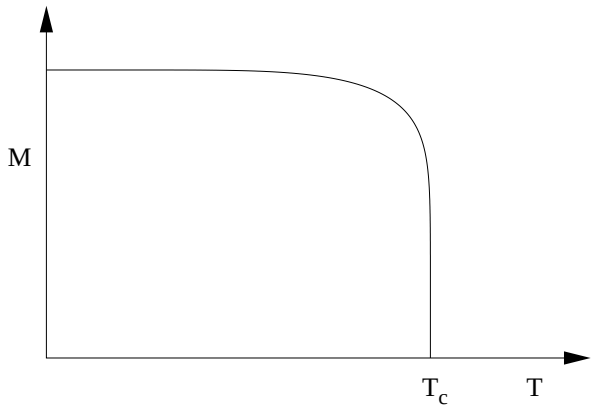

Figure 17.1: The temperature dependence of $m(T)$, the mean magnetization per spin, for the infinite lattice Ising model in two dimensions.

b. Repeat for $L = 16$. Do you need more Monte Carlo steps than in part (a) to obtain statistically independent data? If so, why?

c. The exact value of E/N for the two-dimensional Ising model on a square lattice with $L = 16$ and $T = T_c = 2/\ln(1+\sqrt{2}) \approx 2.269$ is given by $E/N = -1.45306$ (to five decimal places). This value of T_c is exact for the infinite lattice. The exact result for E/N allows us to determine the actual error in this case. Compute $\langle E \rangle$ by averaging E after each Monte Carlo step per spin for `mcs` $\geq 10^6$. Compare your actual error to the estimated error given by (17.19) and (17.20) and discuss their relative values.

17.5 The Ising Phase Transition

Now that we have tested our program for the two-dimensional Ising model, we are ready to explore its properties. We first summarize some of the qualitative properties of infinite ferromagnetic systems in zero magnetic field. We know that at $T = 0$, the spins are perfectly aligned in either direction, that is, the mean magnetization per spin $m(T) = \langle M(T) \rangle / N$ is given by $m(T = 0) = \pm 1$. As T is increased, the magnitude of $m(T)$ decreases continuously until $T = T_c$ at which $m(T)$ vanishes (see Fig. 17.1). Because $m(T)$ vanishes continuously rather than abruptly, the transition is termed *continuous* rather than discontinuous. (The term *first-order* describes a discontinuous transition.)

How can we characterize a continuous magnetic phase transition? Because a nonzero m implies that a net number of spins are spontaneously aligned, we designate m as the *order parameter* of the system. Near T_c, we can characterize the behavior of many physical quantities by power law behavior just as we characterized the percolation threshold (see Table 13.1). For example, we can

write m near T_c as

$$m(T) \sim (T_c - T)^{\beta}, \tag{17.22}$$

where β is a critical exponent (not to be confused with the inverse temperature). Various thermodynamic derivatives such as the susceptibility and heat capacity diverge at T_c. We write

$$\chi \sim |T - T_c|^{-\gamma} \tag{17.23}$$

and

$$C \sim |T - T_c|^{-\alpha}. \tag{17.24}$$

We have assumed that χ and C are characterized by the same critical exponents above and below T_c.

Another measure of the magnetic fluctuations is the linear dimension $\xi(T)$ of a typical magnetic domain. We expect the *correlation length* $\xi(T)$ to be the order of a lattice spacing for $T \gg T_c$. Because the alignment of the spins becomes more correlated as T approaches T_c from above, $\xi(T)$ increases as T approaches T_c. We can characterize the divergent behavior of $\xi(T)$ near T_c by the critical exponent ν:

$$\xi(T) \sim |T - T_c|^{-\nu}. \tag{17.25}$$

The calculation of ξ is considered in Problem 17.9d.

As we found in our discussion of percolation in Chapter 13, a finite system cannot exhibit a true phase transition. Nevertheless, we expect that if $\xi(T)$ is less than the linear dimension L of the system, our simulations will yield results comparable to an infinite system. Of course, if T is close to T_c, our simulations will be limited by finite size effects. In the following problem, we obtain preliminary results for the T dependence of m, $\langle E \rangle$, C, and χ in the neighborhood of T_c. These results will help us understand the qualitative nature of the ferromagnetic phase transition in the two-dimensional Ising model.

Because we will consider the Ising model for different values of L, it will be convenient to compute intensive quantities such as the mean energy per spin, the specific heat (per spin) and the susceptibility per spin. We will retain the same notation for both the extensive and corresponding intensive quantities.

Problem 17.9. Qualitative behavior of the two-dimensional Ising model

a. Use `Program ising` to compute the magnetization per spin m, the mean energy per spin $\langle E \rangle$, the specific heat C, and the susceptibility per spin χ. Choose $L = 4$ and consider T in the range $1.5 \leq T \leq 3.5$ in steps of $\Delta T = 0.2$. Choose the initial condition at $T = 3.5$ so that the orientation of the spins is chosen at random. Use an equilibrium configuration from a previous run at temperature T as the initial configuration for a run at temperature $T - \Delta T$. Because all the spins might overturn and the magnetization change sign during the course of your observation, estimate the mean value of $|m|$ in addition to that of m. Use at least 1000 Monte Carlo steps per spin and estimate the number of equilibrium configurations needed to obtain m and $\langle E \rangle$ to 5% accuracy. Plot $\langle E \rangle$, m, $|m|$, C, and χ as a function of T and describe their qualitative behavior. Do you see any evidence of a phase transition?

b. Repeat the calculations of part (a) for $L = 8$ and $L = 16$. Plot $\langle E \rangle$, m, $|m|$, C, and χ as a function of T and describe their qualitative behavior. Do you see any evidence of a phase transition? For comparison, recent published Monte Carlo results for the two-dimensional Ising model are in the range $L = 10^2$ to $L = 10^3$ with order 10^6 Monte Carlo steps per spin.

c. For a given value of L, for example, $L = 16$, choose a value of T that is well below T_c and choose the directions of the spins at random. Observe the spins evolve in time. Do you see several domains with positive and negative spontaneous magnetization? How does the magnetization evolve with time?

d. The correlation length ξ can be obtained from the r-dependence of the spin correlation function $c(r)$. The latter is defined as:

$$c(r) = \langle s_i s_j \rangle - m^2, \tag{17.26}$$

where r is the distance between sites i and j. We have assumed the system is translationally invariant so that $\langle s_i \rangle = \langle s_j \rangle = m$. The average is over all sites for a given configuration and over many configurations. Because the spins are not correlated for large r, we see that $c(r) \to 0$ in this limit. It is reasonable to assume that $c(r) \sim e^{-r/\xi}$ for r sufficiently large. Use this behavior to estimate ξ as a function of T. How does your estimate of ξ compare with the size of the regions of spins with the same orientation?

One of the limitations of a computer simulation study of a phase transition is the relatively small size of the systems we can study. Nevertheless, we observed in Problem 17.9 that even systems as small as $L = 4$ exhibit behavior that is reminiscent of a phase transition. In Fig. 17.2 we show our Monte Carlo data for the T dependence of the specific heat of the two-dimensional Ising model for $L = 8$ and $L = 16$. We see that C exhibits a broad maximum which becomes sharper for larger L. Does your data for C exhibit similar behavior?

Because we can simulate only finite lattices, it is difficult to obtain estimates for the critical exponents α, β, and γ by using the definitions (17.22)–(17.24) directly. We learned in Section 13.4, we can do a *finite size scaling analysis* to extrapolate finite L results to $L \to \infty$. For example, from Fig. 17.2 we see that the temperature at which C exhibits a maximum becomes better defined for larger lattices. This behavior provides a simple definition of the transition temperature $T_c(L)$ for a finite system. According to finite size scaling theory, $T_c(L)$ scales as

$$T_c(L) - T_c(L = \infty) \sim aL^{-1/\nu}, \tag{17.27}$$

where a is a constant and ν is defined in (17.25). The finite size of the lattice is important when the correlation length

$$\xi(T) \sim L \sim |T - T_c|^{-\nu}. \tag{17.28}$$

As in Section 13.4, we can set $T = T_c$ and consider the L-dependence of M, C, and χ:

$$m(T) \sim (T_c - T)^{\beta} \to L^{-\beta/\nu} \tag{17.29}$$

$$C(T) \sim |T - T_c|^{-\alpha} \to L^{\alpha/\nu} \tag{17.30}$$

$$\chi(T) \sim |T - T_c|^{-\gamma} \to L^{\gamma/\nu}. \tag{17.31}$$

In Problem 17.10 we use the relations (17.29)–(17.31) to estimate the critical exponents β, γ, and α.

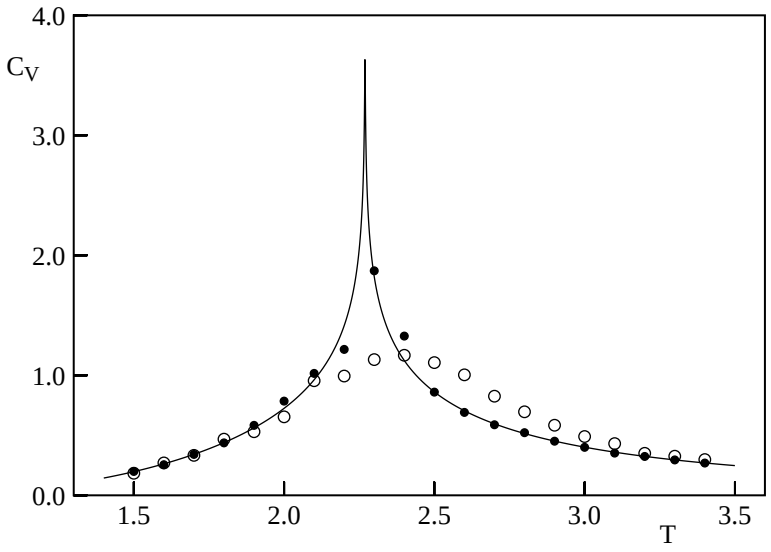

Figure 17.2: The temperature dependence of the specific heat C (per spin) of the Ising model on a $L = 8$ and $L = 16$ square lattice with periodic boundary conditions. One thousand Monte Carlo steps per spin were used for each value of the temperature. The continuous line represents the temperature dependence of C in the limit of an infinite lattice. (Note that C is infinite at $T = T_c$ for an infinite lattice.)

Problem 17.10. Finite size scaling and the critical properties of the two-dimensional Ising model

a. Use the relation (17.27) together with the exact result $\nu = 1$ to estimate the value of T_c on an infinite square lattice. Because it is difficult to obtain a precise value for T_c with small lattices, we will use the exact result $kT_c/J = 2/\ln(1+\sqrt{2}) \approx 2.269$ for the infinite lattice in the remaining parts of this problem.

b. Determine the specific heat C, $|m|$, and the susceptibility χ at $T = T_c$ for $L = 2$, 4, 8, and 16. Use as many Monte Carlo steps per spin as possible. Plot the logarithm of $|m|$ and χ versus L and use the scaling relations (17.29)–(17.31) to determine the critical exponents β and γ. Assume the exact result $\nu = 1$. Do your log-log plots of $|m|$ and χ yield reasonably straight lines? Compare your estimates for β and γ with the exact values given in Table 13.1.

c. Make a log-log plot of C versus L. If your data for C is sufficiently accurate, you will find that the log-log plot of C versus L is not a straight line but shows curvature. The reason for this curvature is that α in (17.24) equals zero for the two-dimensional Ising model, and hence (17.30) needs to be interpreted as

$$C \sim C_0 \ln L. \tag{17.32}$$

Is your data for C consistent with (17.32)? The constant C_0 in (17.32) is approximately 0.4995.

So far we have performed our Ising model simulations on the square lattice. How do the critical temperature and the critical exponents depend on the symmetry and the dimension of the lattice? Based on your experience with the percolation transition in Chapter 13, you might have a good idea what the answer is.

Problem 17.11. The effects of symmetry and dimension on the critical properties of the Ising model

a. The nature of the triangular lattice is discussed in Chapter 8 (see Fig. 8.5). The main difference between the triangular lattice and the square lattice is the number of nearest neighbors. Make the necessary modifications in your Ising program, for example, determine the possible transitions and the values of the transition probabilities. Compute C and χ for different values of T in the interval $[1, 5]$. Assume that $\nu = 1$ and use finite size scaling to estimate T_c in the limit of an infinite triangular lattice. Compare your estimate of T_c to the known value $kT_c/J = 3.641$ (to three decimal places). The simulation of Ising models on the triangular lattice is relevant to the understanding of the experimentally observed phases of materials that can be absorbed on the surface of graphite.

b. No exact results are available for the Ising model in three dimensions. Write a Monte Carlo program to simulate the Ising model on the simple cubic lattice (six nearest neighbors). Compute C and χ for T in the range $3.2 \leq T \leq 5$ in steps of 0.2 for different values of L. Estimate $T_c(L)$ from the maximum of C and χ. How do these estimates of $T_c(L)$ compare? Use the values of $T_c(L)$ that exhibit a stronger L dependence and plot $T_c(L)$ versus $L^{-1/\nu}$ for different values of ν in the range 0.5 to 1 (see (17.27)). Show that the extrapolated value of $T_c(L = \infty)$ does not depend sensitively on the value of ν. Compare your estimate for $T_c(L = \infty)$ to the known value $kT_c/J = 4.5108$ (to four decimal places).

c. Compute $|m|$, C, and χ at $T = T_c \approx 4.5108$ for different values of L on a simple cubic lattice. Do a finite size scaling analysis to estimate β/ν, α/ν, and γ/ν. The best known values of the critical exponents for the three-dimensional Ising model are given in Table 13.1. For comparison, published Monte Carlo results in 1976 for the finite size behavior of the Ising model on the simple cubic Ising lattice are for $L = 6$ to $L = 20$; 2000–5000 Monte Carlo steps per spin were used for calculating the averages after equilibrium had been reached.

Problem 17.12. Critical slowing down

a. Consider the two-dimensional Ising model on a square lattice with $L = 16$. Compute $C_M(t)$ and $C_E(t)$ and determine the correlation times τ_M and τ_E for $T = 2.5, 2.4$, and 2.3. Determine the correlation times as discussed in Problem 17.7d. How do these correlation times compare with one another? Show that τ increases as the critical temperature is approached, a physical effect known as *critical slowing down*.

b. We can define the dynamical critical exponent z by the relation

$$\tau \sim \xi^z. \tag{17.33}$$

On a finite lattice we have the relation $\tau \sim L^z$ at $T = T_c$. Compute τ for different values of L at $T = T_c$ and make a very rough estimate of z. (The value of z for the two-dimensional Ising model with spin flip dynamics is still not definitely known, but appears to be slightly greater than 2.)

The magnitude of τ found in parts (a) and (b) depends in part on our choice of dynamics. Although we have generated a trial change by the attempted flip of one spin, it is possible that other types of trial changes, for example, the simultaneous flip of more than one spin, would be more efficient and lead to smaller correlation times and smaller values of z. A problem of much current interest is the development of more efficient algorithms near phase transitions (see Project 17.23).

17.6 Other Applications of the Ising Model

Because the applications of the Ising model are so wide ranging, we can mention only a few of the applications here. In the following, we briefly describe applications of the Ising model to first-order phase transitions, lattice gases, antiferromagnetism, and the order-disorder transition in binary alloys.

So far we have discussed the continuous phase transition in the Ising model and have found that the energy and magnetization vary continuously with the temperature, and thermodynamic derivatives such as the specific heat and the susceptibility diverge near T_c (in the limit of an infinite lattice). In Problem 17.13 we discuss a simple example of a *first-order* phase transition. Such transitions are accompanied by *discontinuous* (finite) changes in thermodynamic quantities such as the energy and the magnetization.

Problem 17.13. The two-dimensional Ising model in an external magnetic field

a. Modify your two-dimensional Ising program so that the energy of interaction with an external magnetic field H is included. It is convenient to measure H in terms of the quantity $h = \beta H$. We wish to compute m, the mean magnetization per spin, as a function of h for $T < T_c$. Consider a square lattice with $L = 16$ and equilibrate the system at $T = 1.8$ and $h = 0$. Adopt the following procedure to obtain $m(h)$.

   i. Use an equilibrium configuration at $h = 0$ as the initial configuration for $h_1 = \Delta h = 0.2$.

   ii. Run the system for 100 Monte Carlo steps per spin before computing averages.

   iii. Average m over 80 Monte Carlo steps per spin.

   iv. Use the last configuration for h_n as the initial configuration for $h_{n+1} = h_n + \Delta h$.

   v. Repeat steps (ii)–(iv) until $m \approx 0.95$. Plot m versus h. Do the measured values of m correspond to equilibrium averages?

b. Decrease h by $\Delta h = -0.2$ in the same way as in part (a) until h passes through zero and until $m \approx -0.95$. Extend your plot of m versus h to negative h values. Does m remain positive for small negative h? Do the measured values of m for negative h correspond to equilibrium averages? Draw the spin configurations for several values of h. Do you see evidence of domains?

c. Increase h by $\Delta h = 0.2$ until the m versus h curve forms an approximately closed loop. What is the value of m at $h = 0$? This value of m is the spontaneous magnetization.

d. A first-order phase transition is characterized by a discontinuity (for an infinite lattice) in the order parameter. In the present case the transition is characterized by the behavior of m as a function of h. What is your measured value of m for $h = 0.2$? If $m(h)$ is double valued, which value of m corresponds to the equilibrium state, an absolute minima in the free energy? Which value of m corresponds to a *metastable* state, a relative minima in the free energy? What are the equilibrium and metastable values of m for $h = -0.2$? The transition from positive m to negative m is first-order because there is a discontinuous jump in the magnetization. First-order transitions exhibit *hysteresis* and the properties of the system depend on the history of the system, for example, whether h is an increasing or decreasing function. Because of the long lifetime of metastable states near a phase transition, a system in such a state can mistakenly be interpreted as being in equilibrium. We also know that near a continuous phase transition, the relaxation to equilibrium becomes very long (see Problem 17.12), and hence a system with a continuous phase transition can behave as if it were effectively in a metastable state. For these reasons it is very difficult to distinguish the nature of a phase transition using computer simulations. This problem is discussed further in Section 17.8.

e. Repeat the above simulation for $T = 3$, a temperature above T_c. Why do your results differ from the simulations in parts (a)–(c) done for $T < T_c$?

The Ising model also describes systems that might appear to have little in common with ferromagnetism. For example, we can interpret the Ising model as a "lattice gas," where "down" represents a lattice site occupied by a molecule and "up" represents an empty site. Each lattice site can be occupied by at most one molecule, and the molecules interact with their nearest neighbors. The lattice gas is a crude model of the behavior of a real gas of molecules and is a simple lattice model of the gas-liquid transition and the critical point. What properties does the lattice gas have in common with a real gas? What properties of real gases does the lattice gas neglect?

If we wish to simulate a lattice gas, we have to decide whether to do the simulation at fixed density or at fixed chemical potential μ. The implementation of the latter is straightforward because the grand canonical ensemble for a lattice gas is equivalent to the canonical ensemble for Ising spins in an external magnetic field H, that is, the effect of the magnetic field is to fix the mean number of up spins. Hence, we can simulate a lattice gas in the grand canonical ensemble by doing spin flip dynamics. (The volume of the lattice is an irrelevant parameter.)

Another application of a lattice gas model is to the study of phase separation in a binary or A-B alloy. In this case spin up and spin down correspond to a site occupied by an A atom and B atom, respectively. As an example, the alloy β-brass has a low temperature ordered phase in which the two components (copper and zinc) have equal concentrations and form a cesium chloride structure. As the temperature is increased, some zinc atoms exchange positions with copper atoms, but the system is still ordered. However, above the critical temperature $T_c = 742\,\mathrm{K}$, the zinc and copper atoms become mixed and the system is disordered. This transition is an example of an *order-disorder* transition.

Because the number of A atoms and the number of B atoms is fixed, we cannot use spin flip dynamics to simulate a binary alloy. A dynamics that does conserve the number of down and up spins is known as *spin exchange dynamics.* In this dynamics a trial *interchange* of two nearest neighbor spins is made and the change in energy ΔE is calculated. The criterion for the acceptance or rejection of the trial change is the same as before.

Problem 17.14. Simulation of a lattice gas

a. Modify your Ising program so that spin exchange dynamics rather than spin flip dynamics is implemented. For example, determine the possible values of ΔE on the square lattice, determine the possible values of the transition probability, and change the way a trial change is made. If we are interested only in the mean value of quantities such as the total energy, we can reduce the computation time by not interchanging like spins. For example, we can keep a list of bonds between occupied and empty sites and make trial moves by choosing bonds at random from this list. For small lattices such a list is unnecessary and a trial move can be generated by simply choosing a spin and one of its nearest neighbors at random.

b. Consider a square lattice with $L = 8$ and with 32 sites initially occupied. (The number of occupied sites is a conserved variable and must be specified initially.) Determine the mean energy for T in the range $1 \leq T \leq 4$. Plot the mean energy as a function of T. Does the energy appear to vary continuously?

c. Repeat the calculations of part (b) with 44 sites initially occupied, and plot the mean energy as a function of T. Does the energy vary continuously? Do you see any evidence of a first-order phase transition?

d. Because the spins correspond to molecules, we can compute the single particle diffusion coefficient of the molecules. (See Problem 12.5 for a similar simulation.) Use an array to record the position of each molecule as a function of time. After equilibrium has been reached, compute $\langle R(t)^2 \rangle$, the mean square displacement per molecule. Is it necessary to "interchange" two like spins? If the atoms undergo a random walk, the self-diffusion constant D is defined as

$$D = \lim_{t \to \infty} \frac{1}{2dt} \langle R(t)^2 \rangle. \tag{17.34}$$

Estimate D for different temperatures and numbers of occupied sites.

Although you are probably familiar with ferromagnetism, for example, a magnet on a refrigerator door, nature provides more examples of antiferromagnetism. In the language of the Ising model, antiferromagnetism means that the interaction parameter J is negative and nearest neighbor spins prefer to be aligned in opposite directions. As we will see in Problem 17.15, the properties of the antiferromagnetic Ising model on a square lattice are similar to the ferromagnetic Ising model. For example, the energy and specific heat of the ferromagnetic and antiferromagnetic Ising models are identical at all temperatures in zero magnetic field, and the system exhibits a phase transition at the Néel temperature T_N. On the other hand, the total magnetization and susceptibility of the antiferromagnetic model do not exhibit any critical behavior near T_N. Instead, we can define two sublattices for the square lattice corresponding to the red and black squares of a checkerboard and introduce the "staggered magnetization" M_s equal to the difference of the magnetization on the two sublattices. We will find in Problem 17.15 that the temperature dependence of M_s and the staggered susceptibility χ_s are identical to the analogous quantities in the ferromagnetic Ising model.

Problem 17.15. Antiferromagnetic Ising model

a. Modify `Program ising` to simulate the antiferromagnetic Ising model on the square lattice in zero magnetic field. Because J does not appear explicitly in `Program ising`, change the sign of the energy calculations in the appropriate places in the program. To compute the staggered magnetization on a square lattice, define one sublattice to be the sites (x, y) for which the product $\texttt{mod}(x, 2) \times \texttt{mod}(y, 2) = 1$; the other sublattice corresponds to the remaining sites.

b. Choose $L = 16$ and the initial condition to be all spins up. What configuration of spins corresponds to the state of lowest energy? Compute the temperature dependence of the mean energy, specific heat, magnetization, and the susceptibility χ. Does the temperature dependence of any of these quantities show evidence of a phase transition?

c. Compute the temperature dependence of M_s and the staggered susceptibility χ_s defined as (see (17.14))

$$\chi_s = \frac{1}{kT}\left[\langle {M_s}^2\rangle - \langle M_s\rangle^2\right]. \tag{17.35}$$

Verify that the temperature dependence of M_s for the antiferromagnetic Ising model is the same as the temperature dependence of M for the Ising ferromagnet. Could you have predicted this similarity without doing the simulation?

d. In part (b) you might have noticed that χ shows a cusp. Compute χ for different values of L at $T = T_N \approx 2.269$. Do a finite size scaling analysis and verify that χ does not diverge at $T = T_N$.

e. Consider the behavior of the antiferromagnetic Ising model on a triangular lattice. Choose $L \geq 16$ and compute the same quantities as before. Do you see any evidence of a phase transition? Draw several configurations of the system at different temperatures. Do you see evidence of many small domains at low temperatures? Is there a unique ground state? If you cannot find a unique ground state, you share the same frustration as do the individual spins in the antiferromagnetic Ising model on the triangular lattice. We say that this model exhibits *frustration* because there is no spin configuration on the triangular lattice such that all spins are able to minimize their energy (see Fig. 17.3).

The Ising model is one of many models of magnetism. The Heisenberg, Potts, and x-y models are other examples of models of magnetic materials familiar to condensed matter scientists as well as to workers in other areas. Monte Carlo simulations of these models and others have been important in the development of our understanding of phase transitions in both magnetic and nonmagnetic materials. Some of these models are discussed in Section 17.11.

17.7 Simulation of Classical Fluids

The existence of matter as a solid, liquid and gas is well known (see Fig. 17.4). Our goal in this section is to use Monte Carlo methods to gain additional insight into the qualitative differences between these three phases.

Monte Carlo simulations of classical systems are simplified considerably by the fact that the velocity (momentum) variables are decoupled from the position variables. The total energy can be written as $E = K(\{\mathbf{v}_i\}) + U(\{\mathbf{r}_i\})$, where the kinetic energy K is a function of only the particle

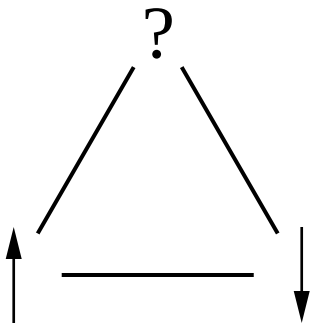

Figure 17.3: An example of frustration on a triangular lattice.

velocities $\{\mathbf{v}_i\}$, and the potential energy U is a function of only the particle positions $\{\mathbf{r}_i\}$. Because the velocity appears quadratically in the kinetic energy, the equipartition theorem implies that the contribution of the velocity coordinates to the mean energy is $\frac{1}{2}kT$ per degree of freedom. Hence, we need to sample only the positions of the molecules, that is, the "configurational" degrees of freedom. Is such a simplification possible for quantum systems?

The physically relevant quantities of a fluid include its mean energy, specific heat and equation of state. Another interesting quantity is the *radial distribution function* $g(r)$ which we introduced in Chapter 8. We will find in Problems 17.16–17.18 that $g(r)$ is a probe of the density fluctuations and hence a probe of the local order in the system. If only two-body forces are present, the mean potential energy per particle can be expressed as (see (**??**))

$$\frac{U}{N} = \frac{\rho}{2}\int g(r)V(r)\,d\mathbf{r}, \tag{17.36}$$

and the (virial) equation of state can be written as (see (8.15))

$$\frac{\beta P}{\rho} = 1 - \frac{\beta\rho}{2d}\int g(r)\,r\frac{dV(r)}{dr}\,d\mathbf{r}. \tag{17.37}$$

Hard core interactions. To separate the effects of the short range repulsive interaction from the longer range attractive interaction, we first investigate a model of *hard disks* with the interparticle interaction

$$V(r) = \begin{cases} +\infty & r < \sigma \\ 0 & r \geq \sigma. \end{cases} \tag{17.38}$$

Such an interaction has been extensively studied in one dimension (hard rods), two dimensions (hard disks), and in three dimensions (hard spheres). Hard sphere systems were the first systems studied by Metropolis and coworkers.

Because there is no attractive interaction present in (17.38), there is no transition from a gas to a liquid. Is there a phase transition between a fluid phase at low densities and a solid at high

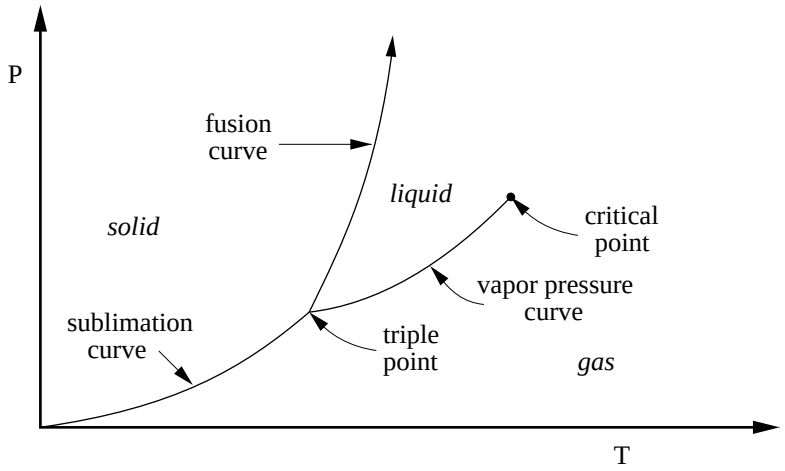

Figure 17.4: A sketch of the phase diagram for a simple material.

densities? Can a solid form in the absence of an attractive interaction? What are the physically relevant quantities for a system with an interaction of the form (17.38)? There are no thermal quantities such as the mean potential energy because this quantity is always zero. The major quantity of interest is $g(r)$ which yields information on the correlations of the particles and the equation of state. If the interaction is given by (17.38), it can be shown that (17.37) reduces to

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3}\rho\sigma^3 g(\sigma) \qquad (d = 3) \tag{17.39a}$$

$$= 1 + \frac{\pi}{2}\rho\sigma^2 g(\sigma) \qquad (d = 2) \tag{17.39b}$$

$$= 1 + \rho\sigma g(\sigma). \qquad (d = 1) \tag{17.39c}$$

We will calculate $g(r)$ for different values of r and then extrapolate our results to $r = \sigma$ (see Problem 17.16b).

Because the application of molecular dynamics and Monte Carlo methods to hard disks is similar, we discuss the latter method only briefly and do not include a program here. The idea is to choose a disk at random and move it to a trial position as implemented in the following:

```
LET itrial = int(N*rnd) + 1
LET xtrial = x(itrial) + (2*rnd - 1)*delta
LET ytrial = y(itrial) + (2*rnd - 1)*delta
```

If the new position overlaps another disk, the move is rejected and the old configuration is retained; otherwise the move is accepted. A reasonable, although not necessarily optimum, choice for the maximum displacement δ is to choose δ such that approximately one half of all trial states are accepted. We also need to fix the maximum amplitude of the move so that the moves are equally probable in all directions.

The major difficulty in implementing this algorithm is determining the overlap of two particles. If the number of particles is not too large, it is sufficient to compute the distances between the trial particle and all the other particles rather than the smaller number of particles that are in the immediate vicinity of the trial particle. For larger systems this procedure is too time consuming, and it is better to divide the system into cells and to only compute the distances between the trial particle and particles in the same and neighboring cells.

The choice of initial positions for the disks is more complicated than it might first appear. One strategy is to place each successive disk at random in the box. If a disk overlaps one that is already present, generate another pair of random numbers and attempt to place the disk again. If the desired density is low, an acceptable initial configuration can be computed fairly quickly in this way, but if the desired density is high, the probability of adding a disk will be very small (see Problem 17.17a). To reach higher densities, we might imagine beginning with the desired number of particles in a low density configuration and moving the boundaries of the central cell inward until a boundary just touches one of the disks. Then the disks are moved a number of Monte Carlo steps and the boundaries are moved inward again. This procedure also becomes more difficult as the density increases. The most efficient procedure is to start the disks on a lattice at the highest density of interest such that no overlap of disks occurs.

We first consider a one-dimensional system of hard rods for which the equation of state and $g(r)$ can be calculated exactly. The equation of state is given by

$$\frac{P}{NkT} = \frac{1}{L - N\sigma}. \tag{17.40}$$

Because hard rods cannot pass through one another, the excluded volume is $N\sigma$ and the available volume is $L - N\sigma$. Note that this form of the equation of state is the same as the van der Waals equation of state (cf. Reif) with the contribution from the attractive part of the interaction equal to zero.

Problem 17.16. Monte Carlo simulation of hard rods

a. Write a program to do a Monte Carlo simulation of a system of hard rods. Adopt the periodic boundary condition and refer to `Program hd` in Chapter 8 for the basic structure of the program. The major difference is the nature of the "moves." Measure all lengths in terms of the hard rod diameter σ. Choose $L = 12$ and $N = 10$. How does the number density $\rho = N/L$ compare to the maximum possible density? Choose the initial positions to be on a one-dimensional grid and let the maximum displacement $\delta = 0.1$. Approximately how many Monte Carlo steps per particle are necessary to reach equilibrium? What is the equilibrium acceptance probability? Compute the pair correlation function $g(x)$.

b. Plot $g(x)$ as a function of the distance x. Why does $g(x) = 0$ for $x < 1$? Why are the values of $g(x)$ for $x > L/2$ not meaningful? What is the physical interpretation of the peaks in $g(x)$? Note that the results for $g(x)$ are for $x > 1$ because none of the hard disks are in contact in the configurations generated by the Monte Carlo algorithm. (Recall that x is measured in units of σ.) Because the mean pressure can be determined from $g(x)$ at $x = 1^+$ (see (17.39)), we need to determine $g(x)$ at contact by extrapolating your results for $g(x)$ to $x = 1$. An easy way to do so is to fit the three points of $g(x)$ closest to $x = 1$ to a parabola. Use your result for $g(x = 1^+)$ to determine the mean pressure.

c. Compute $g(x)$ at several lower densities by using an equilibrium configuration from a previous run and increasing L. How do the size and the location of the peaks in $g(x)$ change?

Problem 17.17. Monte Carlo simulation of hard disks

a. What is the maximum packing density of hard disks, that is, how many disks can be packed together in a cell of area A? The maximum packing density can be found by placing the disks on a triangular lattice with the nearest neighbor distance equal to the disk diameter. Write a simple program that adds disks at random into a rectangular box of area $A = L_x \times L_y$ with the constraint that no two disks overlap. If a disk overlaps a disk already present, generate another pair of random numbers and try to place the disk again. If the density is low, the probability of adding a disk is high, but if the desired density is high most of the disks will be rejected. For simplicity, do not worry about periodic boundary conditions and accept a disk if its center lies within the box. Choose $L_x = 6$ and $L_y = \sqrt{3}L_x/2$ and determine the maximum density $\rho = N/A$ that you can attain in a reasonable amount of CPU time. How does this density compare to the maximum packing density? What is the qualitative nature of the density dependence of the acceptance probability?

b. Adapt your Monte Carlo program for hard rods to a system of hard disks. Begin at a density ρ slightly lower than the maximum packing density ρ_0. Choose $N = 16$ with $L_x = 4.41$ and $L_y = \sqrt{3}L_x/2$. Compare the density $\rho = N/(L_xL_y)$ to the maximum packing density. Choose the initial positions of the particles to be on a triangular lattice. A reasonable first choice for the maximum displacement δ is $\delta = 0.1$. Compute $g(r)$ for $\rho/\rho_0 = 0.95, 0.92, 0.88, 0.85, 0.80, 0.70, 0.60,$ and 0.30. Keep the ratio of L_x/L_y fixed and save a configuration from the previous run to be the initial configuration of the new run at lower ρ. Allow at least 400 Monte Carlo steps per particle for the system to equilibrate and average $g(r)$ for `mcs` ≥ 400.

c. What is the qualitative behavior of $g(r)$ at high and low densities? For example, describe the number and height of the peaks of $g(r)$. If the system is crystalline, then $g(\mathbf{r})$ is not spherically symmetric. How would you compute $g(\mathbf{r})$ in this case and what would you expect to see?

d. Use your results for $g(r = 1^+)$ to compute the mean pressure P as a function of ρ (see (17.39b)). Plot the ratio PV/NkT as a function of ρ, where the "volume" V is the area of the system. How does the temperature T enter into the Monte Carlo simulation? Is the ratio PV/NkT an increasing or decreasing function of ρ? At low densities we might expect the system to act like an ideal gas with the volume replaced by $(V - N\sigma)$. Compare your low density results with this prediction.

e. Take "snapshots" of the disks at intervals of ten to twenty Monte Carlo steps per particle. Do you see any evidence of the solid becoming a fluid at lower densities?

f. Compute an "effective diffusion coefficient" D by determining the mean square displacement $\langle R^2(t)\rangle$ of the particles after equilibrium is reached. Use the relation (17.34) and identify the time t with the number of Monte Carlo steps per particle. Estimate D for the densities considered in part (a), and plot the product ρD as a function of ρ. What is the dependence of D on ρ for a dilute gas? Try to identify a range of ρ where D drops abruptly. Do you observe any evidence of a phase transition?

g. The magnitude of the maximum displacement parameter δ is arbitrary. If δ is large and the density is high, then a high proportion of the trial moves will be rejected. On the other hand, if δ is too small, the acceptance probability will be close to unity, but the successive configurations will be strongly correlated. Hence if δ is too large or is too small, our simulation is inefficient. In practice, δ is usually chosen so that approximately half of the moves are accepted. A better criterion might be to choose δ so that the mean square displacement is a maximum for a fixed time interval. The idea is that the mean square displacement is a measure of the exploration of phase space. Fix the density and determine the value of δ that maximizes $\langle R^2(t)\rangle$. What is the corresponding acceptance probability? If this probability is much less than 50%, how can you decide which criterion for δ is more appropriate?

Continuous potentials. Our simulations of hard disks have led us to conclude that there is a phase transition from a fluid at low densities to a solid at higher densities. This conclusion is consistent with molecular dynamics and Monte Carlo studies of larger systems. Although the existence of a fluid-solid transition for hard sphere and hard disk systems is well accepted, the relatively small numbers of particles used in any simulation should remind us that results of this type cannot be taken as evidence independently of any theoretical justification.

The existence of a fluid-solid transition for hard spheres implies that the transition is primarily determined by the repulsive part of the potential. We now consider a system with both a repulsive and an attractive contribution. Our primary goal will be to determine the influence of the attractive part of the potential on the structure of a liquid.

We adopt as our model interaction the Lennard-Jones potential:

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{17.41}$$

The nature of the Lennard-Jones potential and the appropriate choice of units for simulations was discussed in Chapter 8 (see Table 8.1). We consider in Problem 17.18 the application of the Metropolis algorithm to a system of N particles in a rectangular cell of fixed "volume" V interacting via the Lennard-Jones potential. Because the simulation is at fixed T, V, and N, the simulation samples configurations of the system according to the Boltzmann distribution (17.1).

Problem 17.18. Monte Carlo simulation of a Lennard-Jones system

a. The properties of a two-dimensional Lennard-Jones system with the potential energy of interaction (17.41) have been studied by many workers under a variety of conditions. Write a program to compute the total energy of a system of N particles on a triangular lattice of area $L_x \times L_y$ with periodic boundary conditions. Choose $N = 16, L_x = 4.6$, and $L_y = \sqrt{3}L_x/2$. Why does this energy correspond to the energy at temperature $T = 0$? Does the energy per particle change if you consider bigger systems at the same density?

b. Write a program to compute the mean energy, pressure, and radial distribution function using the Metropolis algorithm. One way of computing the change in the potential energy of the system due to a trial move of one of the particles is to use an array, `pe`, for the potential energy of interaction of each particle. For simplicity, compute the potential energy of particle `i` by considering its interaction with the other $N - 1$ particles. The total potential energy of the system is the sum of the array elements `pe(i)` over all N particles divided by two to account

for double counting. For simplicity, accumulate data after each Monte Carlo step per particle. A reasonable choice for the bin width `dr` for the calculation of $g(r)$ is `dr` $= 0.1$.

c. Choose the same values of N, L_x, and L_y as in part (a), but give each particle an initial random displacement from its triangular lattice site of magnitude 0.2. Do the Monte Carlo simulation at a very low temperature such as $T = 0.1$. Choose the maximum trial displacement $\delta = 0.15$ and consider `mcs` ≥ 400. Does the system retain its hexagonal symmetry? Does the value of δ affect your results?

d. Use the same initial conditions as in part (a), but take $T = 0.5$. Choose $\delta = 0.15$ and run for a number of Monte Carlo steps per particle that is sufficient to yield a reasonable result for the mean energy. Do a similar simulation at $T = 1$ and $T = 2$. What is the best choice of the initial configuration in each case? The harmonic theory of solids predicts that the total energy of a system is due to a $T = 0$ contribution plus a term due to the harmonic oscillation of the atoms. The contribution of the latter part should be proportional to the temperature. Compare your results for $E(T) - E(0)$ with this prediction. Use the values of σ and ϵ given in Table 8.1 to determine the temperature and energy in SI units for your simulations of solid argon.

e. Describe the qualitative nature of $g(r)$ for a Lennard-Jones solid and compare it with your hard disk results for the same density.

f. Decrease the density by multiplying L_x, L_y, and all the particle coordinates by 1.07. What is the new value of ρ? Estimate the number of Monte Carlo steps per particle needed to compute E and P for $T = 0.5$ to approximately 10% accuracy. Is the total energy positive or negative? How do E and P compare to their ideal gas values? Follow the method discussed in Problem 17.17 and compute an effective diffusion constant. Is the system a liquid or a solid? Plot $g(r)$ versus r and compare $g(r)$ to your results for hard disks at the same density. What is the qualitative behavior of $g(r)$? What is the interpretation of the peaks in $g(r)$ in terms of the structure of the liquid? If time permits, consider a larger system at the same density and temperature and compute $g(r)$ for larger r.

g. Consider the same density system as in part (f) at $T = 0.6$ and $T = 1$. Look at some typical configurations of the particles. Use your results for $E(T)$, $P(T)$, $g(r)$ and the other data you have collected, and discuss whether the system is a gas, liquid, or solid at these temperatures. What criteria can you use to distinguish a gas from a liquid? If time permits, repeat these calculations for $\rho = 0.7$.

h. Compute E, P, and $g(r)$ for $N = 16$, $L_x = L_y = 10$, and $T = 3$. These conditions correspond to a dilute gas. How do your results for P compare with the ideal gas result? How does $g(r)$ compare with the results you obtained for the liquid?

17.8 *Optimized Monte Carlo Data Analysis

As we have seen, the important physics near a phase transition occurs on long length scales. For this reason, we might expect that simulations, which for practical reasons are restricted to relatively small systems, might not be useful for simulations near a phase transition. Nevertheless, we have found that methods such as finite size scaling can yield information about how systems behave

in the thermodynamic limit. We next explore some additional Monte Carlo techniques that are useful near a phase transition.

The Metropolis algorithm yields mean values of various thermodynamic quantities, for example, the energy, at particular values of the temperature T. Near a phase transition many thermodynamic quantities change rapidly, and we need to determine these quantities at many closely spaced values of T. If we were to use standard Monte Carlo methods, we would have to do many simulations to cover the desired range of values of T. To overcome this problem, we introduce the use of *histograms* which allow us to extract more information from a single Monte Carlo simulation. The idea is to use our knowledge of the equilibrium probability distribution at one value of T (and other external parameters) to estimate the desired thermodynamic averages at neighboring values of the external parameters.

The first step of the single histogram method for the Ising model is to simulate the system at an inverse temperature β_0 which is near the values of β of interest and measure the energy of the system after every Monte Carlo step per spin (or other fixed interval). The measured probability that the system has energy E can be expressed as

$$P(E,\beta_0) = \frac{H_0(E)}{\sum_E H_0(E)}. \tag{17.42}$$

The histogram $H_0(E)$ is the number of configurations with energy E, and the denominator is the total number of measurements of E (for example, the number of Monte Carlo steps per spin). Because the probability of a given configuration is given by the Boltzmann distribution, we have

$$P(E,\beta) = \frac{W(E)\, e^{-\beta E}}{\sum_E W(E)\, e^{-\beta E}}, \tag{17.43}$$

where $W(E)$ is the number of microstates with energy E. (This quantity is frequently called the *density of states*, and is more generally defined as the number of states per unit energy interval.) If we compare (17.42) and (17.43) and note that $W(E)$ is independent of T, we can write

$$W(E) = a_0 H_0(E) e^{\beta_0 E}, \tag{17.44}$$

where a_0 is a proportionality constant that depends on β_0. If we eliminate $W(E)$ from (17.43) by using (17.44), we obtain the desired relation

$$P(E,\beta) = \frac{H_0(E)\, e^{-(\beta-\beta_0)E}}{\sum_E H_0(E)\, e^{-(\beta-\beta_0)E}}. \tag{17.45}$$

Note that we have expressed the probability at inverse temperature β in terms of $H_0(E)$, the histogram at inverse temperature β_0.

Because β is a continuous variable, we can estimate the β dependence of the mean value of any function A that depends on E, for example, the mean energy and the specific heat. We write the mean of $A(E)$ as

$$\langle A(\beta)\rangle = \sum_E A(E) P(E,\beta). \tag{17.46}$$

If the quantity A depends on another quantity M, for example, the magnetization, then we can generalize (17.46) to

$$\langle A(\beta)\rangle = \sum_{E,M} A(E,M)P(E,M,\beta) \tag{17.47}$$

$$= \frac{\sum_{E,M} A(E,M)H_0(E,M)e^{-(\beta-\beta_0)E}}{\sum_{E,M} H_0(E,M)e^{-(\beta-\beta_0)E}}. \tag{17.48}$$

The histogram method is useful only when the configurations relevant to the range of temperatures of interest occur with reasonable probability during the simulation at temperature T_0. For example, if we simulate an Ising model at low temperatures at which only ordered configurations occur (most spins aligned in the same direction), we cannot use the histogram method to obtain meaningful thermodynamic averages at high temperatures at which most configurations are disordered.

Problem 17.19. Application of the histogram method

a. Consider a 4×4 Ising lattice in zero magnetic field and compute the mean energy per spin, the mean magnetization per spin, the specific heat, and the susceptibility per spin for $T = 1$ to $T = 3$ in steps of $\Delta T = 0.05$. Average over at least 5000 Monte Carlo steps per spin after equilibrium has been reached for each value of T.

b. What are the minimum and maximum values of the total energy E and magnetization M that might be observed in a simulation of a Ising model on a 4×4 lattice? Use these values to set the size of the two-dimensional array needed to accumulate data for the histogram $H(E, M)$. It is suggested that you modify `Program ising` and save $H(E, M)$ in a file. Accumulate data for $H(E, M)$ at $T = 2.27$, a value of T close to T_c, for at least 5000 Monte Carlo steps per spin after equilibration. Write a separate program to read the histogram file and compute the same thermodynamic quantities as in part (a) using (17.48). Compare your computed results with the data obtained by simulating the system directly, that is, without using the histogram method, at the same temperatures. At what temperatures does the histogram method break down?

c. Repeat parts (b) and (c) for a simulation centered about $T = 1.5$ and $T = 2.5$.

d. Repeat parts (b) and (c) for an 8×8 and a 16×16 lattice at $T = 2.27$.

The histogram method can be used to do a more sophisticated finite size scaling analysis to determine the nature of a transition. Suppose that we perform a Monte Carlo simulation and observe a peak in the specific heat as a function of the temperature. What can this observation tell us about a possible phase transition? In general, we can conclude very little without doing a careful analysis of the behavior of the system at different sizes. For example, a discontinuity in the energy in an infinite system might be manifested in small systems by a peak in the specific heat. However, a phase transition in the infinite system in which the energy is continuous, but its derivative diverges at the transition, might manifest itself in the same way in a small system. Another difficulty is that the peak in the specific heat of a small system occurs at a temperature that differs from the transition temperature in the infinite system (see Project 17.25). Finally, there might be no transition at all, and the peak might simply represent a broad crossover from high to low temperature behavior (see Project 17.26).

We now discuss a method due to Lee and Kosterlitz that uses the histogram data to determine the nature of a phase transition (if it exists). To understand this method, we need to introduce the (Helmholtz) free energy F of a system. The statistical mechanics definition of F is

$$F = -kT \ln Z. \tag{17.49}$$

At low T, the factor $e^{-\beta E}$ in the partition function Z determines the dominant contributions to Z, even though there are relatively few such configurations. At high T, the factor $e^{-\beta E}$ is not very large, but the number of disordered configurations with high E is large, and hence high energy configurations dominate the contribution to Z. These considerations suggest that it is useful to define a restricted free energy $F(E)$ that includes only configurations at a particular energy E. We define

$$F(E) = -kT \ln W(E)\, e^{-\beta E}. \tag{17.50}$$

For systems with a first-order phase transition, a plot of $F(E)$ versus E will show two local minima corresponding to configurations that are characteristic of the high and low temperature phases. At low T the minimum at the lower energy will be the absolute minimum, and at high T the higher energy minimum will be the absolute minimum of F. At the transition, the two minima will have the same value of $F(E)$. For systems with no transition in the thermodynamic limit, there will only be one minimum for all T.

How will $F(E)$ behave for the relatively small lattices considered in simulations? In systems with first-order transitions, the distinction between low and high temperature phases will become more pronounced as the system size is increased. If the transition is continuous, there are domains at all sizes, and we expect that the behavior of $F(E)$ will not change significantly as the system size increases. If there is no transition, there might be a spurious double minima for small systems, but this spurious behavior should disappear for larger systems. Lee and Kosterlitz proposed the following method for categorizing phase transitions.

1. Do a simulation at a temperature close to the suspected transition temperature, and compute $H(E)$. Usually, the temperature at which the peak in the specific heat occurs is chosen as the simulation temperature.

2. Use the histogram method to compute $-\ln H_0(E) + (\beta - \beta_0)E \propto F(E)$ at neighboring values of T. If there are two minima in $F(E)$, vary β until the values of $F(E)$ at the two minima are equal. This temperature is an estimate of the possible transition temperature T_c.

3. Measure the difference ΔF at T_c between $F(E)$ at the minima and $F(E)$ at the maximum between the two minima.

4. Repeat steps (1)–(3) for larger systems. If ΔF increases with size, the transition is first-order. If ΔF remains the same, the transition is continuous. If ΔF decreases with size, there is no thermodynamic transition.

The above procedure is applicable when the phase transition occurs by varying the temperature. Transitions also can occur by varying the pressure or the magnetic field. These *field-driven transitions* can be tested by a similar method. For example, consider the Ising model in a magnetic

field at low temperatures below T_c. As we vary the magnetic field from positive to negative, there is a transition from a phase with magnetization $M > 0$ to a phase with $M < 0$. Is this transition first-order or continuous? To answer this question, we can use the Lee-Kosterlitz method with a histogram $H(E, M)$ generated at zero magnetic field, and calculate $F(M)$ instead of $F(E)$. The quantity $F(M)$ is proportional to $-\ln \sum_E H(E, M)\, e^{-(\beta-\beta_0)E}$. Because the states with positive and negative magnetization are equally likely to occur for zero magnetic field, we should see a double minima structure for $F(M)$ with equal minima. As we increase the size of the system, ΔF should increase for a first-order transition and remain the same for a continuous transition.

Problem 17.20. Characterization of a phase transition

a. Use your modified version of `Program ising` from Problem 17.19 to determine $H(E, M)$. Read the $H(E, M)$ data from a file, and compute and plot $F(E)$ for the range of temperatures of interest. First generate data at $T = 2.27$ and use the Lee-Kosterlitz method to verify that the Ising model in two dimensions has a continuous phase transition in zero magnetic field. Consider lattices of sizes $L = 4, 8$, and 16.

b. Perform a Lee-Kosterlitz analysis of the Ising model at $T = 2$ and zero magnetic field by plotting $F(M)$. Determine if the transition from $M > 0$ to $M < 0$ is first-order or continuous. This transition is called field-driven because the transition occurs if we change the magnetic field. Make sure your simulations sample configurations with both positive and negative magnetization by using small values of L such as $L = 4, 6$ and 8.

c. Repeat part (b) at $T = 2.5$ and determine if there is a field-driven transition at $T = 2.5$.

Problem 17.21. The Potts Model

a. In the q-state Potts model, the total energy or Hamiltonian of the lattice is given by

$$H = -J \sum_{i,j=\mathrm{nn}(i)} \delta_{s_i,s_j}, \tag{17.51}$$

where s_i at site i can have the values $1, 2, \cdots, q$; the Kronecker delta function $\delta_{a,b}$ equals unity if $a = b$ and is zero otherwise. As before, we will measure the temperature in energy units. Convince yourself that the $q = 2$ Potts model is equivalent to the Ising model (except for a trivial difference in the energy minimum). One of the many applications of the Potts model is to helium absorbed on the surface of graphite. The graphite-helium interaction gives rise to preferred adsorption sites directly above the centers of the honeycomb graphite surface. As discussed by Plischke and Bergersen, the helium atoms can be described by a three-state Potts model.

b. The transition in the Potts model is continuous for small q and first-order for larger q. Write a Monte Carlo program to simulate the Potts model for a given value of q and store the histogram $H(E)$. Test your program by comparing the output for $q = 2$ with your Ising model program.

c. Use the Lee-Kosterlitz method to analyze the nature of the phase transition in the Potts model for $q = 3, 4, 5, 6$, and 10. First find the location of the specific heat maximum, and then collect data for $H(E)$ at the specific heat maximum. Lattice sizes of order $L \geq 50$ are required to obtain convincing results for some values of q.

17.9 *Other Ensembles

So far, we have considered the microcanonical ensemble (fixed N, V, and E) and the canonical ensemble (fixed N, V, and T). Monte Carlo methods are very flexible and can be adapted to the calculation of averages in any ensemble. Two other ensembles of particular importance are the constant pressure and the grand canonical ensembles. The main difference in the Monte Carlo method is that there are additional "moves" corresponding to changing the volume or changing the number of particles. The constant pressure ensemble is particularly important for studying first-order phase transitions because the phase transition occurs at a fixed pressure, unlike a constant volume simulation where the system passes through a two phase coexistence region before changing phase completely as the volume is changed.

In the NPT ensemble, the probability of a microstate occurring is proportional to $e^{-\beta(E+PV)}$. For a classical system, the mean value of a physical quantity A that depends on the coordinates of the particles can be expressed as

$$\langle A\rangle_{\rm NPT} = \frac{\int_0^\infty dV e^{-\beta PV}\int d\mathbf{r}_1 d\mathbf{r}_2\ldots d\mathbf{r}_N A(\{\mathbf{r}\})\, e^{-\beta U(\{\mathbf{r}\})}}{\int_0^\infty dV e^{-\beta PV}\int d\mathbf{r}_1 d\mathbf{r}_2\ldots d\mathbf{r}_N\, e^{-\beta U(\{\mathbf{r}\})}}. \tag{17.52}$$

The potential energy $U(\{\mathbf{r}\})$ depends on the set of particle coordinates $(\{\mathbf{r}\})$. To simulate the NPT ensemble, we need to sample the coordinates $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N$ of the particles and the volume V of the system. For simplicity, we assume that the central cell is a square or a cube so that $V = L^d$. It is convenient to use the set of scaled coordinates $\{\mathbf{s}\}$, where $\mathbf{s}_i$ is defined as

$$\mathbf{s}_i = \frac{\mathbf{r}_i}{L}. \tag{17.53}$$

If we substitute (17.53) into (17.52), we can write $\langle A\rangle_{\rm NPT}$ as

$$\langle A\rangle_{\rm NPT} = \frac{\int_0^\infty dV e^{-\beta PV} V^N\int d\mathbf{s}_1 d\mathbf{s}_2\ldots d\mathbf{s}_N A(\{\mathbf{s}\})\, e^{-\beta U(\{\mathbf{s}\})}}{\int_0^\infty dV e^{-\beta PV} V^N\int d\mathbf{s}_1 d\mathbf{s}_2\ldots d\mathbf{s}_N\, e^{-\beta U(\{\mathbf{s}\})}}, \tag{17.54}$$

where the integral over $\{\mathbf{s}\}$ is over the unit square (cube). The factor of V^N arises from the change of variables $\mathbf{r}\to\mathbf{s}$. If we let $V^N = e^{\ln V^N} = e^{N\ln V}$, we see that the quantity that is analogous to the Boltzmann factor can be written as

$$e^{-W} = e^{-\beta PV-\beta U(\{\mathbf{s}\})+N\ln V}. \tag{17.55}$$

Because the pressure is fixed, a trial configuration is generated from the current configuration by either randomly displacing a particle and/or making a random change in the volume, for example, $V\to V+\delta V_{\rm max}(2r-1)$, where r is a uniform random number in the unit interval. The trial configuration is accepted if the change $\Delta W\le 0$ and with probability $e^{-\Delta W}$ if $\Delta W>0$. It is not necessary or efficient to change the volume after every Monte Carlo step per particle.

In the grand canonical or μVT ensemble, the chemical potential μ is fixed and the number of particles fluctuates. The average of any function of the particle coordinates can be written as (in three dimensions)

$$\langle A\rangle_{\mu\rm VT} = \frac{\sum_{N=0}^\infty (1/N!)\,\lambda^{-3N}\, e^{\beta\mu N}\int d\mathbf{r}_1 d\mathbf{r}_2\ldots d\mathbf{r}_N A(\{\mathbf{r}\})\, e^{-\beta U_N(\{\mathbf{r}\})}}{\sum_{N=0}^\infty (1/N!)\,\lambda^{-3N} e^{\beta\mu N}\int d\mathbf{r}_1 d\mathbf{r}_2\ldots d\mathbf{r}_N\, e^{-\beta U_N(\{\mathbf{r}\})}}, \tag{17.56}$$

where $\lambda = (h^2/2\pi mkT)^{1/2}$. We have made the N-dependence of the potential energy U explicit. If we write $1/N! = e^{-\ln N!}$ and $\lambda^{-3N} = e^{-N\ln\lambda^3}$, we can write the quantity that is analogous to the Boltzmann factor as

$$e^{-W} = e^{\beta\mu N - N\ln\lambda^3 - \ln N! + N\ln V - \beta U_N}. \tag{17.57}$$

If we write the chemical potential as

$$\mu = \mu^* + kT\ln(\lambda^3/V), \tag{17.58}$$

then W can be expressed as

$$e^{-W} = e^{-\beta\mu^* N - \ln N! - \beta U_N}. \tag{17.59}$$

The parameters are μ^*, V, and T. There are two possible ways of obtaining a trial configuration. The first involves the displacement of a selected particle; such a move is accepted or rejected according to the usual criteria, that is, by the change in the potential energy U_N. In the second possible way, we choose with equal probability whether to attempt to add a particle at a randomly chosen position in the central cell or to remove a particle that is already present. In either case, the trial configuration is accepted if W in (17.59) is increased. If W is decreased, the change is accepted with a probability equal to

$$\frac{1}{N+1}e^{\beta\left(\mu^* - (U_{N+1} - U_N)\right)} \text{(insertion)} \tag{17.60a}$$

or

$$Ne^{-\beta\left(\mu^* + (U_{N+1} - U_N)\right)}. \text{(removal)} \tag{17.60b}$$

In this approach μ^* is an input parameter and μ is not determined until the end of the calculation when $\langle N\rangle_{\mu\mathrm{VT}}$ is obtained.

17.10 More Applications

You probably do not need to be convinced that Monte Carlo methods are powerful, flexible, and applicable to a wide variety of systems. Extensions to the Monte Carlo methods that we have not discussed include multiparticle moves, biased moves where particles tend to move in the direction of the force on them, manipulation of bits for Ising-like models, the *n-fold way* algorithm for Ising-like models at low temperature, use of special processors for specific systems, and the use of parallel processing to update different parts of a large system simultaneously. We also have not described the simulation of systems with long-range potentials such as Coulombic systems and dipole-dipole interactions. For these potentials, it is necessary to include the interactions of the particles in the center cell with the infinite set of periodic images.

We conclude this chapter with a discussion of Monte Carlo methods in a context that might seem to have little in common with the types of problems we have discussed. This context is called *multivariate* or *combinatorial optimization,* a fancy way of saying, "How do you find the minimum of a function that depends on many parameters?" Problems of this type arise in many areas of scheduling and design. We explain the nature of this type of problem by an example known as the *traveling salesperson problem*, a.k.a., the *traveling salesman problem.*

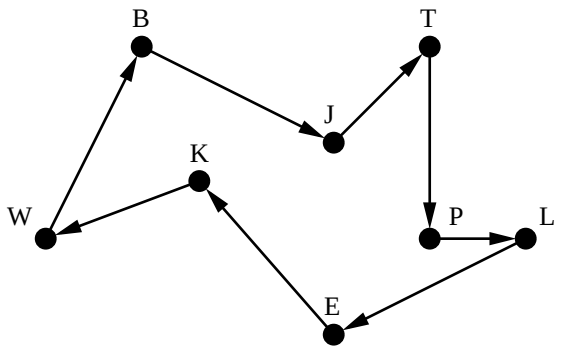

Figure 17.5: What is the optimum route for this random arrangement of $N = 8$ cities? The route begins and ends at city W. A possible route is shown.

Suppose that a salesperson wishes to visit N cities and follow a route such that no city is visited more than once and the end of the trip coincides with the beginning. Given these constraints, the traveling salesperson problem is to find the optimum route such that the total distance traveled is a minimum. An example of $N = 8$ cities and a possible route is shown in Fig. 17.5. All exact methods for determining the optimal route require a computing time that increases as e^N, and in practice, an exact solution can be found only for a small number of cities. The traveling salesperson problem belongs to a large class of problems known as NP-complete. (The NP refers to non-polynomial, that is, such problems cannot be done in a time proportional to some finite polynomial in N.) What is a reasonable estimate for the maximum number of cities that you can consider without the use of a computer?

To understand the nature of the different approaches to the traveling salesperson problem, consider the plot in Fig. 17.6 of the "energy" function $E(a)$. We can associate $E(a)$ with the length of the route and interpret a as a parameter that represents the order in which the cities are visited. If $E(a)$ has several local minima, what is a good strategy for finding the global (absolute) minimum of $E(a)$? One way is to vary a systematically and find the value of E everywhere. This exact enumeration method corresponds to determining the length of each possible route, clearly an impossible task if the number of cities is too large. Another way is to use a *heuristic method,* that is, an approximate method for finding a route that is close to the absolute minimum. One strategy is to choose a value of a, generate a small random change δa, and accept this change if $E(a + \delta a)$ is less than or equal to $E(a)$. This iterative improvement strategy corresponds to a search for steps that lead downhill. Because this search usually becomes stuck in a local and not a global minimum, it is useful to begin from several initial choices of a and to keep the best result. What would be the application of this type of strategy to the salesperson problem?

Let us consider a seemingly unrelated problem. Suppose we wish to make a perfect single crystal. You probably know that we should first melt the material, and then lower the temperature very slowly to the desired low temperature. If we lower the temperature too quickly (a rapid "quench"), the resulting crystal would have many defects or not become a crystal at all. The gradual lowering of the temperature is known as *annealing.*

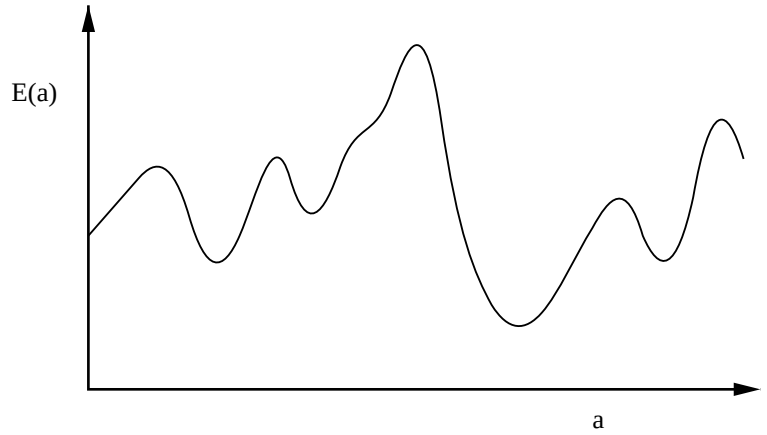

Figure 17.6: Plot of the function $E(a)$ as a function of the parameter a.

The method of annealing can be used to estimate the minimum of $E(a)$. We choose a value of a, generate a small random change δa, and calculate $E(a+\delta a)$. If $E(a+\delta a)$ is less than or equal to $E(a)$, we accept the change. However, if $\Delta E = E(a+\delta a) - E(a) > 0$, we accept the change with a probability $P = e^{-\Delta E/T}$, where T is an effective temperature. This procedure is the familiar Metropolis algorithm with the temperature playing the role of a control parameter. The *simulated annealing* process consists of first "melting" the system, that is, choosing T for which most moves are accepted, and then gradually lowering the temperature. At each temperature, the simulation should last long enough for the system to reach a steady state. The annealing schedule, that is, the rate of temperature decrease, determines the quality of the solution.

The moral of the simulated annealing method is that sometimes it is necessary to climb a hill to reach a valley. The first application of the method of simulated annealing was to the optimal design of computers. In Problem 17.22 we apply this method to the traveling salesperson problem. Perhaps you can think of other applications.

Problem 17.22. Simulated annealing and the traveling salesperson problem

a. Generate a random arrangement of $N = 8$ cities in a square of linear dimension $L = \sqrt{N}$ and calculate the optimum route by hand. Then write a Monte Carlo program and apply the method of simulated annealing to this problem. For example, use two arrays to store the coordinates of each city and an array to store the distances between them. The state of the system, that is, the route represented by a sequence of cities, can be stored in another array. The length of this route is associated with the energy of an imaginary thermal system. A reasonable choice for the initial temperature is one that is the same order as the initial energy. One way to generate random rearrangements of the route is to choose two cities at random and to interchange the order of visit. Choose this method or one that you devise and find a reasonable annealing schedule. Compare your annealing results to exact results whenever possible. Extend your results to larger N, for example, $N = 12, 24$, and 48. For a given annealing schedule, determine the probability of finding a route of a given length. More suggestions can be found in the

references.

b. The microcanonical Monte Carlo algorithm (demon) discussed in Chapter 16 also can be used to do simulated annealing. The advantages of the demon algorithm are that it is deterministic and allows large temperature fluctuations. One way to implement the analog of simulated annealing is to impose a maximum value on the energy of the demon, $E_{d,\max}$ and then gradually lower the value of $E_{d,\max}$. Guo et al. choose the initial value of $E_{d,\max}$ to equal $\sqrt{N}/4$. Their results are comparable to the canonical simulated annealing method, but require approximately half the CPU time. Apply this method to the same routes that you considered in part (a) and compare your results.

17.11 Projects

Many of the original applications of Monte Carlo methods were done for systems of approximately one hundred particles and lattices of order 32^2 spins. Most of these applications can be done with much better statistics and with larger system sizes. In the following, we discuss some recent developments, but this discussion is not complete and we have omitted other important topics such as Brownian dynamics and umbrella sampling. More ideas for projects can be found in the references.

Project 17.23. Overcoming critical slowing down The usual limiting factor of most simulations either is the lack of computer memory or, more likely, the speed of the computer. One way to overcome the latter problem is to use a faster computer. However, near a phase transition, the most important limiting factor on even the fastest available computers is the existence of "critical slowing down" (see Problem 17.12). In this project we discuss the nature of critical slowing down and ways of overcoming it in the context of the Ising model.

The existence of critical slowing down is related to the fact that the size of the correlated regions of spins becomes very large near the Ising critical point. The large size of the correlated regions and the corresponding divergent behavior of the correlation length ξ near T_c implies that the time τ required for a region to lose its coherence becomes very long if a *local* dynamics is used. Near T_c, we have $\tau \sim \xi^z$, which defines the dynamical critical exponent z. At $T = T_c$, we have $\tau \sim L^z$ for L sufficiently large. For the single spin flip (Metropolis) algorithm, $z \approx 2$, and τ becomes very large for $L >> 1$. On a serial computer, the CPU time needed to obtain n configurations increases as L^2, the time needed to visit L^2 spins. This factor of L^2 is not a problem because a larger system contains proportionally more information. However, the time needed to obtain n approximately *independent* configurations is order $\tau L^2 \sim L^{2+z} \approx L^4$ for the Metropolis algorithm. We see that an increase of L by a factor of 10 requires 10^4 more computing time. Hence, the existence of critical slowing down limits the maximum value of L that can be considered.

If we are interested only in the static properties of the Ising model, the choice of dynamics is irrelevant as long as the transition probability satisfies the detailed balance condition (17.10). As we mentioned above, the Metropolis algorithm becomes inefficient near T_c because only single spins are flipped. Hence, it is reasonable to look for a *global* algorithm for which groups or *clusters* of spins are flipped simultaneously. We already are familiar with cluster properties in the context of percolation (see Chapter 13). A naive definition of a cluster of spins might be a domain or group of parallel nearest neighbor spins. We can make this definition more explicit by introducing a bond

between any two nearest neighbor spins that point in the same direction. The introduction of a bond between spins of the same sign defines a "site-bond" percolation problem. More generally, we can assume that such a bond exists with probability p and the randomness associated with the bond probability p depends on the temperature T. The dependence of p on T can be determined by requiring that the percolation transition of the clusters occurs at the Ising critical point, and by requiring that the critical exponents associated with the clusters be identical to the analogous thermal exponents. For example, we can define a critical exponent ν_p to characterize the divergence of the connectedness length of the clusters near p_c. The analogous thermal exponent ν quantifies the divergence of the thermal correlation length ξ near T_c. It is possible to show analytically that these (and other) critical exponents are identical if we define the bond probability as

$$p = 1 - e^{-2J/kT}. \qquad \text{(bond probability)} \tag{17.61}$$

The relation (17.61) holds for any spatial dimension. What is the value of p at $T = T_c$ for the two-dimensional Ising model on the square lattice?

Now that we know how to generate clusters of spins, we use these clusters to construct a global dynamics. One way (known as the Swendsen-Wang algorithm) is to assign all bonds between parallel spins with probability p. No bonds are included between sites that have different spin values. From this configuration of bonds, we can form clusters of spins using the Hoshen-Kopelman algorithm (see Section 13.3). The smallest cluster contains a single spin. After the clusters have been identified, all the spins in each cluster are flipped with probability 1/2.

Because it is nontrivial to determine all the clusters for a given configuration, we instead explore an algorithm that flips single clusters. The idea is to "grow" a single (site-bond) percolation cluster in a way that is analogous to the single (site) percolation cluster algorithm discussed in Section 14.1. The algorithm can be implemented by the following steps:

1. Choose a seed spin at random. Its four nearest neighbor sites (on the square lattice) are the perimeter sites. Form an ordered array corresponding to the perimeter spins that are parallel to the seed spin and define a counter for the total number of perimeter spins.

2. Choose the first spin in the ordered perimeter array. Remove it from the array and replace it by the last spin in the array. Generate a random number r. If $r \leq p$, a bond exists and the spin is added to the cluster.

3. If the spin is added to the cluster, inspect its parallel perimeter spins. If such a spin is not already part of the cluster, add it to the end of the array of perimeter spins.

4. Repeat steps 2 and 3 until no perimeter spins remain.

5. Flip all the spins in the single cluster.

This algorithm is known as single cluster flip or Wolff dynamics. Note that bonds rather than sites are tested so that a spin might have more than one chance to join a cluster. In the following, we consider both the static and dynamical properties of the two-dimensional Ising model using the Wolff algorithm to generate the configurations.

a. Modify your program for the two-dimensional Ising model on a square lattice so that single cluster flip dynamics (the Wolff algorithm) is used. Compute the mean energy and magnetization for $L = 16$ as a function of T for $T = 2.0$ to 2.7 in steps of 0.1. Compare your results to those obtained using the Metropolis algorithm. How many cluster flips do you need to obtain comparable accuracy at each temperature? Is the Wolff algorithm more efficient at every temperature?

b. Fix T at the critical temperature of the infinite lattice ($T_c = 2/\ln(1+\sqrt{2})$) and use finite size scaling to estimate the values of the various static critical exponents, for example, γ and α. Compare your results to those obtained using the Metropolis algorithm.

c. Because we are generating site-bond percolation clusters, we can study their geometrical properties as we did for site percolation. For example, measure the distribution sn_s of cluster sizes at $p = p_c$ (see Problem **??**a). How does n_s depend on s for large s (see Project 14.18)? What is the fractal dimension of the clusters?

d. The natural unit of time for single cluster flip dynamics is the number of cluster flips $t_{\rm cf}$. Measure $C_M(t_{\rm cf})$ and/or $C_E(t_{\rm cf})$ and estimate the corresponding correlation time $\tau_{\rm cf}$ for $T = 2.5, 2.4$, 2.3, and T_c for $L = 16$. As discussed in Problem 17.12, $\tau_{\rm cf}$ can be found from the relation, $\tau_{\rm cf} = \sum_{t_{\rm cf}=1} C(t_{\rm cf})$. The sum is cut off at the first negative value of $C(t_{\rm cf})$. To compare our results for the Wolff algorithm to our results for the Metropolis algorithm, we should use the same unit of time. Because only a fraction of the spins are updated at each cluster flip, the time $t_{\rm cf}$ is not equal to the usual unit of time which corresponds to an update of the entire lattice or one Monte Carlo step per spin. We have that τ measured in Monte Carlo steps per spin is related to $\tau_{\rm cf}$ by $\tau = \tau_{\rm cf}\langle c\rangle/L^2$, where $\langle c\rangle$ is the mean number of spins in the single clusters, and L^2 is the number of spins in the entire lattice. Measure $\langle c\rangle$ and compare your values for τ for the Wolff algorithm to the values of τ that you obtained using the Metropolis algorithm. Which values of τ are smaller?

e. Use the finite size scaling relation $\tau_{\rm cf} \sim L^{z_{\rm cf}}$ at $T = T_c$ to estimate $z_{\rm cf}$. Because $z_{\rm cf}$ is small, you will find it very difficult to obtain a good estimate. Verify that the mean cluster size scales as $\langle c\rangle \sim L^{\gamma/\nu}$ with $\gamma = 7/4$ and $\nu = 1$. (Note that these exponents are identical to the analogous thermal exponents.) To obtain the value of z that is directly comparable to the value found for the Metropolis algorithm, we need to rescale the time as in part (d). We have that $\tau \sim L^z \propto L^{z_{\rm cf}} L^{\gamma/\nu} L^{-d}$. Hence, z is related to the measured value of $z_{\rm cf}$ by $z = z_{\rm cf} - (d - \gamma/\nu)$. It has been suggested that $\tau \propto \ln L$, which would imply that $z = 0$, but the value of z is not known with confidence.

Project 17.24. Physical test of random number generators

In Section 12.6 we discussed various statistical tests for the quality of random number generators. In this project we will find that the usual statistical tests might not be sufficient for determining the quality of a random number generator for a particular application. The difficulty is that the quality of a random number generator for a specific application depends in part on how the subtle correlations that are intrinsic to all deterministic random number generators couple to the way that the random number sequences are used. In this project we explore the quality of two random number generators when they are used to implement single spin flip dynamics (Metropolis algorithm) and single cluster flip dynamics (Wolff algorithm) for the two-dimensional Ising model.

a. Write subroutines to generate sequences of random numbers based on the linear congruential algorithm

$$x_n = 16807\, x_{n-1} \bmod (2^{31} - 1) \tag{17.62}$$

and the generalized feedback shift register (GFSR) algorithm

$$x_n = x_{n-103} \oplus x_{n-250}. \tag{17.63}$$

In both cases x_n is the nth random number. Both algorithms require that x_n be divided by the largest possible value of x_n to obtain numbers in the range $0 \leq x_n < 1$. The GFSR algorithm requires bit manipulation and should be written in C or Fortran (see Appendices **??** or **??**). Which random number generator does a better job of passing the various statistical tests discussed in Problem 12.18?

b. Use the Metropolis algorithm and the linear congruential random number generator to determine the mean energy per spin E/N and the specific heat (per spin) C for the $L = 16$ Ising model at $T = T_c = 2/\ln(1+\sqrt{2})$. Make ten independent runs (that is, ten runs that use different random number seeds), and compute the standard deviation of the means σ_m from the ten values of E/N and C, respectively. Published results by Ferrenberg, Landau, and Wong are for 10^6 Monte Carlo steps per spin for each run. Calculate the differences δ_e and δ_c between the average of E/N and C over the ten runs and the exact values (to five decimal places) $E/N = -1.45306$ and $C = 1.49871$. If the ratio δ/σ_m for the two quantities is order unity, then the random number generator does not appear to be biased. Repeat your runs using the GFSR algorithm to generate the random number sequences. Do you find any evidence of statistical bias?

c. Repeat part (b) using Wolff dynamics. Do you find any evidence of statistical bias?

d. Repeat the computations in parts (b) and (c) using the random number generator supplied with your programming language.

Project 17.25. Kosterlitz-Thouless transition in the planar model

The planar model (also called the x-y model) consists of spins of unit magnitude that can point in any direction in the x-y plane. The energy or Hamiltonian function of the planar model in zero magnetic field can be written as

$$E = -J \sum_{i,j=nn(i)} \left[s_{i,x} s_{j,x} + s_{i,y} s_{j,y} \right], \tag{17.64}$$

where $s_{i,x}$ represents the x-component of the spin at the ith site, J measures the strength of the interaction, and the sum is over all nearest neighbors. We can rewrite (17.64) in a simpler form by substituting $s_{i,x} = \cos\theta_i$ and $s_{i,y} = \sin\theta_i$. The result is

$$E = -J \sum_{i,j=nn(i)} \cos(\theta_i - \theta_j), \tag{17.65}$$

where θ_i is the angle that the ith spin makes with the x axis. The most studied case is the two-dimensional model on a square lattice. In this case the mean magnetization $\langle \mathbf{M} \rangle = 0$ for all

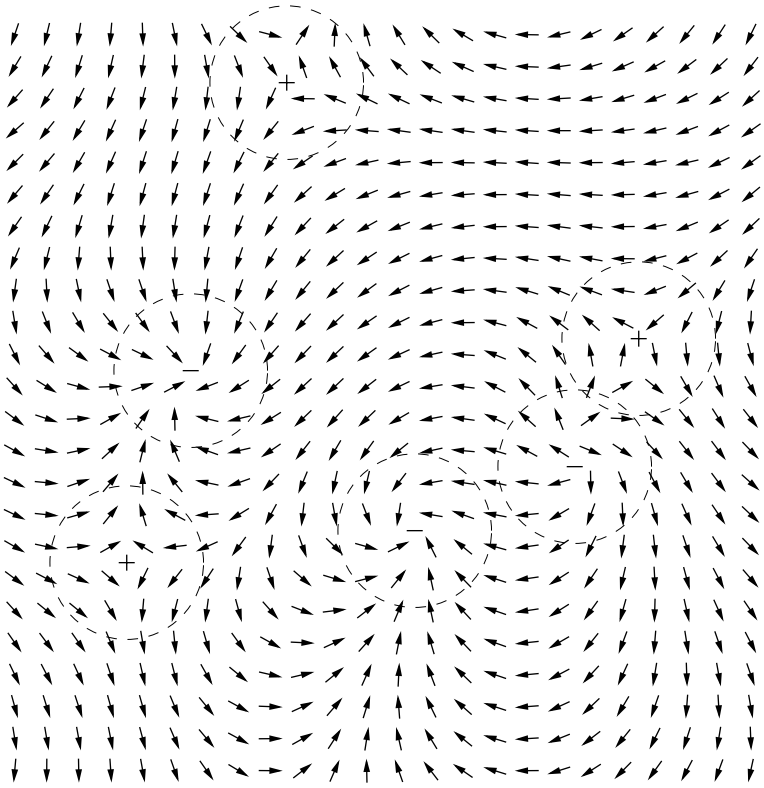

Figure 17.7: A typical configuration of the planar model on a 24×24 square lattice that has been quenched from $T = \infty$ to $T = 0$ and equilibrated for 200 Monte Carlo steps per spin after the quench. Note that there are six vortices. The circle around each vortex is a guide to the eye and is not meant to indicate the size of the vortex.

temperatures $T > 0$, but nevertheless, there is a phase transition at a nonzero temperature, T_{KT}, the Kosterlitz-Thouless (KT) transition. For $T \leq T_{KT}$, the spin-spin correlation function $C(r)$ decreases as a power law for increasing r; for $T > T_{KT}$, $C(r)$ decreases exponentially. The power law decay of $C(r)$ for all $T \leq T_{KT}$ implies that every temperature below T_{KT} acts as if it were a critical point. We say that the planar model has a line of critical points. In the following, we explore some of the properties of the planar model and the mechanism that causes the transition.

a. Write a Monte Carlo program to simulate the planar model on a square lattice using periodic boundary conditions. Because θ and hence the energy of the system is a continuous variable, it is not possible to store the previously computed values of the Boltzmann factor for each possible value of ΔE. Instead, of computing $e^{-\beta \Delta E}$ for each trial change, it is faster to set up an array `w` such that the array element `w(j)` $= e^{-\beta \Delta E}$, where `j` is the integer part of $1000 \Delta E$. This procedure leads to an energy resolution of 0.001, which should be sufficient for most purposes.

b. One way to show that the magnetization $\langle \mathbf{M} \rangle$ vanishes for all T is to compute $\langle \theta^2 \rangle$, where θ is the angle that a spin makes with the magnetization $\mathbf{M}$ at any given instant. (Although the mean magnetization vanishes, $\mathbf{M} \neq 0$ at any given instant.) Compute $\langle \theta^2 \rangle$ as a function of the number of spins N at $T = 0.1$, and show that $\langle \theta^2 \rangle$ diverges as $\ln N$. Begin with a 4×4 lattice and choose the maximum change in θ_i to be $\Delta\theta_{\max} = 1.0$. If necessary, change $\theta_{\max}$ so that the acceptance probability is about 40%. If $\langle \theta^2 \rangle$ diverges, then the spins are not pointing along any preferred direction, and hence there is no mean magnetization.

c. Modify your program so that an arrow is drawn at each site to show the orientation of each spin. We will look at a typical configuration and analyze it visually. Begin with a 32×32 lattice with spins pointing in random directions and do a temperature quench from $T = \infty$ to $T = 0.5$. (Simply change the value of β in the Boltzmann probability.) Such a quench should lock in some long lived, but metastable vortices. A vortex is a region of the lattice where the spins rotate by at least 2π as your eye moves around a closed path (see Fig. 17.7). To determine the center of a vortex, choose a group of four spins that are at the corners of a unit square, and determine whether the spins turn by $\pm 2\pi$ as your eye goes from one spin to the next in a counterclockwise direction around the square. Assume that the difference between the direction of two neighboring spins, $\delta\theta$, is in the range $-\pi < \delta\theta < \pi$. A total rotation of $+2\pi$ indicates the existence of a positive vortex, and a change of -2π indicates a negative vortex. Count the number of positive and negative vortices. Repeat these observations on several configurations. What can you say about the number of vortices of each sign?

d. Write a subroutine to determine the existence of a vortex for each 1×1 square of the lattice. Represent the center of the vortices using a different symbol to distinguish between a positive and a negative vortex. Do a Monte Carlo simulation to compute the mean energy, specific heat, and number of vortices in the range from $T = 0.5$ to $T = 1.5$ in steps of 0.1. Use the last configuration at the previous temperature as the first configuration for the next temperature. Begin at $T = 0.5$ with all $\theta_i = 0$. Draw the vortex locations for the last configuration at each temperature. Use at least 1000 Monte Carlo steps per spin at each temperature to equilibrate and at least 5000 Monte Carlo steps per spin for computing the averages. Use an 8×8 or 16×16 lattice if your computer resources are limited, and larger lattices if you have sufficient resources. Describe the T dependence of the energy, specific heat, and vorticity (equal to the number of vortices per area). Plot the logarithm of the vorticity versus T for $T < 1.1$. What can you conclude about the T-dependence of the vorticity? Explain why this form is reasonable. Describe the vortex configurations. At what temperature can you find a vortex that appears to be free, that is, a vortex that is not obviously paired up with another vortex of opposite sign?

e. The Kosterlitz-Thouless theory predicts that the susceptibility χ diverges above the transition as

$$\chi \sim A\, e^{b/\epsilon^{\nu}}, \tag{17.66}$$

where ϵ is the reduced temperature $\epsilon = (T - T_{KT})/T_{KT}$, $\nu = 0.5$, and A and b are nonuniversal constants. Compute χ from the relation (17.14) with $\mathbf{M} = 0$ because the mean magnetization vanishes. Assume the exponential form (17.66) for χ in the range $T = 1$ and $T = 1.2$ with $\nu = 0.7$, and find the best values of T_{KT}, A, and b. (Although the analytical theory predicts $\nu = 0.5$, simulations for small systems indicate that $\nu = 0.7$ gives a better fit.) One way to

determine T_{KT}, A, and b is to assume a value of T_{KT} and then do a least squares fit of $\ln\chi$ to determine A and b. Choose the set of parameters that minimizes the variance of $\ln\chi$. How does your estimated value of T_{KT} compare with the temperature at which free vortices first appear? At what temperature does the specific heat have a peak? The Kosterlitz-Thouless theory predicts that the specific heat peak does not occur at T_{KT}. This result has been confirmed by simulations (see Tobochnik and Chester). To obtain quantitative results, you will need lattices larger than 32×32.

Project 17.26. Classical Heisenberg model in two dimensions

The energy or Hamiltonian of the classical Heisenberg model is similar to the Ising model and the planar model, except that the spins can point in any direction in three dimensions. The energy in zero external magnetic field is

$$E = -J \sum_{i,j=\mathrm{nn}(i)}^{N} \mathbf{s}_i \cdot \mathbf{s}_j, \tag{17.67}$$

where $\mathbf{s}$ is a classical vector of unit length. The spins have three components, in contrast to the spins in the Ising model which only have one component, and the spins in the planar model which have two components. We will consider the two-dimensional Heisenberg model for which the spins are located on a two-dimensional lattice.

Early simulations and approximate theories led researchers to believe that there was a continuous phase transition, similar to that found in the Ising model. The Heisenberg model received more interest after it was related to the confinement for quarks. Lattice models of the interaction between quarks, called lattice gauge theories, predict that the confinement of quarks can be explained if there are no phase transitions in these models. (The lack of a phase transition in these models implies that the attraction between quarks grows with distance.) The Heisenberg model is a two-dimensional analog of the four-dimensional models used to model quark-quark interactions. Shenker and Tobochnik used a combination of Monte Carlo and renormalization group methods to show that this model does not have a phase transition. Subsequent work on lattice gauge theories showed similar behavior.

a. Modify your Ising model program to simulate the Heisenberg model in two dimensions. One way to do so is to define three arrays, one for each of the three components of the unit spin vectors. A trial Monte Carlo move consists of randomly changing the direction of a spin, $\mathbf{s}_i$. First compute a small vector $\Delta\mathbf{s} = \Delta s_{\max}(p_1, p_2, p_3)$, where $-1 \le p_n \le 1$ is a uniform random number, and $\Delta s_{\max}$ is the maximum change of any spin component. If $|\Delta\mathbf{s}| > \Delta s_{\max}$, than compute another $\Delta\mathbf{s}$. This latter step is necessary to insure that the change in a spin direction is symmetrically distributed around the current spin direction. Next let the trial spin equal $\mathbf{s}_i + \Delta\mathbf{s}$ normalized to a unit vector. The standard Metropolis algorithm can now be used to determine if the trial spin is accepted. Compute the mean energy, specific heat, and susceptibility as a function of T. Choose lattice sizes of $L = 8, 16, 32$ and larger if possible and average over at least 2000 Monte Carlo steps per spin at each temperature. Is there any evidence of a phase transition? Does the susceptibility appear to diverge at a nonzero temperature? Plot the natural log of the susceptibility versus the inverse temperature, and determine the temperature dependence of the susceptibility in the limit of low temperatures.

b. Use the Lee-Kosterlitz analysis at the specific heat peak to determine if there is a phase transition.

Project 17.27. Ground state energy of the Ising spin glass

A spin glass is a magnetic system with frozen-in disorder. An example of such a system is the Ising model with the exchange constant J_{ij} between nearest neighbor spins randomly chosen to be ± 1. The disorder is said to be "frozen-in" because the set of interactions $\{J_{ij}\}$ does not change with time. Because the spins cannot arrange themselves so that every pair of spins is in its lowest energy state, the system exhibits frustration similar to the antiferromagnetic Ising model on a triangular lattice (see Problem 17.15). Is there a phase transition in the spin glass model, and if so, what is its nature? The answers to these questions are very difficult to obtain by doing simulations. One of the difficulties is that we need to do not only an average over the possible configurations of spins for a given set of $\{J_{ij}\}$, but we also need to average over different realizations of the interactions. Another difficulty is that there are many local minima in the energy (free energy at finite temperature) as a function of the configurations of spins, and it is very difficult to find the global minimum. As a result, Monte Carlo simulations typically become stuck in these local minima or metastable states. Detailed finite size scaling analyses of simulations indicate that there might be a transition in three dimensions. It is generally accepted that the transition in two dimensions is at zero temperature. In the following, we will look at some of the properties of an Ising spin glass on a square lattice at low temperatures.

a. Write a program to apply simulated annealing to an Ising spin glass using the Metropolis algorithm with the temperature fixed at each stage of the annealing schedule (see Problem 17.22a). Search for the lowest energy configuration for a fixed set of $\{J_{ij}\}$. Use at least one other annealing schedule for the same $\{J_{ij}\}$ and compare your results. Then find the ground state energy for at least ten other sets of $\{J_{ij}\}$. Use lattice sizes of $L = 5$ and $L = 10$. Discuss the nature of the ground states you are able to find. Is there much variation in the ground state energy E_0 from one set of $\{J_{ij}\}$ to another? Theoretical calculations give an average over realizations of $\overline{E_0}/N \approx -1.4$. If you have sufficient computer resources, repeat your computations for the three-dimensional spin glass.

b. Modify your program to do simulated annealing using the demon algorithm (see Problem 17.22b). How do your results compare to those that you found in part (a)?

Project 17.28. Zero temperature dynamics of the Ising model We have seen that various kinetic growth models (Section 14.3) and reaction-diffusion models (Section 12.4) lead to interesting and nontrivial behavior. Similar behavior can be seen in the zero temperature dynamics of the Ising model. Consider the one-dimensional Ising model with $J > 0$ and periodic boundary conditions. The initial orientation of the spins is chosen at random. We update the configurations by choosing a spin at random and computing the change in energy ΔE. If $\Delta E < 0$, then flip the spin; else if $\Delta E = 0$, flip the spin with 50% probability. The spin is not flipped if $\Delta E > 0$. This type of Monte Carlo update is known as Glauber dynamics. How does this algorithm differ from the Metropolis algorithm at $T = 0$?

The quantity of interest is $f(t)$, the fraction of spins that flip for the first time at time t. As usual, the time is measured in terms of Monte Carlo steps per spin. Published results (Derrida,

Bray, and Godrèche) for $N = 10^5$ indicate that $f(t)$

$$f(t) \sim t^{-\theta} \tag{17.68}$$

for $t \approx 3$ to $t \approx 10,000$ with $\theta \approx 0.37$. Verify this result and extend your results to the one-dimensional q-state Potts model. In the latter model each site is initially given a random integer between 1 and q. A site is chosen at random and set equal to either of its two neighbors with equal probability. The value of the exponent θ is not understood at present, but might be related to analogous behavior in reaction-diffusion models.

Project 17.29. The inverse power law potential

Consider the inverse power law potential

$$V(r) = V_0 \, (\frac{\sigma}{r})^n \tag{17.69}$$

with $V_0 > 0$. One reason for interest in potentials of this form is that thermodynamic quantities such as the mean energy E do not depend on V_0 and σ separately, but depend on a single dimensionless parameter. This dimensionless parameter can be defined as

$$\Gamma = \frac{V_0}{kT} \frac{\sigma}{a}, \tag{17.70}$$

where a is defined in three and two dimensions by $4\pi a^3 \rho/3 = 1$ and $\pi a^2 \rho = 1$, respectively. The length a is proportional to the mean distance between particles. A Coulomb interaction corresponds to $n = 1$, and a hard sphere system corresponds to $n \to \infty$. What phases do you expect to occur for arbitrary n?

a. Compare the qualitative features of $g(r)$ for a "soft" potential with $n = 4$ to a system of hard disks at the same density.

b. Let $n = 12$ and compute the mean energy E as a function of T for fixed density for a three-dimensional system. Fix T and consider $N = 16, 32, 64$, and 128. Does E depend on N? Can you extrapolate your results for the N-dependence of E to $N \to \infty$? Fix N and determine E as a function of Γ. Do you see any evidence of a phase transition? If so, estimate the value of Γ at which it occurs. What is the nature of the transition if it exists?

Project 17.30. Rare gas clusters There has been much recent interest in structures that contain many particles, but that are not macroscopic. An example is the unusual structure of sixty carbon atoms known as a "buckeyball." A less unusual structure is a cluster of argon atoms. Questions of interest include the structure of the clusters, the existence of "magic" numbers of particles for which the cluster is particularly stable, the temperature dependence of the thermodynamic quantities, and the possibility of different phases. This latter question has been subject to some controversy, because transitions between different kinds of behavior in finite systems are not nearly as sharp as they are for infinite systems.

a. Write a Monte Carlo program to simulate a three-dimensional system of particles interacting via the Lennard-Jones potential. Use open boundary conditions, that is, do not enclose the system in a box. The number of particles N and the temperature T should be input parameters.

b. Find the ground state energy E_0 as a function of N. For each value of N begin with a random initial configuration and accept any trial displacement that lowers the energy. Repeat for at least ten different initial configurations. Plot E_0/N versus N for $N = 2$ to 20 and describe the qualitative dependence of E_0/N on N. Is there any evidence of magic numbers, that is, value(s) of N for which E_0/N is a minimum? For each value of N save the final configuration. If you have access to a three-dimensional graphics program, plot the positions of the atoms. Does the cluster look like a part of a crystalline solid?

c. Repeat part (b) using simulated annealing. The initial temperature should be sufficiently low so that the particles do not move far away from each other. Slowly lower the temperature according to some annealing schedule. Do your results for E_0/N differ from part (b)?

d. To gain more insight into the structure of the clusters, compute the mean number of neighbors per particle for each value of N. What is a reasonable criteria for two particles to be neighbors? Also compute the mean distance between each pair of particles. Plot both quantities as a function of N, and compare their dependence on N with your plot of E_0/N.

e. Is it possible to find any evidence for a "melting" transition? Begin with the configuration that has the minimum value of E_0/N and slowly increase the temperature T. Compute the energy per particle and the mean square displacement of the particles from their initial positions. Plot your results for these quantities versus T.

Project 17.31. Hard disks Although we have mentioned (see Section 17.7) that there is reasonable evidence for a transition in a hard disk system, the nature of the transition still is a problem of current research. In this project we follow the work of Lee and Strandburg and apply the constant pressure Monte Carlo method (see Section 17.9) and the Lee-Kosterlitz method (see Section 17.8) to investigate the nature of the transition. Consider $N = L^2$ hard disks of diameter $\sigma = 1$ in a two-dimensional box of volume $V = \sqrt{3}L^2v/2$ with periodic boundary conditions. The quantity $v \geq 1$ is the reduced volume and is related to the density ρ by $\rho = N/V = 2/(\sqrt{3}v)$; $v = 1$ corresponds to maximum packing. The aspect ratio of $2/\sqrt{3}$ is used to match the perfect triangular lattice. We can perform a constant pressure (actually constant $p^* = P/kT$) Monte Carlo simulation as follows. The trial displacement of each disk is implemented as discussed in Section 17.7. Lee and Strandburg find that a maximum displacement of 0.09 gives a 45% acceptance probability. The other type of move is a random isotropic change of the volume of the system. If the change of the volume leads to an overlap of the disks, the change is rejected. Otherwise, if the trial volume $\tilde{V}$ is less than the current volume V, the change is accepted. A larger trial volume is accepted with probability

$$e^{-p^*(\tilde{V}-V)+N\ln\tilde{V}/V)}. \tag{17.71}$$

Volume changes are attempted 40–200 times for each set of individual disk moves. The quantity of interest is $N(v)$, the distribution of reduced volume v. Because we need to store information about $N(v)$ in an array, it is convenient to discretize the volume in advance and choose the mesh size so that the acceptance probability for changing the volume by one unit is 40–50%. Do a Monte Carlo simulation of the hard disk system for $L = 10$ ($N = 100$) and $p^* = 7.30$. Published results are for 10^7 Monte Carlo steps. To apply the Lee-Kosterlitz method, smooth $\ln N(v)$ by fitting it to an eighth-order polynomial. Then extrapolate $\ln N(v)$ using the histogram method to determine

$p_c^*(L = 10)$, the pressure at which the two peaks of $N(v)$ are of equal height. What is the value of the free energy barrier ΔF? If sufficient computer resources are available, compute ΔF for larger L (published results are for $L = 10, 12, 14, 16$, and 20) and determine if ΔF depends on L. Can you reach any conclusions about the nature of the transition?

Appendix 17A: Fluctuations in the Canonical Ensemble

We first obtain the relation of the constant volume heat capacity C_V to the energy fluctuations in the canonical ensemble. We adopt the notation $U = \langle E \rangle$ and write C_V as

$$C_V = \frac{\partial U}{\partial T} = -\frac{1}{kT^2}\frac{\partial U}{\partial \beta}. \tag{17.72}$$

From (17.3) we have

$$U = -\tfrac{\partial}{\partial \beta} \ln Z \tag{17.73}$$

and

$$\frac{\partial U}{\partial \beta} = -\tfrac{1}{Z^2}\tfrac{\partial Z}{\partial \beta}\textstyle\sum_s E_s\, e^{-\beta E_s} - \tfrac{1}{Z}\textstyle\sum_s E_s^2\, e^{-\beta E_s} \tag{17.74}$$

$$= \langle E \rangle^2 - \langle E^2 \rangle. \tag{17.75}$$

The relation (17.12) follows from (17.72) and (17.75). Note that the heat capacity is at constant volume because the partial derivatives were performed with the energy levels E_s kept constant. The corresponding quantity for a magnetic system is the heat capacity at constant external magnetic field.

The relation of the magnetic susceptibility χ to the fluctuations of the magnetization M can be obtained in a similar way. We assume that the energy can be written as

$$E_s = E_{0,s} - HM_s, \tag{17.76}$$

where $E_{0,s}$ is the energy in the absence of a magnetic field, H is the external applied field, and M_s is the magnetization in the s state. The mean magnetization is given by

$$\langle M \rangle = \frac{1}{Z}\sum M_s\, e^{-\beta E_s}. \tag{17.77}$$

Because $\partial E_s/\partial H = -M_s$, we have

$$\frac{\partial Z}{\partial H} = \sum_s \beta M_s\, e^{-\beta E_s}. \tag{17.78}$$

Hence we obtain

$$\langle M \rangle = \frac{1}{\beta}\frac{\partial}{\partial H} \ln Z. \tag{17.79}$$

Number spins up	Degeneracy	Energy	Magnetization
4	1	-8	4
3	4	0	2
2	4	0	0
2	2	8	0
1	4	0	-2
0	1	-8	-4

Table 17.1: The energy and magnetization of the 2^4 states of the zero field Ising model on the 2×2 square lattice. The degeneracy is the number of microstates with the same energy.

If we use (17.77) and (17.79), we find

$$\frac{\partial\langle M\rangle}{\partial H} = -\tfrac{1}{Z^2}\tfrac{\partial Z}{\partial H}\textstyle\sum_s M_s\, e^{-\beta E_s} + \tfrac{1}{Z}\sum_s \beta M_s^2\, e^{-\beta E_s} \tag{17.80}$$

$$= -\beta\langle M\rangle^2 + \beta\langle M^2\rangle. \tag{17.81}$$

The relation (17.14) for the zero field susceptibility follows from (17.81) and the definition (17.13).

Appendix 17B: Exact Enumeration of the 2×2 Ising Model

Because the number of possible states or configurations of the Ising model increases as 2^N, we can enumerate the possible configurations only for small N. As an example, we calculate the various quantities of interest for a 2×2 Ising model on the square lattice with periodic boundary conditions. In Table 17.1 we group the sixteen states according to their total energy and magnetization.

We can compute all the quantities of interest using Table 17.1. The partition function is given by

$$Z = 2\,e^{8\beta J} + 12 + 2\,e^{-8\beta J}. \tag{17.82}$$

If we use (17.73) and (17.82), we find

$$U = -\frac{\partial}{\partial\beta}\ln Z = -\frac{1}{Z}\big[2(8)e^{8\beta J} + 2(-8)e^{-8\beta J}\big]. \tag{17.83}$$

Because the other quantities of interest can be found in a similar manner, we only give the results:

$$\langle E^2\rangle = \tfrac{1}{Z}\big[(2\times 64)\,e^{8\beta J} + (2\times 64)\,e^{-8\beta J}\big] \tag{17.84}$$

$$\langle M\rangle = \tfrac{1}{Z}(0) = 0 \tag{17.85}$$

$$\langle |M|\rangle = \tfrac{1}{Z}\big[(2\times 4)\,e^{8\beta J} + 8\times 2\big] \tag{17.86}$$

$$\langle M^2\rangle = \tfrac{1}{Z}\big[(2\times 16)\,e^{8\beta J} + 8\times 4\big] \tag{17.87}$$

The dependence of C and χ on βJ can be found by using (17.83) and (17.84) and (17.85) and (17.87) respectively.

References and Suggestions for Further Reading

M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press (1987). See Chapter 4 for a discussion of Monte Carlo methods.

K. Binder, editor, *Monte Carlo Methods in Statistical Physics*, second edition, Springer-Verlag (1986). Also see K. Binder, editor, *Applications of the Monte Carlo Method in Statistical Physics*, Springer-Verlag (1984) and K. Binder, editor, *The Monte Carlo Method in Condensed Matter Physics*, Springer-Verlag (1992).

Marvin Bishop and C. Bruin, "The pair correlation function: a probe of molecular order," *Amer. J. Phys.* **52**, 1106 (1984). The authors compute the pair correlation function for a two-dimensional Lennard-Jones model.

James B. Cole, "The statistical mechanics of image recovery and pattern recognition," *Amer. J. Phys.* **59**, 839 (1991). A discussion of the application of simulated annealing to the recovery of images from noisy data.

B. Derrida, A. J. Bray, and C. Godrèche, "Non-trivial exponents in the zero temperature dynamics of the 1D Ising and Potts models," *J. Phys.* A **27**, L357 (1994).

Jerome J. Erpenbeck and Marshall Luban, "Equation of state for the classical hard-disk fluid," *Phys. Rev.* A **32**, 2920 (1985). These workers use a combined molecular dynamics/Monte Carlo method and consider 1512 and 5822 disks.

Alan M. Ferrenberg, D. P. Landau, and Y. Joanna Wong, "Monte Carlo simulations: hidden errors from "good" random number generators," *Phys. Rev. Lett.* **69**, 3382 (1992).

Alan M. Ferrenberg and Robert H. Swendsen, "New Monte Carlo technique for studying phase transitions," *Phys. Rev. Lett.* **61**, 2635 (1988); "Optimized Monte Carlo data analysis," *Phys. Rev. Lett.* **63**, 1195 (1989);"Optimized Monte Carlo data analysis," *Computers in Physics* **3**5, 101 (1989). The second and third papers discuss using the multiple histogram method with data from simulations at more than one temperature.

Harvey Gould and Jan Tobochnik, "Overcoming critical slowing down," *Computers in Physics* **3**4, 82 (1989).

Hong Guo, Martin Zuckermann, R. Harris, and Martin Grant, "A fast algorithm for simulated annealing," *Physica Scripta* **T38**, 40 (1991).

J. Kertész, J. Cserti and J. Szép, "Monte Carlo simulation programs for microcomputer," *Eur. J. Phys.* **6**, 232 (1985).

S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, "Optimization by simulated annealing," *Science* **220**, 671 (1983). See also, S. Kirkpatrick and G. Toulouse, "Configuration space analysis of traveling salesman problems," *J. Physique* **46**, 1277 (1985).

J. M. Kosterlitz and D. J. Thouless, *J. Phys.* C **6**, 1181 (1973); J. M. Kosterlitz, *J. Phys.* C **7**, 1046 (1974).

D. P. Landau, "Finite-size behavior of the Ising square lattice," *Phys. Rev.* B**13**, 2997 (1976). A clearly written paper on a finite-size scaling analysis of Monte Carlo data. See also D. P. Landau, "Finite-size behavior of the simple-cubic Ising lattice," *Phys. Rev.* B**14**, 255 (1976).

D. P. Landau and R. Alben, "Monte Carlo calculations as an aid in teaching statistical mechanics," *Am. J. Phys.* **41**, 394 (1973).

Jooyoung Lee and J. M. Kosterlitz, "New numerical method to study phase transitions," *Phys. Rev. Lett.* **65**, 137 (1990); *ibid.*, "Finite-size scaling and Monte Carlo simulations of first-order phase transitions," *Phys. Rev.* B **43**, 3265 (1991).

Jooyoung Lee and Katherine J. Strandburg, "First-order melting transition of the hard-disk system," *Phys. Rev.* B **46**, 11190 (1992).

N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Keller, "Equation of state calculations for fast computing machines," *J. Chem. Phys.* **6**, 1087 (1953).

J. Marro and R. Toral, "Microscopic observations on a kinetic Ising model," *Am. J. Phys.* **54**, 1114 (1986).

M. A. Novotny, "A new approach to an old algorithm for the simulation of Ising-like systems," *Computers in Physics* **9**1, 46 (1995). The n-fold way algorithm is discussed.

Ole G. Mouritsen, *Computer Studies of Phase Transitions and Critical Phenomena*, Springer-Verlag (1984).

E. P. Münger and M. A. Novotny, "Reweighting in Monte Carlo and Monte Carlo renormalization-group studies," *Phys. Rev.* B **43**, 5773 (1991). The authors discuss the histogram method and combine it with renormalization group calculations.

Michael Plischke and Birger Bergersen, *Equilibrium Statistical Physics*, second edition, Prentice Hall (1994). A graduate level text that discusses some of the more contemporary topics in statistical physics, many of which have been influenced by computer simulations.

William H. Press, Saul A. Teukolsky, William T. Vetterling, and Brian P. Flannery, *Numerical Recipes*, second edition, Cambridge University Press (1992). A Fortran program for the traveling salesman problem is given in Section 10.9.

Stephen H. Shenker and Jan Tobochnik, "Monte Carlo renormalization-group analysis of the classical Heisenberg model in two dimensions," *Phys. Rev.* B **22**, 4462 (1980).

Amihai Silverman and Joan Adler, "Animated Simulated Annealing," *Computers in Physics* **6**, 277 (1992). The authors describe a simulation of the annealing process to obtain a defect free single crystal of a model material.

Zoran Slanič, Harvey Gould, and Jan Tobochnik, "Dynamics of the classical Heisenberg chain," *Computers in Physics* **5**, 630 (1991). Unlike the Ising model, the Heisenberg model has an intrinsic dynamics and can be studied by molecular dynamics methods.

H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press (1971). See Appendix B for the exact solution of the zero-field Ising model for a two-dimensional lattice.

Jan Tobochnik and G. V. Chester, "Monte Carlo study of the planar model," *Phys. Rev.* B **20**, 3761 (1979).

J. P. Valleau and S. G. Whittington, "A guide to Monte Carlo for statistical mechanics: 1. Highways," in *Statistical Mechanics, Part A*, Bruce J. Berne, editor, Plenum Press (1977). See also J. P. Valleau and G. M. Torrie, "A guide to Monte Carlo for statistical mechanics: 2. Byways," *ibid.*

I. Vattulainen, T. Ala-Nissila, and K. Kankaala, "Physical tests for random numbers in simulations," *Phys. Rev. Lett.* **73**, 2513 (1994).