



## Chapter 16

# The Microcanonical Ensemble

©2002 by Harvey Gould, Jan Tobochnik, and Wolfgang Christian  
22 April 2002

We simulate the microcanonical ensemble and “discover” the Boltzmann distribution for systems in thermal contact with a heat bath.

### 16.1 Introduction

The Monte Carlo simulations of the “particles in the box” problem discussed in Chapter 7 and the molecular dynamics simulations discussed in Chapter 8 have exhibited some of the important qualitative features of macroscopic systems, for example, the irreversible approach to equilibrium and the existence of equilibrium fluctuations in macroscopic quantities. In this chapter we apply Monte Carlo methods to the simulation of the equilibrium properties of systems with many degrees of freedom. This application will allow us to explore the methodology of statistical mechanics and to introduce the concept of temperature.

Due in part to the impact of computer simulations, the applications of statistical mechanics have expanded from the traditional areas of dense gases and liquids to the study of phase transitions, particle physics, and theories of the early universe. In fact, the algorithm introduced in this chapter was developed by a physicist interested in using computer simulations to predict experimentally verifiable quantities from lattice gauge theories, theories used to describe the interactions of fundamental particles.

### 16.2 The Microcanonical Ensemble

We first discuss an *isolated* system for which the number of particles  $N$ , the volume  $V$ , and the total energy  $E$  are fixed and the influence of external parameters such as gravitational and magnetic fields can be ignored. In general, an isolated macroscopic system tends to a time-independent equilibrium state of maximum randomness or entropy. The *macrostate* of the system is specified

by the values of  $E$ ,  $V$ , and  $N$ . At the microscopic level there are a large number of different ways or *configurations* in which the macrostate  $(E, V, N)$  can be realized. A particular configuration or *microstate* is *accessible* if its properties are consistent with the specified macrostate.

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

$$P_s = \begin{cases} 1/\Omega, & \text{if } s \text{ is accessible} \\ 0, & \text{otherwise.} \end{cases} \quad (16.1)$$

The sum of  $P_s$  over all  $\Omega$  states is equal to unity.

The averages of physical quantities can be determined in two ways. In the usual laboratory experiment, physical quantities are measured over a time interval sufficiently long to allow the system to sample a large number of its accessible microstates. We already performed such time averages in Chapter 6, where we used the method of molecular dynamics to compute the time-averaged values of quantities such as the temperature and pressure. An interpretation of the probabilities in (16.1) that is consistent with such a time average is that during a sequence of observations,  $P_s$  yields the fraction of times that a single system is found in a given microscopic state.

Although time averages are conceptually simple, it is convenient to formulate statistical averages at a given instant of time. Instead of performing measurements on a single system, imagine a collection or *ensemble* of systems that are identical mental replicas characterized by the same macrostate. The number of systems in the ensemble equals the number of possible microstates. In this interpretation, the probabilities in (16.1) describe an ensemble of identical systems. An ensemble of systems specified by  $E$ ,  $N$ ,  $V$  is called a *microcanonical* ensemble. Suppose that a physical quantity  $A$  has the value  $A_s$  when the system is in the state  $s$ . Then the ensemble average of  $A$  is given by

$$\langle A \rangle = \sum_{s=1}^{\Omega} A_s P_s, \quad (16.2)$$

where  $P_s$  is given by (16.1).

To illustrate these ideas, consider a one-dimensional model of an ideal gas in which the particles are distinguishable, noninteracting, and have only two possible velocities  $v_0$  and  $-v_0$ . Because the particles are noninteracting, the size of the system and the positions of the particles are irrelevant. In Table 16.1 we show the ensemble of systems consistent with  $N = 4$  and  $E = 2v_0^2$ . The mass of the particles is assumed to be unity.

The enumeration of the sixteen systems in the ensemble allows us to calculate ensemble averages for the physical quantities of the system. For example, inspection of Table 16.1 shows that  $P_n$ , the probability that the number of particles moving to the right is  $n$ , is given by  $1/16$ ,  $4/16$ ,  $6/16$ ,  $4/16$ , and  $1/16$  for  $n = 0, 1, 2, 3$ , and  $4$ , respectively. Hence, the mean number of particles

L L L L	L L L R	L L R R	L R R R	R R R R
	L L R L	L R L R	R L R R	
	L R L L	L R R L	R R L R	
	R L L L	R L L R	R R R L	
		R L R L		
		R R L L		

Table 16.1: The sixteen possible microstates for a one-dimensional system of  $N = 4$  noninteracting particles. The letter  $R$  denotes a particle moving to the right and the letter  $L$  denotes a particle moving to the left. Each particle has speed  $v_0$ . The mass of the particles is taken to be unity and the total (kinetic) energy  $E = 4(v_0^2/2)$ .

moving to the right is

$$\langle n \rangle = \sum n P_n = (0 \times 1 + 1 \times 4 + 2 \times 6 + 3 \times 4 + 4 \times 1)/16 = 2. \quad (16.3)$$

### 16.3 The Demon Algorithm

We found in Chapter 8 that we can do a time average of a system of many particles with  $E$ ,  $V$ , and  $N$  fixed by integrating Newton's equations of motion for each particle and computing the time-averaged value of the physical quantities of interest. How can we do an ensemble average at fixed  $E, V$ , and  $N$ ? One way would be to enumerate all the microstates and calculate the ensemble average of the desired physical quantities as we did in the ideal gas example. However, this approach usually is not practical, because the number of microstates for even a small system is much too large to enumerate. In the spirit of Monte Carlo, we wish to develop a practical method of obtaining a representative sample of the total number of microstates. An obvious procedure is to fix  $V$  and  $N$ , change the positions and velocities of the individual particles at random, and retain the configuration if it has the desired total energy. However this procedure is very inefficient, because most configurations would not have the desired total energy and would have to be discarded.

An efficient Monte Carlo procedure has been developed by Creutz and coworkers. Suppose that we add an extra degree of freedom to the original macroscopic system of interest. For historical reasons, this extra degree of freedom is called a *demon*. The demon travels about the system transferring energy as it attempts to change the dynamical variables of the system. If a desired change lowers the energy of the system, the excess energy is given to the demon. If the desired change raises the energy of the system, the demon gives the required energy to the system if the demon has sufficient energy. The only constraint is that the demon cannot have negative energy. The demon algorithm for a classical system of particles is summarized in the following:

1. Choose a particle at random and make a trial change in its position.
2. Compute  $\Delta E$ , the change in the energy of the system due to the change.
3. If  $\Delta E \leq 0$ , the system gives the amount  $|\Delta E|$  to the demon, that is,  $E_d = E_d - \Delta E$ , and the trial configuration is accepted.

4. If  $\Delta E > 0$  and the demon has sufficient energy for this change ( $E_d \geq \Delta E$ ), then the demon gives the necessary energy to the system, that is,  $E_d = E_d - \Delta E$ , and the trial configuration is accepted. Otherwise, the trial configuration is rejected and the configuration is not changed.

The above steps are repeated until a representative sample of states is obtained. After a sufficient number of steps, the demon and the system will reach a compromise and agree on an average energy for each. The total energy remains constant, and because the demon is only one degree of freedom in comparison to the many degrees of freedom of the system, the energy fluctuations of the system will be order  $1/N$ .

How do we know that this Monte Carlo simulation of the microcanonical ensemble will yield results equivalent to the time-averaged results of molecular dynamics? The assumption that the two averages yield equivalent results is called the *ergodic* hypothesis (more accurately, the *quasi-ergodic* hypothesis). Although these two averages have not been shown to be identical in general, they have been found to yield equivalent results in all cases of interest.

## 16.4 One-Dimensional Classical Ideal Gas

We first apply the demon algorithm to the one-dimensional classical ideal gas. Of course, we do not need to use the demon algorithm for an ideal gas because a reduction in the energy of one particle can be easily compensated by the corresponding increase in the energy of another particle. However, it is a good idea to consider a simple example first.

For an ideal gas, the energy of a configuration is independent of the positions of the particles, and the total energy is the sum of the kinetic energies of the individual particles. Hence, for an ideal gas the only coordinates of interest are the velocity coordinates. To change a configuration, we choose a particle at random and change its velocity by a random amount.

`Program ideal` implements a microcanonical Monte Carlo simulation of an ideal classical gas in one dimension. The variable `mcs`, the number of Monte Carlo steps per particle, plays an important role in Monte Carlo simulations. On the average, the demon attempts to change the velocity of each particle once during each Monte Carlo step per particle. We frequently will refer to the number of Monte Carlo steps per particle as the “time,” even though this time has no obvious direct relation to a physical time.

```
PROGRAM ideal
! demon algorithm for the one-dimensional, ideal classical gas
DIM v(100)
CALL initial(N,v(),mcs,E,Ed,Ecum,Edcum,accept,dvmax)
FOR imcs = 1 to mcs
  CALL change(N,v(),E,Ed,Ecum,Edcum,accept,dvmax)
NEXT imcs
CALL averages(N,Ecum,Edcum,mcs,accept)
END

SUB initial(N,v(),mcs,E,Ed,Ecum,Edcum,accept,dvmax)
  RANDOMIZE
```

```

INPUT prompt "number of particles = ": N
INPUT prompt "initial energy of system = ": E
LET Ed = 0                ! initial demon energy
INPUT prompt "number of MC steps per particle = ": mcs
INPUT prompt "maximum change in velocity = ": dvmax
! divide energy equally among particles
LET vinitial = sqr(2*E/N) ! mass unity
! all particles have same initial velocities
FOR i = 1 to N
    LET v(i) = vinitial
NEXT i
! initialize sums
LET Ecum = 0
LET Edcum = 0
LET accept = 0
END SUB

SUB change(N,v(),E,Ed,Ecum,Edcum,accept,dvmax)
FOR i = 1 to N
    LET dv = (2*rnd - 1)*dvmax    ! trial change in velocity
    LET ipart = int(rnd*N + 1)    ! select random particle
    LET vtrial = v(ipart) + dv    ! trial velocity
    ! trial energy change
    LET de = 0.5*(vtrial*vtrial - v(ipart)*v(ipart))
    IF de <= Ed then
        LET v(ipart) = vtrial
        LET accept = accept + 1
        LET Ed = Ed - de
        LET E = E + de
    END IF
NEXT i
! accumulate data after each Monte Carlo step per particle
LET Ecum = Ecum + E
LET Edcum = Edcum + Ed
END SUB

SUB averages(N,Ecum,Edcum,mcs,accept)
LET norm = 1/mcs
LET Edave = Edcum*norm          ! mean demon energy
LET norm = norm/N
LET accept_prob = accept*norm   ! acceptance probability
! system averages per particle
LET Esave = Ecum*norm           ! mean energy per system particle
PRINT "mean demon energy ="; Edave
PRINT "mean system energy per particle ="; Esave
PRINT "acceptance probability ="; accept_prob

```

END SUB

*Problem 16.1.* Monte Carlo simulation of an ideal gas

- a. We will use `Program ideal` to investigate some of the equilibrium properties of an ideal gas. Suppose that we assign the same initial velocity to all the particles. What is the mean value of the particle velocities after equilibrium has been reached? Choose the number of particles  $N = 40$ , the initial total energy  $E = 10$ , the initial demon energy  $E_d = 0$ , the maximum change in the velocity  $dv_{\max} = 2$ , and the number of Monte Carlo steps per particle  $mcs \geq 1000$ . The mass of the particles is set equal to unity.
- b. The configuration corresponding to all particles having the same velocity is not very likely, and it would be better to choose an initial configuration that is more likely to occur when the system is in equilibrium. Because this choice is not always possible, we should let the system evolve for a number of Monte Carlo steps per particle before we accumulate data for the averages. We call this number the *equilibration time*. Modify `Program ideal` so that the changes are made for `nequil` Monte Carlo steps per particle before averages are taken. We can estimate this time from a plot of the time average of the demon energy or other quantity of interest versus the time. Determine the mean demon energy and mean system energy per particle for the parameters in part (a).
- c. Compute the mean energy of the demon and the mean system energy per particle for  $E = 20$  and  $E = 40$ . Choose  $mcs = 50000$  if possible. Use your result from part (b) and obtain an approximate relation between the mean demon energy and the mean system energy per particle.
- d. In the microcanonical ensemble the total energy is fixed with no reference to temperature. Define the temperature by the relation  $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}kT_{\text{kin}}$ , where  $\frac{1}{2}m\langle v^2 \rangle$  is the mean kinetic energy per particle. Use this relation to obtain  $T_{\text{kin}}$ . How is  $T_{\text{kin}}$  related to the mean demon energy? Choose energy units such that Boltzmann's constant  $k$  is equal to unity.
- e. A limitation of any Monte Carlo simulation is the finite number of particles. In part (d) we found that the mean demon energy is approximately twice the mean kinetic energy per particle. In the infinite particle limit this relation would hold exactly. Determine how close your results come to the infinite particle results for  $N = 2$  and  $N = 10$ . If there is no statistically significant difference between your results for the two values of  $N$ , explain why finite  $N$  might not be an important limitation for the ideal gas.

## 16.5 The Temperature and the Canonical Ensemble

Although the microcanonical ensemble is conceptually simple, it does not represent the situation usually found in the laboratory. Most laboratory systems are not isolated, but are in thermal contact with their environment. This thermal contact allows energy to be exchanged between the laboratory system and its environment in the form of heat. The laboratory system is usually small relative to its environment. The larger system with many more degrees of freedom is referred to as the *heat reservoir* or *heat bath*.

We now consider the more realistic case for which the total energy of the *composite* system consisting of the laboratory system and the heat bath is constrained to be constant, but the energy

of the laboratory system can vary. Imagine a large number of mental copies of the laboratory system and the heat bath. Considered together, the composite system is isolated and can be described by the microcanonical ensemble. However, because we are interested in the equilibrium values of the laboratory system, we need to know the probability  $P_s$  of finding the laboratory system in the microstate  $s$  with energy  $E_s$ . The ensemble that describes the probability distribution of the laboratory system in thermal equilibrium with a heat bath is known as the *canonical* ensemble.

In general, the laboratory system can be any macroscopic system that is much smaller than the heat bath. The laboratory system can be as small as an individual particle if the latter can be clearly distinguished from the particles of the heat bath. An example of such a laboratory system is the demon itself. Hence, we can consider the demon to be a system whose microstate is specified only by its energy. The demon is a model of a laboratory system in equilibrium with a heat bath.

One way of finding the form of the probability distribution of the canonical ensemble is to simulate a demon exchanging energy with an ideal gas. The ideal gas serves as the heat bath. The main quantity of interest is the probability  $P(E_d)$  that the demon has energy  $E_d$ . We will find in Problem 16.2 that the form of  $P(E_d)$  is given by

$$P(E_d) = \frac{1}{Z} e^{-E_d/kT}, \quad (16.4)$$

where  $Z$  is a normalization constant such that the sum over all the states of the demon is unity. The parameter  $T$  in (16.4) is called the *absolute temperature* and is measured in Kelvin (K). Boltzmann's constant  $k$  is given by  $k = 1.38 \times 10^{-23}$  J/K. The probability distribution (16.4) is called the *Boltzmann* or the *canonical distribution*, and  $Z$  is called the *partition function*.

The form (16.4) of the Boltzmann distribution provides a simple way of computing  $T$  from the mean demon energy  $\langle E_d \rangle$  given by

$$\langle E_d \rangle = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = kT. \quad (16.5)$$

We see that  $T$  is proportional to the mean demon energy. Note that the result  $\langle E_d \rangle = kT$  in (16.5) holds only if the energy of the demon can take on a continuum of values and if the upper limit of integration can be taken to be  $\infty$ .

**Problem 16.2.** The Boltzmann probability distribution

- Add a subroutine to `Program ideal` to compute the probability distribution  $P(E_d)$  of the demon. Because  $E_d$  is a continuous variable, it is necessary to place the values of  $E_d$  in appropriate bins. Plot the natural logarithm of  $P(E_d)$  versus  $E_d$  and verify the form (16.4) for the Boltzmann distribution. What is the slope of this plot? Choose units such that  $k = 1$  and estimate the corresponding value of  $T$ . Choose the same parameters as were used in Problem 16.1. Be sure to determine  $P(E_d)$  only after thermal equilibrium has been obtained.
- Determine the magnitude of  $T$  from the relation (16.5). Are your two estimates of  $T$  consistent?
- Compare the value of  $T$  obtained in parts (a) and (b) with the value of  $T$  found in Problem 16.1 using the kinetic definition of the temperature. Is the demon in thermal equilibrium with its heat bath?



Figure 16.1: The interaction energy between nearest neighbor spins in the absence of an external magnetic field.

## 16.6 The Ising Model

A popular model of a system of interacting variables in statistical physics is the *Ising* model. The model was proposed by Lenz and investigated by his graduate student, Ising, to study the phase transition from a paramagnet to a ferromagnet (cf. Brush). Ising computed the thermodynamic properties of the model in one dimension and found that the model does not have a phase transition. However, for two and three dimensions the Ising model does exhibit a transition. The nature of the phase transition in two dimensions and the diverse applications of the Ising model are discussed in Chapter 17.

To introduce the Ising model, consider a lattice containing  $N$  sites and assume that each lattice site  $i$  has associated with it a number  $s_i$ , where  $s_i = +1$  for an “up” ( $\uparrow$ ) spin and  $s_i = -1$  for a “down” ( $\downarrow$ ) spin. A particular configuration or microstate of the lattice is specified by the set of variables  $\{s_1, s_2, \dots, s_N\}$  for all lattice sites.

The macroscopic properties of a system are determined by the nature of the accessible microstates. Hence, it is necessary to know the dependence of the energy on the configuration of spins. The total energy  $E$  of the Ising model is given by

$$E = -J \sum_{i,j=\text{nn}(i)}^N s_i s_j - H \sum_{i=1}^N s_i, \quad (16.6)$$

where  $H$  is proportional to a uniform external magnetic field. The first sum in (16.6) is over all nearest neighbor pairs. The *exchange constant*  $J$  is a measure of the strength of the interaction between nearest neighbor spins (see Fig. 16.1). The second sum in (16.6) represents the energy of interaction of the magnetic moments associated with the spins with an external magnetic field.

If  $J > 0$ , then the states  $\uparrow\uparrow$  and  $\downarrow\downarrow$  are energetically favored in comparison to the states  $\uparrow\downarrow$  and  $\downarrow\uparrow$ . Hence for  $J > 0$ , we expect that the state of lowest total energy is *ferromagnetic*, that is, the spins all point in the same direction. If  $J < 0$ , the states  $\uparrow\downarrow$  and  $\downarrow\uparrow$  are favored and the state of lowest energy is expected to be *antiferromagnetic*, that is, alternate spins are aligned. If we subject the spins to an external magnetic field directed upward, the spins  $\uparrow$  and  $\downarrow$  possess an additional internal energy given by  $-H$  and  $+H$  respectively.

An important virtue of the Ising model is its simplicity. Some of its simplifying features are that the kinetic energy of the atoms associated with the lattice sites has been neglected, only nearest neighbor contributions to the interaction energy have been included, and the spins are allowed to have only two discrete values. In spite of the simplicity of the model, we will find that it exhibits very interesting behavior.

For the familiar case of classical particles with continuously varying position and velocity coordinates, the dynamics is given by Newton's laws. For the Ising model the dependence (16.6) of the energy on the spin configuration is not sufficient to determine the time-dependent properties of the system. That is, the relation (16.6) does not tell us how the system changes from one spin configuration to another and we have to introduce the dynamics separately.

In Problem ?? we simulated the Ising model using a cellular automata approach. The major limitation of this approach is that it is difficult for the system to sample a representative set of configurations. In addition, there is no simple measure of the temperature. The demon algorithm is much more effective at exploring the set of possible configurations, because the energy of the lattice can fluctuate slightly allowing the lattice to sample any configuration with nearly the same energy. We implement the demon algorithm by choosing a spin at random. The trial change corresponds to a flip of the spin from  $\uparrow$  to  $\downarrow$  or  $\downarrow$  to  $\uparrow$ .

Because we are interested in the properties of an infinite system, we have to choose appropriate boundary conditions. The simplest boundary condition in one dimension is to choose a "free surface" so that the spins at sites 1 and  $N$  each have one nearest neighbor interaction only. In general, a better choice is periodic boundary conditions. For this choice the lattice becomes a ring and the spins at sites 1 and  $N$  interact with one another and hence have the same number of interactions as do the other spins.

What are some of the physical quantities whose averages we wish to compute? An obvious physical quantity is the *magnetization*  $M$  given by

$$M = \sum_{i=1}^N s_i, \quad (16.7)$$

and the magnetization per spin  $m = M/N$ . Usually we are interested in the average values  $\langle M \rangle$  and the fluctuations  $\langle M^2 \rangle - \langle M \rangle^2$ . We can determine the temperature  $T$  as a function of the energy of the system in two ways. One way is to measure the probability that the demon has energy  $E_d$ . Because we know that this probability is proportional to  $\exp(-E_d/kT)$ , we can determine  $T$  from a plot of the logarithm of the probability as a function of  $E_d$ . An easier way to determine  $T$  is to measure the mean demon energy. However, because the values of  $E_d$  are not continuous for the Ising model,  $T$  is not proportional to  $\langle E_d \rangle$  as it is for the ideal gas. We show in Appendix 16.8 that for  $H = 0$  and the limit of an infinite system, the temperature is related to  $\langle E_d \rangle$  by

$$kT/J = \frac{4}{\ln(1 + 4J/\langle E_d \rangle)}. \quad (16.8)$$

The result (16.8) comes from replacing the integrals in (16.5) by sums over the possible demon energies. Note that in the limit  $|J/E_d| \ll 1$ , (16.8) reduces to  $kT = E_d$  as expected.

**Program demon** implements the microcanonical simulation of the Ising model in one dimension using spin flip dynamics and periodic boundary conditions. Once the initial configuration is chosen, the demon algorithm is similar to that described in Section 16.3. However, in contrast to the ideal gas, the spins in the one-dimensional Ising model must be chosen randomly.

**PROGRAM demon**

**! demon algorithm for the d = 1 Ising model in zero magnetic field**

```

DIM spin(1000)
LIBRARY "mygraphics"
CALL initial(N,spin(),E,Ed,M,mcs,Ecum,Edcum,Mcum,M2cum,accept)
CALL setupscreen(N,spin(),up$,down$)
FOR imcs = 1 to mcs
    CALL change(N,spin(),E,Ed,M,accept,up$,down$)
    CALL data(E,Ed,M,Ecum,Edcum,Mcum,M2cum)
NEXT imcs
CALL averages(N,Ecum,Edcum,Mcum,M2cum,mcs,accept)
END

SUB initial(N,spin(),E,Ed,M,mcs,Ecum,Edcum,Mcum,M2cum,accept)
RANDOMIZE
INPUT prompt "number of spins = ": N
! choose total energy to be multiple of 4J
! coupling constant J is unity
INPUT prompt "desired total energy = ": Etot
LET Etot = 4*int(Etot/4)
INPUT prompt "number of Monte Carlo steps per spin = ": mcs
! initial configuration of spins in minimum energy state
FOR isite = 1 to N
    LET spin(isite) = 1
NEXT isite
LET M = N                ! net magnetization
! compute initial system energy
LET E = -N                ! periodic boundary conditions
LET Ed = (Etot - E)
PRINT "total energy = "; E + Ed
! initialize sums
LET Ecum = 0
LET Edcum = 0
LET Mcum = 0
LET M2cum = 0
END SUB

SUB setupscreen(N,spin(),up$,down$)
LET r = N/(2*pi)
CALL compute_aspect_ratio(r+2,xwin,ywin)
SET WINDOW -xwin,xwin,-ywin,ywin
LET dtheta = 2*pi/N
SET COLOR "red"
BOX AREA 1,1+0.5,1,1+0.5
BOX KEEP 1,1+0.5,1,1+0.5 in up$
CLEAR
SET COLOR "blue"
BOX AREA 1,1+0.5,1,1+0.5

```

```

BOX KEEP 1,1+0.5,1,1+0.5 in down$
CLEAR
FOR i = 1 to N
  CALL showspin(N,spin(i),i,up$,down$)
NEXT i
END SUB

SUB change(N,spin(),E,Ed,M,accept,up$,down$)
FOR i = 1 to N
  LET isite = int(rnd*N + 1)      ! random spin
  ! determine neighboring spin values
  IF isite = 1 then
    LET left = spin(N)
  ELSE
    LET left = spin(isite - 1)
  END IF
  IF isite = N then
    LET right = spin(1)
  ELSE
    LET right = spin(isite + 1)
  END IF
  ! trial energy change
  LET de = 2*spin(isite)*(left + right)
  IF de <= Ed then
    ! spin flip dynamics
    LET spin(isite) = -spin(isite)
    LET M = M + 2*spin(isite)
    LET accept = accept + 1      ! number of changes accepted
    LET Ed = Ed - de
    LET E = E + de
  END IF
  CALL showspin(N,spin(isite),isite,up$,down$)
NEXT i
END SUB

SUB data(E,Ed,M,Ecum,Edcum,Mcum,M2cum)
  ! accumulate data
  LET Ecum = Ecum + E
  LET Edcum = Edcum + Ed
  LET Mcum = Mcum + M
  LET M2cum = M2cum + M*M
END SUB

SUB averages(N,Ecum,Edcum,Mcum,M2cum,mcs,accept)
  SET COLOR "black/white"
  LET norm = 1/mcs              ! collected data after every attempt

```

```

    LET Edave = Edcum*norm
    PRINT "mean demon energy ="; Edave
    LET T = 4/log(1 + 4/Edave)
    PRINT "T ="; T
    LET Eave = Ecum*norm
    PRINT "<E> = "; Eave
    LET Mave = Mcum*norm
    PRINT "<M> ="; Mave
    LET M2ave = M2cum*norm
    PRINT "<M*M> ="; M2ave
    LET accept_prob = accept*norm/N
    PRINT "acceptance probability ="; accept_prob
END SUB

SUB showspin(N,dir,isite,up$,down$)
    LET r = N/(2*pi)
    LET theta = isite/r
    LET x = r*cos(theta)
    LET y = r*sin(theta)
    IF dir = 1 then
        BOX SHOW up$ at x,y
    ELSE
        BOX SHOW down$ at x,y
    END IF
END SUB
END SUB

```

Note that for  $H = 0$ , the change in energy due to a spin flip is either 0 or  $\pm 4J$ . Hence the initial energy of the system plus the demon must be an integer multiple of  $4J$ . Because the spins are interacting, it is difficult to choose an initial configuration of spins with precisely the desired energy. The procedure followed in `SUB initial` is to choose the initial configuration to be all spins up, a minimum energy configuration. The demon energy is chosen so that the total energy of the system and the demon is equal to the desired multiple of  $4J$ .

*Problem 16.3.* One-dimensional Ising model

- Use `Program demon` with  $N = 100$  and the desired total energy  $E_{\text{tot}} = -20$ . What is the initial energy assigned to the demon in `SUB initial`? Note that the program shows the spins as a ring. Describe the evolution of the spins. (It might be useful to insert some `PAUSE` statements in the program.) Change  $E_{\text{tot}}$  and describe any qualitative changes in the evolution.
- Compute the time average of the demon energy and the magnetization  $M$  as a function of the time. As usual, we interpret the time as the number of Monte Carlo steps per spin. What is the approximate time for these quantities to approach their equilibrium values?
- Modify the program so that initial nonequilibrium configurations are not used to determine the averages of physical quantities. What are the equilibrium values of  $\langle E_d \rangle$ ,  $\langle M \rangle$ , and  $\langle M^2 \rangle$ ? The choice of  $\text{mcs} = 100$  is appropriate for testing the program and yields results of approximately 20% accuracy. To obtain better than 5% results,  $\text{mcs}$  should be the order of 1000.

- d. Compute  $T$  and  $E$  for  $N = 100$ , and the cases  $E_{\text{tot}} = -20, -40, -60$ , and  $-80$ . Compare your results to the exact result for an infinite one-dimensional lattice,  $E/N = -\tanh(J/kT)$ . How do your computed results for  $E/N$  depend on  $N$  and on the number of Monte Carlo steps per spin?
- e. Use the same runs as in part (d) to compute  $\langle M^2 \rangle$  as a function of  $T$ . Does  $\langle M^2 \rangle$  increase or decrease with  $T$ ?
- f. Modify Program `demon` and verify the Boltzmann form (16.4) for the energy distribution of the demon.

*Problem 16.4.* Additional applications

- a. Modify Program `demon` so that the antiferromagnetic case ( $J = -1$ ) is treated. Before doing the simulation describe how you expect the spin configurations to differ from the ferromagnetic case. What is the lowest energy or ground state configuration? Run the simulation with the spins initially in their ground state, and compare your results with your expectations. Compute the mean energy per spin versus temperature and compare your results with the ferromagnetic case.
- b. Modify Program `demon` to include a nonzero magnetic field,  $H \neq 0$ , and compute  $\langle E_d \rangle$ ,  $\langle M \rangle$ , and  $\langle M^2 \rangle$  as a function of  $H$  for fixed  $E$ . Read the discussion in Appendix 16.8 and determine the relation of  $\langle E_d \rangle$  to  $T$  for your choices of  $H$ . Is the equilibrium temperature higher or lower than the  $H = 0$  case for the same total energy?

\**Problem 16.5.* The two-dimensional Ising model

- a. Simulate the two-dimensional Ising model on a square lattice with spin-flip dynamics in the microcanonical ensemble. The total number of spins  $N = L^2$ , where  $L$  is the length of one side of the lattice. Use periodic boundary conditions as shown in Fig. 16.2 so that spins in the left-hand column interact with spins in the right-hand column, etc. Do not include nonequilibrium configurations in your averages.
- b. Compute  $\langle E_d \rangle$  and  $\langle M^2 \rangle$  as a function of  $E$ . Convenient choices of parameters are  $L = 10$  and `mcs` = 500. Assume  $J = 1$  and  $H = 0$ . Use (16.8) to determine the dependence of  $T$  on  $E$  and plot  $E$  versus  $T$ .
- c. Repeat the simulations in part (b) for  $L = 20$ . If necessary, increase `mcs` until your averages are accurate to within a few percent. Describe how the energy versus temperature curve changes with lattice size.
- d. Modify your program to make “snapshots” of the spin configurations. Describe qualitatively the nature of the configurations at different energies or temperatures. Are they ordered or disordered? Are there domains of up or down spins?

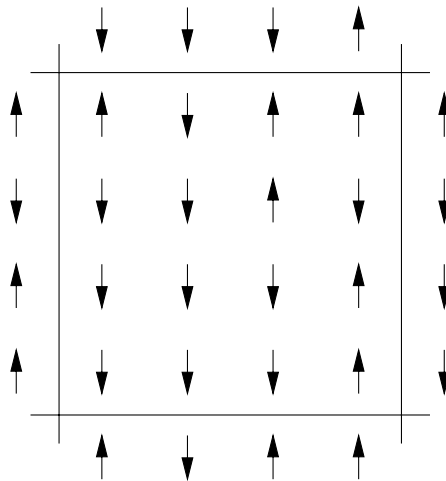


Figure 16.2: One of the  $2^N$  possible configurations of a system of  $N = 16$  Ising spins on a square lattice. Also shown are the spins in the four nearest periodic images of the central cell that are used to calculate the energy. An up spin is denoted by  $\uparrow$  and a down spin is denoted by  $\downarrow$ . Note that the number of nearest neighbors on a square lattice is four. The energy of this configuration is  $E = -8J + 4H$  with periodic boundary conditions.

## 16.7 \*Heat Flow

In our applications of the demon algorithm one demon shared its energy equally with all the spins. As a result the spins all attained the same mean energy of interaction. Many interesting questions arise when the system is not spatially uniform and is in a nonequilibrium but time-independent (steady) state.

Let us consider heat flow in a one-dimensional Ising model. Suppose that instead of all the sites sharing energy with one demon, each site has its own demon. We can study the flow of heat by requiring the demons at the boundary spins to satisfy different conditions than the demons at the other spins. The demon at spin 1 adds energy to the system by flipping this spin so that it is in its highest energy state, that is, in the opposite direction of spin 2. The demon at spin  $N$  removes energy from the system by flipping spin  $N$  so that it is in its lowest energy state, that is, in the same direction as spin  $N - 1$ . As a result, energy flows from site 1 to site  $N$  via the demons associated with the intermediate sites. In order that energy not build up at the “hot” end of the Ising chain, we require that spin 1 can only add energy to the system if spin  $N$  simultaneously removes energy from the system. Because the demons at the two ends of the lattice satisfy different conditions than the other demons, we do not use periodic boundary conditions.

The temperature is determined by the generalization of the relation (16.8), that is, the temperature at site  $i$  is related to the mean energy of the demon at site  $i$ . To control the temperature gradient, we can update the end spins at a rate different than the other spins. The maximum temperature gradient occurs if we update the end spins after every update of an internal spin. A

smaller temperature gradient occurs if we update the end spins less frequently. The temperature gradient between any two spins can be determined from the temperature profile, the spatial dependence of the temperature. The energy flow can be determined by computing the magnitude of the energy per unit time that enters the lattice at site 1.

To implement this procedure we modify `Program demon` by converting the variables `Ed` and `Edcum` to arrays. We do the usual updating procedure for spins 2 through  $N - 1$  and visit spins 1 and  $N$  at regular intervals denoted by `nvisit`.

```

PROGRAM conduct
! many demon algorithm for Ising chain
! heat added at spin 1 and subtracted at spin N
DIM spin(1000),Ed(1000),Edsum(1000),Msum(1000)
CALL initial(N,spin(),nmcs,nvisit)
FOR imcs = 1 to nmcs
  CALL change(N,spin(),Ed(),accept)
  IF mod(imcs,nvisit) = 0 then CALL heat(N,spin(),Edsum())
  CALL data(N,spin(),Ed(),Edsum(),Msum())
NEXT imcs
CALL output(N,Edsum(),Msum(),nmcs,accept)
END

SUB initial(N,spin(),nmcs,nvisit)
  RANDOMIZE
  INPUT prompt "number of spins = ": N
  INPUT prompt "number of MC steps per spin = ": nmcs
  INPUT prompt "MC steps between updates of end spins = ": nvisit
  ! initial random configuration
  FOR i = 1 to N
    IF rnd > 0.5 then
      LET spin(i) = 1
    ELSE
      LET spin(i) = -1
    END IF
  NEXT i
END SUB

SUB change(N,spin(),Ed(),accept) ! spin flip dynamics
! do one Monte Carlo step
FOR i = 2 to N - 1
  ! pick spin at random from spins 2 to N - 1
  LET isite = int(rnd*(N - 2) + 2)
  ! trial energy change
  LET de = 2*spin(isite)*(spin(isite - 1) + spin(isite + 1))
  IF de <= Ed(isite) then
    LET spin(isite) = - spin(isite)
    LET accept = accept + 1
  
```

```

        LET Ed(isite) = Ed(isite) - de
    END IF
NEXT i
END SUB

SUB heat(N,spin(),Edsum())
! attempt to add energy at spin 1 and remove it at spin N
! possible only if spins 1 and 2 are aligned
! and spins N and N - 1 are not aligned
IF (spin(1)*spin(2) = 1) and (spin(N)*spin(N-1) = -1) then
    LET Edsum(1) = Edsum(1) + 2
    LET Edsum(N) = Edsum(N) - 2
    LET spin(1) = -spin(1)
    LET spin(N) = -spin(N)
END IF
END SUB

SUB data(N,spin(),Ed(),Edsum(),Msum())
FOR i = 2 to N - 1
    LET Edsum(i) = Edsum(i) + Ed(i)
    LET Msum(i) = Msum(i) + spin(i)
NEXT i
END SUB

SUB output(N,Edsum(),Msum(),nmcs,accept)
LET norm = 1/nmcs
LET accept_prob = accept*norm/(N - 2)
PRINT "acceptance probability = "; accept_prob
PRINT
PRINT tab(2);"i";tab(16);"Ed(i)";tab(35);"T";tab(46);"M(i) "
PRINT
FOR i = 2 to N-1
    LET edave = Edsum(i)*norm
    LET temperature = 0
    IF Edave <> 0 then
        IF (1 + 4/Edave) > 0 then
            LET temperature = 4/log(1 + 4/Edave)
        END IF
    END IF
    LET M = Msum(i)*norm
    PRINT i,Edave,temperature,M
NEXT i
END SUB

```

*Problem 16.6.* One-dimensional heat flow

- a. As a check on Program conduct, modify the program so that all the demons are equivalent,

that is, impose periodic boundary conditions and do not use `SUB heat`. Compute the mean energy of the demon at each site and use (16.8) to define a local site temperature. Use  $N \geq 22$  and  $\text{mcs} \geq 1000$ . Is the local temperature approximately uniform? How do your results compare with the single demon case?

- b. In `Program conduct` energy is added to the system at site 1 and is removed at site  $N$ . Determine the mean demon energy for each site and obtain the corresponding local temperature and the mean energy of the system. Draw the temperature profile by plotting the temperature as a function of site number. The temperature gradient is the difference in temperature from site  $N - 1$  to site 2 divided by the distance between them. (The distance between neighboring sites is unity.) Because of local temperature fluctuations and edge effects, the temperature gradient should be estimated by fitting the temperature profile in the middle of the lattice to a straight line. Reasonable choices for the parameters are  $N = 22$ ,  $\text{mcs} = 4000$ , and  $\text{nvisit} = 1$ .
- c. The heat flux  $Q$  is the energy flow per unit length per unit time. The energy flow is the amount of energy that demon 1 adds to the system at site 1. The time is conveniently measured in terms of Monte Carlo steps per spin. Determine  $Q$  for the parameters used in part (b).
- d. If the temperature gradient  $\partial T/\partial x$  is not too large, the heat flux  $Q$  is proportional to  $\partial T/\partial x$ . We can determine the *thermal conductivity*  $\kappa$  by the relation

$$Q = -\kappa \frac{\partial T}{\partial x}. \quad (16.9)$$

Use your results for  $\partial T/\partial x$  and  $Q$  to estimate  $\kappa$ . Because of the limited number of spins and Monte Carlo steps, your results should be accurate to only about 20%. More accurate results would require at least  $N = 50$  spins and  $10^4$  to  $10^5$  Monte Carlo steps per spin.

- e. Determine  $Q$ , the temperature profile, and the mean temperature for different values of `nvisit`. Is the temperature profile linear for all `nvisit`? If the temperature profile is linear, estimate  $\partial T/\partial x$  and determine  $\kappa$ . Does  $\kappa$  depend on the mean temperature?

Note that in Problem 16.6 we were able to compute a temperature profile by using an algorithm that manipulated only integer numbers. The conventional approach is to solve a heat equation similar in form to the diffusion equation.

*Problem 16.7. Magnetization profile*

- a. Modify `Program conduct` by removing `SUB heat` and constraining spins 1 and  $N$  to be +1 and -1 respectively. Estimate the magnetization profile by plotting the mean value of the spin at each site versus the site number. Choose  $N = 22$  and  $\text{mcs} \geq 1000$ . How do your results vary as you increase  $N$ ?
- b. Compute the mean demon energy and hence the local temperature at each site. Does the system have a uniform temperature even though the magnetization is not uniform? Is the system in thermal equilibrium?
- c. The effect of this constraint is easier to observe in two and three dimensions than in one dimension. Write a program for a two-dimensional Ising model on a  $L \times L$  square lattice.

Constrain the spins at site  $(i, j)$  to be  $+1$  and  $-1$  for  $i = 1$  and  $i = L$  respectively. Use periodic boundary conditions in the  $y$  direction. How do your results compare with the one-dimensional case?

- d. Remove the periodic boundary condition in the  $y$  direction and constrain all the boundary spins from  $i = 1$  to  $L/2$  to be  $+1$  and the other boundary spins to be  $-1$ . Choose an initial configuration where all the spins on the left half of the system are  $+1$  and the others are  $-1$ . Do the simulation and draw a configuration of the spins once the system has reached equilibrium. Draw a line between each pair of spins of opposite sign. Describe the curve separating the  $+1$  spins from the  $-1$  spins. Begin with  $L = 20$  and determine what happens as  $L$  is increased.

## 16.8 Comment

One advantage of doing simulations using the demon algorithm is that it is not necessary to make any demands on the random number generator. We have done a Monte Carlo simulation without random numbers! (In the one-dimensional Ising model we have to choose the trial spins at random. However, the spins can be chosen sequentially in higher dimensions.) Very fast algorithms have been developed by using one computer bit per spin and multiple demons. There also are several disadvantages associated with the microcanonical ensemble. One disadvantage is the difficulty of establishing a system at the desired value of the energy. However, the most important disadvantage for us is conceptual. That is, it is more natural for us to think of the behavior of macroscopic physical quantities as functions of the temperature rather than the total energy. Hence, we postpone further consideration of the further properties of the Ising model to Chapter 17 in the context of the canonical ensemble.

## Appendix A: Relation of the Mean Demon Energy to the Temperature

We know that the energy of the demon,  $E_d$ , is constrained to be positive and is given by  $E_d = E_{total} - E$ , where  $E$  is the energy of the system and  $E_{total}$  is the total energy. We have found in Problems 16.2 and ?? that the probability for the demon to have energy  $E_d$  is proportional to  $e^{-E_d/kT}$ . We assume that the same form of the probability distribution holds for any macroscopic system in thermodynamic equilibrium. Hence in general,  $\langle E_d \rangle$  is given by

$$\langle E_d \rangle = \frac{\sum_{E_d} E_d e^{-E_d/kT}}{\sum_{E_d} e^{-E_d/kT}}, \quad (16.10)$$

where the summations in (16.10) are over the possible values of  $E_d$ . If an Ising spin is flipped in zero magnetic field, the minimum nonzero decrease in energy of the system is  $4J$  (see Fig. 16.3). Hence the possible energies of the demon are  $0, 4J, 8J, 12J, \dots$ . We write  $x = 4J/kT$  and perform the summations in (16.10). The result is

$$\langle E_d/kT \rangle = \frac{0 + xe^{-x} + 2xe^{-2x} + \dots}{1 + e^{-x} + e^{-2x} + \dots} = \frac{x}{e^x - 1}. \quad (16.11)$$

The form (16.8) can be obtained by solving (16.11) for  $T$  in terms of  $E_d$ . Convince yourself that the relation (16.11) is independent of dimension for lattices with an even number of nearest neighbors.

If the magnetic field is nonzero, the possible values of the demon energy are  $0, 2H, 4J - 2H, 4J + 2H, \dots$ . If  $J$  is a multiple of  $H$ , then the result is the same as before with  $4J$  replaced by  $2H$ , because the possible energy values for the demon are multiples of  $2H$ . If the ratio  $4J/2H$  is irrational, then the demon can take on a continuum of values, and thus  $\langle E_d \rangle = kT$ . The other possibility is that  $4J/2H = m/n$ , where  $m$  and  $n$  are relatively prime positive integers. In this case it can be shown that (see Mak)

$$kT/J = \frac{4/m}{\ln(1 + 4J/m\langle E_d \rangle)}. \quad (16.12)$$

You can test these relations for  $H \neq 0$  by choosing values of  $J$  and  $H$  and computing the sums in (16.10) directly.

## References and Suggestions for Further Reading

- S. G. Brush, "History of the Lenz-Ising model," *Rev. Mod. Phys.* **39**, 883 (1967).
- Michael Creutz, "Microcanonical Monte Carlo simulation," *Phys. Rev. Lett.* **50**, 1411 (1983). See also Gyan Bhanot, Michael Creutz, and Herbert Neuberger, "Microcanonical simulation of Ising systems," *Nuc. Phys. B* **235**, 417 (1984).
- R. Harris, "Demons at work," *Computers in Physics* **4**(3), 314 (1990).
- S. S. Mak, "The analytical demon of the Ising model," *Phys. Lett. A* **196**, 318 (1995).

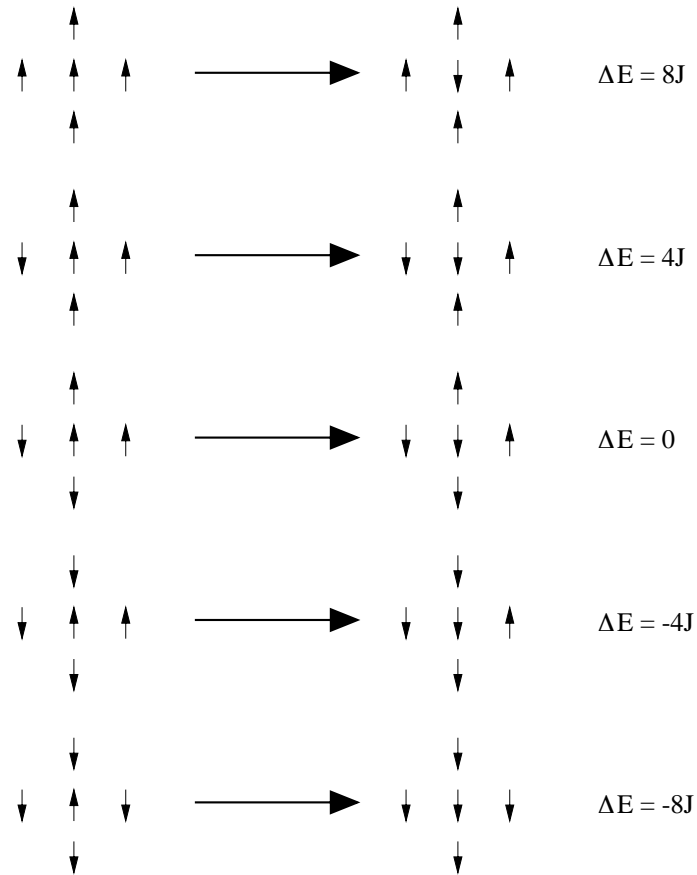


Figure 16.3: The five possible transitions of the Ising model on the square lattice with spin flip dynamics.