22

Thermodynamic Simulations: The Ising Model

22.1 PROBLEM: HOT MAGNETS

Ferromagnetic materials such as bar magnets contain *domains* that are magnetized even in the absence of an external magnetic field. When an external magnetic field is applied, the different domains align and the internal fields become very high. Yet, as the temperature of the ferromagnet is raised, the magnetism decreases and in some cases a *phase transition* occurs in which the magnetism decreases precipitously. Your **problem** is to explain the thermal behavior and the phase transitions of ferromagnets.

We will solve this problem with the quantum mechanical Ising model and the simulated annealing (Metropolis) algorithm. The model is simple but contains much physics, and the simulation gives a visualization of thermal equilibrium that is absent from formal studies. The same algorithm and theory is used for lattice quantum mechanics, and so the present project should be completed before attempting Chapter 23, *Functional Integration on Quantum Paths.*

22.2 THEORY: STATISTICAL MECHANICS

When we say that an object is at a temperature T, we mean that the atoms composing this object are in a state of thermodynamic equilibrium with an environment at temperature T. While this may be an equilibrium state, it is also a dynamic state (it is thermo*dynamics* after all). The system's

energy is continually changing as it exchanges energy with the environment. If the system is at temperature T, then its atoms have an average kinetic energy proportional to T, with larger and larger fluctuations from this average occurring as the temperature increases.

An example of how the equilibrium state changes with temperature is the annealing process (it's one we will simulate on the computer). Let's say that we are making a blade for a sword and are hammering away at it while it's red hot to get its shape just right. At this high a temperature there is a lot of internal motion and not the long-range order needed for a stiff blade. So, as part of the process, we *anneal* the blade; that is, we heat and slow cool it in order to reduce brittleness and increase strength. Too rapid a cooling would not permit long-range equilibration (and ordering) of the blade, and this would lead to brittleness.

In the present problem we deal with the thermal properties of magnetized materials. The magnetism arises from the alignment of the quantum mechanical spins of the atoms. The spin of each atom, in turn, arises from its electrons. When the number of electrons is large, the problem is too difficult to really solve, and so statistical methods are used to obtain average quantities (in most cases that is all we can measure, anyway). If the system is described microscopically by classical or quantum mechanics, then this method is called *statistical mechanics*.

Statistical mechanics starts with the elementary interactions among a system's particles and constructs the macroscopic thermodynamic properties such as temperature T and internal energy U. The essential assumption is that all microscopic configurations of the system consistent with the constraints are equally probable. This leads to a distribution for the states of the system in which state α_j with energy $E(\alpha_j)$ occurs with a probability given by the Boltzmann factor:

$$P(\alpha_j) = \frac{e^{-E(\alpha_j)/kT}}{Z(T)}, \tag{22.1}$$

$$Z(T) = \sum_{\alpha_j} e^{-E_j/kT}. \tag{22.2}$$

Here k is Boltzmann's constant, T is the temperature, and the partition function $Z(T)$ is a weighted sum over states.

Notice that the Boltzmann distribution (22.1) does not require a thermal system to be in the state of lowest energy. Rather, it states that it is less likely for the system to have a high energy. Of course, as $T \to 0$ only the $E = 0$ state has a nonvanishing probability, yet for finite temperatures we expect the system's energy to have fluctuation on the order of kT.

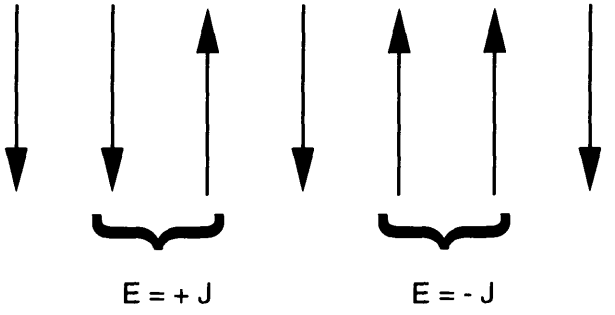

Fig. 22.1 A 1-D lattice of N spins. The interaction energy $V = \pm J$ between nearest-neighbor pairs is shown for aligned and opposing spins.

22.3 MODEL: AN ISING CHAIN

As our model, we consider N magnetic dipoles fixed on the links of a linear chain as shown in Fig. 22.1. (It is a straightforward generalization to handle two- and three-dimensional lattices, and indeed we do it as an exploration.) Because the particle are fixed, their positions and momenta are not dynamical variables, and we need to only worry about their spins.

We assume that the particle at site i has spin s_i, which can be either up or down:

$$s_i \equiv s_{z,i} = \pm\tfrac{1}{2}. \tag{22.3}$$

Each possible configuration or state of the N particles is described by the quantum state vector

$$|\alpha_j\rangle = |s_1, s_2, \ldots, s_N\rangle \tag{22.4}$$

$$= \{\pm\ \tfrac{1}{2}\ , \pm\ \tfrac{1}{2}\ , \ldots\}, \quad j = 1, 2^N. \tag{22.5}$$

Since the spin of each particle can assume that any one of *two* values, there are 2^N different possible states of the N particles in the system. We do not worry about the effect on the state vector of interchanging identical particles because they are all fixed in place and so can't be confused with each other.

The energy of the system arises from the interaction of the spins with each other and with the external magnetic field B. We know from quantum mechanics that an electron's spin and magnetic moment are proportional to each other, so a "dipole–dipole" interaction is equivalent to a "spin–spin" interaction. We assume that each dipole interacts with the external magnetic field and with its nearest neighbor through the potential:

$$V_i = -J\mathbf{s}_i \cdot \mathbf{s}_{i+1} - g\mu\mathbf{s}_i \cdot \mathbf{B}. \tag{22.6}$$

Here the constant J is called the *exchange energy* and is a measure of the strength of the spin–spin interaction. The constant g is the gyromagnetic ratio; that is, the proportionality constant between the angular momentum and magnetic moment. The constant μ is the Bohr magneton, the unit for magnetic moments.

In our model with N particles, there are 2^N possible configurations. Since $2^{20} > 10^6$, we see that even a small number of particles can lead to a prohibitively large number of configurations to consider. For a small number of particles, the computer can examine all possible spin configurations, yet as N gets larger, or as we go to two and three dimensions, a less exact statistical approach is used. We will consequently apply equations (22.1)–(22.2). In addition, we know from our previous studies that Monte Carlo techniques work well on the computer, and so we expect that the simulation may be realistic. Just how large N must be for this to occur depends somewhat on how good a description is needed; for our purposes $N > 200$ should appear statistical, with $N \simeq 2000$ being reliable.

The energy of the system to be used in the Boltzmann distribution (22.1) is the expectation value of the sum of V over the spins of the particles:

$$E(\alpha) = \langle\alpha| \sum_i V_i |\alpha\rangle \tag{22.7}$$

$$= -J \sum_{i=1}^{N-1} s_i s_{i+1} - B\mu \sum_{i=1}^{N} s_i. \tag{22.8}$$

For simplicity of notation, and to be able to compare with an analytic result, we now turn off the magnetic field, that is, assume that $B = 0$. Nonetheless, it is easy to add it back into the final expression for the energy, and we recommend that you do it because giving a preferred direction to space stabilizes the configuration.

The equilibrium alignment of the spins depends critically on the sign of the exchange energy J. If $J > 0$, the lowest energy state will tend to have neighboring spins aligned. If the temperature is low enough, the ground state will be a *ferromagnet* with essentially all spins aligned. If $J < 0$, the lowest energy state will tend to have neighbors with opposite spins. If the temperature is low enough, the ground state will be a *antiferromagnet* with alternating spins.

Unfortunately, a simple model such as this has its limits. Its approach to thermal equilibrium is qualitatively but not quantitatively correct. Further, when $B = 0$ there is no preferred direction in space, which means that the average magnetization may vanish, and this may lead to instabilities in which the spins spontaneously reverse. These instabilities are a type of Bloch-wall transitions in which regions of different spin orientations change size. In addition, the phase transition at the Curie temperature, a characteristic of magnetic materials, does not occur in the 1-D version of the model.

As you will verify in your simulation, a system described by the Boltzmann

distribution (22.1) does not have a single configuration. Rather, there is a continual and random interchange of thermal energy with the environment that leads to fluctuations in the total energy. Even at equilibrium, the system fluctuates with the fluctuations getting larger as the temperature rises.

22.4 SOLUTION, ANALYTIC

For very large numbers of particles, the thermodynamic properties of the 1-D Ising model can be calculated analytically [P&B 89]. This tells us that the average energy (in J units) is

$$\frac{U}{J} = -N \tanh \frac{J}{kT} = -N \frac{e^{J/kT} - e^{-J/kT}}{e^{J/kT} + e^{-J/kT}}, \tag{22.9}$$

$$\Rightarrow \begin{cases} N, & \text{for } kT \to 0, \\ 0, & \text{for } kT \to \infty. \end{cases} \tag{22.10}$$

The analytic result for the specific heat per particle is

$$C(kT) = \frac{1}{N} \frac{dU}{dT} = \frac{(J/kT)^2}{\cosh^2(J/kT)}. \tag{22.11}$$

While the specific heat for the 1-D model does have a maximum as a function of temperature, it does not exhibit the characteristic discontinuity of a phase transition (the 2-D and 3-D models do). For the 1-D Ising model, the magnetization is

$$M(kT) = \frac{N e^{J/kT} \sinh(B/kT)}{\sqrt{e^{2J/kT} \sinh^2(B/kT) + e^{-2J/kT}}}. \tag{22.12}$$

22.5 SOLUTION, NUMERICAL: THE METROPOLIS ALGORITHM

We need an algorithm to evaluate the sums that appear in the partition function (22.2). This is analogous to a 2^N-dimensional numerical integration, and we know from §7.13 that a Monte Carlo approach is best for such high dimensions. Yet we do not want to generate random configurations uniformly for a system in thermal equilibrium because the Boltzmann factor essentially vanishes for those configurations whose energies are not close to the minimum energy. In other words, the vast majority of the terms we sum over to determine the thermodynamic properties of the system make hardly any contribution, and it would be quicker to weight the random numbers we generate such that most of the sum is over large terms.

In their simulation of neutron transmission through matter, Metropolis,

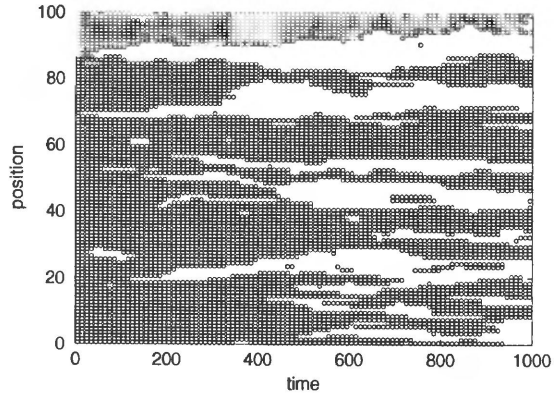

Fig. 22.2 A 1-D lattice of 100 spins. As indicated by the dark circles, initially all the spins are pointing up (a "cold" start). Magnetic domains are seen to form as the system heats up.

Rosenbluth, Teller, and Teller [Metp 53] found an algorithm to improve the Monte Carlo calculation of averages. This *Metropolis algorithm* has now become a cornerstone of computational physics. The sequence of configurations it produces is an example of a *Markov chain*, and in our case simulates the fluctuations in spin configurations that occur during thermal equilibrium. Although not simple or particularly illuminating to prove, this algorithm changes randomly the individual spins in such a way that on the average, the probability of any one configuration occurring follows a Boltzmann distribution.

The Metropolis algorithm involves two steps. First we start off with an arbitrary initial condition and repeatedly apply the algorithm until thermal equilibrium for a specific temperature is reached. For example, in Fig. 22.2 we have an initially "cold" system, whereas the spins would be random for have an initially "hot" system. Once the system reaches thermal equilibrium, the algorithm generates the statistical fluctuations about equilibrium that determine the thermodynamic quantities.

Because the 2^N configurations of N spins can be a lot, the amount of computer time needed can be very long (yet the program is simple). The hope is that the configurations obtained after a small number ($\simeq 10N$) of iterations will be close to those that produce minimum energy. While the answers do get better if we sample more and more configurations, there is a limit to improvement because roundoff error increases as more calculations are made.

Explicitly, the Metropolis algorithm is used to generate a nonuniform, random distribution of spin configurations α_j values, (22.5), with each α_j having

probability

$$\mathcal{P}(\alpha_j) = \frac{1}{Z} e^{-E(\alpha_j)/kT}. \tag{22.13}$$

The technique is a variation of von Neumann rejection (stone throwing of §7.8) in which we start with an initial configuration and vary it randomly to obtain a *trial* configuration. The Boltzmann factor tells us that the relative probability of this trial configuration is proportional to $\Delta\mathcal{P} = \exp(-\Delta E/kT)$, where ΔE is the difference in energy between the previous and the trial configuration. If the trial configuration has a lower energy, ΔE will be negative, the relative probability will be greater than one, and we accept the trial configuration as the new configuration with no further ado. If, on the other hand, the trial configuration has a higher energy, we do not reject it out of hand, but accept it with the relative probability $\Delta\mathcal{P} = \exp(-\Delta E/kT) < 1$.

To accept a configuration with a probability, we pick a uniform random number between 0 and 1, and if the relative probability is greater than this number, we accept the trial configuration; if the Boltzmann factor is smaller than the chosen random number, we reject it. When the trial configuration is not accepted, the next configuration is identical to the preceding one.

The key aspects of the Metropolis algorithm is that the weight given to a trial configuration depends on how far it is from the minimum-energy configuration. Those configurations that stray far from the minimum-energy configuration are deemphasized but not completely discarded. By permitting the system to deviate away from the minimum-energy configuration (go "uphill" for a while), this technique is successful at finding a global extremum for situations in which other techniques are successful at finding only local ones. Its success relies on it not being too quick in "cooling" to the minimum-energy configuration; for this reason the algorithm is sometimes called *simulated annealing*. The algorithm is expected to be good at simulating the fluctuations about minimum energy, and gives explicit results for the thermodynamic quantities like those in Fig. 22.3.

The explicit **rules** for the Metropolis algorithm are

1. Start with an arbitrary spin configuration $\alpha_k = \{s_1, s_2, \ldots, s_N\}$.
2. To generate a new configuration α_{k+1}:
   (a) Pick particle i randomly.
   (b) Reverse i's spin direction to create trial configuration α_{tr}.
   (c) Calculate the energy $E(\alpha_{\text{tr}})$ of the trial configuration.
   (d) If $E(\alpha_{\text{tr}}) \le E(\alpha_k)$, accept the trial; that is, set $\alpha_{k+1} = \alpha_{\text{tr}}$.
   (e) If $E(\alpha_{\text{tr}}) > E(\alpha_k)$, accept with probability $\mathcal{P} = \exp(-\Delta E/kT)$:
      i. Choose a uniform random number: $0 \le r \le 1$,
      ii. Let $\alpha_{k+1} = \begin{cases} \alpha_{\text{tr}}, & \text{if } \mathcal{P} \ge r \quad \text{(accept)}, \\ \alpha_k, & \text{if } \mathcal{P} < r \quad \text{(reject)}. \end{cases}$

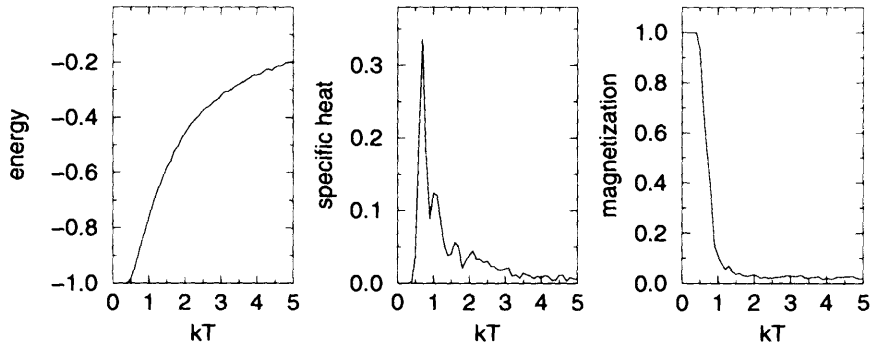

Fig. 22.3 Simulated results for the energy, specific heat, and magnetization of a 1-D lattice of 100 spins as a function of temperature.

How do you start? One possibility, clearly a good choice for high temperatures, is to start with random values of the spins. Another possibility, clearly a good choice for low temperatures, is to start with a ferromagnetic or antiferromagnetic configuration (for positive and negative J, respectively). In general, one tries to remove the importance of the starting configuration by letting the calculation "run a while" ($\simeq N$ rearrangements) before calculating averages. Then you repeat the calculation for different starting configurations, and take the average of the results.

22.6 IMPLEMENTATION, METROPOLIS ALGORITHM, ISING.F (.C)

1. Write a program that implements the Metropolis algorithm, that is, that produces a new configuration α_{k+1} from the present configuration α_k. (Alternatively, use the program supplied on the diskette or the Web.)

2. Make the key data structure in your program an array `s(1:N)` containing the values of s_i. For debugging, print out + and - to give the spins at each lattice point and the trial number.

3. The value for the exchange energy J fixes the scale for energy. Keep it fixed at $J = 1$ (or -1 for an antiferromagnet).

4. The thermal energy kT in units of J is the independent variable that your program should treat as an input parameter. Use $kT = 1$ for debugging.

5. Use periodic boundary conditions on your chain to minimize end effects. (This means that make the first and last spins the same.)

6. Try $N \simeq 20$ for debugging and larger values for production runs.
7. Use the printout to check that the system equilibrates for
   (a) A totally ordered initial configuration (cold start).
   (b) A random initial configuration (hot start).

Your cold start simulation should resemble Fig.22.2.

22.7 ASSESSMENT: APPROACH TO THERMAL EQUILIBRIUM

1. Watch a chain of N atoms attain thermal equilibrium when in contact with a heat bath. At high temperatures, or for small numbers of atoms, you should see large fluctuations, while at lower temperatures you should see smaller fluctuations.
2. The largest kT may be unstable as the system can absorb enough energy to flip all its spin. This is related to the fact that we have eliminated the magnetic field and in this way have no preferred direction to space. Introducing an external magnetic field B will stabilize the system but will also change the total energy and the analytic results.
3. Note how at thermal "equilibrium" the system is still quite dynamic with spins flipping all the time. It is the energy exchange that determines the thermodynamic properties.
4. You may well find that simulations at small kT (say that $kT \sim 0.1$ for $N = 200$) are slow to equilibrate. Higher kT values equilibrate faster yet have larger fluctuations.

22.8 ASSESSMENT: THERMODYNAMIC PROPERTIES

For a given spin configuration α_j, the energy and magnetization are given by

$$E_j = -J \sum_{i=1}^{N-1} s_i s_{i+1}, \tag{22.14}$$

$$\mathcal{M}_j = \sum_{i=1}^{N} s_i. \tag{22.15}$$

At high temperatures we expect a random assortment of spins and so a vanishing magnetization. At low temperature we expect $\mathcal{M}$ to approach $N/2$ as all the spins get aligned.

While the specific heat can be computed from the elementary definition

$$C = \frac{1}{n}\frac{dU}{dT}, \tag{22.16}$$

doing a numerical differentiation of a fluctuating variable is not expected to be accurate. A better way is to first calculate the fluctuations in energy occurring during a number of simulations

$$U_2 = \frac{1}{M}\sum_{t=1}^{M}(E_t)^2, \tag{22.17}$$

and then determine the specific heat from the energy fluctuations:

$$C = \frac{U_2 - (U)^2}{kT^2}. \tag{22.18}$$

1. Extend your program to calculate the total internal energy U (22.14) and the magnetization $\mathcal{M}$ (22.15) for the chain. Notice that you do not have to recalculate entire sums for each new configuration because only one spin changes.

2. Make sure you wait for your system to attain thermal equilibrium before you calculate thermodynamic quantities. (You can check that U is fluctuating about its average.) Your results should resemble those shown in Fig.22.3.

3. The large statistical fluctuations are reduced by running the simulation a number of times with different seeds and taking the average of the results.

4. The simulations you run for small N may be realistic but may not agree with statistical mechanics, which assumes $N \simeq \infty$ (you may assume that $N \simeq 2000$ is close to infinity). Check that agreement with the analytic results for the thermodynamic limit is better for large N than small N.

5. Check that the simulated thermodynamic quantities are independent of initial conditions (within statistical uncertainties). In practice, your cold and hot start results should agree.

6. Make a plot of the internal energy U as a function of kT and compare to the analytic result (22.9).

7. Make a plot of the magnetization $\mathcal{M}$ as a function of kT and compare to the analytic result. Does this agree with how you expect a heated magnet to behave?

8. Compute the fluctuations of the energy U_2 (22.17), and the specific heat C (22.18). Make a graph of your simulated specific heat compared to the analytic result (22.11).

22.9 EXPLORATION: BEYOND NEAREST NEIGHBORS

Extend the model so that the spin–spin interaction (22.6) extends to next-nearest neighbors as well as nearest neighbors. For the ferromagnetic case, this should lead to less fluctuation because we have increased the couplings among spins and thus an increased thermal inertia.

22.10 EXPLORATION: 2-D AND 3-D ISING MODELS

Extend the model so that the ferromagnetic spin–spin interaction (22.6) extends to nearest neighbors in two and then three dimensions. Continue using periodic boundary conditions and keep the number of particles small, at least to start [G&T 96].

1. Form a square lattice and place $\sqrt{N}$ spins on each side.
2. Examine the mean energy and magnetization of the system as it equilibrates.
3. Is the temperature dependence of the average energy qualitatively different from the 1-D model?
4. Print out the spin configurations for small N ($\simeq$ 16–25) and identify the domains.
5. Once your system appears to be behaving properly, calculate the heat capacity of the 2-D Ising model with the same technique used for the 1-D model. Use a total number of particles $100 \leq N \leq 1000$.
6. Look for a phase transition from an ordered to unordered configuration by examining the heat capacity as a function of temperature. It should diverge at the phase transition (you may get only a peak).