follows from the second law of thermodynamics which says that a system with fixed E, V, and N will be in the state of maximum entropy.) We will use the free energy concept in a number of the following sections.

The form (15.4) of $P(E_d)$ provides a simple way of computing the temperature T from the mean demon energy $\langle E_d \rangle$. The latter is given by

$$\langle E_d \rangle = \frac{\int_0^\infty E_d \, e^{-E_d/kT} \, dE_d}{\int_0^\infty e^{-E_d/kT} \, dE_d} = kT. \tag{15.7}$$

We see that T is proportional to the mean demon energy. Note that the result $\langle E_d \rangle = kT$ in (15.7) 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 ∞.

The demon is an excellent example of a thermometer. It has a measurable property, namely, its energy, which is proportional to the temperature. Because the demon is only one degree of freedom in comparison to the many degrees of freedom of the system with which it exchanges energy, it disturbs the system as little as possible. For example, the demon could be added to a molecular dynamics simulation and provide an independent measure of the temperature.

15.5 ■ THE ISING MODEL

A popular model of a system of interacting variables is the *Ising* model. The model was proposed by Lenz and investigated by Ising, his graduate student, to study the phase transition from a paramagnet to a ferromagnet (cf. Brush). Ising calculated 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 some of the diverse applications of the Ising model are discussed in Section 15.7.

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 $s_i = \pm 1$. The s_i are usually referred to as spins. 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

$$E = -J \sum_{i,j=nn(i)}^{N} s_i s_j - B \sum_{i=1}^{N} s_i, \tag{15.8}$$

where B is proportional to the uniform external magnetic field. We will refer to B as the magnetic field, even though it includes a factor of μ. The first sum in (15.8) represents the energy of interaction of the spins and is over all nearest neighbor pairs. The *exchange constant* J is a measure of the strength of the interaction between nearest neighbor spins (see Figure 15.1). The second sum in (15.8) represents the energy of interaction between the magnetic moments of the spins and the 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

Figure 15.1 The interaction energy between nearest neighbor spins in the absence of an external magnetic field.

$\downarrow\uparrow$ 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 energy given by $-B$ and $+B$, 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 are included, and the spins are allowed to have only two discrete values. In spite of the simplicity of the model, we will find that the Ising model exhibits very interesting behavior.

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. Usually a better choice is periodic boundary conditions. For this choice a one-dimensional 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

$$M = \sum_{i=1}^{N} s_i, \tag{15.9}$$

and the magnetization per spin $m = M/N$. Usually we are interested in the average values $\langle M \rangle$ and the fluctuations $\langle M^2 \rangle - \langle M \rangle^2$.

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 (15.8) of the energy on the spin configuration is not sufficient to determine the time-dependent properties of the system. That is, the relation (15.8) does not tell us how the system changes from one configuration to another, and we have to introduce the dynamics separately. This dynamics will take the form of various Monte Carlo algorithms.

We first use the demon algorithm to sample configurations of the Ising model. The implementation of the demon algorithm is straightforward. We first choose a spin at random. The trial change corresponds to a flip of the spin from $\uparrow$ to $\downarrow$ or $\downarrow$ to $\uparrow$. We then compute the change in energy of the system and decide whether to accept or reject the trial change. 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. Another way to determine T is to measure the mean demon energy. However, because the possible values of E_d are not continuous for the Ising model, T is not simply proportional to $\langle E_d \rangle$ as it is for the ideal gas. We show in Appendix 15A that for $B = 0$ and the limit of an infinite system, the temperature is related