

distances. Although this particular problem can be overcome by using a faster computer, there are many problems for which no imaginable supercomputer would be sufficient. One of the biggest current challenges is the *protein folding problem*. The biological function of a protein is determined by its three-dimensional structure which is encoded by the sequence of amino acids in the protein. At present, we know little about how the protein forms its three-dimensional structure. Such formidable computational challenges remind us that we cannot simply put a problem on a computer and let the computer tell us the answer. In particular, for many problems, molecular dynamics methods need to be complemented by other simulation methods, especially Monte Carlo methods (see Chapter 15).

The emphasis in current applications of molecular dynamics is shifting from studies of simple equilibrium fluids to studies of more complex fluids and nonequilibrium systems. For example, how does a solid form when the temperature of a liquid is lowered quickly? How does a crack propagate in a brittle solid? What is the nature of the glass transition? Molecular dynamics and related methods will play an important role in aiding our understanding of these and many other problems.

8.12 ■ PROJECTS

Many of the pioneering applications of molecular dynamics were done on relatively small systems. It is interesting to peruse the research literature of the past three decades to see how much physical insight was obtained from these simulations. Many research-level problems can be generated by first reproducing previously published work and then extending the work to larger systems or longer run times to obtain better statistics. Many related projects are discussed in Chapter 15.

Project 8.22 The classical Heisenberg model of magnetism

Magnetism is intrinsically a quantum phenomenon. One common model of magnetism is the Heisenberg model which is defined by the Hamiltonian or energy function:

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (8.43)$$

where \mathbf{S}_i is the spin operator at the i th lattice site. The sum is over nearest neighbor sites of the lattice, and the (positive) coupling constant J is a measure of the strength of the interaction between spins. The negative sign indicates that the lowest energy state is ferromagnetic. The magnetic moment of a particle on a site is proportional to the particle's spin, and the proportionality constant is absorbed into the constant J .

For many models of magnetism, such as the Ising model (see Section 15.5), there is no obvious dynamics. However, for the Heisenberg model we can motivate a dynamics using the standard rule for the time evolution of an operator given in quantum mechanics texts. For simplicity, we will consider a one-dimensional lattice. The equation for the time development becomes (see Slanić et al.)

$$\frac{d\mathbf{S}_i}{dt} = J\mathbf{S}_i \times (\mathbf{S}_{i-1} + \mathbf{S}_{i+1}). \quad (8.44)$$

In general, \mathbf{S} in (8.44) is an operator. However, if the magnitude of the spin is sufficiently large, the system can be treated classically, and \mathbf{S} can be interpreted as a three-dimensional

unit vector. The dynamics in (8.44) conserves the total energy given in (8.43) and the total magnetization, $\mathbf{M} = \sum_i \mathbf{S}_i$.

We can simulate the classical Heisenberg magnet using an ODE solver to solve the first-order differential equation (8.44).

- Explain why there is no obvious way to determine the mean temperature of this system.
- Write a program to simulate the Heisenberg model on a one-dimensional lattice using periodic boundary conditions. Choose $J = 1$ and $N \geq 100$. Use the RK4 ODE solver, and plot the energy and magnetization as a function of time. These two quantities should be constant within the accuracy of the ODE solver. Also, plot each component of the spin versus position or draw a three-dimensional representation of the spin at each site, so that you can visualize the state of the system.
- Begin with all spins in the positive z direction, except for one spin pointing in the negative z direction. Define the energy of spin i as $\epsilon_i = -\mathbf{S}_i \cdot (\mathbf{S}_{i-1} + \mathbf{S}_{i+1})/2$. Use $N \geq 1000$. Plot the local energy ϵ_i as a function of i . Describe how the local energy diffuses. What patterns do you observe? Do the locations of the peaks in the local energy move with a constant speed?
- One of the interesting dynamical phenomena we can explore is that of *spin waves*. Begin with all $S_{z,i} = 1$ except for a group of 20 spins, where $S_{x,i} = A \cos ki$, $S_{y,i} = A \sin ki$, and $S_{z,i} = \sqrt{1 - S_{x,i}^2 - S_{y,i}^2}$. Choose $A = 0.2$ and $k = 1$. Describe the motion of the spins. Compute the mean position of this spin wave defined by $x = \sum_i i(1 - S_{z,i})$. Show that x changes linearly with time indicating a constant spin wave velocity. Vary k and A to determine what effect their values have on the speed of the spin wave.
- Read about symplectic algorithms in the article by Tsai, Lee, and Landau and write your own ODE solver for one of them. Compare your results to the results you found for the RK4 algorithm. Is the total energy better conserved for the same value of the time step?

Project 8.23 Single particle metrics and ergodic behavior

As mentioned in Section 8.7, the quasi-ergodic hypothesis assumes that time averages and ensemble averages are identical for a system in thermodynamic equilibrium. The assumption is that if we run a molecular dynamics simulation for a sufficiently long time, then the dynamical trajectory will fill the accessible phase space.

One way to confirm the quasi-ergodic hypothesis is to compute an ensemble average by simulating many independent copies of the system of interest using different initial configurations. Another way is to simulate a very large system and compare the behavior of different parts. A more direct measure of ergodicity (see Thirumalai and Mountain) is based on a comparison of the time averaged quantity $\overline{f_i(t)}$ of f_i for particle i to its average for all other particles. If the system is ergodic, then all particles see the same average environment, and the time average $\overline{f_i(t)}$ for each particle will be the same if t is sufficiently long. Note that $\overline{f_i(t)}$ is the average of the quantity f_i over the time interval t and not the value of f_i at time t . The time average of f_i is defined as

$$\overline{f_i(t)} = \frac{1}{t} \int_0^t f_i(t') dt', \quad (8.45)$$