

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 15.25 the application of the Metropolis algorithm to a system of N particles in a cell of fixed volume V (area) 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 (15.4).

Problem 15.25 Monte Carlo simulation of a Lennard–Jones system

- The properties of a two-dimensional Lennard–Jones system 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 $N = 64$, $L_x = 9.2$, 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?
- Write a program to compute the mean energy, pressure, and the 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 the 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.
- 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 $mcs \geq 400$. Does the system retain its symmetry? Does the value of δ affect your results?
- 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.
- 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 at $T = 0.5$ 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 15.24 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 .

- Consider the same density as in part (e) 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 $\rho = 0.7$.
- Compute E , P , and $g(r)$ for $N = 64$, $L_x = L_y = 20$, and $T = 3$. These conditions correspond to a dilute gas. How do your results for P compare with the ideal gas equation of state? How does $g(r)$ compare with the results you obtained for the liquid?
- The chemical potential can be measured using the Widom insertion method. From thermodynamics we know that

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} = -kT \ln \frac{Z_{N+1}}{Z_N} \quad (15.50)$$

in the limit $N \rightarrow \infty$, where F is the Helmholtz free energy and Z_N is the partition function for N particles. The ratio Z_{N+1}/Z_N is the average of $e^{-\beta \Delta E}$ over all possible states of the added particle with added energy ΔE . The idea is to compute the change in the energy ΔE that would occur if an imaginary particle was added to the N particle system at random. Average the value of $e^{-\beta \Delta E}$ over many configurations generated by the Metropolis algorithm. The chemical potential is then given by

$$\mu = -kT \ln \langle e^{-\beta \Delta E} \rangle. \quad (15.51)$$

Note that in the Widom insertion method, no particle is actually added to the system during the simulation. The chemical potential computed in (15.51) is the excess chemical potential and does not include the part of the chemical potential due to the momentum degrees of freedom, which is equal to the chemical potential of an ideal gas. Compute the chemical potential of a dense gas, liquid, and solid. In what sense is the chemical potential a measure of how easy it is to add a particle to the system? ■

15.11 ■ 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 now 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