equation of state (cf. Reif) with the contribution from the attractive part of the interaction equal to zero.

Problem 15.23 Monte Carlo simulation of hard rods

(a) Write a program to do a Monte Carlo simulation of a system of hard rods. Adopt periodic boundary conditions and refer to class `HardDisks` in Chapter 8 for the structure of the program. The major difference is the nature of the trial moves. Measure all lengths in terms of the hard rod diameter σ. Choose $L = 36$ and $N = 30$. How does the number density $\rho = N/L$ compare to the maximum possible density? Choose the initial positions to be on a one-dimensional grid and let the maximum displacement be $\delta = 0.1$. Approximately how many Monte Carlo steps per particle are necessary to reach equilibrium? What is the equilibrium acceptance probability? Compute the pair correlation function $g(x)$.

(b) Compute $g(x)$ as a function of the distance x for $x \leq L/2$. Why does $g(x) = 0$ for $x < 1$? What is the physical interpretation of the peaks in $g(x)$? Because the mean pressure can be determined from $g(x)$ at $x = 1^+$ (see (15.47)), determine $g(x)$ at contact. An easy way to extrapolate your results for $g(x)$ to $x = 1$ is to fit the three values of $g(x)$ closest to $x = 1$ to a parabola. Use your result for $g(x = 1^+)$ to determine the mean pressure.

(c) Compute $g(x)$ at several lower densities by using an equilibrium configuration from a previous run and increasing L. How do the size and the location of the peaks in $g(x)$ change? ■

Problem 15.24 Monte Carlo simulation of hard disks

(a) The maximum packing density can be found by placing the disks on a triangular lattice with the nearest neighbor distance equal to the disk diameter σ. What is the maximum packing density of hard disks; that is, how many disks can be packed together in a cell of area A?

(b) Write a simple program that adds disks at random into a rectangular box of area $A = L_x \times L_y$ with the constraint that no two disks overlap. If a disk overlaps a disk already present, generate another pair of random numbers and try to place the disk again. If the density is low, the probability of adding a disk is high, but if the desired density is high, most of the disks will be rejected. For simplicity, do not worry about periodic boundary conditions and accept a disk if its center lies within the box. Choose $L_x = 6$ and $L_y = \sqrt{3}L_x/2$ and determine the maximum density $\rho = N/A$ that you can attain in a reasonable amount of CPU time. How does this density compare to the maximum packing density? What is the qualitative nature of the density dependence of the acceptance probability?

(c) Modify your Monte Carlo program for hard rods to a system of hard disks. Begin at a density ρ slightly lower than the maximum packing density ρ_0. Choose $N = 64$ with $L_x = 8.81$ and $L_y = \sqrt{3}L_x/2$. Compare the density $\rho = N/(L_x L_y)$ to the maximum packing density. Choose the initial positions of the particles to be on a triangular lattice. A reasonable first choice for the maximum displacement δ is $\delta = 0.1$. Compute $g(r)$ for $\rho/\rho_0 = 0.95, 0.92, 0.88, 0.85, 0.80, 0.70, 0.60$, and 0.30.

Keep the ratio of L_x/L_y fixed and save a configuration from the previous run to be the initial configuration of the new run at lower ρ. (See page 267 for how to save and read configurations.) Allow at least 400 Monte Carlo steps per particle for the system to equilibrate and average $g(r)$ for `mcs` ≥ 400.

(d) What is the qualitative behavior of $g(r)$ at high and low densities? For example, describe the number and height of the peaks of $g(r)$. If the system is crystalline, then $g(\mathbf{r})$ is not spherically symmetric. What would you compute in this case?

(e) Use your results for $g(r = 1^+)$ to compute the mean pressure P as a function of ρ (see (15.47b)). Plot the ratio PV/NkT as a function of ρ, where the volume V is the area of the system. How does the temperature T enter into the Monte Carlo simulation? Is the ratio PV/NkT an increasing or decreasing function of ρ? At low densities we might expect the system to act like an ideal gas with the volume replaced by $(V - N\sigma)$. Compare your low density results with this prediction.

(f) Take snapshots of the disks at intervals of ten to twenty Monte Carlo steps per particle. Do you see any evidence of the solid becoming a fluid at lower densities?

(g) Compute an effective diffusion coefficient D by determining the mean square displacement $\langle R^2(t)\rangle$ of the particles after equilibrium is reached. Use the relation (15.42) and identify the time t with the number of Monte Carlo steps per particle. Estimate D for the densities considered in part (b) and plot the product ρD as a function of ρ. What is the dependence of D on ρ for a dilute gas? Can you identify a range of ρ where D drops abruptly? Do you observe any evidence of a phase transition?

(h) The magnitude of the maximum displacement parameter δ is arbitrary. If the density is high and δ is large, then a high proportion of the trial moves will be rejected. On the other hand, if δ is small, the acceptance probability will be close to unity, but the successive configurations will be strongly correlated. Hence, if δ is too large or is too small, the simulation would be inefficient. One way to choose δ is to find the value of δ that maximizes the mean square displacement over a fixed time interval. The idea is that the mean square displacement is a measure of the exploration of phase space. Fix the density and determine the value of δ that maximizes $\langle R^2(t)\rangle$. What is the corresponding acceptance probability? ■

Continuous potentials. Our simulations of hard disks suggest that there is a phase transition from a fluid at low densities to a solid at higher densities. This conclusion is consistent with molecular dynamics and Monte Carlo studies of larger systems. Although the existence of a fluid-solid transition for hard sphere and hard disk systems is now well accepted, the relatively small numbers of particles used in any simulation should remind us that results of this type cannot be taken as evidence independently of any theoretical justification.

The existence of a fluid-solid transition for hard spheres implies that the transition is determined by the repulsive part of the potential. We now consider a system with both a repulsive and an attractive contribution. Our primary goal will be to determine the influence of the attractive part of the potential on the structure of a liquid.

We adopt as our model interaction the Lennard–Jones potential:

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{15.49}$$