the density, rescale all the positions and the cell size so that the minimum distance is reduced by a factor of two. Repeat this procedure until you reach the desired density. You will need to equilibrate the system between rescalings.

(d) Compute the radial distribution function $g(r)$ for the same densities you considered for the Lennard–Jones interaction. Computing $g(r)$ is more subtle for the hard disk system than it is for a system with a continuous potential. For the latter system, we can accumulate the sums needed to compute $g(r)$ at regular intervals and simply take the average of the computed quantities. However, in an event driven dynamics, the time does not evolve uniformly. The simplest procedure is to keep track of the number of collisions and to compute the necessary sums after a certain number of collisions has occurred. If the number of collisions is sufficiently large, the time elapsed will be approximately the same. The relation of the pressure to $g(r)$ for hard disks is discussed on page 628.

(e) Compare $g(r)$ for the hard disk and Lennard–Jones interactions at the same density. On the basis of your results, which part of the Lennard–Jones interaction plays the dominant role in determining the structure of a dense Lennard–Jones liquid? ■

Simulations of systems of hard disks and hard spheres have shown that the structure of these systems does not differ significantly from the structure of systems with more complicated interactions. Given this insight, our present understanding of liquids is based on the use of the hard sphere (disk) system as a reference system; the differences between the hard sphere interaction and the more complicated interaction of interest are treated as a perturbation about this reference system. Thus, even though the particles interact strongly in a dense gas and a liquid, we now have a perturbation theory of liquids, thanks to the insight gained from simulations. Another important insight that was obtained from simulations is that the solid phase does not require an attractive part of the intermolecular potential. That is, hard spheres and disks have a freezing or melting transition, although the nature of the latter is still a subject of current interest.

In Problem 8.18 we consider two physical quantities associated with the dynamics of a system of hard disks, namely, the mean free time and the mean free path, quantities of interest in kinetic theory.

Problem 8.18 Mean free path and collision time

(a) Class `HardDisks` provides the information needed to determine the mean free time t_c, that is, the average time a particle travels between collisions. For example, suppose we know that 40 collisions occurred in a time $t = 2.5$ for a system of $N = 16$ disks. Because two particles are involved in each collision, there was an average of $80/16$ collisions per particle. Hence, $t_c = 2.5/(80/16) = 0.5$. Write a method to compute t_c and determine t_c as a function of ρ.

(b) The mean free path ℓ is the mean distance a particle travels between collisions. In introductory textbooks, the relation of ℓ to t_c is given by the simple relation $\ell = \overline{v}t_c$, where $\overline{v}$ is the root mean square velocity, $\overline{v} = \sqrt{\overline{v^2}}$. Write a method to compute the mean free path of the particles. Note that the displacement of particle i during the time t is $v_i t$, where v_i is the speed of particle i. What relation do you find between ℓ and t_c?

(c) Write a method to determine the distribution of times between collisions. What is the qualitative form of the distribution? How does the width of this distribution depend on ρ? ■

8.10 ■ DYNAMICAL PROPERTIES

The mean free time and the mean free path are well defined for hard disks for which the meaning of a collision is clear. From kinetic theory we know that both quantities are related to the transport properties of a dilute gas. However, the concept of a collision is not well defined for systems with a continuous interaction, such as the Lennard–Jones potential. In the following, we take a more general approach to the dynamics of a many-body system and discuss how the transport of particles in a system near equilibrium is related to the *equilibrium* properties of the system.

Consider the trajectory of a particular particle, for example, particle 1 in a system that is in equilibrium. At some arbitrarily chosen time $t = 0$, its position is $\mathbf{r}_1(0)$. At a later time t, its displacement is $\mathbf{r}_1(t) - \mathbf{r}_1(0)$. If there was no net force on the particle during this time interval, then $\mathbf{r}_1(t) - \mathbf{r}_1(0)$ would increase linearly with t. However, a particle in a fluid undergoes many collisions, and on the average its net displacement would be zero. A more interesting quantity is the mean square displacement defined as

$$\overline{R(t)^2} = \overline{[\mathbf{r}_1(t) - \mathbf{r}_1(0)]^2}. \tag{8.38}$$

Because the system is in equilibrium, the choice of $t = 0$ is arbitrary, and $\overline{R_1(t)^2}$ depends only on the time difference t. The average in (8.38) is over all possible choices of the time origin.

If the collisions of particle 1 with the other particles are random, then we would suspect that particle 1 undergoes a random walk, and the t-dependence of $\overline{R(t)^2}$ would be given by (see (7.76))

$$\overline{R(t)^2} = 2dDt \quad (t \to \infty), \tag{8.39}$$

where d is the spatial dimension. The coefficient D in (8.39) is known as the *self-diffusion* coefficient and is an example of a transport coefficient. Because the average behavior of all the particles should be the same, we would find better results if we average over all particles. The relation (8.39) relates the macroscopic transport coefficient D to a microscopic quantity $\overline{R(t)^2}$ and gives us a way of computing D.

The easiest way of computing $\overline{R(t)^2}$ is to save in a file the position of a particle at regular time intervals. We can later use a separate program to read the data file and compute $\overline{R(t)^2}$. To understand the procedure for computing $\overline{R(t)^2}$, we consider a simple example. Suppose that the position of a particle in a one-dimensional system is given by $x(t = 0) = 1.65$, $x(t = 1) = 1.62$, $x(t = 2) = 1.84$, and $x(t = 3) = 2.22$. If we average over all possible