if t is sufficiently large. We will not be able to observe the effects of this logarithmic term, and we can interpret our results for $\overline{R(t)^2}$ in terms of an "effective" diffusion coefficient. No such problem exists for three dimensions. See Problem 8.20d.)

(f) Estimate the accuracy of your determination of D. How sensitive is it to the value of Δt? How does this accuracy compare to your estimates of other physical quantities such as the mean pressure?

(g) Compute $\overline{R(t)^2}$ for an equilibrium configuration corresponding to a harmonic solid. What is the qualitative behavior of $\overline{R(t)^2}$?

(h) Compute $\overline{R(t)^2}$ for an equilibrium configuration corresponding to a dilute gas. Is $\overline{R(t)^2}$ proportional to t for small times? Do the particles diffuse over short time intervals? ∎

Another physically important property is the *velocity autocorrelation function* $C(t)$. Suppose that particle i has velocity $\mathbf{v}_i$ at time $t = 0$. If there was no net force on particle i, its velocity would remain constant. However, its interactions with other particles in the fluid will change the particle's velocity, and we expect that after several collisions, its velocity will not be strongly correlated with its velocity at an earlier time. We define $C(t)$ as

$$C(t) = \frac{1}{v_0^2}\overline{\mathbf{v}_i(t) \cdot \mathbf{v}_i(0)}, \tag{8.40}$$

where $v_0^2 = \overline{\mathbf{v}_i(0) \cdot \mathbf{v}_i(0)} = kTd/m$. We have defined $C(t)$ such that $C(t = 0) = 1$. As in our discussion of the mean square displacement, the average in (8.40) is over all possible time origins. Better results would be obtained by averaging over all particles. For large time differences t, we expect $\mathbf{v}_i(t)$ to be independent of $\mathbf{v}_i(0)$, and hence $C(t) \to 0$ for $t \to \infty$. (We have implicitly assumed that $\overline{\mathbf{v}}_i(t) = 0$.)

It can be shown that the self-diffusion coefficient defined by (8.39) can be related to the integral of $C(t)$:

$$D = v_0^2 \int_0^\infty C(t)\, dt. \tag{8.41}$$

Other transport coefficients, such as the shear viscosity and the thermal conductivity, can also be expressed as an integral over a corresponding autocorrelation function. The qualitative properties of the velocity autocorrelation function are explored in Problem 8.20.

Problem 8.20   The velocity autocorrelation function

(a) Modify your hard disk or molecular dynamics program so that the velocity of a particular particle is saved at regular time intervals. Then modify method `computeR2` so that you can compute $C(t)$. The following code might be useful.

```
for(int timeDiff = 1; timeDiff < maxTimeDiff; timeDiff++) {
    for(int time0 = 0; time0 < maxTime0 - timeDiff; time0++) {
        correl[timeDiff] += vxSave[time0 + timeDiff]*vx[time0];
        correl[timeDiff] += vySave[time0 + timeDiff]*vy[time0];
        normalization[timeDiff]++;
    }
}
```

First compute $C(t)$ for a relatively low density system. Plot $C(t)$ versus t and describe its qualitative behavior. Does it more or less decay exponentially?

(b) Increase the density and compute $C(t)$ again. How does the qualitative behavior of $C(t)$ change? Why does $C(t)$ become negative after a relatively short time?

*(c) To obtain quantitative results, modify your program so that $C(t)$ is averaged over all particles. Compute $C(t)$ for time differences in the range 10–40 mean collision times and densities that are about a factor of two less than maximum close packing. Also choose $N \geq 256$. If you are careful, you will be able to observe that $C(t)$ decays as t^{-1} for very long time differences. This long-time tail is due to hydrodynamic effects; that is, part of the velocity of a particle is stored in a microscopic vortex that dies off very slowly. The existence of this tail was first found by simulations and implies that the self-diffusion coefficient is not defined in two dimensions because the integral (8.41) does not exist (the integral diverges for large t). In three dimensions, $C(t) \sim t^{-3/2}$ and the self-diffusion coefficient is well defined.

(d) Compute $C(t)$ for an equilibrium solid. Plot $C(t)$ versus t and describe its qualitative behavior. Explain your results in terms of the oscillatory motion of the particles about their lattice sites.

(e) Contrast the behavior of the mean square displacement, the velocity autocorrelation function, and the radial distribution function in the solid and fluid phases and explain how these quantities can be used to indicate the nature of the phase. ∎

8.11 ∎ EXTENSIONS

The primary goals of this chapter have been to introduce the method of molecular dynamics, some of the concepts of statistical mechanics and kinetic theory, and the qualitative behavior of systems of many particles. Although we found that simulations of systems as small as 64 particles show some of the qualitative properties of macroscopic systems, we would need to simulate larger systems to obtain quantitative results. Most simulations of systems with simple interactions require only several hundred to several thousand particles to obtain reliable results for equilibrium quantities such as the equation of state. How do we know if the size of our system is sufficient to yield quantitative results? The simple answer is to repeat the simulation for a different value of N. In the same spirit, you can determine if your runs are long enough to give statistically meaningful averages.

In general, the most time consuming parts of a molecular dynamics simulation are generating an appropriate initial configuration and doing the bookkeeping necessary for the force and energy calculations. If the force is short range, there are several ways to reduce the equilibration time. For example, suppose we want to simulate a system of 864 particles in three dimensions. We can first simulate a system of 108 particles and allow the small system to come to equilibrium at the desired temperature. After equilibrium has been established, the small system can be replicated twice in each direction to generate the desired system of 864 particles. All of the velocities are reassigned at random using the Maxwell–Boltzmann distribution. Equilibration of the new system is usually established quickly.

The computer time required for our simple molecular dynamics program is order N^2 for each time step. The reason for this N^2-dependence is that the energy and force calculations