2. A system whose macroscopic state is independent of time is said to be in *equilibrium*. The equilibrium macroscopic state is characterized by relatively small fluctuations about a mean that is independent of time. The relative fluctuations become smaller as the number of particles becomes larger.

In Problems 8.3b and 8.3c, we found that the particles filled the box and did not return to their initial configuration. Hence, we were able to define a direction of time. This direction becomes better defined if we consider more particles. Note that Newton's laws of motion are time reversible, and there is no a priori reason that gives the time a preferred direction.

Before we consider other macroscopic quantities, we need to monitor the total energy and verify our claim that the Verlet algorithm maintains conservation of energy with a reasonable choice of Δt. We also introduce a check for momentum conservation.

Problem 8.5 Tests of the Verlet algorithm

(a) One essential check of a molecular dynamics program is that the total energy be conserved to the desired accuracy. Determine the value of Δt necessary for the total energy to be conserved to a given accuracy over a time interval of $t = 2$. One way is to compute $\Delta E_{\max}(t)$, the maximum value of the difference, $|E(t) - E(0)|$, over the time interval t, where $E(0)$ is the initial total energy, and $E(t)$ is the total energy at time t. Verify that $\Delta E_{\max}(t)$ decreases when Δt is made smaller for fixed t. If your application is working properly, $\Delta E_{\max}(t)$ should decrease as approximately $(\Delta t)^2$ because the Verlet algorithm is a second-order algorithm.

(b) A simple way of monitoring how well the program is conserving the total energy is to use a least squares fit of the times series of $E(t)$ to a straight line. The slope of the line can be interpreted as the drift, and the root mean square deviation from the straight line can be interpreted as the noise (σ_y in the notation of Section 7.6). How do the drift and the noise depend on Δt for a fixed time interval t? Most research applications conserve the energy to 1 part in 10^4 or better over the duration of the run.

(c) Because of the use of periodic boundary conditions, all points in the central cell are equivalent and the system is translationally invariant. As you might have learned, translational invariance implies that the total linear momentum is conserved. However, floating point error and the truncation error associated with a finite difference algorithm can cause the total linear momentum to drift. Programming errors might also be detected by checking for conservation of momentum. Hence, it is a good idea to monitor the total linear momentum at regular intervals and reset the total momentum equal to zero if necessary. The method `setVelocities` in Listing 8.3 chooses the velocities so that the total momentum is initially zero. Add a method that resets the total momentum to zero and call it at regular intervals, for example, every 1000–10,000 time steps. How well does class `LJParticles` conserve the total linear momentum for $\Delta t = 0.01$? ■

8.7 ■ THERMODYNAMIC QUANTITIES

In the following, we discuss how some of the macroscopic quantities of interest, such as the temperature and the pressure, can be related to time averages over the phase space trajectories of the particles.

We have already introduced the definition of the kinetic temperature in (8.5). The temperature that we measure in a laboratory experiment is the *mean* temperature, which corresponds to the time average of $T(t)$ over many configurations of the particles. For two dimensions ($d = 2$), we write the mean temperature T as

$$kT = \frac{1}{2N} \sum_{i=1}^{N} m_i \overline{\mathbf{v}_i(t) \cdot \mathbf{v}_i(t)} \quad \text{(two dimensions)}, \tag{8.6}$$

where $\overline{X}$ denotes the time average of $X(t)$. The relation (8.6) is an example of the relation of a macroscopic quantity (the mean temperature) to a time average over the trajectories of the particles. (This definition of temperature is not adequate for particles moving relativistically, or if quantum mechanics is important.)

The relation (8.5) holds only if the momentum of the center of mass of the system is zero—we do not want the motion of the center of mass to change the temperature. In a laboratory system, the walls of the container ensure that the center of mass motion is zero (if the mean momentum of the walls is zero). In our simulation, we impose the constraint that the center of mass momentum (in each of the d directions) be zero. Consequently, the system has $dN - d$ independent velocity components rather than dN components, and we should replace (8.6) by

$$kT = \frac{1}{(N-1)d} \sum_{i=1}^{N} m_i \overline{\mathbf{v}_i(t) \cdot \mathbf{v}_i(t)} \quad \text{(correction for fixed center of mass)}. \tag{8.7}$$

The presence of the factor $(N-1)d$ rather than Nd in (8.7) is an example of a *finite size* correction that becomes unimportant for large N. We shall ignore this correction in the following.

Another macroscopic quantity of interest is the mean pressure. The pressure is related to the force per unit area normal to an imaginary surface in the system. By Newton's second law, this force is related to the momentum that crosses the surface per unit time. We could use this relation to determine the pressure, but this relation uses information only from the fraction of particles that are crossing an arbitrary surface at a given time. Instead, we will use the relation of the pressure to the *virial*, which involves all the particles in the system.

In general, the momentum flux across a surface has two contributions. The contribution, NkT/V, where V is the volume (area) of the system, is due to the motion of the particles and is derived in many texts using simple kinetic theory arguments.

The other contribution to the momentum flux arises from the momentum transferred across the surface due to the forces between particles on different sides of the surface. It can be shown that the instantaneous pressure at time t, including both contributions to the