

and the average of $\overline{f_i(t)}$ over all particles is written as

$$\langle f(t) \rangle = \frac{1}{N} \sum_{i=1}^N \overline{f_i(t)}. \quad (8.46)$$

One of the physical quantities of interest is the energy of a particle e_i defined as

$$e_i = \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} u(r_{ij}). \quad (8.47)$$

The factor of 1/2 is included in the potential energy term in (8.47) because the interaction energy is shared between pairs of particles. The above considerations lead us to define the energy metric, $\Omega_e(t)$, as

$$\Omega_e(t) = \frac{1}{N} \sum_{i=1}^N [\overline{e_i(t)} - \langle e(t) \rangle]^2. \quad (8.48)$$

- (a) Compute $\Omega_e(t)$ for a system of Lennard-Jones particles at a relatively high temperature. Determine $e_i(t)$ at time intervals of 0.5 or less and average Ω_e over as many time origins as possible. If the system is ergodic over the time interval t , then it can be shown that $\Omega_e(t)$ decreases as $1/t$. Plot $1/\Omega_e(t)$ versus t . Do you find that $1/\Omega_e(t)$ eventually behaves linearly with t ? Nonergodic behavior might be found by rapidly reducing the kinetic energy (a temperature quench) and obtaining an amorphous solid or glass rather than a crystalline solid. However, it would be necessary to consider three-dimensional rather than two-dimensional systems because the latter system forms a crystalline solid very quickly.
- (b) Another quantity of interest is the velocity metric Ω_v :

$$\Omega_v(t) = \frac{1}{dN} \sum_{i=1}^N [\overline{\mathbf{v}_i(t)} - \langle \mathbf{v}(t) \rangle]^2. \quad (8.49)$$

The factor of $1/d$ in (8.49) is included because the velocity is a vector with d components. If we choose the total momentum of the system to be zero, then $\langle \mathbf{v}(t) \rangle = 0$, and we can write (8.49) as

$$\Omega_v(t) = \frac{1}{dN} \sum_{i=1}^N \overline{\mathbf{v}_i(t) \cdot \mathbf{v}_i(t)}. \quad (8.50)$$

As we will see, the time dependence of $\Omega_v(t)$ is not a good indicator of ergodicity, but can be used to determine the diffusion coefficient D . We write

$$\overline{\mathbf{v}_i(t)} = \frac{1}{t} \int_0^t \mathbf{v}_i(t') dt' = \frac{1}{t} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]. \quad (8.51)$$

If we substitute (8.51) into (8.50), we can express the velocity metric in terms of the mean square displacement:

$$\Omega_v(t) = \frac{1}{dNt^2} \sum_{i=1}^N [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 = \frac{\overline{R^2(t)}}{dt^2}. \quad (8.52)$$

The average in (8.52) is over all particles. If the particles are diffusing during the time interval t , then $\overline{R^2(t)} = 2dDt$ and

$$\Omega_v(t) = 2D/t. \quad (8.53)$$

From (8.53) we see that $\Omega_v(t)$ goes to zero as $1/t$ as claimed in part (a). However, if the particles are localized (as in a crystalline solid and a glass), then $\overline{R^2}$ is bounded for all t and $\Omega_v(t) \sim 1/t^2$. Because a crystalline solid is ergodic and a glass is not, the velocity metric is not a good measure of the lack of ergodicity. Use the t -dependence of $\Omega_v(t)$ in (8.53) to determine D for the same configurations as in Problem 8.19. ■

Project 8.24 Constant temperature molecular dynamics

In the molecular dynamics simulations we have discussed so far, the energy is constant up to truncation, discretization, and floating point errors, and the temperature fluctuates. However, sometimes it is more convenient to do simulations at constant temperature. In Chapter 15 we will see how to simulate systems at constant T , V , and N (the canonical ensemble) by using Monte Carlo methods. However, we can also do constant temperature simulations by modifying the dynamics.

A crude way of maintaining a constant temperature is to rescale the velocities after every time step to keep the mean kinetic energy per particle constant. This approach is equivalent to a constant temperature simulation when $N \rightarrow \infty$. However, the fluctuations of the kinetic energy can be non-negligible in small systems. For such systems keeping the total kinetic energy constant in this way is not equivalent to a constant temperature simulation.

A better way of maintaining a constant temperature is based on imagining that every particle in the system is connected to a much larger system called a *heat bath*. The heat bath is sufficiently large so that it has a constant temperature even if it loses or gains energy. The particles in the system of interest occasionally collide with particles in this heat bath. The effect of these collisions is to give the particles random velocities with the desired probability distribution (see Problem 8.6). We first list the algorithm and give its rationale later. Add the following statements to method step after all the particles have been moved.

Listing 8.22 Andersen thermostat.

```
for (int i = 0; i < N; i++) {
    if (Math.random() < collisionProbability) {
        double r1 = Math.random();
        double r2 = Math.random()*2.0*Math.PI;
        state[4*i+1] =
            Math.sqrt(-2.0*temperature*Math.log(r1))*Math.cos(r2); // vx
        state[4*i+3] =
            Math.sqrt(-2.0*temperature*Math.log(r1))*Math.sin(r2); // vy
    }
}
```

The parameter `collisionProbability` is much less than unity and determines how often there is a collision with the heat bath. This way of maintaining constant temperature is known as the *Andersen thermostat*.

- (a) Do a constant energy simulation as before, using an initial configuration for which the desired temperature is equal to 1.0. Make sure the total momentum is zero. Choose