

momentum flux, is given by

$$P(t)V = NkT(t) + \frac{1}{d} \sum_{i < j} \mathbf{r}_{ij}(t) \cdot \mathbf{F}_{ij}(t), \quad (8.8)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and \mathbf{F}_{ij} is the force on particle i due to particle j . The second term in (8.8) is related to the virial and represents the correction to the ideal gas equation of state due to the interactions between the particles. (In two and one dimensions, we replace V by the area and length, respectively.)

The mean pressure, $P = \overline{P(t)}$, is found by computing the time average of the right-hand side of (8.8). The computed quantity is not P , but the ratio

$$\frac{PV}{NkT} - 1 = \frac{1}{dNkT} \sum_{i < j} \overline{\mathbf{r}_{ij} \cdot \mathbf{F}_{ij}}. \quad (8.9)$$

In class `LJParticles`, the sum on the right-hand side of (8.9) is computed in the method `computeAcceleration` and stored in the variable `virialAccumulator`.

The relation of information at the microscopic level to macroscopic quantities such as the temperature and pressure is one of the fundamental results of statistical mechanics. In brief, molecular dynamics allows us to compute various time averages of the trajectory in phase space over finite time intervals. One practical question is whether our time intervals are sufficiently long to allow the system to explore phase space and yield meaningful averages. Calculations in statistical mechanics are done by replacing time averages by *ensemble* averages over all possible configurations. The *quasi-ergodic* hypothesis asserts that these two types of averages give equivalent results if the same quantities are held fixed. In statistical mechanics, the ensemble of systems at fixed E , V , and N is called the microcanonical ensemble. Averages in this ensemble correspond to the time averages that we use in molecular dynamics which are at fixed E , V , and N . (Molecular dynamics also imposes an additional, but unimportant, constraint on the center of mass motion.) Ensemble averages are explored using Monte Carlo methods in Chapter 15. A test for determining if a molecular dynamics simulation is exploring a reasonable amount of phase space is discussed in Project 8.23.

The goal of the following problems is to explore some of the qualitative features of gases, liquids, and solids. Because we will consider relatively small systems and relatively short runs, our results will only be qualitatively consistent with averages calculated in the thermodynamic limit where $N \rightarrow \infty$.

Problem 8.6 Distribution of speeds and velocities

- (a) In Section 7.2 we discussed how to use the `HistogramFrame` class from the Open Source Physics library. `LJParticlesApp` uses this class to compute the probability $P(v_x)\Delta v_x$ that a particle has a velocity in the x direction between v_x and $v_x + \Delta v_x$. Add code to determine $P(v_y)$, the probability density for the y -component of the velocity. What are the most probable values for the x and y velocity components? What are their average values? Plot the probability densities $P(v_x)$ versus v_x and $P(v_y)$ versus v_y . Better results can be found by plotting the average $\frac{1}{2}[P(v_x = u) + P(v_y = u)]$ versus u . What is the qualitative form of $P(\mathbf{v})$?

- (b) Write a method to compute the equilibrium probability $P(v)\Delta v$ that a particle has a speed between v and $v + \Delta v$. What is the qualitative form of the probability density $P(v)$? Does it have the same qualitative form as $P(\mathbf{v})$, the probability density for the velocity? What is the most probable value of v ? What is the approximate width of $P(v)$? Compare your measured result to the theoretical form (in two dimensions):

$$P(v)dv = Ae^{-mv^2/2kT}v dv, \quad (8.10)$$

where A is a normalization constant. The form (8.10) of the distribution of speeds is known as the Maxwell-Boltzmann probability distribution.

- (c) Repeat part (b) for different densities and temperatures. Does the form of $P(v)$ depend on the density or temperature? ■

Problem 8.7 Qualitative properties of a liquid and a gas

- (a) Generate an initial configuration using `setRectangularLattice` with $N = 64$ and $L_x = L_y = 12$ and an initial temperature of 2.0. What is the density? Modify your program so that the values of the temperature and pressure are not stored until the system has reached equilibrium. One criterion for equilibrium is to compute the average values of T and P over finite time intervals and check that these averages do not drift with time.
- (b) Choose a value of the time step Δt so that the total energy is conserved to the desired accuracy and run the simulation for a sufficient time to estimate the equilibrium pressure and temperature. Compare your estimate for the ratio PV/NkT with its value for an ideal gas. (We have written V for the area of the system, so that the ideal gas equation of state has a familiar form.) Save the final configuration of your simulation in a file (see Appendix 8A).
- (c) One way of starting a simulation is to use the positions saved from an earlier run. The simplest way of obtaining an initial condition corresponding to a different density, but the same value of N , is to rescale the positions of the particles and the linear dimensions of the cell. The following code shows one way to do so.

```
for (int i = 0; i < N; i++) {
    x[i] *= rescale; // add rescale as a class variable
    y[i] *= rescale;
}
Lx = rescale*Lx
Ly = rescale*Ly
```

Incorporate this code into your program in a separate method and add a button that lets the user call this method without initialization. This method must be used with care when increasing the density. If the density is increased too quickly, it is likely that two particles will become very close to each other, so that the force will become too large and the numerical algorithm will break down. Allow the system to equilibrate after making a small density change and then repeat until you reach the desired density. How do you expect P and T to change when the system is compressed? Gradually increase the density and determine how PV/NkT changes with increasing density. Can you distinguish the different phases? (The determination of the phase boundary between a gas, liquid, and a solid is nontrivial and is discussed in Problem 15.26.) ■