

Another useful thermal quantity is the *heat capacity* at constant volume, which is defined by the relation $C_V = (\partial E / \partial T)_V$. (The subscript V denotes that the partial derivative is taken with the volume held fixed.) C_V is an example of a linear response function, that is, the response of the temperature to a change in the energy of the system. One way to obtain C_V is to determine $T(E)$, the temperature as a function of E . (Remember that a molecular dynamics simulation yields T as a function of E .) The heat capacity is approximately given by $\Delta E / \Delta T$ for two runs that have slightly different temperatures. This method is straightforward, but requires that simulations at different energies be done. An alternative way of determining C_V from the fluctuations of the kinetic energy is discussed in Problem 8.8c.

Problem 8.8 Energy dependence of the temperature and pressure

- We found in Problem 8.7 that the total energy is determined by the initial conditions, and the temperature is a derived quantity found only after the system has reached thermal equilibrium. For this reason it is difficult to study the system at a particular temperature. The temperature can be changed to the desired value by rescaling the velocities of the system, but we have to be careful not to increase the velocities too quickly. Run your program to create an equilibrium configuration for $L_x = L_y = 12$ and $N = 64$ and determine $T(E)$, the energy dependence of mean temperature, in the range $T = 1.0$ to $T = 1.2$. Rescale the velocities by the desired amount over some time interval. For example, multiply all the velocities by a factor λ after each time step for a certain number of time steps. In general, the desired temperature is reached by a series of velocity rescalings over a sufficiently long time such that the system remains close to equilibrium during the rescaling.
- Use your data for $T(E)$ found in part (a) to plot the total energy E as a function of T . Is T a monotonically increasing function of E ? What percentage of the contribution to the heat capacity is due to the potential energy? Why is an accurate determination of C_V difficult to achieve?
- *In Chapter 15 we will find that C_V is related to the fluctuations of the total energy in the canonical ensemble in which T , V , and N are held fixed. In molecular dynamics simulations, the total energy is fixed, but the kinetic and potential energies can fluctuate. Another way of determining C_V is to relate it to the fluctuations of the kinetic energy. It can be shown that (cf. Ray and Graben)

$$\overline{T^2} - \bar{T}^2 = \frac{d}{2} N (k\bar{T})^2 \left[1 - \frac{dNk}{2C_V} \right], \quad (8.11)$$

or

$$C_V = \frac{dNk}{2} \left[1 - \frac{2}{dN} \frac{(\overline{T^2} - \bar{T}^2)}{(k\bar{T})^2} \right]^{-1}. \quad (8.12)$$

Equation (8.12) reduces to the ideal gas result if $\overline{T^2} = \bar{T}^2$. Method `getHeatCapacity` determines C_V from (8.12). Compare your results obtained using (8.12) with the determination of C_V in part (b). What are the advantages and disadvantages of determining C_V from the fluctuations of the temperature compared to the method used in part (b)? ■

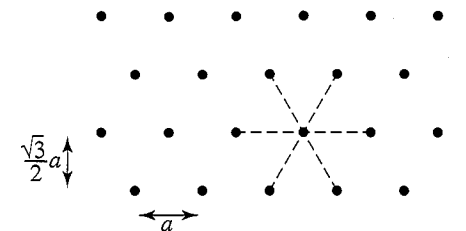


Figure 8.5 Each particle has six nearest neighbors in a triangular lattice.

Problem 8.9 Ground state energy of two-dimensional lattices

To simulate a solid, we need to choose the shape of the central cell to be consistent with the symmetry of the solid phase of the system. This choice is necessary even though we have used periodic boundary conditions to minimize surface effects. If the cell does not correspond to the correct crystal structure, the particles cannot form a perfect crystal, and some of the particles will wander around in an endless search for their “correct” positions. Consequently, a simulation of a small system at a high density and low temperature would lead to spurious results. In the following, we compute the energy of a Lennard–Jones solid in two dimensions for the square and triangular lattices and determine which symmetry has lower energy.

- The symmetry of the triangular lattice can be seen from Figure 8.5. Each particle has six nearest neighbors. Although it is possible to choose the central cell of the triangular lattice to be a rhombus, it is more convenient to choose the cell to be rectangular as in Figure 8.5. For a perfect crystal, the linear dimensions of the cell are L_x and $L_y = \sqrt{3}L_x/2$, respectively. Use method `setTriangularLattice` in Listing 8.13 to generate the positions of the particles in a triangular lattice. Then compute the potential energy per particle of a system of $N = 64$ particles interacting via the Lennard–Jones potential. Determine the potential energy for $L_x = 8$ and $L_x = 9$.
- Determine the potential energy for a square lattice with $L = \sqrt{L_x L_y}$, so that the triangular and square lattices have the same density. Which lattice symmetry has a lower potential energy for a given density? Explain your results in terms of the ability of the triangular lattice to pack the particles closer together. ■

Listing 8.13 Method for generating a triangular lattice.

```
public void setTriangularLattice() {
    double dx = Lx/nx; // distance between particles on same row
    double dy = Ly/ny; // distance between rows
    for(int ix = 0; ix<nx; ++ix) {
        for(int iy = 0; iy<ny; ++iy) {
            int i = ix + iy*ny;
            state[4*i+2] = dy*(iy+0.5);
            if(iy%2==0) {
                state[4*i] = dx*(ix+0.25);
            } else {

```