sum of two-particle interactions:

$$U = u(r_{12}) + u(r_{13}) + \cdots + u(r_{23}) + \cdots = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}), \tag{8.1}$$

where $u(r_{ij})$ depends only on the magnitude of the distance $\mathbf{r}_{ij}$ between particles i and j. The pairwise interaction form (8.1) is appropriate for simple liquids such as liquid argon.

The form of $u(r)$ for electrically neutral molecules can be constructed by a first principles quantum mechanical calculation. Such a calculation is very difficult, and it is usually sufficient to choose a simple phenomenological form for $u(r)$. The most important features of $u(r)$ are a strong repulsion for small r and a weak attraction at large r. The repulsion for small r is a consequence of the Pauli exclusion principle. That is, the electron wave functions of two molecules must distort to avoid overlap, causing some of the electrons to be in different quantum states. The net effect is an increase in kinetic energy and an effective repulsive interaction between the electrons, known as *core repulsion*. The dominant weak attraction at larger r is due to the mutual polarization of each molecule; the resultant attractive potential is called the *van der Waals* potential.

One of the most common phenomenological forms of $u(r)$ is the Lennard–Jones potential:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]. \tag{8.2}$$

A plot of the Lennard–Jones potential is shown in Figure 8.1. The r^{-12} form of the repulsive part of the interaction was chosen for convenience only and has no fundamental significance. The attractive $1/r^6$ behavior at large r corresponds to the van der Waals interaction.

The Lennard–Jones potential is parameterized by a length σ and an energy ϵ. Note that $u(r) = 0$ at $r = \sigma$, and that $u(r)$ is close to zero for $r > 2.5\sigma$. The parameter ϵ is the depth of the potential at the minimum of $u(r)$; the minimum occurs at a separation $r = 2^{1/6}\sigma$.

Problem 8.1 Qualitative properties of the Lennard–Jones interaction
Write a short program to plot the Lennard–Jones potential (8.1) and the magnitude of the corresponding force:

$$\mathbf{f}(r) = -\nabla u(r) = \frac{24\epsilon}{r} \left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \hat{\mathbf{r}}. \tag{8.3}$$

At what value of r is the force equal to zero? For what values of r is the force repulsive? What is the value of $u(r)$ for $r = 0.8\sigma$? How much does u increase if r is decreased to $r = 0.72\sigma$, a 10% change in r? What is the value of u at $r = 2.5\sigma$? ■

8.3 ■ UNITS

As usual, it is convenient to choose units so that the computed quantities are neither too small nor too large. Because the values of the distance and the energy associated with typical liquids are very small in SI units, we choose the Lennard–Jones parameters σ and ϵ as the units of distance and energy, respectively. We also choose the unit of mass to be the mass of one atom m. We can express all other quantities in terms of σ, ϵ, and m. For example, we measure velocities in units of $(\epsilon/m)^{1/2}$ and the time in units of $\sigma(m/\epsilon)^{1/2}$. The values of σ, ϵ, and m for argon are given in Table 8.1. If we use these values, we find that the unit of time is 2.17×10^{-12} s. The units of some of the other physical quantities of interest are also shown in Table 8.1.

All program variables are in reduced units; for example, the time in our molecular dynamics program is expressed in units of $\sigma(m/\epsilon)^{1/2}$. Suppose that we run our molecular dynamics program for 2000 time steps with a time step $\Delta t = 0.01$. The total time of our run is $2000 \times 0.01 = 20$ in reduced units or 4.34×10^{-11} s for argon (see Table 8.1). The duration of a typical molecular dynamics simulation is in the range of 10–10^4 in reduced units, corresponding to a duration of approximately 10^{-11}–10^{-8} s. The longest practical runs are the order of 10^{-6} s.

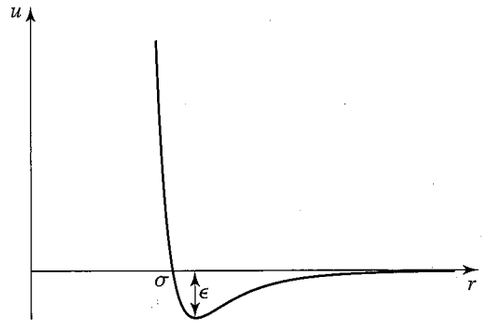

Figure 8.1 Plot of the Lennard–Jones potential $u(r)$. Note that the potential is characterized by a length σ and an energy ϵ.

Table 8.1 The system of units used in the molecular dynamics simulations of particles interacting via the Lennard–Jones potential. The numerical values of σ, ϵ, and m are for argon. The quantity k is Boltzmann's constant and has the value $k = 1.38 \times 10^{-23}$ J/K. The unit of pressure is for a two-dimensional system.

Quantity	Unit	Value for Argon
length	σ	3.4×10^{-10} m
energy	ϵ	1.65×10^{-21} J
mass	m	6.69×10^{-26} kg
time	$\sigma(m/\epsilon)^{1/2}$	2.17×10^{-12} s
velocity	$(\epsilon/m)^{1/2}$	1.57×10^{2} m/s
force	ϵ/σ	4.85×10^{-12} N
pressure	ϵ/σ^2	1.43×10^{-2} N · m^{-1}
temperature	ϵ/k	120 K