CHAPTER 1

Quantum Mechanics and Energy Storage in Particles

This text differs from most statistical thermodynamics textbooks in that it does not deal exclusively with statistical aspects of thermodynamics. Instead, it attempts to weave together statistical and classical elements to develop the full theoretical framework of thermodynamics. Chapter 1 begins this development by establishing the basic features of energy storage at the atomic and molecular levels. It contains a very short introduction to basic aspects of quantum mechanics. The quantum models discussed in this chapter are models of energy storage modes found in common molecules. Conclusions regarding energy levels and their degeneracy for these modes of energy storage are cornerstones of the statistical thermodynamic theory developed in later chapters.

1.1 Microscale Energy Storage

Since this text is designed for graduate-level engineering instruction, it is likely that the reader has already encountered some elements of thermodynamics in previous courses and very likely that he or she has some idea of the usefulness of thermodynamic analysis for systems of scientific and technological interest. Mechanical or chemical engineers who are thoroughly versed in classical equilibrium thermodynamics may wonder what a statistical development of thermodynamics has to offer beyond the tools provided by classical thermodynamics.

In response to such an inquiry, we can identify two main benefits of developing a statistical thermodynamic theory. First, by design, statistical thermodynamics theory provides a link between macroscopic “classical” thermodynamic analysis of system behavior and the microscopic characteristics of the atoms, molecules, or subatomic particles that make up the system. To better understand the nature of establishing such a link, consider the length-scale and time-scale ranges shown in Figure 1.1. The coordinate axes in this diagram span just about the entire range of length and times scales associated with systems and processes in the known universe. The shortest length scales are associated with the interior structure of atoms and the dimensions of subatomic particles, while the largest length scales are associated with intergalactic distances.

In a similar manner, the shortest time scales are associated with microscale interactions of atoms and/or fundamental particles, and the longest is the age of the universe. Relativity theory requires that matter and energy cannot move faster than the speed of light. Since natural processes generally are the result of the motion of matter or photons, processes having very large length scales and very small times scales cannot be attained. Hence the upper left region of the diagram is in some sense a forbidden zone. Statistical thermodynamics is conceptually important because it provides the theoretical link between microscale interactions and systems undergoing processes at much larger length and time scales.

The second benefit of developing statistical thermodynamic theory is that it provides analytical tools for engineering and scientific analysis. With increasing frequency, engineers and scientists are seeking to work with systems whose behavior lies outside the bounds of

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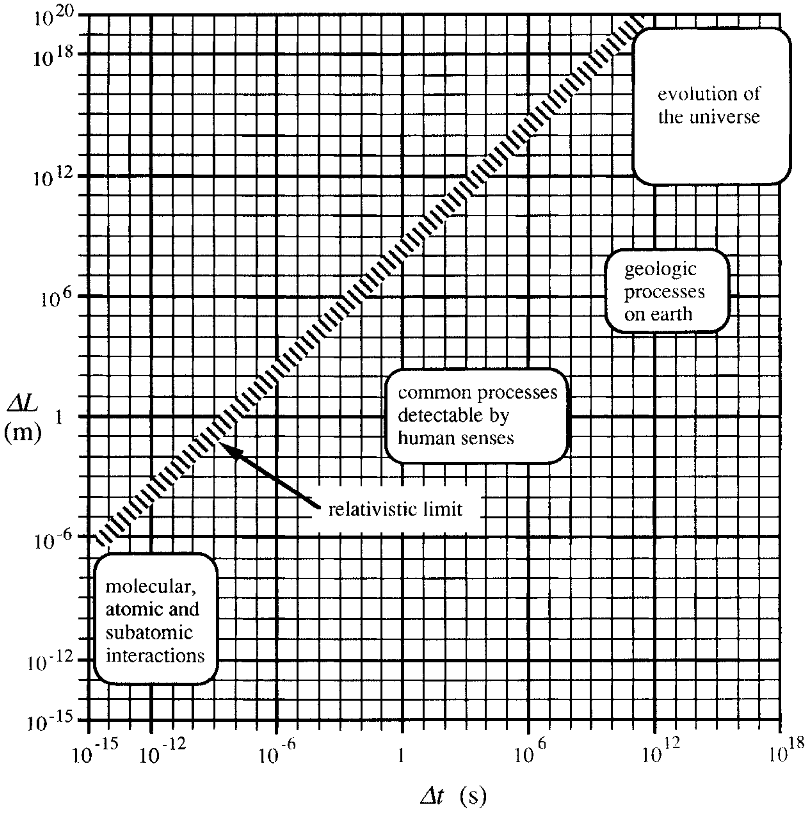

Figure 1.1 Length and time scales of known processes.

classical thermodynamic analysis. The areas of microelectro-mechanical systems (MEMS), fusion reactor development, and ultrafast laser processing of materials are just three examples of engineering applications in which important phenomena are beyond the bounds of classical thermodynamics theory. Engineers specializing in the thermosciences will need tools from statistical thermodynamics and kinetic theory to deal with these and other new applications areas.

In developing the theoretical foundation of thermodynamics, we first seek to define how energy is stored in systems composed of large numbers of particles. In this text, the term *particles* is meant to include subatomic particles, atoms, or molecules. As a first step in dealing with such systems, we must first establish how individual particles themselves store energy. Some insight into this issue can be obtained by considering the simple models of atomic and molecular structures shown in Figure 1.2. In general, such particles may store energy as translational energy or by modifying their internal state. Internal energy storage is directly linked to the internal structure of the particle. In a single atom, internal energy storage or release is accompanied by changes in nuclear or electronic energy levels. Molecules composed of two or more atoms may also store energy internally by altering the nuclear state or electron energy levels of one or more of the atoms. In addition, molecules may store energy in kinetic energy of rotation about the molecule's center of mass and in

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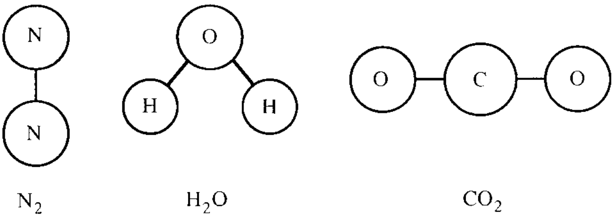

Figure 1.2 Models of typical molecular structures.

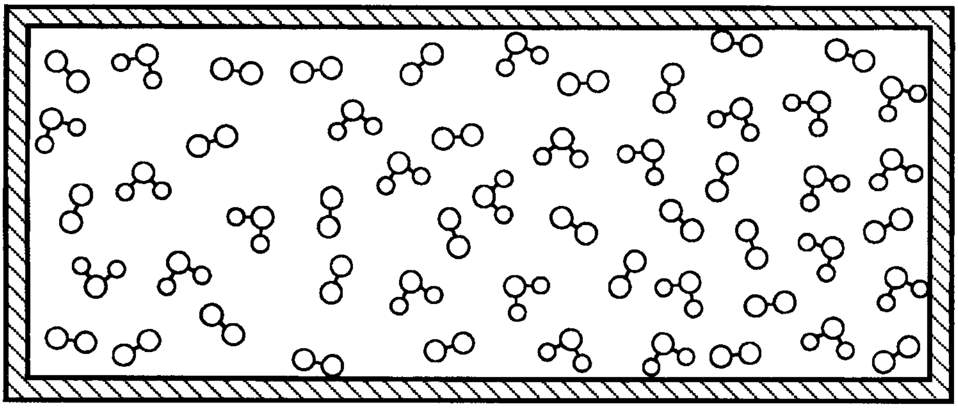

Figure 1.3 A typical system of molecules.

vibration of the molecule. The latter mode of energy storage results when atoms oscillate about their equilibrium positions in the molecular structure.

Our ultimate goal is to develop analytical tools that can be used to analyze a system of particles, like that shown schematically in Figure 1.3. The particles shown in the figure are molecules. The system contains a mixture of diatomic molecules and molecules containing three atoms. Note that translation of the molecules leads to collisions that cause energy to be exchanged among the different modes of energy storage. At the microscopic level, the distribution of energy within each molecule and within the system is constantly changing with time.

In analyzing systems like that shown in Figure 1.3, we will assume that the mass of each species of particle and energy are conserved at both the microscopic and macroscopic level. Conservation of energy is a key foundation element in both classical and statistical thermodynamics. For that reason, conservation of energy is generally referred to as the *first law of thermodynamics*. The volume V and the number of each species of particle in the system $N_a, N_b, \ldots$ are taken to be intrinsic properties of any system. We will assume that they can be measured if necessary and, if desired, we can specify their values.

The *internal energy* of the system, U, is defined as the total energy of the particles in the system, including the translational and internal energy, and any energy stored in force interactions between the particles. If we can isolate the system so no energy crosses its boundary, the first law requires that the internal energy is constant, independent of time, even though particle collisions may alter the way in which the energy is stored within the system. For an isolated system at fixed U, V, N_a, N_b, ..., a system will macroscopically attain an equilibrium state that is unchanging with time. At the microscopic level, the system is constantly changing its configuration. The system thus is in a state of dynamic equilibrium. We will see in later sections of this text that the nature of this dynamic equilibrium strongly influences how the system reacts to changes in the constraints on the system. This issue is central to thermodynamic analysis of systems, since as engineers and scientists, we often want to predict how a system will change if a change occurs in one or more of the macroscopic constraints on the system (such as the specified values of U, V, or particle numbers).

Example 1.1 The mean speed of a helium atom in helium gas at 27°C is about 1,020 m/s. Use this information to estimate the internal energy of the gas per kmol.

Solution The mass per helium atom m is known to be 6.65×10^{-27} kg. Assuming the internal energy is due only to kinetic energy of the molecules, we can estimate the mean kinetic energy per atom as

$$e_k = \frac{1}{2}mc^2 = \left(\frac{1}{2}\right) 6.65 \times 10^{-27}(1{,}020)^2 = 3.46 \times 10^{-21}\ \text{J}.$$

Multiplying by Avogadro's number, we obtain the internal energy per kmol:

$$\hat{u} = (6.02 \times 10^{26})3.46 \times 10^{-21} = 2.082 \times 10^6\ \text{J/kmol} = 2{,}082\ \text{kJ/kmol}$$

Pioneering efforts to construct statistical theories of the behavior of large collections of particles were made by Maxwell, Boltzmann, and Gibbs in the last half of the nineteenth century. Because these efforts preceded the development of quantum theory, simple classical mechanics treatments of molecule energy storage mechanisms were incorporated into these initial statistical mechanics models. In fact, the statistical mechanics models of Maxwell and Boltzmann were highly controversial when they were first proposed because the existence of atoms and molecules was not widely accepted by scientists at that time. The work of Planck, Einstein, and others in the early part of the twentieth century established the existence of atoms, molecules, and eventually the subatomic structure of matter. Quantum theory provided the means for predicting the manner in which energy is stored in atoms, molecules, and subatomic particles. This made it possible to extend the statistical mechanics concepts developed by Boltzmann and Gibbs to a wide variety of system types.

In this text, the current knowledge of the atomic structure of matter is taken as the starting point for development of macroscopic thermodynamics. Macroscopic equilibrium thermodynamics is a consequence of the nature of microscale energy storage and the statistical behavior of very large numbers of particles. We will therefore first establish the basic elements of quantum theory necessary to determine the rules of energy storage and energy exchange in atoms, molecules, and subatomic particles. We will then construct a statistical analysis of a system composed of a large number of particles that obey such rules. Once these two components are blended together to form a statistical thermodynamic framework, we will explore the application of the framework to a variety of system types.

1.2 A Review of Classical Mechanics

Classical mechanics analysis of the motion and mechanical energy storage of a particle can be cast in at least three ways. The Newtonian formulation of classical mechanics can be stated as

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}, \tag{1.1}$$

where **p** is the particle momentum and **F** is the force exerted on the particle.

The Lagrangian formulation of classical mechanics is stated in terms of the *Lagrangian* L defined as

$$L(x, y, z, u, v, w) \equiv K(u, v, w) - \hat{U}(x, y, z), \tag{1.2}$$

where $\hat{U}(x, y, z)$ is the potential energy of the particle and K is the kinetic energy of the particle given by

$$K(u, v, w) = \frac{m}{2}[u^2 + v^2 + w^2]. \tag{1.3}$$

In the above relation, m is the mass of the particle. Noting, for the x direction, that

$$\frac{\partial L}{\partial u} = \frac{\partial K}{\partial u} = mu = p_x, \qquad \frac{\partial L}{\partial x} = -\frac{\partial \hat{U}}{\partial x} = F_x, \tag{1.4}$$

Newton's equation can be written as

$$\frac{d}{dt}\left(\frac{\partial L}{\partial u}\right) = \frac{\partial L}{\partial x}. \tag{1.5}$$

If we generalize the notation as

$$x = q_1, \quad y = q_2, \quad z = q_3, \qquad u = \dot{q}_1, \quad v = \dot{q}_2, \quad w = \dot{q}_3, \tag{1.6}$$

the equations of motion can then be written as

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \frac{\partial L}{\partial q_j}, \qquad j = 1, 2, 3. \tag{1.7}$$

An extraordinary and very useful property of Lagrange's equations of motion is that they have the same form in any coordinate system (useful since it is sometimes easier mathematically to define $\hat{U}$ in a particular coordinate system). A set of equations like (1.7) can be written for each particle in a multiparticle system.

A third formulation of classical mechanics is the Hamiltonian formulation. To construct the Hamiltonian formulation of classical mechanics, we begin by defining generalized momenta as

$$p_j = \frac{\partial L}{\partial \dot{q}_j}, \qquad j = 1, 2, \ldots, 3N \quad \text{(for a system of } N \text{ particles)}. \tag{1.8}$$

Each generalized momentum p_j is said to be conjugate to coordinate q_j. Since each momentum is linearly proportional to the velocity $\dot{q}_j$, it is a simple task to replace any velocity terms in the formulation with the corresponding generalized momentum p_j. We do so throughout the definition of the Lagrangian and define the *Hamiltonian H* for a system of N particles to be

$$\hat{H}(p_1, p_2, \ldots, p_{3N}, q_1, q_2, \ldots, q_{3N}) = \sum_{j=1}^{3N} p_j \dot{q}_j - L(p_1, p_2, \ldots, p_{3N}, q_1, q_2, \ldots, q_{3N}). \tag{1.9}$$

In general, for systems of particles we expect that the total kinetic energy of the particles is given by

$$K = \sum_{j=1}^{3N} a_j(q_1, q_2, q_3, \ldots, q_{3N})\, \dot{q}_j^2, \tag{1.10}$$

and by definition

$$p_j = \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial K}{\partial \dot{q}_j} = 2a_j \dot{q}_j. \tag{1.11}$$

The coefficient a_j varies depending on whether the generalized velocity is linear or angular. Substituting this result and the definition of L into the relation defining $\hat{H}$ yields

$$\hat{H} = K + \hat{U}. \tag{1.12}$$

Note that the Hamiltonian equals the total system energy. If the Lagrangian is not an explicit function of time, we can differentiate the relation defining $\hat{H}$ to obtain

$$d\hat{H} = \sum_j^{3N} (\dot{q}_j dp_j + p_j d\dot{q}_j) - \sum_j^{3N} \frac{\partial L}{\partial \dot{q}_j} d\dot{q}_j - \sum_j^{3N} \frac{\partial L}{\partial q_j} dq_j. \tag{1.13}$$

Using the following relations obtained above:

$$\frac{\partial L}{\partial q_j} = \dot{p}_j, \qquad \frac{\partial L}{\partial \dot{q}_j} = p_j \tag{1.14}$$

the relation for $d\hat{H}$ becomes

$$d\hat{H} = \sum_j^{3N} \dot{q}_j\, dp_j - \sum_j^{3N} \dot{p}_j\, dq_j. \tag{1.15}$$

Since $\hat{H} = \hat{H}(p_1, p_2, \ldots, p_{3N}, q_1, q_2, \ldots, q_{3N})$ it also can be mathematically stated that

$$d\hat{H} = \sum_j^{3N} \left(\frac{\partial \hat{H}}{\partial p_j}\right) dp_j + \sum_j^{3N} \left(\frac{\partial \hat{H}}{\partial q_j}\right) dq_j. \tag{1.16}$$

By equating coefficients of the dp_j and dq_j terms in Eqs. (1.15) and (1.16), we obtain Hamilton's equations of motion

$$\left(\frac{\partial \hat{H}}{\partial p_j}\right) = \dot{q}_j, \qquad \left(\frac{\partial \hat{H}}{\partial q_j}\right) = -\dot{p}_j, \qquad j = 1, 2, \ldots, 3N. \tag{1.17}$$

These $6N$ first-order equations completely describe the dynamics of a system of N particles. Given the initial conditions, we could try to solve these equations to predict the

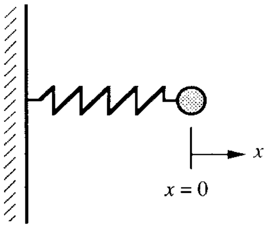

Figure 1.4

macroscopic behavior of a system of molecules. However, to do so is undesirable for two reasons. First, solving so many equations is very difficult, and second, at the microscopic level quantum effects are not included. Hamilton's equations have been presented here because they demonstrate that the energy of the system is a function of appropriately chosen coordinates and conjugate momenta. This concept will be central to our development of a statistical view of the thermodynamics of the system in subsequent chapters.

Example 1.2 The mass in the mass–spring system in Figure 1.4 oscillates about the position $x = 0$. The spring exerts a restoring force F that is linearly dependent on x, obeying the relation

$$F = -kx,$$

where k is a constant that characterizes the spring. Find the Lagrangian and Hamiltonian for the system and show that Eq. (1.5) reduces to Newton's equation of motion.

Solution At any instant, the kinetic energy K is $(1/2)mu^2$, where $u = dx/dt$. The potential energy is

$$\hat{U} = -\int_0^x F\,dx = -\int_0^x -kx\,dx = \frac{1}{2}kx.$$

The Lagrangian and Hamiltonian are therefore given by

$$L = \tfrac{1}{2}mu^2 - \tfrac{1}{2}kx^2$$

and

$$\hat{H} = \tfrac{1}{2}mu^2 + \tfrac{1}{2}kx^2.$$

Substituting the relation for L into Eq. (1.5), we obtain

$$\frac{d}{dt}\left(\frac{\partial L}{\partial u}\right) = \frac{\partial L}{\partial x},$$

$$\frac{d}{dt}(mu) = -kx = F.$$

Thus, Eq. (1.5) reduces to the time derivative of momentum being equal to the applied force, which is essentially Newton's law of motion.

1.3 Quantum Analysis Using the Schrödinger Equation

As a result of the work of Planck and others, by 1920, the dual nature (wave/particle) of radiant energy was widely accepted. Radiant energy is carried in packets called *photons*, each with energy $h\nu$, which have particle and wavelike qualities. Here ν is frequency and $h = 6.63 \times 10^{-34}$ Js is Planck's constant. In 1924, de Broglie argued that if radiant energy could have both wave and particle properties, then perhaps matter particles also have wavelike qualities. By analogy, he postulated that if a particle has total energy ε and momentum p, then it has a wavelength λ and frequency ν associated with it such that

$$\varepsilon = h\nu \tag{1.18a}$$

and

$$p = h/\lambda. \tag{1.18b}$$

For a particle traveling with momentum mv this implies that

$$\lambda = h/mv. \tag{1.19}$$

Example 1.3 In 1927 Davisson and Germer demonstrated the wavelike scattering of an electron beam reflected from a nickel surface. The wavelength of the electron beam determined from the interference pattern and the known spacing of the nickel atoms agreed well with that predicted by de Broglie's formula. The mass of an electron is 9.109×10^{-31} kg. If they travel at 0.05 times the speed of light, it follows that

$$\lambda = \frac{6.63 \times 10^{-34}}{9.109 \times 10^{-31}(.05 \times 3 \times 10^{8})} = 4.85 \times 10^{-11}\text{m} = 0.485\,\text{Å}.$$

For visible light $\lambda = 4{,}000\text{–}8{,}000$ Å. Thus an electron beam can provide higher image resolution since its wavelength is much shorter than visible light. This is the motivation behind the development of the electron microscope.

The coordinates $q_1, q_2, \ldots$ and momenta $p_1, p_2, \ldots$ that quantify the dynamics of an N-particle system define a multidimensional space referred to as *phase space*. The wavelike nature of particles implies that they are really smeared in phase space with no definite position and momentum. It can be argued, based on the de Broglie relations, that for any measurement, the uncertainty in a particle's position, Δx, and in its corresponding momentum, Δp_x, are constrained by the relation

$$|\Delta x \Delta p_x| \geq \frac{h}{4\pi} = \frac{\hbar}{2}, \tag{1.20a}$$

where

$$\hbar = \frac{h}{2\pi}. \tag{1.20b}$$

Equation (1.20a) is a quantitative statement of the *Heisenberg uncertainty principle*. We will consider this issue further in Section 1.6.

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Because matter has some wave characteristics, it is expected that some wave equation governing its behavior should exist. If we consider the following mathematical representation of a one-dimensional (1-D) wave:

$$\Psi = C \exp\{i[2\pi x/\lambda) - 2\pi \nu t]\}, \tag{1.21}$$

and differentiate, it is easy to show that

$$-i\hbar \frac{\partial \Psi}{\partial x} = \frac{h}{\lambda}\Psi = p_x \Psi \tag{1.22}$$

and

$$i\hbar \frac{\partial \Psi}{\partial t} = h\nu\Psi = \varepsilon\Psi. \tag{1.23}$$

This suggests the identification of $-i\hbar(\partial/\partial x)$ with p_x and $i\hbar(\partial/\partial t)$ with ε. In a nonrelativistic, classical (3-D) system, the total Hamiltonian (total energy) for a particle is given by

$$\hat{H} = K + \hat{U} = \frac{p^2}{2m} + \hat{U}(\mathbf{r}), \tag{1.24}$$

where

$$p^2 = p_x^2 + p_y^2 + p_z^2, \tag{1.25a}$$

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}. \tag{1.25b}$$

The above arguments imply that

$$p_x^2 = -i\hbar \frac{\partial}{\partial x}\left(-i\hbar \frac{\partial}{\partial x}\right) = -\hbar^2 \frac{\partial^2}{\partial x^2}, \tag{1.26a}$$

$$p_y^2 = -i\hbar \frac{\partial}{\partial y}\left(-i\hbar \frac{\partial}{\partial y}\right) = -\hbar^2 \frac{\partial^2}{\partial y^2}, \tag{1.26b}$$

$$p_z^2 = -i\hbar \frac{\partial}{\partial z}\left(-i\hbar \frac{\partial}{\partial z}\right) = -\hbar^2 \frac{\partial^2}{\partial z^2}. \tag{1.26c}$$

Substituting Eqs. (1.26) and (1.25a) into (1.24), the right-hand side becomes the Hamiltonian operator

$$\hat{H} = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \hat{U}(\mathbf{r}). \tag{1.27}$$

The Hamiltonian $\hat{H}$ is interpreted as equaling the total energy ε, which, in turn, is identified with $i\hbar(\partial/\partial t)$. Replacing $\hat{H}$ with $i\hbar(\partial/\partial t)$, and applying the operators on both sides to the wave function Ψ, yields

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\Psi + \hat{U}(\mathbf{r})\Psi. \tag{1.28}$$

With a little rearranging this can be written as

$$\nabla^2\Psi - \frac{2m}{\hbar^2}\hat{U}(\mathbf{r})\Psi = \left(\frac{2m}{i\hbar}\right)\frac{\partial \Psi}{\partial t}. \tag{1.29}$$

This is the *Schrödinger equation* for the system wave function Ψ.

The wave version of quantum mechanics theory is built upon the following postulate:

◆ *The state of a quantum-mechanical system is completely specified by a function* $\Psi(\mathbf{r}, t)$ *that depends on the coordinates of the particles and on time. This function, called the* wave function *or* state function, *has the property that* $\Psi^*(\mathbf{r}, t)\,\Psi(\mathbf{r}, t)\,dx\,dy\,dz$ *is the probability that the particle lies in the volume element* $dx\,dy\,dz$ *located at location* $\mathbf{r}$ *at time* t. *(Note that* Ψ^* *is the complex conjugate of* Ψ.*)*

The wave function Ψ is determined by solving the Schrödinger equation.

For Ψ to have the property indicated in the postulate, Ψ must satisfy

$$\int_V \Psi\Psi^*\,dV = 1. \tag{1.30}$$

If solution of the Schrödinger equation is postulated to be of the form

$$\Psi(\mathbf{r}, t) = f(t)\psi(\mathbf{r}) \tag{1.31}$$

then substituting into Eq. (1.29) and rearranging leads to

$$\left(\frac{i\hbar}{f}\right)\frac{df}{dt} = \frac{1}{\psi}\left[\hat{U}(\mathbf{r})\psi - \frac{\hbar^2}{2m}\nabla^2\psi\right]. \tag{1.32}$$

Note that the left side of the above equation is a function only of time whereas the right side is a function only of position. Hence, each side must be a constant, which we will designate as C_0. Setting the left side equal to C_0 yields

$$f = f_0\,\exp\{-iC_0 t/\hbar\}, \tag{1.33}$$

where f_0 is the initial value of f at $t = 0$. Substituting this result into Eq. (1.31) yields

$$\Psi(\mathbf{r}, t) = f_0\psi(\mathbf{r})\exp\{-iC_0 t/\hbar\}. \tag{1.34}$$

Differentiating gives

$$i\hbar\frac{\partial\Psi}{\partial t} = C_0\Psi = \varepsilon\Psi, \tag{1.35}$$

from which we conclude that the separation constant C_0 is the energy,

$$C_0 = \varepsilon. \tag{1.36}$$

The relation for f is therefore

$$f = f_0\exp\{-i\varepsilon t/\hbar\}. \tag{1.37}$$

Thus, the time variation is oscillatory with fixed amplitude. Boundary conditions and potential energy effects are manifested in the spatial variation. Setting the right side of the separated Schrödinger equation equal to ε yields

$$\hat{U}(\mathbf{r})\psi - \frac{\hbar^2}{2m}\nabla^2\psi = \varepsilon\psi. \tag{1.38}$$

The above equation is the *time-independent Schrödinger equation*. The time-independent Schrödinger equation with appropriate boundary conditions generally forms a Sturm–Liouville system for which ε is an eigenvalue. For such a system it is known that solutions exist only for discrete values of ε. Solution of the time-independent Schrödinger equation will specify the allowable quantum energy levels for the system.