Chapter 3
Elements of Statistical Thermodynamics and Quantum Theory

Classical statistical mechanics is based on the assumption that all matters are composed of a myriad of small discrete particles, such as molecules and atoms, in any given macroscopic volume [1–5]. There are about $N = 2.5 \times 10^{16}$ molecules per cubic millimeter of air at standard conditions (25 °C and 1 atm). These particles are in continuous random motion, which generally obeys the laws of classical mechanics. A complete microscopic description of a system requires the identification of the position $\mathbf{r}_i(t)$ and velocity $\mathbf{v}_i(t)$ of each particle (here, subscript i indicates the ith particle) at any time. For a simple system of N molecules in a box of volume V, one can write Newton's law of motion for each molecule as

$$\sum_j \mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j, t) = m_i \frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t}, \ i = 1, 2, \ldots N \tag{3.1}$$

where $\mathbf{F}_{ij}$ is the intermolecular force that the jth molecule exerts on the ith molecule, and m_i is the mass of the ith molecule. The initial position and velocity, as well as the nature of collisions among particles and that between particles and the walls of the box, must be specified in order to solve the N equations. Although this approach is straightforward, there are two major barriers. First, the intermolecular forces or potentials are often complicated and difficult to determine. Second, the solution of Eq. (3.1) requires significant computer resources even for rather simple problems. Statistical methods are often used instead to obtain microscopic descriptions that are related to macroscopic behaviors. *Statistical mechanics* aims at finding the equilibrium distribution of certain type of particles in the velocity space. It provides a linkage between macroscopic thermodynamic properties and the microscopic behavior and a means to evaluate some thermodynamic properties. *Kinetic theory*, on the other hand, deals with nonequilibrium processes. It gives a microscopic description of transport phenomena and helps predict some important transport properties, as will be seen in Chap. 4.

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Along with the rapid development in computing speed and memory, *molecular dynamics* (MD) simulation has become a powerful tool for the investigation of phenomena occurring in nanostructures and/or at very short time scales. In the MD method, the location and the velocity of every particle are calculated at each time step by applying Eq. (3.1) with a suitable potential function [6, 7]. Thermodynamic properties are then evaluated using statistical mechanics formulation. Further discussion about the application of the MD simulation to predict the thermal properties of nanostructures will be given in Chap. 7.

This chapter starts with a statistical model of independent particles and a brief introduction to the basic principles of quantum mechanics. The necessary mathematical background is summarized in Appendix B. It is highly recommended that one review the materials covered in the appendix before studying this chapter. The three important distributions are derived based on the statistics for different types of particles. The microscopic descriptions and results are then linked to macroscopic quantities and the laws of thermodynamics. The application to ideal gases is presented in this chapter, while the applications to blackbody radiation, lattice vibration, free electrons in metals, and electrons and holes in semiconductors will be deferred to later chapters.

3.1 Statistical Mechanics of Independent Particles

We say particles are independent when their energies are independent of each other and the total energy is the sum of the energies of individual particles. Consider a system that has N independent particles of the same type confined in a volume V. The total internal energy of the system is U, which is the sum of the energies of all particles. Particles may have different energies and can be grouped according to their energies. It is of interest to know how many particles are there within certain energy intervals. We can subdivide energy into a large number of discretized energy levels. As illustrated in Fig. 3.1, there are N_i particles on the ith energy level, each with energy exactly equal to ε_i.

From classical mechanics point of view, it appears that the increment between adjacent energy levels can be indefinitely small. The particles are distinguishable, and there is no limit on the number of particles on each energy level. Quantum mechanics predicts that the energy levels are indeed discretized with finite increments between adjacent energy levels, and the particles are unidentifiable (*indistinguishable*) according to quantum statistics. Readers are referred to Appendix B.3 for further discussion about the statistical distinguishability and the resulting different permutation and combination theories. The conservation equations for the system shown in Fig. 3.1 are

$$\sum_{i=0}^{\infty} N_i = N \tag{3.2}$$

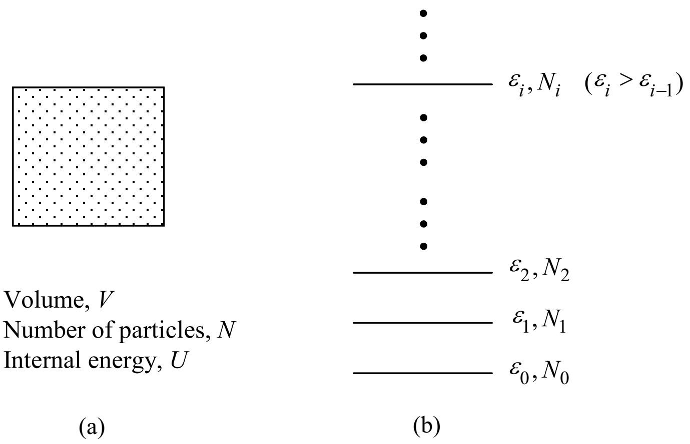


Fig. 3.1 Illustration of **a** a simple system of independent particles and **b** energy levels

and

$$\sum_{i=0}^{\infty} \varepsilon_i N_i = U \tag{3.3}$$

3.1.1 Macrostates Versus Microstates

The thermodynamic state may be viewed in terms of the gross behavior that ignores any differences at the molecular or atomic level, or in terms of the individual particles. A *macrostate* is determined by the values of N_0, N_1, N_2, … for a given volume (which somehow confines the quantized energy levels) though two different macrostates can have the same energy. Each macrostate may be made up of a number of microscopic arrangements; each microscopic arrangement is called a *microstate.* In statistical mechanics, all microstates are assumed *equally probable*. There may be a large number of microstates that correspond to the same macrostate. The number of microstates for each macrostate is termed the *thermodynamic probability* Ω of that macrostate. Unlike the stochastic probability that lies between 0 and 1, the thermodynamic probability Ω is usually a very large number. One of the principles underlying statistical mechanics is that the stable-equilibrium state corresponds to the *most probable macrostate*. Therefore, for given values of U, N, and V, the thermodynamic probability is the largest in the stable-equilibrium state. We will use the following example to illustrate the concepts of microstate and macrostate.

Example 3.1 There are four distinguishable particles in a confined space, and there are two energy levels. How many macrostates are there? How many microstates are there for the macrostate with two particles on each energy level?

Solution There are five macrostates in total with $(N_1, N_2) = (0, 4), (1, 3), (2, 2), (3, 1),$ and (4, 0), respectively. Because the particles are distinguishable, the microstates will be different only if the particles from different energy levels are interchanged. Using the combination theory, we can figure out that $\Omega(N_1, N_2) = N!/(N_1!N_2!) = 4!/(2!2!) = 6$. Hence, there are six microstates for the macrostate with two particles on each energy level. It can be shown that this is also the most probable macrostate.

3.1.2 Phase Space

The phase space is used to describe all possible values of position and momentum variables that can be used to fully characterize the state of a mechanical system at any given time. It is an important concept in classical and quantum statistics. The *phase space* is a six-dimensional "space" formed by three coordinates for the position $\mathbf{r}$ and three coordinates for the momentum $\mathbf{p} = m\mathbf{v}$ or velocity $\mathbf{v}$. Each point in the phase space defines the exact location and momentum of an individual particle. If both the space and the momentum are described with the Cartesian system, then a volume element in the phase space is $\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$. Figure 3.2 shows a phase space projected to the $x - p_x$ plane. The three coordinates (p_x, p_y, p_z) form a *momentum space*. One may choose to use (v_x, v_y, v_z) to form a *velocity space*. If the momentum space is described in spherical coordinates, the volume element is $\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z = p^2 \sin\theta \mathrm{d}p\mathrm{d}\theta\mathrm{d}\phi$. The volume contained in a spherical shell from p to $p + \mathrm{d}p$ is $4\pi p^2\mathrm{d}p$. Figure 3.3 illustrates the momentum space projected to the $p_x - p_y$ plane, with a spherical shell.

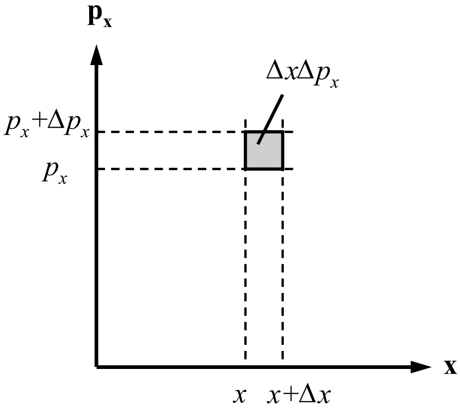


Fig. 3.2 Phase space projected to the $x - p_x$ plane, where $\Delta x \Delta p_x$ is an area element

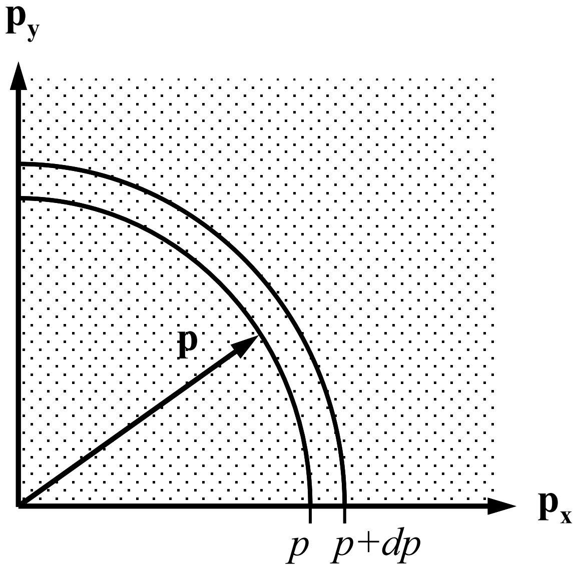


Fig. 3.3 The $p_x - p_y$ plane of the momentum space, showing a spherical shell

3.1.3 Quantum Mechanics Considerations

The principles of quantum mechanics are important for the advancement of statistical thermodynamics, especially when dealing with particles that cannot be treated with classical statistics. An introduction to the basic principles of quantum mechanics is given in this section and a more detailed introduction of the quantum theory is given in Sect. 3.5. The origin of quantum theory can be traced back to about 100 years ago when Planck first used a discrete set of energies to describe the electromagnetic radiation, and thus obtained Planck's distribution (details to be presented in Sect. 8.2). For any given frequency of radiation ν, the smallest energy increment is given by $h\nu$, where $h = 6.626 \times 10^{-34}$ J · s is called Planck's constant. Radiation can be alternatively viewed as electromagnetic waves or traveling energy quanta. The corpuscular theory treats radiation as a collection of energy quanta, called *photons.* The energy of a photon is given by

$$\varepsilon = h\nu \tag{3.4}$$

From the wave theory, the speed of light c is related to the wavelength λ and the frequency by

$$c = \lambda\nu \tag{3.5}$$

In a medium with a refractive index of n, $c = c_0/n$ and $\lambda = \lambda_0/n$, where subscript 0 is used to indicate quantities in vacuum with $n = 1$. The speed of light in vacuum is

$c_0 = 299,792,458\,\text{m/s}$, which is a defined quantity as given in Appendix A. Note that the frequency of an electromagnetic wave does not change from one medium to another.

Based on the relativistic theory, the rest energy E_0 of a particle with mass m is

$$E_0 = mc^2 \tag{3.6}$$

The momentum of the particle traveling with speed v is $p = mv$. Since the energy of a photon is $h\nu$ and its speed is c, the momentum of a (massless) photon is (see Sect. 3.7)

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{3.7}$$

Another hypothesis of quantum theory is that the motion of matter may be wave-like, with characteristic wavelength and frequency. Therefore, for a particle moving with velocity $v \ll c$.

$$\lambda_{\mathrm{DB}} = \frac{h}{p} = \frac{h}{mv} \quad \text{and} \quad \nu_{\mathrm{DB}} = \frac{mc^2}{h} \tag{3.8}$$

which are called *de Broglie wavelength* and *de Broglie frequency*, respectively. In 1923, Louis de Broglie postulated that matter may also possess wave characteristics and thereafter resolved the controversy as per the nature of radiation. Note that the phase speed of the wave defined by Eq. (3.8) is c^2/v, which is greater than the speed of light. The discovery of electron diffraction confirmed de Broglie's hypothesis. For this prediction, de Broglie received the Nobel Prize in Physics in 1929. Seven years later, the 1937 Nobel Prize in Physics was shared by Clinton J. Davisson and George P. Thomson for their independent experiments that demonstrated diffraction of electrons by crystals.

Example 3.2 Calculate the frequency in Hz and photon energy in eV of an ultraviolet (UV) laser beam at a wavelength of $\lambda = 248\,\text{nm}$ and a microwave at $\lambda = 10\,\text{cm}$. Calculate the de Broglie wavelength of a He atom at 200 °C, using the average speed of 1717 m/s, and an electron traveling with a speed of 10^6 m/s.

Solution The equations are $\nu = c/\lambda$ and $\varepsilon = hc/\lambda$. Assume the refractive index is 1. For the UV beam at $\lambda = 248\,\text{nm}$, $\nu = 1.2 \times 10^{15}\,\text{Hz}$ and $\varepsilon = 8.01 \times 10^{-19}\,\text{J} = 5\,\text{eV}$. For $\lambda = 10\,\text{cm}$, $\nu = 3 \times 10^9\,\text{Hz} = 3\,\text{GHz}$ and $\varepsilon = 2 \times 10^{-24}\,\text{J} = 1.24 \times 10^{-5}\,\text{eV} = 124\,\text{meV}$. The mass of a He atom is $m = M/N_{\mathrm{A}} = 6.64 \times 10^{-27}\,\text{kg}$. Hence, $\lambda_{\mathrm{DB}} = h/mv = 5.8 \times 10^{-11}\,\text{m} = 58\,\text{pm}$. From Appendix A, $m_{\mathrm{e}} = 9.11 \times 10^{-31}\,\text{kg}$, therefore, $\lambda_{\mathrm{DB}} = 7.3 \times 10^{-10}\,\text{m} = 0.73\,\text{nm}$, which is in the x-ray region.

The foundation of quantum mechanics is the Schrödinger equation, which is a partial-differential equation of the time-space dependent complex *probability density function*. More details can be found from the texts of Tien and Lienhard [1], Carey [5],

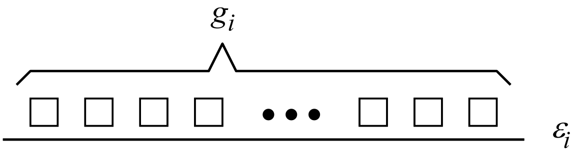


Fig. 3.4 The degeneracy of the *i*th energy level

and Griffiths [8]. The solutions of the Schrödinger equation support the dual nature of wave and matter, and result in discrete quantized energy levels. Furthermore, there are usually more than one distinguishable *quantum states* at each energy level, i.e., the energy levels may be degenerate. The number of quantum states for a given energy level is called the *degeneracy*, denoted by g_i for the *i*th energy level, as shown in Fig. 3.4.

The *uncertainty principle* states that the position and momentum of a given particle cannot be measured simultaneously with arbitrary precision. The limit is given by

$$\Delta x \Delta p_x \geq h/4\pi \tag{3.9}$$

This result implies that we cannot locate the exact position of a particle in the phase space; all we can say is that the particle is somewhere in a domain whose volume is around h^3. The uncertainty principle is one of the cornerstones of quantum mechanics and was formulated in 1927 by Werner Heisenberg, a Nobel laureate in Physics.

For certain particles, such as electrons, each quantum state cannot be occupied by more than one particle. This is *the Pauli exclusion principle,* discovered by Nobel laureate Wolfgang Pauli in 1925. The result, as we will see, is the Fermi-Dirac statistics that can be used to describe the behavior of free electrons. The collection of free electrons in metals is sometimes called the free electron gas, which exhibits very different characteristics from ideal molecular gases.

3.1.4 Equilibrium Distributions for Different Statistics

The characteristics of various types of particles can be described by different statistics. In this section, we will first introduce three statistics and then apply them to obtain the distribution functions, i.e., the number of particles on each energy level. Applications of the distribution functions to various particle systems will also be explained.

- *The Maxwell-Boltzmann (MB) statistics*: Particles are distinguishable and there is no limit for the number of particles on each energy level. From Eq. (B.22) in Appendix B, the thermodynamic probability for the distribution shown in Fig. 3.1b is

$$\Omega = \frac{N!}{N_0!N_1!N_2!\cdots} = \frac{N!}{\prod_{i=0}^{\infty} N_i!}$$

If degeneracy is included as shown in Fig. 3.4, then

$$\Omega_{\mathrm{MB}} = N!\prod_{i=0}^{\infty} \frac{g_i^{N_i}}{N_i!} \tag{3.10}$$

- *The Bose-Einstein (BE) statistics*: Particles are indistinguishable and there is no limit for the number of particles in each quantum state; there are g_i quantum states on the *i*th energy level. From Eq. (B.23), the number of ways of placing N_i indistinguishable objects to g_i distinguishable boxes is $\frac{(g_i+N_i-1)!}{(g_i-1)!N_i!}$. Therefore, the thermodynamic probability for BE statistics is

$$\Omega_{\mathrm{BE}} = \prod_{i=0}^{\infty} \frac{(g_i + N_i - 1)!}{(g_i - 1)!N_i!} \tag{3.11}$$

- *The Fermi-Dirac (FD) statistics*: Particles are indistinguishable and the energy levels are degenerate. There are g_i quantum states on the *i*th energy level, and each quantum state can be occupied by no more than one particle. Using Eq. (B.21), we obtain the thermodynamic probability for FD statistics as

$$\Omega_{\mathrm{FD}} = \prod_{i=0}^{\infty} \frac{g_i!}{(g_i - N_i)!N_i!} \tag{3.12}$$

The three statistics are very important for understanding the molecular, electronic, crystalline, and radiative behaviors that are essential for energy transport processes in both small and large scales. MB statistics can be considered as the limiting case of BE or FD statistics. The thermodynamic relations and the velocity distribution of ideal molecular gases can be understood from MB statistics. BE statistics is important for the study of photons, phonons in solids, and atoms at low temperatures. It is the basis of Planck's law of blackbody radiation, the Debye theory for the specific heat of solids, and the Bose-Einstein condensation, which is important for superconductivity, superfluidity, and laser cooling of atoms. FD statistics can be used to model the electron gas and the electron contribution to the specific heat of solids. It is important for understanding the electronic and thermal properties of metals and semiconductors.

Example 3.3 Four indistinguishable particles are to be placed in two energy levels, each with a degeneracy of 3. Evaluate the thermodynamic probability of all arrangements, considering BE and FD statistics separately. What are the most probable arrangements?

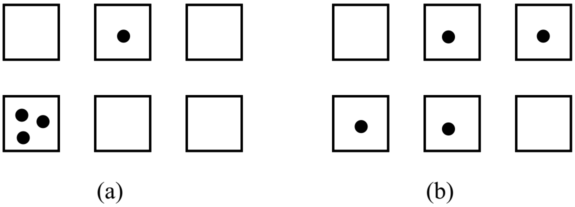


Fig. 3.5 Illustration of the arrangement for four particles on two energy levels, each with a degeneracy of 3. **a** Bose-Einstein statistics. **b** Fermi-Dirac statistics

Solution There are two energy levels, $g_0 = g_1 = 3$ and the total number of particles $N = 4$. The thermodynamic probability is $\Omega = \Omega_0 \times \Omega_1$, which depends on N_0 and $N_1 (N_0 + N_1 = 4)$. Figure 3.5 shows specific cases of the BE and FD distributions.

For BE statistics, we have

$$\Omega_{\mathrm{BE}} = \frac{(N_0 + g_0 - 1)!}{(g_0 - 1)!N_0!} \times \frac{(N_1 + g_1 - 1)!}{(g_1 - 1)!N_1!} = \frac{(N_0 + 2)(N_0 + 1)}{2} \times \frac{(6 - N_0)(5 - N_0)}{2}$$

For FD statistics, we must have $N_i \le g_i$; therefore, $1 \le N_0 \le 3$, and

$$\Omega_{\mathrm{FD}} = \frac{g_0!}{(g_0 - N_0)!N_0!} \times \frac{g_1!}{(g_1 - N_1)!N_1!} = \frac{6}{(3 - N_0)!N_0!} \times \frac{6}{(N_0 - 1)!(4 - N_0)!}$$

The results are summarized in the following table. Clearly, the most probable arrangement for both statistics in this case is $N_0 = N_1 = 2$.

N_0	0	1	2	3	4
N_1	4	3	2	1	0
Ω_{BE}	15	30	36	30	15
Ω_{FD}	–	3	9	3	–

For a given simple thermodynamics system of volume V, internal energy U, and total number of particles N, we wish to find the state (identified by the distribution $N_0, N_1, N_2, \ldots$) that maximizes Ω or $\ln \Omega$, under constrains given by Eqs. (3.2) and (3.3), based on the method of Lagrange multipliers (Appendix B). For MB statistics with degeneracy, from Eq. (3.10),

$$\ln \Omega = \ln N! + \sum_{i=0}^{\infty} N_i \ln g_i - \sum_{i=0}^{\infty} \ln N_i!$$

For a large number of particles, the Stirling formula gives $\ln N! \approx N \ln N - N$ from Eq. (B.11). The above equation can be approximated as

$$\ln \Omega = N \ln N - N + \sum_{i=0}^{\infty} N_i \ln g_i - \sum_{i=0}^{\infty} (N_i \ln N_i - N_i) = N \ln N - N + \sum_{i=0}^{\infty} N_i (\ln \frac{g_i}{N_i} + 1)$$

Notice that N and $g_{i's}$ are fixed and only $N_{i's}$ are variables, therefore,

$$\mathrm{d}(\ln \Omega) = \sum_{i=0}^{\infty} \frac{\partial(\ln \Omega)}{\partial N_i} \mathrm{d}N_i = \sum_{i=0}^{\infty} \left(\ln \frac{g_i}{N_i} + 1 - N_i \frac{1}{N_i} \right) \mathrm{d}N_i = \sum_{i=0}^{\infty} \ln \frac{g_i}{N_i} \mathrm{d}N_i = 0 \tag{3.13}$$

From the constraint equations, Eqs. (3.2) and (3.3), we have

$$-\alpha \sum_{i=0}^{\infty} \mathrm{d}N_i = 0 \tag{3.14a}$$

and

$$-\beta \sum_{i=0}^{\infty} \varepsilon_i \mathrm{d}N_i = 0 \tag{3.14b}$$

where α and β are Lagrangian multipliers and ε_i's are treated as constants. Conventionally, negative signs are chosen because α and β are generally nonnegative for molecular gases. By adding Eqs. (3.14a) and (3.14b) to Eq. (3.13), we obtain

$$\sum_{i=0}^{\infty} \left(\ln \frac{g_i}{N_i} - \alpha - \beta \varepsilon_i \right) \mathrm{d}N_i = 0$$

Because $\mathrm{d}N_i$ can be arbitrary, the above equation requires that $\ln(g_i/N_i) - \alpha - \beta\varepsilon_i = 0$. Hence,

$$N_i = \frac{g_i}{\mathrm{e}^{\alpha} \mathrm{e}^{\beta \varepsilon_i}} \tag{3.15a}$$

or

$$\frac{N_i}{N} = \frac{g_i \mathrm{e}^{-\alpha} \mathrm{e}^{-\beta \varepsilon_i}}{\sum_{i=0}^{N} g_i \mathrm{e}^{-\alpha} \mathrm{e}^{-\beta \varepsilon_i}} \tag{3.15b}$$

This is the MB distribution. The physical meanings of α and β will be discussed later. Using the same procedure described above, we can obtain the following for BE statistics,

$$N_i = \frac{g_i}{\mathrm{e}^{\alpha} \mathrm{e}^{\beta \varepsilon_i} - 1} \tag{3.16}$$

which is the BE distribution. For FD statistics, we can obtain the FD distribution as follows

$$N_i = \frac{g_i}{\mathrm{e}^{\alpha}\mathrm{e}^{\beta\varepsilon_i} + 1} \tag{3.17}$$

The results for all the three statistics are summarized in Table 3.1. Note that N_i/g_i signifies how many particles occupy a quantum state or the probability for a quantum state to be occupied, which is called the *mean occupation number*.

Example 3.4 Derive the BE distribution step by step. Under which condition can it be approximated by the MB distribution?

Solution Using the thermodynamic probability of BE statistics in Eq. (3.11), we have

$$\begin{aligned}\ln\Omega &= \sum_{i=0}^{\infty}[\ln(g_i+N_i-1)! - \ln(g_i-1)! - \ln N_i!]\\ &\approx \sum_{i=0}^{\infty}[(g_i+N_i-1)\ln(g_i+N_i-1) - (g_i+N_i-1) - (g_i-1)\ln(g_i-1) + (g_i-1) - N_i\ln N_i + N_i]\\ &= \sum_{i=0}^{\infty}[(g_i+N_i-1)\ln(g_i+N_i-1) - (g_i-1)\ln(g_i-1) - N_i\ln N_i]\end{aligned}$$

Hence,

$$\begin{aligned}\frac{\partial\ln\Omega}{\partial N_i} &= \ln(g_i+N_i-1) + (g_i+N_i-1)\frac{1}{g_i+N_i-1} - \ln N_i - N_i\frac{1}{N_i}\\ &= \ln\left(\frac{g_i+N_i-1}{N_i}\right) \approx \ln\left(\frac{g_i}{N_i}+1\right), \quad \text{since } N_i \gg 1\end{aligned}$$

To maximize Ω, we set $\mathrm{d}(\ln\Omega) = \sum_{i=0}^{\infty}\frac{\partial(\ln\Omega)}{\partial N_i}\mathrm{d}N_i \approx \sum_{i=0}^{\infty}\ln\left(\frac{g_i}{N_i}+1\right)\mathrm{d}N_i = 0$.

By adding Lagrangian multipliers, Eq. (3.14a), (3.14b), we get $\sum_{i=0}^{\infty}[\ln(g_i/N_i+1) - \alpha - \beta\varepsilon_i]\mathrm{d}N_i = 0$. Hence, $N_i = g_i/(\mathrm{e}^{\alpha}\mathrm{e}^{\beta\varepsilon_i} - 1)$, which is the BE distribution given in Eq. (3.16) and Table 3.1.

Discussion. If $\exp(\alpha + \beta\varepsilon_i) \gg 1$, both Eqs. (3.16) and (3.17) reduce to the MB distribution, Eq. (3.15a), (3.15b). Under the limiting case of $g_i \gg N_i \gg 1$, we have

$$\frac{(g_i+N_i-1)!}{(g_i-1)!\,N_i!} = \frac{\overbrace{(g_i+N_i-1)\cdots(g_i+1)g_i}^{N_i \text{ terms}}}{N_i!} \xrightarrow{g_i \gg N_i \gg 1} \frac{g_i^{N_i}}{N_i!}$$

and

$$\frac{g_i!}{(g_i-N_i)!\,N_i!} = \frac{\overbrace{g_i(g_i-1)\cdots(g_i-N_i+1)}^{N_i \text{ terms}}}{N_i!} \xrightarrow{g_i \gg N_i \gg 1} \frac{g_i^{N_i}}{N_i!}$$

Table 3.1 Summary of the three statistics

Statistics	Maxwell-Boltzmann (MB)	Bose-Einstein (BE)	Fermi-Dirac (FD)
Name of particles	Boltzons	Bosons	Fermions
Examples	Ideal gas molecules and in the limit of bosons and fermions	Photons and phonons	Electrons and protons
Distinguishability	Distinguishable	Indistinguishable	Indistinguishable
Degeneracy	Degenerated	Degenerated	Degenerated
Particles per quantum state	Unlimited	Unlimited	One
Thermodynamic probability (Ω)	$N!\prod_{i=0}^{\infty}\frac{g_i^{N_i}}{N_i!}$	$\prod_{i=0}^{\infty}\frac{(g_i+N_i-1)!}{(g_i-1)!N_i!}$	$\prod_{i=0}^{\infty}\frac{g_i!}{(g_i-N_i)!N_i!}$
In the limit of $g_i \gg N_i$	Ω_{MB} (given above)	$\Omega_{\mathrm{MB}}/N!$	$\Omega_{\mathrm{MB}}/N!$
$\ln\Omega$	$N\ln N - N$ $+\sum_{i=0}^{\infty}N_i[\ln(g_i/N_i)+1]$	$\sum_{i=0}^{\infty}[(g_i+N_i-1)\ln(g_i+N_i-1)$ $-N_i\ln N_i-(g_i-1)\ln(g_i-1)]$	$\sum_{i=0}^{\infty}[g_i\ln g_i - N_i\ln N_i$ $-(g_i-N_i)\ln(g_i-N_i)]$
$\mathrm{d}(\ln\Omega)$	$\sum_{i=0}^{\infty}\ln(\frac{g_i}{N_i})\,\mathrm{d}N_i$	$\sum_{i=0}^{\infty}\ln(\frac{g_i}{N_i}+1)\,\mathrm{d}N_i$	$\sum_{i=0}^{\infty}\ln(\frac{g_i}{N_i}-1)\,\mathrm{d}N_i$
$-\alpha\sum_{i=0}^{\infty}\mathrm{d}N_i-\beta\sum_{i=0}^{\infty}\varepsilon_i\mathrm{d}N_i$	$\ln(\frac{g_i}{N_i})-\alpha-\beta\varepsilon_i=0$	$\ln(\frac{g_i}{N_i}+1)-\alpha-\beta\varepsilon_i=0$	$\ln(\frac{g_i}{N_i}-1)-\alpha-\beta\varepsilon_i=0$
Distribution function (Ni)	$\frac{g_i}{\mathrm{e}^{\alpha}\mathrm{e}^{\beta\varepsilon_i}}$	$\frac{g_i}{\mathrm{e}^{\alpha}\mathrm{e}^{\beta\varepsilon_i}-1}$	$\frac{g_i}{\mathrm{e}^{\alpha}\mathrm{e}^{\beta\varepsilon_i}+1}$
Applications	Ideal gases; Maxwell's velocity distribution; limiting cases of BE and FD statistics	Planck's law; Bose-Einstein condensation; specific heat of solids	Electron gas; Fermi level; electron specific heat in metals

We see that the thermodynamic probability for both the BE and FD statistics reduces to the MB statistics divided by $N!$, which is caused by the assumption of indistinguishable particles. Therefore,

$$\Omega_{\text{MB,corrected}} = \prod_{i=0}^{\infty} \frac{g_i^{N_i}}{N_i!}$$

is called the "corrected" MB statistics. For ideal molecular gases at reasonably high temperatures, $g_i \gg N_i$. For this reason, the MB distribution may be considered as the limiting case of the BE or FD distribution; see Table 3.1.

3.2 Thermodynamic Relations

The thermodynamic properties and relations can be understood from the microscopic point of view. This includes the concept of heat and work, entropy, and the third law of thermodynamics. The partition function is key to the evaluation of thermodynamic properties.

3.2.1 Heat and Work

From Eq. (3.3), we have

$$\mathrm{d}U = \sum_{i=0}^{\infty} \varepsilon_i \,\mathrm{d}N_i + \sum_{i=0}^{\infty} N_i \,\mathrm{d}\varepsilon_i \tag{3.18}$$

The first term on the right is due to a redistribution of particles among the energy levels (which is related to a change in entropy), while the second is due to a shift in the energy levels associated with, e.g., a volume change. Consider a reversible quasi-equilibrium process for a closed system (such as a piston/cylinder arrangement); the work is associated to the volume change that does not change the entropy of the system, while heat transfer changes entropy of the system without affecting the energy levels. Therefore,

$$\delta Q = \sum_{i=0}^{\infty} \varepsilon_i \,\mathrm{d}N_i \quad \text{and} \quad \delta W = -\sum_{i=0}^{\infty} N_i \,\mathrm{d}\varepsilon_i \tag{3.19}$$

In writing the above equation, δQ is positive for heat transferred to the system, and δW is positive for work done by the system. They are related to macroscopic quantities for simple system by $\delta Q = T\mathrm{d}S$ and $\delta W = P\mathrm{d}V$. Hence, we obtain the expression of the first law for a closed system, $\mathrm{d}U = \delta Q - \delta W$. If the system is an open system, then $\sum_{i=0}^{\infty} \varepsilon_i \,\mathrm{d}N_i = \mathrm{d}U + \delta W \neq \delta Q$.

3.2.2 Entropy

The macroscopic property entropy is related to the thermodynamic probability by

$$S = k_\mathrm{B} \ln \Omega \tag{3.20}$$

where k_B is the Boltzmann constant. Consider two separate systems A and B, and their combination as a system C. At a certain time, both A and B are individually in thermodynamic equilibrium. Denote the states as A_1 and B_1, and the combined system as state C_1. The thermodynamic probability of system C at state C_1 is related to those of A_1 and B_1 by

$$\Omega_1^\mathrm{C} = \Omega_1^\mathrm{A} \times \Omega_1^\mathrm{B}$$

The entropy of C_1 is then

$$S_1^\mathrm{C} = k_\mathrm{B} \ln \Omega_1^\mathrm{C} = k_\mathrm{B} \ln(\Omega_1^\mathrm{A} \times \Omega_1^\mathrm{B}) = k_\mathrm{B} \ln \Omega_1^\mathrm{A} + k_\mathrm{B} \ln \Omega_1^\mathrm{B} = S_1^\mathrm{A} + S_1^\mathrm{B}$$

Therefore, this definition of entropy meets the additive requirement.

The largest entropy principle states that the entropy of an isolated system will increase until it reaches a stable-equilibrium state (thermodynamic equilibrium), i.e., $\Delta S_\mathrm{isolated} \geq 0$. The microscopic understanding is that entropy is related to the probability of occurrence of a certain macrostate. For a system with specified U, N, and V, the macrostate that corresponds to the thermodynamic equilibrium is the most probable state and, hence, its entropy is the largest. Any states, including those that deviate very slightly from the stable-equilibrium state, will have a much smaller thermodynamic probability. After the equilibrium state is reached, it is not possible for any macrostate, whose thermodynamic probability is much less than that of the equilibrium state, to occur within an observable amount of time.

3.2.3 The Lagrangian Multipliers

For all the three types of statistics, $\mathrm{d}(\ln \Omega) = \alpha \sum_{i=0}^{\infty} \mathrm{d}N_i + \beta \sum_{i=0}^{\infty} \varepsilon_i \,\mathrm{d}N_i$, where the first term is the change in the total number of particles and the second can be related to the net heat transfer for a closed system; therefore, $\mathrm{d}(\ln \Omega) = \alpha \mathrm{d}N + \beta \delta Q$. In a reversible process in which the total number of particles do not change (closed system), $\mathrm{d}N = 0$, $\mathrm{d}(\ln \Omega) = \mathrm{d}S/k_\mathrm{B}$, and $\delta Q = T\mathrm{d}S$. Hence, we have for all the three statistics

$$\beta \equiv 1/k_{\mathrm{B}}T \tag{3.21}$$

To evaluate α, we must allow the system to change its composition. In this case,

$$\mathrm{d}(\ln\Omega) = \alpha\sum_{i=0}^{\infty}\mathrm{d}N_i + \beta\sum_{i=0}^{\infty}\varepsilon_i\mathrm{d}N_i = \alpha\mathrm{d}N + \beta(\mathrm{d}U + P\mathrm{d}V)$$

or

$$T\mathrm{d}S = k_{\mathrm{B}}T\alpha\mathrm{d}N + \mathrm{d}U + P\mathrm{d}V$$

Substituting the above equation into the definition of the Helmholtz function, $\mathrm{d}A = \mathrm{d}(U - TS) = \mathrm{d}U - TdS - SdT$, we have

$$\mathrm{d}A = -SdT - P\mathrm{d}V - k_{\mathrm{B}}T\alpha\mathrm{d}N$$

Noting that the chemical potential $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -k_{\mathrm{B}}T\alpha$, we obtain

$$\alpha = -\frac{\mu}{k_{\mathrm{B}}T} \tag{3.22}$$

Here, μ is expressed in molecular quantity, and if μ is expressed in molar quantity we have $\alpha = -\mu/\bar{R}T$.

3.2.4 Entropy at Absolute Zero Temperature

The third law of thermodynamics states that the entropy of any pure substance vanishes at the ground state (with absolute zero temperature); see Sect. 2.1.3. For BE statistics, we have

$$N = N_0 + N_1 + N_2 + \cdots = \frac{g_0}{\mathrm{e}^{\alpha+\beta\varepsilon_0} - 1} + \frac{g_1}{\mathrm{e}^{\alpha+\beta\varepsilon_1} - 1} + \frac{g_2}{\mathrm{e}^{\alpha+\beta\varepsilon_2} - 1} + \cdots$$

At very low temperatures ($T \to 0$), $\beta = 1/k_{\mathrm{B}}T \to \infty$. Since $\varepsilon_0 < \varepsilon_1 < \varepsilon_2 < \cdots$,

$$\frac{N_i}{N_0} \approx \frac{g_i}{g_0}\mathrm{e}^{-\beta(\varepsilon_i - \varepsilon_0)} \to 0 \text{ as } T \to 0 \text{ for } i \geq 1 \tag{3.23}$$

Hence, $N \approx N_0$; that is, all particles will be at the lowest energy level (ground state). If $g_0 = 1$, as it is the case for a pure substance, then $\Omega = 1$ and $S = k_{\mathrm{B}}\ln\Omega = 0$ as $T \to 0$; this is consistent with the third law of thermodynamics. The occurrence for particles that obey BE statistics (bosons) to collapse to the ground state at sufficiently low temperatures is called the *Bose-Einstein condensation.* Such a state of matter is called the *Bose-Einstein condensate*, in which quantum effects dominate the macroscopic behavior.

Some important applications of the Bose-Einstein condensation are superfluidity and superconductivity. Liquid helium (^{4}He) becomes a superfluid with no viscosity at temperatures below the λ-transition ($T \approx 2.17\,\text{K}$). The specific heat of helium at this temperature becomes infinitely large, suggesting that a phase transition occurs. Bose-Einstein condensate of atoms has been observed with laser cooling and trapping techniques [9]. Photons from the laser collide with the atoms. The absorption can be tuned using the Doppler shift so that only atoms traveling toward the laser can absorb the photons, resulting in reduced momentums in these atoms. Furthermore, the excited atoms will emit photons spontaneously in all directions. The net effect is a decrease in the velocity of the atoms, resulting in a kinetic temperature down to the nanokelvin range. From 1996 to 2003, the Nobel Prize in Physics was awarded for works related to Bose-Einstein condensation for four times: 1996, 1997, 2001, and 2003.

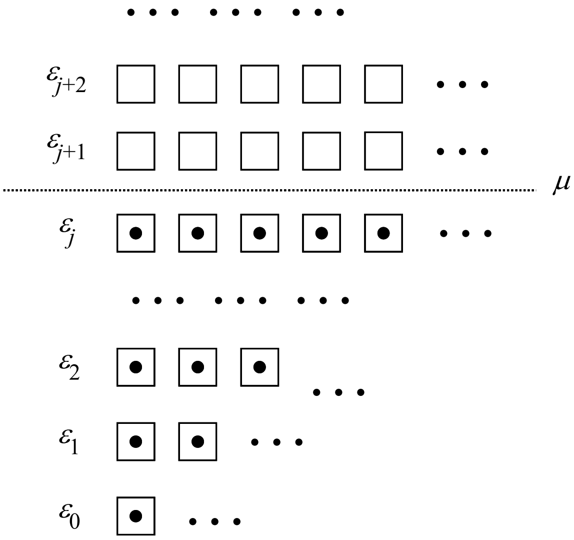
Although electrons are fermions (particles that obey FD statistics) that generally do not condense at zero temperature, they can form pairs at sufficiently low temperatures that behave like bosons. Below the critical temperature, pairs of electrons, called the Cooper pairs can travel freely without any resistance. This is the phenomenon called superconductivity, which was discovered at the beginning of the twentieth century. A large number of elements and compounds can be made superconducting at very low temperatures. Furthermore, some oxides become superconducting at temperatures above 90 K [10]. Superconductors have important applications in magnetic resonance imaging, high-speed and low-noise electronic devices, infrared sensors, and so forth. A similar phenomenon is the superfluidity in helium isotope ^{3}He, which undergoes a phase transition at very low temperatures. The fermionic ^{3}He atoms pair up to form bosonic entities that experience Bose-Einstein condensation at 3 mK.

For FD statistics, from Eqs. (3.17), (3.21), and (3.22), we have

$$\frac{N_i}{g_i} = \frac{1}{\mathrm{e}^{(\varepsilon_i - \mu)/k_\mathrm{B}T} + 1} \tag{3.24}$$

As $T \to 0$, it is found that the occupation number $N_i/g_i = 1$ for all energy levels with $\varepsilon_i < \mu$ and $N_i/g_i = 0$ for energy levels with $\varepsilon_i > \mu$. That is, all quantum states are filled or occupied for $i = 0, 1, 2, \ldots, j$ (with $\varepsilon_j < \mu$), and all quantum states are empty for $i = j + 1, j + 2, \ldots$ (with $\varepsilon_{j+1} > \mu$), as schematically shown in Fig. 3.6. More discussions will be given in Chap. 5 on the behavior of free electrons. For now, it is sufficient to say that the thermodynamic probability $\Omega = 1$ for FD statistics at absolute zero temperature. Therefore, the entropy $S = 0$ at $T \to 0\,\text{K}$ for both the BE and FD statistics. However, MB statistics does not satisfy the third law and is not applicable to very low temperatures.

Fig. 3.6 Schematic of the Fermi-Dirac distribution at 0 K



3.2.5 Macroscopic Properties in Terms of the Partition Function

The *partition function* is an important quantity in statistical thermodynamics. Unlike the characteristics functions (such as the Helmholtz free energy and the Gibbs free energy defined in Chap. 2) used in macroscopic thermodynamics, the physical meaning of the partition function is not immediately clear. However, the introduction of the partition function allows the calculation of macroscopic thermodynamic properties from the microscopic representation. There are different types of partition functions. For MB statistics, the partition function is defined as

$$Z = N\mathrm{e}^{\alpha} = \sum_{i=0}^{\infty} g_i \mathrm{e}^{-\varepsilon_i/k_\mathrm{B}T} \tag{3.25}$$

Therefore,

$$N_i = \frac{N}{Z} g_i \mathrm{e}^{-\varepsilon_i/k_\mathrm{B}T} \tag{3.26}$$

Since

$$\left[\frac{\partial(\ln Z)}{\partial T}\right]_{V,N} = \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N} = \frac{\sum_{i=0}^{\infty} g_i \mathrm{e}^{-\varepsilon_i/k_B T}\left(\frac{\varepsilon_i}{k_\mathrm{B} T^2}\right)}{\sum_{i=0}^{\infty} g_i \mathrm{e}^{-\varepsilon_i/k_\mathrm{B} T}} = \frac{\frac{U\mathrm{e}^{\alpha}}{k_\mathrm{B} T^2}}{N\mathrm{e}^{\alpha}} = \frac{U}{N k_\mathrm{B} T^2}$$

we have

$$U = N k_\mathrm{B} T^2 \left[\frac{\partial(\ln Z)}{\partial T}\right]_{V,N} \tag{3.27}$$

Using the corrected MB statistics by dividing Eq. (3.10) by $N!$, we can express the entropy as

$$\begin{aligned} S &= k_\mathrm{B} \ln(\Omega_\mathrm{MB}/N!) = k_\mathrm{B} \sum_{i=0}^{\infty} N_i \left(1 + \ln\frac{g_i}{N_i}\right) \\ &= k_\mathrm{B} \sum_{i=0}^{\infty} N_i \left(1 + \ln\frac{Z}{N} + \beta\varepsilon_i\right) = N k_\mathrm{B} + N k_\mathrm{B} \ln\frac{Z}{N} + k_\mathrm{B}\beta U \end{aligned} \tag{3.28a}$$

Had we not divided Ω_MB by $N!$, we would get $S = N k_\mathrm{B} \ln Z + k_\mathrm{B}\beta U$, which differs from Eq. (3.28a), (3.28b) by a constant. After substituting β and U into Eq. (3.28a), (3.28b), we obtain

$$S = N k_\mathrm{B} \left\{1 + \ln\frac{Z}{N} + T\left[\frac{\partial(\ln Z)}{\partial T}\right]_{V,N}\right\} \tag{3.28b}$$

The Helmholtz free energy is

$$A = U - TS = -N k_\mathrm{B} T \left(1 + \ln\frac{Z}{N}\right) \tag{3.29}$$

The pressure is

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = N k_\mathrm{B} T \left[\frac{\partial(\ln Z)}{\partial V}\right]_{T,N} \tag{3.30}$$

The enthalpy H and the Gibbs free energy G can also be obtained. The partition function is now related to the macroscopic thermodynamic properties of interest for simple substances.

3.3 Ideal Molecular Gases

An important application of statistical mechanics is to model and predict the thermal properties of materials. In this section, the application of MB statistics to obtain the equation of state and the velocity distributions for ideal molecular gases is presented. The microscopic theories of the specific heat for ideal monatomic and polyatomic gases are given subsequently.

3.3.1 Monatomic Ideal Gases

For a monatomic ideal gas at moderate temperatures, MB statistics can be applied, and the translational energies are

$$\varepsilon = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2}m\mathbf{v}^2 \tag{3.31}$$

Consider a volume element in the phase space, $\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$, where $\mathbf{p} = m\mathbf{v}$ is the momentum of a molecule. The accuracy of specifying the momentum and the displacement is limited by $\Delta x \Delta p_x \sim h$, given by the uncertainty principle. The degeneracy, which is the *number of quantum states* (boxes of size h^3) in a volume element of the phase space, is given by

$$\mathrm{d}g = \frac{\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{h^3} = \frac{m^3}{h^3}\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{3.32}$$

Many useful results were obtained before quantum mechanics by assuming that h^3 is some constant. A more rigorous proof of Eq. (3.32) will be given in Sect. 3.5. When the space between energy levels are sufficiently close, the partition function can be expressed in terms of an integral as $Z_\mathrm{t} = \int \mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\mathrm{d}g$ or

$$Z_\mathrm{t} = \iiint \mathrm{d}x\mathrm{d}y\mathrm{d}z \iiint \frac{m^3}{h^3}\exp\left[-\frac{m}{2k_\mathrm{B}T}\left(v_x^2 + v_y^2 + v_z^2\right)\right]\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{3.33}$$

The space integration yields the volume V, and the velocity integration can be individually performed, viz.

$$\int_{-\infty}^{\infty} \exp\left(-\frac{mv_x^2}{2k_\mathrm{B}T}\right)\mathrm{d}v_x = \sqrt{\frac{2\pi k_\mathrm{B}T}{m}} \tag{3.34}$$

Hence,

$$Z_\mathrm{t} = V\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2} \tag{3.35}$$

Therefore,

$$\mathrm{e}^\alpha = \frac{V}{N}\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2} \tag{3.36}$$

which is indeed much greater than unity at normal temperatures for most substances, suggesting that the MB statistics is applicable for ideal molecular gases. At extremely low temperatures, intermolecular forces cannot be neglected and the molecules are not independent anymore.

From Eq. (3.30), we have $P = Nk_\mathrm{B}T\left[\frac{\partial(\ln Z)}{\partial V}\right]_{T,N} = Nk_\mathrm{B}T/V$; thus,

$$PV = Nk_\mathrm{B}T \quad \text{or} \quad P = nk_\mathrm{B}T \tag{3.37}$$

where $n = N/V$ is the number density. The Boltzmann constant is the ideal (universal) gas constant on the molecular basis, $k_\mathrm{B} = \overline{R}/N_\mathrm{A}$. The internal energy, the specific heats, and the absolute entropy can also be evaluated.

$$U = Nk_\mathrm{B}T^2\left[\frac{\partial(\ln Z)}{\partial T}\right]_{V,N} = \frac{3}{2}Nk_\mathrm{B}T \tag{3.38}$$

which is not a function of pressure. The molar specific internal energy is $\bar{u} = \frac{3}{2}\overline{R}T$, and the molar specific heats are

$$\bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T}\right)_V = \frac{3}{2}\overline{R} \tag{3.39}$$

and

$$\bar{c}_p = \left(\frac{\partial \bar{h}}{\partial T}\right)_p = \frac{5}{2}\overline{R} \tag{3.40}$$

The above equations show that the specific heats of monatomic gases are independent of temperature, except at very high temperatures when electronic contributions become important. The molar specific heats do not depend on the type of molecules, but the same is not true for mass specific heats. Using Eq. (3.28a), the absolute entropy can be expressed as

$$S = Nk_\mathrm{B}\left\{\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2}\right]\right\}$$

Therefore, the molar specific entropy is a function of T and P,

$$\bar{s}(T, P) = \overline{R}\left\{\frac{5}{2} + \ln\left[\frac{k_B T}{P}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]\right\} \tag{3.41}$$

This is the *Sackur-Tetrode equation.*

3.3.2 Maxwell's Velocity Distribution

Rewrite $N_i = g_i e^{-\alpha} e^{-\varepsilon_i/k_B T}$ as $dN = dg e^{-\alpha} e^{-\varepsilon/k_B T}$. In a volume V and from $\mathbf{v}$ to $\mathbf{v} + d\mathbf{v}$ (i.e., v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, and v_z to $v_z + dv_z$), the number of molecules dN per unit volume may be expressed as

$$\frac{dN}{V} = \frac{m^3}{h^3} dv_x dv_y dv_z \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} \exp\left(-\frac{m}{2k_B T}\mathbf{v}^2\right) \tag{3.42}$$

or

$$f(\mathbf{v})d\mathbf{v} = \frac{dN}{V} = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right)d\mathbf{v} \tag{3.43}$$

where $f(\mathbf{v})$ is the Maxwell velocity distribution in a unit volume. Notice that

$$F(\mathbf{v}) = \frac{f(\mathbf{v})}{n} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) \tag{3.44}$$

which is a Gaussian distribution. Notice that $\mathbf{v}^2 = \mathbf{v} \cdot \mathbf{v} = v^2 = v_x^2 + v_y^2 + v_z^2$. The distribution of velocity component is also Gaussian, such that

$$F(\mathbf{v}) = F(v_x)F(v_y)F(v_z) \tag{3.45}$$

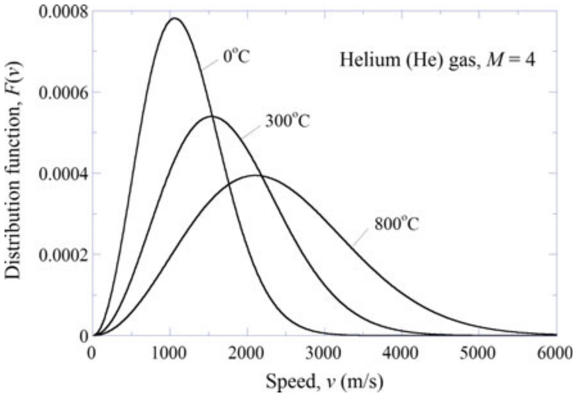
Taking the x-component as an example, we can write

$$F(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2k_B T}\right) \tag{3.46}$$

The speed distribution may be obtained from the following by integrating the velocity distribution in a spherical shell (over the solid angle of 4π).

$$F(v)dv = \iint_{4\pi} F(\mathbf{v})d\mathbf{v} = \iint_{4\pi} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)v^2 \sin\theta dv d\theta d\phi$$

Fig. 3.7 Speed distribution for helium gas at different temperatures



Therefore,

$$F(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{3.47}$$

Figure 3.7 plots the speed distribution of He gas at 0, 300, and 800 °C. When evaluating $k_B T$, we must convert T to absolute temperature. It can be seen that more molecules will be at higher speeds as the temperature increases. It should be noted that $F(v = 0) = 0$ but $F(\mathbf{v})$ is maximum at $v = 0$. In the speed coordinate, an interval between v and $v + \mathrm{d}v$ corresponds to a spherical shell in the velocity space. Even though $F(\mathbf{v})$ is maximum at $v = 0$, the probability of finding a molecule per unit speed interval decreases to 0 as $v \to 0$, which is caused by the associated decrease in the volume of the spherical shell.

Example 3.5 Find the average speed and the root-mean-square speed for a He gas at 200 °C at 100 kPa. What if the pressure is changed to 200 kPa? What are the most probable velocity and the most probable speed?

Solution The average speed may be obtained from either the velocity distribution or the speed distribution. That is

$$\bar{v} = \iiint vF(\mathbf{v})\,\mathrm{d}\mathbf{v} = \int_0^\infty vF(v)\mathrm{d}v = \sqrt{\frac{8k_B T}{\pi m}} \tag{3.48}$$

The average of v^2 is (see Appendix B.5)

$$\overline{v^2} = \iiint v^2 F(\mathbf{v})\,\mathrm{d}\mathbf{v} = \int_0^\infty v^2 F(v)\mathrm{d}v = \frac{3k_B T}{m} \tag{3.49a}$$

Therefore the root-mean-square speed is

$$v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}} \tag{3.49b}$$

Plugging in the numerical values, we have $\bar{v} = 1582\,\mathrm{m/s}$ and $v_{\mathrm{rms}} = 1717\,\mathrm{m/s}$ for He gas at 200 °C. We also notice that the pressure has no effect on the speed distribution, unless it is so high that intermolecular forces cannot be neglected.

The most probable velocity $\mathbf{v}_{\mathrm{mp}} = 0$ because of the symmetry in the Gaussian distribution. We can obtain the most probable speed by setting $F'(v) = 0$, viz.

$$2v \exp\left(-\frac{mv^2}{2k_BT}\right) - v^2\left(\frac{mv}{k_BT}\right)\exp\left(-\frac{mv^2}{2k_BT}\right) = 0$$

The solution gives the most probable speed as $v_{\mathrm{mp}} = \sqrt{2k_{\mathrm{B}}T/m}$. For He gas at 200 °C, it gives $v_{\mathrm{mp}} = 1402\,\mathrm{m/s}$. Note that $v_{\mathrm{mp}} : \bar{v} : v_{\mathrm{rms}} = \sqrt{2} : \sqrt{8/\pi} : \sqrt{3} \approx 1.4 : 1.6 : 1.7$.

Comment. An important consequence for Eqs. (3.49a), (3.49b) is that temperature is related to the mean kinetic energy of the molecule such that

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_z^2} = \frac{1}{2}k_{\mathrm{B}}T \tag{3.50}$$

Thus, the internal energy of a monatomic gas given in Eq. (3.38) is the sum of the kinetic energy of all molecules.

3.3.3 Diatomic and Polyatomic Ideal Gases

Additional degrees of freedom or energy storage modes must be considered for diatomic and polyatomic molecules, besides translation. The molecule may rotate about its center of gravity, and atoms may vibrate with respect to each other. For a molecule consisting of q atoms, each atom may move in all three directions, and there will be a total of $3q$ modes. Consider the translation of the molecule as a whole; there are three translational degrees of freedom or modes: $\phi_{\mathrm{t}} = 3$. For diatomic molecules or polyatomic molecules whose atoms are arranged in a line (such as CO_2), as shown in Fig. 3.8, there are two rotational degrees of freedom or modes: $\phi_{\mathrm{r}} = 2$. Therefore, there are $\phi_{\mathrm{v}} = 3q - 5$ vibrational degrees of freedom or modes. For polyatomic molecules whose atoms are not aligned (such as H_2O and CH_4, see Fig. 3.9), there are three rotational degrees of freedom or $\phi_{\mathrm{r}} = 3$. The number of vibrational degrees of freedom or modes are thus $\phi_{\mathrm{v}} = 3q - 6$.

The total energy of a molecule may be expressed as the sum of translational, rotational, and vibrational energies: $\varepsilon = \varepsilon_{\mathrm{t}} + \varepsilon_{\mathrm{r}} + \varepsilon_{\mathrm{v}}$. For simplicity, we have neglected contributions from the electronic ground state and chemical dissociation, which can be included as additional terms in evaluating the internal energy and the entropy [1].

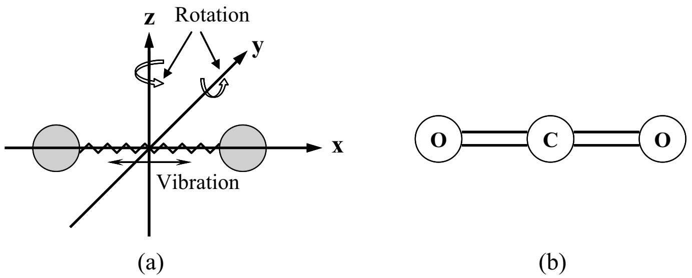
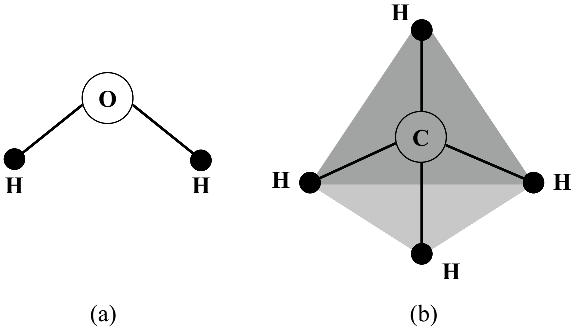


Fig. 3.8 **a** A diatomic molecule, showing two rotational and one vibrational degrees of freedom. **b** CO_2 molecule, where the atoms are aligned

Fig. 3.9 **a** H_2O molecule, for which the atoms are not aligned. **b** The tetrahedral methane (CH_4) molecule



At high temperatures, the vibration mode can be coupled with the rotation mode. Here, however, it is assumed that these modes are independent. The partition function can be written as

$$Z = Z_t Z_r Z_v = \left(\sum g_t e^{-\varepsilon_t/k_B T}\right)\left(\sum g_r e^{-\varepsilon_r/k_B T}\right)\left(\sum g_v e^{-\varepsilon_v/k_B T}\right) \tag{3.51}$$

For polyatomic atoms, Eqs. (3.31) through (3.36) hold for the translational modes. Z_r and Z_v are internal contributions that do not depend on volume; therefore, Eq. (3.37) also holds. Since the degrees of freedom are independent of each other, Maxwell's velocity and speed distributions discussed in Sect. 3.3.2 still hold for polyatomic gases. The problem now is to determine the rotational and vibrational energy levels and degeneracies. Generally speaking, there exists certain characteristic temperature associated with each degree of freedom. The characteristic temperature for translation is very low for molecular gases. On the other hand, the characteristic temperature for rotation is slightly higher, and that for vibration is usually very high, as can be seen from Table 3.2 for selected diatomic molecules. If the temperature is much less than the characteristic temperature of a certain mode, then the contribution of that mode to the energy storage is negligible. For the temperatures

Table 3.2 Characteristic temperatures of rotation and vibration for some diatomic molecules

Substance	Symbol	Θ_r (K)	Θ_v (K)
Hydrogen	H_2	87.5	6320
Deuterium	D_2	43.8	4490
Hydrogen chloride	HCl	15.2	4330
Nitrogen	N_2	2.86	3390
Carbon monoxide	CO	2.78	3120
Nitric oxide	NO	2.45	2745
Oxygen	O_2	2.08	2278
Chloride	Cl_2	0.35	814
Sodium vapor	Na_2	0.08	140

much greater than the characteristic temperature, however, there often exist some asymptotic approximations.

Rotation. A quantum mechanical analysis of a rigid rod, to be derived in Sect. 3.5.3, shows that the rotational energy levels are given by

$$\frac{\varepsilon_l}{k_B T} = l(l+1)\frac{\Theta_r}{T} \tag{3.52}$$

Here, Θ_r is the characteristic temperature for rotation given by $\Theta_r = h^2/(8\pi^2 k_B I)$, where I is the moment of inertia of the molecule about the center of mass. The larger the value of I, the smaller the characteristic temperature will be. This is clearly shown in Table 3.2. The degeneracy of rotational energy levels is

$$g_l = \frac{2l+1}{\sigma} \tag{3.53}$$

where σ is a symmetry number that arises from molecular symmetry: $\sigma = 1$ if the atoms are of different types (such as in a NO or CO molecule), and $\sigma = 2$ if the atoms are the same (such as in a O_2 or N_2 molecule).

$$Z_r = \sum_{l=0}^{\infty} \frac{2l+1}{\sigma} \exp\left[-l(l+1)\frac{\Theta_r}{T}\right] \tag{3.54}$$

This series converges very fast for $\Theta_r/T < 0.5$, since

$$Z_r = \frac{1}{\sigma}\left[1 + 3\exp\left(-\frac{2\Theta_r}{T}\right) + 5\exp\left(-\frac{6\Theta_r}{T}\right) + 7\exp\left(-\frac{12\Theta_r}{T}\right) + \cdots\right]$$

For $T/\Theta_r > 1$, Eq. (3.54) may be expanded to give (see Problem 3.26)

$$Z_{\mathrm{r}} = \frac{T}{\Theta_{\mathrm{r}}\sigma}\left[1 + \frac{1}{3}\left(\frac{\Theta_{\mathrm{r}}}{T}\right) + \frac{1}{15}\left(\frac{\Theta_{\mathrm{r}}}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_{\mathrm{r}}}{T}\right)^3 + \cdots\right] \tag{3.55}$$

At temperatures much higher than the characteristic temperature of rotation, $T/\Theta_{\mathrm{r}} \gg 1$, the above equation reduces to

$$Z_{\mathrm{r}} = \frac{T}{\sigma\Theta_{\mathrm{r}}} \tag{3.56}$$

Under this limit, the contribution of the rotational energy to the internal energy becomes

$$U_{\mathrm{r}} \approx Nk_{\mathrm{B}}T \tag{3.57}$$

The contribution to the molar specific heat by the two rotational degrees of freedom is

$$\bar{c}_{v,\mathrm{r}} = \overline{R} \tag{3.58}$$

Vibration. The vibration in a molecule can be treated as a harmonic oscillator. For each vibration mode, the quantized energy levels are given in Sect. 3.5.5 as

$$\varepsilon_{\mathrm{v},i} = (i + \tfrac{1}{2})h\nu,\ i = 0, 1, 2, \ldots \tag{3.59}$$

where ν is the natural frequency of vibration, and the ground-state energy is $\frac{1}{2}h\nu$. The vibrational energy levels are not degenerated; thus, $g_{\mathrm{v},i} = 1$. Subsequently, we can write

$$Z_{\mathrm{v}} = \sum_{i=0}^{\infty} \mathrm{e}^{-(i+1/2)h\nu/k_{\mathrm{B}}T} = e^{-\Theta_{\mathrm{v}}/2T}\sum_{i=0}^{\infty} \mathrm{e}^{-i\Theta_{\mathrm{v}}/T}$$

where $\Theta_{\mathrm{v}} = h\nu/k_{\mathrm{B}}$ is a characteristic temperature for vibration and is listed in Table 3.2 for several diatomic molecules. The vibrational partition function becomes

$$Z_{\mathrm{v}} = \frac{\mathrm{e}^{-\Theta_{\mathrm{v}}/2T}}{1 - \mathrm{e}^{-\Theta_{\mathrm{v}}/T}} = \frac{\mathrm{e}^{\Theta_{\mathrm{v}}/2T}}{\mathrm{e}^{\Theta_{\mathrm{v}}/T} - 1} \tag{3.60}$$

Its contribution to the internal energy and the specific heat can be written as

$$U_{\mathrm{v}} = Nk_{\mathrm{B}}\Theta_{\mathrm{v}}\left(\frac{1}{2} + \frac{1}{\mathrm{e}^{\Theta_{\mathrm{v}}/T} - 1}\right) \tag{3.61}$$

and

$$\bar{c}_{v,\mathrm{v}} = \overline{R}\frac{\Theta_\mathrm{v}^2}{T^2}\frac{\mathrm{e}^{\Theta_\mathrm{v}/T}}{(\mathrm{e}^{\Theta_\mathrm{v}/T}-1)^2} \tag{3.62}$$

At $T \ll \Theta_\mathrm{v}$, the vibrational mode contributes to the internal energy but not to the specific heat. At $T > 1.5\Theta_\mathrm{v}$, U_v almost linearly depends on T and $\bar{c}_{v,\mathrm{v}} \approx \overline{R}$. In classical statistical mechanics, it is believed that each degree of freedom contributes to the stored thermal energy with an amount of $\frac{1}{2}k_\mathrm{B}T$ and results in a specific heat of $\frac{1}{2}k_\mathrm{B}$ on the particle base. This is called the *equipartition principle*. The contribution of each vibrational mode is $\overline{R}$ not $\overline{R}/2$, due to the fact that each vibrational mode includes a kinetic component and a potential component for energy storage. For this reason, each vibrational mode is equivalent to two degrees of freedom in terms of the energy storage when it is fully excited. It should be noted that the equipartition principle is only applicable at sufficiently high temperatures. Because energy is additive, we can write

$$\bar{c}_v = \bar{c}_{v,\mathrm{t}} + \bar{c}_{v,\mathrm{r}} + \bar{c}_{v,\mathrm{v}} \tag{3.63}$$

The result is schematically shown in Fig. 3.10. One can see that for a diatomic ideal gas,

$$\bar{c}_v = 2.5\overline{R} \quad \text{if} \quad \Theta_\mathrm{r} \ll T \ll \Theta_\mathrm{v} \tag{3.64}$$

which happens to be near room temperature for many gases such as nitrogen and carbon monoxide; see Table 3.2. Figure 3.11 plots the specific heat for several real gases at sufficiently low pressure so that the ideal gas model is applicable. It should be noted that, for hydrogen, nuclear spin is important and Eq. (3.54) needs to be modified to account for the spin degeneracy [1, 2]. However, Eqs. (3.57) and (3.58) predict the right trend and are applicable at temperatures much higher than Θ_r. At extremely high temperatures (say 3000 K), electronic contributions and the coupling between rotation and vibration become important. Although Eq. (3.63) is the correct expression for the specific heat at moderate temperatures, two additional partition

Fig. 3.10 Typical specific heat curve of a diatomic ideal gas

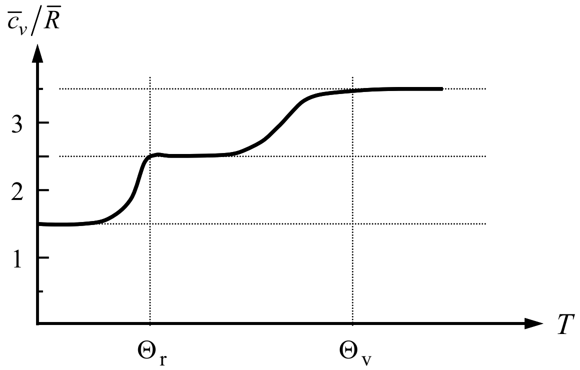
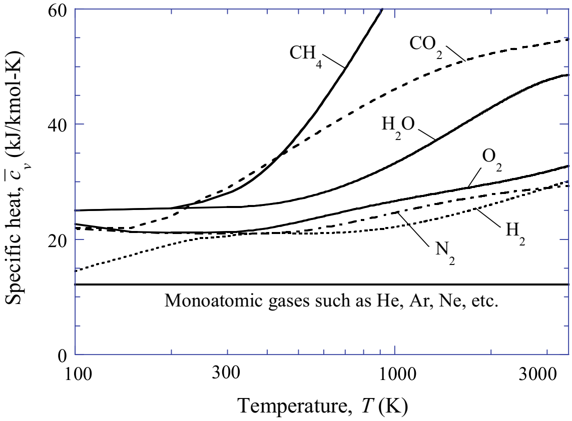


Fig. 3.11 Specific heat at constant volume for several ideal gases



functions must be included to correctly evaluate the internal energy and the entropy (see Problem 3.22). We limit the derivations to the specific heat, which is closely relevant to heat transfer calculations.

The characteristic temperature for rotation is usually very small for polyatomic molecules because of their large moments of inertia. Therefore, the rotational degrees of freedom can be assumed as fully excited in almost any practical situations. Each rotational degree of freedom will contribute $\overline{R}/2$ to the molar specific heat. For molecules whose atoms are aligned (such as CO_2), the rotational contribution to the specific heat is $\overline{R}$, and

$$\bar{c}_v = \frac{5}{2}\overline{R} + \overline{R}\sum_{i=1}^{3q-5} \frac{\zeta_i^2 e^{\zeta_i}}{(e^{\zeta_i} - 1)^2}, \quad \zeta_i = \Theta_{v,i}/T \tag{3.65}$$

If $T \gg \Theta_{v,i}$, then $\bar{c}_v \to \overline{R}(3q - 2.5)$. For molecules whose atoms are not aligned (such as H_2O and CH_4),

$$\bar{c}_v = 3\overline{R} + \overline{R}\sum_{i=1}^{3q-6} \frac{\zeta_i^2 e^{\zeta_i}}{(e^{\zeta_i} - 1)^2} \tag{3.66}$$

In this case, $\bar{c}_v \to \overline{R}(3q - 3)$ at $T \gg \Theta_{v,i}$. Again, electronic contribution may be significant at very high temperatures. Table 3.3 lists the vibrational frequencies for several commonly encountered gases. The unit of frequency is given in inverse centimeter (cm^{-1}), which is often used in spectroscopic analyses. Note that $\Theta_v = h\nu/k_B = hc\bar{\nu}/k_B$, where $\bar{\nu}$ is the wavenumber in cm^{-1} if we take $c = 2.998 \times 10^{10}$ cm/s, giving Θ_v (K) $= 1.44\,\bar{\nu}$ (cm^{-1}). One can use this table to estimate the specific heat of these gases based on Eq. (3.65) or (3.66).

Table 3.3 Vibrational modes of several gases, where the integer in the parentheses indicates the number of degenerate modes

Type	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	Total f_v
CO_2	667 (2)	1343	2349	–	4
H_2O	1595	3657	3756	–	3
CH_4	1306 (3)	1534 (2)	2916	3019 (3)	9

In reality, vibration-rotation interactions result in multiple absorption lines around each vibration mode, which can be observed through infrared absorption spectroscopy. Figure 3.12 shows the molecular absorption spectra of CO_2 and H_2O measured with a Fourier-transform infrared spectrometer. The absorption spectra were obtained by comparing the spectrum when the measurement chamber is open with that when the chamber is purged with a nitrogen gas, which does not absorb in the mid-infrared region. The concentrations of H_2O and CO_2 in the experiments were not controlled since the purpose is to demonstrate the infrared absorption frequencies only. While the resolution of 1 cm^{-1} is not high enough to resolve very fine features, the absorption bands near 670 cm^{-1} due to degenerate bending modes and near 2350 cm^{-1} due to asymmetric stretching mode in CO_2 can be clearly seen. Note that the symmetric vibration mode of CO_2 at 1343 cm^{-1} is infrared inactive. Hence, it does not show up in the absorption spectrum but can be observed with Raman spectroscopy. Furthermore, the vibration-rotation interactions cause multiple lines in the water vapor absorption bands from 1300 to 2000 cm^{-1} and from 3500 to 4000 cm^{-1}.

Example 3.6 How many rotational degrees of freedom are there in a silane (SiH_4) molecule? If a low-pressure silane gas is raised to a temperature high enough to completely excite its rotational and vibrational modes, find its specific heats.

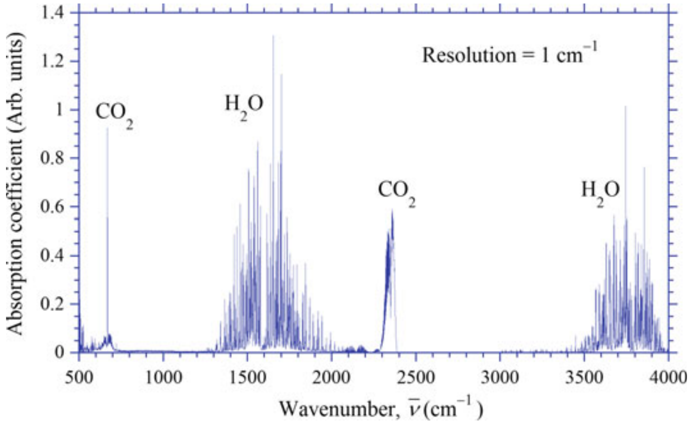


Fig. 3.12 Infrared absorption spectrum of ambient air obtained with a Fourier-transform infrared spectrometer

Solution For SiH_4, there will be three translational degrees of freedom $\phi_t = 3$, three rotational degrees of freedom $\phi_r = 3$, and $\phi_v = 3q - 6 = 9$ vibrational degrees of freedom. If all the modes are excited, the specific heat for constant volume will be $c_v = 1.5R + 1.5R + 9R = 12R$. Given that $M = 32$, we find $c_v = 3.12\,\mathrm{kJ/kg\,K}$, $c_p = 3.38\,\mathrm{kJ/kg\,K}$, and $\gamma = 13/12 = 1.083$. The actual specific heats would be much smaller at moderate temperatures.

3.4 Statistical Ensembles and Fluctuations

We have finished the discussion about statistical thermodynamics of independent particles without mentioning ensembles. In a system of independent particles, there is no energy associated with particle-particle interactions or the configuration of the particles. For dependent particles or dense fluids, the previous analysis can be extended by using *statistical ensembles*, which was pioneered by J. Willard Gibbs (1839–1903) in the late nineteenth century in his 1902 book, *Elementary Principles of Statistical Mechanics.* Statistical ensembles are a large set of macroscopically similar systems. When the properties are averaged over a properly chosen ensemble, the macroscopic properties can be considered as the same as the time-averaged quantity of the same system. There are three basic types of ensembles: microcanonical ensemble, canonical ensemble, and grand canonical ensemble [1, 5].

A *microcanonical ensemble* is composed of a large set of identical systems. Each system in the ensemble is isolated from others by rigid, adiabatic, and impermeable walls. The energy, volume, and number of particles in each system are constant. The results obtained using the microcanonical ensemble for independent particles are essentially the same as what we have obtained in previous sections. It is natural to ask the question as to what extent the statistical mechanics theory presented in previous sections will be valid for nanosystems. If the equilibrium properties are defined based on a large set of microcananical ensembles and considered as the time-averaging properties of the system, there will be sufficiently large number of particles in the whole ensemble to guarantee the basic types of statistics, and the thermodynamics relations derived in Sects. 3.1 and 3.2 are still applicable. On the other hand, the difference between the energy levels due to quantization may be large enough to invalidate the substitution of summation with integration. We will discuss the energy level quantization further in Sect. 3.5. In deriving the properties of ideal gases in Sect. 3.3, the consideration of the translational, rotational, and vibrational degrees of freedom is on the basis of individual molecules. Therefore, the conclusions should be applicable to systems under thermodynamic equilibrium.

In a *canonical ensemble,* each system is separated from others by rigid and impermeable walls, which are diathermal. All systems have the same volume and number of particles. However, the systems can exchange energy. At the equilibrium, the temperature T will be the same for all systems. An important result of applying the canonical ensemble is that the energy fluctuation (i.e., the standard deviation of energy of the system) is proportional to $1/\sqrt{N}$, where N is the total number of independent particles.

In a *grand canonical ensemble,* each system is separated from others by rigid, diathermal, and permeable walls. While the volume is fixed and is the same for each system, the number of particles as well as the energy of each system can vary. The temperature and the chemical potential must be the same for all systems at equilibrium. This allows the study of density fluctuations for each system. The result for monatomic molecules yields that the density fluctuation is also proportional to $1/\sqrt{N}$.

The canonical and grand canonical ensembles are essential for the study of complex thermodynamic systems, such as mixture, chemical equilibrium, dense gases, and liquids, which will not be further discussed in this text. Interested readers can find more details from Refs. [1, 5]. A simple theory based on independent particles of phonons and electrons will be discussed in Chap. 5. While the partition function can also be used to study the thermodynamic relations of solids, the approach used in solid state physics will be adopted in a detailed study of the properties of solids presented in Chap. 6.

3.5 Basic Quantum Mechanics

So far we have largely avoided the derivations and equations involving quantum mechanics, by using the conclusions from quantum theory on a need basis without proof. In this section, we shall present the basics of quantum mechanics to enhance the understanding of the materials already presented and to provide some background for future chapters.

In classical mechanics, the state of a system is completely described by giving the position and the momentum of each particle in the system at any given time. The equation of motion is given in Eq. (3.1), which is also the basis for molecular dynamics. The position and the momentum of each particle are determined using the initial values and precisely the forces exerted on it afterward. According to the wave-particle duality, particles also have wave characteristics. The results are described in quantum mechanics by the Schrödinger wave equation. The solution of the Schrödinger equation is given in the form of a *wavefunction*, which describes the probabilities of the possible outcome rather than the exact position and momentum of the particle. Another important aspect in quantum mechanics is the use of operators in mathematical manipulations.

3.5.1 The Schrödinger Equation

Consider the following equation that describes a wave in the x direction (see Appendices B.6 and B.7):

$$\Psi(x,t) = \widetilde{A}\mathrm{e}^{\mathrm{i}(2\pi x/\lambda - 2\pi \nu t)} \tag{3.67}$$

where $\widetilde{A} = A' + \mathrm{i}A''$ is a complex constant, λ is the wavelength, and ν is the frequency. One can take the real part of Ψ:

$$\mathrm{Re}(\Psi) = A' \cos(2\pi x/\lambda - 2\pi \nu t) - A'' \sin(2\pi x/\lambda - 2\pi \nu t)$$

which is a cosine function of x for any given t. The complex notation is convenient for obtaining derivatives. If Eq. (3.67) is used to describe a moving particle, with a mass m and a momentum p, it can be shown that

$$-\mathrm{i}\hbar \frac{\partial}{\partial x}\Psi = \frac{h}{\lambda}\Psi = p\Psi \tag{3.68a}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi = \frac{p^2}{2m}\Psi = E_\mathrm{K}\Psi \tag{3.68b}$$

and

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi = h\nu\Psi = \varepsilon\Psi \tag{3.68c}$$

where $\hbar$ is the Planck constant divided by 2π, E_K is the kinetic energy of the particle, and ε is the total energy of the particle. In writing Eqs. (3.68a), (3.68b), (3.68c), we have applied the concept of wave-particle duality to relate $p = h/\lambda$ and $\varepsilon = h\nu$. If the particle possesses only the kinetic and potential energies, we have

$$\varepsilon = E_\mathrm{K} + E_\mathrm{P} = \frac{p^2}{2m} + \Phi(\mathbf{r}) \tag{3.69a}$$

where $\Phi(\mathbf{r}) = \Phi(x, y, z)$ is the potential function that depends on the position of the particle. Define the Hamiltonian operator in the three-dimensional (3D) case as

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \Phi(\mathbf{r}) \tag{3.69b}$$

It can be seen that $\widehat{H}\Psi = \varepsilon\Psi$. Hence,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \Phi(\mathbf{r})\Psi = \mathrm{i}\hbar\frac{\partial\Psi}{\partial t} \tag{3.70}$$

which is the time-dependent Schrödinger equation [8]. From $\varepsilon\Psi = \mathrm{i}\hbar\frac{\partial\Psi}{\partial t}$, one can obtain

$$\Psi(\mathbf{r},t) = \Psi_0(\mathbf{r})\mathrm{e}^{-\mathrm{i}\varepsilon t/\hbar} \tag{3.71a}$$

The general time dependence for different energy eigenvalues can be written as a summation:

$$\Psi(\mathbf{r},t) = A_1\Psi_{01}(\mathbf{r})\mathrm{e}^{-\mathrm{i}\varepsilon_1 t/\hbar} + A_2\Psi_{02}(\mathbf{r})\mathrm{e}^{-\mathrm{i}\varepsilon_2 t/\hbar} + \cdots \tag{3.71b}$$

Therefore, the key to solve the Schrödinger equation becomes how to obtain the initial wavefunctions. For this reason, Eq. (3.70) can be rewritten as follows:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \Phi(\mathbf{r})\Psi = \varepsilon\Psi \tag{3.72}$$

which is called the time-independent Schrödinger equation. The solution gives the wavefunction $\Psi(\mathbf{r})$, which is often expressed in terms of a set of eigenfunctions, $\Psi_1, \Psi_2, \Psi_3, \ldots$, each with an eigenvalue energy, $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$, respectively. The solution, or the wavefunction, must satisfy

$$\int\limits_V \Psi\Psi^*\,\mathrm{d}V = 1 \tag{3.73}$$

where the subscript * denotes the complex conjugate since the wavefunction is in general complex, and the integration is over the whole volume. The physical significance is that the probability of finding the particle in the volume must be 1. The wavefunction is also called a state function because it describes the quantum state of the particle, and $\Psi\Psi^*$ is called the probability density function. The average or expectation value of any physical quantity η is calculated by

$$\langle\eta\rangle = \int\limits_V \Psi^*\hat{\eta}\Psi\,\mathrm{d}V \tag{3.74}$$

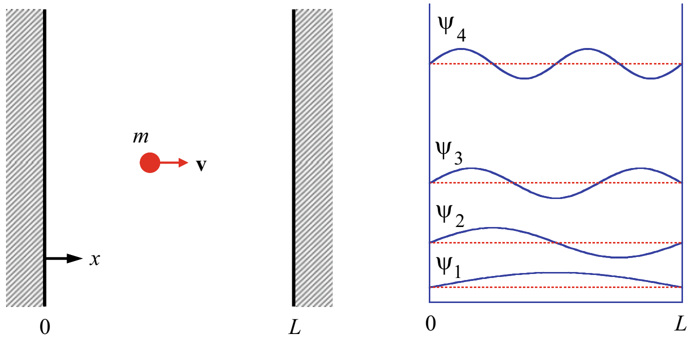
where $\hat{\eta}$ signifies an operator of η. For example, the average energy of the particle is

$$\langle\varepsilon\rangle = \int\limits_V \Psi^*\widehat{H}\Psi\,\mathrm{d}V \tag{3.75}$$

Several examples are discussed in the following sections to show how to obtain the wavefunctions and the physical significance of the solutions.

3.5.2 A Particle in a Potential Well or a Box

The one-dimensional (1D) potential well is illustrated in Fig. 3.13a, where a particle is confined within a physical space between $0 < x < L$ and the particle can move



(a) Potential well (b) Eigenfunctions

Fig. 3.13 Illustration of **a** a 1D potential well and **b** the eigenfunctions

parallel to the x axis only. This is equivalent of saying that the potential energy is zero inside and infinite outside the potential well. Hence,

$$\Phi(x) = \begin{cases} 0, & \text{for } 0 < x < L \\ \infty, & \text{at } x = 0 \text{ or } x = L \end{cases} \tag{3.76}$$

The Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = \varepsilon\Psi \tag{3.77}$$

whose solutions are $\Psi(x) = A\cos(kx) + B\sin(kx)$, where $k = \sqrt{2m\varepsilon/\hbar^2}$. Because the particle is confined inside the well, the wavefunction must be zero outside the potential well. Another requirement for the wavefunction is that it must be continuous. Thus, we must have $\Psi(0) = \Psi(L) = 0$. This requires that $A = 0$ and, by taking only the positive k values, we have

$$kL = n\pi, \ \ n = 1, 2, 3 \ldots \tag{3.78}$$

Therefore, the eigenfunctions are $\Psi_n(x) = B_n \sin\left(\frac{n\pi x}{L}\right)$, which can be normalized by letting $\int_0^L \Psi_n(x)\Psi_n^*(x)\,\mathrm{d}x = 1$ to get

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{3.79}$$

The solution requires the particle to possess discretized energy values, i.e., its energy cannot be increased continuously but with finite differences between neighboring states. It can easily be seen that

$$\varepsilon_n = \frac{h^2 n^2}{8mL^2} \tag{3.80}$$

The quantized energy eigenvalues are called energy levels for each quantum state, and the index n is called a quantum number. The eigenfunctions are standing waves as shown in Fig. 3.13b for the first four quantum states. For molecules, the difference between energy levels is very small and the energy distribution can often be approximated as a continuous distribution. For electrons at very small distances, $L \to 10$ nm for example, quantization may be important. The effects of quantum confinement take place when the quantum well thickness becomes comparable to the de Broglie wavelength of the particle, such as electrons or holes in a semiconductor. Quantum wells can be formed by a sandwiched structure of heterogeneous layers, such as AlGaAs/GaAs/AlGaAs. The bandgap of the two outer layers is larger than that of the inner layer to form an effective potential well. These structures are used for optoelectronic applications such as lasers and radiation detectors. The thickness of the active region can be a few nanometers. In some cases, multiple quantum wells are formed with periodic layered structures, called *superlattices*, which have unique optical, electrical, and thermal properties.

Example 3.7 Derive the uncertainty principle. Suppose the wavefunction is given by Eq. (3.79) for a particle with energy ε_n given in Eq. (3.80).

Solution To find the average position of the particle, we use $\langle x \rangle = \int_0^L \Psi^* x \Psi \mathrm{d}x = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \frac{L}{2}$. The variance of x, $\sigma_x^2 = \langle x - \langle x \rangle \rangle^2 = \langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$.

With $\langle x^2 \rangle = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$, we obtain the standard deviation of x as $\sigma_x = L\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2}$. For the momentum, we use the operator $p \to -\mathrm{i}\hbar\frac{\partial}{\partial x}$. Hence, $\langle p \rangle = \int_0^L \Psi^*\left(-\mathrm{i}\hbar\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right)\mathrm{d}x = -\mathrm{i}\hbar\frac{2n\pi}{L^2}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = 0$ and $\langle p^2 \rangle = \int_0^L \Psi^*(-\hbar^2)\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2}\mathrm{d}x = \left(\frac{n\pi\hbar}{L}\right)^2$. We have $\sigma_p = \frac{n\pi\hbar}{L}$ and obtain the following expression:

$$\sigma_x \sigma_p = \frac{\hbar}{2}\left(\frac{\pi^2 n^2}{3} - 2\right)^{1/2} \tag{3.81}$$

Taking the smallest quantum number, $n = 1$, we get $\sigma_x \sigma_p \approx 0.5678\hbar > \hbar/2$, which is a proof of the uncertainty principle given in Eq. (3.9).

Next, consider a free particle in a 3D box, $0 < x < a,\ 0 < y < b,\ 0 < z < c$. It can be shown that the (normalized) eigenfunctions are

$$\Psi_{x,y,z} = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \tag{3.82}$$

with the energy eigenvalues:

$$\varepsilon_{x,y,z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{3.83}$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$ When $a = b = c = V^{1/3}$, Eq. (3.83) can be simplified as

$$\varepsilon_{x,y,z} = \frac{h^2}{8mV^{2/3}}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{3.84}$$

Let $\eta = (n_x^2 + n_y^2 + n_z^2)^{1/2}$, then we can evaluate the number of quantum states between η and $\eta + \mathrm{d}\eta$, which is nothing but the degeneracy. For sufficiently large V, the quantum states are so close to each other that the volume within the spherical shell between η and $\eta + \mathrm{d}\eta$ is equal to the number of quantum states. Only one-octant of the sphere is considered in Eq. (3.84) because $n_x > 0,\ n_y > 0,\ n_z > 0$. The total volume is therefore one-eighth of the spherical shell; hence,

$$\mathrm{d}g = \frac{1}{8}4\pi\eta^2\mathrm{d}\eta = \frac{2\pi V(2m)^{3/2}}{h^3}\varepsilon^{1/2}\mathrm{d}\varepsilon \tag{3.85}$$

With $\varepsilon = \frac{1}{2}mv^2$ and $\mathrm{d}\varepsilon = mv\mathrm{d}v$, we obtain

$$\mathrm{d}g = \frac{m^3 V}{h^3}4\pi v^2\mathrm{d}v \tag{3.86}$$

This equation is essentially the same as Eq. (3.32), with $\mathrm{d}x\mathrm{d}y\mathrm{d}z = V$ and $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = 4\pi\mathrm{d}v$. Equation (3.86) provides a rigid proof of Eq. (3.32), which is the translational degeneracy. It should be noted that the classical statistical mechanics results in the same expression for U and p, as well as the Maxwell velocity distribution for ideal gases. However, the constant h must be included to correctly express S as in Eq. (3.41). Equation (3.86) will also be used in Chap. 5 to study the free electron gas in metals. When using the momentum $p = mv$ as the variable, we have

$$\mathrm{d}g = \frac{V}{h^3}4\pi p^2\mathrm{d}p \tag{3.87}$$

Because Eq. (3.87) does not involve mass, it is also applicable to phonons and photons as will be discussed in Chaps. 5 and 8.

3.5.3 A Rigid Rotor

The rigid rotor model can be used to study the rotational movement of diatomic molecules as well as the electron around the orbit in a hydrogen atom. Consider two particles separated by a fixed distance $r_0 = r_1 + r_2$ as shown in Fig. 3.14. The masses

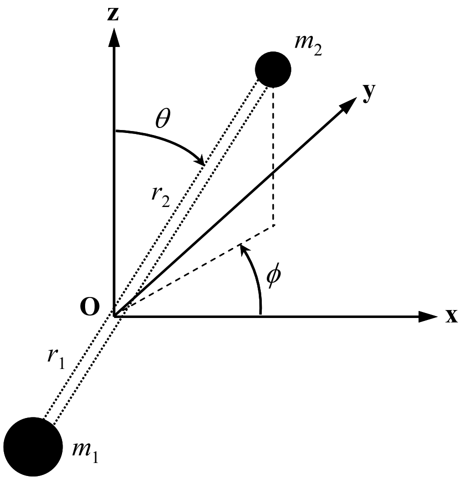


Fig. 3.14 Schematic of a rotor consisting of two particles

of the particles are m_1 and m_2, respectively. Since the center of mass is at the origin, we have $m_1 r_1 = m_2 r_2$. The moment of inertia is

$$I = m_1 r_1^2 + m_2 r_2^2 = m_\mathrm{r} r_0^2 \tag{3.88}$$

where $m_\mathrm{r} = m_1 m_2/(m_1 + m_2)$ is the reduced mass. We can study the rotational movement of the particles by considering a particle with a mass of m_r that rotates around at a fixed distance $r = r_0$ from the origin in the θ and ϕ directions. In the spherical coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} \tag{3.89}$$

Because $r \equiv r_0$, the derivative with respect to r vanishes. The potential energy is zero for free rotation. By setting the mass to be m_r and $\Phi = 0$ in Eq. (3.72) and noticing that $m_\mathrm{r} r_0^2 = I$, we obtain

$$\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Psi}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 \Psi}{\partial \phi^2} = -\frac{2I\varepsilon}{\hbar^2}\Psi \tag{3.90}$$

This partial differential equation can be solved by separation of variables. We get two ordinary differential equations by letting $\Psi(\theta, \phi) = P(\theta)\psi(\phi)$,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\phi^2} = -m^2\psi \tag{3.91}$$

and

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}P}{\mathrm{d}\theta}\right)+\left(\frac{2I\varepsilon}{\hbar^2}-\frac{m^2}{\sin^2\theta}\right)P=0 \tag{3.92}$$

Here, m is a new eigenvalue, and the periodic boundary conditions shall be applied to P and ψ, respectively. The solution of Eq. (3.91) is readily obtained as

$$\psi(\phi)=A\mathrm{e}^{\mathrm{i}m\phi} \tag{3.93}$$

with $m=0,\pm1,\pm2,\ldots,$ to satisfy the periodic boundary conditions: $\psi(\phi)=\psi(2\pi+\phi)$. A transformation, $\cos\theta=\xi$, can be used so that Eq. (3.92) becomes

$$(1-\xi^2)\frac{\mathrm{d}^2P}{\mathrm{d}\xi^2}-2\xi\frac{\mathrm{d}P}{\mathrm{d}\xi}+\left(\frac{2I\varepsilon}{\hbar^2}-\frac{m^2}{1-\xi^2}\right)P=0 \tag{3.94}$$

Because θ is defined from 0 and π, we have $-1\le x\le 1$. In order for Eq. (3.94) to have solutions that are bounded at $x=\pm1$, $\frac{2I\varepsilon}{\hbar^2}=l(l+1)$, where l is an integer that is greater than or at least equal to the absolute value of m. Therefore, the energy eigenvalues are

$$\varepsilon_l=\frac{\hbar^2}{2I}l(l+1),\ l=|m|,\ |m|+1,\ |m|+2,\ \text{etc.} \tag{3.95}$$

Equation (3.94) is called the associated Legendre differential equation. The solutions are the associated Legendre polynomials given as

$$P_l^m(\xi)=\frac{(1-\xi^2)^{m/2}}{l!2^l}\frac{\mathrm{d}^{m+l}}{\mathrm{d}\xi^{m+l}}\left(\xi^2-1\right)^l \tag{3.96}$$

Finally, after normalization, the standing wavefunctions can be expressed as

$$\Psi_l^m(\theta,\phi)=\frac{1}{\sqrt{2\pi}}\left[\frac{(2l+1)(l-m)!}{2(m+1)!}\right]^{1/2}P_l^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi} \tag{3.97}$$

It can be seen that Eq. (3.95) is identical to Eq. (3.52). The energy level is determined by the principal quantum number l. On the other hand, for each l, there are $2l+1$ quantum states corresponding to each individual m, because m can take $0,\pm1,\pm2$ up to $\pm l$. This means that the degeneracy $g_l=2l+1$. When the two atoms are identical, such as in a nitrogen molecule, the atoms are indistinguishable when they switch positions. The degeneracy is reduced by a symmetry number, as given in the expression of Eq. (3.53). It should be noted that the nuclear spin degeneracy is important for hydrogen (also see Problem 3.27).

3.5.4 Atomic Emission and the Bohr Radius

A hydrogen atom is composed of a proton and an electron. Since the mass of the proton is much greater than that of the electron, it can be modeled as the electron moving around the nucleus. The mass of the electron is $m_\mathrm{e} = 9.11 \times 10^{-31}$ kg, and the position of the electron can be described in the spherical coordinates as $\mathbf{r} = (r, \theta, \phi)$. The force exerted on the electron is Coulomb's force, which gives a potential field

$$\Phi(r) = -\frac{C_1}{r} \tag{3.98}$$

where $C_1 = e^2/4\pi\varepsilon_0 = 2.307 \times 10^{-28}\,\mathrm{N\,m^2}$, with the electron charge $e = 1.602 \times 10^{-19}\,\mathrm{C}$ and the dielectric constant $\varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{F/m}$. Let $\Psi(r, \theta, \phi) = R(r)P(\theta)\psi(\phi)$. In doing the separation of variables, we notice that the potential Φ is independent of θ and ϕ, and the total energy is equal to the sum of the rotational energy and the energy associated with r. The dependence of rotational energy is given in Eq. (3.45). Using Eqs. (3.72) and (3.89), we can write the equation for $R(r)$ as follows:

$$\frac{\hbar}{2m_\mathrm{e}r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left(\frac{C_1}{r} + \varepsilon - \frac{l(l+1)\hbar^2}{2I}\right)R = 0 \tag{3.99}$$

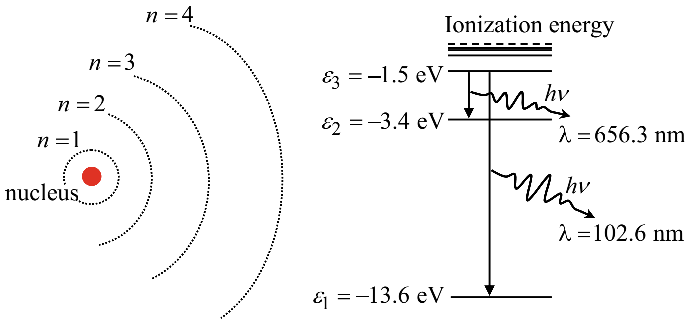
which is the associated Laguerre equation, and its solutions are the associated Laguerre polynomials. The solutions give the energy eigenvalues as [5, 8]

$$\varepsilon_n = -\frac{m_\mathrm{e}C_1^2}{2\hbar^2 n^2} \tag{3.100}$$

where the negative values are used for convenience to show that the energy increases with the principal quantum number n. For $n = 1$, $-m_\mathrm{e}C_1^2/2\hbar^2 = -13.6$ eV, as shown in Fig. 3.15. Note that 1 eV $= 1.602 \times 10^{-19}$ J. When the electron is in a higher energy state, it has a tendency of relaxing to a lower energy state by spontaneously emitting a photon, with precisely the same energy as given by the energy difference between the two energy levels:

$$h\nu = \varepsilon_i - \varepsilon_j = \frac{m_\mathrm{e}C_1^2}{2\hbar^2}\left(\frac{1}{n_j^2} - \frac{1}{n_i^2}\right) \tag{3.101}$$

The emission or absorption of photons by electrons is called *electronic transitions.* When $i = 3$ and $j = 1$, we have $h\nu = 12.1$ eV, corresponding to the wavelength of 102.6 nm (ultraviolet), which is the second line in the Lyman series. When $i = 3$ and $j = 2$, we have $h\nu = 1.89$ eV, corresponding to the wavelength of 656.4 nm (red),



(a) (b)

Fig. 3.15 **a** Electron orbits and **b** energy levels in a hydrogen atom. The ionization energy is the energy required for an electron to escape the orbit

which is the first line in the Balmer series. A more detailed description of the atomic emission lines can be found from Sonntag and van Wylen [2].

The next question is: What is the radius of a particular electron orbit? This is an important question because it gives us a sense of how small an atom is. When a particle is in an orbit, the classical force balance gives that

$$\frac{C_1}{r^2} = m_e\left(\frac{v^2}{r}\right) \tag{3.102}$$

which is to say that $E_K = m_e v^2/2 = C_1/2r$, and the sum of the kinetic and potential energies is

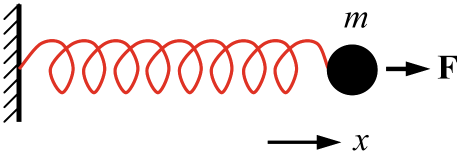
$$\varepsilon = E_K + E_P = \frac{C_1}{2r} - \frac{C_1}{r} = -\frac{C_1}{2r} \tag{3.103}$$

Equations (3.100) and (3.103) can be combined to give discrete values of the radius of each orbit in the following:

$$r_n = \frac{\hbar^2}{m_e C_1} n^2 = a_0 n^2 \tag{3.104}$$

where the electron is in the innermost orbit, with the radius given by $a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} =$ 0.0529 nm, which is called the *Bohr radius*. Niels Bohr (1885–1962) was a Danish physicist who received the Nobel Prize in Physics in 1922 for his contributions to the understanding of the structure of atoms and quantum physics. Therefore, the hydrogen atom in its ground state can be considered as having a diameter of approximately 1 Å (Angstrom), or 0.1 nm. One should accept the quantum interpretation of the electron radius as a characteristic length, not the exact distance that the electron would rotate around the nucleus in the same manner a planet rotates around a star.

Fig. 3.16 A linear spring



3.5.5 A Harmonic Oscillator

The last example of quantum mechanics is the linear spring as shown in Fig. 3.16. Consider a 1D oscillator with a mass m and the spring force $F(x) = -Kx$. The origin can be selected such that $F(0) = 0$. It can be shown that the potential is

$$\Phi(x) = -\int_0^x F(x)\mathrm{d}x = \frac{1}{2}Kx^2 \tag{3.105}$$

From classical mechanics, we can solve Newton's equation $m\ddot{x} + Kx = 0$ to obtain the solution

$$x = A\sin(\omega t + \phi_0) \tag{3.106}$$

where constant A is the amplitude, constant ϕ_0 is the initial phase, and parameter $\omega = \sqrt{K/m}$ is the angular resonance frequency. It can be shown that the total energy $\varepsilon = E_\mathrm{K} + E_\mathrm{P} = KA^2/2$ is a constant and the maximum displacement is A. The velocity is the largest at $x = 0$ and zero at $x = \pm A$.

The Schrödinger wave equation can be written as

$$\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + \left(\varepsilon - \frac{Kx^2}{2}\right)\Psi = 0 \tag{3.107}$$

with the boundary condition being $\Psi(x) = 0$ at $x \to \pm\infty$. The constants can be grouped by using $\alpha = 2m\varepsilon/\hbar^2$ and $\beta = \sqrt{Km}/\hbar$. Then Eq. (3.107) can be transformed by using $\xi = \sqrt{\beta}x$ and $\Psi(x) = Q(\xi)\exp(-\xi^2/2)$ to

$$\frac{\mathrm{d}^2Q}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}Q}{\mathrm{d}\xi} + \left(\frac{\alpha}{\beta} - 1\right)Q = 0 \tag{3.108}$$

This is the Hermite equation, and the solutions are Hermite polynomials given by

$$H_n(\xi) = (-1)^n \mathrm{e}^{\xi^2}\frac{\mathrm{d}^n}{\mathrm{d}\xi^n}\left(\mathrm{e}^{-\xi^2}\right) \tag{3.109}$$

when α and β must satisfy the eigenvalue equation:

$$\frac{\alpha}{\beta} - 1 = 2n, \quad n = 0, 1, 2, \ldots \tag{3.110}$$

The normalized wavefunctions can be written as

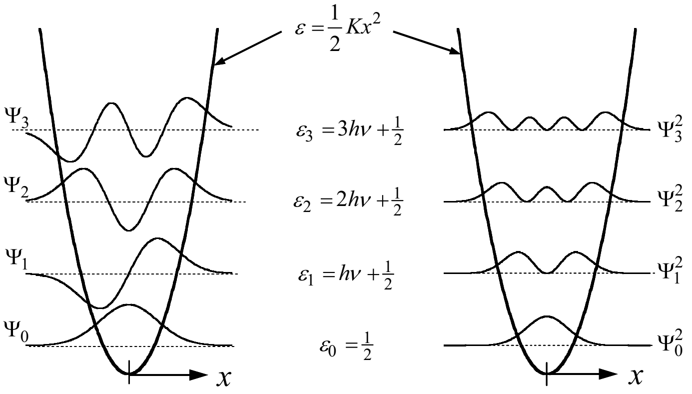
$$\Psi_n(x) = \left(\frac{\sqrt{\beta/\pi}}{n!2^n} \right)^{1/2} H_n(\beta^{1/2}x) \exp\left(-\frac{\beta x^2}{2} \right) \tag{3.111}$$

The energy eigenvalues can be obtained from Eq. (3.110) as

$$\varepsilon_n = (n + \tfrac{1}{2})\hbar\sqrt{K/m} = (n + \tfrac{1}{2})\hbar\omega \tag{3.112}$$

The above equation was used to study the vibrational contributions in diatomic molecules; see Eq. (3.59). The 1/2 term was not included in Planck's original derivation of the blackbody radiation function. The significance lies in that if the ground-state energy is zero, both its kinetic energy and potential energy must be zero, suggesting that both the position and the momentum must be zero. This would violate the uncertainty principle. As mentioned earlier, in classical mechanics, the particle is limited to the region $-A < x < A$, where A is the amplitude given in Eq. (3.106). This is not the case in the quantum theory, as shown in Fig. 3.17, for the first few energy levels and the associated wavefunctions. Notice that probability density function Ψ^2 is nonzero even though the absolute value of x exceeds $\sqrt{2\varepsilon/K}$.

The application of quantum theory allows us to predict the specific heat of ideal gases. In deriving the equations shown in Sect. 3.3.3, we have largely neglected nonlinear and anharmonic vibration, electronic contribution, and dissociation. These factors may become important at very high temperatures. The degeneracy due to the coupling of rotation and vibration can cause multiple absorption/emission lines in the infrared in polyatomic molecular gases, as shown in Fig. 3.12.



(a) (b)

Fig. 3.17 **a** Wavefunctions and **b** probability density functions for vibration energy levels

3.6 Emission and Absorption of Photons by Molecules or Atoms

We have learned that the emission of photons is associated with transitions from a higher energy level to a lower energy level that reduces the total energy of the molecular system. The reverse process is the absorption of photons that increases the energy of the system through transitions from lower energy levels to higher energy levels. As discussed earlier, an electronic transition requires a large amount of energy, and the emitted or absorbed photons are at frequencies from deep ultraviolet ($\lambda \approx 100$ nm) to slightly beyond the red end of the visible region ($\lambda \approx 1$ μm). On the other hand, vibration or rotation-vibration modes lie in the mid-infrared (2.5 μm $< \lambda <$ 25 μm), while their overtones or higher-order harmonics lie in the near-infrared region (0.8 μm $< \lambda$ $<$ 2.5 μm). Rotational modes alone may be active in the far-infrared and microwave regions ($\lambda >$ 25 μm). Transitions between different energy levels of the molecules or atoms are called *bound-bound transitions*, because these energy states are called *bound states*. Bound-bound transitions happen at discrete frequencies due to quantization of energy levels. Dissociation or ionization can also occur at high temperatures. The difference between adjacent energy levels is very small because the electrons can move freely (i.e., not bound to the atom or the molecule). Therefore, *free-free* or *bound-free transitions* happen in a broadband of frequencies. In gases, these broader transitions occur only at extremely high temperatures.

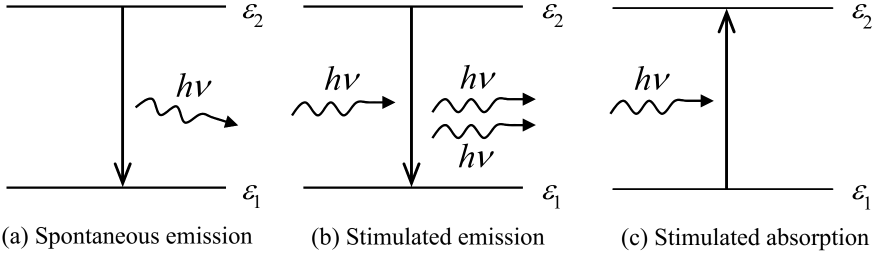
If a molecule at elevated energy states were placed in a surrounding at zero absolute temperature (i.e., empty space), it would lower its energy states by emitting photons in all directions until reaching its ground state. However, the emission processes should occur spontaneously regardless of the surroundings. Suppose the molecule is placed inside an isothermal enclosure, after a long time, the energy absorbed must be equal to that emitted to establish a thermal equilibrium with its surroundings. The thermal fluctuation of oscillators is responsible for the equilibrium distribution of photons governed by Planck's law developed in 1900. Albert Einstein examined how matter and radiation can achieve thermal equilibrium in a fundamental way and published a remarkable paper, "On the quantum theory of radiation" in 1917 [11]. The interaction of radiation with matter is essentially through emission or absorption at the atomistic dimension, although solids or liquids can reflect radiation and small particles can scatter radiation. Einstein noticed that spontaneous emission and pure absorption (i.e., transition from a lower level to a higher level by absorbing the energy from the incoming radiation) alone would not allow an equilibrium state of an atom to be established with the radiation field. He then hypothesized the concept of *stimulated* or *induced emission,* which became the underlying principle of lasers. In a stimulated emission process, an incoming photon interacts with the atom: the interaction results in a transition from a higher energy state to a lower energy state by the emission of another photon of the same energy toward the same direction as the incoming photon. In other words, the stimulated photon is a "clone" of the stimulating photon with the same energy and momentum. Depending on the probability of each event, the incoming photons could either be absorbed or stimulate another photon or pass by without any effect on the atom. Understanding the emission and absorption processes is important not only for coherent emission but also for thermal radiation [12]. While more detailed treatments will be given in later chapters, it is important to gain a basic understanding of the quantum theory of radiative transitions and microscopic description of the radiative properties.

Consider a canonical ensemble of single molecules or atoms, with two nondegenerate energy levels, ε_1 and ε_2 ($\varepsilon_1 < \varepsilon_2$), in thermal equilibrium with an enclosure or cavity at temperature T. Suppose the total number of particles is N, and let N_1 and N_2 be the number of particles at the energy level corresponding to ε_1 and ε_2, respectively. These particles do not interact with each other at all. The concept of canonical ensemble can be understood as if each cavity has only one atom but there are N single-atom cavities with one atom in each cavity. As shown in Fig. 3.18, there are three possible interaction mechanisms: spontaneous emission, stimulated emission, and *stimulated or induced absorption.* Here, stimulated absorption refers to the process that the energy of the photon is absorbed, and consequently, the transition occurs from the lower energy level to the higher energy level. In a stimulated absorption process, the number of photons before the process is 1 and after the process is $1 - 1 = 0$. In a stimulated emission process, the number of photons beforehand is 1 and afterward is $1 + 1 = 2$. Therefore, stimulated emission is regarded also as *negative absorption*. Each of the photons involved in this process will have an energy equal to $h\nu = \varepsilon_2 - \varepsilon_1$ and a momentum $h\nu/c$.

Transition from the higher energy level to the lower energy level cannot take place if the population of atoms on the higher energy level, $N_2 = 0$, and vice versa. Einstein further assumed that the probability of transition is proportional to the population at the initial energy level, and spontaneous transition should be independent of the radiation field. Hence, the rate of transition from ε_2 to ε_1 due to spontaneous emission can be written as

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_\mathrm{A} = -\left(\frac{\mathrm{d}N_2}{\mathrm{d}t}\right)_\mathrm{A} = AN_2 \tag{3.113}$$

where A is *Einstein's coefficient* of spontaneous emission. On the other hand, the transition rate due to stimulated emission should also be proportional to the energy



(a) Spontaneous emission (b) Stimulated emission (c) Stimulated absorption

Fig. 3.18 Illustration of the emission and absorption processes. **a** Spontaneous emission. **b** Stimulated emission. **c** Stimulated absorption density of the radiation field $u(\nu, T)$. Thus,

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_{\mathrm{B}} = BN_2u(\nu, T) \tag{3.114}$$

Stimulated absorption will cause a transition rate that is proportional to N_1 and $u(\nu, T)$:

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_{\mathrm{C}} = -CN_1u(\nu, T) \tag{3.115}$$

In Eqs. (3.114) and (3.115), constants B and C are Einstein's coefficients of stimulated emission and absorption, respectively. The combination of these processes must maintain a zero net change of the populations at equilibrium. Thus,

$$AN_2 + BN_2u(\nu, T) - CN_1u(\nu, T) = 0 \tag{3.116}$$

Atoms or molecules in a thermal equilibrium are described by the Maxwell-Boltzmann statistics of molecular gases given by Eq. (3.26): $N_1/N_2 = \mathrm{e}^{(\varepsilon_2-\varepsilon_1)/k_{\mathrm{B}}T} = \mathrm{e}^{h\nu/k_{\mathrm{B}}T}$. Therefore, Eq. (3.116) can be rewritten as

$$u(\nu, T) = \frac{A/B}{(C/B)e^{h\nu/k_{\mathrm{B}}T} - 1} \tag{3.117}$$

Comparing this equation with Planck's distribution, Eq. (8.41) in Chap. 8, we see that $B = C$ and $A/B = 8\pi h\nu^3/c^3$. The two-level system can easily be generalized to arbitrary energy levels to describe the fundamental emission and absorption processes. The emission and absorption processes not only exchange energy between the field and the atom but also transfer momentum. How will an atom move inside a cavity? The phenomenon of a molecule or atom in a radiation field is like the Brownian motion, in which the radiation quanta exert forces on the molecule or the atom as a result of momentum transfer during each emission or absorption process. Consequently, the molecule or the atom will move randomly following Maxwell's velocity distribution at the same temperature as the radiation field. The equilibrium radiation field, which obeys the quantum statistics (i.e., BE statistics) that was not realized until 1924, and the motion of a molecular gas, which obeys classical statistics, can be coupled to each other at mutual equilibrium. Einstein also asserted that each spontaneously emitted photon must be directional, while the probability of spontaneous emission should be the same in all directions. In fact, Einstein's 1917 paper complemented Planck's 1900 paper on radiation energy quanta and his own 1905 paper on photoelectric emission and, thus, provided a complete description of the quantum nature of photons, although the name "photon" was not coined until 1928 [12].

At moderate temperatures, the population at higher energy states is too small for stimulated emission to be of significance for optical and thermal radiation. Thus, the absorption comes solely from induced absorption. When stimulated emission is important, the contributions of stimulated emission and stimulated absorption cannot be separated by experiments. The effect is combined to give an effective absorption coefficient by taking stimulated emission as negative absorption, whereas the emission of radiation includes solely the spontaneous emission [12]. The effective absorption coefficient is proportional to the population difference, $N_1 - N_2$. On the other hand, if a *population inversion* can be created and maintained such that $N_2 > N_1$, the material is called a *gain medium* or *active medium*. In an active medium, stimulated emission dominates stimulated absorption so that more and more photons will be cloned and the radiation field be amplified coherently. The principle of stimulated emission was applied in 1950s and early 1960s for the development of maser, which stands for *microwave amplification by stimulated emission of radiation,* and laser, which stands for *light amplification by stimulated emission of radiation* [13]. Lasers have become indispensable to modern technologies and daily life.

3.7 Energy, Mass, and Momentum in Terms of Relativity

Special theory of relativity or *special relativity* predicts that energy and mass can be converted to each other. If we retain the definition of mass as in the classical theory, only energy conservation is the fundamental law of physics. The mass does not have to be conserved. On the other hand, for processes that do not involve changes below the atomic level or inside the nuclei, the mass can indeed be considered as conserved. According to the special relativity, the rest energy of a free particle is related to its mass and the speed of light by

$$E_0 = mc^2 \tag{3.118}$$

The rest energy is simply the energy when the particle is not moving relative to the reference frame. Suppose the free particle is moving at a velocity v in a given reference frame, then its momentum is given by [14]

$$p = \frac{mv}{\sqrt{1 - v^2/c^2}} \tag{3.119}$$

When $v \ll c$, Eq. (3.119) reduces to the classical limit $p = mv$. It can be seen that for a particle with nonzero mass, its momentum would increase as $v \to c$ without any bound. There is no way we could accelerate a particle to the speed of light. If there is anything that travels with the speed of light, it has to be massless, i.e., $m = 0$. An example of massless particles is the light quanta or photons. The kinetic energy can be evaluated by integrating the work needed to accelerate a particle, $E_\mathrm{K} = \int_0^x F\mathrm{d}x = \int_0^x \frac{\mathrm{d}p}{\mathrm{d}t}\mathrm{d}x = \int_0^x \frac{\mathrm{d}p}{\mathrm{d}v}\frac{\mathrm{d}v}{\mathrm{d}t}\mathrm{d}x = \int_0^v \frac{\mathrm{d}p}{\mathrm{d}v}v\mathrm{d}v$. Using Eq. (3.119), we find that

$$E_\mathrm{K} = \frac{mc^2}{\sqrt{1 - v^2/c^2}} - mc^2 \tag{3.120}$$

When $v \ll c$, we have $1/\sqrt{1 - v^2/c^2} \approx 1 + v^2/2c^2$ so that $E_\mathrm{K} = mv^2/2 = p^2/2m$ in the low-speed limit. In the relativistic limit, however, E_K will be on the order of mc^2. Because energy is additive, the total energy of a moving free particle is

$$E = E_\mathrm{K} + E_0 = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \tag{3.121}$$

Obviously, the energy of a particle would become infinite if its speed approaches the speed of light, unless its mass goes to zero. It can be shown that $E^2 - E_0^2 = \frac{m^2c^4}{1-v^2/c^2} - m^2c^4 = p^2c^2$, where p is given in Eq. (3.119). This gives another expression of energy in terms of the rest energy, the momentum, and the speed of light as follows:

$$E^2 = m^2c^4 + p^2c^2 \tag{3.122}$$

It should be noted that, in general, pc is not equal to the kinetic energy. For $v \ll c$, the total energy is approximately the same as the rest energy. Comparing Eqs. (3.119) and (3.121), we notice that $E = pc(c/v)$. Therefore, when $v \to c$, we see that $E \to pc$ (which is unbounded unless $m = 0$). For a photon that travels at the speed of light, in order for the above equations to be meaningful, we must set its mass to zero. From Eq. (3.122), we have for photons that

$$p = \frac{E}{c} = \frac{h\nu}{c} \tag{3.123}$$

which is the same as Eq. (3.7) in Sect. 3.1.3. By noting that $\lambda\nu = c$, we obtain

$$\lambda = \frac{h}{p} \tag{3.124}$$

The kinetic energy of a photon is pc or $h\nu$ since its rest energy is zero. One should not attempt to calculate the kinetic energy of a photon by $\frac{1}{2}mc^2$, because photons are not only massless but also *relativistic particles,* for which the energy and momentum must be evaluated according to Eqs. (3.122) and (3.123), respectively. While photons do not have mass, it has been observed that photons can be used to create particles with nonzero mass or vice versa, as in *creation* or *annihilation reactions*. High energy physics has proved that mass is not always conserved. It is commonly said that mass and energy can be interconverted. For example, in a nuclear reaction, a small amount of mass can be converted into a large amount of energy. In these statements, the term energy is used in the classical sense (such as kinetic energy and the emission of high-energy photons). When the rest energy E_0 is included, the total energy is always conserved.

3.8 Summary

This chapter started with very basic independent particle systems to derive the three major statistics, namely, the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics. The classical and quantum statistics were then applied to thermodynamic systems, providing microscopic interpretations of the first, second, and third laws of thermodynamics, as well as Bose-Einstein condensate. The velocity distribution and specific heat of ideal gases were explained based on the semi-classical statistics, followed by a brief description of quantum mechanics to understand the quantization of translational, rotational, and vibrational modes. The fundamental emission and absorption processes of molecules or atoms were discussed along with the concept of stimulated emission. Finally, matter-energy conversion was described within the framework of special relativity. While most of the explanations in this chapter are semi-classical and somehow oversimplified, it should provide a solid background to those who do not have a comprehensive knowledge and background in statistical mechanics and quantum physics. The materials will be frequently referenced in the rest of the book.

Problems

3.1 For a rectangular prism whose three sides are x, y, and z. If $x + y + z = 9$, find the values of x, y, and z so that the volume of the prism is maximum.

3.2 Make a simple computer program to evaluate the relative error of Stirling's formula: $\ln x! \approx x \ln x - x$ for $x = 10$, 100, and 1000.

3.3 For each of the following cases, determine the number of ways to place 25 books on 5 shelves (distinguishable by their levels). The order of books within an individual shelf is not considered.

   (a) The books are distinguishable, and there is no limit on how many books can be put on each shelf.
   (b) Same as (a), except that all the books are the same (indistinguishable).
   (c) The books are distinguishable, and there are 5 books on each shelf.
   (d) The books are distinguishable, and there are 3 books on the 1st shelf, 4 on the 2nd, 5 on the 3rd, 6 on the 4th, and 7 on the 5th.

3.4 For each of the following cases, determine the number of ways to put 4 books on 10 shelves (distinguishable by their levels). Disregard their order on each shelf.

   (a) The books are distinguishable, and there is no limit on how many books you can place on each shelf.
   (b) Same as (a), but there is a maximum of 1 book on any shelf.
   (c) Same as (a), except that the books are identical (indistinguishable).
   (d) Same as (b), except that the books are identical.

3.5 A box contains 5 red balls and 3 black balls. Two balls are picked up randomly. Determine the following:

  (a) What's the probability that the second ball is red?
  (b) What's the probability that both are red?
  (c) If the first one is black, what is the probability that the second is red?

3.6 Suppose you toss two dice, what's the probability of getting a total number (a) equal to 5 and (b) greater than 5?

3.7 Draw 5 cards from a deck of 52 cards.

  (a) What is the probability of getting a royal flush?
  (b) What is the probability of getting a full house? [A royal flush is a hand with A, K, Q, J, and 10 of the same suit. A full house is a hand with three of one kind and two of another (a pair).]

3.8 For a Gaussian distribution function, $f(x) = a\mathrm{e}^{-(x-\mu)^2}$, where a and μ are positive constants.

  (a) Find the normalized distribution function $F(x)$.
  (b) Show that the mean value $\bar{x} = \mu$.
  (c) Determine the variance u_{var} and the standard deviation σ.

3.9 The speed distribution function for N particles in a fixed volume is given by $f(V) = \frac{AV(B-V)}{B^3}$, where V (> 0) is the particle speed, and A and B are positive constants. Determine:

  (a) The probability density function $F(V)$.
  (b) The number of particles N in the volume.
  (c) The minimum speed Vmin and maximum speed Vmax.
  (d) The most probable speed where the probability density function is the largest.
  (e) The average speed $\overline{V}$ and the root-mean-square average speed $V_{\text{rms}} = \sqrt{\overline{V^2}}$.

3.10 Six bosons are to be placed in two energy levels, each with a degeneracy of two. Evaluate the thermodynamic probability of all arrangements. What is the most probable arrangement?

3.11 Four fermions are to be placed in two energy levels, each with a degeneracy of four. Evaluate the thermodynamic probability of each arrangement. What is the most probable arrangement?

3.12 Derive the Fermi-Dirac distribution step by step. Clearly state all assumptions. Under which condition, can it be approximated by the Maxwell-Boltzmann distribution?

3.13 What is the Boltzmann constant and how is it related to the universal gas constant? Show that the ideal gas equation can be written as $P = nk_{\mathrm{B}}T$. What is the number density of air at standard conditions (1 atm and 25 °C)?

3.14 How many molecules are there per unit volume (number density) for the nitrogen gas at 200 K and 20 kPa? How would you estimate the molecular spacing (average distance between two adjacent molecules)?

3.15 Use Eq. (3.28a), (3.28b) and $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ to show that $\beta = \frac{1}{k_B T}$.

3.16 Show that $\beta = 1/k_B T$ and $\alpha = -\mu/k_B T$ for all the three statistics. [Hint: Follow the lecture note with a few more steps.]

3.17 Consider 10 indistinguishable particles in a fixed volume that obey the Bose-Einstein statistics. There are three energy levels with $\varepsilon_0 = 0.5$ eu, $\varepsilon_1 = 1.5$ eu, and $\varepsilon_2 = 2.5$ eu, where "eu" refers to certain energy unit. The degeneracies are $g_0 = 1$, $g_1 = 3$, and $g_2 = 5$, respectively.

(a) If the degeneracy were not considered, in how many possible ways could you arrange the particles on the three energy levels?
(b) You may notice that different arrangements may result in the same energy. For example, both the arrangement with $N_1 = 9$, $N_2 = 0$, $N_3 = 1$ and the arrangement with $N_1 = 8$, $N_2 = 2$, $N_3 = 0$ yield an internal energy $U = 7$ eu. How many arrangements are there with $U = 9$ eu? Calculate the thermodynamic probability for all macrostates with $U = 9$ eu.
(c) The ground state refers to the state corresponding to the lowest possible energy of the system. Determine the ground-state energy and entropy. What is the temperature of this system at the ground state?
(d) How many microstates are there for the macrostate with $U = 25$ eu?

3.18 Consider a system of a single type of constituents, with N particles (distinguishable from the statistical point of view) and only two energy levels $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$ (nondegenerate).

(a) What is the total number of microstates in terms of N. How many microstates are there for the macrostate that has energy $U = (N-1)\varepsilon$? Show that the energy of the most probable macrostate is $N\varepsilon/2$.
(b) What are the entropies of the states with $U = 0$ and $U = (N-1)\varepsilon$. Sketch S as a function of U. Comment on the negative temperature, $1/T = (\partial S/\partial U)_{V,N} < 0$. Is it possible to have a system with a negative absolute temperature?

3.19 A system consists of six indistinguishable particles that obey Bose-Einstein statistics with two energy levels. The associated energies are $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$, and the associated degeneracies are $g_0 = 1$ and $g_1 = 3$. Answer the following questions:

(a) How many possible macrostates are there? How many microstates corresponding to the macrostate with three particles on each energy level?
(b) What is the most probable macrostate, and what are its corresponding energy U and thermodynamic probability Ω?
(c) Show that at 0 K, both the energy and the entropy of this system are zero. Also, show that for this system the entropy increases as the energy increases.

3.20 From the Sackur-Tetrode equation, show that $s_2 - s_1 = c_p \ln(T_2/T_1) - R\ln(P_2/P_1)$.

3.21 Write U, p, A, and S in terms of the partition function Z. Express H and G in terms of the partition function Z. For an ideal monatomic gas, express H and G in terms of T and P.

3.22 For an ideal diatomic gas, the partition function can be written as $Z = Z_t Z_r Z_v Z_e Z_D$, where $Z_e = g_{e0}$ is the degeneracy of the ground electronic level, and $Z_D = \exp(-D_0/k_B T)$ is the chemical partition function that is associated with the reaction of formation. Here, g_{e0} and D_0 can be regarded as constants for a given material. Contributions to the partition function beside the translation are due to internal energy storage and thus are called the *internal contribution*, $Z_{\text{int}} = Z_r Z_v Z_e Z_D$. Find the expressions of U, P, A, S, H, and G in terms of N, T, and P (or V) with appropriate constants, assuming that $\Theta_r \ll T \sim \Theta_v$.

3.23 For an ideal molecular gas, derive the distribution function $f(\varepsilon)$ in terms of the kinetic energy $\varepsilon = mv^2/2$.

3.24 Prove Eqs. (3.48), (3.49a), (3.49b) and (3.50).

3.25 Evaluate and plot the Maxwell speed distribution for Ar gas at 100, 300, and 900 K. Tabulate the average speed, the most probable speed, and the rms speed at these temperatures.

3.26 A special form of the Euler-Maclaurin summation formula is

$$\sum_{j=a}^{\infty} f(j) = \int_a^{\infty} f(x)\mathrm{d}x + \frac{1}{2}f(a) - \frac{1}{12}f'(a) + \frac{1}{720}f^{(3)}(a) - \frac{1}{30,240}f^{(5)}(a) + \cdots$$

Consider the rotational partition function, $Z_r = \sum_{l=0}^{\infty}(2j+1)\exp[-j(j+1)\Theta_r/T]$, and show that $Z_r \approx \frac{T}{\Theta_r}\left[1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \cdots\right]$, which is Eq. (3.55) for $\sigma = 1$.

3.27 Because of the nuclear spin degeneracy, hydrogen H_2 gas is consistent of two different types: *ortho-hydrogen* and *para-hydrogen.* The rotational partition functions can be written, respectively, as

$$Z_{\text{r,ortho}} = 3\sum_{l=1,3,5\ldots}(2l+1)\exp\left[-l(l+1)\frac{\Theta_r}{T}\right]$$

and

$$Z_{\text{r,para}} = \sum_{l=0,2,4\ldots}(2l+1)\exp\left[-l(l+1)\frac{\Theta_r}{T}\right]$$

so that $Z_{\text{r,H}_2} = 3\sum_{l=1,3,5\ldots}(2l+1)\exp\left[-l(l+1)\frac{\Theta_r}{T}\right] + \sum_{l=0,2,4\ldots}(2l+1)\exp\left[-l(l+1)\frac{\Theta_r}{T}\right]$. Evaluate the temperature-dependent specific heat of each of the two types of hydrogen, which can be separated and stay separated for a long time before the equilibrium distribution is restored. Calculate the specific heat of hydrogen in the equilibrium distribution as a function of temperature. The ratio $Z_{\mathrm{r,ortho}}/Z_{\mathrm{r,para}}$ is the same as the equilibrium ratio of the two types and varies from 0 at very low temperatures to 3 near room temperature.

3.28 Calculate the specific heat and the specific heat ratio $\gamma = c_p/c_v$ for nitrogen N_2 at 30, 70, 300, and 1500 K. Assume the pressure is sufficiently low for it to be an ideal gas.

3.29 Calculate the specific heat and the specific heat ratio $\gamma = c_p/c_v$ for oxygen O_2 at 50, 100, 300, and 2000 K. Assume the pressure is sufficiently low for it to be an ideal gas.

3.30 Estimate the mole and mass specific heats of CO gas at 100, 300, and 3000 K. Show in a specific heat versus temperature graph the contributions from different modes.

3.31 (a) How many rotational degrees of freedom are there in a CO_2 molecule and in a H_2O molecule?

(b) If the temperature of a low-pressure CO_2 gas is raised high enough to completely excite its rotational and vibrational modes, what will be its specific heats c_v and c_p? Express answers in both kJ/kg K and kJ/kmol K.

3.32 Compute and plot the temperature-dependent specific heat for the following ideal gases and compare your results with tabulated data or graphs: (a) CO_2, (b) H_2O, and (c) CH_4.

3.33 Write down a few sentences to discuss each of the following topics: (a) the significance of partition functions, (b) the different types of statistical ensembles, and (c) statistical fluctuations.

3.34 We have discussed the translational degeneracy dg in a 3D space with a volume V, as given in Eq. (3.85). Consider the situation when the particle is confined in a 2D square potential well. Find the proper wavefunctions and the energy eigenvalues. Assuming the area A is very large, find the translational degeneracy dg in terms of $A, m, \varepsilon,$ and $d\varepsilon$.

3.35 Estimate the speed an electron needs in order to escape from the ground state of a hydrogen atom. What is the de Broglie wavelength of the electron at the initial speed? If a photon is used to knock out the electron in the ground state, what would be the wavelength of the photon? Why is it inappropriate to consider the electron movement in an atom analog with the movement of the Mars in the solar system?

3.36 For the harmonic oscillator problem discussed in Sect. 3.5.5. Show that Eq. (3.111) is a solution for Eq. (3.107) for $n = 0, 1,$ and 2. Plot $\Psi_0^2, \Psi_1^2,$ and Ψ_2^2 and discuss the differences between classical mechanics and quantum mechanics.

References

1. C.L. Tien, J.H. Lienhard, *Statistical Thermodynamics* (Hemisphere, New York, 1985)
2. R.E. Sonntag, G.J. van Wylen, *Fundamentals of Statistical Thermodynamics* (Wiley, New York, 1966)
3. J.E. Lay, *Statistical Mechanics and Thermodynamics of Matter* (Harper Collins Publishers, New York, 1990)
4. C.E. Hecht, *Statistical Thermodynamics and Kinetic Theory* (W.H. Freeman and Company, New York, 1990)
5. V.P. Carey, *Statistical Thermodynamics and Microscale Thermophysics* (Cambridge University Press, Cambridge, UK, 1999)
6. F.C. Chou, J.R. Lukes, X.G. Liang, K. Takahashi, C.L. Tien, Molecular dynamics in microscale thermophysical engineering. Annu. Rev. Heat Transfer **10**, 144–176 (1999)
7. S. Maruyama, Molecular dynamics method for microscale heat transfer, in *Advances in Numerical Heat Transfer*, vol. 2, ed. by W.J. Minkowycz, E.M. Sparrow (Taylor and Francis, New York, 2000), pp. 189–226
8. D.J. Griffiths, *Introduction to Quantum Mechanics*, 2nd edn. (Prentice Hall, New York, 2005)
9. H.J. Metcalf, P. van der Straten, *Laser Cooling and Trapping* (Springer, New York, 1999)
10. G. Burns, *High-Temperature Superconductivity: An Introduction* (Academic Press, Boston, MA, 1992)
11. A. Einstein, Zur quantentheorie der strahlung. Phys. Z. **18**, 121–128 (1917); English translation in *Sources of Quantum Mechanics,* B.L. Van der Waerden (ed.), (North-Holland Publishing Company, Amsterdam, the Netherlands, 1967)
12. H.P. Baltes, On the validity of Kirchhoff's law of heat radiation for a body in a nonequilibrium environment. Progress Opt. **13**, 1–25 (1976)
13. J.P. Gordon, H.J. Zeiger, C.H. Townes, The maser—New type of microwave amplifier, frequency standard, and spectrometer. Phys. Rev. **95**, 1264–1274 (1955); A.L. Schawlow, C.H. Townes, Infrared and optical masers. Phys. Rev. **112**, 1940–1949 (1958)
14. R. Wolfson, J.M. Pasachoff, *Physics with Modern Physics for Scientists and Engineers*, 3rd edn. (Addison-Wesley, Reading, MA, 1999)