Chapter 1

Fundamentals of Radiation for Atmospheric Applications

This text is intended for the study, understanding, and quantitative analysis of atmospheric radiation, a field in which the interactions of solar and terrestrial radiation with molecules, aerosols, and cloud particles in planetary atmospheres, as well as with the surface, are studied through the theory of radiative transfer and radiometric observations made from the ground, the air, and space. The field is closely associated with the investigation of atmospheric greenhouse effects resulting from external radiative perturbations in climate systems and the development of methodologies for inferring atmospheric and surface parameters by means of remote sensing. In the following, we begin with a discussion of various concepts, definitions, and units that are pertinent to the field of atmospheric radiation.

1.1 Concepts, Definitions, and Units

1.1.1 Electromagnetic Spectrum

The most important process responsible for energy transfer in the atmosphere is electromagnetic radiation. Electromagnetic radiation travels in wave form, and all electromagnetic waves travel at the same speed, the speed of light. This is $2.99793 \pm 1 \times 10^8$ m sec^{-1} in a vacuum and very nearly the same speed in air. Visible light, gamma rays, x-rays, ultraviolet light, infrared radiation, microwaves, television signals, and radio waves constitute the *electromagnetic spectrum*.

The retina of the human eye is sensitive to electromagnetic waves with frequencies between 4.3×10^{14} vibrations per second (usually written as cycles per second and abbreviated cps) and 7.5×10^{14} cps. Hence, this band of frequencies is called the *visible* region of the electromagnetic spectrum. The eye, however, does not respond to frequencies of electromagnetic waves higher than 7.5×10^{14} cps. Such waves, lying beyond the violet edge of the spectrum, are called *ultraviolet* light. The human eye also does not respond to electromagnetic waves with frequencies lower than 4.3×10^{14} cps. These waves, having frequencies lower than the lowest frequency of visible light at the red end of the spectrum and higher than about 3×10^{12} cps, are called *infrared light* or *infrared radiation*. Just beyond the infrared portion of the spectrum are *microwaves,* which cover the frequencies from about 3×10^{10} cps to 3×10^{12} cps. The most significant spectral regions associated with radiative energy transfer in planetary atmospheres lie between ultraviolet light and microwaves.

The *x-ray* region of the electromagnetic spectrum consists of waves with frequencies ranging from about 3×10^{16} cps to 3×10^{18} cps, and is adjacent to the ultraviolet region in the spectrum. The *gamma-ray* region of the spectrum has the highest frequencies of all, ranging upward from about 3×10^{19} cps. *Radio* waves have the lowest frequencies in the spectrum, extending downward from about 3×10^{5} cps.

Electromagnetic waves are often described in terms of their wavelength rather than their frequency. The following general formula connects frequency $\tilde{\nu}$ and wavelength λ:

$$\lambda = c/\tilde{\nu}, \tag{1.1.1}$$

where c represents the speed of light in a vacuum. It is conventional to use micrometers (μm; 1 μm $= 10^{-4}$ cm) to denote the wavelengths of radiation from the sun. Other units, known as nanometers (nm; 1 nm $= 10^{-7}$ cm $= 10^{-3}$ μm) and angstroms (Å; 1 Å $= 10^{-4}$ μm), have also been frequently used, particularly for ultraviolet radiation. Equation (1.1.1) is valid for any type of wave and is not restricted to electromagnetic waves. It is customary to use wavenumber ν to describe the characteristics of infrared radiation. It is defined by

$$\nu = \tilde{\nu}/c = 1/\lambda. \tag{1.1.2}$$

Thus, a 10 micrometer (μm) wavelength is equal to a 1000 cm^{-1} wavenumber. In the microwave region, however, a frequency unit called gigahertz (GHz) is commonly used. One GHz is equal to 10^{9} cycles per second. It follows that 1 cm is equivalent to 30 GHz. Figure 1.1 shows the complete electromagnetic spectrum along with each region's corresponding frequency, wavenumber, and wavelength.

1.1.2 Solid Angle

The analysis of a radiation field often requires the consideration of the amount of radiant energy confined to an element of solid angle. A solid angle is defined as the ratio of the area σ of a spherical surface intercepted at the core to the square of the radius, r, as indicated in Fig. 1.2. It can be written as

$$\Omega = \sigma/r^2. \tag{1.1.3}$$

Units of solid angle are expressed in terms of the steradian (sr). For a sphere whose surface area is $4\pi r^2$, its solid angle is 4π sr.

To obtain a differential elemental solid angle, we construct a sphere whose central point is denoted as O. Assuming a line through point O moving in space and intersecting an arbitrary surface located at a distance r from point O, then as is evident from Fig. 1.3, the differential area in polar coordinates is given by

$$d\sigma = (r d\theta)(r \sin\theta \, d\phi). \tag{1.1.4}$$

Name of region	Wavelength (μm)	Frequency (GHz)	Wavenumber (cm^{-1})
Gamma rays	10^{-5}	3×10^{10}	10^{9}
X rays	10^{-2}	3×10^{7}	10^{6}
Ultraviolet	3×10^{-1}	10^{6}	0.33×10^{5}
Visible			
Infrared	1 10^{3}	3×10^{2}	10^{4} 10
Microwaves	10^{4} (1cm)	3×10^{1}	1
Spacecraft	10^{6}	3×10^{-1}	10^{-2}
Television & FM	10^{7}	3×10^{-2}	10^{-3}
Shortwave	10^{8}	3×10^{-3}	10^{-4}
AM Radio waves	10^{9}	3×10^{-4}	10^{-5}

Violet 0.4μm
Purple
Blue
Green
Yellow
Orange
Red 0.7μm

Figure 1.1 The electromagnetic spectrum in terms of wavelength in μm, frequency in GHz, and wavenumber in cm^{-1}.

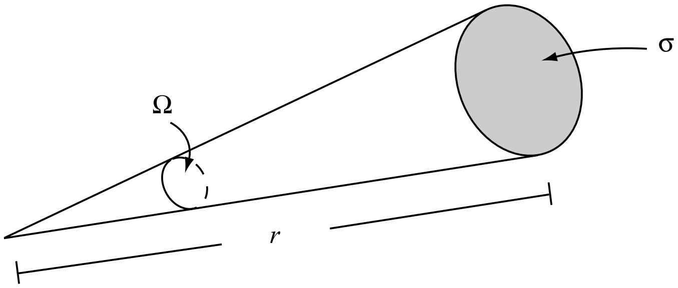

Figure 1.2 Definition of a solid angle Ω, where σ denotes the area and r is the distance.

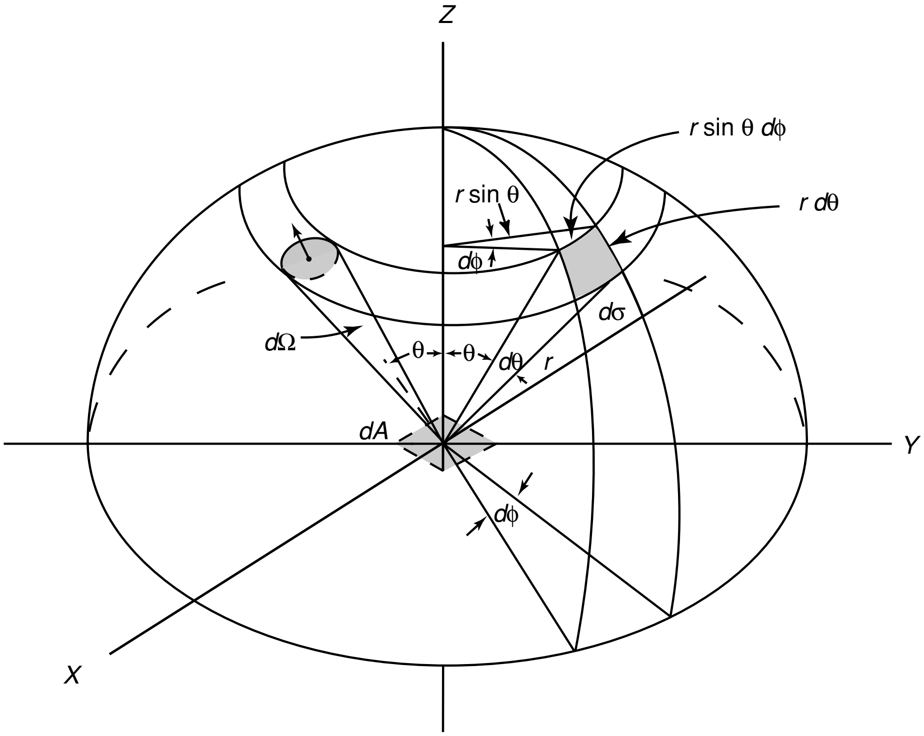

Figure 1.3 Illustration of a differential solid angle and its representation in polar coordinates. Also shown for demonstrative purposes is a pencil of radiation through an element of area dA in directions confined to an element of solid angle $d\Omega$. Other notations are defined in the text.

Hence, the differential solid angle is

$$d\Omega = d\sigma/r^2 = \sin\theta \, d\theta \, d\phi, \tag{1.1.5}$$

where θ and ϕ denote the zenith and azimuthal angles, respectively, in polar coordinates.

1.1.3 Basic Radiometric Quantities

Consider the differential amount of radiant energy dE_λ in a time interval dt and in a specified wavelength interval, λ to $\lambda + d\lambda$, which crosses an element of area dA depicted in Fig. 1.3, in directions confined to a differential solid angle, which is oriented at an angle θ to the normal of dA. This energy is expressed in terms of the specific intensity I_λ by

$$dE_\lambda = I_\lambda \cos\theta \, dA \, d\Omega \, d\lambda \, dt, \tag{1.1.6}$$

where $\cos\theta \, dA$ denotes the effective area at which the energy is being intercepted. Equation (1.1.6) defines the *monochromatic intensity* (or *radiance*) in a general way as follows:

$$I_\lambda = \frac{dE_\lambda}{\cos\theta \, d\Omega \, d\lambda \, dt \, dA}. \tag{1.1.7}$$

Thus, the intensity is in units of energy per area per time per wavelength and per steradian. It is evident that the intensity implies a directionality in the radiation stream. Commonly, the intensity is said to be confined in a pencil of radiation.

The *monochromatic flux density* or the *monochromatic irradiance* of radiant energy is defined by the normal component of I_λ integrated over the entire hemispheric solid angle and may be written as

$$F_\lambda = \int_\Omega I_\lambda \cos\theta \, d\Omega. \tag{1.1.8}$$

In polar coordinates, we write

$$F_\lambda = \int_0^{2\pi} \int_0^{\pi/2} I_\lambda(\theta, \phi) \cos\theta \, \sin\theta \, d\theta \, d\phi. \tag{1.1.9}$$

For isotropic radiation (i.e., if the intensity is independent of the direction), the monochromatic flux density is then

$$F_\lambda = \pi I_\lambda. \tag{1.1.10}$$

The total flux density of radiant energy, or irradiance, for all wavelengths (energy per area per time), can be obtained by integrating the monochromatic flux density over the entire electromagnetic spectrum:

$$F = \int_0^\infty F_\lambda \, d\lambda. \tag{1.1.11}$$

Moreover, the total flux f, or radiant power W (energy per time), is defined by

$$f = \int_A F \, dA. \tag{1.1.12}$$

The monochromatic flux density in the frequency domain may be written in the form

$$F_{\tilde{\nu}} = \frac{dF}{d\tilde{\nu}}. \tag{1.1.13}$$

From the relationship between wavelength and frequency denoted in Eq. (1.1.1), we have

$$F_{\tilde{\nu}} = -(\lambda^2/c)F_\lambda. \tag{1.1.14}$$

Likewise, the intensity in wavelength and frequency domains is connected by

$$I_{\tilde{\nu}} = -(\lambda^2/c)I_\lambda. \tag{1.1.15}$$

A similar relation between the monochromatic flux density, or intensity, in wavenumber and wavelength (or frequency) domains may be expressed by means of Eq. (1.1.2).

When the flux density or the irradiance is from an emitting surface, the quantity is called the *emittance*. When expressed in terms of wavelength, it is referred to as the *monochromatic emittance*. The intensity or the radiance is also called the *brightness* or *luminance* (photometric brightness). The total flux from an emitting surface is

Table 1.1

Symbols, Dimensions, and Units of Various Radiometric Quantities

Symbol	Quantity	Dimension[a]	Unit[b]
E	Energy	ML^2T^{-2}	Joule (J)
f	Flux (luminosity)	ML^2T^{-3}	Joule per second (J sec^{-1}, W)
F	Flux density (irradiance) Emittance	MT^{-3}	Joule per second per square meter (W m^{-2})
I	Intensity (radiance) Brightness (luminance)	MT^{-3}	Joule per second per square meter per steradian (W m^{-2} sr^{-1})

[a] M is mass, L is length, and T is time.
[b] 1 watt (W) = 1 J sec^{-1}.

often called *luminosity*. The basic radiometric quantities are summarized in Table 1.1, along with their symbols, dimensions, and units.

1.1.4 Concepts of Scattering and Absorption

Most of the light that reaches our eyes comes not directly from its source but indirectly through the process of *scattering*. We see diffusely scattered sunlight when we look at clouds or at the sky. Land and water surfaces and the objects surrounding us are visible through the light that they scatter. An electric lamp does not send us light directly from the luminous filament but usually glows with the light that has been scattered by the glass bulb. Unless we look directly at a light source, such as the sun, a flame, or an incandescent filament with a clear bulb, we see light that has been scattered. In the atmosphere, we see many colorful examples of scattering generated by molecules, aerosols, and clouds containing water droplets and ice crystals. Blue sky, white clouds, and magnificent rainbows and halos, to name a few, are all optical phenomena produced by scattering. Scattering is a fundamental physical process associated with light and its interaction with matter. It occurs at all wavelengths throughout the entire electromagnetic spectrum.

Scattering is a physical process by which a particle in the path of an electromagnetic wave continuously abstracts energy from the incident wave and reradiates that energy in all directions. Therefore, the particle may be thought of as a point source of the scattered energy. In the atmosphere, the particles responsible for scattering range in size from gas molecules ($\sim 10^{-4}$ μm) to aerosols (~ 1 μm), water droplets (~ 10 μm), ice crystals (~ 100 μm), and large raindrops and hail particles (~ 1 cm). The effect of particle size on scattering is inferred by a physical term called the *size parameter*. For a spherical particle, it is defined as the ratio of the particle circumference to the incident wavelength, λ; i.e., $x = 2\pi a/\lambda$, where a is the particle radius. If $x \ll 1$, the scattering is called *Rayleigh scattering*. An excellent example of this case is the scattering of visible light (0.4–0.7 μm) by atmospheric molecules, leading to the explanation of blue sky and sky polarization to be discussed in Chapter 3. For

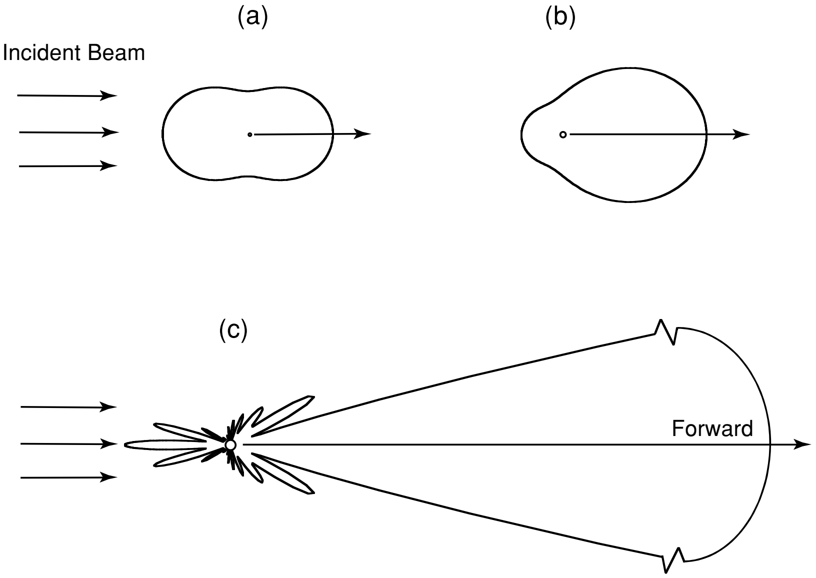

Figure 1.4 Demonstrative angular patterns of the scattered intensity from spherical aerosols of three sizes illuminated by the visible light of 0.5 μm: (a) 10^{-4} μm, (b) 0.1 μm, and (c) 1 μm. The forward scattering pattern for the 1 μm aerosol is extremely large and is scaled for presentation purposes.

particles whose sizes are comparable to or larger than the wavelength, i.e., $x \gtrsim 1$, the scattering is customarily referred to as *Lorenz–Mie scattering*. The mathematical theory of Lorenz–Mie scattering for spherical particles will be presented in Chapter 5. Figure 1.4 illustrates the scattering patterns of spherical aerosols of size 10^{-4}, 0.1, and 1 μm illuminated by a visible light of 0.5 μm. A small particle tends to scatter light equally in the forward and backward directions. When the particle becomes larger, the scattered energy becomes increasingly concentrated in the forward direction with increasingly complex scattering features. Because of the spherical symmetry with respect to the incoming light beam, the scattering patterns for other planes are the same as the ones presented in Fig. 1.4. The scattering of sunlight by spherical cloud droplets and raindrops produces the magnificent rainbows and glory that we see in our daily life.

In situ observations and electronic microscopic photography have shown that aerosols in the atmosphere, such as minerals, soot, and even oceanic particles, exhibit a wide variety of shapes ranging from quasi-spherical to highly irregular geometric figures with internal structure. The shape and size of ice crystals are governed by temperature and supersaturation, but they generally have a basic hexagonal structure. In the atmosphere, if ice crystal growth involves collision and coalescence, the crystal's shape can be extremely complex. Recent observations based on aircraft optical probes and replicator techniques for widespread midlatitude, tropical, arctic, and contrail cirrus show that these clouds are largely composed of ice crystals in the shape of bullet rosettes, solid and hollow columns, plates, and aggregates, and ice crystals with irregular surfaces with sizes ranging from a few micrometers to thousands of micrometers. The scattering of sunlight by some of the defined ice crystals produces

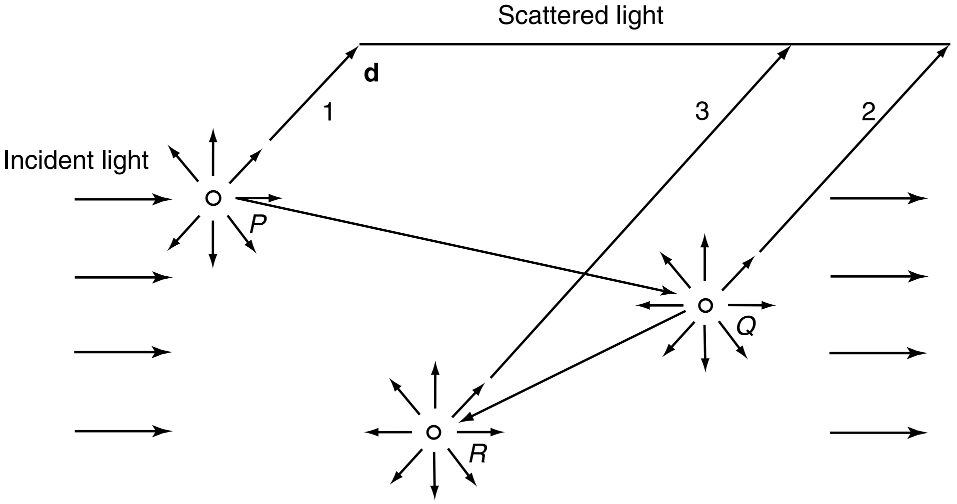

Figure 1.5 Multiple scattering process involving first (P), second (Q), and third (R) order scattering in the direction denoted by **d.**

fascinating optical phenomena including 22° and 46° halos, sundogs, and numerous arcs and bright spots. Light scattering by nonspherical and inhomogeneous particles, a contemporary research subject, will be covered in Chapter 5, which presents a combination of geometric ray-tracing and numerical solution approaches.

In atmospheric scattering, it is generally assumed that the light scattered by molecules and particulates has the same frequency (or wavelength) as the incident light. It is noted, however, that high-energy laser light can produce phenomena such as Raman scattering in shift frequencies, which can be employed for the remote sensing of water vapor. Atmospheric molecules and particulates are separated widely enough so that each particle scatters light in exactly the same way as if all other particles did not exist. This is referred to as *independent scattering*. The assumption of independent scattering greatly simplifies the problem of light scattering by a collection of particles, because it allows the use of energy quantity instead of electric field in the analysis of the propagation of electromagnetic waves in planetary atmospheres.

In a scattering volume, which contains many particles, each particle is exposed to, and also scatters, the light that has already been scattered by other particles. To demonstrate this concept we refer to Fig. 1.5. A particle at position P removes the incident light by scattering just once, i.e., single scattering, in all directions. Meanwhile, a portion of this scattered light reaches the particle at position Q, where it is scattered again in all directions. This is called *secondary scattering*. Likewise, a subsequent third-order scattering involving the particle at position R takes place. Scattering more than once is called *multiple scattering*. It is apparent from Fig. 1.5 that some of the incident light that has been first scattered away from direction **d** may reappear in this direction by means of multiple scattering. Multiple scattering is an important process for the transfer of radiant energy in the atmosphere, especially when aerosols and clouds are involved. Chapter 6 deals with the theory of multiple scattering in planetary atmospheres.

Scattering is often accompanied by absorption. Grass looks green because it scatters green light while it absorbs red and blue light. The absorbed energy is converted into some other form, and it is no longer present as red or blue light. In molecular atmospheres, there is very little absorption of energy in the visible spectrum. Clouds also absorb very little visible light. Both scattering and absorption remove energy from a beam of light traversing the medium. The beam of light is attenuated, and we call this attenuation *extinction*. Thus, extinction is a result of scattering plus absorption. In a nonabsorbing medium, scattering is the sole process of extinction.

In the field of light scattering and radiative transfer, it is customary to use a term called *cross section,* analogous to the geometrical area of a particle, to denote the amount of energy removed from the original beam by the particle. When the cross section is associated with a particle dimension, its units are denoted in terms of area (cm^2). Thus, the extinction cross section, in units of area, is the sum of the scattering and absorption cross sections. However, when the cross section is in reference to unit mass, its units are given in area per mass (cm^2 g^{-1}). In this case, the term mass extinction cross section is used in radiative transfer. The mass extinction cross section is, therefore, the sum of the mass absorption and mass scattering cross sections. Furthermore, when the extinction cross section is multiplied by the particle number density (cm^{-3}), or when the mass extinction cross section is multiplied by the density (g cm^{-3}), the quantity is referred to as the *extinction coefficient,* whose units are given in terms of length (cm^{-1}). In the field of infrared radiative transfer, the mass absorption cross section is simply referred to as the *absorption coefficient*.

The absorption of energy by particles and molecules leads to emission. The concept of emission is associated with blackbody radiation and will be discussed in the following section. In addition, a number of minor atmospheric constituents exhibit complicated absorption line structures in the infrared region. Section 1.3 and Chapter 4 will provide discussions of the fundamentals of line formation and the transfer of infrared radiation in the atmosphere. A fundamental understanding of the scattering and absorption processes in the atmosphere is imperative for the study of the radiation budget and climate of planetary atmospheres and for the exploration of remote sounding techniques to infer atmospheric composition and structure.

1.2 Blackbody Radiation Laws

The laws of blackbody radiation are basic to an understanding of the absorption and emission processes. A blackbody is a basic concept in physics and can be visualized by considering a cavity with a small entrance hole, as shown in Fig. 1.6. Most of the radiant flux entering this hole from the outside will be trapped within the cavity, regardless of the material and surface characteristics of the wall. Repeated internal reflections occur until all the fluxes are absorbed by the wall. The probability that any of the entering flux will escape back through the hole is so small that the interior appears dark. The term *blackbody* is used for a configuration of material where absorption is complete. Emission by a blackbody is the converse of absorption. The flux

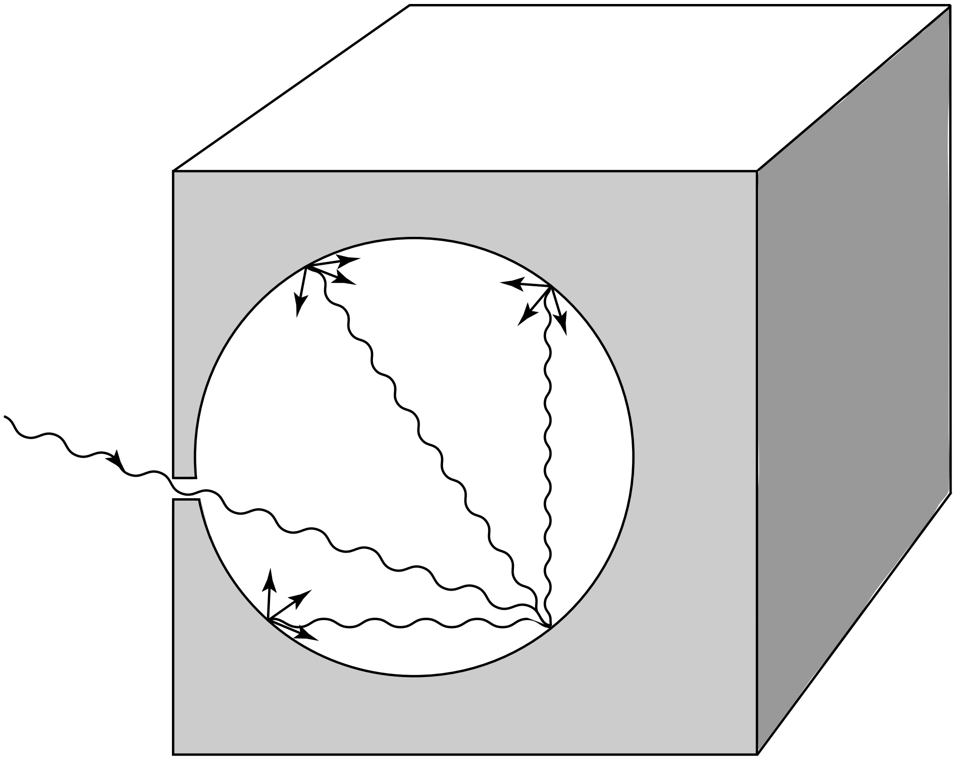

Figure 1.6 A blackbody radiation cavity to illustrate that absorption is complete.

emitted by any small area of the wall is repeatedly reflected and at each encounter with the wall, the flux is weakened by absorption and strengthened by new emission. After numerous encounters, emission and absorption reach an equilibrium condition with respect to the wall temperature. In the following, we present four fundamental laws that govern blackbody radiation, beginning with Planck's law.

1.2.1 Planck's Law

In his pursuit of a theoretical explanation for cavity radiation, Planck (1901) assumed that the atoms that make up the wall behave like tiny electromagnetic oscillators, each with a characteristic frequency of oscillation. The oscillators emit energy into the cavity and absorb energy from it. In his analysis, Planck was led to make two assumptions about the atomic oscillators. First, Planck postulated that an oscillator can only have energy given by

$$E = nh\tilde{\nu}, \tag{1.2.1}$$

where $\tilde{\nu}$ is the oscillator frequency, h is Planck's constant, and n is called the quantum number and can take on only integral values. Equation (1.2.1) asserts that the oscillator energy is quantized. Although later developments revealed that the correct formula for a harmonic oscillator is $E = (n + 1/2)h\tilde{\nu}$ [see Eq. (1.3.7)], the change introduces no difference to Planck's conclusions. Secondly, Planck postulated that the oscillators do not radiate energy continuously, but only in jumps, or in quanta. These quanta of energy are emitted when an oscillator changes from one to another of its quantized energy states. Hence, if the quantum number changes by one unit, the amount of radiated energy is given by

$$\Delta E = \Delta n h\tilde{\nu} = h\tilde{\nu}. \tag{1.2.2}$$

Determination of the emitted energy requires knowing the total number of oscillators with frequency $\tilde{\nu}$ for all possible states in accord with Boltzmann statistics, as presented in Appendix A. Following the two preceding postulations and normalization of the average emitted energy per oscillator, the Planck function in units of energy/area/time/sr/frequency is given by

$$B_{\tilde{\nu}}(T) = \frac{2h\tilde{\nu}^3}{c^2(e^{h\tilde{\nu}/KT} - 1)}, \tag{1.2.3}$$

where K is Boltzmann's constant, c is the velocity of light, and T is the absolute temperature. The Planck and Boltzmann constants have been determined through experimentation and are $h = 6.626 \times 10^{-34}$ J sec and $K = 1.3806 \times 10^{-23}$ J deg^{-1}.

The Planck function relates the emitted monochromatic intensity to the frequency and the temperature of the emitting substance. By utilizing the relation between frequency and wavelength shown in Eq. (1.1.15), Eq. (1.2.3) can be rewritten as follows:

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5(e^{hc/K\lambda T} - 1)} = \frac{C_1\lambda^{-5}}{\pi(e^{C_2/\lambda T} - 1)}, \tag{1.2.4}$$

where $C_1 = 2\pi hc^2$ and $C_2 = hc/K$ are known as the first and second radiation constants, respectively. Figure 1.7 shows curves of $B_\lambda(T)$ versus wavelength for a number of emitting temperatures. It is evident that the blackbody radiant intensity increases with temperature and that the wavelength of the maximum intensity decreases with increasing temperature. The Planck function behaves very differently when $\lambda \to \infty$, referred to as the *Rayleigh–Jeans distribution,* and when $\lambda \to 0$, referred to as the *Wien distribution.*

1.2.2 Stefan–Boltzmann Law

The total radiant intensity of a blackbody can be derived by integrating the Planck function over the entire wavelength domain from 0 to ∞. Hence,

$$B(T) = \int_0^\infty B_\lambda(T)\,d\lambda = \int_0^\infty \frac{2hc^2\lambda^{-5}}{(e^{hc/K\lambda T} - 1)}\,d\lambda. \tag{1.2.5}$$

On introducing a new variable $x = hc/k\lambda T$, Eq. (1.2.5) becomes

$$B(T) = \frac{2k^4T^4}{h^3c^2}\int_0^\infty \frac{x^3dx}{(e^x - 1)}. \tag{1.2.6}$$

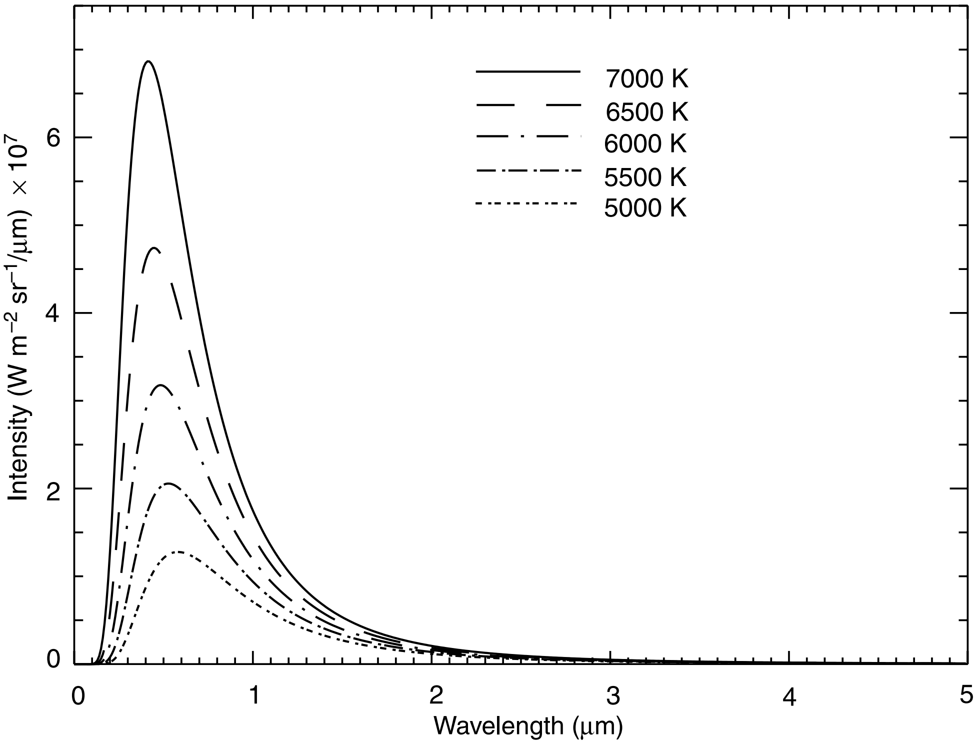

Figure 1.7 Blackbody intensity (Planck function) as a function of wavelength for a number of emitting temperatures.

The integral term in Eq. (1.2.6) is equal to $\pi^4/15$. Thus, defining

$$b = 2\pi^4 K^4/(15c^2h^3), \tag{1.2.7}$$

we then have

$$B(T) = bT^4. \tag{1.2.8}$$

Since blackbody radiation is isotropic, the flux density emitted by a blackbody is therefore [see Eq. (1.1.10)]

$$F = \pi B(T) = \sigma T^4, \tag{1.2.9}$$

where σ is the Stefan–Boltzmann constant and is equal to 5.67×10^{-8} J m^{-2} sec^{-1} deg^{-4}. Equation (1.2.9) states that the flux density emitted by a blackbody is proportional to the fourth power of the *absolute* temperature. This is the Stefan–Boltzmann law, fundamental to the analysis of broadband infrared radiative transfer.

1.2.3 Wien's Displacement Law

Wien's displacement law states that the wavelength of the maximum intensity of blackbody radiation is inversely proportional to the temperature. By differentiating the Planck function with respect to wavelength, and by setting the result equal to zero, i.e.,

$$\frac{\partial B_\lambda(T)}{\partial \lambda} = 0, \tag{1.2.10}$$

we obtain the wavelength of the maximum (Exercise 1.4)

$$\lambda_{\mathrm{m}} = a/T, \tag{1.2.11}$$

where $a = 2.897 \times 10^{-3}$ m deg. From this relationship, we can determine the temperature of a blackbody from the measurement of the maximum monochromatic intensity. The dependence of the position of the maximum intensity on temperature is evident from the blackbody curves displayed in Fig. 1.7.

1.2.4 Kirchhoff's Law

The preceding three fundamental laws are concerned with the radiant intensity emitted by a blackbody, which is dependent on the emitting wavelength and the temperature of the medium. A medium may absorb radiation of a particular wavelength, and at the same time also emit radiation of the same wavelength. The rate at which emission takes place is a function of temperature and wavelength. This is the fundamental property of a medium under the condition of *thermodynamic equilibrium*. The physical statement regarding absorption and emission was first proposed by Kirchhoff (1860).

To understand the physical meaning of Kirchhoff's law, we consider a perfectly insulated enclosure having black walls. Assume that this system has reached the state of thermodynamic equilibrium characterized by uniform temperature and isotropic radiation. Because the walls are black, radiation emitted by the system to the walls is absorbed. Moreover, because there is an equilibrium, the same amount of radiation absorbed by the walls is also emitted. Since the blackbody absorbs the maximum possible radiation, it has to emit that same amount of radiation. If it emitted more, equilibrium would not be possible, and this would violate the second law of thermodynamics. Radiation within the system is referred to as blackbody radiation as noted earlier, and the amount of radiant intensity is a function of temperature and wavelength.

On the basis of the preceding discussion, the emissivity of a given wavelength, ε_λ (defined as the ratio of the emitting intensity to the Planck function), of a medium is equal to the absorptivity, A_λ (defined as the ratio of the absorbed intensity to the Planck function), of that medium under thermodynamic equilibrium. Hence, we may write

$$\varepsilon_\lambda = A_\lambda. \tag{1.2.12}$$

A medium with an absorptivity A_λ absorbs only A_λ times the blackbody radiant intensity $B_\lambda(T)$ and therefore emits ε_λ times the blackbody radiant intensity. For a blackbody, absorption is a maximum and so is emission. Thus, we have

$$A_\lambda = \varepsilon_\lambda = 1 \tag{1.2.13}$$

for all wavelengths. A *gray body* is characterized by incomplete absorption and emission and may be described by

$$A_\lambda = \varepsilon_\lambda < 1. \tag{1.2.14}$$

Kirchhoff's law requires the condition of thermodynamic equilibrium, such that uniform temperature and isotropic radiation are achieved. Obviously, the radiation field of the earth's atmosphere as a whole is not isotropic and its temperatures are not uniform. However, in a localized volume below about 60–70 km, to a good approximation, it may be considered to be isotropic with a uniform temperature in which energy transitions are governed by molecular collisions. It is in the context of this local thermodynamic equilibrium (LTE) that Kirchhoff's law is applicable to the atmosphere. Departure from the LTE conditions will be discussed in Section 1.3.3.

1.3 Absorption Line Formation and Line Shape

1.3.1 Line Formation

Inspection of high-resolution spectroscopy reveals that the emission spectra of certain gases are composed of a large number of individual and characteristic spectral lines. In the previous section, we indicated that Planck successfully explained the nature of radiation from heated solid objects of which the cavity radiator formed the prototype. Such radiation generates continuous spectra, as opposed to line spectra. Planck's quantization ideas, properly extended, however, lead to an understanding of line spectra as well. In the following, we use the simplest hydrogen model to discuss emission and absorption line formation.

1.3.1.1 BOHR'S MODEL

Investigation of the hydrogen spectrum led Bohr (1913) to postulate that the circular orbits of the electrons were quantized; that is, their angular momentum could have only integral multiples of a basic value. Bohr assumed that the hydrogen atom exists, like Planck's oscillators, in certain stationary states in which it does not radiate. Radiation occurs only when the atom makes a transition from one state with energy E_k to a state with lower energy E_j. Thus, we write

$$E_k - E_j = h\tilde{\nu}, \tag{1.3.1}$$

where $h\tilde{\nu}$ represents the quantum of energy carried away by the photon, which is emitted from the atom during the transition. The lowest energy state is called the *ground state* of the atom. When an electron of an atom absorbs energy due to a collision and jumps into a larger orbit, the atom is said to be in an *excited state*. Then, according to Eq. (1.3.1), a sudden transition will take place, and the atom emits a photon of energy and collapses to a lower energy state. This is illustrated in Fig. 1.8 for a hydrogen atom. Also shown in this figure is the absorption of a photon by a stationary hydrogen atom.