

---

## Introduction and Preliminaries

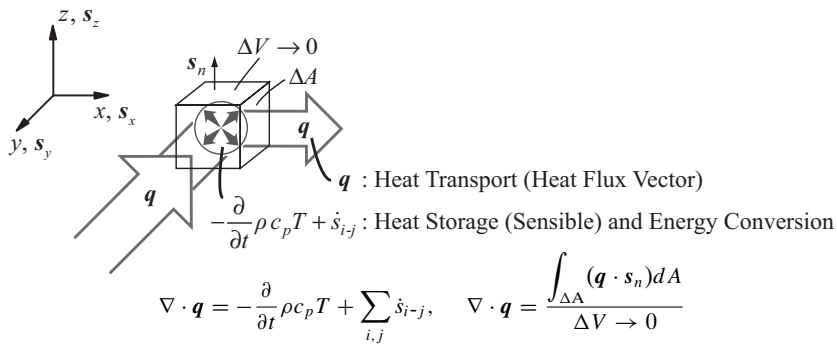
The macroscopic heat transfer rates use thermal-energy related properties, such as the thermal conductivity, and in turn these properties are related to the atomic-level properties and processes. Heat transfer physics addresses these atomic-level processes (e.g., kinetics). We begin with the macroscopic energy equation used in heat transfer analysis to describe the rates of thermal energy storage, transport (by means of conduction  $k$ , convection  $u$ , and radiation  $r$ ), and conversion to and from other forms of energy. The volumetric macroscopic energy conservation (rate) equation is listed in Table 1.1.<sup>†</sup> The sensible heat storage is the product of density and specific heat capacity  $\rho c_p$ , and the time rate of change of local temperature  $\partial T/\partial t$ . The heat flux vector  $\mathbf{q}$  is the sum of the conductive, convective, and radiative heat flux vectors. The conductive heat flux vector  $\mathbf{q}_k$  is the negative of the product of the thermal conductivity  $k$ , and the gradient of temperature  $\nabla T$ , i.e., the Fourier law of conduction. The convective heat flux vector<sup>‡</sup>  $\mathbf{q}_u$  (assuming net local motion) is the product of  $\rho c_p$ , the local velocity vector  $\mathbf{u}$ , and temperature. For laminar flow, in contrast to turbulent flow that contains chaotic velocity fluctuations, molecular conduction of the fluid is unaltered, whereas in turbulent flow this is augmented (phenomenologically) by turbulent mixing transport (turbulent eddy conductivity). The radiative heat flux vector  $\mathbf{q}_r = \mathbf{q}_{ph}$  ( $ph$  stands for photon) is the spatial (angular) and spectral integrals of the product of the unit vector  $s$  and the electromagnetic (EM), spectral (frequency dependent), directional radiation intensity  $I_{ph,\omega}$ , where  $\omega$  is the angular frequency of EM radiation (made up of photons). When the spherical, (solid angle) integral of  $I_{ph,\omega}$  is nonzero, there is a net photon flux in the medium (matter). This intensity is influenced by the spectral emission, absorption, and scattering of photons by matter, i.e., its radiative properties (Table 7.1). Among these properties are the photon spectral, absorption coefficient  $\sigma_{ph,\omega}$ , which results from the interaction

<sup>†</sup> In deriving this equation, it is assumed that  $c_p$  is constant. The more general form is also given in [232].

<sup>‡</sup> The surface-convection heat flux vector  $\mathbf{q}_{ku}$  is the special case of conduction occurring on an interface separating a moving fluid from a generally stationary solid. Then, assuming no fluid slip on this interface, the heat transfer through the fluid is only by conduction, but the interface temperature gradient is influenced by the fluid motion [232].

Table 1.1. Macroscopic energy conservation equation and the heat flux vector [232].

Energy equation



Heat flux vector

$$\mathbf{q} = \mathbf{q}_k + \mathbf{q}_u + \mathbf{q}_r = -k\nabla T + \rho c_p \mathbf{u} T + 2\pi \int_0^\infty \int_{-1}^1 s I_{ph,\omega} d\mu d\omega$$

- A area, m<sup>2</sup>
- $I_{ph,\omega}$  spectral, directional radiation intensity, W/(m<sup>2</sup>-sr-rad/s)
- $c_p$  specific heat capacity, J/kg-K
- $k$  thermal conductivity, W/m-K
- $\mathbf{q}$  heat flux vector, W/m<sup>2</sup>
- $\mathbf{s}_n$  surface normal, unit vector
- $\mathbf{s}$  unit vector
- $\dot{s}_{i-j}$  energy conversion rate between principal carrier  $i$  and carrier  $j$ , W/m<sup>3</sup>
- $T$  temperature, K
- $\mathbf{u}$  velocity, m/s
- $V$  volume, m<sup>3</sup>
- $\rho$  density, kg/m<sup>3</sup>
- $\mu$   $\cos \theta$ ,  $\theta$  is polar angle
- $\omega$  angular frequency, rad/s

of an EM waves with electric entities in its travelling medium (e.g., vibrating electric dipoles, free electrons, electronic bandgap).

In Table 1.1, it is noted that the divergence of  $\mathbf{q}$  is integral to its surface normal component on the differential surface area  $\Delta A$  of a vanishing differential volume  $\Delta V$ . The rate of energy conversion to and from thermal energy  $\dot{s}_{i-j}$  is determined by the nature and frequency of the interactions between the principal energy carriers  $i$  and  $j$ . This rate describes various bond (chemical, nuclear and physical), electromagnetic, and mechanical energy conversions. The rate is related to the available energy transitions as well as the contributions from promoting/limiting mechanisms (e.g., energy distribution probabilities, kinetics, transport, and temperature). It is this interplay among storage, transport, and transformation rates that allows for the behaviors exhibited by energy conversion phenomena and devices.

As mentioned, heat is atomic motion of matter and temperature represents equilibrium distribution of this motion [represented by the equilibrium energy distribution function  $f^o(T)$ ]. Heat transfer results from nonequilibrium distribution function  $f(T)$  which in turn is caused by spatial and/or temporal variation of

1.1 Principal Carriers: Phonon, Electron, Fluid Particle, and Photon 3

temperature or presence of related force fields, and/or thermal energy conversion. In particular, thermal energy conversion creates spectral heat transfer at the atomic level. Here spectral refers to a selected atomic motion mode (e.g., a vibration frequency). The rate of heat transfer is the kinetics of return to equilibrium. The motion of atoms, because of vibration, rotation, and translation, creates kinetic energy within matter and this defines its temperature or sensible heat. Electrons (valence electrons as they orbit the nuclei or conduction electrons as they move among atoms) are also central to the energy contained within matter. Electronic energies (including bond energy between atoms), kinetic energy (created by the motion of atoms), and even the annihilation/creation of mass (i.e., relativistic effects), can all be converted to electromagnetic energy (photons). The energy contained in photons can then, in turn, interact with other matter (through electric entities such as dipole moments) resulting in energy conversion.

The state of an electron (which defines its energy level), as well as its coupling with atomic nuclei (in a free atom, or in molecules), is central to the energy of a system, its interactions (including conversion to other forms of energy), and its transport (both within the system and across its boundaries), especially when the energy per unit mass is much larger than  $k_B T$  (which is 0.026 eV for  $T = 300$  K), where  $k_B$  is the Boltzmann constant.  $k_B T$  is the energy of thermal fluctuations (Section 2.3.3). In ideal electrical insulators, no conduction (free) electrons exist, metals have a large number (over  $10^{21}$  cm<sup>-3</sup>), and intrinsic (undoped) semiconductors have a small, temperature-dependent number (less than  $10^{15}$  cm<sup>-3</sup>) of conduction electrons. Mobile and stationary ions, as intrinsic constituents or as dopants, also have their own particular electronic energy states.

Thus the microscopic model of thermal energy storage, transport, and interactions is assembled through the study of each of the principal energy carriers, namely: phonons ( $p$ ), electrons ( $e$ ), fluid particles ( $f$ ), and photons ( $ph$ ).<sup>†</sup>

This introduction–preliminaries chapter continues with attributes of the four principal heat carries, including their combinatorial energy-state occupational probabilities and their wave, particle, and quasi-particle treatments. Then we present a brief history of contributions to heat transfer physics, and introduce the universal constants and atomic-level (fine-structure) time, length, and energy scales. Then we give examples of atomic-level kinetics controlling energy storage, transport, and conversion, and define the scope of heat transfer physics and this text.

### 1.1 Principal Carriers: Phonon, Electron, Fluid Particle, and Photon

The energy of matter can be divided into potential and kinetic energies  $E_p$  and  $E_k$ . Each of the principal energy carriers can have potential and kinetic energy (for photon it is electric and magnetic field energies). Here we discuss the energy attributes of carriers, including their equilibrium occupancy probabilities, which allow for inclusion of these attributes into statistical presentation of energy of matter.

<sup>†</sup> The suffix “on” indicates having properties of particles.

## 1.1.1 Phonon

Heat as atomic motion is stored in atomic vibration in solids. A phonon is a quantized mode of vibration occurring in rigid atomic lattices, such as those in crystalline solids.<sup>†</sup> The properties of long-wavelength phonons give rise to sound in solids (hence the name phonon). Phonons participate in many of the physical properties of materials, including heat capacity and thermal/electrical conductivities (the propagation of phonons is responsible for the conduction of heat in electrical insulators).

In classical mechanics, any vibration of a lattice can be decomposed into a superposition of nonlocalized normal modes of vibration. When these modes are analyzed by use of quantum mechanics, they are found to possess some quantum particlelike properties (quasi-particles). Thus a phonon is an indistinguishable quasi-particle (see Glossary). When treated as particles, phonons are called bosons (see Table 1.2, and the derivation given in Appendix F) and are said to possess zero spin. The thermal equilibrium particle probability distribution (occupation) function  $f_p^o$  indicates, that at thermal equilibrium (the superscript <sup>o</sup> indicates equilibrium), phonons are distributed based on their scaled energy  $E_p/k_B T$ . This is also shown in Figure 1.1, which shows the phonon energy is the sum of its potential and kinetic energy. Here,  $E_p = \hbar\omega_p$  is the phonon energy, and  $\hbar = h_P/2\pi$ , where  $h_P$  is the Planck<sup>‡</sup> constant (fundamental constants are discussed in Section 1.5.1).

The equilibrium, energy-occupation probability (or distribution) function  $f_i^o$  is based on principles of (a) equal *a priori* probability applied to all energy states of the system (equipartition of the energy states), and (b) ensemble averaging which gives the macroscopic properties of the system and constrains this probability in favor of lower probability of highest energy states (in general). This second principle introduces the system temperature and results in increased occupancy of the higher energy states at higher temperatures. Spin is one of the properties of elementary particles, which can be thought of as rotating tops. Based on spin, the particles are either fermions or bosons. The spin (quantum angular momentum) of a particle is given by  $S = \hbar[s(s + 1)]^{1/2}$  (Section 2.6.6), where  $s$  is 0, 1/2, 3/2, 2, ... If  $s$  is 1, 2, ..., then the particle is called a boson, and if  $s$  is 1/2, 3/2, ..., then it is called a fermion. No two fermions can be found in the same quantum state (because of the Pauli exclusion principle), whereas bosons tend to accumulate in certain favored states.

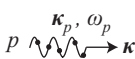
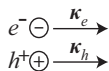
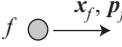
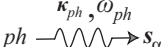
There are two types of phonons: acoustic phonons, denoted with the subscript A, and optical phonons, denoted with the subscript O. Acoustic phonons have frequencies that become small for long wavelengths and correspond to sound waves in the lattice (this is a property of phonon dispersion relation). These long wavelengths correspond to bulk translations. Longitudinal- and transverse-acoustic phonons are often abbreviated as LA and TA phonons, respectively. Optical phonons, which

<sup>†</sup> In lattice dynamics, there are a finite number of vibrational modes, and the energy of each mode is quantized. So, phonons are also these normal modes. Also, although phonons are exclusively a property of periodic media, vibrations exist in all solids.

<sup>‡</sup> The subscript P is for consistency with other fundamental constants (Table 1.4 and also listed in Table A.3) and also is used to avoid confusion with the specific enthalpy  $h$ .

1.1 Principal Carriers: Phonon, Electron, Fluid Particle, and Photon 5

Table 1.2. Thermal equilibrium particle (energy occupancy) distribution (statistical) function  $f_i^0(E_i)$ ,  $i = p, e, f, ph$  and its temperature dependence for principal energy carriers.

Attributes	Phonon	Electron and Hole <sup>a</sup>	Fluid Particle	Photon
Iconic presentation				
Energy presentation	wave vector $\kappa_p$ , dispersion $\kappa_p(\omega_p)$ , and polarization in reciprocal lattice space $\mathbf{g}$	wave vector $\kappa_e$ , band structure (conduction and valence bands), and spins	momentum $\mathbf{p}_f$ , kinetic, potential, and electronic energy states	frequency $\omega_{ph}$ , dispersion $\kappa_{ph}(\omega_{ph})$ , and polarization in real space $s_\alpha$
Particle type	Bose–Einstein (boson)	Fermi–Dirac (fermion)	Maxwell-Boltzmann (M–B)	Bose–Einstein (boson)
Nature of particle	particles are indistinguishable, integer spin (angular momentum), and any number of particles may occupy a given eigenstate	particles are indistinguishable, odd, half-integer spin (angular momentum) and obey the Pauli exclusion principle (only one particle may be found in a given quantum state)	particles are distinguishable, and any number of particles may occupy a given eigenstate (classical particle or nondegenerate limit)	particles are indistinguishable, integer spin (angular momentum), and any number of particles may occupy a given eigenstate
Equilibrium distribution (occupancy) function, $f_i^0(E_i)$	$\frac{1}{\exp(\frac{E_p}{k_B T}) - 1}$	$\frac{1}{\exp(\frac{E_e - \mu}{k_B T}) + 1}$	$\frac{1}{\exp(\frac{E_f}{k_B T})}$	$\frac{1}{\exp(\frac{E_{ph}}{k_B T}) - 1}$
Energy	$E_p = E_{p,p} + E_{p,k} = \hbar\omega_p$	$E_e = E_{e,p} + E_{e,k}$ $E_{e,k} = \frac{\hbar\kappa_e^2}{2m_e}$ $\mu$ is chemical potential $\mu = E_F[1 - \frac{1}{3}(\frac{\pi k_B T}{2E_F})^2]$	$E_f = E_{f,t} + E_{f,v} + E_{f,r} + E_{f,e} + E_{f,p}$ $E_{f,t} = \frac{p_f^2}{2m_f}$ $E_{f,v} = (l + \frac{1}{2})\hbar\omega_f$	$E_{ph} = E_{ph,e} + E_{ph,m}$ $E_{ph} = \hbar\omega_{ph}$

$\hbar = h_P/2\pi$  and  $k_B$  are the reduced Planck and the Boltzmann constants  
 $k_B T = 0.02585$  eV for  $T = 300$  K

<sup>a</sup> Holes are represented by  $h^+$

A general relation can be used for all particles as  $f_i^0 = \frac{1}{e^{(E_i - \mu)/k_B T} + \gamma}$ , where  $\gamma = 1$  (fermion), 0 (M–B),  $-1$  (boson).

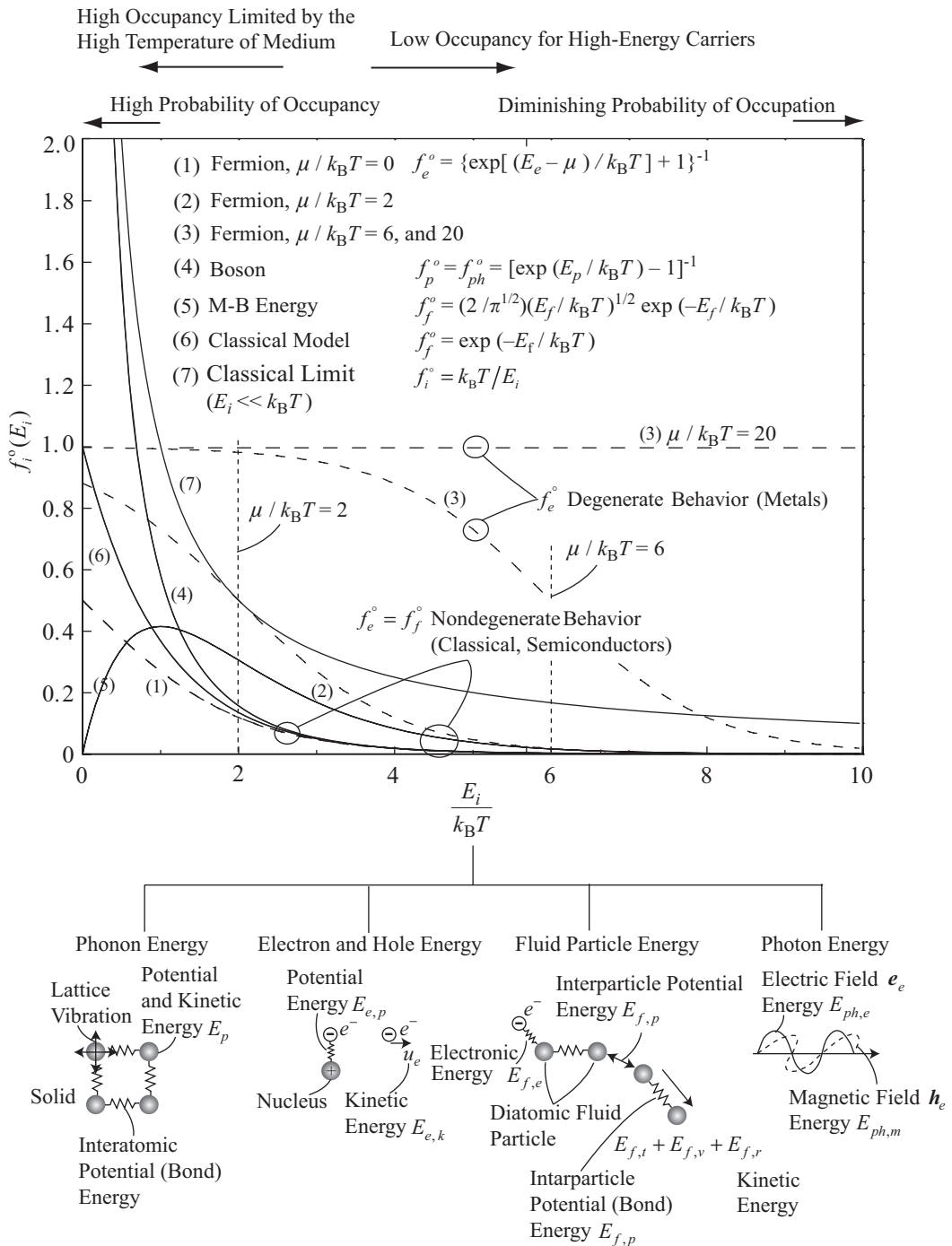


Figure 1.1. Variation of equilibrium particle (energy-state occupation) distribution function with respect to energy (scaled with respect to thermal fluctuation energy  $k_B T$ ) for different energy carriers. For fermions, three different reduced chemical potentials  $\mu / k_B T = E_F / k_B T$  (Fermi energy) are used. Conduction electrons in metals have a highly degenerate behavior. The high-energy (low population) approximation (nondegenerate behavior) for electrons and holes in semiconductors is also shown (discussed in Section F.5 in Appendix F). The classical limit distribution function is also shown. Various contributions (e.g., kinetic and potential) to the total energy of each principal carrier, are also shown. The photon energy is divided between electric and magnetic energies.

arise in lattices with more than one atom per unit cell, always have some minimum frequency of vibration, even when their wavelength is infinite. They are called optical, because in ionic crystals (such as NaCl) they are excited very easily by light (such as infrared radiation). This is because they correspond to a mode of vibration where positive and negative ions at adjacent lattice sites move, thus creating a time-varying electric dipole moment. Optical phonons that interact in this way with light are called infrared active. Optical phonons, which are known as Raman active, can also interact indirectly with light, through Raman scattering (an inelastic scattering of a photon that creates or annihilates an optical phonon). Optical phonons are often abbreviated as LO and TO for the longitudinal and transverse varieties, respectively (although they are readily distinguishable for low-symmetry crystals).

### 1.1.2 Electron (and Hole)

Electrons store heat and potential energy and here are divided into conduction and bound electrons. The electron  $e^-$  is a charged subatomic particle. In an atom, electrons surround the nucleus, made of protons and neutrons, in a manner termed the electronic configuration (or structure). The electron is among a class of subatomic particles called leptons, believed to be fundamental particles (i.e., they cannot be divided into smaller constituents). The electron has a spin of  $1/2$  (which makes it a fermion), and follows the Fermi–Dirac statistical energy distribution  $f_i^0$  (Table 1.2; derivation is given in Appendix F). These distributions are based on the equipartition of energy and the partition function, and are dictated by the statistical mechanics–thermodynamics laws and relations).

Electrons can exhibit properties of both particles and waves, and thus can be treated as quasi-particles. An electron bound to a nucleus behaves as a standing wave (due to the periodic boundary condition).

For matter in the solid state, electrons are responsible for bonding within crystals; they hold the nuclei together. These bonds belong to one of four types: van der Waals, ionic, covalent, or metallic. The Fermi surface is the set of loci in electron momentum space with zero excitation energy. The topology of the Fermi surface is important in understanding the electronic properties of materials. Electrons in solids are divided into core and outer electrons. Core electrons do not participate in bonding and are assumed to move with the nucleus at all times. Outer electrons reside farther away from the nucleus, and are in turn divided into conduction (or free) electrons and valence electrons.

In quantum mechanics, the electron is described by the Dirac equation. In the Standard Model of particle physics, it forms a doublet in  $SU(2)$  with the electron neutrino, as they interact through the weak force.<sup>†</sup> The electron has two variations

<sup>†</sup> The Standard Model is a quantum field theory and is the union of quantum chromodynamics and the electroweak theory. In the Standard Model, there are 16 fundamental particles: 12 particles of matter (fermions of spin  $1/2$ ) and 4 force carrier particles. The fermions are six quarks (up, down, charm, strange, top, bottom) and six leptons (electron, electron neutrino, muon, muon neutrino, tau, tau neutrino). The gauge bosons or force carriers mediate the strong, weak, and electromagnetic

with the same charge but different masses: the muon and the tauon. The antimatter counterpart of the electron, its antiparticle, is the positron. The positron has the same amount of electrical charge, mass and spin as the electron, except that the charge is positive.

The variation of the three equilibrium distribution functions [boson, fermion, and Maxwell–Boltzmann (M–B)] with respect to dimensionless (scaled) energy are shown in Figure 1.1. For electrons, the chemical potential  $\mu$  is the datum of energy, and the results for a few values of the scaled (also called reduced) electron chemical potentials  $\mu/k_B T$  are also shown. All distributions become similar to the classical distributions for large energies (for electrons also in the case of small  $\mu$ ). As will be discussed in Section 2.6.5 (metals) and 5.7 (semiconductors), the number density of conduction electrons is related to the chemical potential (Fermi energy), and because semiconductors have smaller conduction electron density, their chemical potential is smaller than that of metals. As shown in Figure 1.1, whereas the occupation probability of conduction electrons in metals is high and subject to exclusion principle (degenerate), that of semiconductors is low and is generally treated with the nondegenerate, classical distribution.

For a general treatment, the energy of electron (and hole  $h^+$ ) are divided into potential (representing its bond energy) and kinetic (representing its velocity) energy. Electron (or hole) is a charge particle (single charge), other charge particles (e.g., ions) also transport heat (as current). For example in proton transport, this particle is much larger and heavier than an electron, and therefore, has a much smaller velocity and requires vacancy or surface to travel (hop).

### 1.1.3 Fluid Particle

Fluid particles temperature is due to their kinetic energy (thermal motion). Gases and liquids are composed of single atoms or molecules (here broadly termed fluid particles), which can be neutral or charged, in motion. The fluid particle (see Glossary) energy is divided into potential (among atoms), electronic, and kinetic energy. The fluid specific volume is fixed under constant temperature and pressure, and its shape may be determined by the container it fills or through cohesive forces such as surface tension. The moving particles constantly collide with each other (and, possibly, with the container wall). In ideal gas behavior, the collisions between the gas particles are elastic (energy is conserved among colliding particles) and the forces of attraction between the particles are negligible. For ideal gases, the M–B distribution  $f_f^0$  (Table 1.2 and Figure 1.1; derivation is given in Appendix F) can be derived

fundamental interactions. An additional particle, known as the Higgs boson, must also be included to explain why the other 16 have mass. It is also proposed that particles acquire their mass through interactions with an all-pervading field, called the Higgs field, which is carried by the Higgs boson. It is accepted that the Standard Model cannot be a fundamental theory of nature because it does not embrace gravity and only makes sense if viewed as a low-energy approximation. The quantum group theory deals with noncommutative algebra with additional structure, and the special unitary group of degree  $n$ , denoted by  $SU(n)$ , which is the group of  $n \times n$  unitary matrices with determinant 1 [[176]].



by use of statistical mechanics (and the concepts of energy partitioning and symmetry). In polyatomic-gas lasers, e.g.,  $\text{CO}_2$ , the population distribution deviates from equilibrium (population inversion is created). So, in both the energy transport and conversion involving fluid particles, nonequilibrium distribution occurs. Figure 1.1 also shows various contributions to the total energy of the fluid particle (translational, vibrational, rotational, electronic, intraatomic, and interatomic potential). For these ideal, noninteracting particles in the ground state, all energy is only in the form of kinetic energy, and (by use of the equipartition energy principle) each mode has a kinetic energy equal to  $k_B T/2$ . This corresponds to the most probable energy distribution, in a collision-dominated system consisting of a large number of noninteracting particles with no net motion, but with a nonzero root-mean-square (RMS) thermal fluctuation velocity  $\langle u_T^2 \rangle^{1/2}$ . This velocity is related to the speed of sound in fluids  $a_s$ , and is temperature dependent. So, the probability of occurrence of very-high velocity fluid particles decreases as the temperature decreases.

A liquid is considered to be a substance that's particles have enough kinetic energy to stretch the intermolecular forces of attraction, but not completely overcome them (so their densities are close to solids). Collisions thus occur between the particles more often than in gases (ideal or otherwise). As the temperature of a liquid is raised, the velocity of the particles increases. The kinetic energy eventually becomes so great that the particles overcome all intermolecular forces and move freely, thus becoming a gas.

#### 1.1.4 Photon

Photons are emitted from matter according to its temperature and also by other excitations. A photon (Greek for light) is a quantum of excitation of an electromagnetic field, and is also an elementary particle in quantum electrodynamics (QED), which is part of the Standard Model of particle physics. Photons are thus the building blocks of EM radiation, some of which we observe as light. According to quantum mechanics, all particles, including the photon, have some of the properties of a wave. Photons have zero invariant mass, but a definite, finite energy. Because they have energy, the theory of general relativity states that they are affected by gravity, something that has been confirmed by experiment.

Photons have a spin of 1, which makes them bosons ( $f_{ph}^o$  in Table 1.2). This is the equilibrium distribution, as in blackbody radiation. However, lasers have highly nonequilibrium distributions (amplified, stimulated emission). Photons act as mediators to the EM spectrum; they are the particles that enable other particles to interact with each other electromagnetically and with an electromagnetic field. Individual photons are circularly polarized (as compared to electrons that have a spin up or spin down) because of their unit spin. They travel at the speed of light,  $u_{ph}$  (or  $c$ ), and their lifetime is infinite, although they can be created and destroyed.

In general, an EM field consists of plane, monochromatic waves, of frequency  $f$  (angular frequency  $\omega = 2\pi f$ ), wavelength  $\lambda$ , and speed  $u_{ph}$ , with  $\omega_{ph} = 2\pi u_{ph}/\lambda$ .

The quantum property of an EM waves is given by its energy  $E_{ph} = \hbar\omega$ . The photon also has a quantum momentum  $\mathbf{p} = \hbar\boldsymbol{\kappa}$ , where  $\boldsymbol{\kappa}$  is the wave vector and the wave number  $\kappa = 2\pi/\lambda$ . Note that for a classical particle, the energy is  $p^2/2m$ , i.e., it is proportional to  $p^2$ .

In a vacuum, the dispersion relation of photons (the relation between angular frequency or energy and wave vector or momentum) is linear, and the constant of this proportionality is the Planck constant.

In matter, photons couple to the excitations (polarizing vibration, electric and magnetic) of the material. These excitations can often be described as quasi-particles (such as phonons and excitons defined in Glossary) with quantized wave-like or particlelike entities propagating through the material. Photons can transform into these excitations (that is, a photon is absorbed and the medium is excited, creating a quasi-particle) and vice versa (the quasi-particle transforms back into a photon, i.e., the medium relaxes by re-emitting the energy as a photon). These transformations are subject to probability rates and are presented as a polariton (Glossary). This is a quantum-mechanical superposition of the energy quantum being a photon as well as being one of the quasi-particle, matter excitations (such as photons). According to the rules of quantum mechanics, a measurement breaks this superposition; that is, the quantum is either absorbed into the medium and stays there, or it reemerges as a photon.

Matter excitations (photon emissions) have a nonlinear dispersion relation, and their momentum is not proportional to their energy. Hence, these particles propagate more slowly than the speed of light in vacuum (Section 3.3.1). The propagation speed is the derivative of the dispersion relation with respect to momentum (angular frequency with respect to wave vector). A photon, by coupling with the excitation of matter and forming a polariton, acquires an effective mass, which means that it cannot travel at speed of light in vacuum.

## 1.2 Equilibrium and Nonequilibrium Energy Occupancy Distributions

### 1.2.1 Nonequilibrium Energy Carrier Occupancy by Energy Conversion

Nonequilibrium atomic motion (mostly as vibration in solids and in polyatomic fluids) is formed in the initial states of the energy conversions. As examples, in Figures 1.2(a) to (c), the time (and entropy) evolution of the energy in solar, chemical bond, and nuclear fission conversion are shown. Initially the energy is not converted to atomic motion (e.g., phonon in solids), and this period is called the pre-phonon period. In these examples we also show how nonequilibrium atomic motions can be harvested, with early interventions (e.g., prior to thermalization, which creates equilibrium population distributions for these atomic motions, or by the recycling of equilibrium phonons).

When solar energy is absorbed in semiconductors, electron and hole pairs are created and experience various processes of energy conversion as shown in Fig. 1.2(a). Overpopulated electron-hole pairs decay by three recombination mechanisms (radiative, Auger, and Shockley-Read-Hall). The electrons are also relaxed