1

Introduction to Thermal Properties of Materials

Rui Feng and Chengyi Song

State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, P. R. China

This introductory chapter encompasses the basic principles and calculation methods for the heat transfer process and the advanced thermal properties. Various thermal applications of bioinspired functional materials will also be briefly discussed. To elucidate the basic principles of thermal theory, several analytical examples involving heat source and boundary conditions, uniform and nonuniform mesh structures, multiphase transfer, phase change, and convection in fluidic cases are also described. Noticing that micro/nanoscale materials exhibit unique thermal properties in modern materials scientific research, in this chapter the new developments in micro/nanoscale heat transfer theory are also discussed and some of the theoretic solutions drawn in calculating the thermal conductivity of micro/nanomaterials are shown. Biological systems set numerous examples in teaching humans how to collect, convert, and harness thermal energy from nature. In the last section of this chapter, practical approaches are discussed in an overview of bioinspired thermal materials. Typical thermal applications of functional materials (e.g., thermal nanofluids such as nanosuspension of colloidal particles in solution, the rapid charging of thermal energy storage, the phase change energy conversion by photothermal membrane, and the sensing of infrared radiation by bioinspired materials) are presented to show how the modern conventional and micro/nano heat transfer theory is related to advanced thermal functions of bioinspired materials.

1.1 Conventional Macroscale Heat Transfer

Heat transfer forms a vital kinetic force in the maintenance of the basic energy operation of the whole natural system for the activities of all the creatures on earth. As an engineering discipline, the inherent laws of heat transfer do not merely explain the way of energy transportation but also deal with the thermodynamics of both objects and the equilibrium principle under specified conditions. Fundamental learning of the equilibrium principle is provided by the first and second laws of thermodynamics, and follows the classic mechanics of

conduction, convection, and radiation. In the following sections, the conduction, convection, and radiation of macroscale heat transfer problems will be shown and the working principles formulated by energy equations. In thermal physics and engineering problems, we use critical quantitative criteria to characterize the thermal properties of material. These thermal properties are modified as representations of thermal energy transportation and energy conservation models, and can be used to analytically or numerically solve problems in thermal engineering and nature. Therefore, in the following sections, the basic principles of thermal transfer will be introduced first through a discussion of the thermal energy transportation and energy conservation models.

1.1.1 Normalization

To describe the process of heat transfer based on quantitative criteria, the primary quantities involved in a thermal process are listed in Table 1.1 and the quantitative criteria of thermal process are derived by these basic units. For analyzing much more complicated situations, the units of some derived quantities in Table 1.2 are defined as scientific descriptions of thermal properties of materials. Especially in numerical calculations and study of material heat transfer models, these derived units such as specific heat capacity C_p, thermal conductivity κ, heat flux q and thermal diffusivity α in thermodynamics cases will facilitate the systematic learning and understanding of the details of heat transfer.

In developing and judging thermal properties of new materials, normalizing the units of critical parameters may help us to better learn and understand different thermal properties.

1.1.2 Thermal Equilibrium and Nonequilibrium

Thermal equilibrium and nonequilibrium are the descriptions of the energy state of a thermal system. In an isolated steady thermal system, the state of thermal equilibrium will become stable without any external energy input. Once higher/lower temperature occurs at a specific point of the system, local thermal nonequilibrium exists. Meanwhile, the temperature difference will force the thermal energy to be transported from a region with higher temperature to a region with lower temperature. The system will eventually be in an equilibrium state after a spontaneous transformation process. The process of turning

Table 1.1 Basic parameter units.

Primary quantity	Parameter
Length	L (m)
Time	t (s)
Mass	m (kg)
Temperature	T (°C or K)
Current	J_e (A)

Table 1.2 Parameter units driven by the primary quantities in Table 1.1.

Driven quantity	Parameter
Specific heat capacity	C_p (J/kg K)
Energy	E (J or N m)
Force	F (N m/s^2)
Electric charge	C (coulomb or A s)
Thermal conductivity	k (W/m k)
Pressure	p (Pa or N/m^2)
Heat flux	q (W/m^2)
Heat efficiency	Q (W or J/s)
Velocity	V (m/s)
Viscosity	μ (Pa s)
Density	$A \rho$ (kg/m^3)
Potential	Φ (V or W/A or J/C)

nonequilibrium into equilibrium is dominated by temperature difference. The gradient of temperature difference triggers heat diffusion, which can be ascribed to thermal conduction, thermal convection, and thermal radiation. However, temperature difference in a system does not always dominate thermal energy transportation. Thermal energy transportation can also occur in some cases of nonequilibrium heat transfer including phase change and chemical exothermic reaction or chemical endothermic reaction. The kinetic driving forces in these cases are latent heat and chemical energy. Therefore, the thermal nonequilibrium of a system should be described as the nonequilibrium of energy states to some extent rather than the internal temperature differences.

1.1.3 Integral Structural Heat Transfer

Heat transfer in different media that is induced by thermal nonequilibrium may have different characteristics. The numerical analysis of heat transfer in the integral structure with control surface A and control volume V as boundary is defined as

$$q_{\text{heat}} = q_k + q_u + q_r$$
$$Q = \int_A (q_{\text{heat}} \cdot s_n)\mathrm{d}A = \int_A [(q_k + q_u + q_r) \cdot s_n]\,\mathrm{d}A \tag{1.1}$$

With this definition, a schematic of the outward, normal unit vector pointing out a control volume V and control surface A is shown in Figure 1.1a. The dot s_n represents location of the per unit energy state (surface normal vector) on a differential surface area. By integrating the entire surface A, when q is parallel to the surface, the dot product of q and s_n will become zero, which means no heat flows across the control surface. And if q is perpendicular to normal surface s_n,
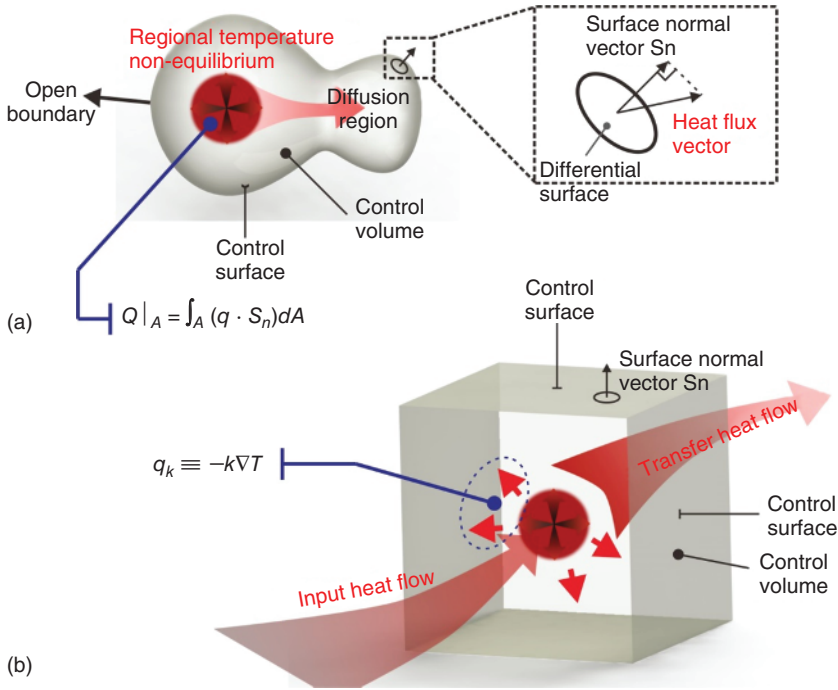
Figure 1.1 Schematic graphs of heat conductance and transfer. (Adapted from Kaviany 2011 [1].)

the dot product will be maximum.

$$Q = \int_A (q \cdot s_n)\mathrm{d}A = \begin{cases} > 0 \\ < 0 \\ 0 \end{cases} \tag{1.2}$$

In Eq. (1.2), when the integration of the dot product is a positive quantity, heat flux flows out of the control surface; when it is negative, heat flux flows into the control surface. When a unit control volume owns a higher/lower energy state than its surrounding medium, the region with higher temperature will transport the thermal energy to a region with lower temperature. The total energy in control volume Q represents the sum of the energy integration of the surface area.

The heat flow through the control surface and volume is shown in Figure 1.1b [1], where a rectangular matter in Cartesian coordinate system receives inward energy from an external medium. The heat energy flow into this rectangular matter implies an increase in total energy. The transport of the heat shows the directional quantity, which can be expressed as a product of thermal conductivity and temperature divergence.

1.1.4 Control Volume and Interface

The boundaries of thermal system in the aforementioned model of a control volume and interface heat conductance will be studied and defined as

limitation condition. Heat is forced to diffuse from a high-temperature point to a low-temperature point by local temperature nonequilibrium, and passes through the control interface into another medium. The boundaries of control surface can be at the interface (gas–liquid or liquid–solid interface) between two phases or just within the integral structure. The configuration is represented in Figure 1.2 where a spherical gas/liquid/solid phase exists at the initial position and with different phase surroundings. Discontinuous thermodynamic and transporting properties occur outside of the spherical phase interface [1]. For a droplet or particle within a higher temperature region than the surrounding atmosphere, the thermal nonequilibrium drives heat diffusion outward from the liquid/solid phase.

Another example is the gas–gas phase heat transfer analysis. Owing to the penetration and diffusion of gas molecules, the initial control surface will be involved in the heat transfer. In addition, mass transfer must also be taken into consideration. A more comprehensive analysis of the heat transfer involving molecule diffusion will be discussed in Section 1.2.2, and typical examples of solid–liquid phase, solid–gas phase, and liquid–gas phase, and even three-phase matter are shown in Section 1.1.5.
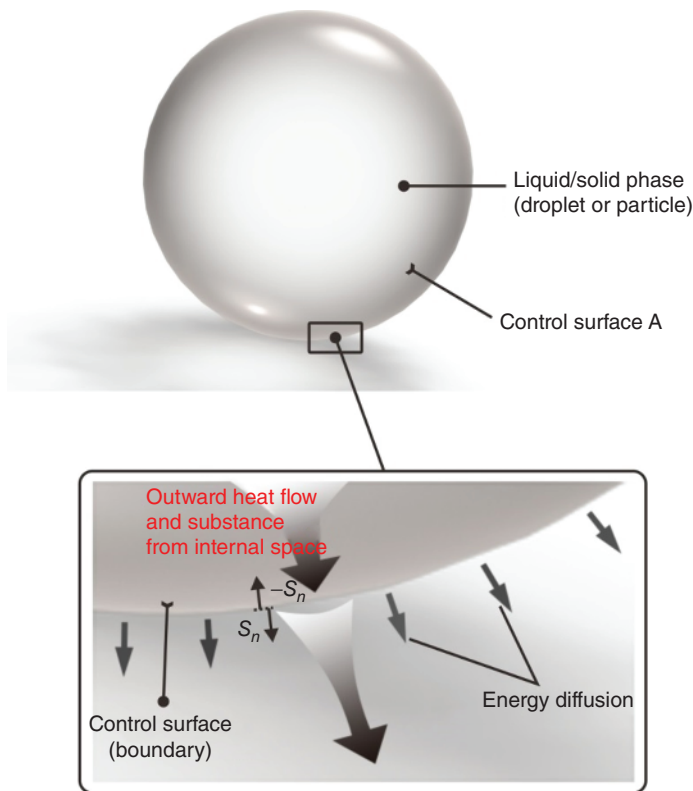

Figure 1.2 Interface between liquid/solid/gas phase. (Adapted from Kaviany 2011 [1].)

1.1.5 Conduction in Single and Multiphase Medium

In many cases, the heat transfer medium can be a single-phase material or multiphase materials. Thus, there are various descriptions of single-phase and multiphase matter; for example, the composite's heat conduction or convection with fluid motion leads to an unambiguous solution because of vast variations in geometry and the uncertainty of the initial interface and boundary conditions. This section discusses the principles of conducting transfer analysis in different phases and provides several typical single-phase and multiphase examples.

1.1.5.1 Single-phase Medium

Thermal energy transportation in the integral structure of only one element can be modeled as a single-phase medium such as saturation gas, purified liquid, solid monocrystal, and compounds made of chemical elements (e.g., water, silica, aluminum oxide). For multidimensional single-phase systems, some materials depend on Fourier's law of heat conduction. For example, cylindrical and spherical structures can be well applied for calculating heat flow power or thermal conductivity of materials.

In a one-dimensional single-phase medium, thermal energy transportation is generally considered as the heat conduction along one direction. The process of heat conduction along the x-axis is formulated by $q = -kA\frac{\mathrm{d}T}{\mathrm{d}x} = -\frac{\mathrm{d}}{\mathrm{d}t}\rho c_p T + \dot{s}$, where q represents heat flux, k is the thermal conductivity of the material, A is the surface area of the thermal energy flowing out, ρ is the density of the material, and C_p is the specify heat capacity. The conductive equation is numerically equal to the differential energy storage equation. In a two-dimensional or three-dimensional single-phase material system, the conductive heat flux q represents the magnitude, direction, and spatial–temporal variations, where $\nabla \cdot q = -\nabla \cdot k\nabla T$ can be defined as the spatial-rate conductive energy equation.

1.1.5.2 Multiphase Composite Medium

In many thermal conduction problems, more than one phase is present (gas, liquid, and solid). A multiphase medium, such as $0°C$ ice–water mixture, displays various conditions; it can be treated as a solid–liquid two-phase medium whose inner thermal energy transportation shows energy differences between ice and water. Normally, multiphase media also can be categorized as continuous and disordered structures: (i) a multilayer composite film is a continuous multiphase material and (ii) a doping alloy or cement brick is a disordered multiphase material. Thermal energy transportations among these different types of multiphase media display different time domain and property domain performances. Furthermore, once the thermal nonequilibrium state turns into a thermal equilibrium state, thermal energy will probably be converted into other forms of energy such as mechanical energy, electrical power, electromagnetic energy, or chemical energy.

Beyond the simple cases of thermal analysis in the single-phase material such as solid, liquid, and gas, the combination of two or three phases or even more phases seems to be more complicated for thermal analysis.

For a multiphase composite material, the interface effect (gas–liquid, gas–solid, liquid–solid) and layer thickness should be considered in thermal analysis. The gas–liquid–solid three-phase interfaces may result in quite different heat conducting performances (Figure 1.3). In Figure 1.3a, a cross section of a double-layered solid composite film is set in a rectangular isolated boundary (ultrahigh thermal resistance) area. The thermal energy unit with nonequilibrium tendency starts to diffuse from its control volume to the surrounding layer, and the local temperature decreases by conduction and body radiation. The interface between the two layers may lead to a critical change in heat transfer rate because of the resistance at the two-phase contact, and the difference in thermal conductivity between two layers leads to different heat transfer rates in each phase. Generally, in the same medium, the thermal energy transfer rate will more or less constant.

However, in a solid–liquid composite case (Figure 1.3b) of condensed liquid on a solid wall, the thermal energy transfer between the solid and liquid layers may induce liquid intermolecular reactions on the two-phase interface (convection). Thermal convection occurs in the liquid layer where fluid convection will accelerate the thermal energy diffusion and cool the liquid faster. Another similar example is the gas–liquid medium, where instant evaporation occurs at the gas–liquid interface. When the liquid is overheated, it will become more "fuzzy" under a fierce phase change procedure and the evaporation rate will be enhanced. The latent heat of the phase change medium should be considered in this case.

The particular example of oil–water emulsion is discussed in Figure 1.3c,d. Besides complex interactions between individual oil droplets and surrounding water, the thermal energy transfer rate in the emulsion also depends on
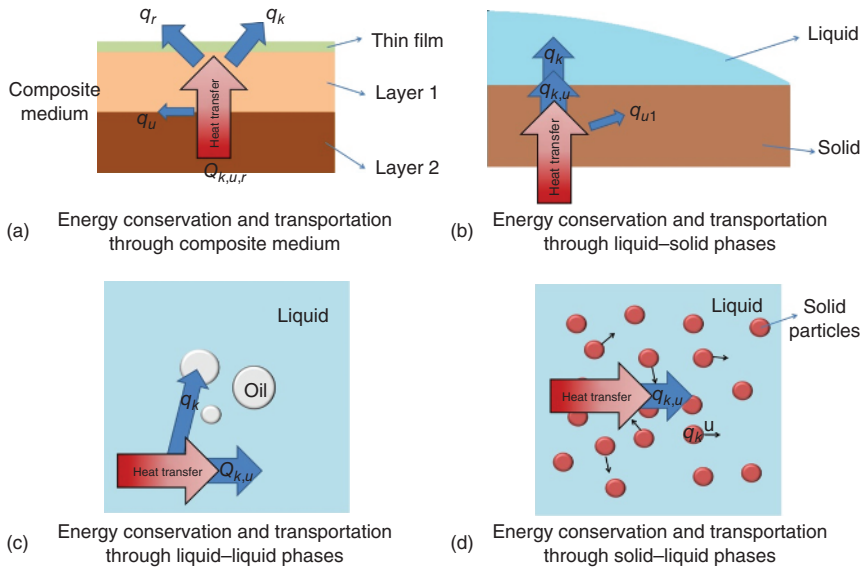

(a) Energy conservation and transportation through composite medium

(b) Energy conservation and transportation through liquid–solid phases

(c) Energy conservation and transportation through liquid–liquid phases

(d) Energy conservation and transportation through solid–liquid phases

Figure 1.3 Various heat transfer cases on solid composite film, condensed liquid on the wall, oil–water solution and solid particles disperse in liquid, respectively.

various physical quantities such as the geometry of oil droplets, the superheat temperature of the droplet, and other hydrodynamic parameters involving the heat transfer behavior under the same conditions. However, the surface tension gradient and viscosity may induce an internal Marangoni convection effect, which will help the energy to diffuse to other spaces. This type of thermal phenomenon can find its model in the heat transfer of liquid/gas in a solid porous medium.

A three-phase heat transfer case is the boiling experiment in a container. When saturated steam bubbles attach on the superheated wall, there occurs the gas–liquid–solid phase situation for the thermal energy transfer process.

More details of heat transfer analysis for thermal materials are shown in the later chapters, where some of the materials are composed of a single medium or can be simplified as one single medium in the practical thermal engineering case. In other complex thermal applications, both continuous and disordered heat transfer analysis for materials consisting of at least two heterogeneous mediums are considered. For example, the mutual diffusion/penetration of various gas molecules in gas/liquid/solid three-phase media displays an extremely complicated situation for heat analysis. It is also necessary to realize that not all mechanisms of conduction, convection, and radiation are obvious in every phase of matter. For example, the thermal radiation from heated carbon is almost the same as blackbody but transparent to air. Thus, in many cases of thermal analysis, volumetric radiation heat transfer of gas is generally neglected. The treatment of heat transfer in a fixed mesh solid material also involves ignoring convection heat transfer.

1.1.6 Heat Capacity

In a system, heat transfer not only passes the thermal energy through different media of single/multiphase material but also raises the temperature of the medium. The quantitative characterization of the ability of a material to store the thermal energy is defined as the *heat capacity*. The specific heat capacity is defined as the energy rise per unit temperature rise per unit mass. The capacity increase (intermolecular reaction) under an apparent specific heat at constant pressure is

$$c_p = \left. \frac{\partial Q}{\partial T} \right|_p \to \infty \tag{1.3}$$

As a consequence of the third law of thermodynamics, a solid material shows heat capacity $C_p = 0$ at $T = 0$ K. In general, molecules with a small molecular weight have a high heat capacity. The comparison of C_p of various common materials is illustrated in Figure 1.4. The arrow in the scheme shows that hydrogen (gas) has the highest heat storage capacity compared to the other elements (at constant room temperature), and heavy metals in general have low heat capacities [1]. Water has a relatively higher heat capacity ($C_p = 4.2$ kJ/kg K) than most liquid elements in the list except helium gas. More specifically, heat capacity changes with the material's temperature, phase of the medium (density),
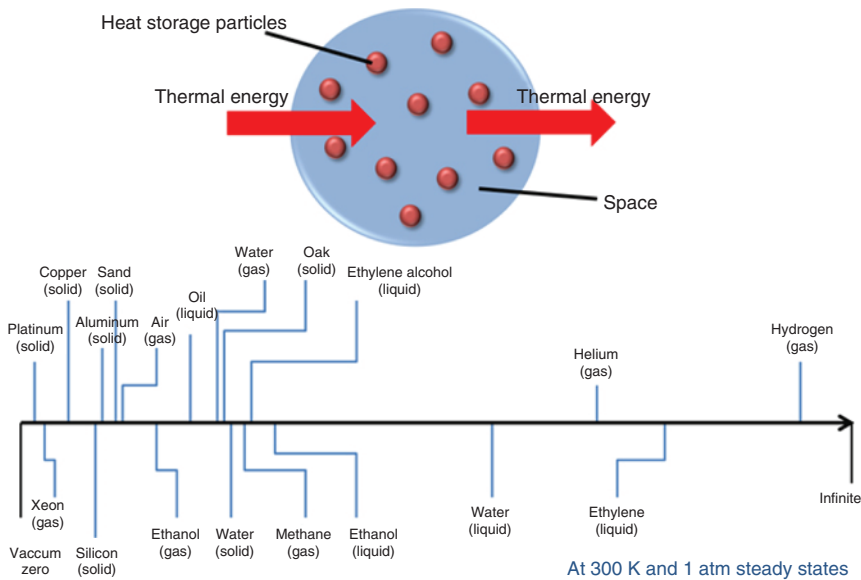
Figure 1.4 Thermal capacity of various materials. (Adapted from Kaviany 2011 [1].)

and the ambient pressure. The change in heat capacity of the liquid phase and the gaseous phase strictly obeys a physical rule: the C_p of these materials increases when their density decreases.

Heat capacity can be characterized by the states of thermal energy such as translational, rotational, and vibrational motions with a collective excitation in molecules or atoms. For a heat conduction process, a phonon is treated as the heat carrier to exchange heat within the integral structure. The specify heat capacity is related to the ability of the phonons to store and release the thermal energy, which can be described as the energy states of material.

1.1.7 Phase Change

As a significant phenomenon of heat storage, a heated burner for boiling water not only involves the temperature change of water but also a phase change process. During the phase change process, the absorbed energy is converted into latent heat to provide the dynamic force for a phase change. The heat that can be sensed before approaching the phase transition point is considered as a thermal storage within the matter. The phase change represents the input energy offsetting the interacting force between molecules or atoms (van der Waals force, electromagnetic force, etc.) by enlarging the kinetic force of molecules or changing the atomic binding modes. Hence, solid melts into liquid by increasing the intermolecular distance. Similarly, liquid evaporates into vapor and gas forms into plasma gases of ions when the cations and anions are separated. Although the classic theory gives empirical solutions of the phase change process based on experiments and energy equations, these solutions cannot thoroughly describe

the molecular reactions in phase change, and also cannot accurately describe the micro/nanoscale heat transfer problems.

The next section presents a brief discussion of the micro/nanoscale thermal transport problems in gases (or liquid). The results show how the thermal conductivity of gases and fluids is related to microscale properties such as velocity, mean free path, molecular density, and microstates. Then, the relation between conduction in liquids and in solids involving phonons and electrons will be described.

1.2 Micro/Nanoscale Heat Transfer

All energetic processes can be derived through quantum mechanics by analyzing the interplay and immigration of protons and photons. Figure 1.5 shows the variation of thermal physics at different mass scales. At minimum scale of this system ($\sim 10^{-30}$ kg), the thermodynamics of protons and electrons can be ascribed to quantum mechanics [2]. Energy transportation of each quantum can be expressed as the interplay of tiny particles, quantized lattice vibration, immigration of ions and electrons, and emission and absorption of photons.

Recognizing the natural law of thermal energy transportation at the microscale range will help us analyze and learn from these phenomena. From continuous media effect to quantum effect at different mass scales, corresponding theories are used to characterize the energy processes among matters. As shown in Figure 1.6 [3], there are four related theories for multiscale heat transfer problems, where these scale effects occur at quantum, atom, molecule, and matter levels.

1.2.1 Micro/Nanoscale Heat Carriers

Each thermal process experienced by a micro/nanomaterial in the nonequilibrium state requires heat carriers. A heat carrier is described as a basic unit vector that has extra heat energy in heat transfer. Heat carriers can be phonons, thermal electrons, crystalline solids, or molecules. For the heat conduction process of a nonequilibrium system, the quantization of heat carriers' excitation or motion achieves thermal energy transfer in the system. In some solid crystal heat transfer problems, the phonon is treated as the heat carrier to exchange heat within the integral structure via lattice vibration.

Among gases, liquid, and the fluidic motion system, random collisions occur during the thermal process. The frequency of these motions is determined by the average distance traveled before collision of one molecule with another in the system, which is called the mean free path. It is the average path of energy delivery charged by random motion displacement within micro/nano objects and is widely used for quantitating the kinetic process occurring in the micro/nanoscale objects.

The measurable value of disorder and randomness in a system that helps statistically predict the energy exchange behavior of a nonequilibrium system is
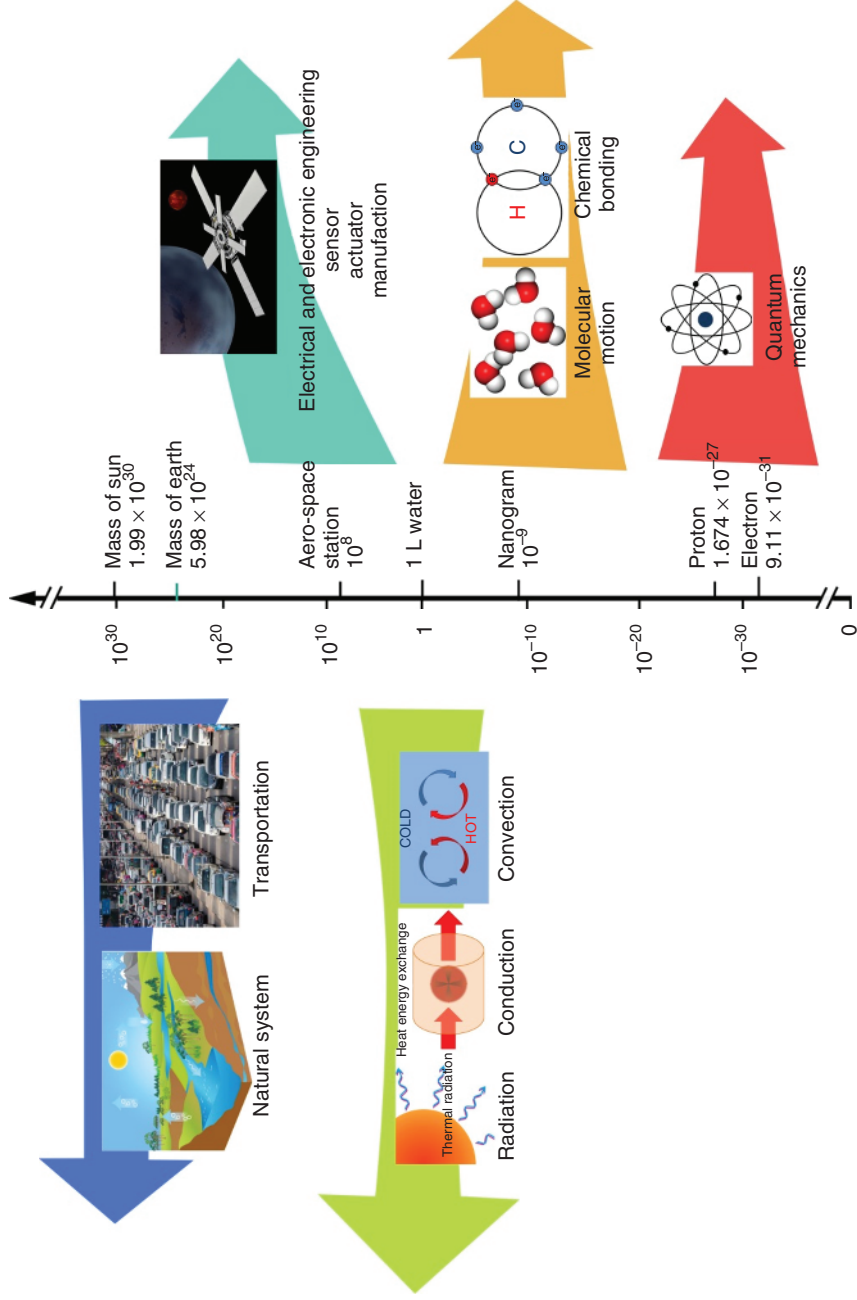
Figure 1.5 Thermal theories at different mass scales: at the known minimum scale of $\sim 10^{-30}$ kg, the corresponding theory is the quantum mechanics that relates the reaction of electrons, proton, atoms, and electromagnetic waves; at larger levels (nanoscale 10^{-9} kg), the related molecular motion and particle reactions can be observed and predicted by manmade microscopic and other instruments. At the normal level of our daily life scale (~ 1 kg), the classic theory of heat transfer involves the basic phenomena of conduction and convection. By applying thermal engineering at aerospace scale ($\sim 10^8$ kg), the utilization of heat energy help us to better explore nature. At about the whole earth scale of 10^{24} kg, the biological water recycling system in nature indicates the essentials of heat transfer.
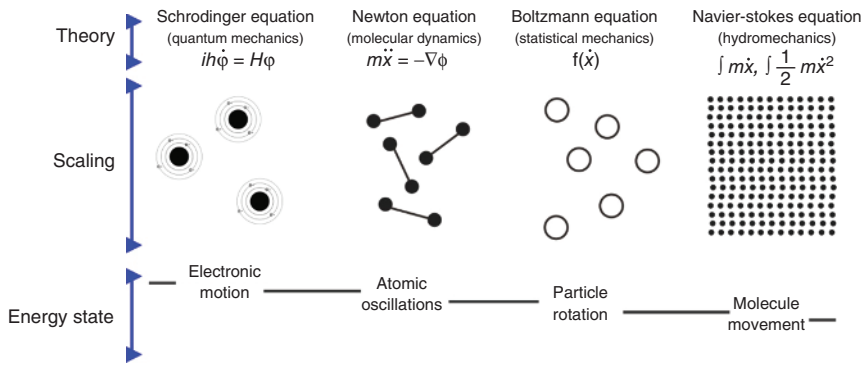
Figure 1.6 Thermal theories at different length scales: For quantum motion problems such as electrons, proton, and atoms, the relative theory is the Schrodinger equation. For elastic bonding or collisions of atoms or molecules, the working principles can be described by Newton's law; for larger rigid particles problems in gaseous or occasionally liquid system, the most used statistical prediction tool is the Boltzmann equation. Furthermore, in integral structure, the motion or the vibration of liquid molecules and crystal can be solved by Navier–Stokes equation [3]

called *entropy*. Entropy is one of the most essential quantities used to describe the number of arrangements or "microstates" in a thermodynamic process. Changing the microstates of material can be treated as the enhancement of the substance's interatomic or intermolecular reactions (Brownian movement), the vibration of the crystalline solids (phonon), and so on. A larger number of microstates mean more randomness of thermal processes in a system. Therefore, the greater the number of possible arrangements for microstates, the higher the entropy is. The randomness includes positional randomness and temperature randomness, which exhibits the distributions of the positional states and energy states of particles/molecules.

In order to predict the randomness and the energy states of a system, relative distributions are required to describe the process of heat exchange and storage under various boundary conditions. There are also several models developed to explain the heat carrier effects of materials at different physical states: (i) Planck distribution for the phonons within the solid state and (ii) Maxwell–Boltzmann distribution for gas molecules. For a more specific case, in a sparsely condensed gaseous system in which gas molecule collisions rarely take place, Bose–Einstein distribution displays a statistic collection of noninteracting tiny particles (nanoparticles (NPs) or molecules) that show local unambiguous energy states at thermodynamic equilibrium. In quantum physics, photons (fermions) that obey the Pauli exclusion principle are generally charged by Fermi–Dirac distribution. Bose–Einstein distribution and Fermi–Dirac distribution can be derived under high-temperature situations while Maxwell–Boltzmann distribution can be derived under low-density gaseous conditions. For most newly developed thermal materials that involve micro/nanoscale, Boltzmann equations and molecular dynamics simulation that are based on direct Monte Carlo simulation method are the general methods to analyze and elucidate their thermal

behavior. The Boltzmann equation is considered a universal analytical theory that deals with molecule dynamic motion and internal reaction. For some referred physical processes that involve quantum effects such as electromagnetic excitation, plasmon effect, or phonon effect, the molecular dynamic equation and Schrodinger equation are assembled in analyzing processes. Otherwise, the adjusted macroscale heat transfer theory can also enable the analysis of some microscale heat transfer cases.

1.2.2   Nanoscale Thermal Dynamic Theory via Boltzmann Equation

Boltzmann transport equation is a widely acknowledged numerical tool. In the particles system of thermal applications, the equation is helpful for analyzing the gaseous/liquid currents with the prediction of particles' species and momentum. Hence, the thermal diffusion of liquid/gaseous system induced by local nonequilibrium can be presented to indicate the kinetic relationship of tiny particles via Boltzmann equation.

A nonequilibrium distribution function determines the probability of a particle with certain position and momentum. Boltzmann transport equation expresses the global nonequilibrium distribution in terms of local equilibrium energy states. Hence, the equation can be used to study a nonequilibrium system by applying the properties of equilibrium systems.

Considering a specific simple example of a two-dimensional system of randomly moving particles with a temperature gradient along the x–y coordinates, whenever a single rigid particle is scattered or collides with the other particles, its processing tendency will be

$$\{f(v + \alpha dt, r + vdt, t + dt) - f(v, r, t)\} dv dt = \left(\frac{\partial f}{\partial t}\right)_{scatter} dv \, dr \, dt \qquad (1.4)$$

where v is the particle velocity, r is the position, t is the current time, and a is the external forcing acceleration. When dt diffuses to zero, we can derive the diffusion equation as

$$\frac{\partial f}{\partial t} + v \cdot \nabla f + a \cdot \frac{\partial f}{\partial v} = \left(\frac{\partial f}{\partial t}\right)_{scatter} \qquad (1.5)$$

The equation, however, does not involve the collisions of the particles. For calculating the energy transportation through particle collisions, an approximated equation of the thermal equilibrium is used, which is called approximation relaxation time mechanics. The colliding function can be written as

$$\left(\frac{\partial f}{\partial t}\right)_{scatter} = \frac{f_0 - f}{\tau(r, a)} \qquad (1.6)$$

where dt can be treated as a function $f(v, a)$ related to velocity and external force. If the period of colliding particles is considered to be a statistical constant, then the Boltzmann equation will be treated as a linear equation, which means

the particles' motion will eventually meet the distribution function f_0 when it reaches equilibrium. Thus, when $a = 0$, the equation will be

$$\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} = -\frac{f - f_0}{\tau} \tag{1.7}$$

This equation simplified by using approximation relaxation time mechanics can be used to derive another heat carrier transportation equation (i.e., energy flux equation):

$$q_{k,r} = \sum_r uf(v, r, t)H(r) = \int uf(v, r, t)H(r)\mathrm{d}r \tag{1.8}$$

To solve the Boltzmann equation containing the distribution function f in Eq. (1.8), where $H(x) = \rho c_p \mathrm{d}x$ is set at the one-dimensional heat conduction of molecules and $\frac{\partial f}{\partial x} = \frac{\mathrm{d}f}{\mathrm{d}T}\frac{\partial T}{\partial x}$ satisfies the approximation condition in this case, Eq. (1.8) can be derived as

$$q_x(x) = -\frac{\partial T}{\partial x} \int v_x^2 \tau \frac{\mathrm{d}f}{\mathrm{d}T} H(x)\mathrm{d}x \tag{1.9}$$

According to the relative energy equation and mean free path mechanics, we can obtain the proper thermal conductivity [1] as

$$\kappa = \int v_x^2 \tau \frac{\mathrm{d}f}{\mathrm{d}T} H(x)\mathrm{d}x = \frac{1}{3}c_v v_x \lambda. \tag{1.10}$$

The heat flux equation of x-direction conduction is shown in Figure 1.7:

For the electron motion or lattice vibration in solids (metal and semiconductors), there will be another problem that is emphasized by the physical coupling
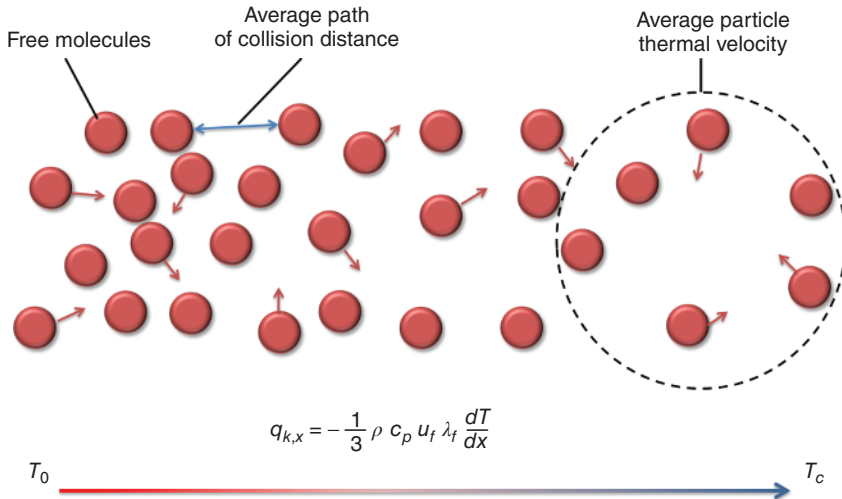

$$q_{k,x} = -\frac{1}{3}\rho \, c_p \, u_f \, \lambda_f \frac{\mathrm{d}T}{\mathrm{d}x}$$

Figure 1.7 The solution of heat carrier collision (heat transfer) as a linear case in Boltzmann equation. (Adapted from Kaviany 2011 [1].)

of thermal energy transportation. The reason is ascribed to the free electrons that play an important role in energy transportation, such as the pyroelectric effect of the metal material, and the semiconductor, which has an intermediate performance between metal and nonmetal solids.

1.2.3 Molecular Dynamics Calculation

Molecular dynamics (MD) is not only a powerful computation-assisted method for understanding the properties of micro/nanostructure but is also a computer simulation technique for exhibiting the behaviors of thermal processes with time evolution. The theoretical assumption of the dynamics of small molecules obeys the classic Newton's law:

$$F_n = m_n a_n \tag{1.11}$$

where each atom n is in a system constituted by N atoms, m_n is the atom mass, $a_n = \frac{d^2 r}{dt^2}$ is the acceleration, and F_n is the force acting upon it due to the interactions with other atoms.

Therefore, in molecular dynamics simulation, the objects are regarded as molecular particles composed of atoms with flexible bonding, which is in contrast with the basic objects in Boltzmann theory that are treated as tiny particles with constant mass and unchangeable structure. It means that in a dynamic process, particles experience not only collisions but also self-rotation, elastic deformation, and even energy conversion during the process [4].

For linear and some simple cases of energy conversion, Boltzmann equation can be derived by MD simulation. It calculates the time-dependent behavior of a molecular system (Figure 1.8). The derivation of Boltzmann equation from Monte Carlo algorithm can be used not only in rare gaseous molecule systems but also to
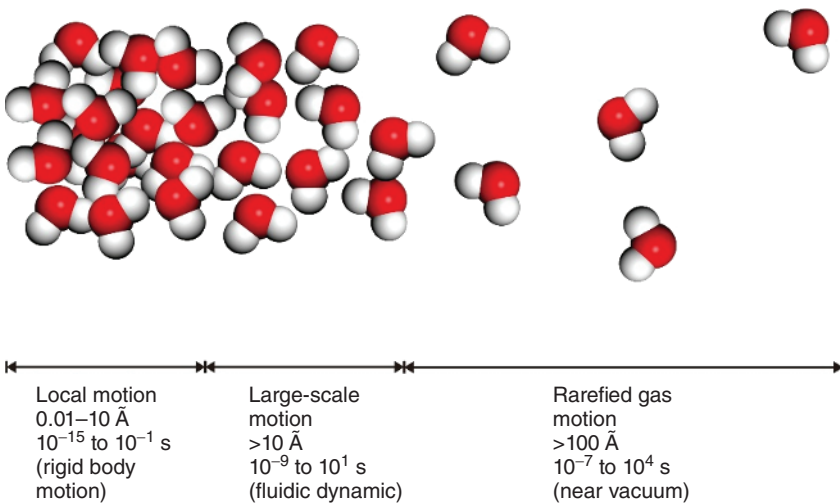

Local motion	Large-scale	Rarefied gas
0.01–10 Å	motion	motion
10^{-15} to 10^{-1} s	>10 Å	>100 Å
(rigid body	10^{-9} to 10^1 s	10^{-7} to 10^4 s
motion)	(fluidic dynamic)	(near vacuum)

Figure 1.8 A typical sample of aqueous molecules in the MD system.

solve the phase change process of materials and the thermal diffusion of mixture of different liquids.

For example, in a typical molecular dynamics problem of diffusion in hot water, once given an initial set of positions and velocities, the subsequent time evolution is completely determined. When nonequilibrium occurs, the water molecules are wandering around (fluid), oscillating in Brownian movement with their neighbors, and sometimes even evaporate away from the system if they are at the free surface.

MD simulations optimize the study of complex, dynamic heat transfer in thermal systems. The Monte Carlo algorithm-based method can be widely applied to many engineering or scientific analyses (e.g., the stability testing of metal nanoparticles in nanofluid systems).

1.2.4 Photothermal Effect via SPR Heating

Surface plasmonic resonance (SPR) is an important nanoscale photothermal effect in the state-of-the-art thermal materials research. It is described as the collective oscillations of the free electron clouds in bulk metals, nanoparticles, and semiconductors. Especially in the photothermal nanomaterials, SPR plays a critical role in converting light energy to thermal energy, which will be briefly discussed in the following sections.

In an environment with ideal dielectric, the excited plasmonic particle does not propagate SPR waves among the group of particles but exhibits localized SPR. Therefore, the free electron gas in the metal is frequently polarized along a specific direction by exhibiting a restoring force. The mobile electrons immigrate in dielectric medium with the loss of electrical power, which is transformed into thermal energy. As shown in Figure 1.9, heat generation occurs under the process of oscillation of the electromagnetic radiation, corresponding to the electron–phonon interaction (Figure 1.9). Part of the intercepted light will be absorbed by the particle and converted into heat, and the remaining portion is transformed into elastic scattering and photon excitation:

$$\sigma = \sigma_{\text{scat}} + \sigma_{\text{excit}} + \sigma_{\text{abs}} \tag{1.12}$$
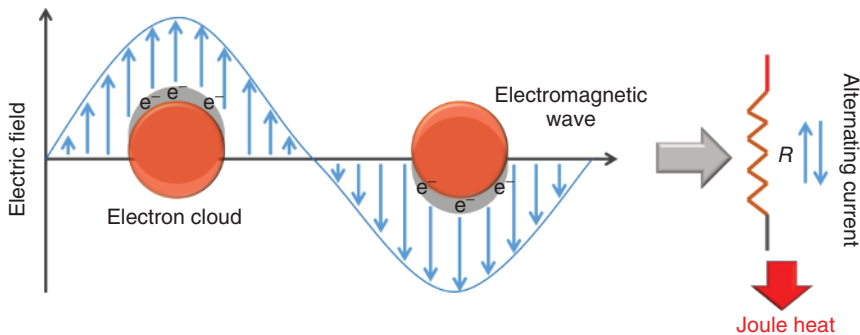

Figure 1.9 Schematic principle of light-induced plasmonic heating on a gold nanoparticle.

The heat dissipation portion depends on the amount and the geometry of the metal particles. The heat generation inside the particle structure can be described as

$$Q = \sigma_{abs}I \qquad (1.13)$$

where σ_{abs} represents the particle cross section of the absorbing light and I is the irradiance of the incoming light [5–8].

1.3 Bioinspired Thermal Materials

The history of human learning from nature spans millions of years. For example, in a low-temperature environment, at the North or South Pole, biological species have to minimize the loss of heat to adapt to the cold weather. Inspired by the use of furs or caves by biological species for minimizing their heat loss in winter, there are some innovations of artificial thermal materials to regulate the temperature or to reduce the thermal loss [9]. In this section, some interesting bioinspired thermal applications are discussed briefly. The critical thermal properties and performances of biological systems are emphasized, which contributes to the development of bioinspired thermal engineering/management.

1.3.1 Bioinspired Thermal Materials for Heat Conduction

Materials with high thermal conductivity are widely used in practical thermal management applications for the purpose of heating or cooling. The newly developed nanomaterials with super-high thermal conductivity, including carbon nanotubes or graphenes, are introduced to promote thermal conduction for the traditional problems. For example, carbon nanotubes have been used in composites for wall heat transfer applications [10–12]. Doping carbon nanotubes or graphene in organic and nonorganic materials helps reduce the interfacial resistance between two phases. Inspired by the natural delicate biological structure, scientists can achieve exceptional thermal properties of functional nanomaterials fabricated with regular raw commercial materials. Spider dragline silk is one of the famous biomimetic examples. As per a previous report, this kind of spider silk consisting of biopolymers can achieve a thermal conductivity as high as 416 W m^{-1} K^{-1}, which is comparable to the thermal conductivity of copper (400 W m^{-1} K^{-1}) [13]. It is evident that the nanofibrils composed of well-organized β-sheets and helical structures allow rapid phonon conduction within the spider silk. Inspired by this natural highly hierarchical alignment of the microstructures, Shen *et al.* fabricated artificial polyethylene nanofibers with a high thermal conductivity of 104 W m^{-1} K^{-1} [14]. Such materials attract wide attention for further developments ranging from rapid cooling of electronic chips and coating of heating elements to components of pulse tube cryocooler.

1.3.2 Bioinspired Materials for Thermal Storage

To date, 80% or more of energy consumed in the human world comes from natural fuel by combusting gas, oil, and coal. Utilizing fuel energy on earth will not only produce heavy pollution but also result in huge amounts of energy loss. In order to improve the energy efficiency, one approach is to store thermal energy from nature and industrial processing. Many animals know how to preserve and store thermal energy. For example, the black butterfly easily absorbs solar light in the daytime and then converts it into heat against the cold night. Inspired by thermal energy storage approaches evolved by biological systems, especially the absorption and conversion of solar light into heat by some butterfly species in cold area, a new thermal storage system has recently been proposed by employing phase change material, a mixture of plasmonic nanoparticles and paraffin to enhance the photothermal energy charging rate [15]. In Wang's work, they have made use of the photothermal effect of noble gold nanoparticles to achieve a rapid charging rate of the paraffin-mixture material with very low volumetric loading concentration (parts per million level) of surface-modified Au NPs and nanorods (NRs) (Figure 1.10). With homogeneously dispersed nanoparticles in the matrix such as paraffin, the light absorber nanoparticles contribute a great enhancement to thermal energy storage rate. When incident light illuminates the surface of nanoparticles-doped paraffin, the surface of the paraffin will rapidly melt due to the large amount of heat generated by the light-absorbing particles. Meanwhile, the doped gels become transparent, which allows the illuminating light to further pass into the inner portion of paraffin [16].
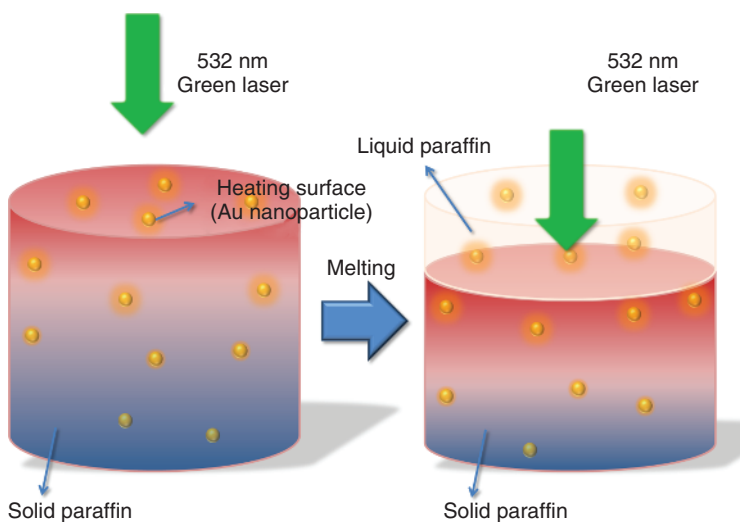

Figure 1.10 The rapid charging of the thermal energy conversion and storage by Au NP–paraffin composite.

1.3.3   Bioinspired Thermal Detection

Inspired by infrared vision of some desert snakes in the night that can detect heat from other creatures, the reflective radiation wave from a heat body can be used as a method of temperature detection. The traditional infrared detection can be categorized as cooled and uncooled IR detection. Cooled IR detection requires expensive cryogenic or thermoelectric cooling devices with relatively high resolution. Uncooled IR detection suffers from low resolution, but the cost is much cheaper than that of the cooled IR detection system. A bioinspired detection approach has been introduced to provide a new mechanism for IR detection technology [17]. Modified butterfly wings were fabricated by depositing a 50 nm layer of Au atoms on the end of lamellae. When the modified butterfly wing is irradiated with IR, the chitin of the lamellae of butterfly wing and the deposited Au thin film will absorb incident IR and expand. The mismatch in the thermal expansion coefficients of the Au film and chitin results in the bending of lamellae of butterfly wing. Subsequently, the reflectance of the visible readout light will change its spectrum structure or position after the IR illumination. By collecting the reflectance spectrum of the deformation of the multilayered butterfly wing structure, the IR signal can be captured. In short, IR radiation is detected as the deformation of the 3D structure of butterfly wing. Also, photonic resonators and thermoplasmonic devices with enhanced sensitivity on 3D multilayered structure for thermal bimorph structure have also been reported [18–21].

1.3.4   Bioinpsired Materials for Energy Conversion

Learning from the energy recycle of the natural leaf transpiration system through solar light-enabled water evaporation, the converted photothermal energy can be utilized in a wide range of applications, including electricity generation and seawater desalination [22–33]. Halas *et al.* comprehensively studied the heat generation and transfer effect in aqueous plasmonic nanoparticle solutions. Since the gold nanoparticles are generally used as heat source due to SPR effect [34]. concentrated plasmonic nanoparticle solution is used to generate high-temperature steam. Their work showed that multiple light scattering from the dispersed nanoparticles enhanced photothermal evaporation efficiency [35, 36]. However, aqueous nanoparticle solution still suffers from plenty of disadvantages such as nonreusable and thermal energy loss to nonevaporative portion of the liquid. In Figure 1.11, inspired by human sweating, Liu *et al.* have developed a new evaporation system that utilizes the assembled Au nanoparticles film coating on a free-floating porous airlaid paper [37]. In this work, the intense plasmonic heating was localized at the evaporative surface (water–air interface), resulting in the generation of vapor bubbles close to the evaporative surface. The results showed that the evaporation efficiency could reach 74%, which was much higher than that of aqueous gold nanoparticle solutions. The free-floating paper-based Au NP films were able to reduce heat
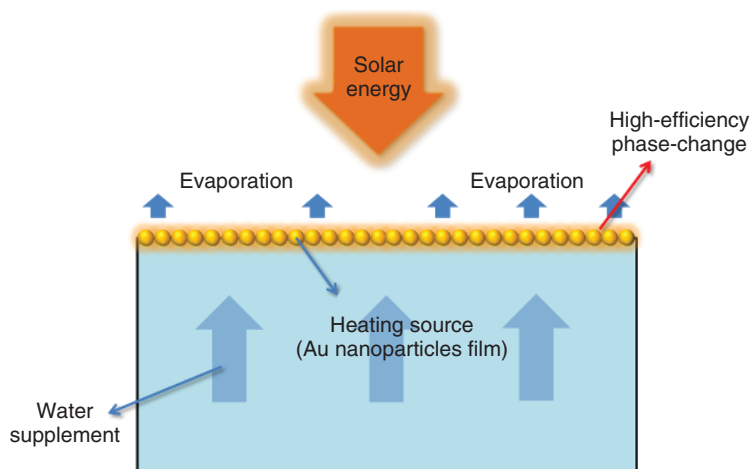
Figure 1.11 A large-scale, renewable, low-cost evaporational photothermal membrane.

loss, that is, the thermal diffusion from heated Au NP film to the nonheated portion of bulk liquid, which is inevitable, to the gold nanoparticle aqueous solution. Also, the low thermal conductivity of airlaid paper and the collective solar energy conversion in a thin film also help reduce thermal energy loss within the evaporation system. The thermal energy conversion of bioinspired materials including the efficient evaporation system will be comprehensively discussed in this book as well.

1.4 Perspective and Outlook

This introductory chapter aims to provide simple descriptions of heat transfer mechanism and the essential thermal properties of bioinspired thermal materials. In Section 1.1, the working principles of macroscale heat transfer are introduced and discussed through some practical examples of heat conduction problems. Besides the introduction of macroscale heat transfer theory, this chapter also emphasizes the theory of microscale heat transfer equation in Section 1.2, which is especially useful to understand the thermal concepts of micro/nanoscale thermal properties of materials. These basic theories will assist in solving and learning the practical problems encountered in the rapidly growing area of bioinspired thermal materials.

In Section 1.3, some typical developments of bioinspired thermal materials are presented to summarize the recent works of thermal engineering approaches. The advanced progress of thermal engineering and management takes advantages of highly sophisticated biological evolution system and eventually benefits industrial development and humans' daily lives. In the near future, improvement of innovative materials science and technology by learning from nature may lead to a revolution in the thermal engineering of materials.

Acknowledgments

References

1 Kaviany, M. (2011) *Essentials of Heat Transfer: Principles, Materials, and Applications*, Cambridge University Press.
2 Kandlikar, S.G. (2010) Scale effects on flow boiling heat transfer in microchannels: a fundamental perspective. *International Journal of Thermal Sciences*, **49** (7), 1073–1085.
3 Kondepudi, D.K. (2008) *Introduction to Modern Thermodynamics*, John Wiley & Sons, Ltd, Chichester.
4 Allen, M.P. (2004) Introduction to molecular dynamics simulation, in *Computational Soft Matter: From Synthetic Polymers to Proteins*, vol. **23** (eds N. Attig, K. Binder, H. Grubmüller, and K. Kremer), John von Neumann Institute for Computing, Julich, pp. 1–28.
5 Baffou, G., Quidant, R., and Girard, C. (2009) Heat generation in plasmonic nanostructures: influence of morphology. *Applied Physics Letters*, **94** (15), 153109.
6 Baffou, G., Quidant, R., and García de Abajo, F.J. (2010) Nanoscale control of optical heating in complex plasmonic systems. *ACS Nano*, **4** (2), 709–716.
7 Zhang, W., Li, Q., and Qiu, M. (2013) A plasmon ruler based on nanoscale photothermal effect. *Optics Express*, **21** (1), 172–181.
8 Baffou, G., Quidant, R., and Girard, C. (2010) Thermoplasmonics modeling: a Green's function approach. *Physical Review B*, **82** (16), 165424.
9 Tao, P., Shang, W., Song, C., Shen, Q., Zhang, F., Luo, Z., Yi, N., Zhang, D., Deng, T. *et al.* (2015) Bioinspired engineering of thermal materials. *Advanced Materials*, **27** (3), 428–463.
10 Bryning, M.B., Milkie, D.E., Islam, M.F. *et al.* (2005) Thermal conductivity and interfacial resistance in single-wall carbon nanotube epoxy composites. *Applied Physics Letters*, **87** (16), 161909.
11 Shenogin, S., Xue, L., Ozisik, R. *et al.* (2004) Role of thermal boundary resistance on the heat flow in carbon-nanotube composites. *Journal of Applied Physics*, **95** (12), 8136–8144.
12 Biercuk, M.J., Llaguno, M.C., Radosavljevic, M. *et al.* (2002) Carbon nanotube composites for thermal management. *Applied Physics Letters*, **80** (15), 2767–2769.
13 Huang, X., Liu, G., and Wang, X. (2012) New secrets of spider silk: exceptionally high thermal conductivity and its abnormal change under stretching. *Advanced Materials*, **24** (11), 1482–1486.
14 Shen, S., Henry, A., Tong, J. *et al.* (2010) Polyethylene nanofibres with very high thermal conductivities. *Nature Nanotechnology*, **5** (4), 251–255.

15 Wang, Z., Tao, P., Liu, Y. *et al*. (2014) Rapid charging of thermal energy storage materials through plasmonic heating. *Scientific Reports*, **4** (1). doi: 10.1038/srep06246.

16 Zheng, Y., Liu, J., Liang, J., Jaroniecc, M., and Qiao, S.Z. (2012) Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis. *Energy & Environmental Science*, **5**, 6717–6731.

17 Zhang, F. *et al*. (2015) Infrared detection based on localized modification of Morpho butterfly wings. *Advanced Materials*, **27** (6), 1077–1082.

18 LeMieux, M.C. *et al*. (2006) Polymeric nanolayers as actuators for ultrasensitive thermal bimorphs. *Nano Letters*, **6** (4), 730–734.

19 Watts, M.R., Shaw, M.J., and Nielson, G.N. (2007) Optical resonators: microphotonic thermal imaging. *Nature Photonics*, **1** (11), 632–634.

20 Yi, F. *et al*. (2013) Plasmonically enhanced thermomechanical detection of infrared radiation. *Nano Letters*, **13** (4), 1638–1643.

21 Park, T., Na, J., Kim, B. *et al*. (2015) Photothermally activated pyroelectric polymer films for harvesting of solar heat with a hybrid energy cell structure. *ACS Nano*, **9** (12), 11830–11839.

22 Szwarcman, D., Vestler, D., and Markovich, G. (2010) The size-dependent ferroelectric phase transition in $BaTiO_3$ nanocrystals probed by surface plasmons. *ACS Nano*, **5** (1), 507–515.

23 Huang, X., El-Sayed, I.H., Qian, W. *et al*. (2006) Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods. *Journal of the American Chemical Society*, **128** (6), 2115–2120.

24 Yilmaz, Ş., Bauer, S., and Gerhard-Multhaupt, R. (1994) Photothermal poling of nonlinear optical polymer films. *Applied Physics Letters*, **64** (21), 2770–2772.

25 Yang, Y., Zhang, H., Zhu, G. *et al*. (2012) Flexible hybrid energy cell for simultaneously harvesting thermal, mechanical, and solar energies. *ACS Nano*, **7** (1), 785–790.

26 Gude, V.G. and Nirmalakhandan, N. (2010) Sustainable desalination using solar energy. *Energy Conversion and Management*, **51** (11), 2245–2251.

27 Shannon, M.A., Bohn, P.W., Elimelech, M. *et al*. (2008) Science and technology for water purification in the coming decades. *Nature*, **452** (7185), 301–310.

28 Elimelech, M. and Phillip, W.A. (2011) The future of seawater desalination: energy, technology, and the environment. *Science*, **333** (6043), 712–717.

29 Gupta, M.K. and Kaushik, S.C. (2010) Exergy analysis and investigation for various feed water heaters of direct steam generation solar–thermal power plant. *Renewable Energy*, **35** (6), 1228–1235.

30 Agrawal, R., Singh, N.R., Ribeiro, F.H. *et al*. (2007) Sustainable fuel for the transportation sector. *Proceedings of the National Academy of Sciences of the United States of America*, **104** (12), 4828–4833.

31 Cartlidge, E. (2011) Saving for a rainy day. *Science*, **334** (6058), 922–924.

32 Zarza, E., Valenzuela, L., Leon, J. *et al*. (2004) Direct steam generation in parabolic troughs: final results and conclusions of the DISS project. *Energy*, **29** (5), 635–644.

33 Fang, C., Shao, L., Zhao, Y., Wang, J., Wu, H. *et al.* (2012) A gold nanocrystal/poly(dimethylsiloxane) composite for plasmonic heating on microfluidic chips. *Advanced Materials*, **24** (1), 94–98.

34 Hogan, N.J., Urban, A.S., Ayala-Orozco, C., Pimpinelli, A., Nordlander, P., and Halas, N.J. (2014) Nanoparticles heat through light localization. *Nano Letters*, **14** (8), 4640–4645.

35 Brongersma, M.L., Halas, N.J., and Nordlander, P. (2015) Plasmon-induced hot carrier science and technology. *Nature Nanotechnology*, **10** (1), 25–34.

36 El-Agouz, S.A., Abd, El-Aziz, G.B., and Awad, A.M. (2014) Solar desalination system using spray evaporation. *Energy*, **76**, 276–283.

37 Liu, Y., Yu, S., Feng, R. *et al.* (2015) A bioinspired, reusable, paper-based system for high-performance large-scale evaporation. *Advanced Materials*, **27** (17), 2768–2774.