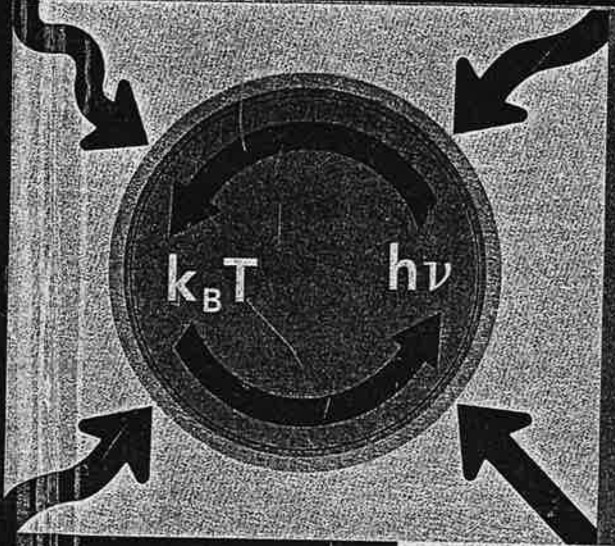
PA ALARDO SERIES IN
MECHANICAL ENGINEERING

NANOSCALE ENERGY TRANSPORT AND CONVERSION



A PARALLEL TREATMENT
OF ELECTRONS,
MOLECULES,
PHONONS,
AND PHOTONS

Fig. 8.12(c): From Fraas L.M., Avery J.E., Huang H.X. and Martinelli, R.U., 2003, "Thermophotovoltaic System Configurations and Spectral Control," *Semiconductor Science Technology*, vol. 18, pp. S165–S173.

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Introduction

The major sources of inspiration for this book are the recent rapid advancements in microtechnology and nanotechnology. Microtechnology deals with devices and materials with characteristic lengths in the range of submicron to micron scales (0.1–100 μm), while nanotechnology generally covers the length scale from 1 to 100 nm. For example, integrated circuits are now built on transistors with characteristic device length scales around 100 nm. The semiconductor industry roadmap predicts that, in 2010, the characteristic length in integrated circuits will further shrink to 25 nm (SEMATECH, 2002). In the late 1980s, microelectronics fabrication technology began to impact mechanical engineering, and the field of microelectromechanical systems, or MEMS, blossomed (Trimmer, 1997). Meanwhile, nanoscience and nanotechnology, explored by a few pioneers (Feynman, 1959, 1983), are currently generating much excitement across all disciplines of science and engineering. The fields of micro- and nanotechnologies are enormous in breadth and cannot be covered completely in any single book. In this book, we focus on microscopic mechanisms behind energy transport, particularly thermal energy transport. As the device or structure characteristic length scales (such as the gate length in field-effect transistors, used to build computers, and the film thickness in coatings) become comparable to the mean free path and the wavelength of energy and information carriers (mainly electrons, photons, phonons, and molecules), some of the classical laws are no longer applicable. By examining the microscopic pictures underlying transport processes, we will develop a consistent framework for treating thermal energy transport phenomena from the nanoscale to the macroscale.

In this chapter, we will first give a few examples of micro- and nanoscale transport phenomena from contemporary technologies to provide motivation for the rest of this book. We will then briefly summarize classical laws governing heat transfer processes and discuss the microscopic pictures behind heat transfer phenomena, followed by a simple derivation of the Fourier law, based on the kinetic theory, to demonstrate that many classical laws we have learned are actually not as fundamental as their names may suggest! The rest of the book will further expand on this chapter and answer in depth some of the questions we raise.

1.1 There Is Plenty of Room at the Bottom

Richard Feynman, who won the 1963 Nobel Prize in physics for his work in quantum electrodynamics, gave a visionary talk in 1959 entitled "There is plenty of room at the bottom" (Feynman, 1959, 1983). In this talk, Feynman described the possibilities of storing all the books in the world in a piece of dust, making micromachines that can go into the human body, shrinking computers, rearranging atoms, and so on. To put his ideas in a historic perspective, the possibility of integrated circuits was first demonstrated in 1958 and, at the time of Feynman's famous lecture, computers filled entire rooms and lasers were shown only to be theoretically possible. Feynman not only spoke of theoretical possibilities, but also provided potential approaches to realize his dreams. Although his talk was considered bold at the time, his insights on what was possible, or, better put, what was not impossible, were based on the laws of physics. Most of the audience at that 1959 talk did not take Feynman's visions seriously—rather, they thought he was trying to be humorous. Subsequent developments in micro- and nanotechnologies, however, have realized many of his dreams, and some have even followed the technical approaches that he envisioned.

Great visionaries like Richard Feynman point to directions and provide inspiration. Often, at the beginning of a revolutionary idea, only a small group appreciates the ideas and begins to work on practical ways to demonstrate the concepts. Some of them make breakthroughs along the way and prove that the idea works in principle; this attracts more attention from wider communities and eventually the general public. This small group is privileged because they have access to the ideas at an earlier stage, but, more importantly, they have the training and judgments to appreciate the importance of these ideas. Some of this small group have insights of their own, enabling them to realize these ideas and generate their own ideas along the way. With the rapid development of information technology, ideas propagate quickly nowadays. Academic training and scientific knowledge become even more important for one to filter through the flood of information for gold and to develop one's own ideas and visions. One objective of this book is to provide a knowledge base to its readers, assuming that most are not familiar with modern physics, with a foundation to understand energy transport and conversion processes, particularly thermal energy, from nanoscale up to macroscale, with an emphasis on nanoscale processes. We will give a few examples here to illustrate the importance of understanding nanoscale transport and energy conversion processes.

One major driver behind microtechnology and nanotechnology is information processing, which includes microelectronics, data storage, and data transmission. The information carriers are electrons in electrical circuits and photons in optical fibers. The transport of electrons and photons often generate unwanted heat. As more and more devices are compacted into a small area, heat generation density increases and thermal management becomes a major challenge for the microelectronics industry. A Pentium4 chip from Intel Corporation, for example, has an area of ~1 cm^2 and dissipates about 60 W of heat. The size of the fan used to maintain the chip temperature below its standard (typically 80–120°C) is much larger than the chip itself. As engineers develop various cooling solutions, it also becomes clearer that heat transfer characteristics must be considered at the device level (Cahill et al., 2002). The most important device in a computer chip is the metal-on-insulator field-effect transistor or MOSFET (Sze, 1981), as shown in figures 1.1(a) and (b). The source, drain, and channel are made of doped silicon (or other types of semiconductor). Electrons (or holes) flow from the source into the drain through the channel under an externally applied voltage between the source and the drain. The width of the channel is controlled by another voltage applied between the back of the substrate and the gate electrode, which is insulated from the channel by a very thin silicon dioxide layer. A MOSFET is thus like a variable resistor with its resistance controlled by the gate voltage. To make faster devices, the channel length (and thus the gate length) is shrinking by about 30% every 2 years, with the current gate length at around 90 nm. Electrons convert most of their energy into heat in a small region in the drain side [figure 1.1(b)]. Both modeling (Chen, 1996a) and experiments (Svedrup et al., 2001) suggest that the temperature rise due to heat generation in the small region is much higher than that predicted by the Fourier law, which can accelerate the failure of the device. As another example, semiconductor lasers used in telecommunication and data storage are often composed of multilayers of thin films, as shown

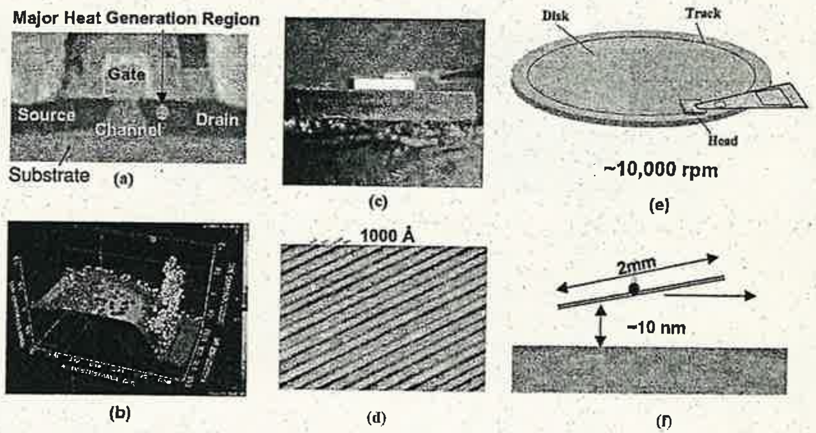


Figure 1.1 Nanoscale transport examples in information-oriented devices. (a) & (b): A MOSFET device (courtesy of IBM) and electron energy dissipation in a MOSFET (courtesy of Dr. S.E. Laux and Dr. M.V. Fischetti), indicating most heat is generated in nanometer region at the drain. Heat conduction from such small source cannot be described by Fourier law; (c) & (d): A InAs/AlSb based quantum cascade laser is made of many layers of thin films, each ranging from a few to hundreds Angstrom thick (courtesy of Dr. S. Pei). These films have thermal conductivity values significantly lower than those of their bulk materials; (e) & (f): A disk drive in magnetic data storage with the slider head hovering about 10 nm on top of the disk rotating at 10,000 rpm. Fluid flow through the gap between the slider and the disk is rarefied and cannot be described by the Newton shear stress law.

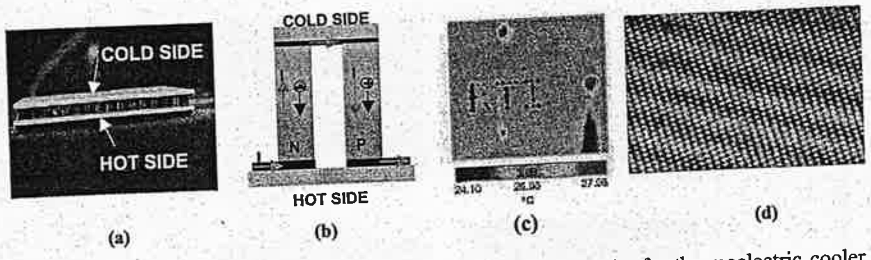


Figure 1.2 Illustration of thermoelectric devices, (a) a photograph of a thermoelectric cooler, (b) illustration of charge flow inside one pair of legs, (c) microcoolers fabricated based on superlattices (Venkatasubramanian et al., 2001; courtesy of Nature Publishing Groups), and (d) an example of a Si/Ge superlattice structure (courtesy of Dr. K.L. Wang).

in figures 1.1(c) and (d). Past studies have shown that the thermal conductivity of these structures is much lower than effective values calculated from their bulk materials on the basis of the Fourier heat conduction theory (Chen, 1996b). These lasers have severe heating problems that limit their performance. The reduced thermal conductivity calls for careful design of the lasers to minimize the number of interfaces. In a different example, figure 1.1(e) sketches the disk head in a magnetic disk drive. The separation between the slider and the magnetic disk [figure 1.1(f)] determines the data storage density. Currently, this separation distance is around 10–50 nm while the disk rotates at ~ 10,000 rotations per minute (rpm). The relative motion between the slider and the disk is analogous to flying a Boeing 747 a few millimeters above the ground. The airflow between the slider and the disk is crucial in maintaining the slider–disk separation and is very different from the prediction of continuum fluid mechanics at this small spacing (Fukui and Kaneko, 1988). Some data storage processes are also based on heat transfer (Chen et al., 2004). Examples are rewritable CDs based on the phase change of the materials upon laser heating and thermomechanical data storage, where data bits are written on polymer substrates by heated atomic force microscope (AFM) tips. For such applications, it is desirable to limit the heating to a small domain. Nanoscale heat transfer effects including reduced thermal conductivity of thin films and nonlocal heat conduction surrounding nanoscale heating spots can be utilized to confine heat for writing smaller spots.

While heat in information technology is, in most cases, undesirable and needs to be "managed," it becomes a dominant factor in energy conversion technology. Nanoscale energy transport phenomena can be used for developing new strategies to improve the energy conversion efficiency. For example, the reduced thermal conductivity observed in semiconductor thin films can potentially be used to develop highly efficient thermoelectric materials for cooling and power generation (Tritt, 2001; Chen and Shakouri, 2002). Thermoelectric devices, as shown in figure 1.2(a–d), use electrons in solids as the media to carry energy from one location to another. Low thermal conductivity materials are required to reduce the thermal leakage between the hot and cold sides. At the same time, the materials must have good electron energy-carrying properties (Goldsmid, 1964). The use of nanostructures to control the thermoelectric transport properties for improving the electron energy carrying capability and reducing the thermal conductivity emerged over the last ten years as a very promising approach for realizing highly

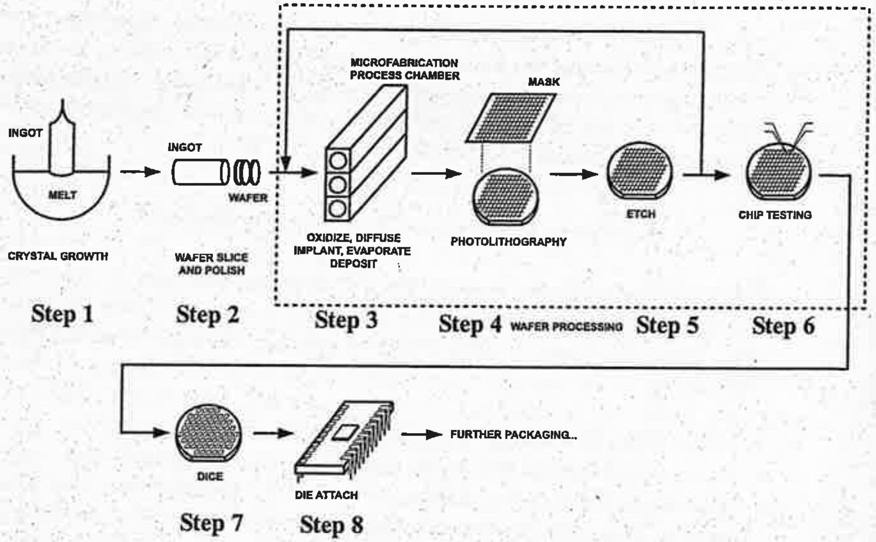
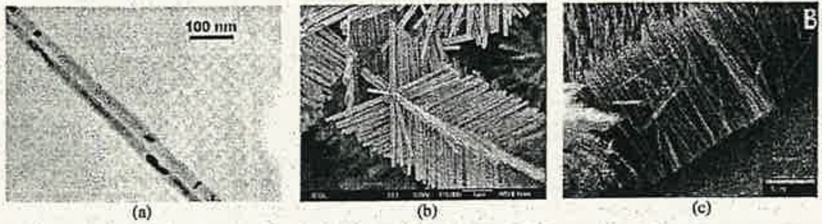


Figure 1.3 Illustration of major microelectronic device fabrication processes.

efficient thermoelectric devices (Dresselhaus et al., 1999; Tritt, 2001; Harman et al., 2002; Chen et al., 2003).

Radiation transport in micro- and nanostructures is also different from that in macrostructures because the wave properties of photons become dominant. For example, radiation exchange between two closely spaced vacuum gaps is much higher than that predicted on the basis of standard view-factor calculations because of tunneling and interference effects (Domoto et al., 1970), which potentially can be used to develop high power density thermophotovoltaic power generators (Whale and Cravalho, 2002). Photonic crystals, a concept developed in 1987 (Yablonovitch, 1987), can be used to design special thermal radiation surfaces with desirable properties (Fleming et al., 2002). Using microstructures, coherent thermal radiation was recently demonstrated (Greffet et al., 2002).

There are many outstanding nanoscale transport problems related to the fabrication of nanodevices and synthesis of nanomaterials. As an example, consider a typical fabrication process, shown in figure 1.3, for an integrated circuit. Important transport issues exist in almost every step and some of them are particularly relevant to the nanoscale transport discussed in this book. With regard to the process illustrated in figure 1.3, in step 1, heat transfer and fluid flow problems in crystal growth are in the continuum range and have been addressed extensively in literature. Many of the material deposition processes (step 3) occur at high temperatures and under low pressures. Atoms or gas molecules have long mean free paths at low pressures, and this must be considered in developing proper working conditions for filling trenches between devices. Lithography processes (step 4) should consider photon transport carefully. Optical interference and scattering effects can be either detrimental or useful for the lithography technology. Heat transfer issues arise in both the mask-making and lithography processes. For example, some candidates for next-generation lithography, such as extreme



(a) (b) (c)

Figure 1.4 Examples of nanowires and nanotubes synthesized by various methods: (a) a pair of bismuth nanowires obtained by pressure injection into a template (Dresselhaus et al., 2001; courtesy of Dr. M.S. Dresselhaus), (b) TiO_2 nanowires obtained by vapor condensation (courtesy of Dr. Z.F. Ren), (c) carbon nanotubes grown by plasma CVD (Ren et al., 1998; courtesy of AAAS).

ultra-violet lithography (EUV) and X-ray lithography, rely on multilayer structures for reflecting light (Hector and Mangat, 2001). The consequence of reduced thermal conductivity on mask reliability has yet to be investigated. The synthesis of nanoscale materials is a wide-open field and many nanomaterial and nanostructure synthesis methods being developed raise intriguing nanoscale transport questions. For example, nanowires and carbon nanotubes, shown in figure 1.4, have been synthesized with several different methods such as chemical or physical vapor deposition, filling of templates, plasma deposition, and laser ablation (Morales and Lieber, 1998; Ren et al., 1998; Dresselhaus et al., 2001). Understanding the transport processes during nanomaterial formation will allow better control of the final material quality.

The preceding examples emphasize the small length scales involved in nanodevices and nanomaterials. Short time scales are also becoming increasingly important. Similar questions can be raised for transport at short time scales as for the small length scales. Lasers can deliver a pulse as short as a few femtoseconds ($1\ \text{fs} = 10^{-15}\ \text{s}$). Energy transduction mechanisms at such short time scales can differ significantly from those at macroscales (Qiu and Tien, 1993). Microelectronic devices are pushing to the tens of gigahertz clock frequency with much shorter transient times. The temperature rise of the device in such short time scales can be very different from that predicted by the Fourier law (Yang et al., 2002).

The examples given above illustrate a few of the motivations behind the rapid development in micro- and nanoscale heat transfer research over the last decade (see Tien and Chen, 1994; Tien et al., 1998). In the meantime, similar developments are occurring in various fields, as evidenced in the strong interest in nanoscience and nanotechnology from numerous fields of science and engineering, as well as from industry. Yet we are only at the entrance, and the room at the bottom is big. The convergence of interests from disparate fields into common subjects also creates confusion because different languages are used in each field for similar phenomena. For newcomers, these differences are often intimidating. One of the objectives of this book is to get the readers familiar with the terminologies. In fact, once they get involved, the readers will find that drastically different equations used in unrelated fields, such as the Fourier law for heat conduction and the drift-diffusion equation for electrical current flow, actually originate from the same principle. For this reason, the text will adopt a parallel treatment of different energy carriers whenever possible.

1.2 Classical Definition of Temperature and Heat

The classical definition of heat transfer from thermodynamics can be stated as follows: "Heat transfer is the energy flow across the boundaries of a system under a temperature difference." We can emphasize several points in this definition: heat transfer is a form of energy flow; heat transfer is associated with a temperature difference; and finally, heat transfer is a boundary phenomenon.

Since heat transfer is driven by temperature differences, it is necessary that we pay attention to the definition of temperature. In classical thermodynamics, temperature is defined on the basis of the concept of thermal equilibrium. If system A is in thermal equilibrium with system B, then system A and system B have the same temperature. In other words, temperature is a quantity that describes thermal equilibrium phenomena.

These definitions of temperature and heat transfer are independent of the material and serve well in establishing the universality of classical thermodynamics. Their strengths, however, are also their weaknesses. These definitions are devoid of the physical microscopic pictures underlying heat transfer processes and the meaning of temperature. This book aims to provide a more detailed picture of thermal energy transport processes. We will study how heat is transferred at the microscopic level and how temperature should be defined for transport processes that are intrinsically nonequilibrium.

1.3 Macroscopic Theory of Heat Transfer

There exist three basic modes of heat transfer: conduction, convection, and thermal radiation. We briefly review the classical laws that are used to describe these modes. Later in this book we will show how these laws can be derived and on what approximations they are built.

1.3.1 Conduction

Heat conduction represents the energy transfer processes through a medium, caused by a temperature difference due to the random motion of heat carriers in the substance. The key is that a medium is needed for heat conduction, and heat is the part of the energy that is carried around through random motion of heat carriers such as molecules. An example is heat transfer through a solid wall separating the inside and the outside of a room, which is due to the random vibrations of atoms within the wall materials. Heat conduction processes are usually modeled on the basis of the Fourier law (Joseph Fourier, 1768–1830) that relates the local heat flux to the local temperature gradient

$$\mathbf{q} = -k\nabla T \tag{1.1}$$

where k is the thermal conductivity, which is a temperature dependent material property and has units of $[\mathrm{Wm^{-1}K^{-1}}]$, $\mathbf{q}$ has units of $[\mathrm{Wm^{-2}}]$, and ∇ is the gradient operator such that

$$\nabla T \equiv \frac{\partial T}{\partial x}\hat{x} + \frac{\partial T}{\partial y}\hat{y} + \frac{\partial T}{\partial z}\hat{z} \tag{1.2}$$

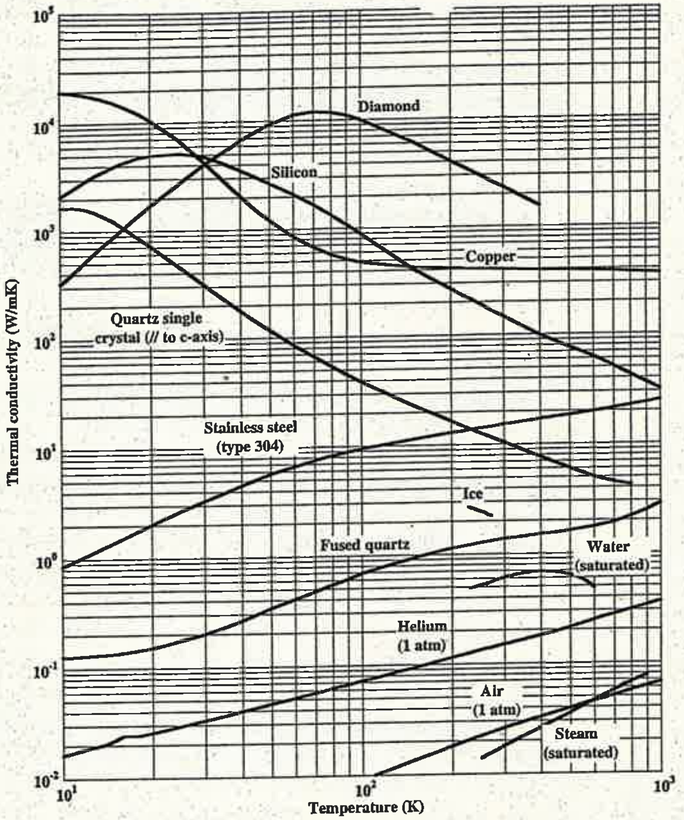


Figure 1.5 Thermal conductivity as a function of temperature for representative materials (data from Touloukian et al., 1970, and http://www.chrismanual.com/Default.htm).

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the unit vectors along coordinate directions. Equation (1.1) is called the Fourier law in honor of the mathematician who first used it to solve heat conduction problems. It is called a law because, at the time of its creation, it was a postulate based on the observation of experimental results. This law applies to most engineering situations and is the foundation of classical heat transfer analysis. Thermal conductivity of materials is a very important material property. The higher the thermal conductivity, the better the material conducts heat. Figure 1.5 shows the thermal conductivity of some common materials. We notice that the temperature dependence of thermal conductivity of various materials is quite different. The value of the thermal conductivity spans several orders of magnitude, from 10^{-2} $\mathrm{Wm^{-1}K^{-1}}$ for gas to 10^5 $\mathrm{Wm^{-1}K^{-1}}$ for solids at low temperatures. Diamond is the best thermal conductor among naturally existing materials.

? At this stage, we raise the following questions for interested readers. Why do thermal conductivities of various materials differ not only in magnitude, but also in their temperature dependence? Is the Fourier law applicable to nanostructures? Do nanostructures have the same thermal conductivity as their bulk counterparts? We will find answers to these questions throughout the text.

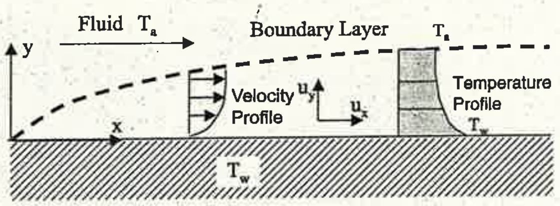


Figure 1.6 Forced convection over a solid surface. Fluids close to the boundary form a boundary layer in which temperature and velocity vary (thermal and momentum boundary layers may have different thicknesses) from their values at the wall to those outside the boundary layer.

1.3.2 Convection

Convection heat transfer occurs when a bulk fluid motion overlaps a temperature gradient. When fluid molecules move from one place to another, they carry internal energy with them. In most situations, like the one shown in figure 1.6, we are interested in the heat transfer between a solid surface and the fluid. The convection heat transfer rate Q [W] between a solid surface at temperature T_w and a fluid at temperature T_a can be expressed by Newton's law of cooling (Isaac Newton, 1643–1727)

$$Q = hA(T_w - T_a) \tag{1.3}$$

where h $[\mathrm{Wm^{-2}K^{-1}}]$ is called the heat transfer coefficient and A is the surface area. Unlike the thermal conductivity, the heat transfer coefficient is not a material property. ! It is a flow property that depends on the flow field, fluid properties, and the geometry of the object over which the fluid flows. Convection is categorized into two types: natural convection in which the fluid motion is created by the buoyancy force due to the difference in the densities of hot and cold fluids, and forced convection in which the fluid is set into motion by some other means such as a pump or a fan. Heat transfer between a solid surface and a liquid undergoing a phase change, that is, boiling or condensation, is also characterized by a heat transfer coefficient.

Although Newton's law of cooling is simple in form, h is difficult to determine in general. The heat transfer coefficient is usually determined by experiment, although analysis and numerical simulation can be performed for certain simple geometries and flow conditions. Table 1.1 gives some empirical relations and ranges of heat transfer coefficients for simple geometries, mostly under laminar flow conditions. These empirical relations are expressed using nondimensional parameters such as the average Nusselt number ($\overline{Nu}_L = \bar{h}L/k$) (Wilhelm Nusselt, 1882–1957), the Reynolds number ($Re_L = uL/\nu$) (Osborne Reynolds, 1848–1912), and the Prandtl number ($Pr = \nu/\alpha$) (Ludwig Prandtl, 1875–1953), where L is a characteristic length, u is the fluid velocity, ν the kinematic viscosity $[\mathrm{m^2s^{-1}}]$, α the thermal diffusivity $[\mathrm{m^2s^{-1}}]$, and the bar indicates average properties.

In convection heat transfer analysis, it is usually assumed that the fluid molecules at the wall are stationary relative to the wall and have temperatures identical to that of the

Table 1.1 Convection heat transfer correlations for common configurations

Configuration	Correlation
1. Forced convection: fully developed laminar flow inside pipes with constant wall temperature	$\overline{Nu}_{D_h} = 3.66$ (circular pipe), 7.54 (parallel plates) $Re_{D_h} \lesssim 2500$, $\overline{Nu}_{D_h} = \bar{h}D_h/k$, $Re_{D_h} = \bar{u}D_h/\nu$, $D_h \equiv 4A_c/p$, $A_c =$ cross-sectional area, $p =$ perimeter; properties evaluated at the average of inlet and outlet temperatures.
2. Forced convection: laminar boundary layer on an isothermal flat plate	$\overline{Nu} = 0.664\, Re_L^{1/2} Pr^{1/3}$ $10^3 < Re_L < 5 \times 10^5$, $Pr > 0.5$
3. Force convection: flow across a cylinder of external diameter D	$\overline{Nu}_D = \frac{1}{0.8237 - \ln(Re_D Pr)^{1/2}}$; $Re_D Pr < 0.2$ $\overline{Nu}_D = 0.3 + \frac{0.62\, Re_D^{1/2} Pr^{1/3}}{[1+(0.4/Pr)^{2/3}]^{1/4}}$; $Re_D < 10^4$, $Pr > 0.5$
4. Forced convection: flow across a sphere of external diameter D	$\overline{Nu}_D = 2 + (0.4\, Re_D^{1/2} + 0.06\, Re_D^{2/3}) Pr^{0.4} (\mu/\mu_w)^{1/4}$; $3.5 < Re_D < 7.6 \times 10^4$; $0.7 < Pr < 380$ All properties except μ_w are evaluated at T_∞
5. Natural convection: boundary layer on an isothermal vertical wall of length L	$\overline{Nu}_L = 0.68 + \frac{0.670\, Ra_L^{1/4}}{[1+(0.492/Pr)^{9/16}]^{4/9}}$; $Ra_L < 10^9$ where Rayleigh number $Ra_L \equiv g\beta(T_s - T_a)L^3/(\alpha\nu)$, $g =$ gravitational acceleration; $\beta =$ thermal expansion coefficient
6. Natural convection on a heated isothermal horizontal plate facing up, or a cooled plate facing down	$\overline{Nu}_L = 0.54\, Ra_L^{1/4}$; $10^4 < Ra_L < 10^7$, Ra_L defined in (5) $L \equiv A_s/p =$ ratio of the plate surface area to perimeter
7. Natural convection on a heated isothermal horizontal plate facing down, or a cooled plate facing up	$\overline{Nu}_L = 0.27\, Ra_L^{1/4}$; $10^5 < Ra_L < 10^{10}$ Ra_L and L defined in (5) and (6), respectively
8. Natural convection on an isothermal horizontal cylinder of external diameter D	$\overline{Nu}_D = 0.36 + \frac{0.518\, Ra_D^{1/4}}{[1+(0.559/Pr)^{9/16}]^{4/9}}$; $10^{-4} < Ra_D < 10^9$
9. Natural convection on a sphere of external diameter D	$\overline{Nu}_D = 2 + \frac{0.589\, Ra_D^{1/4}}{[1+(0.469/Pr)^{9/16}]^{4/9}}$; $Ra_D < 10^{11}$, $Pr \geq 0.7$

Note: All properties should be calculated at the average temperature of the wall and the fluid far away from the wall, unless otherwise mentioned. The Nusselt number is averaged over the area of the fluid–solid interface.

solid. This assumption is called the no-slip boundary condition. Referring to figure 1.6, the no-slip boundary condition is

$$u_x(x, y)|_{y=0} = u_y(x, y)|_{y=0} = 0 \tag{1.4}$$

$$T(x, y)|_{y=0} = T_w \tag{1.5}$$

where u_x and u_y are the fluid velocity components in Cartesian coordinates, T the fluid temperature distribution, and T_w the temperature of the solid surface. Because fluid

particles are stationary on the surface, the heat transfer from the wall to the fluid in the vicinity of the surface is actually through heat conduction. We can calculate this heat transfer rate according to the Fourier law,

$$Q = -kA\left.\frac{\partial T}{\partial y}\right|_{y=0} \tag{1.6}$$

Combining eqs. (1.3) and (1.6) leads to the expression for calculating the heat transfer coefficient

$$h = \frac{-k\left.\frac{\partial T}{\partial y}\right|_{y=0}}{T_w - T_a} \tag{1.7}$$

The above equation furnishes a formula for determining the heat transfer coefficient, provided the fluid temperature gradient at the wall can be determined. This task usually requires solving the velocity and temperature distributions of the whole flow field on the basis of the Navier–Stokes equations. In typical heat transfer or fluid mechanics textbooks, the Navier–Stokes equations are derived on the basis of the conservation principles for mass, momentum, and energy, together with constitutive relations such as the Fourier law, which relates the heat flux to the temperature gradient, and the Newton shear stress law, which relates the local velocity gradient to the local shear stress. We will discuss the Navier–Stokes equations in greater detail further in chapter 6. In its simplest form, assuming that the velocity component u in figure 1.6 depends on y only, the Newton shear stress law can be written as

$$\tau_{xy} = \mu\frac{\partial u_x}{\partial y} \tag{1.8}$$

where the first subscript on τ denotes the direction of the shear stress and the second subscript denotes the plane of action of the shear stress (y = constant plane), and μ [N s m^{-2}] is the dynamic viscosity (or absolute viscosity). A popular unit for μ is P (poise), where 1 P = 0.1 N s m^{-2}. The ratio of the dynamic viscosity to the fluid density, μ/ρ, gives the kinematic viscosity, ν. Viscosity is generally regarded as an intrinsic property of the fluid.

Going back to the theme of this book, microfluidics, which deals with fluid flow at micro- and nanoscales, has attracted significant attention due to its applications in chemical and biological analysis (Ho and Tai, 1998). Many questions can be asked about fluid flow and heat transfer at such scales. Is the Newton shear stress law applicable to fluid flow at these length scales? Is the no-slip boundary condition always correct? In this book, we will answer these questions via the Boltzmann equation, surface force analysis, and molecular dynamics simulations.

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1.3.3 Radiation

Thermal radiation, the third basic heat transfer mode, is different from conduction and convection. Heat transfer by thermal radiation does not require a medium and can propagate in vacuum, and the energy is carried by electromagnetic waves. A blackbody,

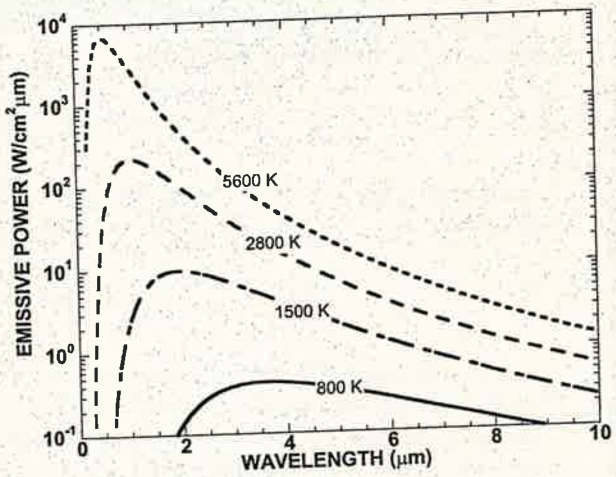


Figure 1.7 Blackbody emissive power as a function of wavelength at different temperatures.

which is an idealized object that emits the maximum amount of thermal radiation, radiates according to Planck's law

$$e_{b,\lambda} = \frac{C_1}{\lambda^5(e^{C_2/\lambda T} - 1)} \tag{1.9}$$

where C_1(= 37,413 W µm^4 cm^{-2}) and C_2(= 14,388 µm K) are constants, λ is the wavelength of the radiation, and T is the absolute temperature. The spectral emissive power, $e_{b,\lambda}$, is defined as the radiated power per unit emitting area and per unit wavelength interval,

$$e_{b,\lambda} = \frac{\text{Power}}{\Delta A \Delta \lambda} \tag{1.10}$$

and has units of Wm^{-2}µm^{-1}. Examples of blackbody radiation spectra are shown in figure 1.7. The wavelength at which the maximum emissive power occurs is given by the Wien displacement law

$$\lambda_{\max} T = 2898\ \mu\text{m K} \tag{1.11}$$

Solar radiation has an equivalent blackbody temperature of 5600 K and peaks around 0.52 µm. Thus, the fact that the human visibility range is between 0.4 and 0.7 µm is not incidental.

Integrating Eq. (1.9) over all wavelengths, we obtain the total emissive power of a blackbody

$$e_b = \int_0^\infty e_{b,\lambda} d\lambda = \sigma T^4 \tag{1.12}$$

What is coherence then? Why & when is it important?

where σ(= 5.67 × 10^{-8} Wm^{-2} K^{-4}) is the Stefan–Boltzmann constant. Equation (1.12) is called the Stefan–Boltzmann Law.

Real objects typically radiate less than a blackbody. The emissivity characterizes the thermal radiation characteristics of a surface. The spectral emissivity is defined as

$$\varepsilon_\lambda = e_\lambda / e_{b,\lambda} \tag{1.13}$$

where e_λ is the spectral emissive power of the surface.

As a form of electromagnetic wave, the propagation of thermal radiation can be described by Maxwell's equations. Calculating the radiative heat transfer, however, seldom requires the solution of these equations. Typically, we neglect the phase information carried by the electromagnetic waves and treat the thermal radiation as incoherent photon particles, or bundles of rays propagating in straight lines. These rays can be scattered, absorbed along the path, or enhanced by emission of the medium along the propagation direction. Upon reaching a surface, the thermal radiation can be reflected, absorbed, or transmitted. Calculating the radiation heat transfer between real surfaces requires information about the surface radiative properties, the geometrical arrangement of the surfaces, and the properties of the media between the surfaces. As an example, consider the simplest situation of two infinite, black, parallel walls separated by a vacuum. The radiation heat transfer per unit area, q, between the two surfaces is the difference of the energy carried by two groups of counter-propagating photons: one from the hot side toward the cold side [σT_1^4], and the other from the cold to the hot side [σT_2^4], !!

$$q = \sigma(T_1^4 - T_2^4) \tag{1.14}$$

In contrast to solving differential equations in heat conduction and convection to get the heat flux, in the case of thermal radiation we usually deal with the trajectory of photons through the use of view factor, or integral equations when scattering is involved. This approach is necessary because photons typically travel a long distance before they are scattered. In many radiation problems, photons collide more frequently with the walls rather than being scattered along their paths. In this sense, thermal radiation is always dealing with size or boundary effects. For heat conduction and convection in nanostructures, the heat carriers experience similar situations to photon transport in macrostructures because electrons, phonons, or molecules collide more often with the boundaries and interfaces than they collide with each other. Thus, many nanoscale transport processes can be understood through an analogy with photon transport on the macroscale. Such an analogy will be pursued throughout the text, whenever applicable. !!!

The transport of photons in micro- and nanostructures usually differs from that in macrostructures because the wavelength becomes comparable to or even longer than the characteristic device dimension. Under such circumstances, the phase information can no longer be ignored and the wave properties of photons, such as interference, diffraction, and tunneling, become important. The treatment of the propagation of electromagnetic waves is well developed in the fields of optics and electromagnetic waves (Born and Wolf, 1980). Many results in these fields can also be applied to thermal radiation in small spaces. In later chapters, we will see that the wave effects in micro- and nanostructures lead to significant deviations from the thermal radiation relations developed for macrostructures. For example, radiation heat transfer between nanoscale objects can be significantly higher than blackbody radiation (Domoto et al., 1970). An !!

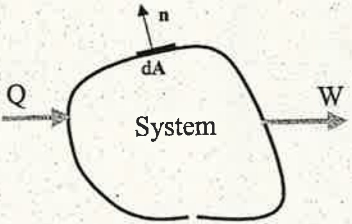


Figure 1.8 Energy conservation applied to a closed system.

understanding of the wave nature of photons provides a basis for comprehending the material waves and quantum size effects on other energy carriers such as electrons and phonons (Chen, 1996b).

1.3.4 Energy Balance

The equations that we have reviewed for different transport processes relate the heat flux to the temperature and the temperature gradient. Equations of this type are called constitutive equations. Each of them is a single equation with two unknowns: the heat flux and the temperature. In general, another equation is needed to solve for T and q. We use conservation principles to establish this other equation. For heat transfer, the most important conservation principle is the first law of thermodynamics (energy conservation), which states that heat transfer into a system minus the work output from a system equals the change of the internal energy of the system. Referring to a closed system, as shown in figure 1.8, the first law of thermodynamics is

$$Q - W = dU/dt \tag{1.15}$$

where Q is the rate of heat transfer into the system, W is the power output, and U is the system energy, that is, the sum of the internal energy, the kinetic energy, and the potential energy. In many heat transfer situations, the changes in the kinetic and potential energy are usually negligible such that U represents the internal energy only.

One major difference between the constitutive equations and the conservation equations is that the former relate to specific materials and processes but may not be valid in all cases, while the latter are universal. For example, the Newton law of shear stress is valid for Newtonian fluids but not for non-Newtonian fluids. Similarly, the Fourier heat conduction equation may not be valid for all heat conduction processes, as we will soon show. On the other hand, no evidence exists that the first law of thermodynamics is not valid, although there are discussions in current literature on the validity of the second law at small length and short time scales (Wang et al., 2002). As we move to the micro- and nanoscale, what may change are the conservation equations. The conservation equations are expected to hold true.

As an example of using the conservation equations, we consider a region with heat conduction as the only mode of heat transfer with no work transfer and no internal heat generation. The heat conduction across the boundary into the solid can be obtained by integrating eq. (1.1) over the surface consisting of the boundary (referring to figure 1.8),

$$Q = -\oint\!\!\oint_S (-k\nabla T)\, d\mathbf{A} \tag{1.16}$$

where $d\mathbf{A}$ is a differential area on the boundary with the norm pointing outward; thus a minus sign is added to eq. (1.16) to indicate heat conduction into the region. Substituting eq. (1.16) into eq. (1.15), we get

$$-\oint\!\!\oint_S (-k\nabla T) \bullet d\mathbf{A} = \frac{\partial}{\partial t}\int_V u\, dV \tag{1.17}$$

where u is the internal energy per unit volume and the integration on the right hand side is over the volume. The left-hand side of eq. (1.17) can be converted into volume integration using Gauss's divergence theorem and the right-hand side can be further related to temperature through the chain rule and the specific heat c,

$$\int_V \nabla \bullet (k\nabla T)\, dV = \int_V \rho c \frac{\partial T}{\partial t}\, dV \tag{1.18}$$

For this equation to be valid in any region, we must have

$$\nabla(k\nabla T) = \rho c \frac{\partial T}{\partial t} \tag{1.19}$$

which is the familiar heat diffusion equation that is used to solve heat conduction problems on the macroscale.

1.3.5 Local Equilibrium

In thermodynamics, we define equilibrium as a state of an isolated system in which no macroscopic change can be observed as a function of time. Quantities such as temperature and pressure are defined only under equilibrium conditions. Transport processes happen when the system is driven out of equilibrium. A system undergoing steady-state heat conduction is not in an equilibrium state. Although no change occurs in such a system, the steady state does not violate the definition of equilibrium, since the system is not isolated. However, the nonequilibrium state of the system does pose a problem because the temperature cannot be defined in accordance with thermodynamics. It would seem the constitutive relations we have introduced are meaningless. This dilemma can be resolved by employing the concept of local equilibrium. Although a system may be out of equilibrium globally, the deviation from equilibrium at each point is usually small. A small region surrounding each space point may be approximated as being in equilibrium, which allows us to define a local temperature, pressure, and chemical potential. We have not, however, established rigorous criteria based on when we can assume local equilibrium and we do not know yet how small this region should be. We can further ask what happens if the system is smaller than this minimal size.

1.3.6 Scaling Trends under Macroscopic Theories

The characteristic length scales at which the classical theories discussed in this section fail are typically on the order of submicrons, although the exact demarcation line depends on the type of energy carriers, the media, and the temperature. A wide range of microdevices exists with characteristic lengths larger than microns for which the classical transport theories are still applicable. It is, however, interesting to consider how the miniaturization will change the heat transfer characteristics. As the device size shrinks, the ratio of surface area to volume increases, leading to significant changes in thermal, electrical, and mechanical behavior. A well-known example in mechanics is the diminishing effect of inertia and the increasing importance of surface tension, as is evident in the fact that ants (with a characteristic dimension of millimeters) are not injured by falling off a table but can be easily trapped in a drop of water, which is contrary to what may happen to humans (with a characteristic length of meters) in similar situations. In table 1.2, we show some examples of the scaling trend for simple heat transfer configurations, assuming that macroscopic transport theories are still applicable.

1.4 Microscopic Picture of Heat Carriers and Their Transport

This section briefly addresses the following questions: (1) What carries heat? (2) How much energy do the carriers possess? (3) How fast do they travel? and (4) How far do they travel? The explanation will be brief here since these questions will be discussed in more detail in subsequent chapters.

1.4.1 Heat Carriers

People used to think that heat was carried by a special form of matter termed calories, which were supposedly massless and colorless. When two objects at different temperatures are in contact with each other, calories from the object at the high temperature would flow into the object at the lower temperature. This view prevailed in the early 19th century and contributed significantly to the development of classical thermodynamics. Of course, we now know that this is an incorrect picture. In fact, the caloric theory, despite its inception in the late 18th century, was completely abandoned by the middle of the 19th century. Yet most of the results on classical thermodynamics derived from such a wrong picture turned out to be correct and are still valid today because, as we mentioned before, classical thermodynamics does not consider detailed pictures of heat carriers.

Heat conduction actually results from the random motion of the material particles in the system carrying thermal energy from one location to another. These material particles are electrons, atoms, and molecules in gases, liquids, and solids. We use heat conduction in a gas, as shown schematically in figure 1.9, to illustrate the microscopic energy transport process. Gas molecules near the hot wall collide with the solid atoms of the wall often and gain a higher kinetic energy, that is, a higher random velocity. These molecules are in random motion and have the possibility of moving toward the lower temperature end. During this process, they collide with molecules having smaller random velocity (and thus cooler) and pass some of the excess energy to those molecules. Such a process cascades for all adjacent molecules until it reaches the molecules in the proximity of the cold wall. These molecules have a higher kinetic energy than the atoms in the solid wall and will impart their excess energy to the wall through collisions.

Table 1.2 Scaling trend under classical transport theories for representative microgeometries

Mode and Example	Quantity	Scaling Trend
Heat conduction (1) Along thin films (2) Perpendicular to thin films	Heat transfer rate: $Q = kA_c\Delta T/L$ Heat flux: $q = k\Delta T/L$ Thermal diffusion time: $\tau = L^2/a$ L: heat conduction path length L = film length (along film plane) L = film thickness (perpendicular) a: thermal diffusivity, $\mathrm{m^2\,s^{-1}}$	Case (1): Q small since A_c is small q larger than bulk, depending on L τ shorter than bulk, depending on L Case (2): Q depending on A_c/L q very large since L is small τ very short
Convection (1) Inside a microchannel (2) Across a microcylinder	Heat transfer rate: $Q = hA(T_w - T_a)$ Heat flux: $q = h(T_w - T_a)$ Nusselt No. for (1): $Nu = hd/k =$ const. h for case (1): $h \propto 1/d$ Nusselt No. for (2): $Nu - 0.3 \propto Re^{1/2}$ h for (2): $h \propto 1/d^{1/2}$ to $1/d$	For case (1): Q independent of d q increases as $1/d$ h increases as $1/d$ For case (2): Q decreases with d^0 to $d^{1/2}$ q increases with $1/d^{1/2}$ to $1/d$ h increases with $1/d^{1/2}$ to $1/d$
Radiation Between two black parallel plates	Heat transfer rate: $Q = \sigma A(T_1^4 - T_2^4)$ Heat flux: $q = \sigma(T_1^4 - T_2^4)$	Q decreases since A decreases q remains constant → near field effects
Coupled conduction and convection (1) Heat conduction along fins (2) Lumped capacitance	Case (1) Temperature: $\frac{[T_b - T(x)]}{T_b - T_a} = e^{-\gamma x}$ Heat transfer rate: $Q = kA_c\gamma(T_b - T_a)$ fin parameter: $\gamma = [hp/(kA_c)]^{1/2}$ Case (2) Temperature: $\frac{[T(t) - T_a]}{T_i - T_a} = e^{-t/\tau}$ Time Constant: $\tau = \rho cV/(hA)$ p = fin perimeter; T_i = initial temperature T_b = fin base temperature	For case (1): γ increases, temperature decreases rapidly along fins Q decreases due to decreasing A_c For case (2): τ decreases due to decreasing V/A and increasing h

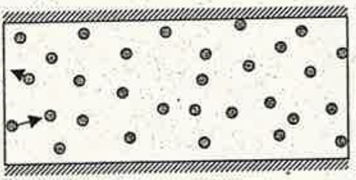


Figure 1.9 Microscopic heat conduction process through a gas.

The resultant effect is that a net energy flows from the hot wall to the cold wall due to the temperature difference between the two walls. It should become clear that the net energy flow is due to the random motion of the molecules and that the molecules do not necessarily move from the hot to the cold side.

In dielectric solid materials (electrical insulators), heat is conducted through the vibration of atoms. The atoms are bonded to each other in a dielectric material through interatomic force interactions. Figure 1.10 shows a schematic of the interatomic potential, ϕ, between two atoms as a function of their separation, x. The force interaction between two atoms is the derivative of such an interatomic potential

$$F = \frac{-d\phi}{dx} \tag{1.20}$$

If the two atoms are far apart, an attractive force exists between the atoms because the electrons of one atom attract the nucleus of the other. When the atoms are close, the interaction force becomes repulsive because the electron orbits, or the nuclei, of different atoms begin to overlap. The minimum potential defines the equilibrium positions of the atoms. Each atom in a solid vibrates around its equilibrium position. The motion of each atom is constrained by its neighboring atoms through the interatomic potential. A simplified picture of the interatomic interactions in crystals can be represented by a mass-spring system, as shown in figure 1.11(a). In such a system, the vibration of any one atom can cause the vibration of the whole system by creating lattice waves in the system. The propagation of sound in a solid is due to long-wavelength lattice waves. If one side of the solid is hotter, the atoms near the hot side will have larger vibrational amplitudes, which will be felt by the atoms on the other side of the system through the propagation and interaction of lattice waves. Quantum mechanical principles dictate that the energy of each lattice wave is discrete and must be a multiple of $h\nu$ (except for a small modification called zero point energy that equals $h\nu/2$), where ν is the frequency of the lattice wave and h the Planck constant (6.6×10^{-34} J s). This minimum energy $h\nu$ of a quantized lattice wave is called a phonon. A phonon at a specific frequency and wavelength is a wave that extends through the entire crystal. The superposition of phonons of multiple frequencies existing in the solid forms wave packets that have a narrow spatial extent. These wave packets can be considered as particles as long as they are much smaller than the crystal size. Using this phonon particle picture, the spring system in figure 1.11(a) can be replaced by a box of phonon particles as in figure 1.11(b). Heat in a dielectric crystal is conducted by such a phonon gas similar to that in a box of gas molecules as shown in figure 1.9. The collision of phonon particles is due to the interaction of phonon waves, which can be further attributed to the nonparabolicity (or anharmonic) potential profile as shown in figure 1.10. A parabolic potential, according to eq. (1.20), would lead to an ideal spring with force linearly proportional to displacement from the minimum potential position. Phonons in such an ideal potential do not collide with each other. !! In chapters 3 and 5 we will explain in more detail the phonon concept and when we can treat phonons as particles rather than waves.

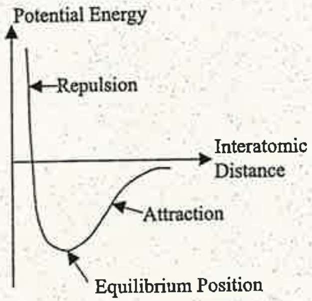


Figure 1.10 A typical interatomic potential profile.

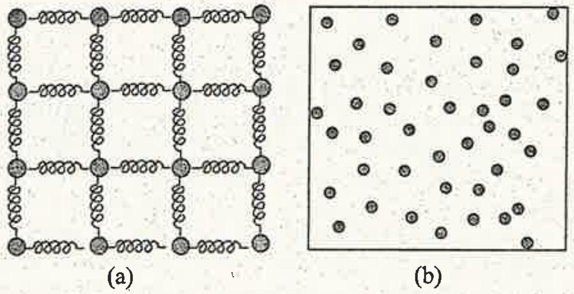


Figure 1.11 (a) A mass-spring system representing interconnected atoms in a crystal, and (b) phonon gas model replaces the solid atoms in a crystal.

In metals, heat is conducted by free electrons as well as by phonons. When atoms are bonded together to form a metal, some of the electrons in the outer orbits of the nuclei become free from the bonding of the nuclei. These free electrons can travel a distance much longer than the interatomic distance until they are scattered by either atoms, electrons, or impurities. Under this picture, the free electrons inside a metal can also be thought of as a gas—an electron gas. The heat conduction process for the electron gas is again similar to that shown in figure 1.9 for molecules. Electrons in a metal travel at a velocity typically three orders of magnitude larger than phonons do. Thus, compared to the energy carried by lattice waves, the energy flux carried by electrons is in general much larger. Therefore, in metals, electrons are usually the dominant heat carriers.

One may guess that, in semiconductors, heat is probably conducted partially by phonons and partially by electrons. That assumption is not completely correct. In fact, heat is carried dominantly by phonons in most semiconductors, because the free electron density in a normal semiconductor is much smaller than that in a metal. As an example, the electron carrier density in a metal is $\sim 10^{23}$ cm^{-3} while in a semiconductor it is typically less than 10^{18} cm^{-3}. In lightly and moderately doped semiconductors, phonons are the dominant heat carriers. However, the electron contribution in a heavily doped semiconductor can be appreciable.

Given the above pictures of heat carriers for heat conduction processes, the convection of heat can be understood rather easily since the only difference of convection from heat conduction is that now heat carriers have a nonvanishing average velocity superimposed on their random velocity. When a liquid or gas molecule moves from one place to another due to its nonzero average velocity, it also carries its internal energy directly from one place to another. This direct motion of internal energy in convection is very different from heat conduction process. In the latter, heat is transferred due to the energy exchange of heat carriers in the collision process. Heat conduction process exists even in convection process because molecules are still doing random motion. In fact, the random motion velocity of the molecules is usually much higher than the nonvanishing average velocity in convection. However, convection is more effective than heat conduction because energy moves directly from one place to another.

Thermal radiation involves another heat carrier, that is, electromagnetic waves. The propagation of electromagnetic waves emitted from a thermal source does not differ fundamentally from those carrying TV and radio signals because all are governed by the Maxwell equations. The major difference lies in how these waves are generated. Thermal radiation typically refers to the electromagnetic waves that are generated by a heat source, while TV and radio signals are generated by an artificial source such as the oscillation of current in a circuit. At the microscopic level, thermal radiation is due to the oscillation of charges in the atoms and crystals. Similarly to lattice waves, electromagnetic waves are also quantized as a result of quantum mechanics. An electromagnetic wave at frequency ν can have energy that is only a multiple of $h\nu$. This smallest energy quantum of an electromagnetic field, $h\nu$, is called a photon. In fact, most people are probably more familiar with the terminology of photon than phonon. Both of them are the basic quantum of a wave; one for electromagnetic waves and the other for lattice vibrational waves.

1.4.2 Allowable Energy Levels of Heat Carriers

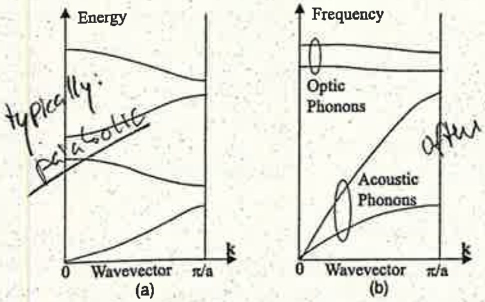
The transport of heat is due to the motion of the energy carriers discussed above and the associated energy they carry. To describe heat transfer quantitatively, we need to know the energy associated with these heat carriers. The possible energy states of heat carriers are determined by quantum mechanical principles, which we will cover in chapters 2 and 3. Here, we will only give the reader some brief idea. For individual atoms and molecules, the energy levels are typically discrete. For example, the allowed energy levels of a harmonic oscillator, which is a good model for the vibrations of a diatomic molecule such as H_2, are given by

$$E_n = h\nu(n + 1/2) \qquad (n = 0, 1, 2, 3, \ldots) \tag{1.21}$$

where ν is the fundamental vibration frequency. The amplitude of the vibration must be such that the total energy of the molecule fits into one of the above discrete energy levels. In crystalline solids, the allowable energy of electrons and phonons is a function of the wavevector. Such functional relations are also called dispersion relations. A wavevector **k** points in the direction of wave propagation (electron and phonon waves) and its magnitude equals 2π divided by the wavelength. Figures 1.12(a) and (b) show examples

def dispersion relation

$$|\vec{k}| = \frac{2\pi}{\lambda}$$



typically: parabolic

often linear

Figure 1.12 Illustration of typical dispersion relation for (a) electrons and (b) phonons in crystals.

of the electron and phonon energy levels, represented by either energy or frequency, in solids along a specific crystallographic direction, where a is the periodicity of the atoms in the direction of the wave propagation and **k** is the wavevector. The allowable energy levels form bands. Within each band, the energy is quasi-continuous because the wavevector is discrete, as we will discuss in more detail in chapter 3. However, there can be substantial gaps between different bands. The filling of the electronic bands by electrons and the magnitude of the gaps determine whether a solid is a metal, a semiconductor, or an insulator. The phonon band differs significantly from that for electrons. Electron bands are typically approximated by a parabolic relationship between the energy and the wavevector, whereas the dispersion relation between the phonon wavelength and the wavevector is often approximated by a linear relationship.

1.4.3 Statistical Distribution of Energy Carriers

Not all the possible energy levels of energy carriers (molecules, electrons, and phonons) will be actually occupied by the carriers. Classical thermodynamics tells us that a non-isolated system at equilibrium tends to minimize its energy. In a system with different allowable energy levels, heat carriers will fill the lowest energy levels at zero temperature. At higher temperatures, some of the carriers will have higher energy levels. The most probable energy distributions of the carriers are governed by statistical principles. Classical statistical theory gives the probability density $f(E)$, defined as the probability of finding the carrier at energy E per energy interval surrounding E, for a particle in an equilibrium system at a temperature T,

$$\boxed{f(E) = Be^{-E/(\kappa_B T)}} \tag{1.22}$$

→ see photonics book.

where κ_B (= 1.38 × 10^{-23} J K^{-1}) is the Boltzmann constant, T is the absolute temperature, and B is a normalization factor. Equation (1.22) is the famous Boltzmann distribution (Ludwig Boltzmann, 1844–1906). For a monoatomic ideal gas system, the only energy of each atom is its translational kinetic energy

monatomic ideal gas:

$$E = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2) \tag{1.23}$$

where m is the mass of the atom and v_x, v_y, and v_z are the components of its random velocity. Since the probability of finding this particle to have energy between zero and infinite speed must be one, we have

$$\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} B \exp\left[-\frac{m(v_x^2+v_y^2+v_z^2)}{2\kappa_B T}\right] dv_z = 1 \tag{1.24}$$

Carrying out the above integration leads to

$$B = \left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \tag{1.25}$$

The probability density of a monatomic gas is thus

$$f(\mathbf{v}) = \left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \exp\left[-\frac{m(v_x^2+v_y^2+v_z^2)}{2\kappa_B T}\right] \tag{1.26}$$

which is called the Maxwell distribution. With this probability density, we can calculate other expectation values (or average values). For example, the average energy (internal energy) of a monatomic gas molecule is

$\langle E \rangle = \int E f(v)\, dv$

$$\langle E\rangle = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} \frac{m}{2}(v_x^2+v_y^2+v_z^2)\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \exp\left[-\frac{m(v_x^2+v_y^2+v_z^2)}{2\kappa_B T}\right] dv_z \tag{1.27}$$

Transforming the Cartesian coordinates v_x, v_y, v_z into spherical coordinates makes the above integration much easier. The final result is

$$\langle E\rangle = \frac{3}{2}\kappa_B T \tag{1.28}$$

average kin. energy of monatomic gas molecule

The above expression means that temperature is a measure of the average kinetic energy for a monoatomic gas. Equation (1.28) is a very useful result to remember and is an example of the equipartition theorem in statistical thermodynamics. The equipartition theorem for classical systems states that at sufficiently high temperatures (such that the Boltzmann distribution is valid) each quadratic term of the molecular energy contributes to the molecule an average energy $\kappa_B T/2$. For a monoatomic gas, each molecule has three quadratic energy components, from its translational motion, as indicated by eq. (1.23), so that the total average kinetic energy is $3\kappa_B T/2$.

Example 1.1 *Speed and specific heat of gas molecules*

Estimate the average speed of helium atoms as an ideal gas at 300 K, and also estimate its specific heat at constant volume.

Solution: The average speed of molecules obeying the Maxwell distribution is

$$\langle v\rangle = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} v\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \exp\left[-\frac{m(v_x^2+v_y^2+v_z^2)}{2\kappa_B T}\right] dv_z$$

$$= \int_0^{\infty} v\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2\kappa_B T}\right) 4\pi v^2 dv = \sqrt{\frac{8\kappa_B T}{\pi m}}$$

The mass of a helium atom is $4 \times 1.67 \times 10^{-27}$ kg, where 4 comes from the fact that a helium atom has two protons and two neutrons, and 1.67×10^{-27} kg is the rest mass of a proton (a neutron has approximately the same weight as a proton). We thus obtain the average velocity of helium atoms as 1257 m s^{-1}. To obtain the specific heat, we know that a mole contains $N_A = 6.02 \times 10^{23}$ (Avogadro's constant) molecules. The total energy of a mole of helium atoms is thus $u = 3N_A\kappa_B T/2$. The specific heat at constant volume is $c_v = \partial u/\partial T = 3\kappa_B N_A/2 = 3R_u/2 = 12.5$ J K^{-1} mol^{-1}, where $R_u = \kappa N_A = 8.314$ J K^{-1} mol^{-1} is the universal gas constant. The actual specific heat of helium is in agreement with this number.

Comment: A quick order-of-magnitude estimation of the average speed can be obtained by setting the average kinetic energy of each atom, $3\kappa_B T/2$, equal to $mv^2/2$, which leads to $v = (3\kappa_B T/m)^{1/2} \approx 1364$ m s^{-1}, which is slightly higher than $\langle v\rangle$.

When energy levels are not continuous, the normalization factor B in eq. (1.22) can no longer be determined as is done in deriving the Maxwell distribution. We will give the distribution functions for electrons and phonons here, leaving the details to chapter 4. The electron probability density is governed by the Fermi–Dirac distribution and that of phonons and photons by the Bose–Einstein distribution, !!

$$\text{Fermi–Dirac distribution: } f(E) = \frac{1}{\exp\left(\frac{E-\mu}{\kappa_B T}\right)+1} \tag{1.29}$$

$$\text{Bose–Einstein distribution: } f(\nu) = \frac{1}{\exp\left(\frac{h\nu}{\kappa_B T}\right)-1} \tag{1.30}$$

where μ is the chemical potential. The Bose–Einstein distribution is expressed in terms of the phonon energy $E = h\nu$ rather than E directly.

From the above discussion, we see that temperature is only meaningful when we deal with a large number of molecules. At equilibrium, the temperature alone determines the statistical distribution of all the heat carriers in the system. It is meaningless to speak of the temperature of one single particle. But it is meaningful to talk about the energy of one particle and the average energy of a cluster of particles, even if the particles are out of equilibrium such that they do not obey the Boltzmann distribution (or other kinds of expected statistical distributions). Later, we will use the concept of temperature for highly nonequilibrium systems. In these situations, temperature should be understood as a measure of the local average energy density, but one cannot determine the statistical distributions of the particles on the basis of temperature alone.

T zu E_{kin}

1.4.4 Simple Kinetic Theory

By definition, heat transfer involves the motion of heat carriers generated by temperature differences. Statistically, heat carriers generated by thermal sources are randomly distributed in all directions. Given the position and velocity of all heat carriers, their subsequent motion determines the energy transport. Although, in principle, the trajectory of these energy carriers can be traced on an individual basis, such an analytical approach is usually impractical due to the large number of carriers existing in the medium. With the rapid advancement of computational power, however, some problems are within

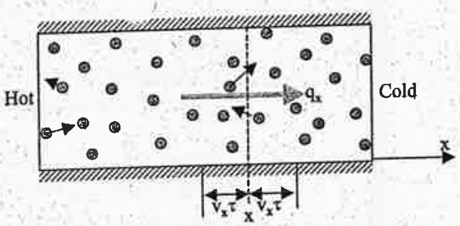


Figure 1.13 Simplified derivation of the Fourier law based on kinetic theory.

the reach of this direct approach. We will devote a chapter (chapter 10) to molecular dynamics, which is based on tracing the trajectory of individual molecules. In most cases, some kinds of averaging are necessary for practical mathematical descriptions of the heat carrier motion. The Fourier law for heat transfer, the Fick law for mass diffusion, and the Ohm law for electrical conduction are the results of averaging the microscopic motion in a sufficiently large region and over a sufficiently long time. The laws are the correct representations of the average behavior of the energy, mass, and current flow in macroscopic systems going through relatively slow processes. Such averaging may no longer be valid in microscale and nanoscale domains and for high-speed processes because the conditions for the average behavior are no longer satisfied. In subsequent chapters, we will take a closer look at the averaged motion of heat carriers in micro- and nanoscale systems. Here, we first introduce a simple derivation of the Fourier law from kinetic theory.

We consider a one-dimensional model as shown in figure 1.13. If we take an imaginary surface perpendicular to the heat flow direction, the net heat flux across this surface is the difference between the energy fluxes associated with all the carriers flowing in the positive and negative directions. Considering the positive direction, the carriers within a distance $v_x\tau$ can go across the interface before being scattered. Here v_x is the x component of the random velocity of the heat carriers and τ is the relaxation time—the average time a heat carrier travels before it is scattered and changes its direction. Thus, the net heat flux carried by heat carriers across the surface is

$$q_x = \frac{1}{2}(nEv_x)\Big|_{x-v_x\tau} - \frac{1}{2}(nEv_x)\Big|_{x+v_x\tau} \tag{1.31}$$

where n is the number of carriers per unit volume and E is the energy of each carrier. The factor 1/2 implies that only half of the carriers move in the positive x direction while the other half move in the negative x direction. Using a Taylor expansion, we can write the above relation as

$$q_x = -v_x\tau\frac{d(Env_x)}{dx} \tag{1.32}$$

Now we assume that v_x is independent of x, and $v_x^2 = (1/3)v^2$, where v is the average random velocity of the heat carriers. The above equation becomes

$$q_x = -\frac{v^2\tau}{3}\frac{dU}{dT}\frac{dT}{dx} \tag{1.33}$$

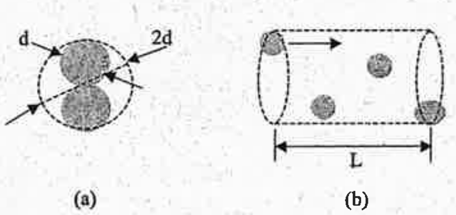


Figure 1.14 Mean free path estimation for a box of gas molecules with effective diameter d for each molecule: (a) effective diameter of two molecules to scatter is $2d$, and (b) mean free path is the average distance between two consecutive scattering.

where $U = nE$ is the local energy density per unit volume and dU/dT is the volumetric specific heat C of the heat carriers at constant volume, which equals the mass specific heat c times the density ρ, i.e., $C = \rho c$. This formulation leads to the Fourier law

$$q_x = -(Cv^2\tau/3)dT/dx = -kdT/dx \tag{1.34}$$

Although the above model is fairly crude, the expression for the thermal conductivity is actually a surprisingly good approximation,

kinetic theory: $$k = Cv^2\tau/3 = Cv\Lambda/3 = \rho cv\Lambda/3 \tag{1.35}$$

where $\Lambda = v\tau$ is the mean free path—the average distance a heat carrier travels before it loses its excess energy due to scattering. Very often, the above equation is used to estimate the mean free path on the basis of experimental results for the other parameters in the equation.

1.4.5 Mean Free Path

We now give a very crude derivation of the mean free path for gas molecules. By definition, the mean free path is the average distance that a gas molecule travels between successive collisions. It is not the distance that separates individual molecules. Suppose that the effective diameter of an atom (or molecule) is d, as shown in figure 1.14.* The effective diameter for two atoms to collide is $2d$ and the collision cross-section is $\pi(2d)^2/4$. If the molecule travels a distance L, it sweeps out a volume $\pi d^2 L$. If the molecular number concentration is n, then the number of molecules that this particle will collide with is $n\pi d^2 L$. The average distance between each collision is (Kittel and Kroemer, 1980)

$$\Lambda = \frac{L}{n\pi d^2 L} = \frac{m}{\pi\rho d^2} \tag{1.36}$$

where we have invoked the relation that the number of molecules per unit volume is the density divided by the molecular weight m. This expression assumes that the molecule being considered moves but the other molecules in the volume are stationary. Dropping this assumption leads to a more accurate expression (Tien and Lienhard, 1979),

$$\Lambda = \frac{m}{\pi\sqrt{2}\,\rho d^2} \tag{1.37}$$

*This is not the diameter of the ion or the electron orbit. It represents the force range that a molecule exerts on its surroundings.

For an ideal gas, $P = \rho \kappa_B T/m$, so

$$\Lambda = \frac{\kappa_B T}{\pi \sqrt{2}\, P d^2} \tag{1.38}$$

Estimating the effective diameter d of an atom or molecule requires detailed information regarding the molecular and electronic structures of the molecule and the atom. We can readily reason that d is proportional to the number of atoms in the molecule and the number of electrons in the atom. Let us take an order-of-magnitude value for d of 2.5 Å. At $P = 101$ kPa, $T = 300$ K, Λ is approximately 0.14 μm. At a low pressure, for example, at $P = 10^{-8}$ torr $= 1.32 \times 10^{-6}$ Pa, $\Lambda \approx 14{,}000$ m, which is a very long traveling distance and means that no collision occurs in practical systems under such a vacuum condition. In thin-film deposition processes, vacuum conditions are often used to avoid contamination and the long mean free path ensures that atoms will travel uninterrupted (ballistically) from the source to the depositing surface. Equation (1.38) shows that the mean free path of gas molecules increases with increasing temperature. In addition, the gas random velocity increases with the square root of the temperature. At room temperature and higher, the molar specific heat remains constant and the density is proportional to P/T. This effect leads to the conclusion that the thermal conductivity increases with $T^{1/2}$ for gases and is independent of pressure. Check figure 1.5 for this trend of thermal conductivity for various gases.

Example 1.2 *Thermal conductivity of gas*

Estimate the thermal conductivity of air.

Solution: We will use eq. (1.35) to estimate the thermal conductivity of air. We can estimate the random velocity of air molecules from $mv^2/2 = 3\kappa_B T/2$, where m is the average mass of an air molecule (average molar weight of air is 29). This gives $v = 524$ m s^{-1}. At room temperature, $\rho = 1.16$ kg m^{-3} and $c = 1007$ J kg^{-1}K^{-1}. Substituting these values and a mean free path of 0.14 μm into eq. (1.35), we obtain $k = 0.028$ W m^{-1}K^{-1}. This is not far from the actual thermal conductivity of air at 300 K, which is 0.026 W m^{-1}K^{-1}.

1.5 Micro- and Nanoscale Transport Phenomena

At small scales, many macroscopic descriptions of heat transfer become invalid. In this section, we will provide examples to illustrate microscale transport phenomena.

1.5.1 Classical Size Effects

One example of the classical size effect is rarefied gas heat conduction. This size effect occurs when the mean free path of gas molecules becomes comparable to or larger than the size of the system. We have seen that the mean free path increases with decreasing gas pressure. The air pressure in the outer atmosphere is very low and thus the mean free path of the molecules is long. A spacecraft going through the outer atmosphere cannot be modeled on the basis of continuum theory; this sparked a substantial amount of work in the past on rarefied gas flow and heat transfer. Certain semiconductor manufacturing processes are often performed in vacuum environments, for which heat transfer and fluid flow may fall into the rarefied gas regime.

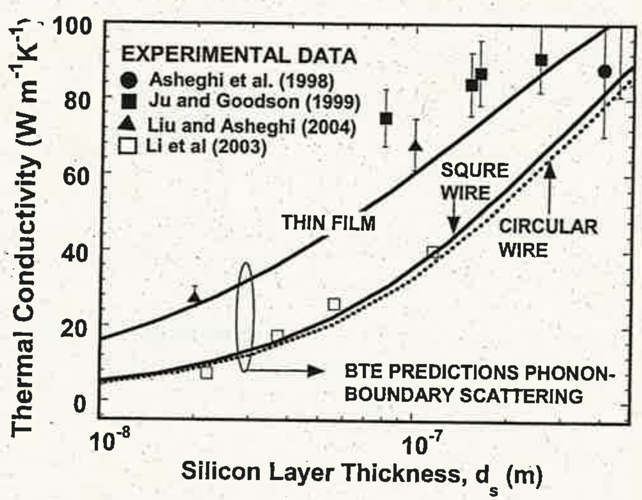


Figure 1.15 Thermal conductivity of silicon films as a function of the film thickness or wire diameter. (Courtesy of M. Ashegli).

Past research interests in rarefied gas dynamics and heat transfer were stimulated by the increasing mean free path encountered in low-pressure environments. Microfabrication and nanotechnology led to micrometer and nanometer structures with the characteristic length comparable to the mean free path of gas molecules, even at normal atmospheric pressures. The rarefaction effects must be considered for gas flow and heat transfer in such structures. The small size also brings in additional factors. For example, despite the fact that liquids molecules have a mean free path only on the order of angstroms, the surface charges that build up may significantly affect the heat transfer and fluid flow in submicron channels.

Size effects, which are well studied for gases, can also be expected for electrons and phonons, since both electrons and phonons can be considered as gases existing within solids (electron gas and phonon gas). When the mean free paths of electrons and phonons become comparable to or larger than an object's characteristic length, heat conduction in solids can deviate significantly from the predictions of the Fourier law. The thermal conductivity of thin films or nanowires is no longer solely a material property, but also depends on the film thickness or the wire diameter. Figure 1.15 shows the thermal conductivity of Si single crystal thin films and nanowires as a function of the film thickness and wire diameter.

1.5.2 Quantum Size Effects

According to quantum mechanics heat carriers such as electrons and phonons are also material waves. The finite size of the system can influence the energy transport by altering

$\frac{n\lambda}{2} = D$

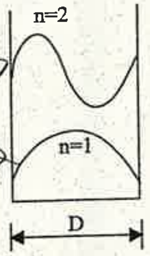


Figure 1.16 Standing waves in a quantum well, the two lowest energy levels.

the wave characteristics, such as forming standing waves and creating new modes that do not exist in bulk materials. For example, electrons in a thin film can be approximated as standing waves inside a potential well of infinite height as shown in figure 1.16. The condition for the formation of such standing waves is that the wavelength λ satisfies the following relation

Condition for standing $n\lambda/2 = D\ (n = 1, 2, \ldots)$ waves (1.39)

where D is the width of the potential well. Given the above electron wavelength, we can calculate its momentum according to the de Broglie relation between wavelength λ and momentum p,

$$p = h/\lambda \tag{1.40}$$

where h is the Planck constant ($h = 6.6 \times 10^{-34}$ J s). The energy of the electron is thus $E = p^2/2m$,

$$E_n = \frac{h^2}{8m}\left[\frac{n}{D}\right]^2 \ (n = 1, 2, \ldots) \tag{1.41}$$

For a free electron, $m = 9.1 \times 10^{-31}$ kg, and $D = 1$ μm, $E_n = 5.9 \times 10^{-25} n^2$ J, so that the energy separation between the $n = 1$ and $n = 2$ levels is 1.8×10^{-24} J. At room temperature, this energy separation is too small compared to the thermal fluctuation energy $\kappa_B T = 41.6 \times 10^{-22}$ J to be distinguishable from thermal fluctuation. In addition, the electron mean free path at room temperature is usually much smaller than 1 μm. Scattering of electrons destroys the condition for forming standing waves, making eq. (1.39) inapplicable. However, as the film size is further reduced, say to $D \approx 100$ Å, scattering is negligible and energy quantization becomes observable in comparison with thermal fluctuation. The electron energy quantization will affect the electrical, optical, and thermal properties of nanostructures and nanomaterials.

1.5.3 Fast Transport Phenomena

Size effects create deviations from commonly used classical laws by imposing new conditions at the boundaries. Transport at short time scales may also differ significantly from that at the longer time scales that we are used to. This difference is because the classical laws are commonly derived for time scales much longer than the time scale of microscopic processes. We can quickly estimate, for example, the average time interval τ between successive collisions of phonons as

Table 1.3 Basic characteristics of energy carriers

	Free Electrons	Phonons	Photons	Molecules
Source	Freed from nucleic bonding	Lattice vibration	Electron and atom motion	Atoms
Propagation media	In vacuum or media	In media	In vacuum or media	In vacuum or media
Statistics	Fermi–Dirac	Bose–Einstein	Bose–Einstein	Boltzmann
Frequency or energy range	0–infinite	Debye cutoff	0–infinite	0–infinite
Velocity (m s^{-1})	$\sim 10^6$	$\sim 10^3$	$\sim 10^8$	$\sim 10^2$

$$\tau = \Lambda / v \tag{1.42}$$

where Λ is the phonon mean free path and v the average phonon velocity. For many materials, this relaxation time is of the order 10^{-12} to 10^{-10} s. Although this appears to be an amazingly short time, a laser pulse can be as short as a few femtoseconds (1 fs = 10^{-15} s). Clearly, if we deal with processes shorter than the relaxation time, the classical Fourier diffusion law will no longer hold true, since the diffusion process is established by considering the multiple collisions of the heat carriers such that their motion is almost random. In addition to the relaxation time, there are also other time scales that need to be considered, such as the time characterizing the energy exchange between electrons and phonons. An example of the latter is the femtosecond laser heating of metals (Qiu and Tien, 1993).

Table 1.3 summarizes the basic characteristics of energy carriers, including:

- Free electrons in solids, which are released from the bonding of the nuclei and can propagate in solids as well in a vacuum;
- Phonons, which are due to atom vibration in crystals and cannot propagate in a vacuum;
- Photons, which are generated from the electron and atom motion and can propagate in a vacuum;
- Molecules, which form due to bonding of atoms.

Electrons obey the Fermi–Dirac statistics and are called fermions, while photons and phonons obey the Bose–Einstein statistics and are called bosons. Molecules obey the Boltzmann statistics (classical) under most temperatures except when approaching absolute zero, when Bose–Einstein statistics must be considered. The quantum mechanically allowable energy (or frequency) of one carrier spans a wide range, from zero to infinite, except for phonons for which the maximum is capped. The allowable energy only tells what is possible, but not the average, which is determined by the temperature and the statistics. The random average velocity of the heat carriers increases from molecules, to phonons, to electrons, and to photons, approximately.

Table 1.4 illustrates the transport regimes of energy carriers. This regime table can be best understood after reading through chapters 5–7. It divides the transport into

Table 1.4 Transport regimes of energy carriers; O represents order of magnitude

Important Length Scales	Regimes		Photon	Electron	Phonon	Fluids
1 Coherence length, ℓ_c 2 Phase-breaking length, ℓ_p ℓ_c: for photon: µm–km for phonon: 10 Å for electron: 100 Å $\ell_p \gtrsim$ Mean free path	Wave regime	$D < O(\ell_p)$ $D < O(\ell_c)$	Maxwell EM theory	Quantum mechanics	Quantum mechanics	Super fluidity
	Transition regime	$D \sim O(\ell_p)$ $D \sim O(\ell_c)$	Coherence theory	Quantum Boltzmann equation		
3 Mean free path, Λ Photon: 100 Å–1 km Electron: 100–1000 Å Photon: 100–1000 Å 4 width of "potential well," D	Particle regime $D > O(\ell_c)$, $D > (\ell_p)$	$D < O(\Lambda)$ ballistic	Ray tracing	Ballistic transport	Ray tracing	Free molecular flow
		$D \sim O(\Lambda)$ quasi-diffusive	Radiative transfer equation	Boltzmann transport equation	Boltzmann transport equation	Boltzmann transport equation
		$D > O(\Lambda)$ diffusive	Diffusion approximation	Ohm's law	Fourier's law	Newton's shear stress

several regimes. The wave regime is where the phase information of the energy carriers must be considered and the transport is coherent, and the particle regime is where the phase information can be neglected and the transport is incoherent. In between is the partially coherent transition regime from wave description to the particle description. The phase-breaking length is the distance needed to completely destroy the phase of the heat carriers through various collision processes such as phonon–phonon collision and phonon–electron collision, and it is usually comparable to or slightly longer than the mean free path. The coherence length measures the distance beyond which waves from the same source can be superimposed without considering the phase information. The overlapping length scales in table 1.4 hint at the complexity in judging when to treat them as waves and when to treat them as particles, but this should become clearer after we treat wave and particle size effects in chapters 5 and 7.

Most engineering courses teach only the classical transport theories; that is, the bottom row of table 1.4. Some engineering disciplines may be more familiar with electromagnetic waves and photon radiative transfer: in other words, the column for photons. A wide range of transport problems fall into territories that are not familiar to classical engineering disciplines but are becoming increasingly important in contemporary technology. This book covers these unfamiliar domains as well as the more familiar regimes to help the reader solve problems on all scales.

1.6 Philosophy of This Book

The introductory discussion thus far suggests that, to deal with micro- and nanoscale thermal energy transport processes, one needs to have a clear picture of the motion of energy carriers and the thermal energy associated with their motion. This book aims to develop a unified microscopic picture on energy transport processes for elementary heat carriers including electrons, phonons, photons, and molecules. Figure 1.17 shows the structure of this book. We will began with the energy states of energy carriers, which are established on quantum mechanical principles, solid-state physics, and electrodynamics (chapters 2 and 3). The association of these energy states with heat transfer comes about through the statistical distribution of heat carriers at equilibrium, where temperature enters the picture. Statistical thermodynamics is discussed in chapter 4. Heat carriers have both wave and particle characteristics, as is implied by quantum-mechanical wave-particle duality. The transport of thermal energy can be analyzed from either the wave or the particle picture. It is important to understand when to treat the carriers as waves and when as particles. A key question is whether the phase information of the carriers is maintained or not in the transport process. Energy transport as waves is treated in chapter 5, together with a discussion on when the wave characteristics can be ignored so that the particle description alone is sufficient. Energy transfer by particles is treated in chapter 6 on the basis of the Boltzmann equation, from which classical laws valid at macroscales are derived, accompanied by discussions on the approximations used behind the derivations. Classical size effects are treated in chapter 7. Energy conversion between different carriers is discussed in chapter 8. Throughout the entire text, attempts are made to treat all the energy carriers—electrons, phonons, photons, and molecules—in parallel so that readers can draw analogies from their previous engineering and scientific backgrounds. Liquid molecules, however, defy such a unified treatment and thus chapter 9 is devoted to a discussion on liquids. Direct simulation tools based on molecular dynamics are becoming increasingly useful. Thus, chapter 10 introduces molecular dynamics techniques, with an emphasis on the statistical foundation for analyzing the trajectory of the molecules obtained in a typical molecular dynamics simulation. It should be noted that the linear response theory introduced in this chapter has much broader applications than just to molecular dynamics.

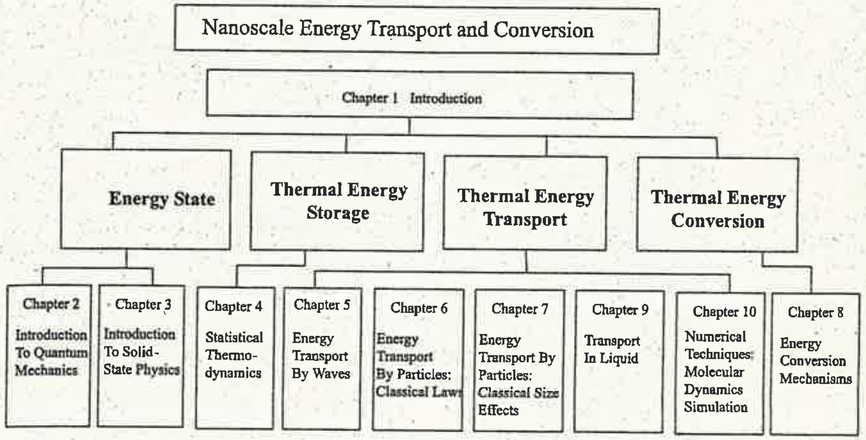


Figure 1.17 Structure of this book.

The text strives to develop connections and analogies among the energy carriers. The transport of these carriers is often discussed in various disciplines and is often considered to be governed by different laws. The underlying principles, however, are either very similar or identical, as is indicated by table 1.4, which justifies the attempt to develop a parallel treatment. In this table, we divide transport into generally the wave regime and the particle regime because all matter has both wave and particle characteristics. In the wave regime, the phase information of the energy carriers must be considered, whereas in the particle regime, only the trajectory is important. The propagation of material waves or electromagnetic waves shares many similarities despite the differences in the governing equations. In the particle regime, the phase information of the energy carriers can be ignored. Particle transport, under most conditions, can be described by the Boltzmann equation. The bottom line of table 1.4 lists the diffusion theories that most readers with an engineering background are familiar with. Some readers may also be familiar with propagation of electromagnetic waves or photon transport (or an acoustic wave equivalent). Other regimes in the table are most likely less familiar for readers in engineering but are often encountered in dealing with nanoscale transport. This book aims to cover the transport in all of the aforementioned regimes, while developing a parallel treatment for all carriers so that readers with different backgrounds can draw on their prior knowledge in exploring the nano-territory. Because of the wide range of topics covered in this book, however, readers should be prepared to embrace new terminologies. I believe that familiarity with different terminologies is a necessity for interdisciplinary work, which is becoming increasingly important in our exploration of the "ample room at the bottom."

1.7 Nomenclature for Chapter 1

a	thermal diffusivity, $m^2 s^{-1}$
A	cross-sectional area for conduction, and surface area for convection, m^2
B	normalization factor
c	specific heat, $J\,kg^{-1}K^{-1}$
C	volumetric specific heat, $J\,m^{-3}K^{-1}$
d	effective diameter of molecules, m
D	diameter of cylinders or spheres; separation of plates, m
D_h	hydraulic diameter, m
e	emissive power per unit area, $W\,m^{-2}$
e_λ	spectral emissive power per wavelength interval, $W\,m^{-2}\mu m^{-1}$
E	allowed energy level, J
f	probability distribution function
F	interatomic force, N
g	gravitational acceleration, $m\,s^{-2}$
h	convection heat transfer coefficient, $W\,m^{-2}\,K^{-1}$; Planck constant, J s
k	thermal conductivity, $W\,m^{-1}\,K^{-1}$
$\mathbf{k}$	wavevector, m^{-1}
L	characteristic length, m
m	mass, kg
n	integer; Particular number density, m^{-3}
N_A	Avogadro constant, mol^{-1}
Nu	Nusselt number
p	perimeter, m; momentum, $kg\,m\,s^{-1}$
Pr	Prandtl number
$\mathbf{q}$	heat flux vector, $W\,m^{-2}$

Q	heat transfer rate, W
Ra	Rayleigh number
Re	Reynolds number
t	time, s
T	temperature, K
u	internal energy per unit volume, $J\,m^{-3}$
$\mathbf{u}$	fluid velocity, $m\,s^{-1}$
U	system or internal energy, J
v	molecular instantaneous random velocity, $m\,s^{-1}$
V	volume, m^3
W	power output, W
β	thermal expansion coefficient, K^{-1}
γ	fin parameter, m^{-1}
κ_B	Boltzmann constant, $J\,K^{-1}$
λ	wavelength, m
Λ	mean free path, m
μ	dynamic viscosity, $N\,s\,m^{-2}$; chemical potential, J
ν	kinematic viscosity, $m^2 s^{-1}$; frequency of phonons and photons, s^{-1}
ρ	density, $kg\,m^{-3}$
σ	Stefan–Boltzmann constant, $W\,m^{-2}K^{-4}$
τ	relaxation time, s; time constant, s
τ_{xy}	shear stress, $N\,m^{-2}$
ϕ	interatomic potential, J

Subscripts

a	ambient
b	blackbody
c	cross-section
λ	per unit wavelength
w	wall
x, y, z	Cartesian components

Superscripts

—	average

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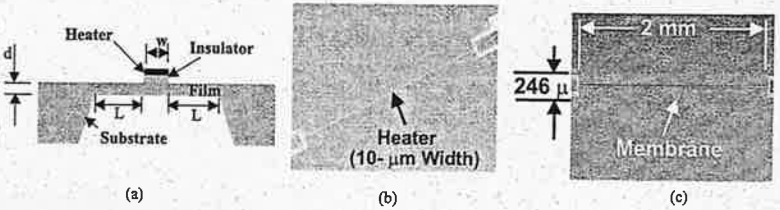
1.9 Exercises

1.1 *Membrane method for thin-film thermal conductivity measurement.* One technique for measuring the thermal conductivity of thin films is to create a freestanding film by removing part of the substrate, as shown in figure P1.1. A thin-film heater is deposited at the center of the film. A thin layer of electrical insulator (such as SiO_2 or Si_3N_4) is used between the film and the heater if the film itself is electrically conducting. The temperature rise of the heater is determined by measuring the change in its electrical resistance. The substrate temperature is assumed to be uniform (alternatively, another temperature sensor can be deposited at the edge of the film and the substrate). Thermal conductivity along the film can be measured but one must be very careful to address various factors that may affect the final results. Answer the following questions.



(a) (b) (c)

Figure P1.1 A thin-film conductivity measurement method (a) schematic of the cross-section, (b) photograph of a fabricated heater, and (c) photograph of a the free-standing silicon membrane.

(a) Derive an expression for determining the thermal conductivity of the film, given the power input to the heater, the temperature rise of the heater, the temperature of the substrates and the geometries, under the following assumptions: (1) heat conduction is one-dimensional, (2) heat losses along the film are negligible, and (3) the thermal resistance of the insulating film is negligible.

(b) For a 3 μm thick silicon membrane, the thermal conductivity at room temperature is 145 $\mathrm{W\,m^{-1}K^{-1}}$. The measured temperature rise of the heater is 2°C. Given the geometries in figure P1.1(b) and (c), estimate how much power input is needed.

(c) For the silicon thermal conductivity measurement, an insulating layer must be placed between the heater and the silicon film for electrical isolation. Assuming a 200 nm thick SiO_2 film with a thermal conductivity of 1.2 $\mathrm{W\,m^{-1}K^{-1}}$ is used, estimate what thermal conductivity you will get if the thermal resistance of the SiO_2 layer is not taken into account in analyzing the experimental data, based on the power input condition given in (b).

(d) Now consider heat losses along the film. The combined heat transfer coefficient due to convection and radiation is 10 $\mathrm{W\,m^{-2}K^{-1}}$. For the silicon membrane example given in (b), determine how much additional power input is needed as a result of this heat loss.

(e) One concern in measuring low thermal conductivity membranes is the heat loss along the heater, which has a relatively high thermal conductivity. Assuming that the heater thickness is t = 200 nm and the material is gold with a thermal conductivity of 315 $\mathrm{W\,m^{-1}K^{-1}}$, develop a model to estimate the heat loss along the heater to the substrate.

1.2 *AC calorimetry method for measuring thin-film thermal diffusivity* (Hatta, 1990). One thin-film thermal diffusivity measurement method is to use a modulated light source to heat up a membrane, as shown in figure P1.2. A small temperature sensor, either a tiny thermocouple or a microfabricated sensor, is placed onto the film. The distance between the film and the temperature sensor is controlled by a mask that blocks part of the light source. Amplitude and phase of the temperature response are measured as a function of the distance L between the temperature sensor and the edge of the light source. This is equivalent to measuring the distribution of the amplitude and phase as a function of x. Derive an expression for determining the thermal diffusivity on the basis of (a) phase signal and (b) amplitude signal. List all the assumptions made in establishing the model.

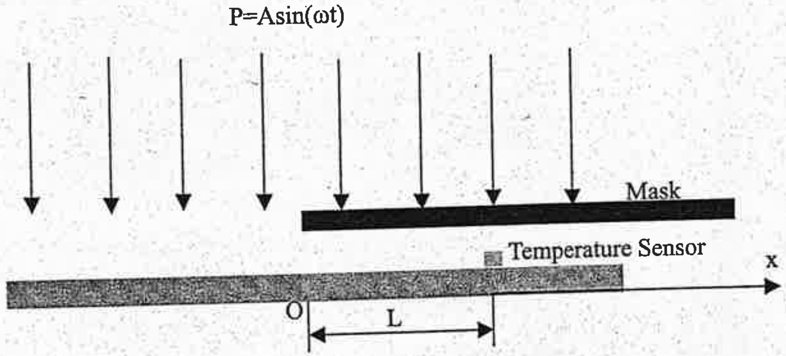


Figure P1.2 AC calorimetry method for determining thermal diffusivity of thin films.

1.3 *Cross-plane thermal conductivity measurement of thin films: steady-state method.* The measurement of the thermal conductivity perpendicular to a thin-film plane (cross-plane) is difficult because the temperature drop across a thin film is small unless a high heat flux is applied. Since thin films are usually deposited on a substrate, one-dimensional heating is unfavorable because a large temperature drop would occur across the substrate rather than the film. To avoid this situation, one solution is to use a narrow heater patterned directly on the film, as shown in figure P1.3. In this case, the heat flux through the film is high but the heat spreading inside the substrate lowers the heat flux, leading to a relatively large temperature drop across the film compared to that in the substrate. For the given configuration, we can assume that the heat flux is uniform from the heater into the substrate. If the substrate thermal conductivity is known, the thin-film thermal conductivity can be determined from the measured heater temperature rise. In this problem, the substrate is silicon with a thermal conductivity of 145 $\mathrm{W\,m^{-1}K^{-1}}$ and the film is SiO_2 with a thermal conductivity of 1.2 $\mathrm{W\,m^{-1}K^{-1}}$.

(a) Assuming heat conduction is two-dimensional, derive an expression for the average temperature rise of the heater.

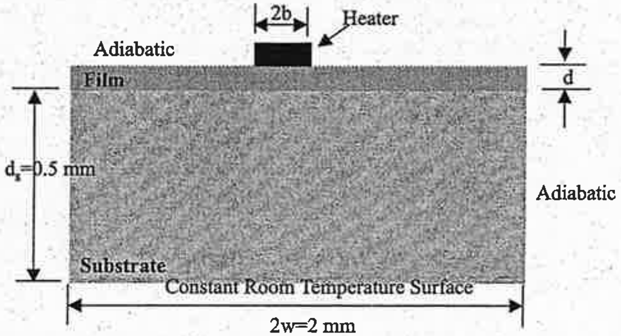


Figure P1.3 Figure for problem 1.3

(b) The ideal case is that heat conduction through the film is one-dimensional. For a 400 nm SiO_2 film on a silicon substrate and a heater 10 μm wide and 2 mm long with a power input of 40 mW, compare the exact solution for the average heater temperature with the approximation that heat conduction inside the SiO_2 is one-dimensional.

(c) Determine the temperature drop across the film and inside the substrate.

(d) Estimate the heat loss through radiation and convection and compare its magnitude with that of heat conduction.

1.4 *Cross-plane thermal conductivity measurement of thin films: 3ω method* (Lee and Cahill, 1997). One disadvantage of the steady-state method in problem 1.3 is that the backside temperature of the substrate must be known. In reality, the substrate is placed on a heat sink and the backside may not be at uniform temperature. In addition, the thermal resistance between the substrate and the heat sink also changes the temperature of the substrate. To avoid this situation, heat input into the heater can be modulated by a sine input current at angular frequency ω. In this case, power will be modulated at 2ω, leading to a 2ω temperature oscillation and corresponding electrical resistance oscillation of the heater, due to the temperature dependence of the resistance. This resistance oscillation at 2ω leads to a third harmonic component in the heater voltage. By measuring the phase and amplitude of this third harmonic, the temperature rise of the heater due to the modulating power input can be determined and, from this, the thermal conductivity of the film can be determined. This is called the 3ω method.

(a) Assuming a power input of the form of A sin $(2\omega t)$, derive an expression for the in-phase (sine function) and out-of-phase (cosine function) components of the heater temperature rise. Assume that all the thermal properties (thermal diffusivity, thermal conductivity, and specific heat) of the film and the substrate are known.

(b) One additional advantage of the 3ω method is that the substrate thermal conductivity can be determined from the frequency dependency of the temperature response under appropriate conditions. Try to identify these conditions.

(c) Another advantage of the 3ω method is that the radiation loss can be minimized, which is particularly important for low thermal conductivity materials and measurements at extreme temperatures (low and high). Explain why.

1.5 *Thermal diffusivity determination of thin films: laser pulse method.* One method for determining the thermal diffusivity of a thin film is to use a short laser pulse to heat up the front side of the film and to measure the decay of the front side temperature by monitoring the change in reflectance of a probe laser beam (see figure P1.5). The short pulse concentrates temperature drop in the film rather than across the substrate. In this case, it is not the absolute surface temperature rise that is measured but the normalized profile of the surface temperature decay as a function of time. For a heating pulse of the following profile,

$$q = \begin{cases} 0 & t < 0 \\ q_0 & 0 < t < t_p \\ 0 & t > t_p \end{cases}$$

(a) Derive an expression for the temporal response of the front surface temperature, assuming all thermal properties (thermal conductivity k, thermal diffusivity a, and specific heat c) are known for both the film and the substrate.

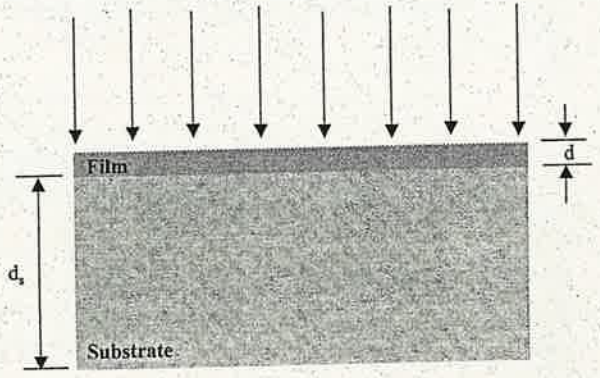


Figure P1.5 Figure for problem 1.5.

(b) What are the requirements on the pulse width that will maximize the sensitivity for measuring the thermal diffusivity of the film?

1.6 *Lumped heat capacitance and time constant.* Develop a lumped capacitance model for a solid sphere at uniform temperature T_i that is suddenly immersed inside a liquid at temperature T_0. In such a model, the temperature of the solid is assumed to be uniform, and the heat transfer coefficient between the solid object and the fluid is taken to be h. Other known parameters are the surface area A, the volume V, the density ρ, and specific heat c of the solid.

(a) Derive the differential equation governing the temperature history of the solid.

(b) Solve the equation and find the time constant of the process.

(c) Investigate how the time constant varies with the diameter of the solid sphere.

1.7 *$\kappa_B T$ energy.* One unit for energy is the electron-volt (eV). It is the energy difference of one electron under a potential difference of 1 V. Convert 1 $\kappa_B T$ at 300 K into milli-eV (meV).

1.8 *Thermal conductivity of gases.* Estimate the thermal conductivity of air and argon as a function of temperature between 300 K and 1000 K at 1 atm.

1.9 *Mean free path in air.* Estimate the mean free path of air molecules as a function of temperature at atmospheric pressure on the basis of (a) kinetic theory and (b) experimental data on the thermal conductivity and specific heat of air.

1.10 *Speed of electrons.* Estimate the average random speed of an electron gas in a semiconductor at 300 K.

1.11 *Thermal conductivity of liquid.* Although the application of kinetic theory to a dense liquid is questionable, estimate the thermal conductivity of water at room temperature on the basis of a simple derivation for the mean free path and the results from the kinetic theory. This estimation is typically smaller than experimental values because, for liquid, potential energy exchange contributes to heat conduction.

1.12 *Phonon mean free path and relaxation time.* Given the thermal conductivity of Si at room temperature as 145 $\mathrm{W\,m^{-1}K^{-1}}$, the speed of sound as 6400 $\mathrm{m\,s^{-1}}$, the volumetric specific heat as $1.66 \times 10^6\ \mathrm{J\,m^{-3}K^{-1}}$,

(a) Estimate the phonon mean free path in Si at room temperature from the kinetic theory. In reality, this estimation usually leads to a much shorter mean free path (about a factor of 10 shorter) than with more sophisticated modeling.

(b) Estimate the relaxation time of phonons in silicon.

1.13 *Fick's law of diffusion.* Using a simple kinetic argument that is similar to the derivation of the Fourier law, derive the Fick law of diffusion, which gives the mass flux for species i under a concentration gradient as

$$J_i = -\rho D \frac{dm_i}{dx}$$

where D is the mass diffusivity, ρ is the density of the mixture, and m_i the local mass fraction of species i.

1.14 *Newton's shear stress law.* Using a simple kinetic argument that is similar to the derivation of the Fourier law, derive the Newton law of shear stress (in one-dimensional form). Hint: consider the momentum exchange across a plane parallel to the flow.

1.15 *Energy quantization.*

(a) Assuming a person weighing 100 kg trapped deep inside a two-dimensional ditch 1 m in width, estimate the energy difference between the first and second quantized energy levels. Compare this energy difference with the thermal fluctuation energy $\kappa_B T$ for $T = 300$ K.

(b) Assuming an electron of mass 9.1×10^{-31} kg is trapped inside a two-dimensional infinitely high potential well, plot the first and second energy levels of the electron as a function of well width between 10 and 100 Å. Also mark the thermal energy $\kappa_B T$ on the graph for $T = 300$ K.

2

Material Waves and Energy Quantization

For macroscopic systems, we take the continuity of many variables for granted, including the continuity in energy. For example, the heat flux along a rod through conduction, according to the Fourier law, can be continuously varied to any desired value by controlling the temperature difference and the material properties. The microscopic picture of energy, however, is entirely different. According to quantum mechanical principles, the permissible energy levels of matter (electrons, crystals, molecules, and so on) are often discontinuous. Differences in allowable energy levels among materials are major factors that distinguish them from each other. For example, why is glass transparent in the visible light range but not silicon, and why are some materials electrical insulators but others are conductors?

In this chapter, we introduce the basic quantum mechanical concepts necessary to appreciate various energy states found in different materials. It should be remembered that these energy states represent the range of possibilities for the matter but do not tell which state the matter will be in. The latter depends on the temperature, a topic we will discuss in chapter 4. Important concepts that should be mastered through this chapter include the wave–particle duality, the Schrödinger equation and the meaning of the wavefunction, the Pauli exclusion principle, quantum states, and degeneracy. Solutions of the Schrödinger equation for various simple yet very common potentials will be given. Key concepts and results of this chapter are summarized in the last section of the chapter.

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