5.19 *Landauer formulation for electron thermal conduction.* A metallic square nanowire is placed between two thermal reservoirs at temperatures T_1 and T_2. Assume that electron transmissivity is equal to one. Derive an expression for the thermal conductivity of the nanowire contributed by the electrons.

5.20 *Coherence length of blackbody radiation.* Estimate the coherence length of a blackbody radiation source at 10 K and 300 K.

5.21 *Coherence length of laser radiation.* Estimate the coherence of a laser radiation with a central wavelength of 1.06 μm and a spectral width of 10 Å.

5.22 *Coherence properties of electrons.* At low temperatures, the Fermi velocity in a material is 2.76×10^5 m s^{-1}, the electron relaxation time is 3.8 ps (1 ps $= 10^{-12}$ s), and the phase-breaking time is 18 ps. Calculate the mean free path and the phase coherence length of an electron.

5.23 *Phonon group velocity.* The phonon dispersion for a monatomic lattice chain is

$$\omega = 2\sqrt{\frac{K}{m}}\left|\sin\frac{ka}{2}\right|$$

Derive an expression of its group velocity. Prove that the group velocity at the zone boundary is zero.

5.24 *Difference between wave and particle approaches (project type).* In section 5.6 we stated that wave optics and geometrical optics do not lead to the same results for the radiative properties of periodic multilayer structures for blackbody radiation. Consider a periodic structure made of two alternating layers with refractive indices of (4,0) and (2,0), that is, nonabsorbing films. Blackbody radiation at 1000 K comes toward the periodic multilayer structure at normal incidence. Assuming both sides of the multilayer structure are vacuum, calculate the reflectivity and transmissivity averaged over the blackbody spectrum for the following cases, using wave optics and ray tracing:

(a) For each layer thickness of 1 μm, 10 μm, and 100 μm calculate the variation of reflectivity and transmissivity as a function of the number of periods in the structure. Compare the results for wave and ray tracing.

(b) For 10, 100, 1000 periods, calculate the average reflectivity and transmissivity as a function of the thickness of each layer, assuming all layers are of equal thickness, for the layer thickness range of 1 μm to 100 μm.

Geometrical optics can be obtained using the following recursive formula for the addition of every interface (Siegel and Howell, 1992, p. 928)

$$R_{n+m} = R_m + \frac{R_n T_m^2}{1 - R_m R_n} \qquad \tau_{m+n} = \frac{\tau_m \tau_n}{1 - R_m R_n}$$

where the subscript m refers to the total reflectivity and transmissivity of the first m interfaces (counted from the incident side) and n represents those of the subsequent n additional interfaces. For example, for one layer with two interfaces (the reflectivity and transmissivity at the first interface are R_1 and τ_1 and those at the second interface are R_2 and τ_2), the above formula becomes

$$R_{1+1} = R_1 + \frac{R_2 \tau_1^2}{1 - R_1 R_2} \qquad \tau_{1+1} = \frac{\tau_1 \tau_2}{1 - R_1 R_2}$$

Hint: one numerical problem with the transfer matrix method for thick film is that the exponential function may blow up. One must find ways to solve this problem for calculating thick films using the transfer matrix method.

6

Particle Description of Transport Processes: Classical Laws

We discussed in the previous chapter when we can ignore the coherence effects and treat heat carriers as individual particles without considering their phase information. In the next few chapters, we will describe how to deal with energy transfer under the particle picture. Most constitutive equations for macroscale transport processes, such as the Fourier law and the Newton shear stress laws, are obtained under such particle pictures. These equations are often formulated as laws summarized from experiments. In this chapter, we will see that most of the classical laws governing transport processes can be derived from a few fundamental principles.

In chapter 4, we studied systems at equilibrium and developed the equilibrium distribution functions (Fermi–Dirac, Bose–Einstein, and Boltzmann distributions). The distribution function for a quantum state at equilibrium is a function of the energy of the quantum state, the system temperature, and the chemical potential. When the system is not at equilibrium, these distribution functions are no longer applicable. Ideally, we would like to trace the trajectory of all the particles in the system, as in the molecular dynamics approach that we will discuss in chapter 10. This approach, however, is not realistic for most systems, because they have a large number of atoms or molecules. Thus, we resort to a statistical description of the particle trajectory.

In the statistical description we use nonequilibrium distribution functions, which depend not only on the energy and temperature of the system but also on positions and other variables. We will develop in this chapter the governing equations for the nonequilibrium distribution functions. In particular, we will rely on the Boltzmann equation, also called the Boltzmann transport equation. From the Boltzmann equation we will derive familiar constitutive equations such as the Fourier law, the Newton shear stress law, and the Ohm law. We will also demonstrate that conservation equations, such as the Navier–Stokes equations for fluids and electrohydrodynamic equations for charged particles, can be obtained from the Boltzmann equation. Special attention will be paid to the approximations made in these derivations, which will be relaxed in the next chapter when we consider various classical size effects. A discussion is also presented in this chapter on thermal waves and their appropriate descriptions.

6.1 The Liouville Equation and the Boltzmann Equation

We discussed, in chapter 4, the probability distribution of an equilibrium system occupying a specific accessible quantum state. Because the system is at equilibrium, the probability distribution take a simple form. For example, the Boltzmann distribution depends only on the energy of the quantum state and on the system temperature. Transport occurs, however, only when the system is in a nonequilibrium state and consequently the equilibrium distribution can no longer describe the state of the system. Conceivably, to describe the state of such a nonequilibrium system, more information is needed. In this section, we will introduce nonequilibrium distribution functions that describe the states of systems and the governing equations for the evolution of the nonequilibrium distribution functions. We will start from the general Liouville equation, which is valid for all classical systems but is difficult to solve, and move on to the simpler Boltzmann equation that serves as the basis for our future analysis. We will also discuss the assumptions made in the Boltzmann equation and see, consequently, its limitations.

6.1.1 The Phase Space and Liouville's Equation

Consider a system with N particles, where each particle can be described by the generalized coordinate $\mathbf{r}$ and momentum $\mathbf{p}$. For example, the generalized coordinates of a diatomic molecule, $\mathbf{r}_1$, include the position (x_1, y_1, z_1), the vibrational coordinate (the separation between the two atoms, Δx_1), the rotational coordinates (polar and azimuthal angles, θ_1 and φ_1); likewise, the generalized momentum, $\mathbf{p}_1$, includes the translational momenta $(mv_{x1}, mv_{y1}, mv_{z1})$, the vibrational momentum proportional to the relative velocity of the two atoms $(md\Delta x_1/dt)$, and the rotational momenta (angular momenta of rotation corresponding to θ and φ directions). We assume here that there are m degrees of freedom in space, that is, m generalized spatial coordinates, and m degrees of freedom in momentum for each particle. The number of the degree of freedom of the whole system is $2n = 2m \times N$. These $2n$ variables form a $2n$-dimensional space that is called a *phase space*. The system at any instant can be described as one point in such a space. The time evolution of the system, that is, the time history of all the particles in the system, traces one line in such a $2n$-dimensional *phase space*, which we will call the flow line as in fluid mechanics.

Now we consider an ensemble of systems—a collection of many systems satisfying the same macroscopic constraints—as we did in chapter 4. At time $t = 0$, each system in the ensemble is represented by a different point in the phase space, as shown in figure 6.1. From classical mechanics, we know that with a given initial condition the trajectory of the system is uniquely determined. Since the initial condition for each system differs from that of other systems in the ensemble, the traces of systems in such an ensemble never intersect, so that the flow lines in phase space do not intersect each other.

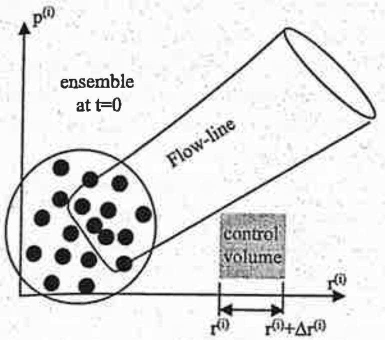

Figure 6.1 Phase space, and an ensemble in the phase space.

The number of systems in an ensemble is usually very large, much larger than the number of the particles in one system. Because of the large number of systems in one ensemble, we can treat the points of the ensemble, each representing one microstate of the original macroscopic system, as forming a continuum in the phase space, just as we treat atoms or molecules in a macroscopic system as a continuous medium in real space. We define a particle density $f^{(N)}$ such that, surrounding any point $(\mathbf{r}^{(n)}, \mathbf{p}^{(n)})$ in the phase space, where $\mathbf{r}^{(n)} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = (r^{(1)}, r^{(2)}, r^{(3)}, \ldots, r^{(n)})$ includes all the space coordinates of N particles and similarly $\mathbf{p}^{(n)}$ represents all the momentum coordinates, the number of systems is

$$\text{No. of systems} = f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)})\Delta\mathbf{r}^{(n)}\Delta\mathbf{p}^{(n)} \qquad (6.1)$$

in a small volume of the phase space, $\Delta\mathbf{r}^{(n)}\Delta\mathbf{p}^{(n)}$, where $\Delta\mathbf{r}^{(n)} = \Delta\mathbf{r}_1\Delta\mathbf{r}_2\ldots\Delta r_N = \Delta r^{(1)}\Delta r^{(2)}\ldots\Delta r^{(n)}$ and $\Delta\mathbf{p}^{(n)} = \Delta\mathbf{p}_1\Delta\mathbf{p}_2\ldots\Delta\mathbf{p}_N = \Delta p^{(1)}\Delta p^{(2)}\ldots\Delta p^{(n)}$. We use superscript (n) to denote the generalized space and momentum coordinates, and superscript (N) to represent the N particles. The particles density in the phase space $f^{(N)}(t, \mathbf{p}^{(n)}, \mathbf{p}^{(n)})$ is called the N-particle distribution function, which represents the probability density of finding a particular system at a specific state defined by $\mathbf{r}^{(n)}$ and $\mathbf{p}^{(n)}$. If we assume that the ensemble is ergodic for all time, this distribution function also represents the probability of observing one system at a particular state $\mathbf{r}^{(n)}$ and $\mathbf{p}^{(n)}$ over a period of time (such a time period should be smaller than the characteristic time we use in tracing the trajectory, or the relaxation time that we will discuss later).

The time evolution of $f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)})$ in the phase space is governed by the *Liouville equation*, which can be derived on the basis that the flow lines of systems in the ensemble do not intersect. Consider a tube formed by the traces of a set of points (a subset of systems in the ensemble) as shown in figure 6.1. Since the flow lines do not intersect, the points in the phase space are conserved. We want to derive an equation for the distribution function $f^{(N)}$ based on this conservation requirement. Recall that in fluid mechanics or heat transfer, we often use the control volume method rather than tracing the trajectory of individual fluid particles. We could do the same for the points in phase space and examine a small control volume in phase space, as shown in figure 6.1.

The net rate of points flowing into the control volume should equal the rate of change of points inside the control volume. This leads to

$$-\sum_{i=1}^{n}\frac{\partial}{\partial r^{(i)}}\left(f^{(N)}\frac{\partial r^{(i)}}{\partial t}\right)-\sum_{i=1}^{n}\frac{\partial}{\partial p^{(i)}}\left(f^{(N)}\frac{\partial p^{(i)}}{\partial t}\right)=\frac{\partial f^{(N)}}{\partial t} \qquad (6.2)$$

where $\partial p^{(i)}/\partial t = \dot{p}^{(i)}$ and $\partial r^{(i)}/\partial t = \dot{r}^{(i)}$ represents the flow rate of the points. The left-hand side of eq. (6.2) is the net rate of points flowing into the control volume and the right-hand side is the rate of change of the points in the control volume. The above relation can be further written as

$$\frac{\partial f^{(N)}}{\partial t}+\sum_{i=1}^{n}\dot{r}^{(i)}\times\frac{\partial f^{(N)}}{\partial r^{(i)}}+\sum_{i=1}^{n}\dot{p}^{(i)}\times\frac{\partial f^{(N)}}{\partial p^{(i)}}=0 \qquad (6.3)$$

where we have used $\partial\dot{r}^{(i)}/\partial r^{(i)}+\partial\dot{p}^{(i)}/\partial p^{(i)}=0$, which is a result that we will obtain in chapter 10 on the basis of the Hamilton equations of motion.

Equation (6.3) is the Liouville equation that governs the time evolution of the N-particle distribution function $f^{(N)}$. The equation is valid for all classical systems and has quantum mechanical counterparts for quantum systems (Liboff, 1998). It has a large number of variables since n is of the order of 10^{23}, that is, the Avogadro constant, in macroscale systems. Direct solution of the Liouville equation for nonequilibrium systems is impossible, not only because of the large number of variables, but also because we are hampered by the necessity to determine the exact initial states of the ensemble. However, the Liouville equation provides a good starting point for further simplification. The Boltzmann equation, to be discussed below, is one example. In chapter 10, we will develop another approach for transport problems, the linear response theory, based on the perturbation analysis of the Liouville equation.

6.1.2 The Boltzmann Equation

The Liouville equation involves $2n$ variables in the phase space, plus time. This large number of variables makes it impractical in terms of the boundary and initial conditions, as well as for analytical and numerical solutions. One way to simplify the Liouville equation is to consider one particle in a system. This is a representative particle having coordinate $\mathbf{r}_1$ and momentum $\mathbf{p}_1$; each of the vectors has m components, that is, m degrees of freedom. We introduce a *one-particle distribution function* by averaging the N-particle distribution function over the rest of the $(N-1)$ particles in the system,

$$f^{(1)}(t,\mathbf{r}_1,\mathbf{p}_1)=\frac{N!}{(N-1)!}\int\cdots\int f^{(N)}(t,\mathbf{r}^{(n)},\mathbf{p}^{(n)})d\mathbf{r}_2\ldots d\mathbf{r}_N d\mathbf{p}_2\ldots d\mathbf{p}_N \qquad (6.4)$$

where, again, each vector $\mathbf{r}_i$ and $\mathbf{p}_i$ has m degrees of generalized freedom, so that $n=m\times N$, as we discussed before. For a monatomic atom, $m=3$, and for a diatomic atom, $m=6$ (neglecting the electronic states). The factorials are normalization factors. For simplicity in notation, we will drop the subscript 1 and use $(\mathbf{r},\mathbf{p})$ as the coordinates and momenta of the particle. Since $f^{(N)}(t,\mathbf{r}^{(n)},\mathbf{p}^{(n)})$ represents the number density of systems having generalized coordinates $(\mathbf{r}^{(n)},\mathbf{p}^{(n)})$ in the ensemble, the one-particle distribution function represents the number density of systems having $(\mathbf{r},\mathbf{p})$,

$$f(t,\mathbf{r},\mathbf{p})d^3\mathbf{r}d^3\mathbf{p}=\text{number of systems in } d^3\mathbf{r}d^3\mathbf{p}$$

This one-particle distribution function features a significant reduction of variables. For one mole of monatomic gas with 6×10^{23} atoms, the number of variables in the generalized phase space is $6\times6\times10^{23}$, because of the three space and three momentum coordinates. The one-particle phase space for monatomic atoms, however, has only three space coordinates and three momentum coordinates. The one-particle phase space can be thought of as the projection of the N-particle phase space, similarly to the projection of a volume in three-dimensional space into the area of a two-dimensional space.

With the introduction of the averaging method to obtain the one-particle distribution function, one can start from the Liouville equation, eq. (6.3), and carry out the averaging over the space and momentum coordinates of the other $(N-1)$ particles. This procedure leads to (Liboff, 1998)

$$\frac{\partial f}{\partial t}+\frac{d\mathbf{r}}{dt}\bullet\nabla_{\mathbf{r}}f+\frac{d\mathbf{p}}{dt}\bullet\nabla_{\mathbf{p}}f=\left(\frac{\partial f}{\partial t}\right)_c \qquad (6.5)$$

where the subscripts ($\mathbf{r}$ and $\mathbf{p}$) in the gradient operators represent the variables of the gradients:

$$\nabla_{\mathbf{r}}f=\frac{\partial f}{\partial x}\hat{\mathbf{x}}+\frac{\partial f}{\partial y}\hat{\mathbf{y}}+\frac{\partial f}{\partial z}\hat{\mathbf{z}}$$

$$\nabla_{\mathbf{p}}f=\frac{\partial f}{\partial p_x}\hat{\mathbf{p}}_x+\frac{\partial f}{\partial p_y}\hat{\mathbf{p}}_y+\frac{\partial f}{\partial p_z}\hat{\mathbf{p}}_z$$

Unlike the $2n$-phase space for the derivation of the Liouville equation, in which one point represents a system and the flow lines of the points do not intersect, the particle as represented by the one-particle distribution function interacts with other particles in the system, and thus the number of particles along a flow line in the one-particle phase space is no longer conserved. The right-hand side of eq. (6.5) lumps the interaction of this one particle with the rest of the particles in the system and represents the nonconserving nature of the one-particle distribution function. This scattering term should not be considered as a derivative, but rather as a symbol representing the net rate of gaining particles at point $(\mathbf{r},\mathbf{p})$. We will give more detailed expressions for the scattering term in section 6.2.

Equation (6.5), together with the expressions to be given in section 6.2 for $\left(\frac{\partial f}{\partial t}\right)_c$, is called the *Boltzmann equation* or Boltzmann transport equation. Rather than using momentum $\mathbf{p}$, we can also use velocity $\mathbf{v}(\mathbf{p}=m\mathbf{v})$ or wavevector $\mathbf{k}(\mathbf{p}=\hbar\,\mathbf{k})$ to rewrite the Boltzmann equation as

$$\frac{\partial f}{\partial t}+\mathbf{v}\bullet\nabla_{\mathbf{r}}f+\frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}}f=\left(\frac{\partial f}{\partial t}\right)_c \qquad (6.6)$$

$$\frac{\partial f}{\partial t}+\mathbf{v}\bullet\nabla_{\mathbf{r}}f+\frac{\mathbf{F}}{\hbar}\bullet\nabla_{\mathbf{k}}f=\left(\frac{\partial f}{\partial t}\right)_c \qquad (6.7)$$

where $\mathbf{F} = d\mathbf{p}/dt$ is the external force acting on the particle. The use of $\hbar$ in eq. (6.7) implies that the Boltzmann equation can also be applied to quantum particles as long as we do not consider the phase coherence of the particles. In connection with the discussion in the previous chapter on the group velocity and the crystal momentum, it should be understood that $\mathbf{v}$ in these forms of the Boltzmann equation is the group velocity, while $\hbar\,\mathbf{k}$ in eq. (6.7) is the crystal momentum. In the following treatment, we will use $\mathbf{p}$, $\mathbf{v}$, and $\mathbf{k}$ as momentum variables interchangeably. Variables $\mathbf{v}$ or $\mathbf{p}$ are often used as continuum variables when treating gases, and variables $\mathbf{k}$ are often used for treating electron and phonon transport in crystals. Please be reminded that $\mathbf{v} = \nabla_{\mathbf{k}}\omega$ is the group velocity.

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The Boltzmann equation gives the distribution function at $\mathbf{r}$ and $\mathbf{p}$ (or $\mathbf{k}$ or $\mathbf{v}$) in the phase space. Typically, we are interested in the quantities averaged over $\mathbf{p}$, for example, the average velocity and energy. If the solution of the Boltzmann equation is known for a problem, we can calculate the volume-average of any microscopic property X of the particle from

$$\langle X(\mathbf{r})\rangle = \frac{1}{V}\sum_{\mathbf{k},s} X(\mathbf{r},\mathbf{k})f = \frac{1}{(2\pi)^3}\int X(\mathbf{r},\mathbf{k})f\,d^3\mathbf{k} \tag{6.8}$$

where s is the polarization, if appropriate. When going from the summation over discrete wave vector $\mathbf{k}$ to the integration, the factor $(2\pi)^3$ comes from the fact that the volume of one quantum state in k-space is $V/(2\pi)^3$.

There are two directions in exploring the solution of the Boltzmann equation. One is to solve for f and to calculate the average quantities of interest according to eq. (6.8). This approach will be used in section 6.3 to derive constitutive equations such as the Fourier law and the Ohm law, and the Newton shear stress law. It will also be used in the next chapter when considering the classical size effects. The other approach is to take the moments of the Boltzmann equation, from which conservation equations such as the Navier–Stokes equations can be derived.

The above arguments leading to the Boltzmann equation are by no means a rigorous derivation. The derivation of the Boltzmann equation from the Liouville equation is a fundamental topic in statistical physics (Kubo et al., 1991; Liboff, 1998). Here it is appropriate to comment on the range of validity of the Boltzmann equation. We use the one-particle distribution instead of the N-particle distribution function and assume that this one-particle distribution function is an appropriate representation of all the particles in the system. This will only be true if the N-particle distribution function can be factorized as the product of the distribution function for each particle, that is,

$$f^{(N)}(t,\mathbf{r}^{(n)},\mathbf{p}^{(n)}) = f^{(1)}(t,\mathbf{r}_1,\mathbf{p}_1)f^{(1)}(t,\mathbf{r}_2,\mathbf{p}_2)\ldots f^{(1)}(t,\mathbf{r}_N,\mathbf{p}_N) \tag{6.9}$$

Such a factorization means that the particles in the system are quite independent of each other, even though collisions between particles can affect the one-particle distribution function. Consider the collision of two particles. Before and after the collision, the distribution functions of one particle are independent of the coordinates and momentum of the other particle. This is the so-called *molecular chaos* assumption. Such factorization is only valid when the interactions of the particles are infrequent. Thus, the Boltzmann equation is appropriate only for dilute systems such as molecular gases, electron gases, phonon gases, and photon gases. It is not valid for dense fluids such as liquids. The Boltzmann equation does not include explicitly wave effects such as interference and tunneling. Extension of the classical particle picture to the quantum wave picture involves the so-called Wigner function (Liboff, 1998), which we will not discuss here. Despite these restrictions, the Boltzmann equation is powerful and can be applied to a wide range of problems from nanoscale to macroscale.

6.1.3 Intensity for Energy Flow

The single-particle distribution function f is a scalar in the one-particle phase space. Sometimes we try to map this and related quantities into the real space $\mathbf{r}$. At each point in real space, the possible wavevectors lie in all directions. Along each wavevector direction, the particle moves at the group velocity $\mathbf{v}_g(\mathbf{k})$ and the energy flows at the rate of $E \times \mathbf{v}_g(\mathbf{k}) \times f$ for the specific quantum state. In section 3.4.4, we introduced the differential density-of-states $dD(E,\mathbf{k})$ as

$$dD(E,\mathbf{k}) = \frac{\text{No. of States within }(E, E+dE)\text{ and }d\Omega}{V\,dE\,d\Omega} = \frac{D(E)}{4\pi} \tag{6.10}$$

where the last equality is valid only for isotropic media. The rate of energy propagating along this direction per unit solid angle is then

$$\begin{aligned} I(t,E,\mathbf{k}) &= E \times v_g(\mathbf{k})f(t,\mathbf{r},\mathbf{k})dD(E,\mathbf{k}) \\ &= \frac{1}{4\pi}E \times v_g(\mathbf{k})f(t,\mathbf{r},\mathbf{k})D(E) \end{aligned} \tag{6.11}$$

In thermal radiation, $E = h\nu$ for photons, and I is called the intensity. Majumdar (1993) extended the intensity concept to phonons. Equation (6.11) shows that intensity is a simple transformation of the distribution function. It is usually defined, without referring to the phase space, as the power flowing along direction $\hat{\Omega}$ per unit solid angle, per unit frequency interval, and per unit area normal to the direction of propagation:

$$I_\nu = \frac{\text{Power}}{dA_\perp\,d\Omega\,d\nu} \tag{6.12}$$

where $dA_\perp$ is a differential area perpendicular to the direction of propagation.

Comparing eq. (6.12) with (6.11), we see that the solid angle, which is usually considered as an angle in real space, is actually sustained by the wavevectors in the phase space. In phase space, intensity is a scalar. Without considering the phase space, it is difficult to tell whether intensity is a scalar or a vector. Although the concept of intensity is widely used in thermal radiation, it is not very common in the treatment of charge transport since the major concern is not energy but the flux of charges. In the following treatment, we will use both f and the intensity, in accordance with the customs in each field, while attempting to present different carriers in a parallel fashion.

6.2 Carrier Scattering

The key to the Boltzmann equation lies in the description of the scattering term. This term, in its most general form, is a complex multi-variable integral that contains the

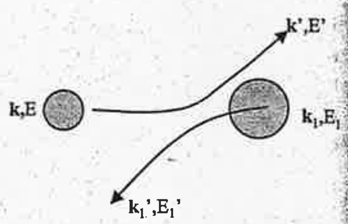

Figure 6.2 Collision of two particles with initial wavevector and energy ($\mathbf{k}$, E) and ($\mathbf{k}_1$, E_1). After the collision, the two particles are at states ($\mathbf{k}'$, E') and ($\mathbf{k}_1'$, E_1').

distribution function, making the Boltzmann equation an integro-differential equation that is extremely difficult to solve. The relaxation time approximation is often made to simplify the scattering term. In this section, we will first give the general expression for the scattering integral and then introduce the relaxation time approximation, followed by a more detailed discussion of the scattering mechanisms of various carriers.

6.2.1 Scattering Integral and Relaxation Time Approximation

We consider the collision process between two particles as shown in figure 6.2. After the collision, the energy and the velocity of each particle may change. Clearly, the collision is a time-dependent process. The rigorous way of dealing with the collision process is to solve the corresponding time-dependent Schrödinger equation for the combined system of both particles. This approach is, however, usually very complicated and not practical. A simpler way to treat the collision is to use the perturbation method (Landau and Lifshitz, 1977). This method considers the time-dependent interaction between the two particles as a small perturbation in energy, $H'(\mathbf{r},t)$, from the original steady-state, non-interacting energy H_0 of the two particles, such that the total system energy is

$$H = H_0(\mathbf{r}) + H'(\mathbf{r},t)$$

For example, when we use the harmonic oscillator approximation for the actual interatomic potentials, the higher order term $O[(x'-x_0)^3]$ in eq. (2.51) can be considered as the perturbation from the harmonic potential. In quantum mechanics, we must treat H as an operator and solve the Schrödinger equation for the two-particle system with the new H, the Hamiltonian of the system, as in eq. (2.22). By treating H' as a small perturbation to the unperturbed Hamiltonian H_0, the solution of the Schrödinger equation for the new H can be obtained through the perturbation method and expressed in terms of the wave functions Ψ of the unperturbed two-particle system with Hamiltonian H_0. Using the perturbation solution, one can calculate the probability for the system jumping from one quantum state Ψ_i to another quantum state Ψ_f, both being accessible quantum states of the original two-particle system. The rate of this transition probability is the transition rate and is given by

$$\begin{aligned} W_i^f &= \frac{2\pi}{\hbar}\left|\int \Psi_f^* H' \Psi_i d^3\mathbf{r}\right|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar}|\langle i|\mathrm{H}'|f\rangle|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar} M_{if}^2 \delta(E_f - E_i) \end{aligned} \tag{6.13}$$

where $d^3\mathbf{r} = dx\,dy\,dz$ means integration over the whole volume of the system and

$$M_{if} \equiv \langle i|H'|f\rangle \equiv \int \Psi_f^* H' \Psi_i d^3\mathbf{r} \tag{6.14}$$

is called the scattering matrix. The delta function, $\delta(E_f - E_i)$, defined as

$$\delta(E_f - E_i) = \begin{cases} 1 & E_i = E_f \\ 0 & E_i \neq E_f \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x)dx = 1 \tag{6.15}$$

is a manifestation of the requirements of the conservation of energy. According to eq. (6.15), $\delta(E_f - E_i)$ has a unit of J^{-1}. Equation (6.13) is often-referred to the *Fermi golden rule*. It should be kept in mind that E_i and E_f are the initial and final total energies of the two-particle system.

The Fermi golden rule gives the transition rate from one set of quantum states of the two particles into another set due to the scattering. The scattering term in the Boltzmann equation is the net gain of particles in one quantum state. This net gain consists of two components: one is the increase in the number of particles due to scattering from other quantum states into the quantum state under consideration ("in-scattering"); the other is the decrease of the number of particles due to scattering from the current quantum state to other quantum states ("out-scattering"). We again take the two-particle scattering process as an example. The initial wavevector of one particle is $\mathbf{k}$ and it collides with another particle with a wavevector $\mathbf{k}_1$. The corresponding distribution functions for the two particles are $f(t,\mathbf{r},\mathbf{k})$ and $f(t,\mathbf{r}_1,\mathbf{k}_1)$. After scattering, the momenta of the two particles are $\mathbf{k}'$ and $\mathbf{k}_1'$ and their distribution functions are $f(t,\mathbf{r}',\mathbf{k}')$ and $f(t,\mathbf{r}_1',\mathbf{k}_1')$, respectively. The scattering term for the particle at state $\mathbf{k}$ can be expressed as

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_c &= -\sum_{\mathbf{k}_1,\mathbf{k}',\mathbf{k}_1'} f(t,\mathbf{r},\mathbf{k}) f(t,\mathbf{r},\mathbf{k}_1) W(\mathbf{k},\mathbf{k}_1 \to \mathbf{k}',\mathbf{k}_1') \\ &\quad + \sum_{\mathbf{k}_1,\mathbf{k}',\mathbf{k}_1'} f(t,\mathbf{r},\mathbf{k}') f(t,\mathbf{r},\mathbf{k}_1') W(\mathbf{k}',\mathbf{k}_1' \to \mathbf{k},\mathbf{k}_1) \\ &= -K\int f(t,\mathbf{r},\mathbf{k}) f(t,\mathbf{r},\mathbf{k}_1) W(\mathbf{k},\mathbf{k}_1 \to \mathbf{k}',\mathbf{k}_1') d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1' \\ &\quad + K\int f(t,\mathbf{r},\mathbf{k}') f(t,\mathbf{r},\mathbf{k}_1') W(\mathbf{k}',\mathbf{k}_1' \to \mathbf{k},\mathbf{k}_1) d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1' \end{aligned} \tag{6.16}$$

where $K = V^3/(2\pi)^9$ is a factor that converts the summation over wavector into integration over the phase space. The first term represents the rate of particles being scattered out of quantum states determined by $\mathbf{k}$ and $\mathbf{k}_1$, and the second term represents the rate of particles scattered into the quantum state. We have used the same $\mathbf{r}$, assuming that at the point of scattering all the particles are at the same location. This means that the particles do not have a finite volume. The integration must be done over all other possible particles in the initial states $\mathbf{k}_1$ and counts all possibilities of the final states $\mathbf{k}'$ and $\mathbf{k}_1'$. For a particle with only translational motion, as we will assume from here on, $d^3\mathbf{k} = dk_x dk_y dk_z$. Equation (6.16) thus contains a nesting of nine integrals.

However, the conservation of energy and momentum, which is included in the transition probability, eq. (6.13), and the scattering matrix

$$E(\mathbf{k}) + E(\mathbf{k}_1) = E(\mathbf{k}') + E(\mathbf{k}_1') \tag{6.17}$$

$$\mathbf{k} + \mathbf{k}_1 = \mathbf{k}' + \mathbf{k}_1' \tag{6.18}$$

lead to a reduction in the number of integrals. Also, the following reciprocity relation

$$W(\mathbf{k}, \mathbf{k}_1 \rightarrow \mathbf{k}', \mathbf{k}_1') = W(\mathbf{k}', \mathbf{k}_1' \rightarrow \mathbf{k}, \mathbf{k}_1) \tag{6.19}$$

arising from the principle of detailed balance, is valid and can be used to write eq. (6.16) as

$$\begin{aligned}\left(\frac{\partial f}{\partial t}\right)_c = &-K\int W \times [f(t,\mathbf{r},\mathbf{k})f(t,\mathbf{r},\mathbf{k}_1)\\ &- f(t,\mathbf{r},\mathbf{k}')f(t,\mathbf{r},\mathbf{k}_1')]d^3\mathbf{k}_1\, d^3\mathbf{k}' d^3\mathbf{k}_1{}'\end{aligned} \tag{6.20}$$

Combining eqs. (6.20) and. (6.7), we see that the *Boltzmann equation*

$$\begin{aligned}&\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f\\ &= -K\int W \times [f(t,\mathbf{r},\mathbf{k})f(t,\mathbf{r},\mathbf{k}_1)\\ &\quad - f(t,\mathbf{r},\mathbf{k}')f(t,\mathbf{r},\mathbf{k}_1')]d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1'\end{aligned} \tag{6.21}$$

is a complicated integral-differential equation with seven variables $(t, \mathbf{r}, \mathbf{k})$, due to our assumption of translational motion only.

The integral-differential Boltzman equation, eq. (6.21), is very difficult to solve in general. Most solutions rely on a drastic simplification of the scattering integral by the relaxation time approximation

$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f - f_0(T, E, \mu)}{\tau(\mathbf{r}, \mathbf{k})} \tag{6.22}$$

where $\tau(\mathbf{r}, \mathbf{k})$ is the *relaxation time*, and f_0 represents the equilibrium distribution of the carriers, such as the Boltzmann, the Fermi–Dirac, and the Bose–Einstein distributions given in chapter 4. The relaxation time approxi-mation is also called the BGK approximation in gas dynamics in honor of the joint work of Bhatnagar, Gross, and Krook (1954). In chapter 8, we will go through the scattering integrals more carefully for the case of electron–phonon scattering and show that the approximation is valid only for elastic scattering. Despite this limitation, the relaxation time approximation is actually used widely, even for processes including inelastic scattering, with correct end results for most situations.

We can understand the meaning of τ easily by neglecting the spatial nonuniformity of the distribution function. Equation (6.7) becomes

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau} \tag{6.23}$$

and thus

$$f - f_0 = Ce^{-t/\tau} \tag{6.24}$$

So the relaxation time is a measure of how long it takes for a nonequilibrium system to relax back to an equilibrium distribution. Often, the relaxation time is expressed in terms of the energy rather than the velocity, $\tau = \tau(E)$, which implies isotropic scattering.

The scattering may be caused by the coexistence of different processes and a relaxation time can be defined for each process. The total relaxation time, τ_t, can be calculated from individual relaxation times, τ_j, according to the *Matthiessen rule*,

$$\frac{1}{\tau_t} = \sum_j \frac{1}{\tau_j} \tag{6.25}$$

The Matthiessen rule assumes that the scattering mechanisms are independent of each other (Ashcroft and Mermin, 1976).

Under the relaxation time approximation, the Boltzmann equation becomes

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau} \tag{6.26}$$

where we have used $\mathbf{v}$ rather than $\mathbf{k}$ as the variable. The corresponding equation using $\mathbf{k}$ as the variable is, from eq. (6.7),

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = -\frac{f - f_0}{\tau} \tag{6.27}$$

Equations (6.26) and (6.27) are also called the *Krook equation* in gas dynamics (Chapman and Cowling, 1970). In the rest of this section, we will discuss in greater detail the scattering mechanisms and the relaxation time of various energy carriers.

6.2.2 Scattering of Phonons

The derivation of the phonon modes in chapter 3 is based on the assumption of harmonic interatomic potential. Under this assumption, the lattice waves are decomposed into normal modes which do not interact with each other. For such an ideal case, there is no resistance to heat flow and the thermal conductivity is infinite. In contrast, real crystals clearly have a finite thermal conductivity, which is caused by the scattering of phonons.

In a pure dielectric crystal, the phonon scattering is primarily due to the scattering of phonons among themselves. Anharmonic force interaction is the source of scattering among phonons. The second-order term in the Taylor expansion of the interatomic potential around the equilibrium point, as in eq. (2.51), gives the harmonic oscillator model that we used to represent phonons. By considering the third-order term in the potential as a perturbation to the original Hamiltonian, $H' \sim x^3$, and through the use of the Fermi golden rule, it is found that this anharmonic force term acts as a mechanism for two phonons to merge into a third phonon or for one phonon to split into two phonons, as shown in figure 6.3 (Ziman, 1960). Such scattering processes are called three-phonon scattering. The two-particle collision picture shown in figure 6.2 must now be modified

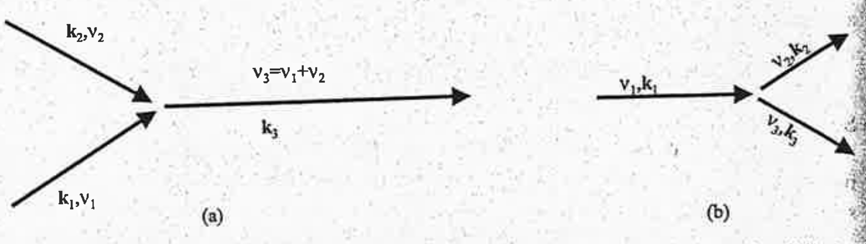

Figure 6.3 Three-phonon scattering processes: (a) two phonons merge into one (annihilation process); (b) one phonon splits into two (creation process).

in accordance with figure 6.3, with corresponding changes to the general scattering integral expressed by eq. (6.20) and the energy and momentum conservation rules expressed by eqs. (6.17) and (6.18). For the merging of two phonons into one, energy conservation gives

$$h\nu_1 + h\nu_2 = h\nu_3 \tag{6.28}$$

and a similar equation can be written for the process in which one phonon splits into two.

Momentum conservation during the three-phonon interaction processes takes a special form. For the phonon merging process, the momentum conservation can be written as

$$\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 = \mathbf{G} \tag{6.29}$$

where the reciprocal lattice vector **G** can be zero or a linear combination of the reciprocal lattice vectors. If $(\mathbf{k}_1 + \mathbf{k}_2)$ falls within the first Brillouin zone wavevector, then $\mathbf{G} = \mathbf{0}$; otherwise, $\mathbf{G} \neq \mathbf{0}$ (figure 6.4). The latter result comes from the requirement that the phonon wavelength cannot be smaller than the lattice constant, as discussed in chapter 3. The $\mathbf{G} = \mathbf{0}$ phonon scattering process is called the *normal process* and the $\mathbf{G} \neq \mathbf{0}$ is the *umklapp process*. Without the umklapp process, the thermal conductivity of a crystal would still be infinite because in a normal scattering process, the generated third phonon preserves both the energy and the direction of the two original phonons. The extra reciprocal lattice wavevector in the umklapp process changes the net direction of phonon propagation and thus creates resistance to the heat flow (Peierls, 1929).

The evaluation of the scattering integral for phonons is very difficult (Ziman, 1960). Instead, approximate expressions for the relaxation time, based on eq. (6.20), have been developed (Klemens, 1958). For example, an often-used expression for the three-phonon umklapp process is

$$\tau_u^{-1} = Be^{-\theta_D/bT}T^3\omega^2 \tag{6.30}$$

where B and b are constants and θ_D is the Debye temperature. The values of B and b for different materials can be obtained by matching the model predictions for thermal conductivity with experimental results, as we will see later.

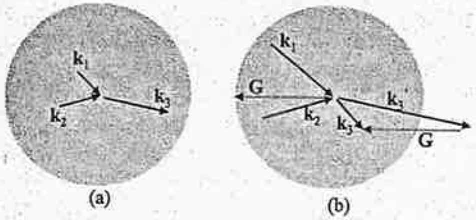

Figure 6.4 Three-phonon (a) normal and (b) umklapp scattering processes, using the merging of two phonons into one as an example. The gray region represents the first Brillouin zone. In the umklapp process, $\mathbf{k}_3'$, which is the sum of $\mathbf{k}_1$ and $\mathbf{k}_2$, is outside the first Brillouin zone. It is brought back into the first Brillouin zone by the reciprocal lattice wavevector **G**. Energy must be conserved during both scattering processes. The normal processes in (a) do not create thermal resistance because the merged phonon carries the same amount of energy and momentum as the original two phonons. Umklapp scattering causes thermal resistance because the momenta of the two original phonons are changed after scattering.

In real crystals, there are defects such as impurities, dislocations, and grain boundaries. These can all scatter phonons; details can be found in the given references (Ziman, 1960; Klemens, 1958). For impurities, the scattering obeys the familiar Rayleigh law

$$\tau_I^{-1} = A\omega^4 \tag{6.31}$$

Boundary scattering is also sometimes included in the total relaxation time, using the Matthiessen rule. The relaxation time due to boundary scattering is of the order of

$$\tau_b^{-1} = b_s v/L \tag{6.32}$$

where L is a characteristic length, such as the diameter of a circular rod for heat conduction along the axial direction, and b_s is a shape factor that can be modeled similarly to the radiation shape factor (Berman et al., 1955).

The total relaxation time is obtained by combining the expressions for individual relaxation processes according to the Matthiessen rule. We should point out, however, that incorporating the boundary scattering with the Matthiessen rule is questionable because the boundary scattering is a surface process whereas the phonon–phonon and phonon–impurity scattering occur inside the volume. In chapter 7, we will consider many size effects by imposing interfaces and boundaries as boundary conditions of the Boltzmann equation rather than being based on the Matthiessen rule. Although τ_t can include several potential mechanisms, typically, in a certain temperature range, there is a dominant scattering mechanism. We will come back to this point when discussing thermal conductivity.

Phonons cannot be acted upon by external force. Under the relaxation time approximation, the force term in eq. (6.27) drops out in the phonon Boltzmann equation.

6.2.3 Scattering of Electrons

Electrons are predominantly scattered by phonons. Electron–electron scattering is typically much weaker. An electron can create or annihilate a phonon in the scattering process, and must obey the energy conservation and momentum conservation during the process. For a phonon creation process, the energy and momentum conservation rules are

$$E_i = E_f + h\nu_p \tag{6.33}$$

$$\mathbf{k}_i = \mathbf{k}_f + \mathbf{k}_p + \mathbf{G} \tag{6.34}$$

where $h\nu_p$ and $\mathbf{k}_p$ are the energy and wavevector of the created phonon, respectively. Again, the process can be a normal or an umklapp one, depending on whether $\mathbf{G} = \mathbf{0}$ or not. In most cases, the dominant scattering process has $\mathbf{G} = \mathbf{0}$.

In metals, at temperatures higher than the Debye temperature, the number of phonons is proportional to temperature T, as the temperature independent specific heat suggests. The more phonons, the more chance that the electron will experience scattering by phonons; consequently, the electron–phonon relaxation time is (Ashcroft and Mermin, 1976)

$$\frac{1}{\tau} \propto T \tag{6.35}$$

Scattering in semiconductors is more complicated and one must determine whether the scattering is caused by acoustic or optical phonons. The optical phonons can be further divided into nonpolar, such as in silicon and germanium, or polar, such as in gallium arsenide (GaAs). In chapter 8, we will discuss in more detail the electron–phonon scattering in relation to energy exchange mechanisms. Impurity scattering in semiconductors is also a very important mechanism. Refer to Lundstrom (2000) and Hess (2000) for a more detailed discussion of various electron scattering mechanisms.

6.2.4 Scattering of Photons

Photon scattering is often divided into two parts: the inelastic and the elastic processes. In the inelastic process, photons are absorbed or emitted. The absorption coefficient is often used to represent the process. Under the relaxation time approximation, inelastic scattering that includes absorption and emission of photons can be expressed as

$$\left(\frac{\partial f}{\partial t}\right)_{c,\text{inelastic}} = -\frac{f - f_0}{\tau} \tag{6.36}$$

and the steady-state Boltzmann equation becomes

$$v\frac{\partial f}{\partial s} = -\frac{f - f_0}{\tau} + \left(\frac{\partial f}{\partial t}\right)_{c,\text{elastic}} \tag{6.37}$$

where we have used

$$\mathbf{v} \bullet \nabla_{\mathbf{r}} f = v\frac{\partial f}{\partial s}$$

s is the distance along the direction of propagation and v is the speed of light in the medium. The term $\nabla_{\mathbf{k}} f$ in the Boltzmann equation for photons drops out because photons do not interact with external force. The elastic scattering term can be obtained from solving the Maxwell equations. A familiar example is the Mie scattering theory, which represents the full solution of the Maxwell equations for a plane wave interacting with a spherical particle with given optical constants (Bohren and Huffman, 1983).

As mentioned before, for thermal radiation it is customary to use intensity rather than the distribution function. Using the intensity notation, eq. (6.37) can be written as

$$\frac{\partial I_\nu}{\partial s} = -\frac{I_\nu - I_{\nu 0}}{\Lambda} + \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,\text{elastic}} \tag{6.38}$$

where $\Lambda = v\tau$ is the photon inelastic scattering mean free path, and I_0 is the blackbody radiation intensity, as we have proven in chapter 4. Here we have added the subscript ν to denote that the quantities are frequency dependent. Using the terminology that is more frequently used in thermal radiation, the absorption coefficient is the inverse of inelastic scattering mean free path,

$$\alpha_\nu = \frac{1}{\Lambda} = \frac{1}{v\tau} = \frac{4\pi\kappa}{\lambda_0} \tag{6.39}$$

where the last equality is the expression we introduced in eq. (5.40) and is valid only for a homogeneous medium with κ as the imaginary part of the complex refractive index. For other systems such as a system with particulates, the absorption coefficient can be obtained from solving the Maxwell equations (Bohren and Huffman, 1983; Siegel and Howell, 1992). The elastic scattering term is also divided into two parts: the outgoing scattering, which is proportional to the scattering coefficient, and the incoming scattering,

$$\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,\text{elastic}} = -\sigma_{s\nu} I_\nu + \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,\text{elastic, in}} \tag{6.40}$$

where $\sigma_{s\nu}$ is the scattering coefficient. The incoming scattering is often expressed as

$$\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,\text{elastic,in}} = \frac{\sigma_{s\nu}}{4\pi}\int I'_\nu(\hat{\Omega}')\phi(\hat{\Omega}' \to \Omega)d\Omega' \tag{6.41}$$

where ϕ is called the scattering phase function, representing the fraction of photons scattered from direction Ω' to Ω per unit solid angle of the incident direction. The integration in eq. (6.41) is thus the total radiation scattered into the Ω direction. The final equation, which is called the equation of radiative transfer, becomes (Siegel and Howell, 1992)

$$\frac{\partial I_\nu}{\partial s} = -K_{e\nu} I_\nu + \alpha_\nu I_{\nu 0} + \frac{\sigma_{s\nu}}{4\pi}\int I'_\nu(\hat{\Omega}')\phi(\hat{\Omega}' \to \Omega)d\Omega' \tag{6.42}$$

where the extinction coefficient, $K_{e\nu} = \alpha_\nu + \sigma_{s\nu}$, combines absorption and outgoing scattering into an extinction term.

Although the equation of radiative heat transfer, eq. (6.42), looks quite different from the Boltzmann equation, eq. (6.21), the above explanation illustrates that it does come from the Boltzmann equation. This point was exploited by Majumdar (1993), who transformed the phonon Boltzmann equation into a form that is similar to the equation of radiative heat transfer by introducing phonon intensity. We see that the analogy is natural because all of these equations originate from the Boltzmann equation. For electron transport, the intensity concept is not customarily used, although it can be similarly introduced, not in terms of the energy flux but in terms of the particle flux.

6.2.5 Scattering of Molecules

In eq. (1.37), we gave the mean free path between successive collisions of two molecules as

$$\Lambda = \frac{m}{\sqrt{2}\pi \rho d^2} \tag{6.43}$$

where d is the molecule diameter, m is the molecular weight, and ρ is the density. From the mean free path, the relaxation time can be obtained,

$$\frac{1}{\tau} = \frac{\bar{v}}{\Lambda} = \frac{\sqrt{2}\pi \rho \bar{v} d^2}{m} \tag{6.44}$$

where $\bar{v}$ is the average speed of the molecules,

$$\bar{v} = \int_0^\infty \int_0^\infty \int_0^\infty v f_0(v)\, dv_x\, dv_y\, dv_z = \sqrt{\frac{8\kappa_B T}{\pi m}} \tag{6.45}$$

and f_0 is the Maxwell velocity distribution given by eq. (1.26).

6.3 Classical Constitutive Laws

Using the Boltzmann equation under the relaxation time approximation, we can investigate the transport of energy carriers. We will show in this section that classical laws, such as the Fourier law, the Newton shear stress law, the Ohm law, and so on, are special solutions of the Boltzmann equation under the assumption of local thermal equilibrium. The limitations of this assumption can be appreciated through the derivations.

Consider the Boltzmann equation under the relaxation time approximation, that is, eqs. (6.26) and (6.27). Let us introduce a deviation function g,

$$g = f - f_0 \tag{6.46}$$

and write eq. (6.26) as

$$\frac{\partial g}{\partial t} + \frac{\partial f_0}{\partial t} + \mathbf{v} \bullet \nabla_\mathbf{r} f_0 + \mathbf{v} \bullet \nabla_\mathbf{r} g + \frac{\mathbf{F}}{m} \bullet \nabla_\mathbf{v} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_\mathbf{v} g = -\frac{g}{\tau} \tag{6.47}$$

All the diffusion laws can be obtained under the following assumptions: (1) the transient terms are negligible; (2) the gradient of g is much smaller than the gradient of f_0; and similarly, (3) g is much smaller than f_0. Under these assumptions, eq. (6.47) becomes

$$g = -\tau \left(\mathbf{v} \bullet \nabla_\mathbf{r} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_\mathbf{v} f_0 \right) \tag{6.48}$$

or

$$f = f_0 - \tau \left(\mathbf{v} \bullet \nabla_\mathbf{r} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_\mathbf{v} f_0 \right) \tag{6.49}$$

This solution for the distribution function can also be obtained by treating g as the first-order expansion of f (f_0 is the 0th-order expansion) and neglecting higher order terms. The Boltzmann equation thus obtained is said to be the linearized Boltzmann equation. From the distribution function, we can calculate the flux of various quantities of interest (charge, momentum, energy). We will narrow our focus next to examine some of the fluxes associated with various carriers.

6.3.1 Fourier Law and Phonon Thermal Conductivity

We first consider the heat conduction by phonons. In this case, there is no external force. Since the Bose–Einstein distribution

$$f_0 = \frac{1}{\exp\left(\hbar\omega / k_B T\right) - 1} \tag{6.50}$$

depends only on temperature, we can write eq. (6.49) as

$$f(\mathbf{r}, \mathbf{k}) = f_0 - \tau \frac{df_0}{dT} \mathbf{v} \bullet \nabla T \tag{6.51}$$

where T is a function of coordinate $\mathbf{r}$, i.e., $T(t, \mathbf{r})$. We have dropped the subscript $\mathbf{r}$ in the gradient operator. The nonequilibrium carrier distribution depends on both $\mathbf{r}$ and $\mathbf{v}$.

For simplicity, we consider a temperature gradient along the x-direction without loss of generality. We can calculate the heat flux from

$$J_{qx}(x) = \sum_s \left[\frac{1}{V} \sum_{k_{x1}=-\infty}^{\infty} \sum_{k_{y1}=-\infty}^{\infty} \sum_{k_{z1}=-\infty}^{\infty} v_x \hbar\omega f \right] \tag{6.52}$$

where s represents the summation over all polarizations. It is interesting to compare this expression with eq. (5.152) which we used in deriving the Landauer formalism. In eq. (5.152), we are considering only the heat flux going from point 1 to point 2 but there also exists a reverse heat flux from point 2 to point 1. In eq. (6.52), we are considering the net heat flux at any constant x-plane inside the domain. There are carriers going across the plane in both directions, as determined by eq. (6.51) and sketched in figure 6.5. Following a similar procedure to that used before, we can transform eq. (6.52) first into an integration over all wavevectors and then into an integration over energy and solid angle, using a spherical coordinate system for the wavevectors as shown in figure 6.6.

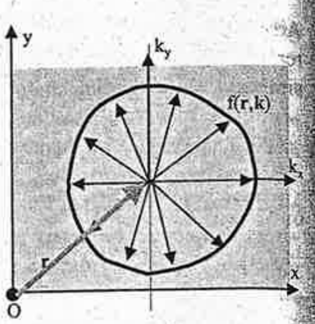

Figure 6.5 In the calculation of heat flux at a constant x plane, carriers moving in all directions may contribute to the net heat flux in the x-direction, depending on the velocity component v_x of the carriers. Note that we align k_x parallel to x, but the **k**-space origin is located at **r**.

$$
\begin{aligned}
J_{qx}(x) &= (1/V)\sum_{s}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x\hbar\omega f\, dk_x\, dk_y\, dk_z/(2\pi/L)^3 \\
&= \int_0^{\omega_{\max}} d\omega\left[\int_0^{2\pi}\left\{\int_0^{\pi} v\cos\theta\hbar\omega f\frac{D(\omega)}{4\pi}\sin\theta d\theta\right\} d\varphi\right]
\end{aligned}
\tag{6.53}
$$

where $\omega_{\max}$ represents the highest phonon frequency, such as the Debye frequency in the Debye model. Substituting eq. (6.51) into the above equation, we obtain

$$
\begin{aligned}
&J_{qx}(x) \\
&= \int_0^{\omega_{\max}} d\omega\left[\int_0^{2\pi}\left\{\int_0^{\pi} v\cos\theta\hbar\omega\left[f_0-\tau\frac{df_0}{dT}\frac{dT}{dx}v\cos\theta\right]\frac{D(\omega)}{4\pi}\sin\theta d\theta\right\} d\varphi\right] \\
&= -\frac{1}{2}\frac{dT}{dx}\int_0^{\omega_{\max}} d\omega\left\{\int_0^{\pi}\tau v^2\sin\theta\cos^2\theta\times\hbar\omega D(\omega)\frac{df_0}{dT}d\theta\right\}
\end{aligned}
\tag{6.54}
$$

We see that the first term f_0 in eq. (6.51) naturally drops out of the integration. This is because f_0 represents the equilibrium distribution and it contributes an equal amount of energy going from left to right as in the reverse direction. Equation (6.54) can be written as the *Fourier law*

$$
J_{qx} = -k\frac{dT}{dx}
\tag{6.55}
$$

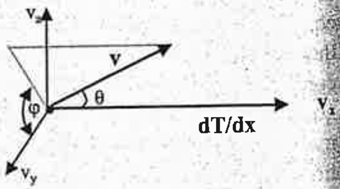

Figure 6.6 Polar coordinates for the momentum components. Note that we align the momentum and space Cartesian components in the same direction.

with the following expression for thermal conductivity

$$
k = \frac{1}{2}\int_0^{\omega_{\max}}\left\{\int_0^{\pi}\tau v^2 C_\omega\sin\theta\times\cos^2\theta d\theta\right\} d\omega
\tag{6.56}
$$

where $C_\omega = \hbar\omega D(\omega)\, df_0/dT$ is the specific heat per unit frequency at frequency ω and temperature T. When v and τ are isotropic, eq. (6.56) can be integrated to

$$
k = \frac{1}{3}\int \tau v^2 C_\omega\, d\omega
\tag{6.57}
$$

In the case that both τ and v are independent of frequency, the above expression reverts to the kinetic relation, eq. (1.35), that we obtained in chapter 1,

$$
k = \frac{1}{3}Cv\Lambda
\tag{6.58}
$$

where $\Lambda = \tau v$ is the phonon mean free path.

Our previous discussion suggests that the relaxation time is highly frequency dependent. On the basis of the Mathiessen rule, and considering the following phonon scattering mechanisms: (1) phonon–phonon umklapp scattering, (2) phonon–impurity scattering, and (3) phonon–boundary scattering, we have

$$
\frac{1}{\tau} = \frac{b_s v}{L} + A\omega^4 + Be^{-\theta_D/bT}T^3\omega^2
\tag{6.59}
$$

We cautioned before that our treatment of boundary scattering is very crude and should be taken as a rough approximation. Substituting eq. (6.59) into (6.57), we obtain an expression to calculate the thermal conductivity. There are three unknown parameters, particularly A, B and b, since b_s can be modeled (Berman et al., 1955). These parameters can be determined from fitting eq. (6.57) with experimental temperature-dependent thermal conductivity data. In figure 6.7, we show a fit of the thermal conductivity of GaAs (Chen and Tien, 1993). The thermal conductivity of a crystalline solid typically shows a dome shape with a peak around 20 K, depending on the size of the crystals. At high temperature, the dominant scattering mechanism is due to phonon–phonon scattering and thermal conductivity is approximately inversely proportional to temperature,

$$
k \propto \frac{1}{T}
\tag{6.60}
$$

In practice, the high temperature dependence is often T^{-n} with $n = 1 - 1.5$. At low temperature, phonon–boundary scattering dominates heat conduction. Thermal conductivity is proportional to specific heat and also to the size of the crystal (Casimir, 1938),

$$
k \propto T^3
\tag{6.61}
$$

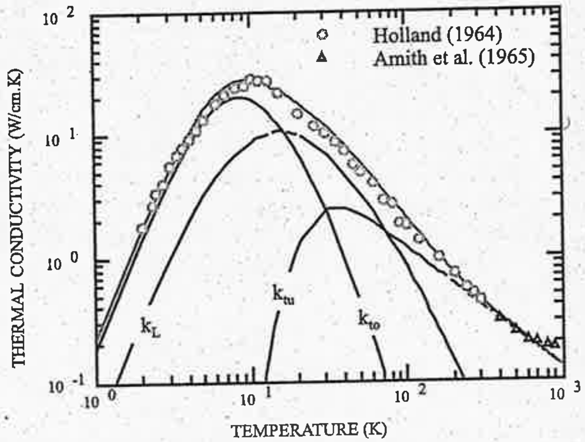

Figure 6.7 Thermal conductivity of GaAs, based on a model that considers phonon dispersion and contributions from different phonon branches, k_{to} from low-frequency transverse phonons and k_{tu} from high-frequency ones, and k_L from longitudinal phonons (Chen and Tien, 1993).

The reader should be reminded that the fitting of the thermal conductivity model based on eq. (6.57) and (6.59) with experimental data has some arbitrariness since the model also depends on the treatment of the density of states, the phonon group velocity v, and the dispersion of phonons. Often, the Debye model is used with a constant phonon group velocity. In addition, expressions for phonon–phonon scattering such as eq. (6.30) are obtained with a number of assumptions that also involve phonon dispersion. The fitting of the GaAs thermal conductivity data in figure 6.7 was based on Holland's model (Holland, 1963; Chen and Tien, 1993), which considered, approximately, the changing group velocity of phonons as a function of frequency, and used different relaxation time expressions for different branches of phonons. It was found that, depending on how the dispersion is approximated, the experimental data can be fitted equally well with different sets of parameters. Thus, extracting the exact relaxation time is, to a large extent, a still unsolved question even for bulk materials. Another point that should be mentioned is that although the normal three-phonon scattering process does not create resistance, it can redistribute phonons and thus indirectly affect the umklapp scattering process. A phenomenological model, based on displaced equilibrium distribution for the normal process, was established by Callaway (1959) to take the normal scattering process into consideration and this model has become a standard in thermal conductivity modeling.

Rather than being a convenient way of calculating thermal conductivity, eq. (6.58) is often used to estimate the mean free path on the basis of the experimental values of thermal conductivity, the specific heat, and the speed of sound in a material. This way of estimating the phonon mean free path, however, usually leads to an underestimation of the mean free path for those phonons that are actually carrying the heat because of the following reasons (Chen, 2001a):

1. Phonons are dispersive and their group velocity varies from the speed of sound at the Brillouin zone center to zero at the zone edge. The average phonon group velocity is much smaller than the speed of sound.
2. Optical phonons contribute to the specific heat but typically contribute little to heat flux, due to their low group velocity and their high scattering rates.
3. Phonon scattering is highly frequency dependent. High-frequency phonons are usually scattered more strongly than low-frequency phonons.

For example, the simple kinetic theory based on eq. (6.58) leads to a mean free path for silicon of ~410 Å. More careful consideration of the phonon dispersion and optical phonons (Chen, 1998) and experimental results (Ju and Goodson, 1999) indicate that the mean free path of those phonons actually carrying the heat is ~2500–3000 Å, much longer than what simple kinetic theory would give.

6.3.2 Newton's Shear Stress Law

To derive the Newton shear stress law for gas, we again consider a one-dimensional flow along the x-direction with the average velocity variation along the y-direction, as shown in figure 6.8. Because the molecules have an average velocity superimposed on their random velocity, we can no longer use the Maxwell velocity distribution as given in eq. (1.26), which would lead to a zero average velocity. As an approximation, the following *displaced Maxwell velocity distribution* is often used for the probability of finding one particle having velocity **v**

$$P(v_x, v_y, v_z) = \left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} e^{-m[(v_x-u)^2+v_y^2+v_z^2]/2\kappa_B T} \tag{6.62}$$

where u is the average velocity along the x-direction. On the basis of this distribution, it can be shown that the average velocity is indeed u (this is left as an exercise). Assuming that the number density of particles is n, the number density of particles having velocity **v** is

$$f_0(v_x, v_y, v_z) = nP(v_z, v_y, v_z) = n\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} e^{-m[(v_x-u)^2+v_y^2+v_z^2]/2\kappa_B T} \tag{6.63}$$

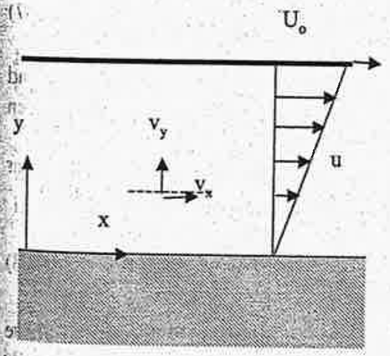

Figure 6.8 One-dimensional laminar viscous flow for deriving the Newton shear stress law.

From eq. (6.49), the distribution function is

$$f = f_0 - \tau v_y \frac{\partial f_0}{\partial y} = f_0 - \tau v_y \frac{\partial f_0}{\partial u} \frac{\partial u}{\partial y} \tag{6.64}$$

The shear stress along the x-direction on a plane perpendicular to the y-axis can be calculated by considering the momentum exchange across the plane,

$$\begin{aligned} \tau_{xy} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_y[mv_x] f \, dv_x \, dv_y \, dv_z \\ &= -\frac{\partial u}{\partial y}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \tau v_y^2 m v_x \frac{\partial f_0}{\partial u} dv_x \, dv_y \, dv_z = \mu \frac{\partial u}{\partial y} \end{aligned} \tag{6.65}$$

where mv_x is the momentum of one particle along the x-direction and the $v_y(mv_x)f$ represents the rate of momentum change along the x-direction due to the flow of molecules across the constant y-plane. Such a rate of change of momentum equals the shear force acting on the constant y-plane, according to Newton's second law. The dynamic viscosity is

$$\begin{aligned} \mu &= -\int\int\int \tau v_y^2 (mv_x) \frac{\partial f_0}{\partial u} dv_x \, dv_y \, dv_z \\ &= m^2 \tau n \left(\frac{m}{2\pi \kappa_B T}\right)^{3/2} \int_{-\infty}^{\infty} e^{-mv_z^2/(2\kappa_B T)} dv_z \\ &\times \int_{-\infty}^{\infty} v_y^2 e^{-mv_y^2/(2\kappa_B T)} dv_y \int_{-\infty}^{\infty} \frac{v_x'^2}{\kappa_B T} e^{-mv_x'^2/(2\kappa_B T)} dv_x' \end{aligned} \tag{6.66}$$

In the last equation, we assume that the relaxation time is a constant and use $v_x' = v_x - u$. Carrying out the above integration, we obtain the following expression for the dynamic viscosity:

$$\mu = n\tau\kappa_B T = \frac{1}{4d^2}\sqrt{\frac{m\kappa_B T}{\pi}} \tag{6.67}$$

In writing the last step, we have used the mean free path expression [eq. (1.36)] and $\tau = \Lambda/\langle v \rangle$, where the average speed of molecules is $\langle v \rangle = [8\kappa_B T/(\pi m)]^{1/2}$, as given in example 1.1.

Following a similar procedure, we can also calculate the energy flux due to molecular heat conduction and obtain the thermal conductivity for a gas as

$$k = \frac{5}{2}\left(\frac{k_B}{m}\right) n\tau\kappa_B T = \frac{5}{2}\left(\frac{\kappa_B}{m}\right)\mu \tag{6.68}$$

Thus the thermal conductivity and viscosity are related to each other, because all these quantities arise from the same microscopic carrier motion. The difference is that for the shear stress we examine the momentum of the carriers, whereas for heat conduction we examine the energy of the carriers. Relationships as such are often found between kinetic coefficients. We will see similar relations in the next few sections between the electrical conductivity and mobility, the electrical and thermal conductivity of electrons, and the Seebeck and Peltier coefficients.

Equations (6.67) and (6.68) for viscosity and thermal conductivity are obtained on the basis of the relaxation time approximation. Enskog and Chapman, independently, solved the Boltzmann equation in its integral form (Chapman and Cowling, 1970) by series expansion of the distribution function. The final results for the viscosity and thermal conductivity for gas molecules, approximated as elastic spheres, are (Vincenti and Kruger, 1986)

$$\mu = \frac{5}{16d^2}\sqrt{\frac{m\kappa_B T}{\pi}} \quad \text{and} \quad k = \frac{15}{4}\left(\frac{\kappa_B}{m}\right)\mu \tag{6.68a}$$

6.3.3 Ohm's Law and the Wiedemann–Franz Law

Having considered phonon and molecule transport, let us turn our attention now to electron transport. We first limit our consideration to electron flow in an isothermal conductor driven by an external electric field. The force acting on the electron from the external field is

$$\mathbf{F} = -e\mathscr{E} = e\nabla\varphi_e \tag{6.69}$$

where e is the unit charge, the charge of an electron is $(-e)$, $\mathscr{E}$ is the electric field, and φ_e is the electrostatic potential that is related to the field by $\mathscr{E} = -\nabla\varphi_e$. Consider the one-dimensional case with charge flow in the x-direction due to a field of magnitude $\mathscr{E}$. Substituting eq. (6.69) into (6.49), we have

$$f = f_0 - \tau\left(v_x \frac{\partial f_0}{\partial x} - \frac{e\mathscr{E}}{m}\frac{\partial f_0}{\partial v_x}\right) \tag{6.70}$$

where f_0 obeys the Fermi–Dirac distribution

$$f_0(E, E_f, T) = \frac{1}{\exp\left(\frac{E-E_f}{\kappa_B T}\right) + 1} \tag{6.71}$$

Here we are using E_f to represent the chemical potential. In chapter 4, we used E_f for the Fermi level and μ for the chemical potential, but in this chapter μ is used for the dynamic viscosity. Sometimes the distinction between the Fermi level and the chemical potential is not rigorously made. In electrical engineering, chemical potential is usually called the Fermi level. To calculate $\partial f_0/\partial x$ in eq. (6.70), we should be careful where we place the reference for E and E_f. In a semiconductor, the conduction band energy is [Eq. (4.60)]

$$E = E_c + \frac{\hbar^2}{2m_*}(k_x^2 + k_y^2 + k_z^2)$$

where E_c is the location of the band edge. If we choose a common flat reference point for E_c, E_f, and E, such as shown in figure 6.9(a), it is clear that all three quantities

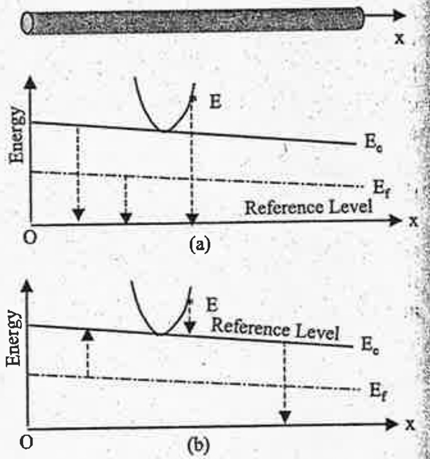

Figure 6.9 Choice of reference level for E_f and E. In (a), E_f, E_c, and E are relative to an absolute reference level. In this case all three quantities are x-dependent. In (b), E_f and E are relative to E_c and E_c is relative to an absolute reference level. The arrows in the dashed lines mark the reference point of the quantities.

are dependent on x. It is easier, however, to measure E_f relative to E_c. For a given carrier concentration, for example, the chemical potential should be measured relative to the bottom of the conduction band for electrons, as is clearly seen from eq. (4.64). In this reference system, E_f is actually the sum of the chemical potential $(E_f - E_c)$ and E_c, that is, $E_f = (E_f - E_c) + E_c$. The bottom of the conduction band E_c is related to the electrostatic potential φ_e from the relation between force and potential (for electrons with a negative charge)

$$F = -\frac{dE}{dx} = -\frac{dE_c}{dx} = e\frac{d\varphi_e}{dx} \tag{6.72}$$

Thus, $-E_c/e$ is parallel to the *electrostatic potential*. We can usually take $\varphi_e = -E_c/e$.

Note the difference of the "potential" used in electricity from what we normally call the potential energy. The sum of the electrostatic potential φ_e and chemical potential (divided by charge) $(E_f - E_c)/(-e)$ is often called the *electrochemical potential*, Φ,

$$\Phi = \varphi_e - (E_f - E_c)/e = -E_f/e \tag{6.73}$$

Thus, in a reference system as shown in figure 6.9(a), E_f itself includes both electrostatic and chemical potential contributions.

A different reference system, as shown in figure 6.9(b), is to have E_f and E always relative to E_c while E_c refers to an absolute potential level. This reference system has the advantage that E_f always represents the chemical potential and E is independent of x. This can also be seen from eq. (6.71), if we write $(E - E_f)$ in the Fermi–Dirac distribution as

$$E - E_f = (E - E_c) - (E_f - E_c) = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2) - (E_f - E_c)$$

Under this reference, the electrochemical potential is then

$$\Phi = -(E_c + E_f)/e = \varphi_e - E_f/e \tag{6.73a}$$

where we have taken $\varphi_e = -E_c/e$.

Because of its simplicity, we will choose figure 6.9(b) as the reference system in our subsequent derivations. The end results are independent of the reference system. In the chosen reference system

$$\frac{\partial f_0}{\partial x} = \frac{\partial f_0}{\partial E_f}\frac{dE_f}{dx} = -\frac{\partial f_0}{\partial E}\frac{dE_f}{dx} \tag{6.74}$$

and eq. (6.70) becomes

$$\begin{aligned} f &= f_0 + \tau\left(v_x\frac{dE_f}{dx}\frac{\partial f_0}{\partial E} + \frac{e\mathscr{E}\partial f_0}{m}\frac{\partial E}{\partial E}\frac{\partial E}{\partial v_x}\right) \\ &= f_0 + \tau v_x\left(\frac{dE_f}{dx} + e\,\mathscr{E}\right)\frac{\partial f_0}{\partial E} \end{aligned} \tag{6.75}$$

In eq. (6.74), we used the relation $\partial f/\partial E_f = -\partial f/\partial E$. The current density (A m^{-2}) is then

$$\begin{aligned} J_e &= \frac{1}{V}\sum_{k_z=-\infty}^{\infty}\sum_{k_y=-\infty}^{\infty}\sum_{k_z=-\infty}^{\infty}(-e)v_x f \\ &= -\frac{2}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e v_x f\, dk_x\, dk_y\, dk_z \\ &= -\frac{e}{4\pi}\int_{4\pi}\left\{\int_0^{\infty} v_x^2\tau\left(\frac{dE_f}{dx} + e\,\mathscr{E}\right)\frac{\partial f_0}{\partial E}D(E)dE\right\}d\Omega \\ &= -\frac{e}{3}\left(\frac{dE_f}{dx} + e\,\mathscr{E}\right)\int_0^{\infty}\tau v^2 D(E)\frac{\partial f_0}{\partial E}dE = \frac{e^2}{3}\frac{d\Phi}{dx}\int_0^{\infty}\tau v^2 D(E)\frac{\partial f_0}{\partial E}dE \end{aligned} \tag{6.76}$$

where we have used the same angle notation as in figure 6.6 and the integration over the entire solid angle (4π) is carried out over θ and φ similar to eq. (6.54). We see from eq. (6.76) that the driving force for current flow is the electrochemical potential, not just the electrostatic potential alone. Because the chemical potential is related to the carrier concentration, the chemical potential gradient is representative of the carrier concentration gradient and the current due to the chemical potential gradient is thus the diffusion current. In metals and semiconductors, the relative importance of the two terms in the electrochemical potential is different, so we will discuss metals and semiconductors separately.

6.3.3.1 Metals

The electron density in metals is very large, such that the transport does not affect the chemical potential since the chemical potential is a measure of the electron number density. Equation (6.76) becomes

$$J_e = -\frac{e^2}{3}\mathscr{E}\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE = \sigma\,\mathscr{E} \tag{6.77}$$

where σ is the electrical conductivity. Equation (6.77) is the Ohm law. The electrical conductivity is

$$\sigma = -\frac{e^2}{3}\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE = L_{11} \tag{6.78}$$

where L_{11} is a notation to be used later. Because $\partial f_0/\partial E$ is zero everywhere except close to the chemical potential or Fermi level, we can use a delta function to approximate it, $\partial f_0/\partial E = -\delta(E - E_f)$. Equation (6.78) becomes

$$\sigma = \frac{\tau_F D_F e^2 v_F^2}{3} \tag{6.79}$$

where subscript F represents the values at the Fermi level. Equation (6.79) means that not all the electrons in a metal actually participate in carrying the current. Only those close to the Fermi level are actively contributing to current flow. From eq. (3.53), we have

$$n = \frac{2}{3}E_F D_F = \frac{1}{3}mv_F^2 D_F$$

so that

$$\sigma = \frac{ne^2}{m}\tau_F \tag{6.80}$$

In the above derivation, we have used the relation $E_f = mv_F^2/2$.

6.3.3.2 Semiconductors

For transport in semiconductors, the carrier concentration changes with position and thus the chemical potential is not constant. We can start from eq. (6.70) to rewrite eq. (6.76) as

$$J_e = -\frac{e}{3}\int v^2\tau\left(e\mathscr{E}\frac{\partial f_0}{\partial E}\right)D(E)dE + \frac{e}{3}\int v^2\tau\frac{\partial f_0}{\partial x}D(E)dE \tag{6.81}$$

The first term represents current flow caused by the electrostatic field and the second term arises from the concentration gradient. Equation (6.81) is often written as

$$J_e = en\mu_e\mathscr{E} + e\frac{\partial(an)}{\partial x} \approx en\mu_e\mathscr{E} + ea\frac{\partial n}{\partial x} \tag{6.82}$$

where μ_e is called the *mobility* [$\mathrm{m^2\,V^{-1}\,s^{-1}}$] and a is the *diffusivity* [$\mathrm{m^2\,s^{-1}}$]. The approximation is valid only when the diffusivity is independent of location (Hess, 2000). The latter expression in eq. (6.82) is called the drift–diffusion equation. The electrostatic field causes the drifting of electrons while the concentration gradient drives the diffusion of electrons. The product of the mobility and the electric field

$$v_d = \mu_e\mathscr{E} \tag{6.83}$$

defines a velocity which is called the drift velocity. It is the average velocity that the electrons gain under the external field. Equation (6.83) is often used as the definition of mobility (Sze, 1981). Because the drift current density is equal to env_d, the electrical conductivity is related to mobility through

$$\sigma = en\mu_e \tag{6.84}$$

For semiconductors, because the carrier concentration is not fixed, the mobility is a measure of the mobile properties of individual electrons and thus is more useful. From eqs. (6.81) and (6.82), we can write the following expressions for the mobility and the diffusivity

$$\mu_e = -\frac{\frac{e}{3}\int_0^\infty v^2\tau(\partial f_0/\partial E)D(E)dE}{\int_0^\infty f_0 D(E)dE} = \frac{e\tau_m}{m} \tag{6.85}$$

$$a = \frac{\frac{1}{3}\int_0^\infty v^2\tau f_0 D(E)dE}{\int_0^\infty f_0 D(E)dE} \approx \frac{\kappa_B T}{e}\mu_e \tag{6.86}$$

where τ_m is called the momentum relaxation time and the approximate relationship between the diffusivity and the mobility, eq. (6.86), which is valid only when the distribution function obeys the Boltzmann distribution, is called the *Einstein relation.*

6.3.3.3 Wiedemann–Franz Law

The thermal conductivity of electrons can be derived in a similar manner to the derivation for phonons. Assuming no current flow, the thermal conductivity due to electrons can be expressed as

$$k_e = \frac{1}{3}C_e v_F^2\tau_E \tag{6.87}$$

where τ_E is the energy relaxation time of electrons and is an average of τ weighed against the energy of the electrons, and C_e is the volumetric specific heat of electrons. τ_E represents the average time for an electron to lose its excess energy. In general, the energy relaxation time can be different from the momentum relaxation time. Typically, however, the two relaxation times are very close. From eqs. (6.80) and (6.87), and neglecting the difference between the relaxation times, we get

$$L = \frac{k_e}{\sigma T} = \frac{mC_e v_F^2}{3nTe^2} = \frac{\pi^2}{3}\left(\frac{\kappa_B}{e}\right)^2 = 2.45\times10^{-8}(\mathrm{W\,\Omega\,K^{-2}}) \tag{6.88}$$

where we have used the specific heat of metal obtained in chapter 4, eq. (4.71). This is called the *Wiedemann–Franz law* and L is called the Lorentz number. Many metals obey this law, with slight changes in the value of the Lorentz number. For semiconductors, the Lorentz number should be calculated since the relation between n and the Fermi level depends on doping, but the magnitude of the Lorentz number remains close to the value. The Wiedemann–Franz law is often used to estimate the electron contribution to the thermal conductivity. For metals, it is sometimes used to calculate the thermal conductivity directly from the electrical conductivity because electrons are the dominant heat carriers in most metals.

6.3.4 Thermoelectric Effects and Onsager Relations

We have considered electron transport under the condition of either uniform temperature or no current flow (heat conduction by electrons). Now, let's examine the coupling of the temperature gradient with the electric field. In this case, both the Fermi level and temperature are functions of location, and $\partial f_0/\partial x$ can be expressed as

$$\frac{\partial f_0}{\partial x} = -\frac{\partial f_0}{\partial E}\cdot\frac{dE_f}{dx} - \frac{E-E_f}{T}\frac{\partial f_0}{\partial E}\frac{dT}{dx} \tag{6.89}$$

Substituting the above equation into eq. (6.70) and further into eq. (6.76), we obtain

$$J_e = -\frac{e}{3}\int v^2\tau\left(\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx} + e\mathscr{E}\right)\frac{\partial f_0}{\partial E}D(E)dE \tag{6.90}$$

or

$$\begin{aligned} J_e &= L_{11}\left(\mathscr{E} + \frac{1}{e}\frac{dE_f}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right) \\ &= L_{11}\left(-\frac{d\Phi}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right) \end{aligned} \tag{6.91}$$

where L_{11} is the electrical conductivity as given by eq. (6.78), and L_{12} is the coupling coefficient between current and the temperature gradient

$$L_{12} = \frac{e}{3T}\int v^2\tau(E-E_f)\frac{\partial f_0}{\partial E}D(E)dE \tag{6.92}$$

The first term in eq. (6.91) is the normal electrical conduction due to the electrochemical potential gradient. The second term arises from the thermal diffusion of electrons under a temperature gradient. Under an open circuit, equation (6.91) leads to

$$\frac{d\Phi}{dx} = -\frac{L_{12}}{L_{11}}\frac{dT}{dx} = -S\frac{dT}{dx} \tag{6.93}$$

where S [V K^{-1}] is called the *Seebeck coefficient*, defined as

$$\begin{aligned} S &= \frac{-d\Phi/dx}{dT/dx} = \frac{L_{12}}{L_{11}} \\ &= -\frac{1}{eT}\frac{\int v^2\tau(E-E_f)\frac{\partial f_0}{\partial E}D(E)dE}{\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE} \end{aligned} \tag{6.94}$$

where the negative sign arises because we are dealing with electrons. Similar treatment for holes would lead to a positive sign. This expression shows that the Seebeck coefficient is a measure of the average energy of an electron above the Fermi level under the open circuit condition, weighted against the differential electrical conductivity at each energy level. As we will show later, $(E - E_f)$ is related to the heat carried by an electron and $(E - E_f)/T$ is related to the entropy. Thus the Seebeck coefficient is a measure of the average heat current carried per electron.

Equation (6.93) can also be written as

$$-(\Phi_2 - \Phi_1) = S(T_2 - T_1) = -V \tag{6.95}$$

where V is the voltage drop measured from point 2 (hot point) to point 1 (cold point). Thus, in a conductor or semiconductor, a temperature difference generates a voltage difference. Physically, when one side of the conductor (or semiconductor) is hot, electrons have higher thermal energy and will diffuse to the cold side. The higher charge concentration in the cold side builds an internal electric field that resists the diffusion. The Seebeck voltage is the steady-state voltage accumulated under the open-circuit condition. If the conductor is a uniform material such that S is constant, the voltage difference does not depend on the temperature profile. This is the principle behind the thermocouple for temperature measurement. A thermocouple employs two conductors for ease of measuring the voltage difference. The same effect can also be used for power generation. We will present more discussion in chapter 8 on thermoelectric effects for energy conversion applications (Goldsmid, 1986).

We can also examine the heat flow when temperature and voltage gradients coexist in the conductor. When calculating the heat flow, we must carefully distinguish the energy flux from the heat flux because we are treating an open system with particles flowing across the boundaries. Consider a small control volume of fixed volume. The first law of thermodynamics should be written as

$$dU = dQ + E_f dN \tag{6.96}$$

In terms of energy flux, the above equation can be expressed as

$$d\mathbf{J}_q = d\mathbf{J}_E - E_f d\mathbf{J}_n \tag{6.97}$$

where $\mathbf{J}_q$ is the heat flux, $\mathbf{J}_E$ the energy flux, and $\mathbf{J}_n$ the particle flux. Considering again one-dimensional flow along the x-direction, these fluxes can be expressed as

$$J_E = \int E v_x f dv_x dv_y dv_z \text{ and } J_n = \int v_x f\, dv_x dv_y dv_z \tag{6.98}$$

so that the heat flux along the x-direction can be calculated from

$$J_q = \int (E - E_f)\, v_x f dv_x dv_y dv_z \tag{6.99}$$

Substituting eqs. (6.70) and (6.89) into the above expression and following the same procedure as we used for the electrical current, we obtain the following expression for the heat flux

$$J_q = L_{21}\left(\mathscr{E} + \frac{1}{e}\frac{dE_f}{dx}\right) + L_{22}\left(-\frac{dT}{dx}\right) \tag{6.100}$$

The first term is the energy carried due to the convection of electrons under an electrochemical potential gradient, and the second term is due to the diffusion of electrons under a temperature gradient. The expressions for the coefficients are

$$L_{21} = \frac{e}{3}\int (E-E_f)v^2\tau\frac{\partial f_0}{\partial E}D(E)dE = TL_{12} \tag{6.101}$$

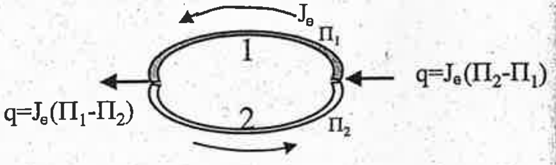

Figure 6.10 Cooling or heating at the junction of two materials occurs because of the difference between the Peltier coefficients of the two materials.

and

$$L_{22} = -\frac{1}{3T}\int (E - E_f)^2 v^2 \tau \frac{\partial f_0}{\partial E} D(E) dE \tag{6.102}$$

Eliminating the electrochemical potential in eqs. (6.91) and (6.100) leads to

$$J_q = \frac{L_{21}}{L_{11}} J_e + \left(L_{22} - \frac{L_{12}L_{21}}{L_{11}}\right)\left(-\frac{dT}{dx}\right) = \Pi J_e - k\frac{dT}{dx} \tag{6.103}$$

where

$$\Pi = \frac{L_{21}}{L_{11}} = TS \text{ and } k = L_{22} - \frac{L_{12}L_{21}}{L_{11}} \tag{6.104}$$

Π [J K^{-1}] is called the *Peltier coefficient* and k is the electronic thermal conductivity. The relationship between the Peltier coefficient and the Seebeck coefficient is one of the *Kelvin relations*.

Equation (6.103) shows that in addition to the normal heat conduction by electrons, the charge flow also carries another heat that is proportional to the current. When two materials are joined together and a current passes through the junction, heat must be supplied or rejected at the interface because of the difference between the Peltier coefficients of the two materials, as shown in figure 6.10. The energy absorbed ($q > 0$) or rejected ($q < 0$) is

$$q = (\Pi_2 - \Pi_1) J_e$$

depending on the sign of q. The rejection or absorption of heat depends on the current direction and therefore, unlike heat conduction, the Peltier heat is reversible. This effect has been used to make thermoelectric refrigerators and heat pumps (Goldsmid, 1986).

A third thermoelectric effect, the Thomson effect, refers to reversible heating or cooling along a conductor when both a current and a temperature gradient are applied to the conductor. The energy deposited inside a differential volume along the conductor includes contributions from the heat flux variation and the electrochemical potential drop,

$$\begin{aligned}\dot{q} &= -\frac{dJ_q}{dx} + J_e\left(-\frac{d\Phi}{dx}\right)\\ &= -\frac{d\Pi}{dx} \bullet J_e + \frac{d}{dx}\left(k\frac{dT}{dx}\right) + J_e\left(-\frac{d\Phi}{dx}\right)\end{aligned}$$

$$\begin{aligned}&= -J_e\frac{d\Pi}{dT}\frac{dT}{dx} + \frac{d}{dx}\left(k\frac{dT}{dx}\right) - SJ_e\left(\frac{dT}{dx}\right) - J_e\frac{d\Phi}{dx}\\ &= -\left(T\frac{dS}{dT}\right)J_e\frac{dT}{dx} + \frac{d}{dx}\left(k\frac{dT}{dx}\right) + \frac{J_e^2}{\sigma}\end{aligned} \tag{6.105}$$

In the above derivation we have used eqs. (6.91), (6.103), and (6.104). In the last equation, the second term is due to heat conduction and the third term is due to Joule heating. These two terms are quite familiar in a heat conduction equation. The first term, however, is not familiar. It shows that heat can be absorbed or released, depending on the current direction. This reversible heat absorption or rejection is called the Thomson effect. The *Thomson coefficient* [V K^{-1}] is defined as the rate of cooling

$$\beta = \dot{q}_c \Big/ \left(J_e\frac{dT}{dx}\right) = T\frac{dS}{dT} \tag{6.106}$$

where the negative sign in the first term of eq. (6.105) does not appear because a positive Thomson effect is based on cooling whereas $\dot{q}$ is the heat generation. Equations (6.104) and (6.106), relating the three thermoelectric coefficients, S, Π, and β, are called the Kelvin relations.

Throughout this section, we have seen that the transport coefficients are often related, as for example in the Kelvin relations between the thermoelectric coefficients and the Einstein relation for the electrical diffusivity and the mobility. The fact that many of these coefficients are related has a more profound origin than a result from the Boltzmann equation. It is a requirement of the "time reversal invariance" of the mechanical equations of motion, that is, the particles retrace their former paths if all velocities are reversed. On the basis of this principle, Onsager (1931) derived the famous *Onsager reciprocity relations*. Here we will give a brief explanation of the reciprocity relations without proof (Callen, 1985). The flux of any extensive variable of a system (such as energy flux, particle flux) or at a local point of a system can be expressed as a linear combination of all the generalized driving forces F_j,

$$J_k = \sum_j L_{jk} F_j \tag{6.107}$$

where L_{jk} are called the kinetic coefficients. The generalized forces are the driving forces for entropy production. The Onsager reciprocal relations are

$$L_{jk} = L_{kj} \tag{6.108}$$

For local thermoelectric transport, the generalized forces are $\nabla(1/T)$ for heat flow and $(-\nabla\Phi)/T$ for electrical current, which leads to a relation between the two coefficients L_{12} and L_{21} as given by eq. (6.101).

Example 6.1

The relaxation time usually depends on the electron energy as $\tau \sim E^{\gamma}$, where r differs among scattering mechanisms for electron transport ($\gamma = -1/2$ for acoustic phonon scattering, $\gamma = 1/2$ for optical phonon scattering, and $\gamma = 3/2$ for impurity scattering). Derive an expression for the Seebeck coefficient of a nondegenerate semiconductor.

Solution: A nondegenerate semiconductor is one with the Fermi level inside the bandgap. In this case, the Fermi–Dirac distribution function can be approximated by the Boltzmann distribution

$$f = \frac{1}{\exp\left(\frac{E-E_f}{\kappa_B T}\right)+1} \approx \exp\left(-\frac{E-E_f}{\kappa_B T}\right) \tag{E6.1.1}$$

The Seebeck coefficient can be calculated from eq. (6.94). Assuming a parabolic band, the density of states is

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2} \tag{E6.1.2}$$

Substituting (E6.1.2) and the relaxation time into eq. (6.94), we obtain the Seebeck coefficient as

$$\begin{aligned} S &= -\frac{1}{eT}\frac{\int_0^\infty (E-E_f)E^{\gamma+3/2}\exp\left(-\frac{E-E_f}{\kappa_B T}\right)dE}{\int_0^\infty E^{\gamma+3/2}\exp\left(-\frac{E-E_f}{\kappa_B T}\right)dE} \\ &= -\frac{\kappa_B}{e}\left[-\frac{E_f}{\kappa_B T}-\left(\gamma+\frac{5}{2}\right)\right] \end{aligned} \tag{E6.1.3}$$

where E_f is the chemical potential, which can be controlled by doping. Using eq. (4.64) ($E_c = 0$ for the reference system here), we can write the above equation as

$$S = -\frac{\kappa_B}{e}\left[\ln\left(\frac{n}{N_c}\right)-\left(\gamma+\frac{5}{2}\right)\right] \tag{E6.1.4}$$

Comment. The value of κ_B/e is 86 μV K^{-1}, which gives an idea of the order of the magnitude of the Seebeck coefficient in many materials.

6.3.5 Hyperbolic Heat Conduction Equation and Its Validity

One assumption we made in the derivation of the classical constitutive equations, such as the Fourier law, is that the transient effect on the distribution function is negligible,

$$\tau\frac{\partial f}{\partial t} \ll \tau\mathbf{v}\bullet\nabla f \tag{6.109}$$

This will be valid if the variation of the distribution function in the time scale is much smaller than the variation of the distribution function in the length scale. Now, let's relax this approximation but still make the assumption that deviation from spatial equilibrium is small. Equation (6.49) becomes

$$\tau\frac{\partial f}{\partial t} + f = f_0 - \tau\left(\mathbf{v}\bullet\nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}} f_0\right) \tag{6.110}$$

Let's consider one-dimensional phonon transport as the case for study and neglect the force term. We can transform the above expression by considering the energy flux of the left- and right-hand sides:

$$\begin{aligned} &\int_{4\pi}\left[\int v_x\hbar\omega\left(\tau\frac{\partial f}{\partial t}+f\right)\frac{D(\omega)}{4\pi}d\omega\right]d\Omega \\ &= \int_{4\pi}\left[\int v_x\hbar\omega\left(f_0-\tau v_x\frac{df_0}{dx}\right)\frac{D(\omega)}{4\pi}d\omega\right]d\Omega \end{aligned} \tag{6.111}$$

where we have used 4π under the integral to denote that the solid angle integration is over all directions. Eq. (6.111) can be written as

$$\bar{\tau}\frac{\partial J_q}{\partial t} + J_q = -k\frac{\partial T}{\partial x} \tag{6.112}$$

where $\bar{\tau}$ is a weighted average of the relaxation time relative to the heat flux expression. Equation (6.112) is the *Cattaneo equation* (Cattaneo, 1958; Joseph and Preziosi, 1989; Tamma and Zhou, 1997). Combining this equation with the energy conservation equation (no heat generation considered)

$$\frac{\partial J_q}{\partial x} = \rho c\frac{\partial T}{\partial t} \tag{6.113}$$

and eliminating J_q, we arrive at the following governing equation for the temperature distribution

$$\bar{\tau}\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{k}{\rho c}\frac{\partial^2 T}{\partial x^2} \tag{6.114}$$

This is a *hyperbolic* type of equation, or telegraph equation. It differs from the parabolic heat conduction equation obtained under the Fourier law, eq. (1.19), by adding the first term on the left-hand side. The parabolic heat conduction equation implies that if a temperature perturbation is applied at the boundary, it will be immediately felt through the whole region (the temperature rise at infinity may be infinitely small but it is still not absolutely zero). The hyperbolic heat conduction equation overcomes this dilemma since the heat propagation is in the form of a wave and the temperature rise is zero on the other side of the wave front. The solution is typically a damped wave due to the existence of the second term on the left-hand side. In addition to the Cattaneo equation, there are also other accepted modifications such as the Jeffreys type of equation (Joseph and Preziosi, 1989),

$$\bar{\tau}\frac{\partial q}{\partial t} + q = -k\frac{\partial T}{\partial x} - \bar{\tau}k_1\frac{\partial}{\partial t}\left(\frac{\partial T}{\partial x}\right) \tag{6.115}$$

where k_1 is another physical property similar to thermal conductivity.

We comment here that although these equations can overcome the dilemma of infinite speed of Fourier's heat conduction equation, neither should be taken as generally applicable. There are many mathematical studies on the solution of the hyperbolic type of heat

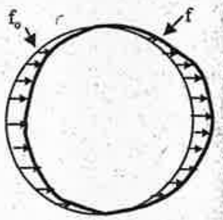

Figure 6.11 Local distribution f under the local-equilibrium distribution deviates slightly from the equilibrium distribution f_0. The difference between f and f_0, that is, the arrowed area, is the driving force for the heat and current flux.

conduction equation with various boundary conditions, but few experimental reports on the observation of hyperbolic heat conduction. Most of the theoretical studies are for conditions that are difficult to realize in practice. This is because heat conduction in a fast heat transfer process is typically confined in a very small region such that the assumption of small deviation from equilibrium in space is no longer valid. For such cases, one should resort to the Boltzmann equation (Majumdar, 1993) or to other approximations such as the ballistic–diffusive equations that take the spatial deviation from local equilibrium into consideration (Chen, 2001b). Although there is also experimental evidence on the wave type of response in different media, these are mostly caused by energy exchange between two fluids such as electrons and phonons (Qiu and Tien, 1993) or between solids and liquids in porous media.

Thermal waves in dielectrics have been observed experimentally (Landau, 1941; Ackerman et al., 1966; Narayanamurti and Dynes, 1972) and are often used as support for the hyperbolic heat conduction equations. These thermal waves can only be observed under special conditions when the mean free path of the umklapp scattering is long compared to the specimen size and that of the normal scattering process is relatively short (Guyer and Krumhansl, 1966). In this case, heat waves will propagate at a speed of $v/\sqrt{3}$; this speed is called the second sound. In section 6.4.3, we will discuss in more detail the origin of the second sound. It will be seen there that the second sound cannot be attributed to the approximation made in eq. (6.110). Rather, it is due to the fact that in a transport process dominated by normal scattering, the equilibrium distribution must be replaced by the displaced function, as in the displaced Maxwell distribution we used in section 6.3.2. Thus it is justifiable to say that the hyperbolic heat conduction equation, as derived in this section, cannot be used in most situations.

6.3.6 Meaning of Local Equilibrium and Validity of Diffusion Theories

From the derivation of the classical constitutive laws, the meaning of local equilibrium that underlies all these relations becomes clear. From eq. (6.47) to eq. (6.49) we assumed that the deviation of the distribution function from equilibrium is small, such that the local distribution function can be represented by its equilibrium value modified by a small deviation term that is proportional to the local gradient, as implied by eq. (6.49). In this sense, the local equilibrium is not equilibrium at all. In figure 6.11, we illustrate the equilibrium distribution function f_0 and the actual distribution function represented by eq. (6.49). The distortion of f from f_0 is small under the local equilibrium assumption. Because f_0 is isotropically distributed, it does not contribute to any net flux. Only the difference between f and f_0, that is, the arrowed area, contributes to the next current or heat fluxes.

Thus, for the (drift) diffusion theories to be valid, the deviation from the equilibrium must be small:

$$f_0 \gg \tau \left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 \right) \tag{6.116}$$

Taking phonon heat conduction as an example, multiplying the above inequality by $\hbar\omega$ and summing over all the phonon states, we have

$$\sum_{\mathbf{k}} \hbar\omega f_0 \gg \sum_{\mathbf{k}} \hbar\omega\tau \mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 \tag{6.117}$$

The left-hand side is the phonon internal energy and the right-hand side is of the order of $q/\bar{v}$, where $\bar{v}$ is the average phonon velocity; thus,

$$U \gg -\frac{k}{\bar{v}}\frac{dT}{dx} \sim -C\Lambda\frac{dT}{dx} \tag{6.118}$$

where we used $k = C\bar{v}\Lambda/3$.

If we make the approximation that the specific heat is independent of temperature such that $U = CT$, the above condition becomes

$$\frac{\Lambda}{T}\frac{dT}{dx} \ll 1 \tag{6.119}$$

Equation (6.119) means that the temperature variation within one mean free path must be small compared to the absolute temperature for the diffusion theory to be valid.

Another assumption that we made in our derivations, in going from eq. (6.47) to (6.48), is that the deviation term g is much larger than the gradient of g:

$$\frac{g}{\tau} \gg \mathbf{v} \bullet \nabla g \tag{6.120}$$

If we approximate $\nabla g \approx g/L$, where L is a characteristic length that can be associated with, for example, the film thickness, the above inequality becomes

$$\frac{\tau v}{L} = \frac{\Lambda}{L} = Kn \ll 1 \tag{6.121}$$

where Kn is called the *Knudsen number*. The above relation means the characteristic length must be much larger than the mean free path for the diffusion theory to be valid.

Temporal wise, for the term $\partial f/\partial t$ to be negligible, we must have

$$\frac{\partial f}{\partial t} \ll \frac{f - f_0}{\tau} \tag{6.122}$$

For a transient phenomenon occurring with a characteristic time scale τ_c (such as a laser pulse width), the above inequality requires

$$\tau_c \gg \tau \tag{6.123}$$

which means that the transient process must be slow compared to the relaxation time.

If any of the conditions (6.119), (6.121), or (6.123) are not satisfied, one must be careful about whether the drift–diffusion relations discussed in this section are still valid. Sometimes, eq. (6.121) can be violated but (6.119) is still valid, as in the case of heat conduction along a thin film. In this case, the Fourier law, for example, is still valid for heat conduction along the film, but the thermal conductivity must be modified. In chapter 7, we will discuss various size effects for which one or several of these conditions are no longer valid.

6.4 Conservation Equations

In the previous section we saw how constitutive equations, for example, relations between heat flux and temperature gradient, or between electric current density and the electrochemical potential gradient, can be derived from the Boltzmann equation. In this section we will derive conservation equations, such as the particle continuity equation, Navier–Stokes equations, and so on, from the Boltzmann equation. For simplicity in notation, we will change the Cartesian coordinate notation from (x, y, z) to (x_1, x_2, x_3) and from (v_x, v_y, v_z) to (v_1, v_2, v_3). This will permit us to write long summations using the so-called *Einstein summation convention*, for example

$$\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}+\frac{\partial v_z}{\partial z}=\frac{\partial v_1}{\partial x_1}+\frac{\partial v_2}{\partial x_2}+\frac{\partial v_3}{\partial x_3}=\frac{\partial v_i}{\partial x_i} \tag{6.124}$$

where i is a dummy index and the repeating of i means summation over i. As another example, $v_i v_i = v_1^2 + v_2^2 + v_3^2$.

From the probability distribution function f we can calculate the average quantities of every microscopic variable X,

$$\langle X\rangle=\frac{\int Xf\,d^3\mathbf{v}}{\int f\,d^3\mathbf{v}}=\frac{\int Xf d^3\mathbf{v}}{n}=\frac{m}{\rho}\int Xf\,d^3\mathbf{v} \tag{6.125}$$

where we have used the short notation $d^3\mathbf{v} = dv_1dv_2dv_3$, ρ is the density, m is the mass per particle, and the integration, which is a triple integration, is over all the possible values of v_1, v_2, v_3, that is, $(-\infty, \infty)$. In the previous section we solved the distribution function first and then proceeded to find the average quantities such as the heat and current fluxes, or the shear stress as a function of the generalized driven force. Here, we do not seek a solution for the distribution function. Rather, we will seek equations governing the average value of X. We multiply both sides of the Boltzmann equation by X and integrate over the momentum space (Reif, 1965; Vincenti and Kruger, 1986)

$$\int X\left(\frac{\partial f}{\partial t}+\mathbf{v}\bullet\nabla_{\mathbf{r}}f+\frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}}f\right)d^3\mathbf{v}=\int X\left(\frac{\partial f}{\partial t}\right)_c d^3\mathbf{v} \tag{6.126}$$

From the above equation, one can derive the Navier–Stokes equations for gas flow, and similar "convective" type of equation for electron and phonon transport, as will be demonstrated below.

6.4.1 Navier–Stokes Equations

If we take the quantity X as meaning conserved quantities (such as mass, momentum, and energy), the net scattering term, that is, the right-hand side of eq. (6.126), should vanish. In these cases, the averaged Boltzmann equation can be significantly simplified. The microscopic expressions for these conserved quantities per particle of a dilute gas are

$$\text{Mass } X = m \tag{6.127}$$

$$\text{Momentum } \mathbf{X} = m\mathbf{v} \tag{6.128}$$

$$\text{Energy } X = mv^2/2 + m\psi_{\text{int}} \tag{6.129}$$

Where ψ_{int} is the potential energy per unit mass of a particle.

Substituting eq. (6.127) into (6.126), the three terms on the left-hand side of eq. (6.126) become, respectively,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} m\frac{\partial f}{\partial t}dv_1dv_2dv_3=\frac{\partial(mn)}{\partial t}=\frac{\partial\rho}{\partial t} \tag{6.130}$$

$$\begin{aligned}&\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} m\mathbf{v}\bullet\nabla_{\mathbf{r}}f\,dv_1dv_2dv_3\\&=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{\partial(mv_1f)}{\partial x_1}+\frac{\partial(mv_2f)}{\partial x_2}+\frac{\partial(mv_3f)}{\partial x_3}\right)dv_1dv_2dv_3\\&=\frac{\partial(mnu_i)}{\partial x_i}=\frac{\partial(\rho u_i)}{\partial x_i}\end{aligned} \tag{6.131}$$

$$\begin{aligned}&\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} m\frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}}f\,dv_1dv_2dv_3\\&=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{\partial(F_if)}{\partial v_i}\right)dv_1dv_2dv_3=0\end{aligned} \tag{6.132}$$

where $\mathbf{u}$ is the average velocity. Equation (6.132) ends in zero because f approaches zero as v approaches infinity. We also used the fact that t, $\mathbf{r}$, $\mathbf{v}$ are independent variables. Although the average quantity, such as $\mathbf{u}$, depends on $\mathbf{r}$, this dependence is due to the dependence of f on $\mathbf{r}$. Using eqs. (6.126, 6.130–6.132), the mass conservation equation can be written as

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x_i}(\rho u_i)=0 \tag{6.133}$$

Next, we examine the momentum equation. In this case, $m\mathbf{v}$ is a vector and as an example, we choose one component, $X = mv_j$. The three terms on the left-hand side of eq. (6.126) become

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} mv_j \frac{\partial f}{\partial t} dv_1 dv_2 dv_3 = \frac{\partial}{\partial t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\partial (mv_j f)}{\partial t} dv_1 dv_2 dv_3$$
$$= \frac{\partial (m \times nu_j)}{\partial t} = \frac{\partial (\rho u_j)}{\partial t} \tag{6.134}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} mv_j \mathbf{v} \bullet \nabla_{\mathbf{r}} f \, dv_1 dv_2 dv_3$$
$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(\frac{\partial (mv_j v_i f)}{\partial x_i}\right) dv_1 dv_2 dv_3 \tag{6.135}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} mv_j \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f \, dv_1 dv_2 dv_3$$
$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(v_j \frac{\partial (F_i f)}{\partial v_i}\right) dv_1 dv_2 dv_3$$
$$= -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} F_j f \, dv_1 dv_2 dv_3 = -nF_j = -\Psi_j \tag{6.136}$$

where Ψ is the force per unit volume or the body force. To further simplify eq. (6.135), we now decompose the velocity into a random component and an average component,

$$\mathbf{v} = \mathbf{u} + \mathbf{v}' \tag{6.137}$$

such that

$$\mathbf{u} = \frac{\int \mathbf{v} f d^3\mathbf{v}}{\int f d^3\mathbf{v}} = \mathbf{u}(t, \mathbf{r}) \tag{6.138}$$

$$\langle \mathbf{v}' \rangle = \frac{\int (\mathbf{v} - \mathbf{u})\, f d^3\mathbf{v}}{\int f d^3\mathbf{v}} = 0 \tag{6.139}$$

Equation (6.135) can be written as

$$\int m \frac{\partial (f v_i v_j)}{\partial x_i} d^3 v = \frac{\partial (\rho u_i u_j)}{\partial x_i} + \frac{\partial (m \int v_i' v_j' f d^3 v)}{\partial x_i}$$
$$= \frac{\partial (\rho u_i u_j)}{\partial x_i} + \frac{\partial (\rho \langle v_i' v_j' \rangle)}{\partial x_i} \tag{6.140}$$

With eqs. (6.134), (6.136), and (6.140), the averaged Boltzmann equation, (6.126), becomes

$$\frac{\partial (\rho u_j)}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_i} + \frac{\partial (\rho \langle v_i' v_j' \rangle)}{\partial x_i} = \Psi_i \tag{6.141}$$

We can write the cross term as

$$\rho \langle v_i' v_j' \rangle = P - \tau_{ij} \tag{6.142}$$

where P is the pressure, which comprises the normal components of the random thermal velocity

$$P = \frac{\rho}{3}(\langle v_1'^2 \rangle + \langle v_2'^2 \rangle + \langle v_3'^2 \rangle) = \frac{\rho}{3}\langle v_i' v_i' \rangle \tag{6.143}$$

and τ_{ij} is the shear stress

$$\tau_{ij} = -[\rho \langle v_i' v_j' \rangle - P\delta_{ij}] \tag{6.144}$$

where δ_{ij} is again the Kronecker delta function, which equals 1 when $i = j$ and zero when $i \neq j$. Equation (6.141) then becomes

$$\rho \frac{\partial (\rho u_j)}{\partial t} + \rho \frac{\partial (\rho u_i u_j)}{\partial x_i} = -\frac{\partial P}{\partial x_j} + \frac{\partial \tau_{ij}}{\partial x_i} + \Psi_j \tag{6.145}$$

This is the momentum conservation equation for the component in the j-direction. Similarly, we can derive the energy conservation equation by setting $X = mv^2/2 + m\psi_{\text{int}}$ (Vincenti and Kruger, 1986).

$$\frac{\partial}{\partial t}\left(\rho\psi + \frac{1}{2}\rho u_i u_i\right) + \frac{\partial}{\partial x_i}\left[\rho u_i \left(H + \frac{1}{2}u_j u_j\right)\right]$$
$$= \frac{\partial}{\partial x_i}(\tau_{ik} u_k - J_{qi}) + \rho \langle F_i v_i \rangle \tag{6.146}$$

where

$$\psi = \frac{1}{2}\langle v_j' v_j' \rangle + \psi_{\text{int}} \tag{6.147}$$

is the total internal energy (translational plus other forms of internal energy) and H is the enthalpy per unit mass [J kg^{-1}]

$$H = \psi + \frac{P}{\rho} \tag{6.148}$$

The heat flux is defined as

$$J_{q_i} = \frac{1}{2}\rho\langle v_i{}'v'^2\rangle + \rho\langle v_i{}'\psi_{\text{int}}\rangle \tag{6.149}$$

Equations (6.133), (6.145), and (6.146) are the conservation equations for mass, momentum, and energy. To further simply the equation, we need the relation between the shear stress and the average velocity, and between heat flux and temperature. The previous section has shown how to derive these constitutive equations. Following eqs. (6.63–6.65) and maintaining a more general three-dimensional velocity profile, one can show that the shear stress can be expressed as

$$\tau_{ij} = n\kappa_B T\tau\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right] = \mu\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right] \tag{6.150}$$

Substituting the above-generalized Newton shear stress law into eq. (6.145), we obtain the familiar *Navier–Stokes* equations.

6.4.2 Electrohydrodynamic Equation

When electrons flow in an electric field, they acquire a nonzero average velocity. We can perform similar operations for electron transport as we did above for gas molecules to derive the governing equations for electron transport. There is, however, one complication. In a semiconductor, the numbers of electrons and holes can vary. An electron in the conduction band can fall back into the valence band, a process called recombination which we will discuss in more detail in chapter 8. Due to electron and hole recombination, the number of electrons in the conduction band and the number of holes in the valence band are reduced. During this process, the excess energy of the electron is lost, either by emitting a photon or by generating phonons. The latter becomes heat dissipation. The reverse process, that an electron is excited from the valence band to the conduction band by absorbing photons and phonons, or kicked by other electrons, thus creating an electron in the conduction band and a hole in the valence band, is called generation. The existence of the generation and recombination processes means that the scattering term is no longer zero. Other than this major difference, the derivation of the electron mass, momentum, and energy conservation equation is very similar to the derivation of the Navier–Stokes equations given in the previous section (Blotekjaer, 1970; Lundstrom, 2000). Without the detailed derivation, we write down the continuity equation as

$$\frac{\partial n}{\partial t} + \frac{\partial(nu_i)}{\partial x_i} = G - R \tag{6.151}$$

where n is the number density of electrons or holes, $\mathbf{u}$ is the average velocity of the electrons defined according to eq. (6.138) and is called the drift velocity, G is the rate of generation of electrons, and R is the rate of recombination. We can also write the above equation in terms of the current density for electrons

$$\frac{\partial n}{\partial t} + \frac{1}{(-e)}\frac{\partial J_{ei}}{\partial x_i} = G - R \tag{6.152}$$

The momentum equation can be written as (Lundstrom, 2000)

$$\frac{\partial(nu_j)}{\partial t} + \frac{\partial(nu_iu_j)}{\partial x_i} + \frac{ne\mathscr{E}_j}{m} + \frac{1}{m}\frac{\partial(n\kappa_B \overline{\overline{T}}_{ij})}{\partial x_i} = \left[\frac{\partial p_j}{\partial t}\right]_c \tag{6.153}$$

where the *temperature tensor* is defined as

$$\kappa_B \overline{\overline{T}}_{ij} = \frac{1}{2}m\int (v_i - u_i)(v_j - u_j) f d^3\mathbf{v} \tag{6.154}$$

Equation (6.154) actually corresponds to eq. (6.142). In fluid mechanics, this term is split into the normal stress (pressure) and shear stress. In electrohydrodynamics, this term is often directly related to the electron temperature T by treating the tensor as diagonal and isotropic so that

$$\frac{\partial \overline{\overline{T}}_{ij}}{\partial x_i} = \frac{\partial T}{\partial x_j} \tag{6.155}$$

The right-hand side of eq. (6.153) is the rate of momentum scattering, which is often expressed using the relaxation time approximation

$$\left[\frac{\partial p_j}{\partial t}\right]_c = -\frac{nu_j}{\tau_m} \tag{6.156}$$

Using eqs. (6.155) and (6.156), we can write the momentum conservation equation as

$$\frac{\partial(nu_j)}{\partial t} + \frac{\partial(nu_iu_j)}{\partial x_i} + \frac{ne\mathscr{E}_j}{m} + \frac{1}{m}\frac{\partial(n\kappa_B T)}{\partial x_i} = -\frac{nu_j}{\tau_m} \tag{6.157}$$

The second term on the left-hand side represents the inertia effects of the electrons. When these effects are negligible, the steady-state solution for the electron velocity is

$$nu_j = -\frac{\tau_m ne\mathscr{E}_j}{m} - \frac{\tau_m}{m}\frac{\partial(n\kappa_B T)}{\partial x_j} \tag{6.158}$$

The current is $\mathbf{J}_e = -en\mathbf{u}$, and thus

$$\begin{aligned} J_{ej} &= \frac{\tau_m ne^2}{m}\mathscr{E}_j + \frac{e\tau_m}{m}\frac{\partial(nk_B T)}{\partial x_j} \\ &\approx \sigma\mathscr{E}_j + ea\frac{\partial n}{\partial x_j} \end{aligned} \tag{6.159}$$

where we have neglected the variation of T with x. If this variation is included, we obtain an additional term corresponding to the thermoelectric effect. Equation (6.159) is identical to eq. (6.82), the drift–diffusion equation.

Taking the moment from the Boltzmann equation for the kinetic energy of electrons leads to the following energy conservation equation

$$\frac{\partial \psi_e}{\partial t} + \frac{\partial(u_i\psi_e)}{\partial x_i} = J_{ei}\mathscr{E}_i - \frac{\partial J_{qi}}{\partial x_i} + \left(\frac{\partial \psi_e}{\partial t}\right)_c - \dot{q} \tag{6.160}$$

where the energy Ψ_e comprises the thermal energy plus the average kinetic energy:

$$\psi_e = \frac{3}{2}n\kappa_B T + \frac{m}{2}nu_i u_i = \frac{3}{2}n\kappa_B T + \frac{m}{2}n\mathbf{u}^2 \tag{6.161}$$

The heat flux is expressed by the Fourier law

$$J_{qi} = -k\frac{\partial T}{\partial x_i} \tag{6.162}$$

and the energy scattering rate must be determined for different scattering processes (Blotekjaer, 1970). One example, which considers the electron and phonon at nonequilibrium temperatures, is

$$\left(\frac{\partial \psi_c}{\partial t}\right)_c = -\frac{n\kappa_B\left(T - T_p\right)}{\tau_e} + \frac{nm\mathbf{u}^2}{3}\left(\frac{2}{\tau_m} - \frac{1}{\tau_e}\right) \tag{6.163}$$

where τ_e is the energy relaxation time, T_p is the phonon temperature, and τ_m is the momentum relaxation time. This equation is valid only for electrons in the same conduction band. Similar equations can be written for holes and for electrons in different bands. The equation can be coupled to the phonon heat conduction equation to form a closed set of equations. Further consideration of different phonon groups, such as optical and acoustic phonons, has also been undertaken (Fushinobu et al., 1995; Lai and Majumdar, 1996).

Equations (6.152), (6.157), and (6.160) form a set of closed equations, called electrohydrodynamic equations, that can be used to solve for the electron density, drift velocity, and temperature distributions. These equations were studied quite intensively in investigations of "hot electron" effects, that is, when the electron temperature is significantly higher than the phonon temperature. Such hot electrons can be generated under a high electric field. Small electronic devices, such as the field-effect transistors used in integrated circuits, are often operated with a high electric field and often have an electron temperature much higher than that of phonons. The electrohydrodynamic equations are sometimes used to study submicron devices. The applicability of the electrohydrodynamic equations to very small devices, however, is highly questionable because these equations are derived under the assumption of local equilibrium, which may not be valid when the electron mean free path is much larger than the characteristic length of the device.

The above summary shows although the electrohydrodynamic equations share many similarities with the Navier–Stokes equation, there are clearly places where different concepts are used, such as the temperature tensor rather than the stress tensors. The consequences of these subtle differences have not been examined in detail.

6.4.3 Phonon Hydrodynamic Equations

In analogy to the hydrodynamic equations for molecules and electrons, theories have been developed for the hydrodynamics of phonons (Gurevich, 1986). The motivation behind phonon hydrodynamics is the relative importance of the normal scattering process (N-process) that conserves crystal momentum versus the umklapp scattering that does not conserve the momentum. Denoting the relaxation times for these two processes as τ_N and τ_u, the phonon hydrodynamic equations are established for the regime when $\tau_N \ll \tau_u$, and the time constant of heat transfer τ_c is comparable with or smaller than τ_u. When $\tau_c \ll \tau_u$, that is, there exist no momentum-destroying scattering processes, the phonon energy is redistributed in the normal scattering processes but the total momentum along the direction of heat flow does not change. In this case, phonons have a nonzero average velocity, $\mathbf{u}$, as do molecules or electrons. The equilibrium distribution function for the normal process is the drifted Bose–Einstein distribution

$$f_d = \frac{1}{\exp\left(\frac{\hbar\omega - \mathbf{k}\bullet\mathbf{u}}{\kappa_B T}\right) - 1} \tag{6.164}$$

where $\mathbf{u}$ is the average phonon drift velocity and $\mathbf{k}$ is the phonon wavevector. The phonon Boltzmann equation can be written as

$$\frac{\partial f}{\partial t} + \mathbf{v}\bullet\nabla_{\mathbf{r}} f = -\frac{f - f_0}{\tau_u} - \frac{f - f_d}{\tau_N} \tag{6.165}$$

We define the local energy and momentum density variables as

$$U = \frac{3}{(2\pi)^3}\int \hbar\omega f d^3\mathbf{k} \tag{6.166}$$

$$\mathbf{P} = \frac{3}{(2\pi)^3}\int \hbar\mathbf{k} f d^3\mathbf{k} \tag{6.167}$$

Here, for simplicity in notation, we have assumed that the three phonon polarizations are identical. Because phonons can be created and annihilated, the number density is not conserved and no continuity equation is needed. Multiplying eq. (6.165) by $\hbar k_i$ and integrating over all wavevectors leads to the following momentum equation,

$$\frac{\partial P_i}{\partial t} + \frac{\partial \Sigma_{ij}}{\partial x_j} = -\frac{3}{(2\pi)^3}\int \frac{f - f_0}{\tau_u}\hbar k_i d^3\mathbf{k} \tag{6.168}$$

where the term related to τ_N is zero because momentum is conserved for the N-process, and

$$\Sigma_{ij} = \frac{3}{(2\pi)^3}\int \hbar k_i v_j f d^3\mathbf{k} \tag{6.169}$$

is similar to the inertia terms in the Navier–Stokes equations.

Multiplying eq. (6.165) by $\hbar\omega$ and integrating over all wavevectors, we obtain the energy equation as

$$\frac{\partial U}{\partial t} + \frac{\partial J_{qi}}{\partial x_i} = 0 \tag{6.170}$$

where

$$J_{qi} = \frac{3}{(2\pi)^3}\int \hbar\omega v_i f d^3\mathbf{k} \tag{6.171}$$

The above derivations have not made any assumption and are thus generally applicable. Now we will follow strategies similar to those used in deriving the thermal conductivity in order to further evaluate various terms in the momentum and energy equations. From eq. (6.165), we see that the distribution function approaches

$$f \to \frac{f_0/\tau_u + f_d/\tau_N}{1/\tau_u + 1/\tau_N} \tag{6.172}$$

When $\tau_N \ll \tau_u$, the dominant term is f_d. As a 0th-order approximation, we first examine how a nonzero drift velocity affects the momentum and energy transport. In this case, we can approximate

$$f \approx f_d \approx f_0 - \frac{\partial f_0}{\partial \omega}\mathbf{k} \bullet \mathbf{u} = f_0 + f_0(1+f_0)\frac{\hbar \mathbf{k} \bullet \mathbf{u}}{\kappa_B T} \tag{6.173}$$

Using this distribution function, eq. (6.167) becomes

$$\begin{aligned}
P_{i0} &= \frac{3}{(2\pi)^3}\int \hbar k_i f_d d^3\mathbf{k} \\
&\approx \frac{3}{(2\pi)^3}\int \hbar k_i \left(f_0 + f_0(1+f_0)\frac{\hbar \mathbf{k}\bullet\mathbf{u}}{\kappa_B T}\right) d^3\mathbf{k} \\
&= \frac{3}{(2\pi)^3}\int \hbar k_i \left(f_0(1+f_0)\frac{\hbar k_j u_j}{\kappa_B T}\right) d^3\mathbf{k} \\
&= u_j \frac{3}{(2\pi)^3}\int \hbar k_i \left(f_0(1+f_0)\frac{\hbar k_j}{\kappa_B T}\right) d^3\mathbf{k} = \eta_{ij} u_j
\end{aligned} \tag{6.174}$$

where η_{ij} is a second-order tensor,

$$\eta_{ij} = \frac{3}{(2\pi)^3}\int \hbar k_i \left(f_0(1+f_0)\frac{\hbar k_j}{\kappa_B T}\right) d^3\mathbf{k} \tag{6.175}$$

and has units of kg m^{-3}, which makes the $\mathbf{P}$ term in eq. (6.168) similar to the $\rho\mathbf{u}$ term in the Navier–Stokes equations. Substituting eq. (6.173) into (6.169) and maintaining only the leading terms, we obtain the following expression for the second derivative term in eq. (6.168):

$$\begin{aligned}
\frac{\partial \Sigma_{ij0}}{\partial x_j} &= \frac{3}{(2\pi)^3}\int \hbar k_i v_j \frac{\partial f_d}{\partial x_j} d^3\mathbf{k} \\
&= \frac{3}{(2\pi)^3}\int \hbar k_i v_j \left(\frac{\partial f_d}{\partial T}\frac{\partial T}{\partial x_j} + \frac{\partial f_d}{\partial u_k}\frac{\partial u_k}{\partial x_j}\right) d^3\mathbf{k} \\
&\approx \frac{3}{(2\pi)^3}\int \hbar k_i \frac{\partial \omega}{\partial k_j}\left(f_0(1+f_0)\frac{\hbar\omega}{\kappa_B T^2}\frac{\partial T}{\partial x_j} + f_0(1+f_0)\frac{\hbar k_k}{\kappa_B T}\frac{\partial u_k}{\partial x_j}\right) d^3\mathbf{k} \\
&= \frac{3}{(2\pi)^3}\int \hbar k_i \frac{\partial \omega}{\partial k_j}\left(-\frac{1}{\hbar}\frac{\partial s}{\partial \omega}\frac{\partial T}{\partial x_j}\right) d^3\mathbf{k} = -\frac{\partial T}{\partial x_j}\frac{3}{(2\pi)^3}\int k_i \frac{\partial s}{\partial k_j} d^3\mathbf{k} \\
&= \delta_{ij}\frac{3}{(2\pi)^3}\int s\, d^3\mathbf{k}\left(\frac{\partial T}{\partial x_j}\right) = S_p \frac{\partial T}{\partial x_j}
\end{aligned} \tag{6.176}$$

In the above derivation, s is the entropy of one phonon quantum state and S_p is the phonon entropy density. We have used integration by parts in carrying out the second-to-last step, and the following relationship for the entropy of one phonon state,*

$$\frac{\hbar\omega}{T} f_0(1+f_0) = -\frac{\kappa_B T}{\hbar}\frac{\partial s}{\partial \omega} \tag{6.177}$$

Substituting eq. (6.173) into (6.171), we obtain a 0th-order expression for the second term in eq. (6.170):

$$\begin{aligned}
\frac{\partial J_{qi}}{\partial x_i} &= \frac{3}{(2\pi)^3}\int \hbar\omega v_i \frac{\partial f}{\partial x_i} d^3\mathbf{k} \\
&= \frac{3}{(2\pi)^3}\int \hbar\omega \frac{\partial \omega}{\partial k_i}\left(f_0(1+f_0)\frac{\hbar\omega}{\kappa_B T^2}\frac{\partial T}{\partial x_i} + f_0(1+f_0)\frac{\hbar k_k}{\kappa_B T}\frac{\partial u_k}{\partial x_i}\right) d^3\mathbf{k} \\
&= \frac{3}{(2\pi)^3}\int \hbar\omega \frac{\partial \omega}{\partial k_i} f_0(1+f_0)\frac{\hbar k_k}{\kappa_B T}\frac{\partial u_k}{\partial x_i} d^3\mathbf{k} \\
&= \frac{\partial u_k}{\partial x_i}\frac{3}{(2\pi)^3}\int \frac{\partial \omega}{\partial k_i}\left(-k_k T\frac{\partial s}{\partial \omega}\right) d^3\mathbf{k} \\
&= \frac{\partial u_k}{\partial x_i}\frac{3}{(2\pi)^3}\int \left(-k_k T\frac{\partial s}{\partial k_i}\right) d^3\mathbf{k} \\
&= T\frac{\partial u_k}{\partial x_i}\frac{3}{(2\pi)^3}\int (\delta_{ki} s)\, d^3\mathbf{k} = TS_p\frac{\partial u_i}{\partial x_i}
\end{aligned} \tag{6.178}$$

Substituting eqs. (6.174), (6.176), and (6.178) into (6.168) and (6.170), we obtain

$$\frac{\partial(\eta_{ij}u_j)}{\partial t} + S_p\frac{\partial T}{\partial x_i} = 0 \tag{6.179}$$

$$C\frac{\partial T}{\partial t} + TS_p\frac{\partial u_i}{\partial x_i} = 0 \tag{6.180}$$

where we have used

$$\frac{\partial U}{\partial t} = C\frac{\partial T}{\partial t} \tag{6.181}$$

Equations (6.179) and (6.180) constitute the 0th-order phonon hydrodynamic equation, that is, the inviscid phonon flow since we have completely neglected the umklapp scattering. Elminating u_i from eqs. (6.179) and (6.180), we obtain

$$\frac{\partial^2 T}{\partial t^2} = \frac{TS_p^2}{C\eta_{ij}}\frac{\partial^2 T}{\partial x_i \partial x_j} \tag{6.182}$$

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*Equation (6.177) can be proven based on eqs. (4.14) and (4.40). See exercise 4.20.

This equation is a hyperbolic one that implies that the temperature field propagates as a wave. In an isotropic medium, η_{ij} degenerates into a scalar η and the corresponding speed of wave propagation is called the *second sound* (Ward and Wilks, 1952):

$$v_s = \sqrt{\frac{TS_p^2}{C\eta}} \tag{6.183}$$

In helium-II (Gurevich, 1986),

$$\eta = \frac{2\pi^2\kappa_B^4 T^4}{45\hbar^3 v^5}; \quad C = \frac{2\pi^2\kappa_B^4 T^3}{15\hbar^3 v^3} \text{ and } C = 3S_p \tag{6.184}$$

where v is the speed of sound. Substituting the above expressions into eq. (6.183) leads to $v_s = v/\sqrt{3}$. This thermal wave has a very different origin to that of the hyperbolic heat conduction equation discussed in section 6.3.5. The latter is derived under the relaxation time approximation while keeping the time derivative of the distribution function. The former is derived on the basis of the displaced Bose–Einstein distribution for processes dominated by normal scattering. Although the hyperbolic heat conduction equation can be applied to umklapp-dominated processes, its derivation implies that the spatial deviation from equilibrium is small. This condition is unlikely to be realized in fast transport processes, which are usually accompanied by a steep temperature gradient or masked by other carrier transport, as in fast laser experiments (Qiu and Tien, 1993). The derivation of the phonon hydrodynamic equation does not consider the steep temperature gradient either. However, its premise is built on the assumption that the normal scattering is much faster than the umklapp scattering, such that phonons have a large drift velocity. This condition can be satisfied only at low temperatures. Thus, at room temperature, the wave types of equation, either the hyperbolic heat conduction equation discussed in section 6.3.5 or the hydrodynamic equation discussed here, are unlikely to be applicable.

If the umklapp scattering is included, the phonon hydrodynamic equations can be expressed as (Gurevich, 1986)

$$\frac{\partial P_i}{\partial t} + S_p\frac{\partial T}{\partial x_i} - \xi_{ijmn}\frac{\partial^2 u_j}{\partial x_m \partial x_n} + \frac{TS_p^2}{k_{ij}}u_j = 0 \tag{6.185}$$

$$C\frac{\partial T}{\partial t} + \frac{\partial J_{q_i}}{\partial x_i} = 0 \tag{6.186}$$

$$J_{q_i} = TS_p u_i - \chi_{ij}\frac{\partial T}{\partial x_j} \tag{6.187}$$

$$P_i = \eta_{ij} u_j \tag{6.188}$$

where ζ_{ijmn} is analogous to viscosity for normal scattering processes, and χ_{ij} is the thermal conductivity tensor due to normal scattering processes, whereas κ_{ij} is the thermal conductivity tensor due to non-momentum-conserving scattering processes such as Umklapp scattering. These coefficients can be derived similarly to what we have done in section 6.3 for other transport coefficients, that is, by substituting eq. (6.164) in the left-hand side of the Boltzmann equation and solving for from eq. (6.165), followed by substituting f into eqs. (6.169) and (6.171). Details can be found in Gurevich (1986).* Here we will give only the final results:

$$\xi_{\ell mnp} = \frac{\hbar^2}{\kappa_B T}\frac{3}{(2\pi)^3}\int \tau_n f_0(f_0+1) \times \left(k_\ell v_m - \delta_{\ell m}\omega\frac{S_p}{C}\right)\left(k_n v_p - \delta_{np}\omega\frac{S_p}{C}\right) d^3\mathbf{k} \tag{6.189}$$

$$\chi_{ij} = \frac{\hbar^2}{\kappa_B T^2}\frac{3}{(2\pi)^3}\int \tau_n f_0(f_0+1)\left(\omega v_i - \frac{TS_p}{\eta_{im}}k_m\right)\left(\omega v_j - \frac{TS_p}{\eta_{jm}}k_m\right) d^3\mathbf{k} \tag{6.190}$$

$$k_{ij}^{-1} = \frac{\hbar^2}{\kappa_B T^2 S_p^2}\frac{3}{(2\pi)^3}\int \frac{1}{\tau_u} f_0(f_0+1)k_i k_j d^3\mathbf{k} \tag{6.191}$$

where v_i is the component of the group velocity. Their orders of magnitude are

$$\xi \sim \kappa_B T\left(\frac{T}{\hbar v}\right)^3 \tau_n, \quad \chi \sim \kappa_B^4 v^2 \tau_n\left(\frac{T}{\hbar v}\right)^3,$$
$$\eta \sim \frac{\kappa_B^4 T^4}{\hbar^3 v^5}, \quad k \sim \kappa_B^4\left(\frac{T}{\hbar v}\right)^3 v^2\tau_u \tag{6.192}$$

Equations (6.185) and (6.186) are very similar to the Navier–Stokes equations. Similar flow regimes can also be expected. For example, the phonon Poiseuille flow has been observed and discussed in literature (Guyer and Krumhansl, 1966; Gurevich, 1986).

6.5 Summary of Chapter 6

This chapter has two major aims: one is to introduce the Boltzmann equation, and the other is to illustrate that classical laws can be derived from the Boltzmann equation under appropriate approximations.

The Boltzmann equation, or the Boltzmann transport equation, can be derived from the general Liouville equation. These equations are all established in phase space, which is multidimensional. The state of a system, described by the generalized coordinates $\mathbf{r}^{(n)}$ and momentum $\mathbf{p}^{(n)}$ of all the particles in the system, is one point in the phase space at any specific time. The Liouville equation of motion describes the evolution of the distribution function for an ensemble of systems in phase space. The Boltzmann equation is simplified from the Liouville equation through the use of the one-particle distribution function. The interaction of this particle with the rest of the particles in the system is represented by the

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*Gurevich's book does not carry κ_B in the Boltzmann factor. Expressions given here included κ_B for consistency.

scattering term. The Boltzmann equation is valid only for a dilute system of particles, such as gases, electrons, photons, and phonons in the particle regime. Because the Boltzmann equation is based on the one-particle distribution function, the phase-space coordinates comprise six coordinates: position **r** and translational momentum **p** (we did not consider other modes of motion, such as rotation).

The key to the Boltzmann equation is the scattering term. Quantum mechanical principles are often used to deal with scattering. The time-dependent perturbation treatment in quantum mechanics leads to the Fermi golden rule for calculating the scattering probability from one quantum state to another. A general expression of the scattering integral can be formally written down on the basis of the scattering probability and the distribution function. This leads to an integral-differential form of the Boltzmann equation, which is difficult to solve but has often been treated in thermal radiation transport in the form of the equation of radiative transfer. For phonon and electron transport, as well as gas transport, we often use the relaxation time approximation. In chapter 8, we will further examine the cases in which the relaxation time approximation is invalid. The relaxation times for different carriers, including electrons, phonons, photons, and molecules, are discussed. These typically involve unknown constants that are determined by fitting experimental data on transport properties. When multiple scattering coexists, the Matthiessen rule is often used to obtain the total relaxation time.

Starting from the Boltzmann equation under the relaxation time approximation, we proceed to derive the classical constitutive equations including the Fourier law, the Newton shear stress law, the Ohm law, the drift–diffusion equations, and the thermoelectric relations. The common assumptions made in all these relations are that (1) the transport process occurs in a time scale much longer than the relaxation time, and (2) deviation from equilibrium at every point is small—that is, the local equilibrium assumption. We showed that the kinetic coefficients of a particular type of carrier are often related, because of their common origin, such as the relationship between viscosity and thermal conductivity, the Einstein relation between diffusivity and mobility, and the Wiedmann–Franz law linking electrical and thermal conductivity. The relationship of kinetic coefficients culminates in the Onsager reciprocal relations. We also commented on the appropriateness of the hyperbolic heat conduction equation. The key message is that all the constitutive relations are derived under certain approximations, which may no longer be valid for transport at micro- and nanoscales, as we will discuss in more detail in the next chapter.

From the Boltzmann equation, we can also derive the familiar conservation equations. We explained the derivation of the Navier–Stokes equations. Along a similar line of derivation, one can obtain the electrohydrodynamic equations for charged carriers and the phonon hydrodynamic equations. For phonons, we showed the phonon hydrodynamic equations that originate from the difference between the normal scattering and momentum-destroying scattering processes. The phonon hydrodynamic equations lead to second sound and temperature waves, which occur only when the time scale of the transport is longer than the relaxation time of normal scattering but much shorter than the umklapp or other momentum-destroying processes. From our discussion, it should become clear that the hyperbolic heat conduction equation, which often invokes the existence of the second sound at low temperatures as a proof of its validity, has a limited validity range that is difficult to realize through experiments, at least for single-carrier systems. In multiple-carrier systems, such as electron–phonon interactions, a subject we will discuss in more detail in chapter 8, the coupling of electrons and phonons, with their different heat capacities, can lead to hyperbolic types of heat conduction equation, even though the governing equation for each carrier is still of the diffusion type. Such wave-like equations should not be confused with the wave behavior of single carrier systems.

We again followed the tradition of parallel development for electrons, photons, phonons, and molecules. Through this effort, we hope that the reader can see that divisions between different disciplines are quite arbitrary. Although the languages are very different, due to the historical developments within each field, common grounds exist among them.

6.7 Nomenclature for Chapter 6

a	diffusivity, $\mathrm{m^2\,s^{-1}}$
A	coefficient in eq. (6.31), $\mathrm{s^3}$
b	coefficient in eq. (6.30)
B	coefficient in eq. (6.30), $\mathrm{K^{-3}s}$
c	specific heat, $\mathrm{J\,kg^{-1}\,K^{-1}}$
C	volumetric specific heat, $\mathrm{J\,m^{-3}\,K^{-1}}$
d	molecule diameter, m
D	density of states per unit volume, $\mathrm{m^{-3}}$
e	unit charge, C
E	energy of one particle, J
E_c	conduction band edge, J
E_f	chemical potential, J
$\mathscr{E}$	magnitude of electric field, $\mathrm{V\,m^{-1}}$
$\boldsymbol{\mathscr{E}}$	electric field vector, $\mathrm{V\,m^{-1}}$
f	one-particle distribution function
f_0	equilibrium distribution function
$f^{(N)}$	N-particle distribution function
$\mathbf{F}$	external force on the particle, N
g	deviation from equilibrium distribution
G	rate of generation per unit volume, $\mathrm{s^{-1}\;m^{-3}}$
h	Planck constant, J s
$\hbar$	Planck constant divided by 2π, J s
H	enthalpy, $\mathrm{J\,kg^{-3}}$
I	intensity, $\mathrm{W\,m^{-2}\,srad^{-1}}$
$\mathbf{J}$	flux of heat transfer rate, $\mathrm{W\,m^{-2}}$; energy transfer rate, $\mathrm{W\,m^{-2}}$; current, $\mathrm{A\,m^{-2}}$, and particles, $\mathrm{s^{-1}\;m^{-2}}$
k	thermal conductivity, $\mathrm{W\,m^{-1}\;K^{-1}}$
k_{ij}	thermal conductivity tensor due to umklapp process, $\mathrm{W\,m^{-1}\;K^{-1}}$
$\mathbf{k}$	wavevector, $\mathrm{m^{-1}}$
$\hat{\mathbf{k}}$	unit vector along the wavevector direction
K_e	extinction coefficient, $\mathrm{m^{-1}}$
L	characteristic length or crystal length, m; Lorentz number, $\mathrm{W\,\Omega\,K^{-2}}$; coefficients
m	space or momentum degrees of freedom of one particle; mass, kg
M_{if}	scattering matrix element, J
n	total degree of freedom in space or momentum for N particles; particle number density, $\mathrm{m^{-3}}$
N	number of particles in the system
$p^{(i)}$	ith component of the momentum in phase space, $\mathrm{kg\,m\,s^{-1}}$

$\mathbf{p}$	momentum coordinate vector of one particle, kg m s^{-1}
$\mathbf{p}_i$	momentum coordinate vector of particle i, kg m s^{-1}
P	pressure, N m^{-2}
$\mathbf{P}$	average momentum per unit volume, kg m^{-2} s^{-1}
q	heat absorbed or rejected, W m^{-2}
$\dot{q}$	heat generation, W m^{-3}
$r^{(i)}$	ith component of the space coordinates, m
$\mathbf{r}$	space coordinate vector of one particle, m
r_i	space coordinate vector of particle i, m
R	rate of recombination, s^{-1} m^{-3}
s	polarization index; entropy J K^{-1}
S	Seebeck coefficient, V K^{-1}
S_p	entropy density, J K^{-1} m^{-3}
t	time, s
T	temperature, K
$\bar{\bar{T}}$	temperature tensor, K
u	average velocity, m s^{-1}
U	total energy density, J
$\mathbf{v}$	velocity, m s^{-1}
v_d	drift velocity, m s^{-1}
v_F	Fermi velocity, m s^{-1}
$\mathbf{v}_g$	group velocity, m s^{-1}
v_s	second sound, m s^{-1}
V	volume, m^3
W	transition rate from initial state i to final state f, s^{-1}
x, y, z	Cartesian coordinates
X	microscopic quantity
α	absorption coefficient, m^{-1}
β	Thomson coefficient, V K^{-1}
γ	parameter in the energy dependence of electron scattering
δ	delta function
η_{ij}	second-order tensor defined by eq. (6.175), kg m^{-3}

θ	polar angle
θ_D	Debye temperature, K
Λ	mean free path, m
μ	dynamic viscosity, N s m^{-2}
μ_e	electron mobility, m^2 V^{-1} s^{-1}
ξ	viscosity defined by eq. (6.189), kg m^{-1} s^{-1}
Π	Peltier coefficient, V
ρ	density, kg m^{-3}
σ	electrical conductivity, Ω^{-1} m^{-1}
$\sigma_{s\nu}$	frequency-dependent scattering coefficient, m^{-1}
Σ_{ij}	defined by eq. (6.169), J m^{-4}
τ	relaxation time, s
τ_c	characteristic time of a process, s
ϕ	scattering phase function
φ	azimuthal angle
φ_e	electrostatic potential, V
Φ	electrochemical potential, V
χ_{ij}	thermal conductivity tensor due to normal process, W m^{-1} K^{-1}
Ψ	internal energy of molecules, J kg^{-3}
Ψ_e	electron energy density, J m^{-3}
Ψ_{int}	potential energy, J kg^{-3}
Ψ	body force, N m^{-3}
ω	angular frequency, Hz
Ω	solid angle, srad
$\langle\rangle$	ensemble average

Subscripts

0	zeroth order
1, 2, 3	components of Cartesian coordinates, corresponding to x, y, z
b	boundary
d	drift
e	electron
E	energy
f	final state
F	Fermi level
g	group velocity
i	initial state; coordinate index
I	impurity
m	momentum
n	total degree
N	normal process
p	phonon
q	heat
t	total
u	umklapp scattering
x, y, z	Cartesian component
ν	frequency dependent, spectral quantity

Superscripts

(n)	n component in the phase space
(N)	N-particle
.	time derivative
-	average

6.8 References

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6.9 Exercises

6.1 *Phonon thermal conductivity at intermediate temperature.* The phonon–phonon scattering relaxation time in the intermediate range of temperature (when $T < \theta_D$) can be approximated as

$$\frac{1}{\tau} = A \exp\left[-\frac{\Theta}{aT}\right] T^3 \omega^2$$

On the basis of the Debye model (linear dispersion), derive an expression for the thermal conductivity and discuss its dependence on temperature.

6.2 *High-temperature thermal conductivity.* At high temperature, the phonon relaxation time in a crystal is

$$\frac{1}{\tau} = \frac{\kappa_B T}{mva}$$

where a is of the order of distance between atoms and m is the atomic weight.

(a) Prove that the high-temperature thermal conductivity is proportional to $1/T$.

(b) The thermal conductivity of silicon at 300 K is 145 $\text{W m}^{-1}\text{K}^{-1}$. Estimate its thermal conductivity at 400 K.

6.3 *Rosseland diffusion approximation for phonon transport.* Consider an absorbing and emitting medium for thermal radiation transport. When the photon mean free path is much smaller than the characteristic length in the transport direction, the local equilibrium approximation is valid. Prove that under this condition (called optically thick) the radiative heat flux can be expressed as

$$q = -\frac{4\pi}{3\alpha}\frac{dI_b}{dx}$$

where α is the absorption coefficient. This is called the Rosseland diffusion approximation.

6.4 *Wiedemann–Franz law.* The electrical resistivity of gold at 300 K is $3.107 \times 10^{-8}\ \Omega$ m. Estimate its thermal conductivity.

6.5 *Wiedemann–Franz law.* The thermal conductivity of copper is 401 $\text{W m}^{-1}\text{K}^{-1}$ at 300 K. Estimate its electrical conductivity at the same temperature.

6.6 *Energy and momentum relaxation time.* The electrical resistivity and thermal conductivity of gold at 300 K are $3.107 \times 10^{-8}\Omega$ m and 315 $\text{W m}^{-1}\text{K}^{-1}$. Estimate the momentum and energy relaxation time, and the momentum and energy relaxation length, of electrons in gold.

6.7 *Thermal conductivity and viscosity.* The thermal conductivity of air is 0.025 $\text{W m}^{-1}\text{K}^{-1}$. Estimate its dynamic viscosity.

6.8 *Electrons in semiconductors.* An n-type semiconductor has a carrier concentration of 10^{18} cm^{-3} and a mobility of 200 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ at 300 K. Estimate the following: (a) electrical conductivity; (b) electron diffusivity; (c) momentum relaxation time; and (d) electron mean free path. Take the electron effective mass as that of a free electron.

6.9 *Thermal conductivity of gases.* Prove that the thermal conductivity of a dilute monatomic gas is

$$k = \frac{5}{2}\left(\frac{\kappa_B}{m}\right) n\tau\kappa_B T$$

6.10 *Thermoelectric cooler.* A thermoelectric device is typically made of p–n junctions as shown in figure P6.10. When a current flows through the p–n junction, both electrons and holes carry energy from the cold side to the hot side. The Peltier coefficients of both p and n materials are equal in magnitude, Π, but of opposite sign. The cooling rate due to current flow is $2\Pi \times I$. In addition to this cooling, there is also Joule heating and reverse heat conduction. Assuming that the electrical and thermal conductivities of both legs are the same, derive an expression for the net cooling power at the cold side in terms of the temperatures at the cold and the hot side, the current, and the cross-sectional area and length of the leg. Show that the cooling power reaches a maximum at a certain optimum current value.

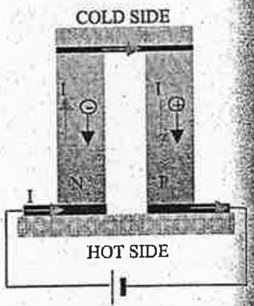

Figure P6.10 Figure for problem 6.10.

6.11 *Seebeck coefficients of a quantum well.* Derive an expression for the Seebeck coefficient of a quantum well of well-width d and with an infinite potential barrier height, as a function of the doping concentration.

6.12 *Power factor of a quantum well.* Because of Joule heating and reverse heat conduction, the efficiency of a thermoelectric device is determined by the figure of merit, defined as $Z = S^2\sigma/k$, where S is the Seebeck coefficient, σ the electrical conductivity, and k the thermal conductivity. The numerator $S^2\sigma$ is also called the power factor.

(a) Derive an expression for the power factor $S^2\sigma$ for a quantum well of width d and with an infinite barrier height, in terms of electron effective mass, relaxation time, chemical potential, and quantum well width.

(b) Assuming constant relaxation time and Boltzmann distribution, simplify the results obtained.

6.13 *Seebeck coefficient of nondegenerate silicon.* For silicon with doping concentration between 10^{16} and 10^{18} cm^{-3}, the Boltzmann distribution can be used instead of the Fermi–Dirac distribution. Silicon has six identical conduction bands with an effective mass of $0.33\ m_e$ for each conduction band, where m_e is the mass of a free electron. Assume a constant relaxation time.

(a) Calculate the Fermi level as a function of the carrier concentration from both the Fermi–Dirac and the Boltzmann distribution, and show that the levels do not differ much in the given doping range.

(b) Calculate the Seebeck coefficient as a function of the dopant concentration.

6.14 *Seebeck coefficient of a metal.*

(a) Assuming a constant relaxation time, prove that the Seebeck coefficient of a metal is given by

$$|S| = \frac{\pi^2\kappa_B^2 T}{2eE_f}$$

(b) Prove that ZT for a metal satisfies the following inequality

$$ZT \leq \frac{3\pi^2\kappa_B^2 T^2}{4E_f^2}$$

(c) Estimate the Seebeck coefficient of copper.

6.15 *Einstein relation.* When the Boltzmann approximation is valid, prove the Einstein relation between mobility and diffusivity for electrons

$$a = \frac{k_B T}{e}\mu$$