

where the parameter τ is an arbitrary large quantity. The quantum expression of the conductivity of Eq. (11.44) holds only in the ideal case of negligible broadening (or very large lifetime) of electronic states. On the contrary, the semiclassical Boltzmann approach of Eq. (11.38) holds also for finite lifetimes, and could be extended to more realistic materials characterized by energy-dependent broadening parameters.

The above considerations help to clarify some aspects of the semiclassical approach and of the quantum treatment. Within the adopted approximations, the Boltzmann framework appears suitable in treating intraband transitions, where relaxation times play a key role. On the other side, the higher energy band-to-band transitions are relatively less sensible to broadening effects, which often may be ignored in the quantum treatment of interband optical properties. For these reasons, in the present chapter on intraband transport we focus on the semiclassical Boltzmann approach, while in the next chapter on interband transitions the quantum approach is followed.

11.6 The Boltzmann Equation in Electric Fields and Temperature Gradients

11.6.1 The Transport Equations in General Form

In the previous sections we have studied transport effects due to the presence of electric fields in samples at uniform temperature (i.e. in *isothermal* conditions); we consider now transport equations in the presence of electric fields and temperature gradients. As usual, we consider the simplest possible electronic structure of the metal with a single conduction band of interest of energy $E(\mathbf{k})$; the influence (if any) of the temperature on the energy band structure $E(\mathbf{k})$ is assumed to be negligible.

In a crystal kept at non-uniform temperature, it is convenient to define the local equilibrium distribution function $f_0(\mathbf{k}, \mathbf{r})$ as

$$f_0(\mathbf{k}, \mathbf{r}) = \frac{1}{\exp[(E(\mathbf{k}) - \mu(\mathbf{r}))/k_B T(\mathbf{r})] + 1}; \quad (11.45)$$

the local equilibrium distribution function $f_0(\mathbf{k}, \mathbf{r})$, in addition to \mathbf{k} , depends implicitly on \mathbf{r} since the local temperature $T = T(\mathbf{r})$ is a function of \mathbf{r} , and the chemical potential $\mu = \mu(T(\mathbf{r}), n(\mathbf{r})) = \mu(\mathbf{r})$ depends on \mathbf{r} via the local temperature $T(\mathbf{r})$ and the local electron density $n(\mathbf{r})$. Notice that the local chemical potential $\mu(\mathbf{r})$ at the point \mathbf{r} , entering in Eq. (11.45), is just the *chemical potential of an ideal infinite sample at thermodynamic equilibrium, characterized by band structure $E(\mathbf{k})$, uniform temperature T equal to $T(\mathbf{r})$, and uniform electron density n equal to $n(\mathbf{r})$.*

In the following we need the gradients of f_0 with respect to \mathbf{k} and \mathbf{r} ; these are given by

$$\frac{\partial f_0}{\partial \mathbf{r}} = \frac{\partial f_0}{\partial E} k_B T \frac{\partial}{\partial \mathbf{r}} \frac{E(\mathbf{k}) - \mu}{k_B T} = \frac{\partial f_0}{\partial E} \left[-\frac{\partial \mu}{\partial \mathbf{r}} - \frac{E(\mathbf{k}) - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \right], \quad (11.46a)$$

and

$$\frac{1}{\hbar} \frac{\partial f_0}{\partial \mathbf{k}} = \frac{1}{\hbar} \frac{\partial f_0}{\partial E} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}} = \frac{\partial f_0}{\partial E} \mathbf{v}(\mathbf{k}). \quad (11.46b)$$

To simplify somewhat the notations, the \mathbf{k} -dependence of the group velocity and of the energy band is often left implicit.

The Boltzmann equation (11.28) for the stationary distribution $f(\mathbf{r}, \mathbf{k})$ in the presence of an electric field \mathbf{E} and temperature gradient is

$$\frac{\partial f}{\partial \mathbf{r}} \cdot \mathbf{v} + \frac{1}{\hbar} \frac{\partial f}{\partial \mathbf{k}} \cdot (-e)\mathbf{E} = -\frac{f - f_0}{\tau} = -\frac{f_1}{\tau}.$$

Since the electric field and temperature gradient are usually small, we can assume that f_1 is linear in these variables; then we can put $f = f_0$ on the left-hand side of the above equation and obtain

$$f_1 = -\tau \frac{\partial f_0}{\partial \mathbf{r}} \cdot \mathbf{v} - \frac{\tau}{\hbar} \frac{\partial f_0}{\partial \mathbf{k}} \cdot (-e)\mathbf{E}.$$

Using Eqs. (11.46), the stationary nonequilibrium distribution function becomes

$$f_1 = \left(-\frac{\partial f_0}{\partial E} \right) \tau \left[-e\mathbf{E} - \nabla\mu - \frac{E - \mu}{T} \nabla T \right] \cdot \mathbf{v}, \quad (11.47)$$

where $\nabla = \partial/\partial \mathbf{r}$ indicates the gradient with respect to space variable \mathbf{r} .

We remind the general charge and energy transport equations (11.29), here re-written in a slightly different form

$$\mathbf{J} = \frac{1}{4\pi^3} \int (-e) \mathbf{v} f_1 d\mathbf{k}; \quad \mathbf{U} = \frac{1}{4\pi^3} \int (E - \mu) \mathbf{v} f_1 d\mathbf{k} - \frac{\mu}{e} \mathbf{J}. \quad (11.48)$$

Furthermore (though not strictly necessary) we suppose that the system is isotropic, so that transport kinetic parameters become scalar quantities, rather than tensors. Inserting Eq. (11.47) into Eq. (11.48) one obtains

$$\begin{cases} \mathbf{J} = e K_0 [e\mathbf{E} + \nabla\mu] + e \frac{K_1}{T} \nabla T, \\ \mathbf{U} = -K_1 [e\mathbf{E} + \nabla\mu] - \frac{K_2}{T} \nabla T - \frac{\mu}{e} \mathbf{J}. \end{cases} \quad (11.49)$$

The expressions of the *kinetic coefficients* K_0, K_1, K_2 are

$$K_n = \frac{1}{4\pi^3} \int \tau (\hat{\mathbf{e}} \cdot \mathbf{v})^2 (E - \mu)^n \left(-\frac{\partial f_0}{\partial E} \right) d\mathbf{k}, \quad n = 0, 1, 2, \quad (11.50)$$

where $\hat{\mathbf{e}}$ is the unit vector in the direction of the electric field; under the assumption of isotropy, the direction of $\hat{\mathbf{e}}$ becomes irrelevant, and can be taken, for instance, in the x -direction.

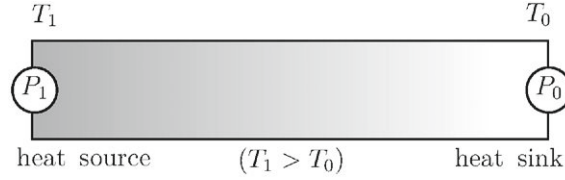


Figure 11.11 Schematic representation of a bar of homogeneous material, whose ends are kept at different temperatures.

It is convenient to rewrite the two basic transport equations (11.49) in a slightly different form, which is more suitable for the interpretation of the thermoelectric phenomena. The first of Eq. (11.49) can be cast in the form

$$\mathbf{J} = e^2 K_0 \left[\mathbf{E} + \frac{1}{e} \nabla \mu - S(T) \nabla T \right] \quad \text{with} \quad S(T) = -\frac{1}{e T} \frac{K_1}{K_0}, \quad (11.51)$$

where the transport coefficient S is called *absolute thermoelectric power* or *Seebeck coefficient*. From Eqs. (11.51) we see that the current density \mathbf{J} consists of three contributions. The first term $e^2 K_0 \mathbf{E}$ is the standard drift term $\sigma_0 \mathbf{E}$, where σ_0 is the conductivity of the metal. The second one is due to the inhomogeneity (i.e. to the \mathbf{r} -dependence) of the chemical potential. The third is due to the presence of a temperature gradient. It is interesting to notice that the energy dissipated per unit time and unit volume

$$\mathcal{P} = \mathbf{E} \cdot \mathbf{J} = \frac{J^2}{\sigma_0} - \frac{1}{e} \nabla \mu \cdot \mathbf{J} + S(T) \nabla T \cdot \mathbf{J},$$

besides the essentially positive Joule term J^2/σ_0 (irreversible heat), contains two additional terms linear in J , which can be either positive or negative (reversible heat).

For what concerns the transport equation for the energy flux, it is convenient to obtain $[e \mathbf{E} + \nabla \mu]$ from the first of Eqs. (11.49) and replace it into the second one; this gives

$$\mathbf{U} = \left[-\frac{K_1}{e K_0} - \frac{\mu}{e} \right] \mathbf{J} - k_e \nabla T \quad \text{with} \quad k_e = \frac{1}{T} \left(K_2 - \frac{K_1^2}{K_0} \right), \quad (11.52)$$

where the transport parameter k_e is called *electron thermal conductivity*.

The physical meaning of k_e is easily established if one considers a metal in the presence of a uniform temperature gradient ∇T and in open circuit situation, so that $\mathbf{J} = 0$ (see Figure 11.11). In this case, Eq. (11.52) takes the form $\mathbf{U} = -k_e \nabla T$; this shows that the energy density (or heat density) flowing through the device is opposite and linear to the temperature gradient, with proportionality constant k_e .

11.6.2 Thermoelectric Phenomena

We discuss now some applications of Eqs. (11.51) and (11.52), which are the basic equations controlling transport in (isotropic) materials. After a few preliminary

considerations on equilibrium conditions and isothermal conditions, we pass to study some typical thermoelectric circuits.

Drift and Diffusion Currents in Isothermal Conditions

As a first application, consider the electron current density in a metal in isothermal conditions, but with a non-uniform carrier concentration $\nabla n \neq 0$; this implies $\nabla \mu \neq 0$. Putting $\nabla T = 0$ into Eq. (11.51) we have

$$\mathbf{J} = \sigma_0 \left[\mathbf{E} + \frac{1}{e} \nabla \mu \right]. \quad (11.53)$$

We can thus distinguish a *drift current density* $\mathbf{J}_{\text{drift}} = \sigma_0 \mathbf{E}$ and a *diffusion current density* $\mathbf{J}_{\text{diff}} = \sigma_0 \nabla \mu / e$.

Consider, for example, a metal with free-electron-like conduction band. In this case $\sigma_0 = n e^2 \tau / m^*$, the chemical potential reads $\mu = (\hbar^2 / 2m^*) (3\pi^2 n)^{2/3}$ and $\nabla \mu / \mu = (2/3) \nabla n / n$. The current density (11.53) in the metal can thus be written as

$$\boxed{\mathbf{J} = n e \mu_e \mathbf{E} + e D \nabla n}, \quad (11.54)$$

where $\mu_e = e \tau / m^*$ is the *electron mobility*, and D is the *diffusion coefficient*

$$\boxed{D = \frac{2}{3} \frac{E_F}{e} \mu_e}, \quad (11.55a)$$

where the chemical potential has been here indicated with E_F .

In the case the free-electron gas is non-degenerate and follows the Boltzmann distribution, we have $\nabla n / n = \nabla \mu / k_B T$. The current density is again given by Eq. (11.54), but now the diffusion coefficient becomes

$$\boxed{D = \frac{k_B T}{e} \mu_e}. \quad (11.55b)$$

Relations (11.55a) and (11.55b) are the *Einstein relations* between mobility and diffusion coefficient for the degenerate and non-degenerate electron gas, respectively.

Consider now Eq. (11.51) in isothermal conditions $\nabla T = 0$ and in open circuit situation $\mathbf{J} = 0$. Indicating with $\phi(\mathbf{r})$ the electrostatic potential we have

$$-\nabla \phi + \frac{1}{e} \nabla \mu = 0 \implies (-e)\phi + \mu \equiv \text{const.}$$

As expected the electrochemical potential $\mu + (-e)\phi$ is uniform throughout the sample in equilibrium conditions.

Seebeck Effect and Thermoelectric Power

When a temperature gradient is established in a long bar (in open circuit situation) an electric field has to set in, so to prevent any net carrier flux. Consider in fact a specimen

with a cool end at temperature T_0 and a hot end at temperature T_1 (see [Figure 11.11](#)). In open circuit situation $\mathbf{J} = 0$ and the electric field can be obtained from [Eq. \(11.51\)](#) in the form

$$\mathbf{E} = -\frac{1}{e}\nabla\mu + S(T)\nabla T. \quad (11.56)$$

The potential difference between the end points P_0 and P_1 , at temperatures T_0 and T_1 , is

$$\phi_1 - \phi_0 = -\int_{P_0}^{P_1} \mathbf{E} \cdot d\mathbf{l} = \frac{1}{e}(\mu_1 - \mu_0) - \int_{T_0}^{T_1} S(T) dT. \quad (11.57)$$

Thus the difference of the electrochemical potentials at the ends of the bar is related to the line integral of the Seebeck coefficient.

The thermoelectric power $S(T)$ of a material can be measured by means of the standard bimetallic circuit of [Figure 11.12](#), in which the two junctions between metal A and metal B are kept at different temperatures. Using the relation

$$-\nabla\phi = -\frac{1}{e}\nabla\mu + S(T)\nabla T,$$

it is easy to evaluate the potential difference at the extremal points P_0 and P_3 (kept at the same temperature $T_0 = T_3$ so that $\mu_{0A} \equiv \mu_{3A}$). The integrand is the scalar product of the above expression for $d\mathbf{l}$, and the integral can be carried out along any line going from P_0 to P_3 within the circuit (conveniently broken into five parts). We have

$$\phi_{1A} - \phi_{0A} = \frac{1}{e}(\mu_{1A} - \mu_{0A}) - \int_{T_0}^{T_1} S_A(T) dT,$$

$$\phi_{1B} - \phi_{1A} = \frac{1}{e}(\mu_{1B} - \mu_{1A}),$$

$$\phi_{2B} - \phi_{1B} = \frac{1}{e}(\mu_{2B} - \mu_{1B}) - \int_{T_1}^{T_2} S_B(T) dT,$$

$$\phi_{2A} - \phi_{2B} = \frac{1}{e}(\mu_{2A} - \mu_{2B}),$$

$$\phi_{3A} - \phi_{2A} = \frac{1}{e}(\mu_{3A} - \mu_{2A}) - \int_{T_2}^{T_3} S_A(T) dT,$$

where $T_i = T(P_i)$. Summing up the above relations we have

$$\phi_{3A} - \phi_{0A} = -\int_{T_0}^{T_1} S_A(T) dT - \int_{T_1}^{T_2} S_B(T) dT - \int_{T_2}^{T_0} S_A(T) dT.$$

It follows

$$\boxed{\phi_{3A} - \phi_{0A} = \int_{T_1}^{T_2} S_A(T) dT - \int_{T_1}^{T_2} S_B(T) dT}. \quad (11.58)$$

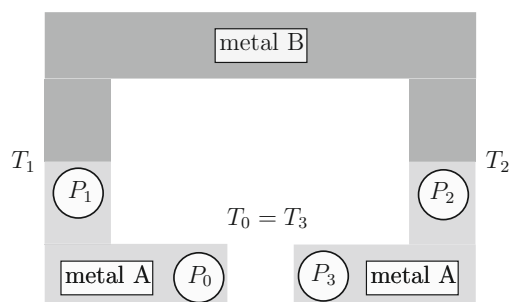


Figure 11.12 Standard bimetallic circuit to measure the thermoelectric effect. The two junctions between the metals are kept at different temperatures ($T_1 \neq T_2$); a voltage appears between points P_0 and P_3 .

Thus if we choose a material B with $S_B(T)$ known (often lead is taken because its thermoelectric power is negligible) and vary T_2 with respect to T_1 we can obtain an experimental determination of $S_A(T)$, by measuring the potential difference $\phi_{3A} - \phi_{0A}$.

Thomson Effect

When an electric current flows in a given homogeneous material in the presence of a temperature gradient, heat is released or absorbed reversibly at a rate depending on the current density and on the nature of the material; if the direction of current is reversed, the Thomson effect also changes sign (contrary to the Joule heating effect).

To study the Thomson effect, we imagine that temperature gradient, electric field and density current depend on a single direction (say x), and we consider a (small) cylinder of section Σ_0 and length d_0 with its axis parallel to \mathbf{J} , and two sections at the temperatures T_A and T_B , respectively; for simplicity we also suppose that the temperature is kept constant and equal to T_A on the left side of the cylinder, while it is kept constant and equal to T_B on the right side of the cylinder. The geometry is schematically indicated in Figure 11.13.

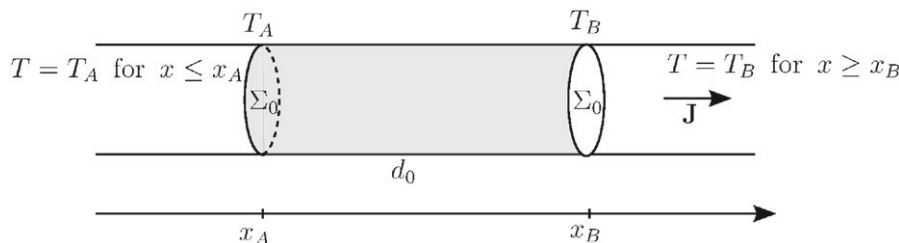


Figure 11.13 Schematic figure for the calculation of the Thomson coefficient.

When a current \mathbf{J} flows from a point at temperature T_A to a point at temperature T_B reversible heat is generated in the cylinder at the rate

$$\frac{\delta Q}{dt} = -J \Sigma_0 \int_{T_A}^{T_B} K_{\text{rev}}(T) dT, \quad (11.59)$$

where $K_{\text{rev}}(T)$ is known as Thomson coefficient, and $J \Sigma_0 = I$ is the current through the cylinder of section Σ_0 under consideration. We now prove that the *Thomson coefficient* is related to the absolute thermoelectric power through the relationship

$$\boxed{K_{\text{rev}}(T) = T \frac{dS(T)}{dT}}. \quad (11.60)$$

The internal energy fluxes across the basis of the cylinder at sections A and B are respectively

$$\mathbf{U}_A = \left[-\frac{K_1(T_A)}{eK_0(T_A)} - \frac{\mu_A}{e} \right] \mathbf{J} \quad \text{and} \quad \mathbf{U}_B = \left[-\frac{K_1(T_B)}{eK_0(T_B)} - \frac{\mu_B}{e} \right] \mathbf{J},$$

as can be seen from Eq. (11.52) (taking into account that temperature gradients at the left and right sides of the cylinder are assumed to be zero).

The heat δQ generated in the time dt in the cylinder of volume $V = \Sigma_0 d_0$ is given by

$$\delta Q = dU + \delta L,$$

where dU is the energy which accumulates in the time dt because of the unbalance between energy flowing in and out of the considered cylinder, and δL is the work performed by the electric field in the time dt . We have

$$\frac{dU}{dt} = \left[-\frac{K_1(T_A)}{eK_0(T_A)} - \frac{\mu_A}{e} + \frac{K_1(T_B)}{eK_0(T_B)} + \frac{\mu_B}{e} \right] J \Sigma_0. \quad (11.61a)$$

Similarly, using Eq. (11.51) for the electric field, we have

$$\begin{aligned} \frac{\delta L}{dt} &= \Sigma_0 \int_A^B \mathbf{J} \cdot \mathbf{E} dl = \Sigma_0 \int_A^B J \left[\frac{1}{\sigma_0} J - \frac{1}{e} \nabla \mu + S(T) \nabla T \right] dl \\ &= \Sigma_0 \left[\frac{1}{\sigma_0} J^2 d_0 - \frac{J}{e} (\mu_B - \mu_A) + J \int_{T_A}^{T_B} S(T) dT \right]. \end{aligned} \quad (11.61b)$$

From Eqs. (11.61), and disregarding the Joule heating $J^2 V / \sigma_0$, we obtain for the reversible heat generation rate

$$\begin{aligned} \frac{\delta Q}{dt} &= \left[-\frac{K_1(T_A)}{eK_0(T_A)} + \frac{K_1(T_B)}{eK_0(T_B)} \right] J \Sigma_0 + J \Sigma_0 \int_{T_A}^{T_B} S(T) dT \\ &= [T_A S_A(T) - T_B S_B(T)] J \Sigma_0 + J \Sigma_0 \int_{T_A}^{T_B} S(T) dT. \end{aligned}$$

Performing an integration by parts, it follows

$$\frac{\delta Q}{dt} = -J \Sigma_0 \int_{T_A}^{T_B} T dS(T) = -J \Sigma_0 \int_{T_A}^{T_B} T \frac{dS}{dT} dT \quad (11.62)$$

and this proves the anticipated Eq. (11.60) for the Thomson coefficient.

Peltier Effect

Heat is generated reversibly not only when current flows in a given homogeneous material in the presence of temperature gradient, but also when current flows across a junction between two contacting materials (Peltier effect). If the direction of current changes, the Peltier effect changes sign (contrary to the Joule heating effect).

For a quantitative analysis consider the standard bimetallic circuit of Figure 11.14 in isothermal conditions ($\nabla T = 0$) and with a current density J flowing throughout the circuit. Across the contact between metal A and metal B the rate (per unit time and section of area Σ_0) of reversible heat released or absorbed is

$$\frac{\delta Q}{dt} = \Pi_{AB} J \Sigma_0, \quad (11.63)$$

where J is supposed to flow from metal A to metal B. The Peltier coefficient of a given metal is connected to the Seebeck coefficient by the simple equality

$$\boxed{\Pi(T) = T S(T)}, \quad (11.64)$$

together with the relation $\Pi_{AB} = \Pi_A - \Pi_B$.

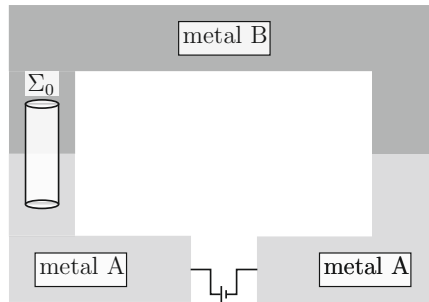


Figure 11.14 Standard bimetallic circuit for illustration of the Peltier effect; the temperature is uniform throughout the whole circuit.

To show this, we can use Eq. (11.62) (with a trivial extension of its meaning) keeping T constant, and S changing not because of temperature but because of inhomogeneity in the material. We have

$$\frac{\delta Q}{dt} = -J \Sigma_0 T [S_B(T) - S_A(T)],$$

and Eq. (11.64) is thus proved.

Considerations on Other Transport Effects

We have seen that the Boltzmann equation is very useful for the description of transport effects in metals. The transport phenomena we have investigated have been confined to the simplest situations in which the driving perturbation is a static or oscillating electric field (electrical conductivity effects), or a static electric field and a temperature gradient (thermal conductivity, Seebeck, Peltier, and Thomson effects).

The Boltzmann equation is of major help for several other transport phenomena. These include transport effects in the presence of electric and magnetic fields (Hall and magnetoresistivity effects), galvanomagnetic effects (Righi-Leduc effect, Nernst effect, Ettingshausen effect, etc.), “anomalies” or “giant effects” (in particular situations, for instance in the presence of magnetic impurities). A variety of challenging situations occur when the “phonon thermal bath,” that usually ensures relaxation toward equilibrium of the electron distribution function, is itself dragged out from thermal equilibrium.

The Boltzmann equation has been widely applied to describe transport properties in semiconductors, following essentially the same semiclassical concepts given for metals, but keeping in mind some obvious differences. Among these, the fact that the distribution of conduction electrons in a semiconductor is in general non-degenerate, because of the low density of carriers. Furthermore we have to consider both electrons in the conduction band and holes in the valence band; and in general their contribution to a given transport phenomenon is not simply additive. These differences may lead to profound effects with respect to metals. For instance the electronic conductivity of a semiconductor is in general several orders of magnitude lower than that of a metal; nevertheless the thermoelectric power of a semiconductor, due to the presence of the energy gap, is in general much higher than typical thermopowers of metals. We do not dwell on other semiclassical aspects of transport properties, except for the discussion in Section 15.5 of magnetoresistivity and the Hall effect.

11.6.3 Transport Coefficients and Efficiency of Good Thermoelectric Materials

Thermoelectric Materials and Efficiency Parameter

Thermoelectric materials, for solid state devices without moving parts, have always attracted great technological interest especially for realization of refrigerators or power generators. Thermoelectric generators use the Seebeck effect to produce a voltage difference, while refrigerators make use of the Peltier effect for cooling purpose; these

solid state devices are extremely reliable, although at the moment not yet competitive with conventional vapor-compressors or other mechanical systems, because of low efficiency. In this section we analyze more closely the transport properties of crystals, and, most importantly, we try to infer qualitatively what should be the features of electronic band structure, that characterize good thermoelectric materials.

So far in the study of the thermoelectric effects, we have considered several transport coefficients (electric conductivity, Seebeck coefficient, thermal conductivity of electrons, etc.). However there is an important parameter, dubbed as efficiency parameter, that is routinely used to characterize thermoelectric materials. The efficiency parameter p of thermoelectric materials (also called *figure of merit* $p = ZT$) is the dimensionless quantity defined as

$$p = \frac{T\sigma S^2}{k_e + k_l}, \quad (11.65a)$$

where T is the temperature, σ is the conductivity, S is the Seebeck coefficient, k_e is the thermal electron conductivity, and k_l is the thermal lattice conductivity. In situations in which the lattice contribution to the thermal conductivity is (or can be made) sufficiently smaller with respect to electron contribution, the efficiency parameter can be approximated by the upper value

$$p_e = \frac{T\sigma S^2}{k_e} \quad (k_l \ll k_e), \quad (11.65b)$$

where the subscript to p denotes that we are here taking into account only the electronic thermal conductivity. Similarly, in situations in which $k_e \ll k_l$ (typically, but not exclusively, doped semiconductors because of the small number of carriers) the efficiency parameter can be approximated by the value

$$p_l = \frac{T\sigma S^2}{k_l} \quad (k_e \ll k_l). \quad (11.65c)$$

One of the best and most studied thermoelectric materials is Bi_2Te_3 , which at room temperature has efficiency parameter near unity; however competitive thermoelectrics should have values significantly higher. This explains the continued search of novel thermoelectric materials with high efficiency parameters, and the importance of guidelines and qualitative criteria to design them. Thermoelectric materials are usually heavily doped semiconductors in degenerate regime and the theory of metals may be applied.

General Expression of the Kinetic Coefficients

The general expression of the kinetic coefficients for isotropic materials in the one-band approximation is given by Eq. (11.50) here re-written

$$K_n = \frac{1}{4\pi^3} \int \tau (\hat{\mathbf{e}} \cdot \mathbf{v})^2 (E - \mu)^n \left(-\frac{\partial f_0}{\partial E} \right) d\mathbf{k}, \quad n = 0, 1, 2.$$

The three-dimensional integral in $d\mathbf{k}$ throughout the Brillouin zone is conveniently broken into a two-dimensional integral on constant energy surfaces and an integration on the energy variable. For this purpose we introduce the *generalized transport distribution function* $\Sigma(E)$ so defined

$$\Sigma(E) = \frac{1}{4\pi^3} \int \tau(\hat{\mathbf{e}} \cdot \mathbf{v})^2 \delta[E(\mathbf{k}) - E] d\mathbf{k} = \frac{1}{4\pi^3} \int_{E(\mathbf{k})=E} \frac{\tau(\hat{\mathbf{e}} \cdot \mathbf{v})^2}{|\nabla E_{\mathbf{k}}|} dS. \quad (11.66)$$

For instance, for the free-electron gas and energy-independent relaxation time, the generalized transport distribution function has the power law form $\Sigma(E) = C E^p$ with $p = 3/2$; this and other models of transport distribution functions will be considered for qualitative considerations.

In terms of the generalized transport distribution function of the material under investigation, the kinetic parameters take the form

$$K_n = \int \left(-\frac{\partial f_0}{\partial E} \right) (E - \mu)^n \Sigma(E) dE, \quad n = 0, 1, 2. \quad (11.67)$$

Without entering in the details of specific materials, it is instructive to estimate the kinetic coefficients and the transport parameters in some simple but significant models for the transport distribution function $\Sigma(E)$.

Case of Smooth $\Sigma(E)$ and the Sommerfeld Expansion

Consider now the case that the generalized distribution function $\Sigma(E)$ is reasonably smooth around the chemical potential, so that we can exploit the Sommerfeld expansion for the calculation of the kinetic parameters. In the case of simple metals, for example, we have already seen that the Sommerfeld expansion is well justified.

The Sommerfeld expansion, introduced in [Section 3.2](#), applies to any function $G(E)$ sufficiently smooth in the thermal shell $k_B T$ around the Fermi energy, and reads

$$\int \left(-\frac{\partial f_0}{\partial E} \right) G(E) dE = G(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \left(\frac{d^2 G}{dE^2} \right)_{E=\mu} + O(T^4).$$

Setting $G(E) = (E - \mu)^n \Sigma(E)$ in the above equation, the kinetic coefficients (11.67), taking into account for simplicity only the leading terms, become

$$K_0 = \Sigma(\mu) + O(T^2), \quad (11.68a)$$

$$K_1 = \frac{\pi^2}{3} k_B^2 T^2 \Sigma'(\mu) + O(T^4), \quad (11.68b)$$

$$K_2 = \frac{\pi^2}{3} k_B^2 T^2 \Sigma(\mu) + O(T^4), \quad (11.68c)$$

where the function $\Sigma(E)$ and its derivative are calculated at the Fermi energy $E = \mu$. Using [Eqs. \(11.68\)](#), we can obtain the conductivity, the Seebeck coefficient, the electron

thermal conductivity, and the figure of merit (for what concerns the electronic part) of a thermoelectric material. In all the cases where the Sommerfeld expansion is applicable, they have the expression

$$\sigma_0(\mu, T) \equiv e^2 K_0 = e^2 \Sigma(\mu), \quad (11.69a)$$

$$S(\mu, T) \equiv -\frac{1}{e} \frac{K_1}{T K_0} = -\frac{\pi^2 k_B}{3 e} k_B T \frac{\Sigma'(\mu)}{\Sigma(\mu)}, \quad (11.69b)$$

$$k_e(\mu, T) \equiv \frac{1}{T} \left(K_2 - \frac{K_1^2}{K_0} \right) = \frac{\pi^2 k_B^2}{3 e^2} T \sigma_0, \quad (11.69c)$$

$$p_e(\mu, T) \equiv \frac{T \sigma_0 S^2}{k_e} = \frac{\pi^2}{3} k_B^2 T^2 \left[\frac{\Sigma'(\mu)}{\Sigma(\mu)} \right]^2. \quad (11.69d)$$

A few comments on the above results are worthwhile. First, consider the thermoelectric power $S(T)$, whose natural unit of measure is

$$\frac{k_B}{e} \equiv 86.17 \mu\text{V/K};$$

this value also sets the order of magnitude of interesting thermoelectric materials. The validity of Eqs. (11.69) automatically implies that the distribution function is reasonably smooth around the Fermi energy; this means $k_B T \Sigma'(\mu)/\Sigma(\mu) \ll 1$. The occurrence of this condition, tendentially depresses the Seebeck coefficient given by Eq. (11.69b), and this effect is even stronger on the efficiency parameter given by Eq. (11.69d).

Transport coefficients in simple metals can be well-described within the Sommerfeld expansion, because of the smooth character of the density-of-states and related generalized transport distribution function. It is instructive to estimate the transport coefficients in simple metals, noticing however that the specific transport properties of actual materials are rather sensitive to the energy dependence of the relaxation time and to the peculiarities of the Fermi surface. From Eq. (11.69b), it is seen that the thermoelectric power can be either negative or positive depending on the sign of $d\Sigma/dE$ at the Fermi energy. To evaluate the order of magnitudes, suppose that the generalized distribution function has a power law form of the type $\Sigma(E) \approx C E^p$ (for the free-electron gas $p = 3/2$). Then we can estimate

$$k_B T \frac{\Sigma'(\mu)}{\Sigma(\mu)} \approx \frac{k_B T}{\mu} = \frac{k_B T}{k_B T_F} = \frac{T}{T_F}; \quad (11.70a)$$

from Eqs. (11.69b,d) it follows

$$S(T) \approx -\frac{k_B}{e} \frac{T}{T_F} \quad \text{and} \quad p_e(T) \approx \left(\frac{T}{T_F} \right)^2. \quad (11.70b)$$

With $T \approx 300$ K and $T_F \approx 100$ T we expect a (negative) thermoelectric power of the order of $\mu\text{V/K}$ in normal metals at room temperature. It is also evident that the figure of merit of ordinary simple metals is very poor.

Another consideration concerns the relation between the electron thermal conductivity and the electrical conductivity. From the expression (11.69c) of the electron thermal conductivity k_e , we see that the ratio of thermal to electrical conductivity is proportional to T (Wiedemann-Franz law). Consider now the ratio

$$\frac{k_e}{T\sigma_0} = L \equiv \frac{\pi^2 k_B^2}{3 e^2},$$

which is known as *Lorentz number*. The Lorentz number would actually be a universal constant (independent from the specific metal, temperature and relaxation time), provided the approximations done in the transport equations are justified. If one goes over the whole treatment, one realizes that the most vulnerable point is the relaxation time approximation of the collision term. This approximation is justified above the Debye temperature, where the electron-phonon scattering is the dominant process, and at very low temperature, where the impurity scattering is dominant. In both temperature regimes, the ratio $k_e/T\sigma_0$ is approximately the same for all metals. At intermediate temperatures, however significant deviations may occur.

Case of Peaked Generalized Transport Distribution Function $\Sigma(E)$

What can be learned from Eqs. (11.69) and the comments done so far, is that smooth distribution functions are not likely to produce good thermoelectric materials. From this matter-of-fact consideration, several investigations in the literature have focused on metals and materials with sharp transport distribution functions. Without entering in specific details, we limit our considerations to a few qualitative remarks.

To model a peaked generalized distribution function $\Sigma(E)$, we choose for simplicity a Lorentzian function of the type

$$\Sigma(E) = C \frac{\Gamma}{(E - E_0)^2 + \Gamma^2}, \quad (11.71)$$

where E_0 is the resonance energy, Γ is the width, and C is taken as constant. We study the qualitative dependence of the kinetic parameters for large and small values of Γ with respect to the thermal energy $k_B T$.

We examine first the case $k_B T \ll \Gamma$. This assumption mimics the situation where the generalized distribution function changes smoothly on the thermal energy scale, and the Sommerfeld expansion is still applicable; then the results expressed by Eqs. (11.69) are still valid. We observe that for the Lorentzian function (11.71) it holds

$$\frac{\Sigma'(E)}{\Sigma(E)} = \frac{-2(E - E_0)}{(E - E_0)^2 + \Gamma^2} \quad \text{and} \quad -\frac{1}{\Gamma} \leq \frac{-2(E - E_0)}{(E - E_0)^2 + \Gamma^2} \leq \frac{1}{\Gamma}.$$

We can thus estimate

$$\frac{\Sigma'(\mu)}{\Sigma(\mu)} \approx \pm \frac{1}{\Gamma} \quad \text{for} \quad \mu \approx E_0 \mp \Gamma. \quad (11.72a)$$

In the case the chemical potential can be settled at or near the energies $E_0 \mp \Gamma$, from Eqs. (11.72a) and (11.69b,d) we obtain for the thermoelectric coefficient and the efficiency parameter

$$S(T) \approx \mp \frac{k_B k_B T}{e \Gamma} \quad \text{and} \quad p_e(T) \approx \left(\frac{k_B T}{\Gamma} \right)^2. \quad (11.72b)$$

From the comparison of these results with the ones of Eq. (11.70b), it is evident the significant benefit achieved in thermoelectric power and efficiency values when the broadening width Γ is in the range $k_B T < \Gamma \ll k_B T_F$. However, the benefit cannot be extended too much, since the condition $k_B T < \Gamma$ must be satisfied, and the Wiedemann-Franz law of Eq. (11.69c) is still at work.

We discuss now the opposite case of extremely narrow resonances, such that $\Gamma \ll k_B T$. Evidently in this situation the Sommerfeld expansion cannot be applied; nevertheless, an instructive discussion can be elaborated assuming for simplicity a δ -like shape for the transport distribution function

$$\Sigma(E) = C \delta(E - E_0), \quad (11.73a)$$

where E_0 is the resonance energy, and C is an appropriate constant. Inserting Eq. (11.73a) into the expression (11.67) of the kinetic parameters gives

$$K_n = C \left(-\frac{\partial f_0}{\partial E} \right)_{E=E_0} (E_0 - \mu)^n, \quad n = 0, 1, 2. \quad (11.73b)$$

From the above results, it is worthwhile to notice that the electron thermal conductivity $k_e = (1/T)(K_2 - K_1^2/K_0)$ becomes exactly zero, and the corresponding efficiency parameter p_e becomes ideally infinity (of course in such a situation k_l cannot be neglected any more). This occurs because k_e is proportional to the variance of an appropriate distribution function, and the variance of a δ -like function is exactly zero. The physical reason of the vanishing of the electron thermal conductivity is due to the fact that no heat flow is possible without a spread of allowed energies; if the band width of allowed energies is much smaller than $k_B T$, charge current can flow without being accompanied by heat flow, and any limitation on the performance of thermoelectrics originated by the Wiedemann-Franz law is overcome.

Without taking too seriously the above results (based on the hypothetical model of δ -like transport distribution function), it is evident the general message that sharp transport distribution functions could lead to increased performance. This explains the wide attention in the literature devoted to transition-metal compounds, rare-earth compounds, multiband metals and alloys, superlattices and other low-dimensional systems, where sharp structures in the density-of-states and in the generalized transport function can occur in the operative range of interest. For what concerns the quest of materials with lattice thermal conductivity as low as possible, much attention has been focused on thermoelectric crystals with great chemical complexity, and in particular on skutterudites (such as CoAs_3 and CoSb_3) and clathrates (such as $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_{24}\text{Si}_{136}$). A prominent feature of these compounds is the presence of ‘‘cavities,’’ where interstitially placed atoms can act as phonon-scattering centers to depress the thermal conductivity. [For further information see for instance the review by Mahan (1998), the review by Singh (2001), or the book of Nolas et al. (2001), and references quoted therein.]