

# 7 Transport Properties

In investigating thermodynamic properties like specific heat, magnetic susceptibility, or the thermal expansion coefficient, an implicit assumption is made that the system is in quasistatic equilibrium: The change of externally controlled parameters (temperature, magnetic field, etc.) is very slow, and the processes are reversible. However, the time evolution of the system, or the behavior under nonequilibrium conditions, is of great importance as well. This is the subject of *irreversible thermodynamics*, which is related to the corresponding microscopic *transport theory*.

In this chapter we will concentrate on systems where the deviation from equilibrium is small. When the external perturbation (the temperature gradient, electric potential gradient . . .) is switched off, the system returns to its equilibrium state in the time scale set by the *relaxation time*. If the perturbation is maintained over a time scale much longer than the relaxation time then a steady flow of energy, particles, charge, and so forth, develops. For small perturbations the response can be characterized by the proportionality constants (called *transport coefficients*) between these quantities.

Here are the definitions for a few commonly used transport coefficients. Note that while one of the parameters of the system is modified (*e.g.*, a temperature gradient is imposed), other, well-specified parameters must be kept under control (*e.g.*, no electric current is allowed):

–Thermal conductivity :	$\kappa = -j_Q/\nabla T,$	$j_e = 0$
–Electrical conductivity :	$\sigma = j_e/E,$	$\nabla T = 0$
–Peltier coefficient :	$\Pi = j_Q/j_e,$	$\nabla T = 0$
–Thermopower :	$S = E/\nabla T,$	$j_e = 0$
–Hall coefficient :	$R_H = E_y/(H j_x),$	$j_y = 0, \nabla T = 0$

where  $j_Q, j_e, \nabla T, E,$  and  $H$  are the heat current, electric current, temperature gradient, electric field, and magnetic field, respectively.<sup>1</sup>

Due to the time-reversible nature of microscopic processes, the transport coefficients are not entirely independent. The *Onsager relations* can be used

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<sup>1</sup> To illustrate the concept, while keeping the formalism simple, a one-dimensional flow was assumed for the first four items; in the definition of the Hall coefficient the current density, electric field, and magnetic field point in the  $x, y,$  and  $z$  directions of a Cartesian coordinate system, respectively.

to calculate some coefficients if some others are known. The most commonly used relation connects electric and heat transports; it can be best formulated in terms of the  $L_{pq}$  *generalized transport coefficients*.<sup>2</sup> In zero magnetic field we have

$$\begin{aligned} j_e &= L_{11} \mathbf{E} - L_{12} \frac{\nabla T}{T} && \text{Electric current} \\ j_Q &= L_{21} \mathbf{E} - L_{22} \frac{\nabla T}{T} && \text{Thermal current.} \end{aligned} \quad (\text{I.7.1})$$

The Onsager relation turns out to be a symmetry condition on the  $L_{pq}$  coefficients:

$$L_{21} = L_{12} \quad (\text{I.7.2})$$

Using the definition of the transport coefficients, along with Eqs. I.7.1 and I.7.2, straightforward calculations result in

$$\begin{aligned} \sigma &= L_{11} \\ \kappa &= \left( -\frac{L_{12}^2}{L_{11}} + L_{22} \right) \frac{1}{T} \\ \Pi &= L_{12}/L_{11} \\ S &= \frac{L_{12}}{TL_{11}}. \end{aligned} \quad (\text{I.7.3})$$

For simplicity, we assumed that the system is isotropic, and we replaced the  $L$  tensors by  $L$  scalars.

In a multicomponent system, or in the presence of a magnetic field, many other transport coefficients can be defined. Here we will discuss only the Hall effect. If a magnetic field  $H$  points in the  $z$  direction of a Cartesian coordinate system, and the electric current is constrained to be in the  $xy$  plane, then for an isotropic sample with no temperature gradient, the relationship between the electric field and the electric current is

$$\begin{aligned} E_x &= \rho j_x - H R_H j_y \\ E_y &= H R_H j_x + \rho j_y, \end{aligned} \quad (\text{I.7.4})$$

where  $\mathbf{j}$  is the electric current, and  $\rho$  is the resistivity.

Inverting Eq. I.7.4 yields

$$\begin{aligned} j_x &= \frac{\sigma}{(\sigma R_H H)^2 + 1} E_x + \frac{\sigma^2 R_H H}{(\sigma R_H H)^2 + 1} E_y \\ j_y &= -\frac{\sigma^2 R_H H}{(\sigma R_H H)^2 + 1} E_x + \frac{\sigma}{(\sigma R_H H)^2 + 1} E_y. \end{aligned} \quad (\text{I.7.5})$$

In this context the tensor in the equation  $\mathbf{E} = \hat{\rho}(\mathbf{H})\mathbf{j}$  is called the *Hall resistivity* tensor and  $\hat{\sigma} = \hat{\rho}^{-1}$  is the *Hall conductivity* tensor. The antisymmetric

<sup>2</sup> For each  $p, q = 1, 2$ ,  $L_{pq}$  is a tensor having components  $L_{pq}^{ij}$ , where  $i, j = x, y, z$ .

character of  $\hat{\rho}(\mathbf{H})$  can be derived from the appropriate Onsager relation by taking into account that time-reversal transformations switch the direction of the magnetic field. Similarly, one can show that the first nonvanishing term in the magnetic field dependence of the diagonal element is second-order in  $H$ :

$$\rho(\mathbf{H}) = \rho_0 + \beta_1 \mathbf{H}^2 + \beta_2 \mathbf{H}(\mathbf{j} \cdot \mathbf{H})/|\mathbf{j}|. \quad (\text{I.7.6})$$

The coefficients  $\beta_1$  and  $\beta_2$  characterize the *magnetoresistance* – that is, the change in resistivity due to the application of magnetic field. Eq. I.7.6 illustrates that the transverse magnetoresistance (measured with the magnetic field perpendicular to the current) and the longitudinal magnetoresistance (in magnetic field parallel to the current) may be different.

Many more transport coefficients can be defined in a finite temperature gradient and a magnetic field. For example, there is a nonzero coefficient relating the the generation of a temperature gradient in the  $y$ -direction by a current flow in the  $y$ -direction (the Ettingshausen effect). For a more general discussion of *thermomagnetic effects* see Callen [10] pp. 305–307, or Ziman [14] pp. 495–501.

In crystalline materials, the transport coefficients are often anisotropic even if  $H = 0$ . For simplicity, let us consider the the isothermal electric conductivity. Since the electric field and current are vectors, the most general linear relation between them is described by a tensor:  $\mathbf{j} = \hat{\sigma} \mathbf{E}$  or  $\mathbf{E} = \hat{\rho} \mathbf{j}$ , where  $\hat{\sigma}$  and  $\hat{\rho}$  are the conductivity and resistivity tensors, respectively. The number of independent components of the tensors are constrained by the requirement that the physical properties must not change when the crystal is subjected to a symmetry operation. Furthermore, the Onsager relation ensures that the conductivity tensor is symmetric.<sup>3</sup> The  $\hat{\sigma}$  tensor is also positive definite, so that the power dissipation,  $P = \mathbf{j} \cdot \mathbf{E}$ , is always positive.

The *Drude model* is a widely used, phenomenological approach en route towards a true microscopic theory of transport: The particles are characterized by a single effective mass  $m$ , the interactions are represented by a single relaxation time  $\tau$ , and the underlying picture is that of a classical ideal gas. In the Drude model of the electronic transport, the conductivity and the Hall coefficients are<sup>4</sup>

$$\sigma = \frac{ne^2\tau}{m} = \frac{1}{3}e^2gv_F^2\tau \quad (\text{I.7.7})$$

$$R_H = -\frac{1}{ne}, \quad (\text{I.7.8})$$

where  $n$  is the number density of the electrons, and the negative sign is due to the electrons' negative charge. [In Eq. I.7.7 we also expressed the conductivity

<sup>3</sup> As Eq. I.7.4 suggests, this is true only if the magnetic field is zero. Anisotropic materials in a magnetic field are discussed by Landau and Lifshitz [9] Vol. 8, pp. 87–91.

<sup>4</sup> For further details, see Ashcroft and Mermin [1] p. 1.

in terms of the density of states at the Fermi level,  $g(E_F)$ , and Fermi velocity,  $v_F$ , using the free-electron values in terms of  $n$  and  $m$ .] These expressions work surprisingly well for metals and (with clever choices of  $n$  and the charge) for semiconductors. Similarly, the Drude result for the thermal conductivity of metals,

$$\kappa_e = \frac{3}{2} \frac{k_B^2}{e} T \sigma, \quad (\text{I.7.9})$$

is close to reality (only when written in terms of the electrical conductivity, as above). For phonons a similar model yields

$$\kappa_{ph} = \frac{1}{3} c v^2 \tau = \frac{1}{3} c v \ell, \quad (\text{I.7.10})$$

where  $c$  is the specific heat,  $v$  is a typical phonon velocity, and the *mean free path*  $\ell$  is defined as  $\ell = v \tau$ .

To obtain estimates of the thermoelectric power, it is often useful to think of it as  $S = \Pi/T = j_Q/j_e T$ . Under the influence of an electric field or a temperature gradient the particles transporting heat and charge start to move with some drift velocity  $v_d$ . A crude estimate of the heat current is obtained by taking  $j_Q = \Delta Q v_d = n(\int c dT) v_d$ ; for the electric current,  $j_e = v_d n e$ . These yield  $S = (\int c dT)/(T e)$ . For free-electrons we then obtain

$$S \approx \frac{\pi^2}{4} \frac{k_B}{e} \frac{k_B T}{E_F} \quad (\text{metals}), \quad (\text{I.7.11})$$

again in reasonable agreement with experiment. In a disordered electronic conductor, exhibiting *hopping conductivity*, the electrons carry a constant entropy of the order of  $\ln 2$ ; the electronic specific heat is independent of temperature, and the thermopower

$$S \approx \ln 2 \, k_B/e = 60 \text{ mV/K} \quad (\text{hopping conductors}) \quad (\text{I.7.12})$$

is also independent of temperature. In semiconductors, the electrons must be excited across the energy gap  $E_g$  and the corresponding energy quanta are dissipated in the form of heat. Consequently the heat current is  $j_Q = E_g n v_d$  and the thermopower becomes<sup>5</sup>

$$S \approx (k_B/e)(E_g/k_B T) \quad (\text{semiconductors}). \quad (\text{I.7.13})$$

The true microscopic theory of transport properties is based on the *Boltzmann equation*. The underlying assumption of the Boltzmann equation is that large portions of the system can still be described by a distribution function similar to the equilibrium distribution function  $f(E(\mathbf{k})) \equiv f(\mathbf{k})$ , as discussed in Eqs. I.6.21 – I.6.23. But to account for the inhomogeneities created by the external perturbation, the distribution function is made position-dependent. (For an introductory discussion see Ashcroft and Mermin [1] pp. 316–320,

<sup>5</sup> These types of arguments are used extensively by Mott [15] and by Ziman [3].

Ziman [3] pp. 211–213, Ibach and Lüth [4] pp. 168–170, or Harrison [5] pp. 253–255. For a more detailed survey, see Ref. [14].) In its most general (and least useful) form the Boltzmann transport equation summarizes the balance between the various ways the distribution function can change:

$$\left. \frac{\partial f}{\partial t} \right|_{\text{field}} + \left. \frac{\partial f}{\partial t} \right|_{\text{diff}} + \left. \frac{\partial f}{\partial t} \right|_{\text{scatt}} = 0. \quad (\text{I.7.14})$$

where the terms correspond to field induced motion, diffusion, and scattering (or collisions) of particles. For electrons the first term is related to the externally applied electric and magnetic fields, the diffusion term is due to the free propagation of the particles in a perfectly periodic crystal field, and the collision term describes the interaction of electrons with lattice imperfections (impurities, dislocations, lattice vibrations) and with other electrons. For phonons the first term is usually zero.

The *linearized Boltzmann equation* is obtained if we assume that  $f$  is close to the equilibrium distribution function  $f^0$  and the difference,  $\delta f = f - f^0$ , is small. The first two terms in Eq. I.7.14 can be treated by appropriate expansion of the  $f^0$  function, as discussed by several textbooks. The scattering term represents the greatest challenge. To obtain the total change in  $f$ , one has to consider all processes taking away from and adding to the particle number for state  $|\mathbf{k}\rangle$ . If the transition probability from state  $|\mathbf{k}\rangle$  to state  $|\mathbf{k}'\rangle$  is denoted by  $W_{\mathbf{k}\mathbf{k}'}$ , then one obtains

$$\left. \frac{\partial f}{\partial t} \right|_{\text{scatt}} = \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k}\mathbf{k}'} [f(\mathbf{k}) - f(\mathbf{k}')]. \quad (\text{I.7.15})$$

The principle of *microscopic reversibility*,  $W_{\mathbf{k}\mathbf{k}'} = W_{\mathbf{k}'\mathbf{k}}$ , was used.<sup>6</sup> However, even with that simplification Eq. I.7.15 turns Eq. I.7.14 into an integro-differential equation which is hard to solve. Most often the *relaxation time approximation* is used:

$$\left. \frac{\partial f}{\partial t} \right|_{\text{scatt}} = -\frac{1}{\tau(\mathbf{k})} \delta f(\mathbf{k}). \quad (\text{I.7.16})$$

Some of the complex wavenumber dependence of  $W_{\mathbf{k}\mathbf{k}'}$  may be condensed into a wavenumber-dependent relaxation time,  $\tau(\mathbf{k})$ ; sometimes this is further simplified to  $\tau \equiv \tau(E)$  or to a single relaxation time  $\tau$ . For example, when the scattering is isotropic and elastic, the relaxation time can be calculated (by comparing Eqs. I.7.16 and I.7.15):

$$\frac{1}{\tau(\mathbf{k})} = \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k}\mathbf{k}'} (1 - \cos \Theta), \quad (\text{I.7.17})$$

<sup>6</sup> The scattering of a single particle by an impurity is often calculated by using the Golden Rule,  $W_{\mathbf{k}\mathbf{k}'} = 2\pi/\hbar \delta(E(\mathbf{k}) - E(\mathbf{k}')) |\langle \mathbf{k} | U | \mathbf{k}' \rangle|^2$ , where  $U$  is the perturbation potential. As the Dirac  $\delta$  function indicates, this scattering is elastic. The condition for microscopic reversibility is also satisfied. For a discussion of the Golden Rule, see Landau and Lifshitz [9] Vol. 3.

where  $\Theta$  is the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ .

To complete the microscopic description of the transport properties, we have to define how currents are calculated from the distribution function:

$$\begin{aligned}
 j_n &= \int \frac{2d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) \mathbf{v}(\mathbf{k}) && \text{Particle current} \\
 j_e &= e \int \frac{2d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) \mathbf{v}(\mathbf{k}) && \text{Electric current} \quad (\text{I.7.18}) \\
 j_E &= \int \frac{2d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) E(\mathbf{k}) \mathbf{v}(\mathbf{k}) && \text{Energy current} \\
 j_Q &= \int \frac{2d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) (E(\mathbf{k}) - \mu) \mathbf{v}(\mathbf{k}) && \text{Heat current.}
 \end{aligned}$$

For the last equation we used  $\Delta Q = TdS = E - \mu dN$  from Eq. I.6.1. The integrations are over the first Brillouin zone. Except for the electric current and the difference in the distribution functions, similar equations work for phonons and other quasiparticles as well. Due to the  $f^0(\mathbf{k}) = f^0(-\mathbf{k})$  symmetry of the Fermi function,<sup>7</sup> we may use  $\delta f = f - f^0$  in Eqs. I.7.18. By substituting the solution of the Boltzmann equation into the above currents, the transport coefficients can be evaluated. For example, the conductivity tensor is

$$\sigma_{ij} = e^2 \int \frac{d\mathbf{k}}{4\pi^3} \left( \frac{-\partial f^0}{\partial E} \right) \tau v_i(\mathbf{k}) v_j(\mathbf{k}) . \quad (\text{I.7.19})$$

In general, the thermoelectric transport coefficients defined in Eq. I.7.1 are

$$\begin{aligned}
 L_{11} &= e^2 \int \frac{d\mathbf{k}}{4\pi^3} \left( \frac{-\partial f^0}{\partial E} \right) \tau \mathbf{v}(\mathbf{k}) \circ \mathbf{v}(\mathbf{k}) \\
 L_{12} &= L_{21} = -Te \int \frac{d\mathbf{k}}{4\pi^3} \left( \frac{-\partial f^0}{\partial E} \right) \tau \mathbf{v}(\mathbf{k}) \circ \mathbf{v}_j(\mathbf{k}) (E(\mathbf{k}) - \mu) \\
 L_{22} &= T \int \frac{d\mathbf{k}}{4\pi^3} \left( \frac{-\partial f^0}{\partial E} \right) \tau \mathbf{v}(\mathbf{k}) \circ \mathbf{v}_j(\mathbf{k}) (E(\mathbf{k}) - \mu)^2 . \quad (\text{I.7.20})
 \end{aligned}$$

Here we used the “dyadic product”  $(\mathbf{v} \circ \mathbf{v})_{ij} \equiv v_i v_j$  to define each component of the L tensors.<sup>8</sup> Note that the Onsager relation (Eq. I.7.2) is automatically satisfied. The integrals can be evaluated in terms of the Bethe–Sommerfeld expansion (Eqs. I.6.30 and I.6.31). Keeping the first nonvanishing terms results in

<sup>7</sup> This symmetry relies on the time-reversal symmetry of the Schrödinger equation, which leads to  $E(\mathbf{k}) = E(-\mathbf{k})$ . In most cases the unperturbed system is in thermal equilibrium (described by the equilibrium distribution function of the quasiparticles,  $f^0$ ) and does not carry any current. Notable exceptions are superconductors and superfluids.

<sup>8</sup> For isotropic systems, the L tensors are described by a diagonal matrix with the diagonal components  $L_{xx} = L_{yy} = L_{zz}$ . In this case the identity  $\mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$  allows us to replace  $\mathbf{v} \circ \mathbf{v}$  by  $\frac{1}{3}v^2$ , and the L tensors may be replaced by scalars.

$$\begin{aligned}
L_{11} &= \hat{\sigma} = e^2 \tau \int \frac{d\mathbf{k}}{4\pi^3} \delta(E(\mathbf{k}) - E_F) \mathbf{v}(\mathbf{k}) \circ \mathbf{v}(\mathbf{k}) \\
L_{12} &= -\frac{\pi^2}{3e} (k_B T)^2 \left\{ \frac{1}{\tau} \frac{d\tau}{dE} \hat{\sigma} + e^2 \tau \int \frac{d\mathbf{k}}{4\pi^3} \delta(E(\mathbf{k}) - E_F) \frac{\partial^2 E}{\partial \mathbf{k} \partial \mathbf{k}} \right\} \\
L_{12} &= \frac{\pi^2}{3e} (k_B T)^2 \hat{\sigma} .
\end{aligned} \tag{I.7.21}$$

Here we have allowed for an energy-dependent relaxation time. In this approximation (which is well-justified for the degenerate Fermi gas, with  $T_F \gg T$ ) the thermal conductivity in Eq. I.7.3 reduces to  $\kappa = L_{22}$ , and it satisfies the *Wiedemann–Franz law*:  $\kappa = \alpha T \sigma$ , where the constant of proportionality is  $\alpha = (\pi^2/3)(k_B/e)^2$ . The thermoelectric power is  $S = -\frac{\pi^2}{3}(k_B/e)k_B T/E^0$ , where  $E^0$  depends on the band structure and can be evaluated from Eq. I.7.21.  $E^0 \approx E_F$  is a good estimate. For free electrons these results justify the Drude results, Eqs. I.7.7–I.7.9, and the simple estimate for the thermopower, Eq. I.7.11. However, the agreement is in part due to the fact that we did not solve the “real” Boltzmann equation after all; instead we used the relaxation time approximation.

The electrical resistivity of metals has an important contribution due to electron–phonon scattering. A simple estimate yields a relaxation rate proportional to the number of phonons  $N_{ph}$ . At high temperatures  $N_{ph}$  varies linearly with temperature (see Problem 6.2), leading to the observed linear temperature dependence of the resistance. A more sophisticated calculation takes into account the directional dependence (Eq. I.7.17) and the inelastic nature of the scattering. The result is the Bloch–Grüneisen formula:

$$\rho \sim \frac{T}{\Theta_D} \int_0^{T/\Theta_D} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})} , \tag{I.7.22}$$

where  $\Theta_D$  is the Debye temperature. This function is tabulated in Landolt–Börnstein [21] Vol. 15, p. 287.

If the relaxation time  $\tau$  is independent of the electron wavenumber the solution of the Boltzmann transport equation gives an electrical conductivity tensor

$$\sigma_{i,j} = \frac{1}{4\pi^3} \frac{e^2 \tau}{\hbar} \int \frac{v_i v_j dS_F}{|v|} . \tag{I.7.23}$$

$v_i$  is the  $i$ th component of the Fermi velocity, and  $|v|$  is the absolute value of  $v$ . The integration is over the Fermi surface.

The Hall effect and the magnetoresistance can be treated similarly. The solution of the Boltzmann equation is searched for in terms of a power series of the operator  $(e\tau/\hbar c)[\mathbf{v} \times \mathbf{H}] \partial/\partial \mathbf{k}$ . Here we reproduce the result for a two-dimensional electronic system. It is assumed that the electronic energy has no dispersion in the direction of the applied magnetic field, which points

in the  $z$ -direction.<sup>9</sup>

$$\sigma_{xy} = \frac{2e^3}{\hbar} \int \frac{d\mathbf{k}}{4\pi^3} \left( \frac{-\partial f^0}{\partial E} \right) v_y \tau(\mathbf{k}) \left\{ v_y \frac{\partial}{\partial k_x} - v_x \frac{\partial}{\partial k_y} \right\} v_x \tau(\mathbf{k}). \quad (\text{I.7.24})$$

Note that the momentum-dependence of the relaxation rate is retained here.

## 7.1 Problem: Temperature Dependent Resistance

Resistors made of pure Pt metal are often used to measure temperature down to about 20 K (below that temperature the sensitivity dramatically decreases). In Table I.7.1 we reproduced the calibration points for a standard, “100  $\Omega$ ” Pt resistor. Show that the Bloch–Grüneisen formula gives a satisfactory fit to these data for temperatures below 350 K. (The Debye temperature of Pt is 230 K. The Bloch–Grüneisen function, Eq. I.7.22, is tabulated in Landolt–Börnstein [21] Vol. 15, p. 287. It can also be calculated by numerical integration.)

T(K)	R( $\Omega$ )	T(K)	R( $\Omega$ )
14.0	1.797	100.0	29.987
20.0	2.147	150.0	50.815
30.0	3.508	200.0	71.073
40.0	5.938	300.0	110.45
50.0	9.228	400.0	148.62
70.0	17.128	1000.0	353.402

**Table I.7.1.** Calibration data for a typical “100  $\Omega$ ” Pt resistor.

## 7.2 Problem: Conductivity Tensor

Prove that for a tetragonal crystal the conductivity is isotropic in the plane perpendicular to the  $c$  axis. (Note how powerful a statement this is. For example, in an electrical conductivity measurement one obtains the same value if the current flows along the CuO bonds of Figure I.1.6 or if it flows in a direction  $45^\circ$  to them.)

<sup>9</sup> The more general result, and details of the derivation, can be found in Ziman [14] pp. 501–504. The two-dimensional formula is quoted by Ong [22], who also provides a transparent geometrical representation of the magnetotransport in two-dimensional systems.