

Chapter 1

Transport properties

In this section transport phenomena in crystals will be treated within the semiclassical Boltzmann transport formalism. This is a statistical treatment of the electrons, since the complex problem of many-body interacting electrons can not be solved, and even if it were, it would be too complex a solution for extracting transport properties which are average properties taken over large time and lengthscales. So a statistical treatment is needed to deal with such fluctuating phenomena.

Resistance of a metal, and in general resistance to flow is caused by scattering. In a metal or semiconductor, the main sources of scattering are impurities and defects at low temperatures, and phonons at high temperatures, where their concentration increases linearly with T .

Before studying the statistical formulation, we will discuss electron dynamics in a perfect crystal.

1.1 Electron Dynamics

As we have seen from the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory, the expectation value of the velocity operator is, within a factor of $1/\hbar$ the derivative of the energy with respect to wavenumber. Indeed, if we assume that the electron is in the Bloch state $\lambda\mathbf{k}$ where λ is the band index, it satisfies the following Schroedinger equation:

$$\left[\frac{p^2}{2m} + V(r) - E_{\lambda\mathbf{k}}\right]\psi_{\lambda\mathbf{k}} = 0$$

which by using $\psi_{\lambda\mathbf{k}} = u_{\lambda\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$ gives the following equation for the periodic function $u_{\lambda\mathbf{k}}(\mathbf{r})$:

$$\left[\frac{(\mathbf{p} + \hbar\mathbf{k})^2}{2m} + V(r) - E_{\lambda\mathbf{k}} \right] u_{\lambda\mathbf{k}} = 0 \quad (1.1)$$

Now if we consider a nearby k-point $\mathbf{k} + \delta\mathbf{k}$, and use the Taylor expansion of the eigenvalue at \mathbf{k} we have:

$$E_{\lambda,\mathbf{k}+\delta\mathbf{k}} = E_{\lambda\mathbf{k}} + \delta\mathbf{k} \cdot \frac{\partial E_{\lambda\mathbf{k}}}{\partial \mathbf{k}} + O(\delta\mathbf{k}^2)$$

On the other hand, eq. 1.1 written at $\mathbf{k} + \delta\mathbf{k}$ gives:

$$\left[\frac{(\mathbf{p} + \hbar\mathbf{k} + \hbar\delta\mathbf{k})^2}{2m} + V(r) - E_{\lambda\mathbf{k}+\delta\mathbf{k}} \right] u_{\lambda\mathbf{k}+\delta\mathbf{k}} =$$

Identifying the terms linear in $\delta\mathbf{k}$ gives:

$$\delta\mathbf{k} \cdot \left(\frac{1}{m} \langle u_{\lambda\mathbf{k}} | \mathbf{p} + \hbar\mathbf{k} | u_{\lambda\mathbf{k}} \rangle - \frac{\partial E_{\lambda\mathbf{k}}}{\partial \mathbf{k}} \right) = 0 \quad (1.2)$$

implying that the velocity of the Bloch electron in the crystal, is just the group velocity. Note that m is the bare electron mass.

$$\mathbf{v}_{\lambda\mathbf{k}} = \langle \psi_{\lambda\mathbf{k}} | \frac{\mathbf{p}}{m} | \psi_{\lambda\mathbf{k}} \rangle = \frac{1}{m} \langle u_{\lambda\mathbf{k}} | \mathbf{p} + \hbar\mathbf{k} | u_{\lambda\mathbf{k}} \rangle = \partial E_{\lambda\mathbf{k}} / \hbar \partial \mathbf{k}$$

Identifying the second order terms in the expansion of eq. 1.1 gives the definition of the effective mass tensor:

$$\frac{1}{2} \delta\mathbf{k}_\alpha \delta\mathbf{k}_\beta \left(\frac{1}{m} + 2 \sum_{\mu \neq \lambda} \frac{\langle \psi_{\lambda\mathbf{k}} | \mathbf{p}_\alpha | \psi_{\mu\mathbf{k}} \rangle \langle \psi_{\mu\mathbf{k}} | \mathbf{p}_\beta | \psi_{\lambda\mathbf{k}} \rangle}{m^2 (E_{\lambda\mathbf{k}} - E_{\mu\mathbf{k}})} - \frac{\partial^2 E_{\lambda\mathbf{k}}}{\partial k_\beta \partial k_\alpha} \right) = 0$$

implying that for each band ($\lambda\mathbf{k}$), the effective mass is really a tensor (3x3 matrix) whose inverse elements are given by:

$$\left(\frac{1}{M} \right)_{\alpha\beta} (\lambda\mathbf{k}) = \frac{\delta_{\alpha\beta}}{m} + 2 \sum_{\mu \neq \lambda} \frac{\langle \psi_{\lambda\mathbf{k}} | \mathbf{v}_\alpha | \psi_{\mu\mathbf{k}} \rangle \langle \psi_{\mu\mathbf{k}} | \mathbf{v}_\beta | \psi_{\lambda\mathbf{k}} \rangle}{(E_{\lambda\mathbf{k}} - E_{\mu\mathbf{k}})} \quad (1.3)$$

This relation for the effective mass tensor is usually used at $\mathbf{k} = 0$ since in semiconductors usually the bottom of the conduction band or the top of the valence band which are mostly populated by the carriers are at $\mathbf{k} = 0$.

1.1.1 Semiclassical approximation

In a semiclassical approximation, we assume that we can define a wavepacket constructed from a superposition of plane wave states, so that its extent dr is much smaller than its **mean free path** l , i.e. the length travelled by an electron between two successive collisions, so that we can talk about a localized or point-like quasi-particle. It should also be localized enough in the k -space so that we can talk about its mean wavenumber \mathbf{k} within dk , i.e. $dk \ll k$. Heisenberg uncertainty principle $dr \cdot dk \approx 1$ implies that the mean wavelength of the electron $\lambda = 2\pi/k$ should be much smaller than the mean free path l : $\lambda \ll dr \ll l$. This is what we mean by a wavepacket. Its mathematical representation is:

$$\psi(r, k_o) = \int dk A(k) e^{i(k \cdot r - \omega_k t)}$$

with the amplitude $A(k)$ being a function centered around k_o decaying away from k_o with a width of order δk (something like $A(k) = e^{-(k-k_o)^2/2\delta k^2}$). Expanding $\omega_k = E_k/\hbar$ around k_o up to first order ($\omega_k \approx \omega_o + v_g \delta k$), we obtain:

$$\psi(r, k_o) = e^{i(k_o r - \omega_o t)} \int d\delta k A(k_o + \delta k) e^{i\delta k(r - v_k t)}$$

showing that the wavepacket is like a plane wave with phase $(k_o r - \omega_o t)$ whose center travels without spreading at a speed of $v_k = d\omega_k/dk$ which is the group velocity. This representation is what we mean by a semiclassical electron whose motion is described statistically by the Boltzmann equation. The location \mathbf{r} is really of width $d\mathbf{r}$ which should be larger than the electron wavelength λ , and the wavenumber \mathbf{k} is specified to within $\delta k \ll 2\pi/\lambda$.

The work done on a Bloch electron subject to an external force within the time dt is equal to $dE_{\lambda\mathbf{k}}/dt = \mathbf{v}_{\lambda\mathbf{k}} \cdot \mathbf{F}$. But since the eigenvalue $E_{\lambda\mathbf{k}}$ changes with time through \mathbf{k} , we have:

$$\frac{dE_{\lambda\mathbf{k}}}{dt} = \frac{dE_{\lambda\mathbf{k}}}{d\mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} = \hbar \mathbf{v}_{\lambda\mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} = \mathbf{v}_{\lambda\mathbf{k}} \cdot \mathbf{F} \quad (1.4)$$

from which we can deduce the equation of motion for the quantum number \mathbf{k} :

$$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}$$

which has a very familiar form. But we should keep in mind that in deriving this equation, we did not make any assumption about the dispersion relation

Figure 1.1: Band diagram of an ideal solid. Lowest energy states are filled by single electrons (neglecting their spin). Under an applied force, the electrons change their state, if allowed by Pauli exclusion principle, to move to higher k states with higher or lower energies (depending on the dispersion relation). (a) Bragg scattering occurs at the Brillouin zone boundary where $2k.G = G^2$ and the wavenumber k is changed from π/a to $-\pi/a$. (b) Electrons are back-scattered due to collisions with defects or phonons, until a steady state situation is reached.

like it being quadratic in \mathbf{k} or anything alike. This equation implies that the wave number of the electron, which is also a quantum number characterizing its state, increases (linearly) with time under the influence of a (constant) force.

1.1.2 Bloch oscillations

For an ideal crystal without defect, we can assume a band which is partially filled by electrons up to the Fermi level (see fig.1.1).

The application of an electric field will force the wavenumber k of each electron to increase according to $\hbar d\mathbf{k}/dt = \mathbf{F}$. As a result the sequence of filled \mathbf{k} states will slide to the right until it reaches the Brillouin zone boundary, at which point electrons are projected to the other side of the BZ, and this leads to a lowering of the total momentum of the electrons and the total current. If this process continues, most of the occupied states will end up after some time to the left of the BZ, and this will cause a current with the opposite sign compared to the initial current. Therefore, as a function of time, in the absence of any scattering mechanism, the current will show an oscillatory behavior with very large amplitude. These oscillations are called “Bloch oscillations”.

In a real system, scatterings dominate transport, and the sequence of occupied states slides only slightly to the right (along the applied force) and scatterings prevent further motion of the Fermi sea, after a steady state has been reached (see fig. 1.1 (b)).

1.2 The Boltzmann Transport Equation

In a real system with 10^{23} electrons, it would be futile to solve the equation of motion for every electron and thus a statistical treatment is needed. It is not important to know, not to mention impossible, what each electron does. It would be useful to know what electrons do “on the average”. The Boltzmann equation describes the time evolution of the electron distribution function $f(\mathbf{r}, \mathbf{k}, t)$. Its physical interpretation is that $f(\mathbf{r}, \mathbf{k}, t) d\mathbf{r} d\mathbf{k}$ is the number of electrons (wavepackets) at point \mathbf{r} with wavenumber \mathbf{k} in the phase space volume $d\mathbf{r} d\mathbf{k}$. If integrated in all space over \mathbf{k} , we would get the electron density at point \mathbf{r} , and if further integrated over \mathbf{r} , we would get the total number of electrons. Its time variation is due to 3 effects: diffusion, drift and collisions. Diffusion is caused by any gradient in the electron concentration, or $\frac{\partial f}{\partial \mathbf{r}}$, whereas the drift is caused by external forces (diffusion in \mathbf{k} space). Collisions of course also change the distribution function. They are also due to forces seen by an electron, but the internal forces causing collisions are separated from the external ones which cause drifts.

Let us take a fixed \mathbf{k} ¹, and see what is the change in $f(\mathbf{r})$ under the flow: the particles in the small volume $d\mathbf{r}$ at \mathbf{r} at time t are those who were at the point $\mathbf{r} - \mathbf{v}_k dt$ at time $t - dt$. So $f(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r} - \mathbf{v}_k dt, \mathbf{k}, t - dt) = f(\mathbf{r}, \mathbf{k}, t - dt) - dt \mathbf{v}_k \cdot \frac{\partial f}{\partial \mathbf{r}}$. We write this as:

$$\left(\frac{\partial f}{\partial t} \right)_{diffusion} = -\mathbf{v}_k \cdot \frac{\partial f}{\partial \mathbf{r}} \quad (1.5)$$

Likewise at a fixed position \mathbf{r} , one can say that electrons of wavenumber \mathbf{k} are those who had wavenumber $\mathbf{k} - dt d\mathbf{k}/dt$ at time $t - dt$. So $f(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r}, \mathbf{k} - \dot{\mathbf{k}} dt, t - dt) = f(\mathbf{r}, \mathbf{k}, t - dt) - dt \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}}$. We write this as:

$$\left(\frac{\partial f}{\partial t} \right)_{drift} = -\dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} \quad (1.6)$$

Finally, the time evolution of the distribution function is given by the Boltzmann equation:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{diffusion} + \left(\frac{\partial f}{\partial t} \right)_{drift} + \left(\frac{\partial f}{\partial t} \right)_{collisions}$$

¹Here for simplicity, we will be dropping the band index λ from the formalism, but in the general case, one should replace every occurrence of \mathbf{k} by $\lambda \mathbf{k}$

$$= -\mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{r}} - \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} + \left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} \quad (1.7)$$

where the collision term depends on the microscopic scattering mechanisms present in the system. If we call $W_{\mathbf{k} \rightarrow \mathbf{k}'}$ the scattering rate to go from state \mathbf{k} to the state \mathbf{k}' , then the rate of change of the distribution function due to collisions can be written for electrons (or fermions) as follows:

$$\left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} = \sum_{\mathbf{k}'} W_{\mathbf{k}' \rightarrow \mathbf{k}} f_{\mathbf{k}'} (1 - f_{\mathbf{k}}) - W_{\mathbf{k} \rightarrow \mathbf{k}'} f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) \quad (1.8)$$

and for different scattering mechanisms, $W_{\mathbf{k} \rightarrow \mathbf{k}'}$ would be the sum of the rates due to each mechanism. This assumes that different mechanisms do not interfere with each other. In the above formula the occupation factors f and $1 - f$ assure that one is going from an occupied to an empty state. To calculate the scattering rates, the well-known **Fermi Golden Rule** based on second-order time-dependent perturbation theory is generally used:

$$W_{\mathbf{k} \rightarrow \mathbf{k}'} = \frac{2\pi}{\hbar} | \langle \mathbf{k} | V | \mathbf{k}' \rangle |^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'})$$

assuming that the perturbation V does not vary with time after it is applied instantaneously. Note that all this formalism is developed in the single particle picture, and the labels \mathbf{k}, \mathbf{k}' refer to single-particle electronic states.² For electron-phonon interactions, there is a slight modification to this formula, as the initial and final states also involve phonons. In this case, many-body theory should be used, but one will end up with a similar formula:

$$W_{\mathbf{k} \rightarrow \mathbf{k}'} = \frac{2\pi}{\hbar} | \langle i | H_{\text{e-ph}} | f \rangle |^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'} \pm \hbar\omega) (n_{\text{ph}}(\omega) + \eta)$$

with $\eta = 0$ or 1 depending on whether the phonon was emitted or absorbed, and i and f refer to the initial and final states of the electron+phonon system.

²To treat electron-electron interactions, one could use the mean-field approximation and include this interaction in the macroscopic field which is the sum of the external field and that due to other electrons. The latter can be taken to be the gradient of the Hartree potential, or one could even add the exchange-correlation potential calculated within the DFT. There are other ways to handle this problem; we refer the reader to other specialized textbooks on this subject[1, 2].

1.2.1 Detailed Balance

When steady state is reached, the partial derivative of f is zero, and in the absence of any driving field, one is in the equilibrium state: $f = f^o$ which is the Fermi-Dirac distribution function. The collision term is zero, meaning that there are as many electrons who leave a state \mathbf{k} , as there are electrons who come to the state \mathbf{k} . This will give a relationship that must be satisfied by the scattering rates:

$$W_{\mathbf{k}' \rightarrow \mathbf{k}} f_{\mathbf{k}'}^o (1 - f_{\mathbf{k}}^o) = W_{\mathbf{k} \rightarrow \mathbf{k}'} f_{\mathbf{k}}^o (1 - f_{\mathbf{k}'}^o) \quad (1.9)$$

For elastic collisions, e.g. electron-impurities or electron-acoustic phonon, the electron energy does not change after scattering: $E_{\mathbf{k}} = E_{\mathbf{k}'}$. The principle of microscopic reversibility implies that $W_{\mathbf{k}' \rightarrow \mathbf{k}} = W_{\mathbf{k} \rightarrow \mathbf{k}'}$. This can also be seen from eq. 1.9, since $f_{\mathbf{k}'}^o = f_{\mathbf{k}}^o$.

For inelastic collisions, however, all we have is eq. 1.9, which can be slightly simplified if second order terms in f are neglected. In this case, $W_{\mathbf{k}' \rightarrow \mathbf{k}} = W_{\mathbf{k} \rightarrow \mathbf{k}'} f_{\mathbf{k}}^o / f_{\mathbf{k}'}^o$. We can furthermore assume that this relation also holds for small driving fields. Then

$$\left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} = \sum_{\mathbf{k}'} W_{\mathbf{k} \rightarrow \mathbf{k}'} \left[f_{\mathbf{k}'} \frac{f_{\mathbf{k}}^o}{f_{\mathbf{k}'}^o} - f_{\mathbf{k}} \right] \quad (1.10)$$

1.2.2 The Relaxation Time Approximation (RTA)

Solving Boltzmann equation 1.7 as stated above, even if scattering rates W are known is a difficult task since it is an integro-differential equation. It involves, in addition to 7 partial derivatives of the distribution function, the integral of its square (in the collision term). In practice, one has to make simplifying assumptions, and the biggest one, which gets rid of the integral, and the second power of f is the relaxation time approximation (RTA). In this approximation, one replaces the collision term by $(f^o - f)/\tau_{\mathbf{k}}$, where f^o is the equilibrium distribution given by the Fermi-Dirac function, and $\tau_{\mathbf{k}}$ is the so-called relaxation time. It specifies essentially after how long the system relaxes to its equilibrium or steady state. Indeed collisions serve to “randomize” the momentum distribution, and help the system to relax or equilibrate. Of course inelastic as well as elastic interactions are also needed so that energy can also be exchanged between the particles, and their energy distribution can also be relaxed.

We can therefore make the distinction between three different relaxation times: the shortest one is the **collision time** which is the average time between two successive collisions of a particle. Then comes the **momentum relaxation time**, which is the time needed for the momentum distribution to relax. This is typically an order longer than the collision time, because it takes many collisions to randomize the momentum distribution. Finally we have the **energy relaxation time**, which is the longest of all, and is the time needed for the energy distribution to reach steady state. Inelastic collisions are needed for this purpose, and the ratio between inelastic rates and elastic ones essentially determines this energy relaxation time. In this approximation, the collision integral for each scattering mechanism is replaced by a corresponding inverse collision time. Therefore, if many types of scatterings are involved, one needs to sum their inverse characteristic times in order to obtain the total relaxation time. This is also referred to as the **Matthiessen's rule** : $1/\tau_k = \sum_s 1/\tau_k^s$, where the superscript s labels different scattering mechanisms.

We should first note that the system goes out of equilibrium under the influence of driving forces such as gradients of temperature, chemical or electrostatic potentials. To a good approximation (if the driving forces are not too large), the deviation of the distribution function from its equilibrium value is linear in the forces. This is called the linear response theory. One can in general expand the distribution function in powers of the driving fields as: $f = f^o + f^1 + f^2 + \dots$ where the superscript tells us to what power of the field a given term is proportional. Plugging this in Boltzmann equation 1.7 we arrive at the simplified equation giving directly the distribution function:

$$\begin{aligned} \frac{\partial f^1}{\partial t} + \frac{f^1}{\tau_{\mathbf{k}}} + \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f^o}{\partial \mathbf{r}} + \frac{\mathcal{F}}{\hbar} \cdot \frac{\partial f^o}{\partial \mathbf{k}} &= 0 \quad (1.11) \\ \frac{f^1}{\tau_{\mathbf{k}}} + \mathbf{v}_{\mathbf{k}} \cdot \left(\frac{\partial T}{\partial \mathbf{r}} \frac{\partial f^o}{\partial T} + \frac{\partial \mu}{\partial \mathbf{r}} \frac{\partial f^o}{\partial \mu} \right) + \mathcal{F} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f^o}{\partial E_{\mathbf{k}}} &= 0 \end{aligned}$$

In the second line, we have assumed steady state, and considered uniform systems so that there is no gradient of f^1 with respect to \mathbf{r} , but assumed that locally the equilibrium distribution is given by $f^o[(E_{\mathbf{k}} - \mu(\mathbf{r}))/k_B T(\mathbf{r})]$. We have also neglected terms of higher order in driving fields. This equation gives the distribution function f^1 explicitly as a function of the driving fields $(\mathcal{F}, \nabla T, \nabla \mu)$ and the relaxation time. Before writing it out, we need to work

out the partial derivatives of f^o :

$$\frac{\partial f^o}{\partial T} = \frac{\partial f^o}{\partial E_{\mathbf{k}}} \frac{E_{\mathbf{k}} - \mu}{T}, \quad \frac{\partial f^o}{\partial \mu} = -\frac{\partial f^o}{\partial E_{\mathbf{k}}}$$

We will express everything as a function of $-(\partial f^o/\partial E_{\mathbf{k}})$ as this function is common and looks like a Dirac δ function centered at the Fermi energy μ for metals. But for semiconductors, where $E_c - \mu \gg k_B T$ and E_c refers to the bottom of the conduction band, it can be approximated by $f^o/k_B T$.³ To summarize,

$$\begin{aligned} -\left(\frac{\partial f^o}{\partial E_{\mathbf{k}}}\right) &= \frac{f^o(1-f^o)}{k_B T} \approx \delta(E_{\mathbf{k}} - \mu) \text{ for metals} \\ -\left(\frac{\partial f^o}{\partial E_{\mathbf{k}}}\right) &= \frac{f^o(1-f^o)}{k_B T} \approx \frac{f^o}{k_B T} \text{ for n-doped semiconductors} \end{aligned} \quad (1.12)$$

Consequently, the non-equilibrium part of the distribution function, within the relaxation time approximation can be written as:

$$f^1 = \tau_{\mathbf{k}} \left(-\frac{\partial f^o}{\partial E_{\mathbf{k}}} \right) \mathbf{v}_{\mathbf{k}} \cdot \left(-\nabla T \frac{E_{\mathbf{k}} - \mu}{T} - \nabla \mu + \mathcal{F} \right) = \tau_{\mathbf{k}} \left(-\frac{\partial f^o}{\partial E_{\mathbf{k}}} \right) \mathbf{v}_{\mathbf{k}} \cdot \mathcal{D} \quad (1.13)$$

where we represented the driving fields by \mathcal{D} . This expression can be seen as the first term in the Taylor expansion of the distribution function in powers of the fields:

$$f_{\mathbf{k}} \approx f_{\mathbf{k}}^o + \tau_{\mathbf{k}} \left(-\frac{\partial f^o}{\partial E_{\mathbf{k}}} \right) \mathbf{v}_{\mathbf{k}} \cdot \mathcal{D} = f_{\mathbf{k}-\tau_{\mathbf{k}}\mathcal{D}/\hbar}^o = f^o(E_{\mathbf{k}} - \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \cdot \mathcal{D}) \quad (1.14)$$

This means that to lowest order in the fields, one can assume that the distribution function is the equilibrium one shifted by a “drift” momentum $\mathbf{p}_d = \hbar \mathbf{k}_d = \langle \tau_{\mathbf{k}} \rangle \mathcal{D}$, which is the average momentum change between two collisions. Note that this is an approximate picture as the relaxation time really depends on \mathbf{k} or $E_{\mathbf{k}}$. That is why we replaced it by its “average” value $\langle \tau_{\mathbf{k}} \rangle$ which needs to be specified better. We will go over this averaging when transport properties will be calculated.

³This relation is used for n-doped semiconductors where electrons are the only carriers present and μ is much closer to E_c , but one could also consider p-doped semiconductors with holes as carriers, and in this case, $-(\partial f^o/\partial E_{\mathbf{k}}) \approx (1-f^o)/k_B T$.

1.2.3 Currents and Response Functions

The equilibrium part of the distribution function does not contribute to currents as it is an even function of the velocities and the currents are odd in velocity. The non-equilibrium part f^1 , however, is odd in \mathbf{v} so that its product with the velocity is even and will give a non zero contribution to the currents. The particle⁴, energy and heat currents are defined as:

$$\begin{aligned}\mathbf{J}_{\mathcal{N}} &= \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}^1 \\ \mathbf{J}_E &= \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} E_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}^1 \\ \mathbf{J}_Q &= \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} (E_{\mathbf{k}\sigma} - \mu) \mathbf{v}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}^1\end{aligned}\quad (1.15)$$

Since the internal energy is related to heat through the first principle of thermodynamics: $dE = TdS - Pd\Omega + \mu d\mathcal{N}$, we can also define currents for these quantities so that each satisfies a conservation equation. Since at zero pressure we have $\delta Q = dE - \mu d\mathcal{N}$, a similar relation holds for their corresponding currents $\mathbf{J}_Q = \mathbf{J}_E - \mu \mathbf{J}_{\mathcal{N}}$. Therefore if energies are measured with respect to the chemical potential, energy current becomes heat current. An electron of energy $E_{\mathbf{k}} > \mu$ is called hot and if $E_{\mathbf{k}} < \mu$, it is called cold. If we define the driving fields as $(\mathcal{F} - \nabla\mu, -\nabla T/T)$, then we can relate the currents to the driving fields via a response function matrix defined as:

$$\begin{pmatrix} \mathbf{J}_{\mathcal{N}} \\ \mathbf{J}_Q \end{pmatrix} = \begin{bmatrix} L_0 & L_1 \\ L_1 & L_2 \end{bmatrix} \begin{pmatrix} \mathcal{F} - \nabla\mu \\ -\nabla T/T \end{pmatrix}$$

Substituting the expression for f^1 from eq.1.13 into eq.1.15 gives us the following expressions for the matrix elements:

$$L_n = \int dE \sigma(E) \left(-\frac{\partial f^0}{\partial E_{\mathbf{k}}}\right) (E - \mu)^n \quad (1.16)$$

with

$$\sigma(E) = \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} \tau_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} \delta(E - E_{\mathbf{k}\sigma}) \quad (1.17)$$

⁴To get the electrical current, one needs to multiply the particle current by the charge of the carriers.

which can be interpreted as the average diffusivity per unit energy and unit volume. Its integral over the energy gives the electrical conductivity divided by the square of the carrier charge. For this reason, it is called the differential conductivity.

1.2.4 Thermoelectric Properties

The above defined response functions characterize the thermoelectric properties of the system. An applied voltage can give rise to an electrical current, that is proportional to the coefficient L_0 . It can also give rise to heat current which is proportional to the coefficient L_1 . A temperature gradient can cause a voltage difference across an open circuit. This is the Seebeck effect. It can also cause heat flow, which is proportional to L_2 . So from the thermoelectric matrix defined above, one can clearly generate different types of currents by applying different types of driving fields. Thermoelectric transport coefficients are historically defined in a different way, which we will describe below and then relate them to the above thermoelectric matrix elements.

The **electrical conductivity** is the ratio of the electrical current density to the applied voltage gradient (or electric field) $\mathbf{J}_e = \sigma \mathcal{E}$ with $q\mathcal{E} = \mathcal{F} - \nabla\mu$, when no thermal gradient is present ($\nabla T = 0$). We have therefore $\sigma = q^2 L_0$.

The **thermal conductivity** is the ratio of the heat current density to the applied temperature gradient $\mathbf{J}_Q = -\kappa \nabla T$ when no current is flowing in the system. We have therefore $\kappa = (L_2 - L_1^2/L_0)/T$.

The **Seebeck coefficient** is the ratio of the induced electric field to the applied temperature gradient $S = \mathcal{E}/\nabla T$, when the circuit is open and no current flows ($\mathbf{J}_e = 0$). It is therefore $S = L_1/T L_0$. It is zero or very small for metals, because the function $(-\partial f^o/\partial E_{\mathbf{k}})(E - \mu)$ in L_1 is odd around the Fermi level. It can become important when there is an asymmetry in the DOS around the Fermi level, namely in doped semiconductors.

The **Peltier coefficient** is the ratio of the heat current density to the electrical current density $\Pi = \mathbf{J}_Q/\mathbf{J}_e$ when no temperature gradient is present in the system ($\nabla T = 0$). It is therefore $\Pi = L_1/qL_0$, and by definition represents the average heat carried by each charged particle. As we can notice, the following relation holds: $\Pi = ST$, which can be proven thermodynamically exactly (even if no RTA holds), and is coming from **Onsager reciprocity theorem**. Consequently, the Seebeck coefficient can also be interpreted as the average entropy carried per charged particle.

1.2.5 Relaxation rates and scattering time

Using the relaxation time approximation, one can obtain a relationship between $\tau_{\mathbf{k}}$ and its corresponding relaxation rate $W_{\mathbf{k}\rightarrow\mathbf{k}'}$. This helps to simplify the formalism and for a given rate, one can deduce its τ which will be used in eq.1.13. To obtain this relationship, we need to equate the collision term to $-f^1/\tau$, and also replace the distribution functions in the collision integral by $f^0 + f^1$:

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}} &= \sum_{\mathbf{k}'} W_{\mathbf{k}\rightarrow\mathbf{k}'} [f_{\mathbf{k}'} \frac{f_{\mathbf{k}}^o}{f_{\mathbf{k}'}^o} - f_{\mathbf{k}}] = -f^1/\tau_{\mathbf{k}} \\ &= \sum_{\mathbf{k}'} W_{\mathbf{k}\rightarrow\mathbf{k}'} [f_{\mathbf{k}'}^1 \frac{f_{\mathbf{k}}^o}{f_{\mathbf{k}'}^o} - f_{\mathbf{k}}^1] \end{aligned}$$

Dividing through by $f_{\mathbf{k}}^1$ one obtains

$$\frac{1}{\tau_{\mathbf{k}}} = \sum_{\mathbf{k}'} W_{\mathbf{k}\rightarrow\mathbf{k}'} \left[1 - \frac{f_{\mathbf{k}'}^1 f_{\mathbf{k}}^o}{f_{\mathbf{k}}^1 f_{\mathbf{k}'}^o}\right] \quad (1.18)$$

For **elastic scatterings** such as impurity scattering, this can be further simplified since $E_{\mathbf{k}} = E_{\mathbf{k}'}$ and $f_{\mathbf{k}}^o = f_{\mathbf{k}'}^o$.

$$\frac{1}{\tau_{\mathbf{k}}} = \sum_{\mathbf{k}'} W_{\mathbf{k}\rightarrow\mathbf{k}'} \left[1 - \frac{\mathbf{v}_{\mathbf{k}'} \cdot \mathcal{E}}{\mathbf{v}_{\mathbf{k}} \cdot \mathcal{E}}\right] = \sum_{\mathbf{k}'} W_{\mathbf{k}\rightarrow\mathbf{k}'} (1 - \cos\theta) \quad (1.19)$$

where θ is the angle between \mathbf{k} and \mathbf{k}' . From this integral, we see that backward scatterings where $\theta = \pi$ have the most weight in determining the inverse relaxation time. In other words, they are most effective in limiting the collision time. Although the collision time (between two successive collisions) is the inverse of $W_{\mathbf{k}\rightarrow\mathbf{k}'}$, the (momentum) relaxation time $\tau_{\mathbf{k}}$ is found from the above integration and turns out to be larger than a typical $1/W_{\mathbf{k}\rightarrow\mathbf{k}'}$. In terms of an electrical circuit analog, since the resistivity is proportional to the relaxation rates, and the latter add, we can think of the total resistivity as the sum of resistivities due to each process, i.e. the resistances due to each process are arranged in series and add. Therefore processes with a long relaxation time (e.g. forward scattering and weak interactions) do not contribute to the total resistance, because they do not help in relaxing or randomizing the momentum of carriers. Backward scatterings and strong interactions, on the other hand, do this job of randomization effectively, and they have the major contribution to the total resistance.

1.2.6 Examples

Here we will illustrate the application of the relaxation time approximation to the calculation of electrical conductivity for metals and semiconductors. Although the final expressions in both cases is the well-known Drude formula, the definition of the relaxation time is quite different in each case.

Let us assume for simplicity that the dispersion relation is isotropic $E_{\mathbf{k}} = E_k$. We first need to use eq. 1.17 and calculate the energy-dependent differential conductivity. We see that it involves an average of $v^2\tau$ over constant energy surfaces. The sum over states \mathbf{k} can be replaced by an integral of the idensity of states (DOS) over energies. The volume factor in the denominator reduces the DOS to $dos(E)$ which we use as the DOS per unit volume, and finally we obtain:

$$\sigma(E) = \int dos(E') \frac{v^2(E')}{d} \tau(E') \delta(E - E') = dos(E) \frac{v^2(E)}{d} \tau(E)$$

In general, due to the vectorial nature of the velocities, σ is a second-rank tensor, but in the isotropic case it becomes a scalar. In d dimensions, we have replaced the product v_x^2 by v^2/d .

Then L_0 essentially takes the average of $\sigma(E)$ weighted by the derivative of the Fermi function, which is like a delta function for metals, and a Boltzmann factor for semiconductors.

$$L_0 = \int dos(E) \frac{v^2(E)}{d} \tau(E) (-\partial f^o / \partial E) dE$$

Note that if we define the diffusion coefficient by $D = \langle v^2\tau/d \rangle$, where the weighting factor is $dos(E)(-\partial f^o / \partial E)$, then we also obtain the **Einstein relation** relating the conductivity to the diffusion coefficient: $\sigma = q^2 D \text{dos}_T$, where

$$\text{dos}_T = \left(\frac{\partial n}{\partial \mu} \right)_T = \int dos(E) (-\partial f^o / \partial E) dE$$

is called the **thermodynamic density of states**.

As the electrical conductivity is usually proportional to the number of charge carriers, we will also calculate this quantity. The carrier density is given by:

$$n = \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma} = \frac{1}{\Omega} \sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}^o$$

Since the function f^1 is odd in velocities or momenta, it will not contribute to the above integral.

$$n = \int dos(E) f^o(E) dE = \int n(E) (-\partial f^o / \partial E) dE \quad (1.20)$$

where an integration by parts was performed to involve $\partial f^o / \partial E$ in the integral. Here $n(E)$ is the integral of $dos(E)$, which is the DOS per unit volume.

Case of metals: In this case the derivative of the distribution function is just a Dirac delta function centered at the Fermi energy:

$$L_0 = dos(\mu) \frac{v^2(\mu)}{d} \tau(\mu)$$

and $n = n(\mu)$ so that $\sigma = q^2 dos(\mu) \tau v^2(\mu) / d = n q^2 \tau(\mu) / m^*$. Note that in this formula, τ is the average relaxation time over the Fermi sphere, and we have to assume that the dispersion is quadratic in order to replace dos/d by $n/2\mu$ and μ by $m^* v^2(\mu)/2$. This is the well-known **Drude formula** for the electrical conductivity. The thermodynamic density of states in metals is obviously $dos(\mu)$ and the Einstein relation in metals becomes: $\sigma = q^2 D dos(\mu)$.

Case of semiconductors: For semiconductors, there is no Fermi surface, and only the tail of the distribution function contributes to the integrals. The density and L_0 are respectively given by:

$$n = \int dos(E) f^o(E) dE$$

$$L_0 = \int dos(E) \frac{v^2(E)}{d} \tau(E) \frac{f^o}{k_B T} dE$$

so that the conductivity becomes $\sigma = n q^2 \langle v^2 \tau \rangle / k_B T$. But since $k_B T \times (d/2) = m^* \langle v^2 \rangle$ for an ideal gas following Maxwell-Boltzmann statistics, we finally obtain : $\sigma = n q^2 \ll \tau \gg / m^*$ where we have defined

$$\ll \tau \gg = \frac{\langle v^2 \tau \rangle}{\langle v^2 \rangle} = \frac{\int dos(E) v^2(E) \tau(E) f^o(E) dE}{\int dos(E) v^2(E) f^o(E) dE}$$

The thermodynamic density of states in semiconductors is $dos_T = n/k_B T$ and the Einstein relation in semiconductors becomes: $\sigma = q^2 D n / k_B T$.

Bibliography

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