

FIP10601 – Text 7

Transport properties – Boltzmann Equation

Distribution function

We have seen in Text 6 that the semiclassical approximation assigns a position \mathbf{r} and a wavevector \mathbf{k} to *each* independent electron, and describes its dynamics in the presence of external fields by means of equations of motion. The study of transport properties in metallic solids involves the *collective* behavior of conduction electrons. We thus need to know the *distribution function* of these electrons. It is denoted by $f(\mathbf{r}, \mathbf{k}, t)$, and defined so that the product

$$f(\mathbf{r}, \mathbf{k}, t) d^3r \frac{d^3k}{(2\pi)^3} \quad (1)$$

gives the *average number* of electrons (with a given spin orientation) within a volume element $d^3r d^3k$ around a generic point (\mathbf{r}, \mathbf{k}) of *phase space* at time t . Considering a system with \mathcal{N} electrons in a volume V , and taking into account the spin degeneracy, we can write

$$2 \int f(\mathbf{r}, \mathbf{k}, t) d^3r d^3k / (2\pi)^3 = \mathcal{N} . \quad (2)$$

If the distribution is spatially uniform, with $f(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{k}, t)$, we have

$$2 \int f(\mathbf{k}, t) \frac{d^3k}{(2\pi)^3} = \frac{\mathcal{N}}{V} . \quad (3)$$

This last equation allows to interpret $f(\mathbf{k}, t)$ as the probability of finding an electron in the state of wavevector \mathbf{k} at time t , since $V d^3k / (2\pi)^3$ gives the number of states in a volume element d^3k . In the absence of external fields and in thermodynamic equilibrium we must recover quantum statistics, that is, the equilibrium distribution function is the *Fermi-Dirac distribution*, which is independent of \mathbf{r} and t (uniform and stationary system). Using a superscript 0 (zero) to indicate equilibrium, we have

$$f^0(\mathbf{r}, \mathbf{k}, t) = \frac{1}{e^{(\varepsilon_{\mathbf{k}} - \mu)/k_B T} + 1} \equiv f^0(\mathbf{k}) . \quad (4)$$

Consistently with a semiclassical approach, this is a quantum distribution, involving the energy spectrum of an electron subjected to the lattice potential.

Applied external fields take the system out of equilibrium, and $f(\mathbf{r}, \mathbf{k}, t)$ must be recalculated. This is done, as we will see below, through a differential equation known as *Boltzmann equation*. Before introducing this equation, it is important to discuss a necessary

extension of the model that we have been dealing with so far. In our quantum treatment of Bloch electrons under a static electric field we saw that each individual electron would visit all possible wavevector states in a band as time went on. This would include velocity reversals and would give rise to an alternate electric current induced by a static field. The experimental observation in metals is that a constant current results as a response to an applied static potential difference. To obtain such a steady state in our model of a metal, we must include some momentum-dissipation mechanism to oppose the field effect. This can be called a *scattering mechanism*, whose microscopic origin will be discussed later.

Boltzmann equation

One of the fundamental theorems of Classical Statistical Mechanics, *Liouville's Theorem*, states that the **causal** evolution of a classical system occurs conserving the probability of finding the system in a given volume element of phase space, which in our case implies that

$$\frac{d}{dt}f(\mathbf{r}, \mathbf{k}, t) = 0 . \quad (5)$$

However, if non-causal evolution processes are present, the net changes of $f(\mathbf{r}, \mathbf{k}, t)$ are due to them. Since the distribution function depends on time also through the time dependence of \mathbf{r} and \mathbf{k} , we have

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} + \frac{\partial f}{\partial \mathbf{k}} \cdot \dot{\mathbf{k}} = \left(\frac{\partial f}{\partial t} \right)_{\text{col}} , \quad (6)$$

which is the usual form known as *Boltzmann equation*. The right-hand side is the scattering term (also called *collision term*).

As we mentioned before, transport phenomena involve *steady states*, in which there is no explicit variation of the distribution function with time. In this case, the Boltzmann equation becomes

$$\frac{\partial f}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} + \frac{\partial f}{\partial \mathbf{k}} \cdot \dot{\mathbf{k}} = \left(\frac{\partial f}{\partial t} \right)_{\text{col}} . \quad (7)$$

In this last equation, $\dot{\mathbf{r}}$ and $\dot{\mathbf{k}}$ depend on the external fields as given by the semiclassical equations of motion obtained earlier (Text 6). Therefore, to use Boltzmann's equation for practical calculations we need to specify the scattering term.

Collision term

Within the context of independent-electron and semiclassical approximations, we can suppose that a scattering event involving an electron fullfills the following conditions: (1) it is essentially local, (2) it is essentially instantaneous in comparison to the relevant time scale of transport phenomena, and (3) it does not affect other electrons. Thus, only the electron

wavevector is changed, and the scattering term may be written as

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \int \frac{d^3 k'}{(2\pi)^3} [W(\mathbf{k}' \rightarrow \mathbf{k}) - W(\mathbf{k} \rightarrow \mathbf{k}')] . \quad (8)$$

$W(\mathbf{k}' \rightarrow \mathbf{k})$ represents the electron scattering rate from (the volume element around) point \mathbf{k}' to point \mathbf{k} . We are not considering the possibility of spin-dependent scattering.

Taking explicitly into account the availability of states for the scattering to occur (due to the exclusion principle), we can write

$$\begin{aligned} W(\mathbf{k}' \rightarrow \mathbf{k}) &= W(\mathbf{k}', \mathbf{k}) f(\mathbf{k}') [1 - f(\mathbf{k})] , \\ W(\mathbf{k} \rightarrow \mathbf{k}') &= W(\mathbf{k}, \mathbf{k}') f(\mathbf{k}) [1 - f(\mathbf{k}')] . \end{aligned} \quad (9)$$

Now, $W(\mathbf{k}', \mathbf{k})$ and $W(\mathbf{k}, \mathbf{k}')$ are **intrinsic** scattering rates, that is, rates corresponding to an occupied initial state and empty final one.

With the above notation, the collision term of Boltzmann's equation is written as

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \int \frac{d^3 k'}{(2\pi)^3} \{W(\mathbf{k}', \mathbf{k}) f(\mathbf{k}') [1 - f(\mathbf{k})] - W(\mathbf{k}, \mathbf{k}') f(\mathbf{k}) [1 - f(\mathbf{k}')] \} . \quad (10)$$

Taking this expression to equation Eq. (7), we conclude that Boltzmann's equation is a **nonlinear integro-differential equation** for $f(\mathbf{r}, \mathbf{k})$.

Nonlinear equations are difficult to deal with. There is an obvious condition for which Boltzmann's equation is linearized, which is equality between $W(\mathbf{k}', \mathbf{k})$ and $W(\mathbf{k}, \mathbf{k}')$. As these rates are intrinsic, we can check this possibility for the system in equilibrium, when we have

$$W(\mathbf{k}', \mathbf{k}) f^0(\mathbf{k}') [1 - f^0(\mathbf{k})] = W(\mathbf{k}, \mathbf{k}') f^0(\mathbf{k}) [1 - f^0(\mathbf{k}')] . \quad (11)$$

Using the explicit form of $f^0(\mathbf{k})$, that is, the Fermi-Dirac distribution, one easily obtains that

$$W(\mathbf{k}', \mathbf{k}) e^{\varepsilon_{\mathbf{k}}/k_B T} = W(\mathbf{k}, \mathbf{k}') e^{\varepsilon_{\mathbf{k}'}/k_B T} . \quad (12)$$

Therefore, the two rates are equal for **elastic** collisions. When this happens, Boltzmann's equation is linearized, and the collision term becomes

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{\text{col}} &= \int \frac{d^3 k'}{(2\pi)^3} \{f(\mathbf{k}') [1 - f(\mathbf{k})] - f(\mathbf{k}) [1 - f(\mathbf{k}')] \} W(\mathbf{k}, \mathbf{k}') \\ &= \int \frac{d^3 k'}{(2\pi)^3} [f(\mathbf{k}') - f(\mathbf{k})] W(\mathbf{k}, \mathbf{k}') . \end{aligned} \quad (13)$$

The elastic-scattering condition is (at least approximately) satisfied for the two dominant mechanisms in metals: scattering by *impurities* and by lattice vibrations (*phonons*). In the first case, there is generally no low-energy internal degrees of freedom to be excited during a collision. Scattering by phonons is not rigorously elastic, but the energy transfer

is much smaller than ε_F , and the Fermi factors restrict collision processes to electrons near the Fermi level.

Introducing the notation

$$\delta f(\mathbf{k}) \equiv f(\mathbf{k}) - f^0(\mathbf{k}) , \quad (14)$$

and taking into account that restriction to equal energies implies that $f^0(\mathbf{k}') = f^0(\mathbf{k})$, we have

$$f(\mathbf{k}') - f(\mathbf{k}) = \delta f(\mathbf{k}') - \delta f(\mathbf{k}) . \quad (15)$$

On the other hand, this same restriction, written in the form

$$W(\mathbf{k}, \mathbf{k}') \equiv \mathcal{W}(\mathbf{k}, \mathbf{k}') \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}) , \quad (16)$$

transforms the volume integral in Eq. (13) into a surface integral (over the surface $S_{\mathbf{k}}$ defined by the equality $\varepsilon_{\mathbf{k}'} = \varepsilon_{\mathbf{k}}$), so that

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = \frac{1}{(2\pi)^3} \int_{S_{\mathbf{k}}} \frac{dS_{\mathbf{k}'}}{|\nabla_{\mathbf{k}'} \varepsilon(\mathbf{k}')|} \mathcal{W}(\mathbf{k}, \mathbf{k}') [\delta f(\mathbf{k}') - \delta f(\mathbf{k})] . \quad (17)$$

We can formally rewrite this equation as

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = -\frac{1}{\tau_{\mathbf{k}}} \delta f(\mathbf{k}) , \quad (18)$$

where

$$\frac{1}{\tau_{\mathbf{k}}} \equiv \frac{1}{(2\pi)^3} \int_{S_{\mathbf{k}}} \frac{dS_{\mathbf{k}'}}{|\nabla_{\mathbf{k}'} \varepsilon(\mathbf{k}')|} \mathcal{W}(\mathbf{k}, \mathbf{k}') \left[1 - \frac{\delta f(\mathbf{k}')}{\delta f(\mathbf{k})} \right] . \quad (19)$$

The quantity $\tau_{\mathbf{k}}$, as defined above, can be seen as a wavevector-dependent *relaxation time*. It should be noticed that this definition is entirely **formal**, because $\tau_{\mathbf{k}}$ depends on the values of $\delta f(\mathbf{k})$ for all \mathbf{k} , that is, the very solution of Boltzmann's equation. But it is convenient to express the collision term as in Eq. (18) for the purpose of an approximate solution to be discussed next.

Relaxation-time approximation

The *relaxation time approximation* consists in assuming a constant relaxation time (τ), independent of \mathbf{k} , which allows to write the collision term as

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = -\frac{\delta f(\mathbf{k})}{\tau} . \quad (20)$$

Solving Boltzmann's equation in this approximation for a non-stationary case in which the external fields are turned off at $t = 0$ yields $\delta f(t) = \delta f(0) \exp(-t/\tau)$. Therefore, the electronic distribution relaxes *exponentially* to equilibrium with a characteristic time τ .

Validity of the relaxation-time approximation

It is reasonable to assume that in a steady state the constant-energy surfaces are **rigidly** displaced by a vector $\delta\mathbf{k}_0$ from the origin of \mathbf{k} -space, with this vector depending on the external applied fields. Then, in the (most often applicable) **linear-response limit**, since $\delta\mathbf{k}_0$ itself is already linear in the applied fields, we can write

$$\delta f(\mathbf{k}) \simeq \frac{\partial f^0}{\partial \varepsilon_{\mathbf{k}}} \nabla_{\mathbf{k}} \varepsilon(\mathbf{k}) \cdot \delta\mathbf{k}_0 . \quad (21)$$

Note that the factor $\partial f^0/\partial \varepsilon_{\mathbf{k}}$ restricts us to the vicinity of the Fermi surface if the temperature is $T \ll T_F$. Therefore, the relaxation time depends essentially on the Fermi energy. If the Fermi surface is roughly *spherical*, we can consider that $\nabla_{\mathbf{k}} \varepsilon(\mathbf{k}) \parallel \mathbf{k}$, and therefore $\delta f(\mathbf{k}')$ and $\delta f(\mathbf{k})$ differ only by the orientations of \mathbf{k}' and \mathbf{k} with respect to $\delta\mathbf{k}_0$. So, representing by Θ and Θ' respectively the angles that \mathbf{k} and \mathbf{k}' make with $\Delta\mathbf{k}_0$, we have, within the integral appearing in the definition of $\tau_{\mathbf{k}}$,

$$\frac{\delta f(\mathbf{k}')}{\delta f(\mathbf{k})} = \frac{\cos \Theta'}{\cos \Theta} . \quad (22)$$

It is also reasonable to assume that $\mathcal{W}(\mathbf{k}, \mathbf{k}') = \mathcal{W}(\varepsilon_F, \theta)$, where θ is the relative angle between \mathbf{k}' and \mathbf{k} . Choosing the k'_z -axis to be parallel to \mathbf{k} when integrating over \mathbf{k}' , and using spherical coordinates (k', θ, ϕ) , only the \mathbf{k}' projection onto \mathbf{k} will survive, the transverse part averaging to zero upon integration over ϕ . Thus, the expression for the relaxation time is reduced to the form

$$\frac{1}{\tau} = \frac{1}{(2\pi)^3} \int_{S_F} \frac{dS_{\mathbf{k}'}}{|\nabla_{\mathbf{k}'} \varepsilon(\mathbf{k}')|} \mathcal{W}(\varepsilon_F, \theta) (1 - \cos \theta) , \quad (23)$$

where S_F is the Fermi surface.

This last equation shows that we do obtain a constant (\mathbf{k} -independent) relaxation time within the adopted restrictions. We then conclude that the relaxation-time approximation is justified if:

- the scattering mechanisms justify the hypothesis of nearly elastic collisions (linearization of Boltzmann's equation);
- the relevant temperatures are low compared to T_F (restriction to the Fermi surface);
- the Fermi surface is approximately spherical.

The relaxation time is often viewed as a *phenomenological parameter*. However, once the validity conditions of the relaxation-time approximation are verified, this parameter can be actually evaluated. It suffices to know $\mathcal{W}(\varepsilon_F, \theta)$, which is basically the *scattering cross section* at the Fermi energy for the specific collision mechanism that is being considered.

In most cases, it is reasonable to assume that different scattering mechanisms (e.g., impurities and phonons) do not interfere with each other, so that the collision term is a sum

of terms, one for each mechanism. Therefore, we can define an effective relaxation time τ such that

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots \quad (24)$$

In summary, under appropriate conditions, the steady-state Boltzmann's equation can be written in the relaxation-time approximation as

$$\frac{\partial f}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} + \frac{\partial f}{\partial \mathbf{k}} \cdot \dot{\mathbf{k}} = -\frac{\delta f}{\tau} . \quad (25)$$

Our next Text will make use of this result to study the evaluation of transport coefficients in metals.