Notes on the semiclassical theory of transport phenomena in metals
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1 Transport phenomena. Whenever a system is put out of equilibrium, it will host processes that tend to bring it back to equilibrium. These processes are called *transport phenomena*. For instance, if different parts of the system have different temperatures, heat will flow from the hotter to the colder parts, so as to restore a uniform temperature across the system. The causes that produce the non-equilibrium conditions will henceforth be called *forces*. There are two possibilities: if the *forces* are removed after producing the non-equilibrium conditions, the system will relax back to equilibrium. Once equilibrium is regained, the transport processes will stop. If the system is permanently forced out of equilibrium, the transport processes will continuously attempt to restore equilibrium, without stopping. If the *forces* are stationary, a steady non-equilibrium states will be reached and the system will host steady transport processes.

2 Distribution function. When characterising the non-equilibrium state of a metal, within a semiclassical picture, one is led to consider the distribution of conduction electrons with a given quasi-momentum $\boldsymbol{k}$. The distribution function $g_n(\boldsymbol{r}, \boldsymbol{k}, t)$ is such that the number of electrons belonging to the n-th band, with quasi-momentum $\boldsymbol{k}$ in the infinitesimal volume element $\mathrm{d}\boldsymbol{k}$ of reciprocal space and whose position $\boldsymbol{r}$ is comprisedvwithin the infinitesimal volume element $\mathrm{d}\boldsymbol{r}$, at time t, is

$$\mathrm{d}N_n = g_n(\boldsymbol{r}, \boldsymbol{k}, t) \frac{\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{k}}{4\pi^3},$$

where the factor of 2 accounting for spin degeneracy has been included.

3 Local equilibrium. We can define the concept of *local equilibrium* in the infinitesimal volume element as the condition such that the distribution function is of the form

$$g_n^0(\boldsymbol{r}, \boldsymbol{k}, t) = \frac{1}{\mathrm{e}^{[\varepsilon_n(\boldsymbol{k}) - \mu(\boldsymbol{r},t)]/\kappa_B T(\boldsymbol{r},t)} + 1},$$

i.e., it corresponds to the Fermi-Dirac distribution function for given local and instantaneous values of the chemical potential μ and temperature T, κ_B being the Boltzmann constant, whereas $\varepsilon_n(\boldsymbol{k})$ indicates henceforth the dispersion of Bloch electrons belonging to the n-th band.

4 Boltzmann equation. In a system of independent particles (perfect gas), the distribution function is conserved along the time evolution of the system (Liouville's theorem), hence

$$\frac{\mathrm{d}g_n}{\mathrm{d}t} = \frac{\partial g_n}{\partial \boldsymbol{r}} \cdot \frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} + \frac{\partial g_n}{\partial \boldsymbol{k}} \cdot \frac{\mathrm{d}\boldsymbol{k}}{\mathrm{d}t} + \frac{\partial g_n}{\partial t} = 0,$$

which, considering the semiclassical equations of motion for Bloch electrons

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{v}_n(\boldsymbol{k}), \qquad \hbar \frac{\mathrm{d}\boldsymbol{k}}{\mathrm{d}t} = -e\left[\boldsymbol{E}(\boldsymbol{r}, t) + \frac{1}{c}\boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{H}(\boldsymbol{r}, t)\right],$$

can be rewritten as

$$\frac{\partial g_n}{\partial \boldsymbol{r}} \cdot \boldsymbol{v}_n(\boldsymbol{k}) + \frac{(-e)}{\hbar} \frac{\partial g_n}{\partial \boldsymbol{k}} \cdot \left[\boldsymbol{E}(\boldsymbol{r}, t) + \frac{1}{c}\boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{H}(\boldsymbol{r}, t)\right] + \frac{\partial g_n}{\partial t} = 0,$$

the velocity of Bloch electrons being

$$\boldsymbol{v}_n(\boldsymbol{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n}{\partial \boldsymbol{k}}.$$

Of course, in a perfect Fermi gas, where all interactions between the electrons are neglected, no relaxation to equilibrium is possible for g_n. To describe relaxation process, we are forced to consider collisions between the electrons (or with other degrees of freedom). In such a case, the r.h.s. of the equation for g_n will be nonzero,

$$\frac{\partial g_n}{\partial \boldsymbol{r}} \cdot \boldsymbol{v}_n(\boldsymbol{k}) + \frac{(-e)}{\hbar} \frac{\partial g_n}{\partial \boldsymbol{k}} \cdot \left[\boldsymbol{E}(\boldsymbol{r}, t) + \frac{1}{c}\boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{H}(\boldsymbol{r}, t)\right] + \frac{\partial g_n}{\partial t} = \mathcal{I}_{\mathrm{coll}}[g_n].$$

This is the Boltzmann equation, describing the evolution of a given system under arbitrary non-equilibrium conditions, where the so-called *collision integral* $\mathcal{I}_{\mathrm{coll}}[g_n]$ is a non-linear functional of g_n, whose expression was deduced by

Boltzmann. The resulting equation in a non-linear integro-differential equation, which is quite difficult to tackle in general.

5 On the nature of collisions. Collisions are the mechanisms that restores equilibrium, or allows the system to reach a steady state under stationary non equilibrium conditions. For Bloch electrons, quasi-momentum is a conserved quantity in equilibrium, so the interaction with a perfectly periodic crystal lattice cannot produce relaxation. Collisions arise when electrons are scattered by imperfections of the lattice (crystal defects, impurities, vacancies, substitutional or interstitial atoms, ...), by lattice vibrations (electron-phonon interactions), or by other electrons, when the electron-electron interaction is taken into account. The first mechanism is nearly temperature independent and dominates the transport properties of metals at low temperatures (e.g., the residual resistivity of a metal). The other mechanisms usually depend on the temperature as a power law $\propto T^n$ and are thus ineffective at low temperatures: for electron-phonon interactions usually $n = 5$ at low temperature and $n = 1$ above the Debye temperature; for electron-electron interactions usually $n = 2$.

6 Relaxation time approximation. In many circumstances, the empirical experience shows that, if a system is weakly out of equilibrium, the relaxation is exponential, and is governed by a characteristic relaxation time, which is the characteristic time scale of the fastest collision mechanism. In any case, the assumption of an exponential relaxation, will usually provide a first crude description of the relaxation to equilibrium (or to a steady non-equilibrium state). The mathematical formulation of such a relaxation time approximation is entailed in the explicit form of the collision integral $\mathcal{I}_{\text{coll}}[g_n] = -(g_n - g_n^0)/\tau$, where $\tau \equiv \tau_n(\boldsymbol{r}, \boldsymbol{k})$ is the relaxation time. This expression guarantees that g_n relaxes exponentially to its (local) equilibrium value. In weak non-equilibrium conditions the band index n is not involved in the relaxation process and will be omitted henceforth. Then, the Boltzmann equation reads

$$\frac{\partial g}{\partial \boldsymbol{r}} \cdot \boldsymbol{v}(\boldsymbol{k}) + \frac{(-e)}{\hbar} \frac{\partial g}{\partial \boldsymbol{k}} \cdot \left[\boldsymbol{E}(\boldsymbol{r}, t) + \frac{1}{c} \boldsymbol{v}(\boldsymbol{k}) \times \boldsymbol{H}(\boldsymbol{r}, t) \right] + \frac{\partial g}{\partial t} = -\frac{g - g^0}{\tau(\boldsymbol{r}, \boldsymbol{k})}.$$

7 Linear response. Further insight is gained considering situations where the *forces* that bring the system out of equilibrium are weak enough, so that g deviates but slightly from the equilibrium value. For instance, since the electric and magnetic fields that bring the system out of equilibrium appear explicitly on the l.h.s. of the Boltzmann equation, the prefactor can be calculated at equilibrium, neglecting higher order terms in the *forces* (linear response),

$$\frac{(-e)}{\hbar} \frac{\partial g}{\partial \boldsymbol{k}} \approx \frac{(-e)}{\hbar} \frac{\partial g^0}{\partial \boldsymbol{k}} = \frac{(-e)}{\hbar} \frac{\partial g^0}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial \boldsymbol{k}} = (-e) \frac{\partial g^0}{\partial \varepsilon} \boldsymbol{v}(\boldsymbol{k}),$$

where we used the fact that g^0 depends on $\boldsymbol{k}$ only through $\varepsilon(\boldsymbol{k})$, and substituted the expression for the velocity of Bloch electrons. Analogously

$$\frac{\partial g}{\partial \boldsymbol{r}} \approx \frac{\partial g^0}{\partial T} \frac{\partial T}{\partial \boldsymbol{r}} + \frac{\partial g^0}{\partial \mu} \frac{\partial \mu}{\partial \boldsymbol{r}},$$

where the *forces* that bring the system out of equilibrium can be identified as the spacial gradients of temperature and chemical potential on the r.h.s., and the expression is explicitly linear in the *forces*. We can further simplify the above expressions noting the identities

$$\frac{\partial g^0}{\partial T} = -\frac{\partial g^0}{\partial \varepsilon} \frac{\varepsilon - \mu}{T}, \quad \frac{\partial g^0}{\partial \mu} = -\frac{\partial g^0}{\partial \varepsilon},$$

and indicating with the symbol ∇ the derivative with respect to $\boldsymbol{r}$, so that we can cast the Boltzmann equation in the form

$$\left(-\frac{\partial g^0}{\partial \varepsilon} \right) \boldsymbol{v} \cdot \left[\frac{\varepsilon - \mu}{T} \nabla T + \nabla \mu + e \boldsymbol{E} \right] + \frac{\partial g}{\partial t} = -\frac{g - g^0}{\tau}.$$

This equation shows that a stationary non-equilibrium state is reached in the presence of constant temperature and chemical potential gradients, and constant electric field, in which the deviation of g from its equilibrium value g^0 is linear in the *forces* that keep the system out of equilibrium. Non-linear corrections will arise beyond the linear response theory. We point out that the magnetic field disappeared from the linearized Boltzmann equation because the term $\boldsymbol{v} \times \boldsymbol{H}$ is perpendicular to $\boldsymbol{v}$, hence $\boldsymbol{v} \cdot (\boldsymbol{v} \times \boldsymbol{H}) = 0$. This does not mean that the magnetic field disappears altogether, because it still determines the time evolution of $\boldsymbol{k}$ through the semiclassical equations of motion for Bloch electrons.

Notice also that, even in the simple relaxation time approximation, the Boltzmann equation is apt to describe all thermo-electric effects that occur in metals under non-equilibrium conditions.

8 Electric current. To illustrate how the transport properties of a metal can be described within the approach developed so far, let us consider the simple case in which temperature and chemical potential gradients are absent, and a uniform electric field is present, which depends on time as a simple harmonic

$$\boldsymbol{E}(t) = \boldsymbol{E}_\omega \, \mathrm{e}^{\mathrm{i}\,\omega t}.$$

Let us call $\delta g \equiv g - g^0$ the deviation of the distribution from its equilibrium value. We can look for a solution of the Boltzmann equation where δg has the same time dependence as the electric field,

$$\delta g(t) = \delta g_\omega \, \mathrm{e}^{\mathrm{i}\,\omega t}.$$

When T and μ are constant, g^0 does not depend on time, so that

$$\frac{\partial g}{\partial t} = \frac{\partial \delta g}{\partial t} = \mathrm{i}\,\omega\,\delta g$$

and the Boltzmann equation reads

$$\left(\mathrm{i}\,\omega + \frac{1}{\tau}\right)\delta g = \left(-\frac{\partial g^0}{\partial \varepsilon}\right)(-e)\boldsymbol{v}\cdot\boldsymbol{E}.$$

Simplifying the factor $\mathrm{e}^{\mathrm{i}\,\omega t}$ on both sides and solving for δg_ω, we find

$$\delta g_\omega = \frac{1}{\mathrm{i}\,\omega + \frac{1}{\tau}}\left(-\frac{\partial g^0}{\partial \varepsilon}\right)(-e)\boldsymbol{v}\cdot\boldsymbol{E}_\omega,$$

confirming that the explicit solution of the Boltzmann equation is linear in the field that keeps the system out of equilibrium.

The value of the current density $\boldsymbol{j}$ (the transport phenomenon that is induced by the electric field) is found calculating the average value of the velocity with the non-equilibrium distribution g, times the charge of an electron,

$$\boldsymbol{j} = (-e)\int \boldsymbol{v}\,g\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = (-e)\int \boldsymbol{v}\,(g - g^0)\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = (-e)\int \boldsymbol{v}\,\delta g\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3},$$

where the integral is carried out over the entire first Brillouin zone and we have used the fact that the average velocity vanishes when calculated with the equilibrium distribution g^0. Then, using the explicit solution for δg, we find $\boldsymbol{j} = \boldsymbol{j}_\omega \, \mathrm{e}^{\mathrm{i}\,\omega t}$ with

$$\boldsymbol{j}_\omega = \int \left(-\frac{\partial g^0}{\partial \varepsilon}\right)\frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\,\boldsymbol{v}(\boldsymbol{v}\cdot\boldsymbol{E}_\omega)\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}.$$

To gain insight, a customary approximation, which cannot be justified on general grounds, but provides a simpler yet reasonable description of the electric current, is to assume that the relaxation time τ depends on $\boldsymbol{k}$ only through the energy $\varepsilon(\boldsymbol{k})$. Since the quantity $\left(-\frac{\partial g^0}{\partial \varepsilon}\right)$ forces the integrand to be evaluated at the Fermi surface, $\tau(\boldsymbol{k}) = \tau(\varepsilon(\boldsymbol{k}))$ becomes a constant $\tau(\varepsilon_F)$, henceforth simply indicated with τ. Then, the factor containig τ can be taken out of the integral and

$$\boldsymbol{j}_\omega = \frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int \left(-\frac{\partial g^0}{\partial \varepsilon}\right)\boldsymbol{v}(\boldsymbol{v}\cdot\boldsymbol{E}_\omega)\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}.$$

9 Ohm's law. The relation between the current density and the electric field is in agreement with Ohm's law, except that in a crystal the properties are anisotropic and the conductivity is a tensor rather than a scalar, i.e., $j_\alpha = \sum_\beta \sigma_{\alpha\beta}\,E_\beta$. Thus, the current is linear in the field, but is not parallel to it, except when it lies along a direction of high symmetry (principal axis) of the crystal. We can read the expression for the conductivity tensor off the expression for the current density,

$$\sigma_{\alpha\beta} = \frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int \left(-\frac{\partial g^0}{\partial \varepsilon}\right)v_\alpha v_\beta\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}.$$

The tensor is evidently symmetric. The final expression is found relying on the identities

$$\int \left(-\frac{\partial g^0}{\partial \varepsilon}\right) v_\alpha v_\beta \,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \int \left(-\frac{\partial g^0}{\partial \varepsilon}\right) \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k_\alpha}\frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k_\beta}\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \int \frac{1}{\hbar^2}\left(-\frac{\partial g^0}{\partial k_\alpha}\right)\frac{\partial \varepsilon}{\partial k_\beta}\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \int \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k_\alpha \partial k_\beta}\,g^0\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3},$$

where we obtained the last term integrating by part and considering that the integrand is periodic so that the contribution evaluated at the boundaries of the first Brillouin zone vanishes. We reckognize now the expression for the inverse mass tensor

$$M_{\alpha\beta}^{-1} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k_\alpha \partial k_\beta},$$

whence

$$\sigma_{\alpha\beta} = \frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int M_{\alpha\beta}^{-1}\,g^0\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}.$$

10 Electrons and holes. The Fermi distribution function g^0 selects the occupied states. However, the inverse mass tensor is a periodic function, its integral over the entire first Brillouin zone vanishes, hence the integral over the unoccupied (unocc) portion is just minus the integral over the occupied (occ) portion, and

$$\sigma_{\alpha\beta} = \frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int_{\mathrm{occ}} M_{\alpha\beta}^{-1}\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = -\frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int_{\mathrm{unocc}} M_{\alpha\beta}^{-1}\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \frac{e^2}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int_{\mathrm{unocc}} \left(-M_{\alpha\beta}^{-1}\right)\,\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}.$$

The last term is just the conductivity of holes, which shows that the conductivity of a metal is the same, regardless of the fact that we attribute the current to electrons or to holes.

11 Drude conductivity. For free electrons the inverse mass tensor is proportional to the identity matrix, $M_{\alpha\beta}^{-1} = \delta_{\alpha\beta}/m$, m being the free electron mass. Thus $\sigma_{\alpha\beta} = \sigma\delta_{\alpha\beta}$, where

$$\sigma = \frac{\frac{e^2}{m}}{\mathrm{i}\,\omega + \frac{1}{\tau}}\int_{\mathrm{occ}} \frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \frac{ne^2\tau}{m}\frac{1}{1+\mathrm{i}\,\omega\tau},$$

the integral over the occupied states yielding the conduction electron density n. This result had been obtained by Drude within a purely classical approach, where the equation of motion of an electron in an electric field was equipped with a friction term proportional to the electron velocity, to obtain a steady-state solution.

At $\omega = 0$ we find the DC conductivity of a metal $\sigma_0 = \frac{ne^2\tau}{m}$. The inverse of this quantity is the resistivity. The main temperature dependence comes from the relaxation time τ, which saturates to a constant at low temperature, where the relaxation is dominated by the scattering of electrons on the defects of the crystal lattice.

At finite frequency, considering the real (dissipative) part of the complex conductivity, we find

$$\mathrm{Re}\,\sigma = \frac{\sigma_0}{1+\omega^2\tau^2},$$

which has a maximum at $\omega = 0$ (Drude peak) and decreases as $1/\omega^2$ at high frequencies, $\omega \gg 1/\tau$. It is worth noticing that the area under the Drude peak does not depend on τ,

$$\int_{-\infty}^{+\infty} \mathrm{Re}\,\sigma(\omega)\,\mathrm{d}\omega = \frac{\pi ne^2}{m}.$$