

# Boltzmann Equation and Semi-classical Transport

Lectures on Condensed Matter Physics

J. M. B. Lopes dos Santos\*

March 26, 2022

Departamento de Física e Astronomia,  
Faculdade de Ciências da Universidade do Porto  
4169-007 Porto

Introduction to semi-classical transport in metals and semiconductors with Boltzmann equation

## 1. Linearized Boltzmann Equation

The semi-classical approach to transport treats carriers as particles with well defined Bloch momentum and spatial position. Wave packets describing these particles satisfy the uncertainty principle restriction

$$\Delta k \Delta r \geq 1 \quad (1)$$

Good momentum definition means

$$\Delta k \ll k_F \sim \frac{1}{a}; \quad a, \text{lattice parameter}, \quad (2)$$

and good position definition,

$$\Delta r \ll L; \quad L \text{ scale of perturbation, system size} \quad (3)$$

It is possible to have

$$\begin{aligned} \Delta k &\ll k_F \\ a &\ll \Delta r \ll L \end{aligned}$$

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\*jlsantos@fc.up.pt

without violating (1), provided  $L \gg a$ .

Carriers described by wave-packets with well defined Bloch momentum  $\mathbf{k}$  and position  $\mathbf{r}$ . The motion of carriers described by wave-packets with well defined Bloch momentum  $\mathbf{k}$  and position  $\mathbf{r}$  includes two effects:

- drift terms, determined by the semi-classical equations of motion;
- scattering events, originating from deviations of the lattice from perfect periodicity (lattice vibrations, impurities, defects, vacancies etc.). These events are local (or quasi-local) in real space but non-local in momentum space.

The Boltzmann equation (BE) refers to the density of such particles in  $(\mathbf{k}, \mathbf{r})$  space

$$f(\mathbf{k}, \mathbf{r}, t) \frac{d^d k}{(2\pi)^d} d^d r = \text{number of carriers in cell } d^d k d^d r \quad (4)$$

with marginal distributions

$$\int \frac{d^d k}{(2\pi)^d} f(\mathbf{k}, \mathbf{r}, t) = \rho(\mathbf{r}, t) \quad (\text{real space density}) \quad (5)$$

$$\int d^d r f(\mathbf{k}, \mathbf{r}, t) = n(\mathbf{k}, t) \quad (\text{momentum space density}) \quad (6)$$

$$\int \frac{d^d k}{(2\pi)^d} \int d^d r f(\mathbf{k}, \mathbf{r}, t) = N_c \quad (\text{number of carriers}) \quad (7)$$

Time changes  $f(\mathbf{k}, \mathbf{r}, t)$  at fixed point in phase space  $(\mathbf{k}, \mathbf{r})$

$$\frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) = \left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{drift} + \left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{col}$$

Drift term arises from smooth variation of  $\mathbf{k}$  and  $\mathbf{r}$  that result in a current in phase space

$$\mathbf{J} = (\dot{\mathbf{k}}, \dot{\mathbf{r}}) f(\mathbf{k}, \mathbf{r}, t)$$

leading to a continuity equation describing the conservation of number of carriers,

$$\begin{aligned} \left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{drift} &= -\nabla_{\mathbf{k}} \left[ \dot{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) \right] - \nabla_{\mathbf{r}} \left[ \dot{\mathbf{r}} f(\mathbf{k}, \mathbf{r}, t) \right] \\ &= -\nabla_{\mathbf{k}} \left[ \dot{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) \right] - \nabla_{\mathbf{r}} \left[ \mathbf{v}_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) \right] \end{aligned} \quad (8)$$

There is an important result (Liouville's theorem), if the  $(\mathbf{k}, \mathbf{r})$  follow Hamiltonian dynamics

$$\hbar \dot{\mathbf{k}} = -\nabla_{\mathbf{r}} \mathcal{H} \quad (9)$$

$$\dot{\mathbf{r}} = \nabla_{\mathbf{k}} \mathcal{H} \quad (10)$$

In that case

$$\nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}} + \nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} = (-\nabla_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} + \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}}) \mathcal{H} = 0 \quad (11)$$

and

$$\left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right| = -\dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f - \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f \quad (12)$$

In the case where both the magnetic field  $\mathbf{B}$  and the Berry curvature  $\boldsymbol{\omega}(\mathbf{k})$  are non-zero, Liouville's theorem does not apply because  $\mathbf{k}$  and  $\mathbf{r}$  are not canonically conjugate (see appendix A). For the moment we assume that either  $\mathbf{B}$  or  $\boldsymbol{\omega}$  are zero.

The semi-classical equations of motion are

$$\hbar \dot{\mathbf{k}} = q (\mathbf{E} + \mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \quad (13)$$

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} - \dot{\mathbf{k}} \times \boldsymbol{\omega}_{\mathbf{k}} \quad (14)$$

$$\left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{drift} = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f - \frac{q}{\hbar} (\mathbf{E} + \mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} f \quad (15)$$

We will proceed with the BE as

$$\frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f - \frac{q}{\hbar} (\mathbf{E} + \mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} f + \left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{col} \quad (16)$$

For stationary (DC) transport the first term is zero and

$$\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f + \frac{q}{\hbar} (\mathbf{E} + \mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} f = \left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{col} \quad (17)$$

## 2. Local Equilibrium Hypothesis

In the usual situation in transport one can define in a small, but macroscopic, region local values of the temperature and chemical potential,  $T(\mathbf{r}, t)$  and  $\mu(\mathbf{r}, t)$ . We can also, in general, define a global temperature and chemical potential. For instance, we can measure a thermal conductivity as a function of a global temperature  $T_0$  using a probing temperature gradient such that  $|T(\mathbf{r}) - T_0| \ll T_0$ . This allows the following definitions:

- Global equilibrium distribution:

$$f_{\mathbf{k}}^0 = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1} \quad (18)$$

- Local equilibrium distribution (LED)

$$f_{\mathbf{k}}^{(le)}(\mathbf{r}, t) = \frac{1}{e^{\beta(\mathbf{r}, t)(\epsilon_{\mathbf{k}} - \mu(\mathbf{r}, t))} + 1} \quad (19)$$

The deviation of the actual distribution from the global equilibrium can then be written as

$$\begin{aligned} \delta f(\mathbf{k}, \mathbf{r}, t) &= \left[ f(\mathbf{k}, \mathbf{r}, t) - f_{\mathbf{k}}^{(le)}(\mathbf{r}, t) \right] + \left[ f_{\mathbf{k}}^{(le)}(\mathbf{r}, t) - f_{\mathbf{k}}^0 \right] \\ &= \bar{\delta} f(\mathbf{k}, \mathbf{r}, t) + \delta f_{\mathbf{k}}^{(le)}(\mathbf{r}, t) \end{aligned} \quad (20)$$

The hydrodynamic regime of transport assumes that the distribution is close to the local equilibrium one

$$\overline{\delta f}(\mathbf{k}, \mathbf{r}, t) \ll \delta f_{\mathbf{k}}^{(le)}(\mathbf{r}, t) \quad (21)$$

so that a definition of time and space varying temperature and chemical potential fields is possible. The collision term, however, is zero for the local equilibrium distribution because collisions are local in real space. In other words, collisions do not change the LED. We then write the collision term as a linear functional of the deviation  $\overline{\delta f}$

$$\left. \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) \right|_{col} := I_{\mathbf{k}}[\overline{\delta f}] = \int \frac{d^d k'}{(2\pi)^2} I(\mathbf{k}, \mathbf{k}') \overline{\delta f}_{\mathbf{k}'}$$

The term  $\nabla_{\mathbf{r}} f^0$  is zero and, in the hydrodynamic regime, we replace  $f(\mathbf{k}, \mathbf{r}, t)$  by  $\delta f_{\mathbf{k}}^{(le)}(\mathbf{r}, t)$  in the drift terms and linearize in the driving fields

$$\nabla_{\mathbf{r}} \delta f_{\mathbf{k}}^{le}(\mathbf{r}, t) = \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \left[ \left( \frac{\epsilon_{\mathbf{k}} - \mu}{\beta} \right) \nabla_{\mathbf{r}} \beta - \nabla_{\mathbf{r}} \mu \right] = \left( - \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \right) \left[ \frac{\epsilon_{\mathbf{k}} - \mu}{T} \nabla_{\mathbf{r}} T + \nabla_{\mathbf{r}} \mu \right] \quad (22)$$

$$\nabla_{\mathbf{k}} f_{\mathbf{k}}^{le}(\mathbf{r}, t) = \left( \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \right) \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}$$

The term with  $\nabla_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t)$  is trickier to linearize. The reason is twofold:

- $\nabla_{\mathbf{k}} f_{\mathbf{k}}^0$  is not zero;
- it would seem that since we already have the external fields multiplying  $\nabla_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t)$  we could just replace  $f \rightarrow f^0$ . This is true for the  $\mathbf{E}$  term, but semi-classical transport is not linear in  $\mathbf{B}$ .

We will proceed with specific cases.

## 2.1. Linearized Boltzmann Equation

In this case

$$\nabla_{\mathbf{k}} f^0 = \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} = \hbar \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \mathbf{v}_{\mathbf{k}} \quad (23)$$

and

$$\frac{q}{\hbar} (\mathbf{E} + \mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} f \rightarrow -q (\mathbf{E} \cdot \mathbf{v}_{\mathbf{k}}) \left( - \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \right) \quad (24)$$

The magnetic field term cancels, since

$$\begin{aligned} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot f_{\mathbf{k}}^{le} &= (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} \left( \frac{\partial f_{\mathbf{k}}^{le}}{\partial \epsilon_{\mathbf{k}}} \right) \\ &= \hbar \left( \frac{\partial f_{\mathbf{k}}^{le}}{\partial \epsilon_{\mathbf{k}}} \right) (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \mathbf{v}_{\mathbf{k}} = 0 \end{aligned}$$

To include magnetic field terms we cannot be content stick with the LED and must include

$$\frac{q}{\hbar} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} \bar{\delta f} \quad (25)$$

as the lowest order contribution. The linearized BE becomes

$$\left( -\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}} \right) \mathbf{v}_{\mathbf{k}} \cdot \left[ \frac{\epsilon_{\mathbf{k}} - \mu}{T} \nabla_{\mathbf{r}} T + \nabla_{\mathbf{r}} \mu - q \mathbf{E} \right] = I_{\mathbf{k}} [\bar{\delta f}] - \frac{q}{\hbar} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} \bar{\delta f}_{\mathbf{k}} \quad (26)$$

to be solved for  $\bar{\delta f}$ .

## 2.2. The currents

What can we calculate with the solution of the BE,  $f(\mathbf{k}, \mathbf{r}) = f_{\mathbf{k}}^0 + \delta f_{\mathbf{k}}^{(le)} + \bar{\delta f}_{\mathbf{k}}$ ?

- the electric current density

$$\mathbf{j}_e = 2q \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}) = 2q \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} \bar{\delta f}(\mathbf{k}, \mathbf{r})$$

we are assuming that there is no current for the equilibrium distribution for any  $T$  or  $\mu$ . But if

$$\int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}^0 = 0 \quad (27)$$

clearly

$$\int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}^{(le)} = 0 \quad (28)$$

- Heat current

$$\mathbf{j}_h = 2 \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) f(\mathbf{k}, \mathbf{r}) = 2 \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) \bar{\delta f}(\mathbf{k}, \mathbf{r}) \quad (29)$$

How can we justify this expression? From thermodynamics

$$dU = TdS - PdV + \mu dN \quad (30)$$

for a infinitesimal (but macroscopic) cell of fixed volume  $d^d r$ ,  $TdS = dU - \mu dN$  and

$$\mathbf{j}_h = \mathbf{j}_u - \mu \mathbf{j}_n \quad (31)$$

where  $\mathbf{j}_u$  is the energy current and  $\mathbf{j}_n$  the particle current.

$$\mathbf{j}_u := \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} \epsilon_{\mathbf{k}} \bar{\delta f}(\mathbf{k}, \mathbf{r}) \quad (32)$$

$$\mathbf{j}_n := \int \frac{d^d k}{(2\pi)^d} \mathbf{v}_{\mathbf{k}} \bar{\delta f}(\mathbf{k}, \mathbf{r}) \quad (33)$$

### 3. The Relaxation Time Approximation

#### 3.1. Electric and Thermal conductivities

The Linearized Boltzmann Equation (LBE), Eq. 26 turn out to be an equation for the deviation  $\delta\bar{f}(\mathbf{k}, \mathbf{r})$ , appearing only in the collision integral and the magnetic field term. No solution can be sought until we specify the collision integral. There is, however, a quite general approximation for this term.

We know that, in the absence of driving fields, any deviation from equilibrium should relax to equilibrium distribution. We make the rather drastic approximation that this relaxation is exponential and that at each  $\mathbf{k}$ ,  $\delta\bar{f}(\mathbf{k}, \mathbf{r})$  relaxes with its own relaxation time, independent of the the occupation of other states

$$I_{\mathbf{k}} [\delta\bar{f}] = -\frac{\delta\bar{f}_{\mathbf{k}}}{\tau_{\mathbf{k}}} \quad (34)$$

In the absence of the magnetic field, this leads at once to an explicit solution

$$\delta\bar{f}_{\mathbf{k}} = \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \mathbf{v}_{\mathbf{k}} \cdot \left[-\frac{\epsilon_{\mathbf{k}} - \mu}{T} \nabla_{\mathbf{r}} T + q \left(\mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu\right)\right] \tau_{\mathbf{k}} \quad (35)$$

and expression for the currents

$$\begin{aligned} j_e^i &= 2q \int \frac{d^d k}{(2\pi)^d} v_{\mathbf{k}}^i \delta\bar{f}_{\mathbf{k}} \\ &= 2q^2 \int \frac{d^d k}{(2\pi)^d} \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) v_{\mathbf{k}}^i v_{\mathbf{k}}^j \tau_{\mathbf{k}} \left(\mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu\right)^j \\ &\quad + 2q \int \frac{d^d k}{(2\pi)^d} \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) v_{\mathbf{k}}^i v_{\mathbf{k}}^j \tau_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) \left(\frac{-\nabla T}{T}\right)^j \end{aligned} \quad (36)$$

Since the driving fields are  $\left(\mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu\right)$  and  $-\nabla T$  this defines the transport coefficients

$$j_e^i = q^2 \sum_j L_0^{ij} \left(\mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu\right)^j + q \sum_j L_1^{ij} \left(\frac{-\nabla T}{T}\right)^j \quad (37)$$

with similar expression for the heat current

$$j_h^i = q \sum_j L_1^{ij} \left(\mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu\right)^j + \sum_j L_2^{ij} \left(\frac{-\nabla T}{T}\right)^j \quad (38)$$

where in general

$$L_n^{ij} := 2 \int \frac{d^d k}{(2\pi)^d} \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) v_{\mathbf{k}}^i v_{\mathbf{k}}^j \tau_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu)^n \quad (39)$$

These expressions allow the calculation of the transport coefficients provided we know the band structure and can calculate the relaxation time. The presence of the Fermi

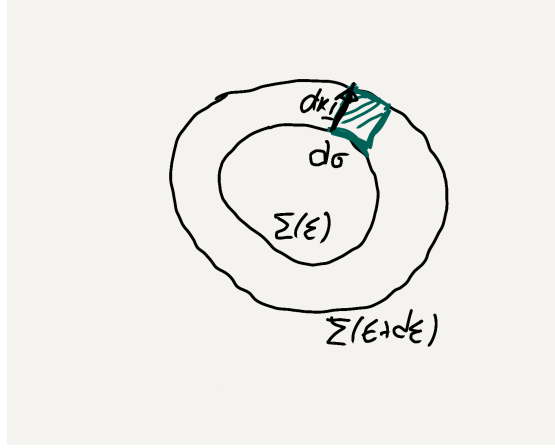


Figure 1: changing coordinates to integration over energy and constant energy surfaces

factor is telling, We know that in the degeneracy limit,  $k_B T \ll \epsilon_F$ ,  $(-\partial f / \partial \epsilon_{\mathbf{k}})$  is peaked about  $\epsilon_{\mathbf{k}} = \mu$ , with exponential decay for  $|\epsilon_{\mathbf{k}} - \mu| \gtrsim k_B T$  and with area 1

$$\int_{-\infty}^{+\infty} d\epsilon_{\mathbf{k}} \left( -\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}} \right) = f(+\infty) - f(-\infty) = 1 - 0 \quad (40)$$

and thus forms the basis of the Sommerfeld expansion. For a degenerate Fermi system, all the transport is then due to the states close to the Fermi surface: the expressions for the velocities, density of states and relaxation rates are only relevant close to the Fermi Surface. As with the specific heat or the Pauli susceptibility, transport is also a Fermi surface property.

To reduce to a convenient form for the Sommerfeld expansion we perform the  $\mathbf{k}$  integration by integrating over constant energy surfaces  $\Sigma(\epsilon)$  and energy

$$\int \frac{d^d k}{(2\pi)^d} (\dots) = \frac{1}{(2\pi)^d} \int dk_{\perp} \int_{\Sigma(k_{\perp})} d\sigma (\dots) \quad (41)$$

$$= \frac{1}{(2\pi)^d} \int d\epsilon \int_{\Sigma(\epsilon)} \frac{d\sigma}{|\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}|} (\dots) \quad (42)$$

$$\frac{1}{(2\pi)^d} \int d\epsilon \int_{\Sigma(\epsilon)} \frac{d\sigma}{\hbar |\mathbf{v}_{\mathbf{k}}|} (\dots) \quad (43)$$

and

$$L_n^{ij} := \int d\epsilon (\epsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \epsilon} \right) K^{ij}(\epsilon) \quad (44)$$

where

$$K^{ij}(\epsilon) := \frac{2}{(2\pi)^d} \int_{\Sigma(\epsilon)} \frac{d\sigma}{\hbar |\mathbf{v}_{\mathbf{k}}|} v_{\mathbf{k}}^i v_{\mathbf{k}}^j \tau_{\mathbf{k}} \quad (45)$$

In the Sommerfeld expansion of Eq.(44) we express the transport coefficients in  $K^{ij}(\epsilon)$  and its derivatives at the Fermi surface.

### 3.1.1. Low temperature properties

The Sommerfeld expansion is obtained by expanding  $K^{ij}(\epsilon)$  in a power series around  $\mu$ .

$$\begin{aligned} L_n^{ij} &:= \int d\epsilon (\epsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \epsilon} \right) K^{ij}(\epsilon) \\ &= \int d\epsilon (\epsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \epsilon} \right) \left[ K^{ij}(\mu) + \frac{dK^{ij}}{d\epsilon} \Big|_{\mu} (\epsilon - \mu) + \frac{1}{2} \frac{d^2 K^{ij}}{d\epsilon^2} \Big|_{\mu} (\epsilon - \mu)^2 + \dots \right] \end{aligned} \quad (46)$$

The integrals can be computed with the substitution  $x = \beta(\epsilon - \mu)$

$$\int d\epsilon (\epsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \epsilon} \right) = (k_B T)^n \int_{-\infty}^{+\infty} dx \frac{x^n e^x}{(e^x + 1)^2} = I_n (k_B T)^n \quad (47)$$

where the Fermi integrals

$$I_n = \begin{cases} 0 & n \text{ odd} \\ 1 & n = 0 \\ \frac{\pi^2}{3} & n = 2 \end{cases} \quad (48)$$

If we estimate a characteristic scale of  $K^{ij}(\epsilon)$  as  $W$ , which we take to be of order of the Fermi energy  $\epsilon_F$ , so that

$$\frac{dK^{ij}}{d\epsilon} \Big|_{\mu} \sim \mathcal{O} \left( \frac{K^{ij}}{W} \right) \quad (49)$$

$$\frac{d^2 K^{ij}}{d\epsilon^2} \sim \mathcal{O} \left( \frac{K^{ij}}{W^2} \right) \quad (50)$$

we see that the Sommerfeld expansion is a power series in the dimensionless parameter  $k_B T/W$ . Keeping the lowest order terms

$$L_0^{ij} = K^{ij}(\epsilon_F) \quad (51)$$

$$L_1^{ij} = \frac{\pi^2}{3} \frac{dK^{ij}}{d\epsilon} \Big|_{\epsilon_F} (k_B T)^2 \quad (52)$$

$$L_2^{ij} = \frac{\pi^2}{3} K^{ij}(\epsilon_F) (k_B T)^2 \quad (53)$$

Computing  $K^{ij}(\mu)$  requires knowledge of the details of the scattering mechanisms (to compute  $\tau$ ) but also of the band dispersion, which determines the domain of integration  $\Sigma(\epsilon)$  and the integrand that appears in  $K^{ij}$ . Rather simple results can be obtained for isotropic Fermi surfaces, though, where  $\mathbf{v}_k = v(\epsilon)\hat{\mathbf{k}}$ .



For  $d = 3$

$$\begin{aligned}
K^{ij}(\epsilon) &:= \frac{2}{(2\pi)^3} \int_{\Sigma(\epsilon)} \frac{d\sigma}{\hbar |\mathbf{v}_{\mathbf{k}}|} v_{\mathbf{k}}^i v_{\mathbf{k}}^j \tau_{\mathbf{k}} \\
&= \frac{1}{4\pi^3} \int \frac{k^2 d\Omega}{|\hbar v(\epsilon)|} v^2(\epsilon) \hat{k}^i \hat{k}^j \tau(\epsilon) \\
&= \frac{k^2(\epsilon) v(\epsilon) \tau(\epsilon)}{4\pi^3 \hbar} \int d\Omega \hat{k}^i \hat{k}^j
\end{aligned} \tag{54}$$

The angular integral is trivial

$$\int d\Omega \hat{k}^i \hat{k}^j = \frac{4\pi}{3} \delta_{ij} \tag{55}$$

so

$$K^{ij}(\epsilon) = \frac{k^2(\epsilon) v(\epsilon) \tau(\epsilon)}{3\pi^2 \hbar} \delta^{ij} \tag{56}$$

It is useful to express this in terms of the density of states

$$\rho(\epsilon) = \frac{1}{8\pi^3} \int_{\Sigma(\epsilon)} \frac{d\sigma}{\hbar |\mathbf{v}_{\mathbf{k}}|} = \frac{1}{2\pi^2} \frac{k^2(\epsilon)}{\hbar v(\epsilon)} \tag{57}$$

Defining the effective mass by

$$v(\epsilon) = \frac{\hbar k(\epsilon)}{m^*} \tag{58}$$

so

$$K(\epsilon) = \frac{2\rho(\epsilon) v^2(\epsilon) \tau(\epsilon)}{3} \tag{59}$$

With this result, for electron carriers  $q = -e$ ,

$$\begin{aligned}
\mathbf{j}_e &= e^2 K(\epsilon_F) \left( \mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu \right) + \frac{\pi^2}{3} (-e) K'(\epsilon_F) (k_B T)^2 \left[ \frac{-\nabla T}{T} \right] \\
\mathbf{j}_h &= \frac{\pi^2}{3} (-e) K'(\epsilon_F) (k_B T)^2 \left( \mathbf{E} - \frac{1}{q} \nabla_{\mathbf{r}} \mu \right) + \frac{\pi^2}{3} K(\epsilon_F) (k_B T)^2 \left[ \frac{-\nabla T}{T} \right]
\end{aligned}$$

From this expression we can obtain the electrical and thermal conductivities, and the thermo-electric coefficient.

**Drude conductivity** The definition of conductivity is

$$\mathbf{j}_e = \sigma \mathbf{E} \tag{60}$$

If we consider a sample at uniform temperature, our analysis gives

$$\mathbf{j}_e = e^2 K(\epsilon_F) \left( \mathbf{E} + \frac{1}{e} \nabla_{\mathbf{r}} \mu \right) \tag{61}$$

The extra term in  $e^{-1} \nabla_{\mathbf{r}} \mu$  is in fact expected because in an experimental situation the

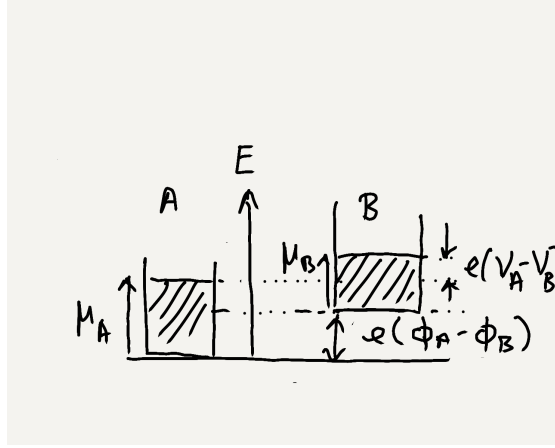


Figure 2: The energy drop when an electron travels from  $B$  to  $A$  (current flowing from  $A$  to  $B$ ) is  $e(V_A - V_B)$  equal to  $e(\phi_A - \phi_B) + \mu_B - \mu_A$  where  $\phi$  is the electric potential.

electric field that appears in the definition of the conductivity, we may call it  $\mathbf{E}_{obs}$ , is *not*  $-\nabla\phi$ , with  $\phi$  the electric potential. The reason is the following. If we are measuring a conductivity, with current flowing between two metallic electrodes, from  $A$  to  $B$ , and have a potential difference between  $V_A - V_B$ , the change in energy of an electron in moving between  $B$  and  $A$  is  $\Delta E = e(V_A - V_B) = e \int_A^B \mathbf{E}_{obs} \cdot d\mathbf{l}$ . But this change in energy is

$$\Delta E = e(\phi_A - \phi_B) + \mu_B - \mu_A \quad (62)$$

The electron moves from the Fermi level of  $B$  to the Fermi level at  $A$ . Hence the “electric field” that appears in Drude’s law is

$$e \int_A^B \mathbf{E}_{obs} \cdot d\mathbf{l} = e \int_A^B \left( -\nabla\phi + \frac{1}{e} \nabla_r \mu \right) \cdot d\mathbf{l} \quad (63)$$

$$\mathbf{E}_{obs} = \mathbf{E} + \frac{1}{e} \nabla_r \mu \quad (64)$$

In other words, the potential difference that we measure with a voltmeter includes a electric potential and a chemical potential term. So

$$\sigma = e^2 \frac{k_F^2 v_F \tau_F}{3\pi^2 \hbar} \quad (65)$$

$$= \frac{2e^2 \rho_F v_F^2 \tau_F}{3} \quad (66)$$

If we look at the first form of the expression and recall the definition of effective mass (also a Fermi surface property)

$$v_F = \frac{\hbar k_F}{m^*} \quad (67)$$

we obtain

$$\sigma = e^2 \frac{k_F^3}{3\pi^2} \frac{\tau_F}{m^*} \quad (68)$$

which is none other than Drude's classical result

$$\sigma_{Drude} = \frac{n_e e^2 \tau}{m^*}$$

since  $n_e = k_F^3/(3\pi^2)$  for an isotropic Fermi system. If the conductivity is determined entirely by Fermi surface terms how come it is expressed in the electronic density, as if all electrons participate in the current?

The explanation lies in the form of the solution of Boltzmann equation

$$\bar{\delta} f_{\mathbf{k}} = -e \left( -\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}} \right) \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}_{\tau F} \quad (69)$$

which can be regarded as the expansion of a shifted equilibrium distribution to first order in  $\mathbf{E}$ :

$$f_{\mathbf{k}} = f_{\mathbf{k}+e\mathbf{E}\tau_F/\hbar}^0 \approx f_{\mathbf{k}}^0 + \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} (\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}) \cdot e\mathbf{E}\tau_F/\hbar = f_{\mathbf{k}}^0 + e \frac{\partial f_{\mathbf{k}}^0}{\partial \epsilon_{\mathbf{k}}} \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}_{\tau F} \quad (70)$$

Hence, we can compute the current as

$$\mathbf{j}_e = -2e \int \frac{d^3 k}{(2\pi)^3} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}+e\mathbf{E}\tau_F/\hbar}^0 = -2e \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar \mathbf{k}}{m^*} f_{\mathbf{k}+e\mathbf{E}\tau_F/\hbar}^0 \quad (71)$$

Even though we have shifted the whole distribution, as long as  $eE\tau/\hbar \ll k_F$  only states near  $k_F$  see their occupation changed relative to the unshifted distribution. So it is permissible to use the result  $\mathbf{v}_{\mathbf{k}} = \hbar \mathbf{k}/m^*$  valid near the FS, with  $m^*$  is the FS effective mass. But now, a simple change of variable,

$$\begin{aligned} \mathbf{j}_e &= -2e \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar \mathbf{k} - e\mathbf{E}\tau_F}{m^*} f_{\mathbf{k}}^0 \\ &= \frac{e^2 \tau_F}{m^*} \mathbf{E} \times 2 \int \frac{d^3 k}{(2\pi)^3} f_{\mathbf{k}}^0 = \frac{e^2 \tau_F}{m^*} n_e \mathbf{E} \end{aligned} \quad (72)$$

because

$$\int \frac{d^3 k}{(2\pi)^3} \hbar \mathbf{k} f_{\mathbf{k}}^0 = 0 \quad (73)$$

and we re-obtain Drude's result.

### 3.1.2. The thermal conductivity

If  $\mathbf{j}_e = 0$

$$\mathbf{E}_{obs} = \frac{\pi^2}{3e} \frac{K'(\epsilon_F)}{K(\epsilon_F)} (k_B T)^2 \left[ \frac{-\nabla T}{T} \right] \quad (74)$$

This means that the thermo-electric coefficient,  $S$ , is

$$\mathbf{E}_{obs} = S\nabla T \quad (75)$$

$$S = -\frac{\pi^2}{3e} \frac{K'(\epsilon_F)}{K(\epsilon_F)} k_B^2 T \quad (76)$$

and the heat current

$$\mathbf{j}_h = -\left(\frac{\pi^2}{3}\right)^2 \frac{[K'(\epsilon_F)]^2}{K(\epsilon_F)} (k_B T)^4 \left(\frac{-\nabla T}{T}\right) + \frac{\pi^2}{3} K(\epsilon_F) (k_B T)^2 \left[\frac{-\nabla T}{T}\right] \quad (77)$$

The first term can be is smaller than the second by a factor of order

$$\frac{\pi^2}{3} \left[\frac{K'(\epsilon_F)}{K(\epsilon_F)}\right]^2 (k_B T)^2 \sim \left(\frac{k_B T}{W}\right)^2 \ll 1 \quad (78)$$

so we obtain for the thermal conductivity

$$\mathbf{j}_h = -\kappa \nabla T \quad (79)$$

$$\kappa = \frac{\pi^2}{3} K(\epsilon_F) k_B^2 T \quad (80)$$

and the famous Wiedemann-Franz Law

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2} = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2} \quad (81)$$

actually followed closely by several metals at low temperatures, when elastic scattering dominates. This constant is known as the Lorentz number.

### 3.2. Classical Hall Effect

The classical form of the Hall effect is relatively easy to obtain in the for an isotropic Fermi surface (FS). We assume that  $\tau_{\mathbf{k}}$  only depends on the energy (at least near the FS) and that

$$\mathbf{v}_{\mathbf{k}} = \frac{\hbar \mathbf{k}}{m^*} \quad (82)$$

With the magnetic field term, BE is

$$\left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \mathbf{v}_{\mathbf{k}} \cdot [-q\mathbf{E}] \tau_{\mathbf{k}} = -\overline{\delta f}_{\mathbf{k}} - \frac{q}{\hbar} \tau_{\mathbf{k}} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}} \overline{\delta f}_{\mathbf{k}} \quad (83)$$

It is still true that  $\overline{\delta f}_{\mathbf{k}}$  is only significant in the vicinity of the FS. Instead of solving this, let us compute the electric current directly

$$j_e^i = 2q^2 \int \frac{d^d k}{(2\pi)^d} v_{\mathbf{k}}^i \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) v_{\mathbf{k}}^j \tau_{\mathbf{k}} E^j - 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau_{\mathbf{k}} v_{\mathbf{k}}^i (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \frac{\partial}{\partial k^j} \overline{\delta f}_{\mathbf{k}} \quad (84)$$

If  $\tau_{\mathbf{k}}$  is a function of  $\epsilon_{\mathbf{k}}$  only, integrating by parts the second term, we get

$$\begin{aligned}
-2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau_{\mathbf{k}} v_{\mathbf{k}}^i (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \frac{\partial}{\partial k^j} \bar{\delta} f_{\mathbf{k}} &= 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \left[ \frac{\partial}{\partial k^j} \tau_{\mathbf{k}} v_{\mathbf{k}}^i (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \right] \bar{\delta} f_{\mathbf{k}} \\
&= 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \frac{\partial \tau_{\mathbf{k}}}{\partial \epsilon_{\mathbf{k}}} \hbar v_{\mathbf{k}}^j \left[ v_{\mathbf{k}}^i (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \right] \bar{\delta} f_{\mathbf{k}} \\
&\quad + 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau_{\mathbf{k}} \frac{\partial}{\partial k^j} \left[ v_{\mathbf{k}}^i (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \right] \bar{\delta} f_{\mathbf{k}} \quad (85)
\end{aligned}$$

The term of the second line is zero because it involves the factor  $\mathbf{v}_{\mathbf{k}} \cdot (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})$ . Also

$$\frac{\partial}{\partial k^j} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j = \nabla \cdot (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) = \mathbf{B} \cdot (\nabla \times \epsilon_{\mathbf{k}}) = 0 \quad (86)$$

because the curl of a gradient is zero. Therefore

$$\begin{aligned}
\mathbf{j}_e &= \sigma \mathbf{E} + 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau_{\mathbf{k}} \frac{\partial v_{\mathbf{k}}^i}{\partial k^j} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^j \bar{\delta} f_{\mathbf{k}} \\
&= \sigma \mathbf{E} + 2\frac{q^2}{\hbar} \int \frac{d^d k}{(2\pi)^d} \tau_{\mathbf{k}} \frac{\hbar}{m^*} (\mathbf{v}_{\mathbf{k}} \times \mathbf{B})^i \bar{\delta} f_{\mathbf{k}} \quad (87)
\end{aligned}$$

$$\mathbf{j}_e = \sigma \mathbf{E} + \frac{q\tau_F}{m^*} \mathbf{j}_e \times \mathbf{B} \quad (88)$$

which we can rewrite in the form

$$\mathbf{E} = \frac{1}{\sigma} \mathbf{j}_e + \frac{q\tau_F}{m^*\sigma} \mathbf{j}_e \times \mathbf{B} \quad (89)$$

For the Hall effect geometry,  $\mathbf{B} = B\hat{e}_z$ ,  $\mathbf{j}_e = j_e\hat{e}_x$ , we get

$$E_x = \frac{1}{\sigma} j_x + \frac{q\tau_F}{m^*\sigma} B j_y \quad (90)$$

$$E_y = \frac{1}{\sigma} j_y - \frac{q\tau_F}{m^*\sigma} B j_x \quad (91)$$

Note that the classical precession frequency of electron orbits is

$$\omega_c = \frac{eB}{m^*}$$

and so

$$E_x = \frac{1}{\sigma} j_x - \frac{\omega_c \tau_F}{\sigma} j_y \quad (92)$$

$$E_y = \frac{1}{\sigma} j_y + \frac{\omega_c \tau_F}{\sigma} j_x \quad (93)$$

$\sigma$  is given by the Drude's formula,

$$\sigma = \frac{ne^2}{m^*} \tau_F$$

and the resistivity tensor becomes

$$\rho_{xx} = \rho_{yy} = \frac{1}{\sigma} \quad (94)$$

$$\rho_{xy} = -\rho_{yx} = -\frac{B}{nq} \quad (95)$$

which is the classical Hall effect result.

## 4. Elastic scattering

The relaxation time approximation is a brutal simplification, and solving the Boltzmann equation without it can be a daunting task, often impossible to address analytically. These is, however, an important situation where the relaxation time approximation can be justified through a microscopic analysis of the collision integral. That is the case when all scattering events are elastic, in other words, the perfect crystal is perturbed by a static potential, created by impurities, vacancies, lattice defects, anything not endowed with dynamics.

Let us then assume that the perturbation induces electronic transitions from  $\mathbf{k} \rightarrow \mathbf{k}'$  with a certain probability rate in the form of Fermi's Golden rule,

$$\frac{1}{\Omega} \omega(\mathbf{k}', \mathbf{k}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}); \quad (96)$$

the rate of change of  $f_{\mathbf{k}}(\mathbf{r}, t)$  is

$$\left( \frac{\partial f_{\mathbf{k}}}{\partial t} \right)_{col} = -\frac{1}{\Omega} \sum_{\mathbf{k}'} [\omega(\mathbf{k}', \mathbf{k}) f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) - \omega(\mathbf{k}, \mathbf{k}') f_{\mathbf{k}'} (1 - f_{\mathbf{k}})] \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \quad (97)$$

where the occupation factors express the probability that the initial state is occupied and the final one empty. Since we expect

$$\omega(\mathbf{k}', \mathbf{k}) \propto |\langle \mathbf{k} | V | \mathbf{k}' \rangle|^2 = |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2$$

the collision integral can simplify to

$$\left( \frac{\partial f_{\mathbf{k}}}{\partial t} \right)_{col} = -\frac{1}{\Omega} \sum_{\mathbf{k}'} \omega(\mathbf{k}', \mathbf{k}) (f_{\mathbf{k}} - f_{\mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}).$$

As  $f_{\mathbf{k}}^0$  and  $\delta f_{\mathbf{k}}^{le}$  only depend on  $\mathbf{k}$  through the energy  $\epsilon_{\mathbf{k}}$ , we can make the replacement

$$(f_{\mathbf{k}} - f_{\mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \rightarrow (\delta \bar{f}_{\mathbf{k}} - \delta \bar{f}_{\mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \quad (98)$$

and the collision integral becomes

$$I_{\mathbf{k}} [\delta f] = \frac{1}{\Omega} \sum_{\mathbf{k}'} \omega(\mathbf{k}', \mathbf{k}) (\delta \bar{f}_{\mathbf{k}} - \delta \bar{f}_{\mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}). \quad (99)$$

Recall the form of BE, without magnetic field

$$\left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \mathbf{v}_{\mathbf{k}} \cdot \mathbf{D}_{\mathbf{k}}(\mathbf{r}, t) = I_{\mathbf{k}} [\overline{\delta f}] \quad (100)$$

Solving BE is finding the function  $\overline{\delta f}$  that satisfies this equation. The LHS is zero away from the Fermi surface, so for  $|\epsilon_{\mathbf{k}} - \epsilon_F| \gg k_B T$ ,  $\delta f_{\mathbf{k}} = 0$  does solve the equation. In other words, in the collision integral we can assume that  $\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}'} \sim \epsilon_F$ . Now suppose that the dispersion relation is isotropic near the Fermi level (spherical Fermi surface) and the scattering rate between two  $\mathbf{k}$  values at the Fermi surface depends only on the angle between them,

$$\omega(\mathbf{k}', \mathbf{k}) = \omega(k_F, \theta_{\mathbf{k}, \mathbf{k}'}) \quad (101)$$

Also the isotropy of the Fermi surface allows us to write

$$\mathbf{v}_{\mathbf{k}} = v_F \hat{\mathbf{k}}, \quad (k \sim k_F) \quad (102)$$

The driving field  $\mathbf{D}_{\mathbf{k}}$  only depends on the modulus of  $\mathbf{k}$ ,  $\mathbf{D}_{\mathbf{k}} \rightarrow \mathbf{D}_k$  and,  $\delta f_{\mathbf{k}}$  can only depend on the angle of  $\mathbf{k}$  and  $\mathbf{D}_k$ . The following Ansatz is easily seen to solve BE

$$\delta \overline{f}_{\mathbf{k}} = - \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \eta(\epsilon_{\mathbf{k}}) \hat{\mathbf{k}} \cdot \mathbf{D} \quad (103)$$

By inserting it in the collision integral and taking into account that the delta function imposes  $\epsilon_{\mathbf{k}'} = \epsilon_{\mathbf{k}}$ ,

$$I_{\mathbf{k}} [\overline{\delta f}] = \left[ \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \eta(\epsilon_{\mathbf{k}}) \mathbf{D}_k \right] \cdot \left[ \frac{1}{\Omega} \sum_{\mathbf{k}'} \omega(k_F, \theta_{\mathbf{k}, \mathbf{k}'}) (\hat{\mathbf{k}} - \hat{\mathbf{k}}') \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \right]$$

We can write

$$\hat{\mathbf{k}}' = (\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') \hat{\mathbf{k}} + \mathbf{q}_{\perp} = \hat{\mathbf{k}} \cos \theta_{\mathbf{k}, \mathbf{k}'} + \mathbf{q}_{\perp} \quad (104)$$

with  $\mathbf{q}_{\perp} \cdot \hat{\mathbf{k}} = 0$ . Using  $\hat{\mathbf{k}}$  as the  $Oz$  axis in the integral over  $\mathbf{k}'$

$$\mathbf{q}_{\perp} = \sin \theta_{\mathbf{k}, \mathbf{k}'} (\cos \varphi_{\mathbf{k}'}, \sin \varphi_{\mathbf{k}'}, 0). \quad (105)$$

The angular integral of the  $\mathbf{q}_{\perp}$  term over  $\varphi_{\mathbf{k}'}$  yields zero because the scattering rate only depends on  $\theta_{\mathbf{k}, \mathbf{k}'}$ . Hence

$$\begin{aligned} I_{\mathbf{k}} [\overline{\delta f}] &= \left[ \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \eta(\epsilon_{\mathbf{k}}) \mathbf{D}_k \cdot \hat{\mathbf{k}} \right] \times \frac{1}{\Omega} \sum_{\mathbf{k}'} \omega(k_F, \theta_{\mathbf{k}, \mathbf{k}'}) (1 - \cos \theta_{\mathbf{k}, \mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \\ &= \left[ \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \eta(\epsilon_{\mathbf{k}}) \mathbf{D}_k \cdot \hat{\mathbf{k}} \right] \frac{1}{\tau_{tr}} \end{aligned} \quad (106)$$

$$= -\frac{\delta \overline{f}_{\mathbf{k}}}{\tau_{tr}} \quad (107)$$

exactly as hypothesised in the relaxation time approximation, with

$$\begin{aligned}\frac{1}{\tau_{tr}} &:= \frac{1}{\Omega} \sum_{\mathbf{k}'} \omega(k_F, \theta_{\mathbf{k}, \mathbf{k}'}) (1 - \cos \theta_{\mathbf{k}, \mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}}) \\ &= \int \frac{d^3k}{(2\pi)^3} \omega(k_F, \theta_{\mathbf{k}, \mathbf{k}'}) (1 - \cos \theta_{\mathbf{k}, \mathbf{k}'}) \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}})\end{aligned}\quad (108)$$

Comparing with the driving term

$$\left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \mathbf{v}_{\mathbf{k}} \cdot \mathbf{D}_{\mathbf{k}}(\mathbf{r}, t) = \left[\left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \eta(\epsilon_{\mathbf{k}}) \mathbf{D}_{\mathbf{k}} \cdot \hat{\mathbf{k}}\right] \frac{1}{\tau_{tr}} \quad (109)$$

we get

$$\eta(\epsilon_{\mathbf{k}}) = v_F \tau_{tr}$$

and

$$\delta \bar{f}_{\mathbf{k}} = - \left(-\frac{\partial f^0}{\partial \epsilon_{\mathbf{k}}}\right) \mathbf{v}_{\mathbf{k}} \cdot \mathbf{D}_{\mathbf{k}} \tau_{tr}$$

is the solution of BE, exactly in the form of the relaxation rate approximation, now with an explicit expression for the elastic transport time, namely, Eq.(108).

Although we solved BE without magnetic field, the derivation of the classical Hall effect, presented in section (3.2) is still valid because all it used is the form of the collision integral of Eq.(107).

## A. Liouville's Theorem in semi-classical dynamics

In deriving BE we assumed

$$\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} + \nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}} = 0 \quad (110)$$

This is true only if  $\mathbf{r}$  and  $\mathbf{k}$  are canonically conjugate, obeying Hamilton's equations of motion. With the semi-classical equations of motion this is not true. In the following we calculate this term with liberal use use the identity

$$\nabla \times (\mathbf{A} \times \mathbf{B}) = (\mathbf{B} \cdot \nabla) \mathbf{A} + (\nabla \cdot \mathbf{B}) \mathbf{A} - (\mathbf{A} \cdot \nabla) \mathbf{B} + (\nabla \cdot \mathbf{A}) \mathbf{B} \quad (111)$$

$$\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} = -\nabla_{\mathbf{r}} \cdot \dot{\mathbf{k}} \times \boldsymbol{\omega}(\mathbf{k}) = -\boldsymbol{\omega}(\mathbf{k}) \cdot (\nabla_{\mathbf{r}} \times \dot{\mathbf{k}}) \quad (112)$$

$$\nabla_{\mathbf{k}} \dot{\mathbf{k}} = \frac{q}{\hbar} \nabla_{\mathbf{k}} \cdot (\mathbf{v}_{\mathbf{k}} \times \mathbf{B}) = \frac{q}{\hbar} \mathbf{B} \cdot (\nabla_{\mathbf{k}} \times \mathbf{v}_{\mathbf{k}}) \quad (113)$$

Using the equation of motion

$$\dot{\mathbf{r}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon(\mathbf{k}) - \dot{\mathbf{k}} \times \boldsymbol{\omega}(\mathbf{k}) \quad (114)$$

$$\hbar \dot{\mathbf{k}} = q(\mathbf{E} + \dot{\mathbf{r}} \times \mathbf{B}) \quad (115)$$



$$\begin{aligned}
\nabla_{\mathbf{r}} \times \dot{\mathbf{k}} &= \frac{q}{\hbar} [\nabla_{\mathbf{r}} \times \mathbf{E} + \nabla_{\mathbf{r}} \times (\dot{\mathbf{r}} \times \mathbf{B})] \\
&= \frac{q}{\hbar} \left[ -\frac{\partial \mathbf{B}}{\partial t} + (\mathbf{B} \cdot \nabla_{\mathbf{r}}) \dot{\mathbf{r}} + (\nabla_{\mathbf{r}} \cdot \mathbf{B}) \dot{\mathbf{r}} - (\dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}}) \mathbf{B} - (\nabla_{\mathbf{r}} \dot{\mathbf{r}}) \mathbf{B} \right] \\
&= \frac{q}{\hbar} \left[ -\frac{d\mathbf{B}}{dt} - \mathbf{B}(\nabla_{\mathbf{r}} \dot{\mathbf{r}}) + (\mathbf{B} \cdot \nabla_{\mathbf{r}}) \dot{\mathbf{r}} \right]
\end{aligned} \tag{116}$$

and

$$\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} = -\frac{q}{\hbar} \left[ -\frac{d\mathbf{B}}{dt} \cdot \boldsymbol{\omega}(\mathbf{k}) - \mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k}) (\nabla_{\mathbf{r}} \dot{\mathbf{r}}) - \mathbf{B}(\mathbf{B} \cdot \nabla_{\mathbf{r}}) \dot{\mathbf{r}} \cdot \boldsymbol{\omega}(\mathbf{k}) \right] \tag{117}$$

The divergence of a curl,  $\mathbf{B}$ , is zero; the last term is also zero because the anomalous velocity term is orthogonal to the Berry curvature;

$$\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} \left( 1 - \frac{q}{\hbar} \mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k}) \right) = \frac{q}{\hbar} \frac{d\mathbf{B}}{dt} \cdot \boldsymbol{\omega}(\mathbf{k}) \tag{118}$$

Now we consider the second term. Not surprisingly it will have a similar structure:

$$\begin{aligned}
\nabla_{\mathbf{k}} \times \mathbf{v}_{\mathbf{k}} &= -\nabla_{\mathbf{k}} \times [\dot{\mathbf{k}} \times \boldsymbol{\omega}(\mathbf{k})] = -\left[ (\boldsymbol{\omega}(\mathbf{k}) \cdot \nabla_{\mathbf{k}}) \dot{\mathbf{k}} + (\nabla_{\mathbf{k}} \cdot \boldsymbol{\omega}(\mathbf{k})) \dot{\mathbf{k}} - (\dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}}) \boldsymbol{\omega}(\mathbf{k}) - (\nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}}) \boldsymbol{\omega}(\mathbf{k}) \right] \\
&= -\left[ -\frac{d}{dt} \boldsymbol{\omega}(\mathbf{k}) - (\nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}}) \boldsymbol{\omega}(\mathbf{k}) + (\boldsymbol{\omega}(\mathbf{k}) \cdot \nabla_{\mathbf{k}}) \dot{\mathbf{k}} \right]
\end{aligned} \tag{119}$$

and

$$\begin{aligned}
\nabla_{\mathbf{k}} \dot{\mathbf{k}} &= \frac{q}{\hbar} \left[ \mathbf{B} \cdot \frac{d}{dt} \boldsymbol{\omega}(\mathbf{k}) + (\nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}}) \boldsymbol{\omega}(\mathbf{k}) - (\boldsymbol{\omega}(\mathbf{k}) \cdot \nabla_{\mathbf{k}}) \dot{\mathbf{k}} \cdot \mathbf{B} \right] \\
\nabla_{\mathbf{k}} \dot{\mathbf{k}} \left( 1 - \frac{q}{\hbar} \mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k}) \right) &= \frac{q}{\hbar} \mathbf{B} \cdot \frac{d}{dt} \boldsymbol{\omega}(\mathbf{k})
\end{aligned} \tag{120}$$

So the final result is

$$(\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} + \nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}}) \left( 1 - \frac{q}{\hbar} \mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k}) \right) = \frac{q}{\hbar} \frac{d}{dt} [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})] \tag{121}$$

which we can write as a total time derivative

$$(\nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} + \nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}}) := -\frac{d}{dt} \ln \left[ 1 - \frac{q}{\hbar} [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})] \right] \tag{122}$$

The LHS is the divergence of the velocity field in phase space. This results expresses the violation of Liouville's theorem: the volume of phase space is not conserved in evolution. In general for a velocity field  $\mathbf{v}(\mathbf{q})$  we have

$$\frac{d}{dt} \int_{V(t)} d^d q = \int_{\partial V} d\sigma \hat{\mathbf{n}} \cdot \mathbf{v} = \int_{V(t)} d^d q \nabla_{\mathbf{q}} \cdot \mathbf{v}; \tag{123}$$

for a infinitesimal volume

$$\frac{d}{dt} \Delta V = \nabla_{\mathbf{q}} \cdot \mathbf{v} \Delta V \tag{124}$$

or

$$\frac{d}{dt} \ln \Delta V = \nabla_{\mathbf{q}} \cdot \mathbf{v} \quad (125)$$

In our case this becomes

$$\frac{d}{dt} \ln \Delta V = -\frac{d}{dt} \ln \left[ 1 - \frac{q}{\hbar} [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})] \right] \quad (126)$$

or

$$\Delta V \left( 1 - \frac{q}{\hbar} [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})] \right) = \text{const.} \quad (127)$$

This result is presented in Xiao et. al. [4] where it is stated that the correct way to compute averages in the semi-classical limit is to use the invariant phase space volume element

$$\frac{d^d k}{(2\pi)^d} d^d r \left( 1 - \frac{q}{\hbar} [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})] \right) \quad (128)$$

Why should this be so? The number of states is invariant under unitary quantum evolution. In a semi-classical approach, a given cell in phase space should contain a certain number of states. Under evolution by the equations of motion the number of states should not change. If, under time evolution the volume element  $d^d r d^d k / (2\pi)^d$  changes, this means that the density of quantum states is not constant in  $\mathbf{r}, \mathbf{k}$  space. But the measure of Eq.(128) is invariant. This implies that the density of states per unit  $k$  and  $r$  volumes is  $D(\mathbf{k}, \mathbf{r}) / (2\pi)^d$  with

$$D(\mathbf{k}, \mathbf{r}) := (1 - (q/\hbar) [\mathbf{B} \cdot \boldsymbol{\omega}(\mathbf{k})]) . \quad (129)$$

Therefore, the mean density of carriers in  $\mathbf{r}, \mathbf{k}$  space is

$$\rho(\mathbf{k}, \mathbf{r}, t) := D(\mathbf{k}, \mathbf{r}) f(\mathbf{k}, \mathbf{r}, t) \quad (130)$$

where  $f(\mathbf{k}, \mathbf{r}, t)$  is the mean occupation of state  $\mathbf{k}, \mathbf{r}$ . It is  $\rho(\mathbf{k}, \mathbf{r}, t)$  that satisfies a continuity equation

$$\begin{aligned} \frac{\partial}{\partial t} D(\mathbf{k}, \mathbf{r}) f(\mathbf{k}, \mathbf{r}, t) &= -\nabla_{\mathbf{r}} (\mathbf{v}_{\mathbf{k}} D f) - \nabla_{\mathbf{k}} (\dot{\mathbf{k}} D f) \\ &= \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} D f - \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} D f - \left( \nabla_{\mathbf{r}} \cdot \dot{\mathbf{r}} + \nabla_{\mathbf{k}} \cdot \dot{\mathbf{k}} \right) D f \\ &= \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} D f - \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} D f + \left( \frac{d}{dt} D \right) f \end{aligned} \quad (131)$$

The total derivative of  $D(\mathbf{k}, \mathbf{r})$  is

$$\frac{d}{dt} D(\mathbf{k}, \mathbf{r}) = \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} D + \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} D \quad (132)$$

so the result is

$$\frac{\partial}{\partial t} D(\mathbf{k}, \mathbf{r}) f(\mathbf{k}, \mathbf{r}, t) = D(\mathbf{k}, \mathbf{r}) \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) = -D \left[ \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f \right] \quad (133)$$

$$\frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{r}, t) = - \left[ \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f(\mathbf{k}, \mathbf{r}, t) + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) \right] \quad (134)$$

The BE is unchanged for  $f(\mathbf{k}, \mathbf{r}, t)$ . It merely states that, with drift terms only,

$$\frac{df(\mathbf{k}, \mathbf{r}, t)}{dt} = 0 \quad (135)$$

as expected for the mean occupation of a quantum state. The BE equation does not change, but it is  $\rho(\mathbf{k}, \mathbf{r}, t)$  that satisfies a continuity equation. The current expression should involve a sum over all states and therefore should be

$$\mathbf{j} = \int \frac{d^d k}{(2\pi)^d} d^d r D(\mathbf{k}, \mathbf{r}) \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} \quad (136)$$

## B. Anomalous Hall effect in 2D materials

There is a very important consequence of the existence of the Berry Curvature in 2D system. In that case both  $\mathbf{r}$  and  $\mathbf{k}$  are 2D vectors and we can keep the form of the equations of motion by interpreting

$$\boldsymbol{\omega}(\mathbf{k}) = \left( \frac{\partial \xi^y}{\partial k^y} - \frac{\partial \xi^x}{\partial k^x} \right) \hat{\mathbf{e}}_z \quad (137)$$

and it follows for  $\mathbf{B} = 0$

$$\begin{aligned} \mathbf{v}_{\mathbf{k}} &= \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} + \frac{e}{\hbar} \mathbf{E} \times \boldsymbol{\omega}(\mathbf{k}) \\ &= \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} + \frac{e}{\hbar} \boldsymbol{\omega}(\mathbf{k}) (\mathbf{E} \times \hat{\mathbf{e}}_z) \end{aligned} \quad (138)$$

For a single band

$$\mathbf{j}_e = 2 \times (-e) \int \frac{d^2 k}{4\pi^2} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} = -\frac{2e^2}{\hbar} \left[ \int \frac{d^2 k}{4\pi^2} \boldsymbol{\omega}(\mathbf{k}) f_{\mathbf{k}} \right] (\mathbf{E} \times \hat{\mathbf{e}}_z) \quad (139)$$

This expression identifies a Hall conductance

$$j_x = \sigma_{xy} E_y \quad (140)$$

as

$$\sigma_{xy} := -\frac{2e^2}{\hbar} \left[ \int \frac{d^2 k}{4\pi^2} \boldsymbol{\omega}(\mathbf{k}) f_{\mathbf{k}} \right] \quad (141)$$

This is a possible mechanism for the existence of a Hall effect in the absence of a magnetic field, the so called Anomalous Hall effect (AHE). There are, however other possible mechanisms [2], although in many materials this appears to be the dominant one [4]. But a very important case occurs when the system is an insulator. In that case we have a filled band,  $f_{\mathbf{k}} = 1$ , and the equation of motion of the Bloch momentum does not change the equilibrium distribution. It follows that

$$\sigma_{xy} := -\frac{2e^2}{\hbar} \left[ \int \frac{d^2 k}{4\pi^2} \boldsymbol{\omega}(\mathbf{k}) \right] = -\frac{2e^2}{h} c_n \quad (142)$$

where

$$c_n := \int \frac{d^2k}{2\pi} \omega(\mathbf{k})$$

is called the Band Chern number and can be proven to be an *integer*, a topological invariant of the band structure. Haldane provided the first example of a model with non-zero Chern number giving a quantized Hall effect in the absence of a magnetic field[1].

Curiously, the quantized Hall effect in a 2D electron system in the presence of a strong magnetic field can be understood under the same principle, if we consider the generalization of the semi-classical equations of motion to magnetic Bloch bands. When the magnetic field is commensurate with the lattice, Bloch's theorem still applies, but the semi-classical equations of motion in magnetic Bloch bands *do not include this field*. Therefore Eq.(142) still applies. This account of the quantized Hall conductivity in terms of the Chern number of the magnetic Bloch Bands is the main result of the famous Thouless, Kohmoto, Nightingale and den Nijs, the TKNN result [3]. It was obtained from a full quantum mechanical calculation, though, without reference to a semi-classical approach.

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