



## Chapter 5 Semi-classical treatment of electrical transport

The electric transport is a response to external perturbations as important as the optical response. Treatment of non-equilibrium to some extent is inevitable for the discussion of transport. A big difference between the electric transport and the optical response is, however, in the former the characteristic energy scale is much smaller than that in the latter ( $\sim E_g$ ). In this chapter, we have a brief look at very basic part of the transport in the linear response regime, in semi-classical treatment. We will go into the quantum transport in the later chapters.

### 5.1 Classical transport phenomena

Among transport phenomena interests of physicist mainly lies in quantum transport such as the quantum Hall effect. In earth-flooding semiconductor devices, however, dominant is the classical transport <sup>\*1</sup>.

The reason that the classical theories are applicable to transport in semiconductors at room temperatures mainly lies in the low density of carriers. In bulk transport, for example, the Fermi level  $E_F$  lies in band-gap, that is, there is no density of states around  $E_F$ . When we are looking at the energy distribution of electrons, what we actually see is the tail of the Fermi distribution function, which can be approximated with Maxwellian.

Heavy doping changes semiconductors into disordered metals, or spatial modulation of materials which shift the positions of Fermi levels above the conduction band edges provide low-dimensional metallic systems. Even in many of such systems, classical approximations hold around room temperatures. The Fermi degeneration temperature for a system with density  $n$  and particle mass  $m$  is

$$T_F = \frac{\hbar^2}{2mk_B} (3\pi^2 n)^{2/3} \quad :3D, \quad \frac{\hbar^2}{16\pi mk_B} n \quad :2D. \quad (5.1)$$

Substitution of typical values for semiconductors give, *e.g.* for a two-dimensional electron system, which has comparatively large Fermi energy, about 70K for  $T_F$ . That is, the distribution of kinetic energy is still described by a Maxwellian. Furthermore, the width of distribution is as large as the Fermi energy making the quantum mechanical interference effect obscure. In this chapter we thus concentrate on the phenomena, which can be described within classical theories for electron kinematics in solids.

#### 5.1.1 Transport phenomena and transport coefficient

“Transport” here means transportation of some physical quantity in real space. In the treatment of such a problem, we often map the problem onto a set of particles and the transport is transfer of the particles in the model. For example, consider a stretched string and some local shift from the stretched line. The shift is transmitted on the string as a wave but we can also treat the shift as a particle, which brings some potential energy. We may consider, then, the transport of the

<sup>\*1</sup> In many devices quantum confinement is working and low-dimensional systems are realized though the transport can be understood within classical theories.

shift. In solids, we actually have various elementary excitations such as phonons, spin-waves (magnons), etc. In electric conduction, which is a representative transport in semiconductors, the physical quantity is charge and a particle bringing it is called a “carrier”. Examples are, of course, electrons and holes, many-body states of band electrons actually.

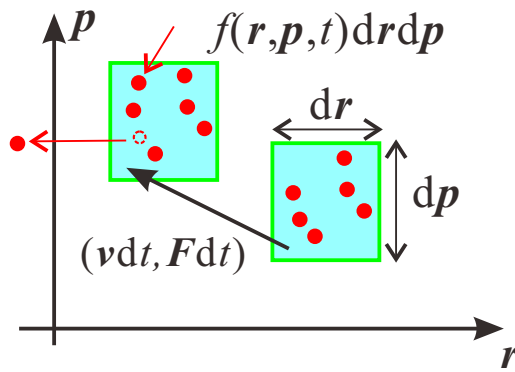
Needless to say, we first need to exclude trivial motion of the center of mass due to arbitrary selection of inertial system. We thus assume that the center of mass for the system under consideration sits still in equilibrium without perturbation. Transport is a response flow of some physical quantity to an external perturbation.<sup>\*2</sup> In the case of linear response, like electric current for voltage in Ohm law, the coefficient is called **transport coefficient**.

We often have strongly non-linear response in electric transport in semiconductors though we begin with linear response. As a typical example, in the electric current response to the field, the linear response between the current density  $\mathbf{j}$  and the field  $\mathbf{E}$  is written as

$$\mathbf{j} = \boldsymbol{\sigma}\mathbf{E}, \quad \mathbf{E} = \boldsymbol{\rho}\mathbf{j} = \boldsymbol{\sigma}^{-1}\mathbf{j}, \quad (5.2)$$

where  $\boldsymbol{\sigma}$  is the **conductivity tensor**,  $\boldsymbol{\rho}$  is the **resistivity tensor**. These two are inverse tensor to each other.

### 5.1.2 Boltzmann equation



**Fig. 5.1** Illustration of time evolution for particles in an infinitesimal volume  $dr dp$  in an infinitesimal time  $dt$  with a scattering.

Let us consider a distribution function  $f(\mathbf{r}, \mathbf{p}, t)$  in a six-dimensional space of spatial coordinate  $\mathbf{r}$  and momentum  $\mathbf{p}$ , *i.e.*, a phase space. The meaning of  $f$  is that the ratio of particles in the volume  $dr dp$  around the point  $(\mathbf{r}, \mathbf{p})$  in the whole system is  $f(\mathbf{r}, \mathbf{p}, t) dr dp$ .

In the absence of scattering, the classical equation of motion is described as

$$d\mathbf{r}/dt = \mathbf{v} = \mathbf{p}/m^*, \quad d\mathbf{p}/dt = \mathbf{F}, \quad (5.3)$$

with  $\mathbf{F}$  as the force working on the particle. Kinematic states of particles in  $dr dp$  are the same in the first order and so are the time evolution during  $dt$ , giving

$$f(\mathbf{r} + \mathbf{v}dt, \mathbf{p} + \mathbf{F}dt, t + dt) = f(\mathbf{r}, \mathbf{p}, t).$$

Some scatterings bring shifts in  $f$  as illustrated in Fig. 5.1. We write the coefficient in the shifts as  $(\partial f/\partial t)_c$ , that is,

$$f(\mathbf{r} + (\mathbf{p}/m^*)dt, \mathbf{p} + \mathbf{F}dt, t + dt) + (\partial f/\partial t)_c dt = f(\mathbf{r}, \mathbf{p}, t).$$

Expanding  $f$  in the left hand side to the first order, we get

**Boltzmann equation**

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m^*} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = - \left( \frac{\partial f}{\partial t} \right)_c \quad (5.4)$$

Equation (5.4) is called **Boltzmann equation**, and the right hand side is called the collision term.

<sup>\*2</sup> This definition cannot include supercurrent or diamagnetic current at edge states of quantum Hall effect. But we usually include them into transport phenomena taking the reference of coordinate to crystal lattices.

The collision term depends on the scattering mechanism and the nature of scattering centers and is generally difficult for us to calculate. The simplest approximation of this term is the constant relaxation time approximation, in which we consider a relaxation time  $\tau$  independent of energy and put

Constant relaxation time approximation

$$-\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f - f_0}{\tau}, \quad (5.5)$$

where  $f_0$  is the equilibrium distribution function for  $\mathbf{F} = \mathbf{0}$ ,  $\tau$ , the relaxation time, is the time for recovery from non-equilibrium states. In spatially uniform systems,  $\partial f / \partial \mathbf{r} = \mathbf{0}$ , and the approximation (5.5) can be generalized to the one with energy or momentum dependence in  $\tau$ .

Below, to avoid trivial failure in pure classical pictures, we use some quantum mechanical relation like  $\mathbf{p} = \hbar \mathbf{k}$  or quantum statistics.

### 5.1.3 Drift current, diffusion current

As currents we here consider electric currents. Net particle flow appears when the distribution function  $f$  gets some anisotropy in  $\mathbf{p}$  space. Hence we need to consider perturbations in (5.4) other than anisotropy or non-uniformity in  $\mathbf{p}$ . The candidates are then  $\mathbf{F} (= -e\mathbf{E})$ , and  $\partial / \partial \mathbf{r}$ . The former perturbation, *e.g.* acceleration by external electric field, brings about non-uniformity of distribution function  $f(\mathbf{r}, \hbar \mathbf{k}, t)$  in  $\mathbf{k}$ -space resulting in the flow of carriers in the real space. That kind of flow is called **drift current**. The latter is non-uniformity of the distribution in the real space and also causes carrier transport, which is called **diffusion current**.

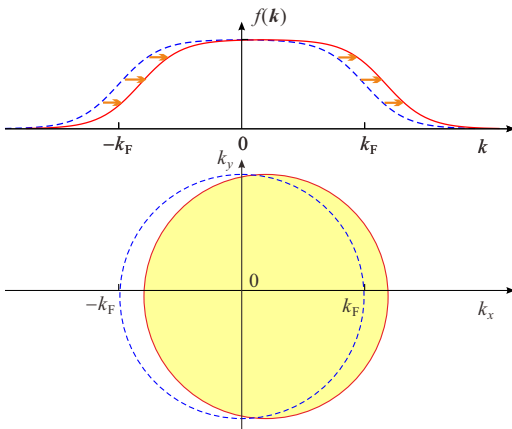
First let us consider a steady uniform electron system under uniform electric field  $\mathbf{E}$ . From this assumption,  $\partial f / \partial t = 0$  (steady) and  $\partial f / \partial \mathbf{r} = 0$  (uniform). We further assume  $\tau$  only depends on  $\mathbf{p}$ . Then eq.(5.4) becomes

$$-e\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f_0}{\tau(\mathbf{p})} \quad \therefore f(\mathbf{p}) = f_0(\mathbf{p}) + e\tau(\mathbf{p})\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}}.$$

In the next step of approximation, we take  $\mathbf{E}$  as a small perturbation. Hence, the 1st order expansion is obtained with replacing  $f$  in the right hand side with  $f_0$  as

$$f(\mathbf{p}) \simeq f_0(\mathbf{p}) + e\tau(\mathbf{p})\mathbf{E} \cdot (\partial f_0 / \partial \mathbf{p}). \quad (5.6)$$

Higher order terms can be obtained by successive replacements. Now eq.(5.6) can be viewed as the first order expansion of  $f(\mathbf{p}) \simeq f_0(\mathbf{p} + e\tau(\mathbf{p})\mathbf{E})$  with  $\mathbf{E}$ , which means this  $f(\mathbf{p})$  is the one shifted by  $-e\tau(\mathbf{p})\mathbf{E}$  in  $\mathbf{p}$  space from  $f_0(\mathbf{p})$ . If  $\tau$  is constant for  $\mathbf{p}$ , the shift is uniform as illustrated in Fig. 5.2.



**Fig. 5.2** Schematic view for constant shift of Fermi sphere of electrons under acceleration by external electric field in the space of wavenumber. The distribution  $f(\mathbf{k})$  shifts from the equilibrium position (indicated by broken line) by a wavevector indicated by small arrows. The upper shows the shift in the distribution and the lower shows the shift of Fermi sphere in two-dimensional systems. In realistic systems, the shifts are much smaller than that illustrated here.

We need to integrate  $\mathbf{v}(\mathbf{k})f(\mathbf{k})$  in  $\mathbf{k}$  space to obtain the current. Without losing generality we take  $\mathbf{E} = (\mathcal{E}_x, 0, 0)$  and erasing integrals of odd functions we obtain

$$\int \frac{d^3k}{(2\pi)^3} \mathbf{v}(\mathbf{k}) \left( f_0 + e\tau \mathbf{E} \cdot \frac{\partial f_0}{\hbar \partial \mathbf{k}} \right) = \int \frac{d^3k}{(2\pi)^3} \frac{\hbar k_x}{m} e\tau \mathcal{E}_x \frac{\partial f_0}{\hbar \partial k_x} = \frac{e\mathcal{E}_x}{m} \int \mathcal{D}(E) \tau(E) \frac{\hbar^2 k_x^2}{m} \frac{\partial f_0}{\partial E} dE, \quad (5.7)$$

where we assume  $\tau$  depends only on energy.  $\hbar^2 k_x^2/2m$ , the kinetic energy along  $x$ -direction is  $E/3$  from the equipartition condition.

For a metallic Fermi-degenerated system,  $\partial f_0/\partial E$  can be approximated as  $-\delta(E - E_F)$  in (5.7). For a three-dimensional system the density of states is  $\mathcal{D}(E) = A\sqrt{E}$  with a coefficient  $A$ , then (5.7) is

$$\langle v_x \rangle = -A \frac{e\mathcal{E}_x}{m} \frac{2\tau(E_F)}{3} E_F^{3/2},$$

while the particle density is calculated as

$$n = \int_0^{E_F} \mathcal{D}(E) dE = A \frac{2}{3} E_F^{3/2}.$$

Putting together the above expressions we obtain the expression for  $\sigma = j/E = -e\langle v_x \rangle/\mathcal{E}_x$  as

Drude conductivity

$$\sigma = \frac{e^2 n \tau(E_F)}{m} \quad (5.8)$$

which is well known **Drude conductivity**.

When the temperature is high, or the particle density is low and the Maxwellian approximation holds, from  $f_0 \approx A \exp(-E/k_B T)$ ,

$$-\frac{\partial f_0}{\partial E} = -\frac{A}{k_B T} \exp\left[-\frac{E}{k_B T}\right] = -\frac{f_0}{k_B T} = -\frac{f_0}{(2\langle E \rangle/3n)}$$

is obtained, in the last equation of which we have used averaged kinetic energy  $k_B T/2$  for single kinetic degree of freedom. The electric conductivity is again given in the Drude form as

$$\sigma = e^2 \int \tau(E) \mathcal{D}(E) \frac{2E}{3m} \frac{3n f_0}{2\langle E \rangle} dE = \frac{n e^2 \langle \tau \rangle_E}{m}. \quad (5.9)$$

Here,  $\langle \tau \rangle_E$  represents the average with weight  $E^{3/2}$ :

$$\langle \tau \rangle_E = \frac{\langle \tau E \rangle}{\langle E \rangle} = \frac{\int_0^\infty \tau(E) E^{3/2} f_0 dE}{\int_0^\infty E^{3/2} f_0 dE}. \quad (5.10)$$

We then proceed to the diffusion current caused by non-uniformity of  $f$  in real space. In Boltzmann equation (5.4),  $\mathbf{F}$  is set to zero and constant relaxation time approximation (5.5) is applied to the space distribution of  $f = f_0 + f_1$  as

$$\mathbf{v} \cdot \nabla f = -f_1/\tau, \quad \text{take to the first order of } f_1 \quad f_1 = -\tau \mathbf{v} \cdot \nabla f_0. \quad (5.11)$$

When a constant diffusion current  $\mathbf{J}$  is flowing through a spatial volume  $V$ , it is written as

$$\mathbf{J} = (-e) \int_V \tau \mathbf{v} (\mathbf{v} \cdot \nabla f_0) d\mathbf{r}.$$

The direction of  $\nabla f_0$  is assumed to be constant and along  $x$ -axis then the components in  $\mathbf{v}$  other than  $v_x$  vanish with integration since they are odd functions.  $\langle v_x^2 \rangle = \langle v^2 \rangle/3$  and we further assume that the temperature is uniform and constant, no spatial variation in  $\langle v^2 \rangle$ , then the current density is

$$j_x \text{ (current density)} = -e \int_{\text{unit volume}} \tau v_x^2 \frac{\partial f_0}{\partial x} d\mathbf{r} = -e \left\langle \frac{\tau v^2}{3} \right\rangle \frac{\partial n}{\partial x}.$$

That is,

$$\mathbf{j} = (-e)D\nabla n, \quad D = \langle \tau v^2 / 3 \rangle. \quad (5.12)$$

Here  $D$  is **diffusion constant** and within constant relaxation time approximation,

Einstein relation

$$D = \frac{\tau}{3} \langle v^2 \rangle = \frac{\tau k_B T}{m^*} = \frac{\mu}{e} k_B T \quad (5.13)$$

Equation (5.13) is called **Einstein relation**.  $\mu$  in the right end is the **mobility**, defined in (5.19), which appears later.

### 5.1.4 Hall effect

The drift current under magnetic field (flux density  $\mathbf{B}$ ) can be calculated with substituting Lorentz force into  $\mathbf{F}$  in (5.4). The straightforward but a bit long calculation is summarized in Appendix A. Here we consider the situation shown in Fig. 5.3, that is, the sample has a finite length along  $y$ -axis and infinitely elongated along  $x$ -axis and the electric field  $\mathbf{E} = (\mathcal{E}_x, 0, 0)$  is applied.  $j_y$  brings the carriers and accumulates them to the edges. The charges at the edges form electric field  $\mathbf{E}_{\text{int}} = (0, \mathcal{E}_y, 0)$  and in the ultimate steady state  $j_y = 0$ .

This phenomenon, which generates an electric field vertical both to the current and the magnetic field is the **Hall effect**. The linear response coefficient

$$R_H = \frac{\mathcal{E}_y}{J_x B_z} \quad (5.14)$$

is called **Hall coefficient**. Hall field  $\mathcal{E}_y$  is obtained as follows. From  $j_y = 0$ ,

$$\mathcal{E}_y = -(A_t/A_l)\mathcal{E}_x. \quad (5.15)$$

Substituting the above and (5A.11b) into (5.14), we obtain the conductivity tensor defined in  $\mathbf{j} = \hat{\sigma}\mathbf{E}$  as

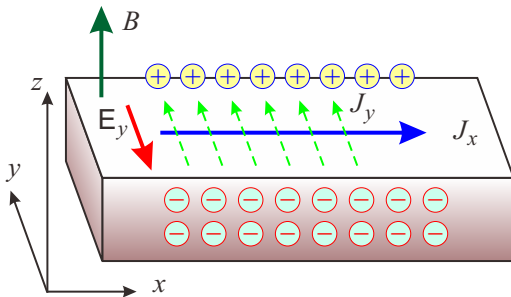
$$\sigma_{xx} = \frac{ne^2}{m^*} A_l = \frac{ne^2}{m^*} \left\langle \frac{\tau}{1 + (\omega_c \tau)^2} \right\rangle_E, \quad \sigma_{xy} = \frac{ne^2}{m^*} \left\langle \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \right\rangle_E, \quad (5.16)$$

$$R_H = -\frac{1}{ne} \frac{A_t}{\omega_c (A_l^2 + A_t^2)}. \quad (5.17)$$

In weak fields, from  $\omega_c \tau \ll 1$ ,

$$R_H = -\frac{1}{ne} \frac{\langle \tau^2 \rangle_E}{\langle \tau \rangle_E^2} = \frac{1}{n(-e)} \frac{\Gamma(2s + 5/2)\Gamma(5/2)}{(\Gamma(s + 5/2))^2} = \frac{r_H}{n(-e)} \left( = \frac{1}{n(-e)} \right). \quad (5.18)$$

Knowing  $s$ , we obtain the carrier concentration as well as the sign of charge from the Hall measurement (for holes  $-e$  is replaced with  $e$ ).  $r_H$ , which is called Hall factor, takes in many cases values around 1 depending on the scattering mechanism at high temperatures (see Tab. 5.1). Within constant relaxation time approximation ( $s = 0$ ) or when the system is Fermi-degenerated,  $r_H = 1$ . When  $s = 0$ , as eq.(5A.9) tells, eq.(5.18) holds giving the expression shown in the last parentheses.



**Fig. 5.3** Magnetic field is applied along  $z$ -axis. Current along  $x$ -axis generates  $y$ -component  $J_y$  through the Lorentz force. The  $y$ -component in current results in charge accumulation at the sample edges, which creates Hall electric field along  $y$ -axis. In steady state,  $J_y$  is canceled by the Hall field and the total current is along  $x$ -axis.

Let  $v$  be the average velocity gained by the electrons from the electric field  $\mathcal{E}$ , the **mobility** is defined as  $v/|\mathcal{E}|$ , and in the relaxation time approximation, written as

$$\mu = \frac{v}{|\mathcal{E}|} = \frac{nev}{ne|\mathcal{E}|} = \frac{j}{ne|\mathcal{E}|} = \frac{\sigma}{ne} = \sigma|R_H| = \frac{e\tau}{m^*}. \quad (5.19)$$

Scattering mechanism	$E$ exponent	$T$ exponent	Hall factor
Acoustic phonon	-1/2	-3/2	1.18
Ionized impurity (weak screening)	+3/2	+3/2	1.93
Ionized impurity (strong screening)	+1/2	+1/2	1.18
Neutral impurity	0		1.00
Piezoelectric phonon	+1/2		1.10

**Tab. 5.1** Hall factors for various scattering mechanism.  $E$ ,  $T$ -exponents are for scattering time. See *e.g.* [1].

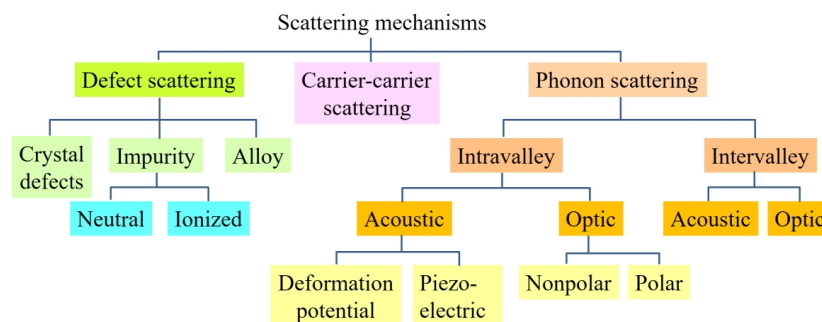
### 5.1.5 Various scatterings

We have considered the Boltzmann equation by relaxation time approximation, but various mechanisms such as scattering with phonons and other degrees of freedom in solids contribute to relaxation. We consider relaxation time for each relaxation mechanism, and index each relaxation time  $\tau_\alpha$  with index  $\alpha$ . Then the frequencies of the relaxations ( $\propto \tau_\alpha^{-1}$ ) is summed up to give the total relaxation. This gives the Matthiessen's rule

$$\tau^{-1} = \sum_{\alpha} \tau_{\alpha}^{-1}. \quad (5.20)$$

In the relaxation time approximation of classical transport, the carrier scatterings are taken into account through the averaged scattering time and the Matthiessen's rule(5.20) into the total relaxation time. Therefore we can infer the scattering mechanism dominating the present transport by tuning, for example, a parameter which gives different effects on different scattering times. Scattering of band electrons (holes) have many origins as shown in Fig. 5.4. In this section, representative scatterings and their characteristics are listed.

**Phonon scattering:** Quantization of lattice vibration gives phonons. The phonons are classified into acoustic phonons, which have the dispersion  $E(k_p) \rightarrow 0$  for wavenumber  $k_p \rightarrow 0$ , and optical phonons, which have finite  $E(k_p \rightarrow 0)$ . In a plain expression, the difference comes from whether the oscillations of neighboring atoms are in phase or out of phase. For the band electrons the lattice vibration is distortion in the lattice potential and causes scattering. The scattering of electrons causes rebounding of nuclei resulting in the phonon scattering. Such phonon scattering is, from the electron side, inelastic associated with the energy gain/loss.



**Fig. 5.4** Classification of scatterings mostly by the origins.

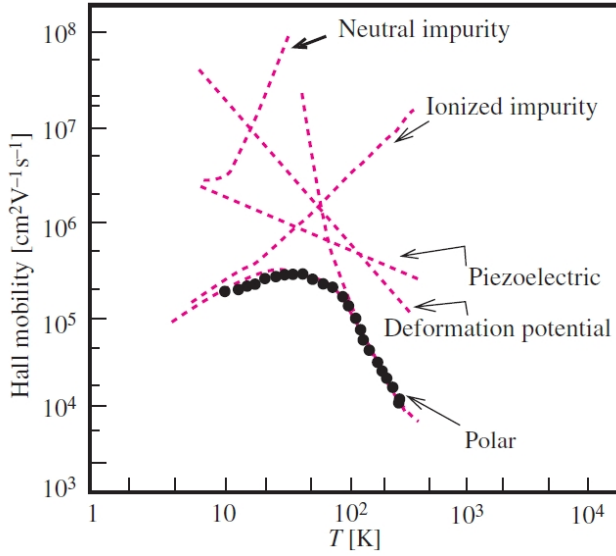
The relaxation time due to the acoustic phonon has energy dependence as  $\tau(E) = a_{\text{ph}}E^{-1/2}$ . The averaged scattering time with energy-weight  $\langle\tau_{\text{ph}}\rangle_E$  is

$$\langle\tau_{\text{ph}}\rangle_E = a_{\text{ph}}(k_{\text{B}}T)^{-1/2} \frac{\Gamma(2)}{\Gamma(5/2)} = \frac{8\sqrt{\pi}a_{\text{ph}}}{3\sqrt{k_{\text{B}}T}}. \quad (5.21)$$

In high temperature approximation, the energy distribution of phonons gives  $a_{\text{ph}} \propto (k_{\text{B}}T)^{-1}$ , then the mobility limited by the acoustic phonons  $\mu_{\text{ph}}$  has the temperature dependence as

$$\mu_{\text{ph}} \propto \langle\tau\rangle_E \propto (k_{\text{B}}T)^{-3/2}. \quad (5.22)$$

On the other hand, optical phonons have large energies around  $k \approx 0$  and do not affect the transport for weak electric field. In hot electron transport, in which the electrons are very far from equilibrium by the effect of strong electric field, the optical phonon scatterings are very important.



**Fig. 5.5** Hall mobility in GaAs(experiments, points) and fitting by putting various scattering mechanisms with temperature dependence into (5.20). Red broken lines indicate temperature dependences of various scattering mechanisms[2].

with a very short  $L_{\text{D}}$ , the scattering is  $\delta$ -function like and the contribution is

$$\tau_{\text{ion}} \propto T^{1/2}, \quad \mu_{\text{ion}} \propto T^{1/2}. \quad (5.24)$$

The mobility in GaAs obtained from Hall and conductivity measurements, and the result of fitting by considering various types of scatterings included in eq.(5.20) are shown in Fig. 5.5. The broken lines show temperature dependences of the scatterings. We see all of these limit the mobility.

## 5.2 Thermal transport and electric transport

In the Boltzmann equation (5.4), the second and the third term in left hand side representing non-uniformity in the phase space, correspond to drift current and diffusion current respectively. In this subsection we treat the thermoelectric effect, in which coexistence of the both types of currents should be considered. A temperature gradient in solids causes a heat current (or thermal flux). Here we consider heat transport by charge carriers, *i.e.* electrons and holes though lattice vibrations (phonons) also carry heat in solids. Below, we do not consider Joule heating for a while.

**Ionized impurity scattering** : Impurity atoms in solids often emit electrons to become positive or trapped negative ions, forming a Coulomb potential for band electrons and causing scattering. In most cases, such potentials are screened by surrounding charge carriers and have the Yukawa-type ( $e^{-r/L_{\text{D}}}/r$ ) distance ( $r$ ) dependence rather than the Coulomb-type  $1/r$ . When the ionized impurities have magnetic moments due to the electron spins, they also cause magnetic impurity scattering the the internal freedom causes peculiar effects like the Kondo effect. If there is no internal freedom the scattering is simple potential scattering and elastic.

Scattering by Yukawa potential of carriers with Maxwell distribution, contributes to the scattering time as

$$\tau_{\text{ion}} \propto T^{3/2}, \quad \mu_{\text{ion}} \propto \frac{T^{3/2}}{\ln(1+x) - \frac{x}{1+x}}, \quad x \equiv \frac{24m^* \lambda k_{\text{B}}T}{\hbar^2} \quad (5.23)$$

for weak screening, *i.e.* a long  $L_{\text{D}}$ . For strong screening

## 5.2.1 Thermal conductivity

Thermal flux density along  $x$ -direction with carrier concentration  $n$  is defined as

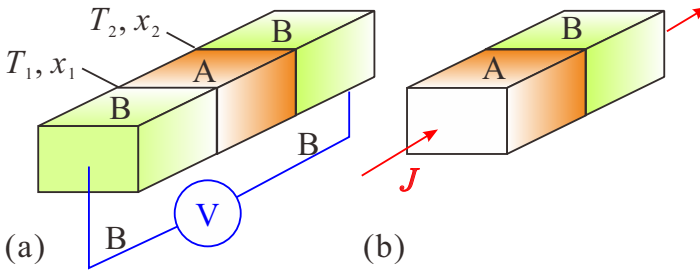
$$j_{qx} = \langle nv_x(E - \mu) \rangle = \int_0^\infty v_x(E - \mu) f(E) \mathcal{D}(E) dE. \quad (5.25)$$

Then thermal conductivity  $\kappa_n$  under temperature gradient  $\nabla T$  is defined as

$$\kappa_n = -\frac{j_{qx}}{\partial T / \partial x}. \quad (5.26)$$

In vector format  $\mathbf{j}_q = -\hat{\kappa} \nabla T$ .

## 5.2.2 Thermoelectric effects



The heat flux in (5.26) should also lead to some electric effect. Such complex effects of temperature gradient and electric response are called **thermoelectric effects**.

Let the temperatures at edges of a conductor A  $T_1$  and  $T_2$  respectively. Two conductors of another material B with the same lengths are connected to the edges. Other ends of conductors (material B) are connected to a voltmeter with infinite input impedance ((a) in the left figure).

In the steady state, there is no net current and the electric current driven by heat flow should be compensated by the voltage  $V_{AB}$  measured at the voltmeter. This is called **Seebeck effect**, and the ratio of the voltage to the temperature difference ( $\Delta T = T_1 - T_2$ )

$$S_{AB} = \frac{V_{AB}}{\Delta T} \quad (5.27)$$

is called **Seebeck coefficient**. On the other hand as in (b), when there is a junction of A and B set at a uniform temperature, a current  $J$  causes heat fluxes  $Q_A$  and  $Q_B$ . In a steady state there is no charge accumulation and  $J$  is uniform, that means  $Q_A$  and  $Q_B$  are different reflecting difference in the thermal transport coefficients. The difference results in heating at the interface. This is called **Peltier effect** and the ratio of the heating speed to  $J$ ,

$$\Pi_{AB} = \frac{Q_{AB}}{J} \quad (5.28)$$

is called **Peltier coefficient**. If we apply a current  $J$  to a BAB type junction as in (a), the same current flows with inverted directions through the two interfaces. Hence if a heating occurs at one interface, a cooling of the same amount of heat occurs at the other end.

In a uniform conductor with a current  $J$  and a temperature gradient (assume along  $x$ -direction)  $\partial T / \partial x$ , cooling or heating occurs. Heat creation per unit length  $\partial Q / \partial x$  is proportional to the product of  $J$  and  $\partial T / \partial x$ . This is **Thomson effect** and the coefficient

$$\tau = \frac{\partial Q / \partial x}{J(\partial T / \partial x)} \quad (5.29)$$

is called **Thomson coefficient**.

Among the above three kinds of coefficient, **Kelvin (Thomson) relations**

$$\Pi_{AB} = S_{AB} T, \quad \tau_A - \tau_B = T \frac{dS_{AB}}{dT} \quad (5.30)$$



hold (Appendix B). From the relations we can define material specific (combination free) Seebeck coefficient as

$$S_A(T) \equiv \int_0^T \frac{\tau_A(T')}{T'} dT'. \quad (5.31)$$

The relation with the coefficient in (5.27) is

$$S_{AB} = S_A - S_B. \quad (5.32)$$

In the measurement of Seebeck effect, we need to connect the sample and the voltmeter with leads, which also have Seebeck coefficient. Hence the measured voltage is the difference between the Seebeck effects of the sample and the leads. Equation (5.32) indicates the fact. **Thermocouple** works as a sensor for temperature difference  $\Delta T$  with knowledge of Seebeck coefficients for the two components.

### 5.2.3 Boltzmann equation and thermoelectric coefficients

Let us look for the relation between the thermoelectric coefficients and the distribution function with Boltzmann equation under relaxation time approximation (5.4), (5.5). In a steady state  $\partial f / \partial t = 0$  we rewrite the equation as

$$\mathbf{v} \cdot \nabla f + \frac{\mathbf{F}}{m} \nabla_v f = -\frac{f - f_0}{\tau(E)}. \quad (5.33)$$

We take the approximation that the shifts from equilibrium are small and replace  $f$  in the left hand side with  $f_0$ .

$\nabla f_0$  due to temperature gradient  $\nabla T$  is written as

$$\nabla f_0 = \nabla T \frac{\partial f_0}{\partial T}.$$

In  $f_0$ ,  $E$  and  $T$  always appear in the expression  $-(E - E_F)/k_B T$ , which we write  $a$  here for short description. Then

$$\frac{\partial f_0}{\partial T} = \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial a} \frac{\partial a}{\partial T} = \frac{\partial f_0}{\partial E} (-k_B T) \frac{E - E_F}{k_B T^2} = \frac{\partial f_0}{\partial E} \frac{E_F - E}{T},$$

$$\text{therefore } \nabla f_0 = \nabla T \frac{E_F - E}{T} \frac{\partial f_0}{\partial E}. \quad (5.34a)$$

$$\text{And } \nabla_v f_0 = \nabla_v E \frac{\partial f_0}{\partial E} = m \mathbf{v} \frac{\partial f_0}{\partial E}. \quad (5.34b)$$

When the electric field  $\mathbf{E}$  and the temperature gradient  $\nabla T$  coexist, (5.33) can be written with (5.34) as

$$f = f_0 - \tau(E) \mathbf{v} \cdot \left[ -e \mathbf{E} + \frac{E_F - E}{T} \nabla T \right] \frac{\partial f_0}{\partial E}. \quad (5.35)$$

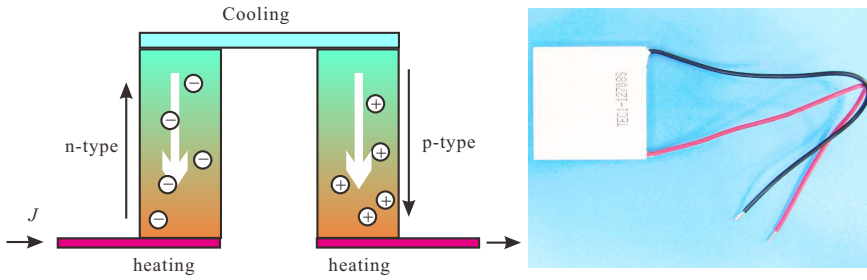
We take  $\mathbf{E} = (\mathcal{E}_x, 0, 0)$  and the current along  $x$ -direction is

$$j_x = -e \langle n v_x \rangle = -e \int_0^\infty v_x f(E) \mathcal{D}(E) dE = e \int_0^\infty v_x^2 \tau \left[ -e \mathcal{E}_x + \frac{E_F - E}{T} \frac{\partial T}{\partial x} \right] \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE.$$

The Seebeck coefficient is obtained with putting  $j_x = 0$  as

$$S = \frac{\mathcal{E}_x}{\partial T / \partial x} = \int_0^\infty v_x^2 \tau \frac{E_F - E}{eT} \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \Big/ \int_0^\infty v_x^2 \tau \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \\ = \frac{1}{eT} \left[ E_F - \int_0^\infty \tau E^2 \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \Big/ \int_0^\infty \tau E \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \right]. \quad (5.36)$$

Here  $v_x^2$  is replaced with  $2E/3m$ .



**Fig. 5.6** Left panel: Schematic of Peltier device. p-type semiconductors and n-type semiconductors are placed staggered (in the figure just a single pair) along the current path. While electric current meanders heat flows one way. Right panel: Photo of a Peltier device. From Akizuki-denshi web site.

In eq.(5.35) inside the parentheses at right hand side, the first term represents the drift current while the second the diffusion current caused by the temperature distribution. The canceling of these term results in the Seebeck effect, therefore the Seebeck effect is the result of diffusion current which causes charge non-uniformity inside the sample. The non-uniformity creates electric field, of which the drift current cancels the diffusion current.

In Maxwellian approximation,  $\partial f_0 / \partial E = -f_0 / k_B T$ , and we further assume the energy dependence of the relaxation time as  $\tau \propto E^s$ , then

$$S = -\frac{1}{eT} \left[ \frac{\langle \tau E \rangle_E}{\langle \tau \rangle_E} - E_F \right] = -\frac{1}{eT} \left[ \left( \frac{5}{2} + s \right) k_B T - E_F \right]. \quad (5.37)$$

This equation tells that if we can measure the temperature dependence of  $S$ , we obtain  $E_F$  and  $s$ . The above calculation is for electrons and for holes  $-e$  is replaced with  $+e$ , hence measurement of  $S$  also gives the sign of carriers. This result for Maxwellian approximation does not depend on the carrier concentration, which can be understood as follows. The Einstein relation (5.13) connects the diffusion constant and the mobility, which are material constants for diffusion and drift currents respectively. Hence these constants disappear from the balancing equation leaving the temperature. The carrier concentration also included as the first order in both currents and dropped. In the case of Hall coefficient, the drift current by external field comes into one side and the carrier concentration remains in the expression.

## 5.2.4 Peltier device

Peltier and Thomson coefficients can also be obtained from the Kelvin relations. Peltier coefficient also changes its sign with that of carriers. In a material with junctions to  $n$  and  $p$ -type semiconductors, a current flow through this structure thus causes heating at one junction and cooling at the other resulting in a heat flow. Such a device is called **Peltier device**.

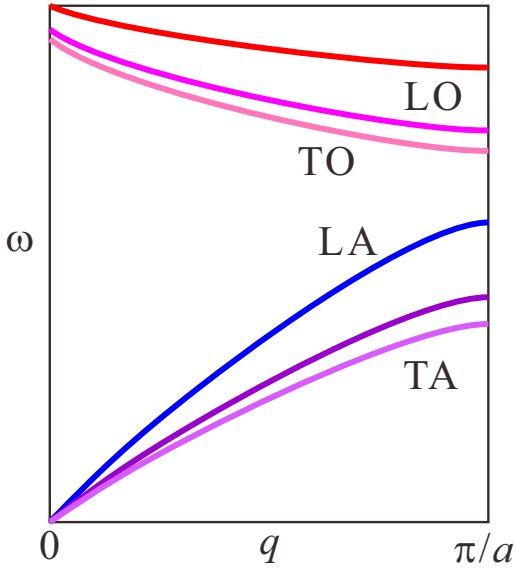
Peltier devices once were frequently used in combination with cooling fans for cooling CPUs in PCs. They have long been used where we need cooling without noises such as refrigerators in bedrooms.

## Appendix 4C: Lattice vibration in semiconductors (continued)

Continuing from the last time, let us briefly look at the lattice vibration of sphalerite-type crystals as an example of three-dimensional crystal lattice vibration.

### 4C.2 Lattice vibration in zinc-blende crystals

We consider zinc-blende (ZB) crystals as an example of three-dimensional crystal which has two species of atoms in the unit cell. The Bravais lattice is fcc but the ZB crystalline structure can be considered as an overlapp of two “fcc crystals”, in which one atom is placed at the lattice point of fcc lattice. We consider two such fcc-crystals with different atoms with common lattice constant  $a$ . We obtain a ZB crystal by placing these two with the shift of  $a(1/4, 1/4, 1/4)$ .



**Fig. 4C.3** Schematic diagram of lattice vibration modes (dispersion relation) in a zinc-blende crystal.

Let  $\mathbf{u}_{\alpha,\mathbf{R}}$  be the atomic shift vectors. Here  $\alpha$  is the index of the two sublattice,  $\mathbf{R}$  is the lattice point. The lattice kinetic energy can be written as

$$E_K = \sum_{\alpha,\mathbf{R}} \frac{1}{2} M_\alpha \dot{\mathbf{u}}_{\alpha,\mathbf{R}}^2. \quad (4C.6)$$

On the other hand, with expanding the potential  $V(\mathbf{r})$  to the second order, the potential energy is written as

$$E_P = \sum_{\alpha\alpha',\mathbf{R}\mathbf{R}',j,j'} u_{\alpha,\mathbf{R}}^j u_{\alpha',\mathbf{R}'}^{j'} \frac{\partial^2 V}{\partial u_{\alpha,\mathbf{R}}^j \partial u_{\alpha',\mathbf{R}'}^{j'}}, \quad j = x, y, z. \quad (4C.7)$$

The equation of motion can be obtained by defining the Lagrangian  $\mathcal{L} \equiv E_K - E_P$ , and general coordinate  $q_k \equiv u_{\alpha,\mathbf{R}}^j$  from the Lagrange equation;

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{q}_k} \right) - \frac{\partial \mathcal{L}}{\partial q_k} = 0.$$

In the present case from (4C.6), (4C.7) we get

$$M_\alpha \ddot{u}_{\alpha,\mathbf{R}}^j = - \sum_{\alpha',\mathbf{R}',j'} \frac{\partial^2 V}{\partial u_{\alpha,\mathbf{R}}^j \partial u_{\alpha',\mathbf{R}'}^{j'}} u_{\alpha',\mathbf{R}'}^{j'} \equiv - \sum_{\alpha',\mathbf{R}'} \mathbf{C}_{\alpha\alpha',\mathbf{R}\mathbf{R}'} \mathbf{u}_{\alpha',\mathbf{R}'}. \quad (4C.8)$$

Tensor  $\mathbf{C}$  corresponds to “force constant” and just depends on the combination  $\alpha\alpha'$ , and on the relative position of unit cell  $\mathbf{R}'' = \mathbf{R}' - \mathbf{R}$ . Then with  $\mathbf{C}_{\alpha\alpha',\mathbf{R}\mathbf{R}} = \mathbf{C}_{\alpha\alpha'}(\mathbf{R}'')$  we can write

$$M_\alpha \ddot{u}_{\alpha,\mathbf{R}}^j = - \sum_{\alpha,\mathbf{R}''} \mathbf{C}_{\alpha\alpha'}(\mathbf{R}'') \mathbf{u}_{\alpha',\mathbf{R}+\mathbf{R}''}. \quad (4C.9)$$

This equation is invariant against the shifts among the lattice points  $\mathbf{R} \rightarrow \mathbf{R}'$ . Then we can write the solution in the form of Bloch function

$$\mathbf{u}_{\alpha,\mathbf{R}}(t) = \mathbf{u}_\alpha(\mathbf{q}, t) \exp(i\mathbf{q} \cdot \mathbf{R}_\alpha). \quad (4C.10)$$

As the time dependence, we consider the oscillation with angular frequency of  $\omega$ , and assume

$$\mathbf{u}_{\alpha,\mathbf{r}}(t) = \frac{1}{\sqrt{M_\alpha}} \mathbf{u}_\alpha(\mathbf{q}, \omega) \exp[i(\mathbf{q} \cdot \mathbf{R}_\alpha - \omega t)]. \quad (4C.11)$$

Substituting this to (4C.9) results in

$$\omega^2 \mathbf{u}_\alpha(\mathbf{q}, \omega) = \sum_{\alpha'} \left[ \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \sum_{\mathbf{R}} \mathbf{C}_{\alpha\alpha'}^{jj'}(\mathbf{R}) \exp(i\mathbf{q} \cdot \mathbf{R}) \right] \mathbf{u}_{\alpha'}(\mathbf{q}, \omega) \equiv \sum_{\alpha'} \mathbf{D}_{\alpha\alpha'}(\mathbf{q}) \mathbf{u}_{\alpha'}(\mathbf{q}, \omega). \quad (4C.12)$$

For (4C.12) to have solutions other than the trivial  $\vec{0}$ ,

$$|D_{\alpha\alpha'}^{jj'}(\mathbf{q}) - \omega^2 \delta_{\alpha\alpha'} \delta_{jj'}| = 0. \quad (4C.13)$$

The dispersion relations can be obtained by solving this numerically. The 6th order equation gives 6 modes, in which 3 acoustic modes and 3 optical modes exist. The each 3 are separated into 2 transverse modes and 1 longitudinal mode. The namings are, then, TA, LA, TO, LO.

## Appendix 5A: Galvanomagnetic effect

We consider the response of drift current to magnetic flux  $\mathbf{B}$ . In the Boltzmann equation (5.4),  $\mathbf{F}$  is taken as  $\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$  and the relaxation approximation (5.5) is applied. With  $f_1 \equiv f - f_0$ ,

$$-\frac{e}{\hbar}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \frac{\partial f}{\partial \mathbf{k}} = -\frac{f_1}{\tau} \quad (\mathbf{p} = \hbar \mathbf{k}). \quad (5A.1)$$

In the first term of the left hand side,  $f$  in  $\partial f / \partial \mathbf{k}$  is replaced with  $f_0$ . Form  $dE = \mathbf{v} \cdot d\mathbf{p}$ , the second term is  $\partial f_0 / \partial \mathbf{k} = \hbar(\partial f_0 / \partial E)\mathbf{v}$  and the term of  $f_0$  is orthogonal with  $\mathbf{v} \times \mathbf{B}$  and vanishes (magnetic field driven force is orthogonal with  $\mathbf{v}$  and does not give work). In the second term we take terms to  $f_1$  and obtain

$$-e\mathbf{v} \cdot \mathbf{E} \frac{\partial f_0}{\partial E} - \frac{e}{\hbar}(\mathbf{v} \times \mathbf{B}) \cdot \frac{\partial f_1}{\partial \mathbf{k}} = -\frac{f_1}{\tau}. \quad (5A.2)$$

Here we introduce a vector  $\mathbf{E}_a$  with the physical dimension of electric field satisfying

$$f_1 = e\tau(\mathbf{v} \cdot \mathbf{E}_a) \frac{\partial f_0}{\partial E}. \quad (5A.3)$$

This is from the concept that the Lorentz force shifts the Fermi sphere as in Fig. 5.2 and the origin of the shift is represented as an electric field. Then the equation is

$$-\mathbf{v} \cdot \mathbf{E} = -\mathbf{v} \cdot \mathbf{E}_a + \frac{e\tau}{m}(\mathbf{v} \times \mathbf{B}) \cdot \mathbf{E}_a, \quad \therefore \mathbf{E} = \mathbf{E}_a - \frac{e\tau}{m^*} \mathbf{B} \times \mathbf{E}_a. \quad (5A.4)$$

The solution to eq.(5A.4) is given as follows.

$$\mathbf{E}_a = \frac{1}{1 + \omega_c^2 \tau^2} \left[ \mathbf{E} + \frac{e\tau}{m^*} \mathbf{B} \times \mathbf{E} + \left( \frac{e\tau}{m^*} \right)^2 (\mathbf{B} \cdot \mathbf{E}) \mathbf{B} \right], \quad (5A.5)$$

$$\omega_c = \frac{e|\mathbf{B}|}{m^*}. \quad (5A.6)$$

$\omega_c$  is the **cyclotron frequency**. Then  $f_1$  is given as follows.

$$f_1 = \frac{e\tau \mathbf{E}}{1 + \omega_c^2 \tau^2} \cdot \left[ \mathbf{v} + \frac{e\tau}{m^*} \mathbf{v} \times \mathbf{B} + \left( \frac{e\tau}{m^*} \right)^2 (\mathbf{B} \cdot \mathbf{v}) \mathbf{B} \right] \frac{\partial f_0}{\partial E}. \quad (5A.7)$$

We take the case  $\mathbf{B} = (0, 0, B_z)$ ,  $\mathbf{E} = (\mathcal{E}_x, \mathcal{E}_y, 0)$ . From  $v_z = 0$  and eq.(5A.7),  $f_1$  is calculated as

$$f_1 = e \frac{\partial f_0}{\partial E} \left[ v_x \left( \frac{\tau}{1 + (\omega_c \tau)^2} \mathcal{E}_x - \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \mathcal{E}_y \right) + v_y \left( \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \mathcal{E}_x + \frac{\tau}{1 + (\omega_c \tau)^2} \mathcal{E}_y \right) \right]. \quad (5A.8)$$

For example, to obtain  $j_x = -en\langle v_x \rangle$  from this equation take the expectation value of  $v_x$  with  $f = f_0 + f_1$ . The expectation value for  $f_0$  is zero and odd components in  $v$  is dropped from the integration over  $\mathbf{k}$ . Then

$$j_x = 2 \int (-e)v_x f(\mathbf{k}) \frac{d\mathbf{k}}{(2\pi)^3} = -\frac{e^2}{4\pi^3} \int \frac{\tau v_x^2}{1 + (\omega_c \tau)^2} (\mathcal{E}_x - (\omega_c \tau) \mathcal{E}_y) \frac{\partial f_0}{\partial E} d\mathbf{k}. \quad (5A.9)$$

The integrand in (5A.9) is the same as that in equilibrium other than  $v_x^2$  and is a function of kinetic energy  $E$ . For a general function  $\xi(E)$ , the principle of energy equipartition gives

$$\int v_x^2 \xi(E) d\mathbf{k} = \frac{2}{3m^*} \int E \xi(E) d\mathbf{k}. \quad (5A.10)$$

With the Maxwellian approximation  $f_0 = A \exp(-E/k_B T)$ , and density of states  $\mathcal{D}(E) = A_D E^{1/2}$ , eq.(5A.10) leads to

$$\frac{\partial f_0}{\partial E} = \frac{f_0}{-k_B T}, \quad n = A_D \int_0^\infty f_0 E^{1/2} dE = \frac{2A_D}{3k_B T} \int_0^\infty E^{3/2} f_0 dE.$$

These being substituted into (5A.9) and we obtain

$$j_x = \frac{ne^2}{m^*} \left[ \left\langle \frac{\tau}{1 + (\omega_c \tau)^2} \right\rangle_E \mathcal{E}_x - \left\langle \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \right\rangle_E \mathcal{E}_y \right], \quad (5A.11a)$$

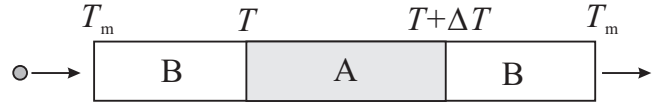
$$\equiv (ne^2/m^*)(A_l \mathcal{E}_x - A_t \mathcal{E}_y) \quad (\text{definitions of } A_l \text{ and } A_t). \quad (5A.11b)$$

$\langle \dots \rangle_E$  is defined in eq.(5.10).  $j_y$  is obtained in the same way and the conductivity tensor in  $xy$ -plane is expressed as

$$\mathbf{j} = \frac{ne^2}{m^*} \begin{pmatrix} A_l & -A_t \\ A_t & A_l \end{pmatrix} \mathbf{E}. \quad (5A.12)$$

## Appendix 5B: Kelvin relations

We consider two species of metals A, B and a junction BAB as shown in the right figure. The temperature at the two edges is kept to  $T_m$  and a unit charge moves from one edge to the other quasi-statically. As indicated in the figure, temperatures at the two junctions are  $T$  and  $T + \Delta T$ . The voltage between the two edges is  $V_{AB}$ .



From the requirement of quasi-static assumption, we apply the first and the second laws of thermodynamics to obtain the conditions,

$$V_{BA} + \Pi_{BA}(T) - \Pi_{BA}(T + \Delta T) + (\tau_B - \tau_A) \Delta T = 0$$

$$\frac{\Pi_{BA}(T)}{T} - \frac{\Pi_{BA}(T + \Delta T)}{T + \Delta T} + \frac{\tau_B - \tau_A}{T} \Delta T = 0.$$

In the differential formula with  $\Delta T \rightarrow 0$ ,

$$\frac{dV_{BA}}{dT} - \frac{d\Pi_{BA}}{dT} + \tau_B - \tau_A = 0, \quad \frac{d}{dT} \left( \frac{\Pi_{BA}}{T} \right) = \frac{\tau_B - \tau_A}{T}.$$

From the second equation

$$\tau_B - \tau_A = T \frac{d}{dT} \left( \frac{\Pi_{BA}}{T} \right) = \frac{d\Pi_{BA}}{dT} - \frac{\Pi_{BA}}{T},$$

and we reach

$$\therefore S_{AB} = \frac{\Pi_{AB}}{T}, \quad \frac{dS_{AB}}{dT} = \frac{\tau_A - \tau_B}{T} \quad (5B.1)$$

with exchange of A and B.

## References

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