

Physics of Semiconductors (7)

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Preface to the latter half series of lectures

Materials called “semiconductors” are insulators with comparatively narrow energy gaps. A vague expression like “comparatively” tells that the boundary between semiconductors and non-semiconductors is not sharply determined. Recently we take more practical definition that the materials with **externally controllable carrier distributions**. The change turns many insulators into semiconductors. Or in some cases, one material serves as a semiconductor as well as an insulator depending on the roles in human-made devices.

In this series of lectures after Prof. Akiyama’s six lectures on the band structures, carrier statistics and other fundamentals of semiconductors and also on basics of optical response, I would like to concentrate on transport phenomena. Semiconductor optics is a huge field, which has many intriguing topics but there are series of lectures on “Advanced optical science” and several experts give lectures of semiconductor optics. So students who have strong interests on the field would better take the lectures.

Ch.1 Classical Transport

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 ¹.

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

$$T_F = \frac{\hbar^2}{2mk_B} (3\pi^2 n)^{2/3} \quad :3D, \quad \frac{\hbar^2}{16\pi mk_B} n \quad :2D. \quad (1.1)$$

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.

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

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 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.² 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.

1.1.1 Boltzmann equation

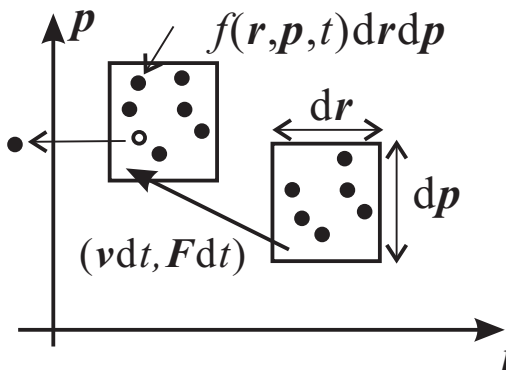


Figure 1.1: Illustration of time evolution for particles in an infinitesimal volume $drdp$ in an infinitesimal time dt with a scattering.

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 $drdp$ around the point (\mathbf{r}, \mathbf{p}) in the whole system is $f(\mathbf{r}, \mathbf{p}, t) drdp$.

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

$$d\mathbf{r}/dt = \mathbf{v} = \mathbf{p}/m^*, \quad d\mathbf{p}/dt = \mathbf{F}, \quad (1.2)$$

with \mathbf{F} as the force working on the particle. Kinematic states of particles in $drdp$ 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.1.1. 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

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m^*} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = - \left(\frac{\partial f}{\partial t} \right)_c. \quad (1.3)$$

²This 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.

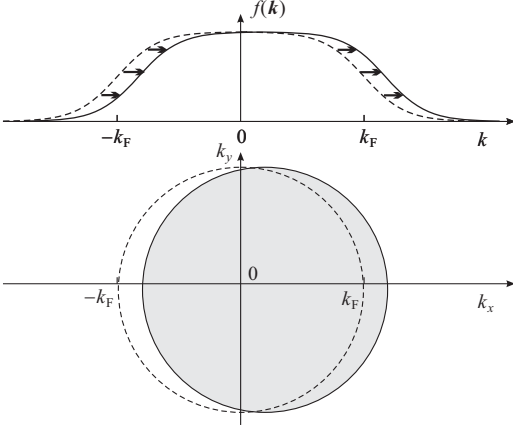


Figure 1.2: Schematic view for constant shift of Fermi sphere of electrons under acceleration by external electric field in the space of wavenumber. The distribution $f(\mathbf{k})$ shifts from the equilibrium position (indicated by broken line) by a wavevector indicated by small arrows. The upper shows 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.

Equation (1.3) is called **Boltzmann equation**, and the right hand side is called the collision term.

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 τ independent of energy and put

$$-(\partial f / \partial t)_c = -(f - f_0) / \tau, \quad (1.4)$$

where f_0 is the equilibrium distribution function for $\mathbf{F} = \mathbf{0}$, τ , 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 (1.4) can be generalized to the one with energy or momentum dependence in τ .

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

1.1.2 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 (1.3) other than anisotropy or non-uniformity in \mathbf{p} . The candidates are then $\mathbf{F} (= -e\mathbf{E})$, and $\partial f / \partial \mathbf{r}$. 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 τ only depends on \mathbf{p} . Then eq.(1.3) 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

$$f(\mathbf{p}) \simeq f_0(\mathbf{p}) + e\tau(\mathbf{p})\mathbf{E} \cdot (\partial f_0 / \partial \mathbf{p}). \quad (1.5)$$

Higher order terms can be obtained by successive replacements. Now eq.(1.5) can be viewed as the first order expansion of $f(\mathbf{p}) \simeq f_0(\mathbf{p}) + e\tau(\mathbf{p})\mathbf{E} \cdot \frac{\partial f_0}{\partial \mathbf{p}}$ 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 τ is constant for \mathbf{p} , the shift is uniform as illustrated in Fig.1.2.

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

$$\int \frac{d^3 k}{(2\pi)^3} \mathbf{v}(\mathbf{k}) \left(f_0 + e\tau \mathbf{E} \cdot \frac{\partial f_0}{\hbar \partial \mathbf{k}} \right) = \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar k_x}{m} e\tau \mathcal{E}_x \frac{\partial f_0}{\hbar \partial k_x} = \frac{e\mathcal{E}_x}{m} \int \mathcal{D}(E) \tau(E) \frac{\hbar^2 k_x^2}{m} \frac{\partial f_0}{\partial E} dE, \quad (1.6)$$

where we assume τ 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 (1.6). For a three-dimensional system the density of states is $\mathcal{D}(E) = A\sqrt{E}$ with a coefficient A , then (1.6) 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

$$\sigma = \frac{e^2 n \tau(E_F)}{m}, \quad (1.7)$$

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

$$\sigma = e^2 \int \tau(E) \mathcal{D}(E) \frac{2E}{3m} \frac{3n f_0}{2\langle E \rangle} dE = \frac{n e^2 \langle \tau \rangle_E}{m}. \quad (1.8)$$

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

$$\langle \tau \rangle_E = \frac{\langle \tau E \rangle}{\langle E \rangle} = \frac{\int_0^\infty \tau(E) E^{3/2} f_0 dE}{\int_0^\infty E^{3/2} f_0 dE}. \quad (1.9)$$

We then proceed to the diffusion current caused by non-uniformity of f in real space. In Boltzmann equation (1.3), \mathbf{F} is set to zero and constant relaxation time approximation (1.4) is applied to the space distribution of $f = f_0 + f_1$ as

$$\mathbf{v} \cdot \nabla f = -f_1/\tau, \quad \text{take to the first order of } f_1 \quad f_1 = -\tau \mathbf{v} \cdot \nabla f_0. \quad (1.10)$$

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 ∇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,

$$\mathbf{j} = (-e) D \nabla n, \quad D = \langle \tau v^2 / 3 \rangle. \quad (1.11)$$

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

$$D = \frac{\tau}{3} \langle v^2 \rangle = \frac{\tau k_B T}{m^*} = \frac{\mu}{e} k_B T. \quad (1.12)$$

Equation (1.12) is called **Einstein relation**.

1.1.3 Hall effect

The drift current under magnetic field (flux density \mathbf{B}) can be calculated with substituting Lorentz force into \mathbf{F} in (1.3). The straightforward but a bit long calculation is summarized in Appendix A. Here we consider the situation shown in Fig.1.3, 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 $j_y = 0$.

| 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 |

Table 1.1: Hall factors for various scattering mechanism. E , T -exponents are for scattering time. See *e.g.* [1].

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

$$R_H = \frac{\mathcal{E}_y}{J_x B_z} \quad (1.13)$$

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

$$\mathcal{E}_y = -(A_t/A_l)\mathcal{E}_x. \quad (1.14)$$

Substituting the above and (A.11b) into (1.13), we obtain the conductivity tensor defined in $\mathbf{j} = \hat{\sigma}\mathbf{E}$ as

$$\sigma_{xx} = \frac{ne^2}{m^*} A_l = \frac{ne^2}{m^*} \left\langle \frac{\tau}{1 + (\omega_c \tau)^2} \right\rangle_E, \quad \sigma_{xy} = \frac{ne^2}{m^*} \left\langle \frac{\omega_c \tau^2}{1 + (\omega_c \tau)^2} \right\rangle_E, \quad (1.15)$$

$$R_H = -\frac{1}{ne} \frac{A_t}{\omega_c (A_l^2 + A_t^2)}. \quad (1.16)$$

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

$$R_H = -\frac{1}{ne} \frac{\langle \tau^2 \rangle_E}{\langle \tau \rangle_E^2} = \frac{1}{n(-e)} \frac{\Gamma(2s + 5/2)\Gamma(5/2)}{(\Gamma(s + 5/2))^2} = \frac{r_H}{n(-e)} \left(= \frac{1}{n(-e)} \right). \quad (1.17)$$

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.1.1). Within constant relaxation time approximation ($s = 0$) or when the system is Fermi-degenerated, $r_H = 1$. When $s = 0$, as eq.(A.9) tells, eq.(1.17) holds giving the expression shown in the last parentheses.

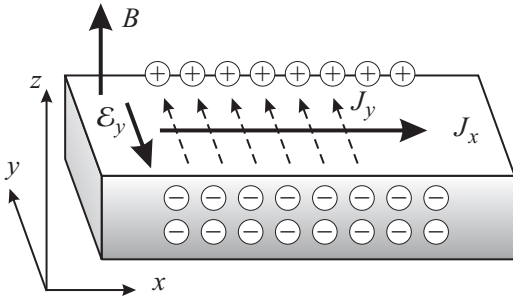


Figure 1.3: Magnetic field is applied along z -axis. Current along x -axis generates y -component J_y through the Lorentz force. The y -component in current results in charge accumulation at the sample edges, which creates Hall electric field along y -axis. In steady state, J_y is canceled by the Hall field and the total current is along x -axis.

1.2 Thermal transport and electric transport

In the Boltzmann equation (1.3), 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.

1.2.1 Thermal conductivity

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

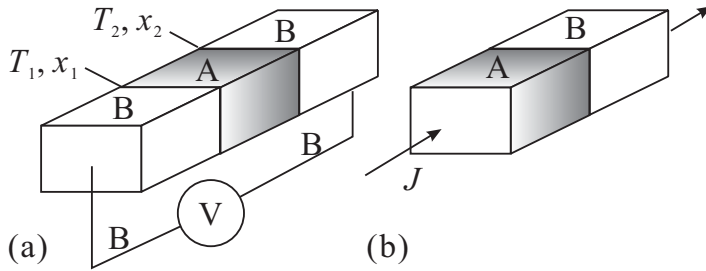
$$j_{qx} = \langle nv_x(E - \mu) \rangle = \int_0^\infty v_x(E - \mu) f(E) \mathcal{D}(E) dE. \quad (1.18)$$

Then thermal conductivity κ_n under temperature gradient ∇T is defined as

$$\kappa_n = -\frac{j_{qx}}{\partial T / \partial x}. \quad (1.19)$$

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

1.2.2 Thermoelectric effects



The heat flux in (1.19) 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 ($\Delta T = T_1 - T_2$)

$$S_{AB} = \frac{V_{AB}}{\Delta T} \quad (1.20)$$

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 ,

$$\Pi_{AB} = \frac{Q_{AB}}{J} \quad (1.21)$$

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

$$\tau = \frac{\partial Q / \partial x}{J(\partial T / \partial x)} \quad (1.22)$$

is called **Thomson coefficient**.

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

$$\Pi_{AB} = S_{AB}T, \quad \tau_A - \tau_B = T \frac{dS_{AB}}{dT} \quad (1.23)$$

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

$$S_A(T) \equiv \int_0^T \frac{\tau_A(T')}{T'} dT'. \quad (1.24)$$

The relation with the coefficient in (1.20) is

$$S_{AB} = S_A - S_B. \quad (1.25)$$

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 (1.25) indicates the fact. **Thermocouple** works as a sensor for temperature difference ΔT with knowledge of Seebeck coefficients for the two components.

1.2.3 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 (1.3), (1.4). In a steady state $\partial f / \partial t = 0$ we rewrite the equation as

$$\mathbf{v} \cdot \nabla f + \frac{\mathbf{F}}{m} \nabla_v f = -\frac{f - f_0}{\tau(E)}. \quad (1.26)$$

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

∇f_0 due to temperature gradient ∇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

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

$$\text{therefore } \nabla f_0 = \nabla T \frac{E_F - E}{T} \frac{\partial f_0}{\partial E}. \quad (1.27a)$$

$$\text{And } \nabla_v f_0 = \nabla_v E \frac{\partial f_0}{\partial E} = m\mathbf{v} \frac{\partial f_0}{\partial E}. \quad (1.27b)$$

When the electric field \mathbf{E} and the temperature gradient ∇T coexist, (1.26) can be written with (1.27) as

$$f = f_0 - \tau(E)\mathbf{v} \cdot \left[-e\mathbf{E} + \frac{E_F - E}{T} \nabla T \right] \frac{\partial f_0}{\partial E}. \quad (1.28)$$

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

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

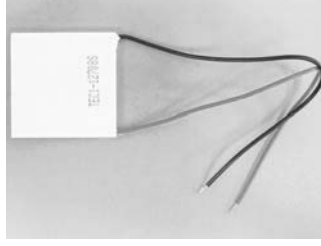
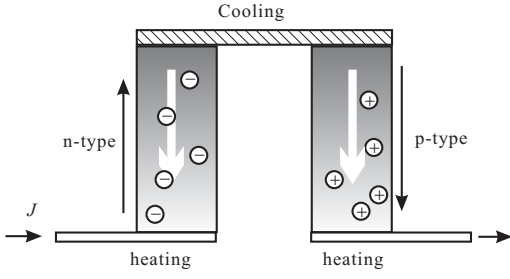


Figure 1.4: Left panel: Schematic of Peltier device. p-type semiconductors and n-type semiconductors are placed staggered (in the figure just a single pair) along the current path. While electric current meanders heat flows one way. Right panel: Photo of a Peltier device. From Akizuki-denshi web site.

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

$$S = \frac{\mathcal{E}_x}{\partial T / \partial x} = \int_0^\infty v_x^2 \tau \frac{E_F - E}{eT} \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \Big/ \int_0^\infty v_x^2 \tau \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE$$

$$= \frac{1}{eT} \left[E_F - \int_0^\infty \tau E^2 \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \Big/ \int_0^\infty \tau E \frac{\partial f_0}{\partial E} \mathcal{D}(E) dE \right]. \quad (1.29)$$

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

In eq.(1.28) 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

$$S = -\frac{1}{eT} \left[\frac{\langle \tau E \rangle_E}{\langle \tau \rangle_E} - E_F \right] = -\frac{1}{eT} \left[\left(\frac{5}{2} + s \right) k_B T - E_F \right]. \quad (1.30)$$

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 (1.12) 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.

1.2.4 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.

Ch.2 Transport in pn junctions

2.1 Thermal equilibrium

A pn junction, as it expresses, is a junction of a p -type semiconductor and an n -type semiconductor. Here we consider homo-junctions, in which the same species of semiconductor is used for p - and n -layers. In such a junction, the electron density is high in the n -layer and the hole density in the p -layer. Hence there should be diffusion pressures which drive electrons to the p -layer and holes to the n -layer for increase of entropy S . On the other hand, such diffusions charge up the p -layer to negative and the n -layer to positive creating charge double layer at the junction (charge **depletion layer**). This electro-magnetically enhances the internal energy U . In thermal equilibrium, the double layer width is determined from the condition for free energy ($U - TS$) minimum.

We take a simple model of an abrupt junction (Fig.2.1), and $p \sim n \sim n_i$ in the depletion layer. We write the **built-in voltage** due to the pn structure at the interface across the depletion layer V_{bi} . In the process that an electron moves from the n -layer to the p -layer, the energy increases by eV_{bi} . In the n -layer the electron density $n_n \sim N_D$, and in the p -layer the semiconductor equation tells $n_p \sim n_i^2/N_A$. We consider a general case that N_1 and N_2 electrons are respectively distributed in two boxes with site number N . The number of cases is $W = {}_N C_{N_1} {}_N C_{N_2}$. Here only particle exchanges are considered hence $dN_1 = -dN_2$. Under assumption $N \gg N_{1,2}$, $d(\ln W) \approx \ln(N_2/N_1)dN_1$ (**mixing entropy** of gases). Applying this to the pn -junction with $dN_1 = -1$, $N_1 = n_n$, $N_2 = n_p$, condition $d(U - TS)/dn_n = 0$ gives

$$eV_{bi} = k_B T \ln \frac{n_n}{n_p} \sim k_B T \ln \frac{N_D N_A}{n_i^2} = E_g - k_B T \ln \frac{N_c N_v}{N_D N_A}. \quad (2.1)$$

($n_n \sim N_D, p_p \sim N_A$).

In equilibrium it is also required that the chemical potential (Fermi energy) is constant through the junction, independent of the spatial coordinate. Far inside p, n -layers apart from the junction, the band structure should recover the bulk states. Hence the band diagram in Fig.2.1(c) is drawn. Let the depletion layer widths in p and n -layers w_p, w_n respectively, then $E(x)$ is given as

$$-\epsilon\epsilon_0 E(x) = N_A(2x + w_p) + N_D w_n \quad (x < 0), \quad N_A w_p + N_D(w_n - 2x) \quad (x \geq 0), \quad (2.2)$$

where ϵ is the dielectric constant. Then V_{bi} is calculated as

$$V_{bi} = \int_{-w_p}^{w_n} (-E(x))dx = \frac{e}{\epsilon\epsilon_0} (N_D + N_A) w_n w_p = \frac{e}{\epsilon\epsilon_0} (N_D + N_A) \frac{N_D}{N_A} w_n^2 \quad \because w_n N_D = w_p N_A. \quad (2.3)$$

From eqs.(2.1) and (2.3), we obtain the relation between the doping concentrations and the depletion layer width.

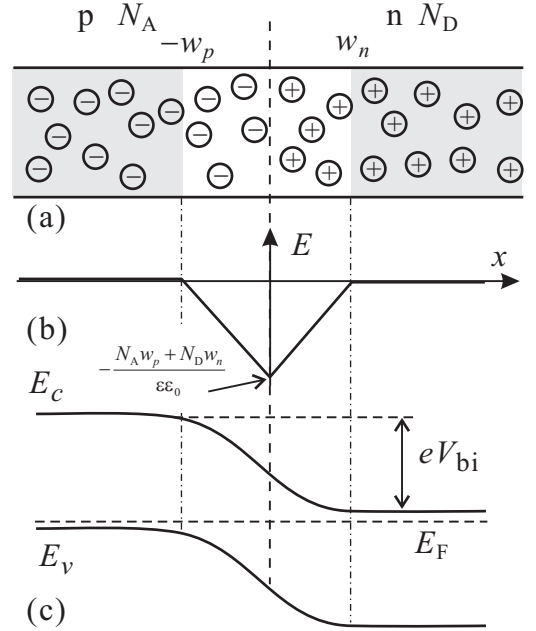


Figure 2.1: (a) Schematic of an abrupt pn -junction. (b) Electric field $E(x)$ in depletion layer. x -direction is taken as positive for the field. (c) Band diagram.

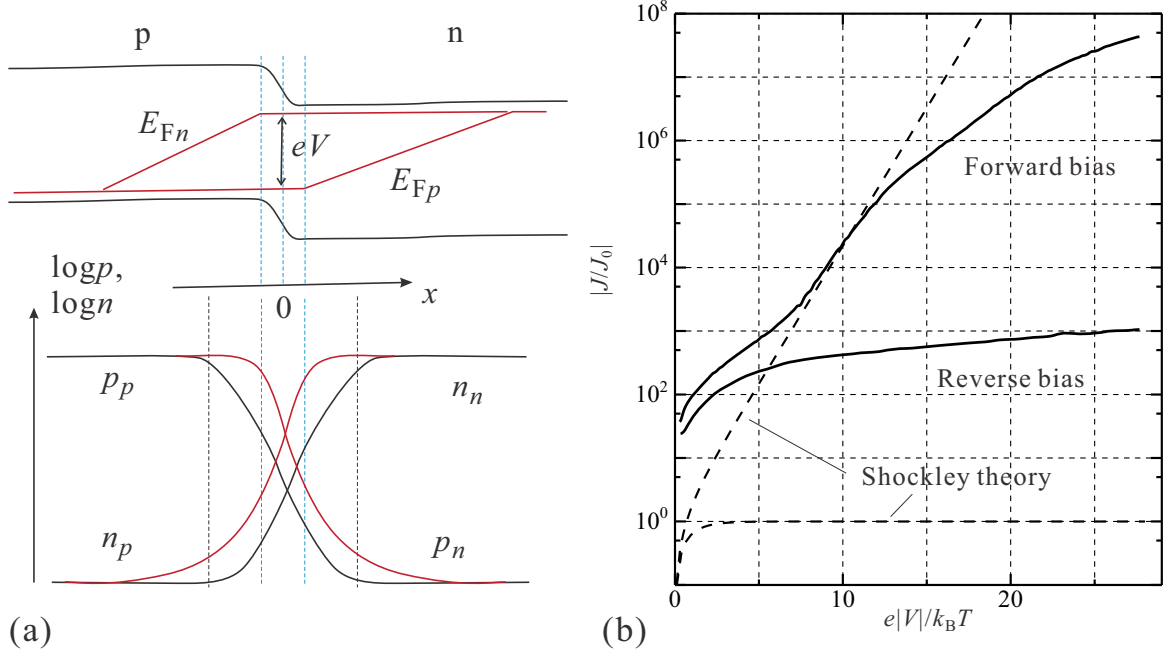


Figure 2.2: (a) Upper panel: quasi-Fermi levels in a pn -junction under external forward voltage V . Lower panel: Spatial variation of carrier densities. (b) Broken line: I-V characteristics of Shockley theory (eq.(2.11)). Normalized with J_0 , which is the coefficient in eq.(2.11). Solid line: Realistic I-V characteristics, in which series resistance, recombination inside the depletion layer, tunneling through localized states are taken into account. The inset is a linear plot of (2.11).

2.2 Current-Voltage characteristics

In equilibrium of a pn -junction, the net current is zero as a result of balance between the entropy and the internal energy. An externally applied voltage pushes off the balance and a current flows as a result. When the energy cost is lowered by the voltage, the diffusion current causes **injection of minority carriers**. Minority carrier injection is an action that increases density of minority carrier dynamically. The minority carrier injection breaks the semiconductor equation $np = n_i^2$ locally. Even in such circumstances, by introducing **quasi-Fermi level**, we can treat electrons and holes as in quasi-equilibriums and apply the Boltzmann equation to obtain carrier fluxes. The semiconductor equation (law of mass action) can also be recovered in a bit modified manner. The goal here is to give the net current as a function of external voltage.

We model the effect of external voltage V as follows. All the voltage drops outside the depletion layer are ignored and V is applied inside it. Far from the junction, the current is carried by majority carriers, which have high concentration and the gradient in the chemical potential in such regions is ignorable. Around the depletion layer, imbalance between the internal energy cost and the increase of entropy causes a flow of carriers. V is applied against V_{bi} lowering the barrier for diffusion currents, then the majority carriers flows into the counter layers increasing the minority carrier densities at the depletion layer edges. The injected minority carriers diffuse into the bulk, recombine with majority carriers and disappear. The diffusion-annihilation process forms an exponential decay in the steady minority carrier density distribution.

In the above model, we assume that local thermal equilibrium is attained in each thin layer parallel to yz plane through the carrier-carrier interaction and the particles can be exchanged between neighboring layers. Quasi-Fermi levels, which depends on x -coordinate, for electrons ($\mu_e(x)$) and holes ($\mu_h(x)$) are introduced as follows,

$$n(x) = N_c \exp[-(E_c(x) - \mu_e(x))/k_B T], \quad p(x) = N_v \exp[-(\mu_h(x) - E_v(x))/k_B T], \quad (2.4a)$$

$$i.e., \quad \mu_e(x) = E_c(x) + k_B T \ln \frac{n(x)}{N_c}, \quad \mu_h(x) = E_v(x) - k_B T \ln \frac{p(x)}{N_v}. \quad (2.4b)$$

The diffusion of minority carriers (densities n_p, p_n) is described by the following diffusion equations.

$$D_e \frac{d^2 n_p}{dx^2} = \frac{n_p - n_{p0}}{\tau_e} - G(x), \quad D_h \frac{d^2 p_n}{dx^2} = \frac{p_n - p_{n0}}{\tau_h} - G(x), \quad (2.5)$$

where $G(x)$ represents minority carrier creation *e.g.* by light illumination and in the dark $G(x) = 0$. n_{p0}, p_{n0} are minority carrier concentrations in the bulk regions, $D_{e,h}, \tau_{e,h}$ are the diffusion constant and the lifetime respectively (e for electrons, h for holes). Then **minority carrier diffusion lengths** for electrons and holes are

$$L_e = \sqrt{D_e \tau_e}, \quad L_h = \sqrt{D_h \tau_h}. \quad (2.6)$$

The solution for (2.5) (p_n for $x > w_n, n_p$ for $x < -w_p$) which satisfies the boundary condition $n_p \rightarrow n_{p0}$ ($x \rightarrow -\infty$) and $p_n \rightarrow p_{n0}$ ($x \rightarrow \infty$), is obtained as

$$n_p(x) = \delta n_0 \exp\left(\frac{x + w_p}{L_e}\right) + n_{p0}, \quad p_n(x) = \delta p_0 \exp\left(-\frac{x - w_n}{L_h}\right) + p_{n0}, \quad (2.7)$$

where $\delta n_0, \delta p_0$ are concentrations of injected minority carriers at the edges of the depletion layer. From the definition (2.4b), in the region of diffusion and with ignoring n_{p0}, p_{n0} in (2.7), the quasi-Fermi levels linearly depend on the distances as

$$\mu_e(x) = E_c + k_B T \left[\frac{x + w_p}{L_e} + \ln \frac{\delta n_0}{N_c} \right], \quad \mu_h(x) = E_v - k_B T \left[\frac{x - w_n}{L_h} + \ln \frac{\delta p_0}{N_v} \right]. \quad (2.8)$$

These should join the bulk values $E_F^{(p),(n)}$ at $x \rightarrow \pm\infty$ respectively and $E_F^{(p),(n)}$ differ by eV , *i.e.*, $E_F^{(p)} - E_F^{(n)} = eV$. Therefore they are schematically drawn as in Fig.2.2(a).

We ignore electron-hole recombination inside the depletion layer and assume the currents are limited by the diffusion of minority carriers. Then the net current density is the sum of minority carrier diffusion currents at the two edges of the depletion layer. From eq.(2.7) and eq.Fig.2.2(a),

$$\delta n_0 + n_{p0} = n(-w_p) = n_{p0} \exp \frac{eV}{k_B T}, \quad \delta p_0 + p_{n0} = p(w_n) = p_{n0} \exp \frac{eV}{k_B T}. \quad (2.9)$$

The electron diffusion current density at $x = -w_p$ in the process (2.5) is thus

$$j_e = e D_e \left. \frac{dn_p}{dx} \right|_{-w_p} = \frac{e D_e \delta n_0}{L_e} = \frac{e D_e}{L_e} n_{p0} \left[\exp \frac{eV}{k_B T} - 1 \right]. \quad (2.10)$$

The hole current can be calculated in the same way and the net current is given as

$$j = e \left[\frac{D_e}{L_e} n_{p0} + \frac{D_h}{L_h} p_{n0} \right] \left[\exp \frac{eV}{k_B T} - 1 \right] \approx e n_i^2 \left[\frac{D_e}{L_e N_A} + \frac{D_h}{L_h N_D} \right] \left[\exp \frac{eV}{k_B T} - 1 \right]. \quad (2.11)$$

Equation (2.11) is the very basics of the Schottky theory of pn -junction. Though the model grabs the essence, real pn junctions are much more complicated. Important modifications are series resistance, recombination in depletion layer and tunneling conductance through localized level inside energy gap (parallel Ohmic resistance). With these modifications, a realistic characteristics shown in Fig.2.2(b) differs considerably from the Shockley theory.

2.3 Photo-response of pn -junctions

Let us take the simplest model for a pn -junction under illumination assuming majority carrier generation $G(x)$ does not depend on x (a constant G) in the diffusion equation (2.5). Just as before, the solution for $n_p(x)$ and

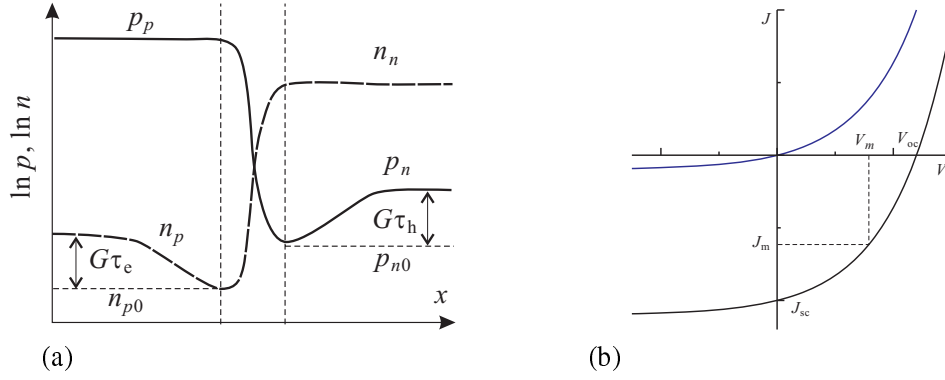


Figure 2.3: (a) Carrier density distribution around a pn -junction under photo-generation of minority carriers G . Depletion layer edges are indicated by perpendicular broken lines. Bias is taken as shortage $V = 0$. (b) Schematic I-V characteristics in the dark and under illumination.

$p_n(x)$ which satisfies the boundary condition $n_p \rightarrow n_{n0} + G\tau_e$ for $x \rightarrow -\infty$, and $p_n \rightarrow p_{n0} + G\tau_h$ for $x \rightarrow \infty$ is

$$n_p(x) = n_{p0} + G\tau_e + \left[n_{p0} \left(\exp \left(\frac{eV}{k_B T} \right) - 1 \right) - G\tau_e \right] \exp \left(\frac{x + w_p}{L_e} \right), \quad (2.12a)$$

$$p_n(x) = p_{n0} + G\tau_h + \left[p_{n0} \left(\exp \left(\frac{eV}{k_B T} \right) - 1 \right) - G\tau_h \right] \exp \left(-\frac{x - w_n}{L_h} \right). \quad (2.12b)$$

The solution for $V = 0$ is schematically drawn in Fig.2.3(a).

From the solution, the net current density is given as

$$j = j_0 \left[\exp \frac{eV}{k_B T} - 1 \right] - eG(L_e + L_h), \quad (2.13)$$

where j_0 is the coefficient in front of the parentheses in (2.11). Equation (2.13) is a simple negative shift of (2.11) by $j_{sc} \equiv G(\tau_e + \tau_h)$. Figure 2.3(b) shows the characteristics. Real solar cells are more complicated but the common is the negative shift of the current characteristics with illumination. The parameters which characterize each device are the negative shift at short-circuit condition $|J_{SC}|$ (**short circuit current**) and the voltage at open-circuit condition V_{OC} (**open circuit voltage**). These depend, of course, on the strength and the spectrum of illumination.

In the characteristics shown in Fig.2.3(b), the cell pumps out an electric energy under the bias condition in the fourth quadrant. Current J and voltage V give power $W = |JV|$. In the fourth quadrant $|J| \leq |J_{SC}|$, $|V| \leq |V_{OC}|$ then $W \leq |J_{SC}V_{OC}|$. Then J_{max} , V_{max} which give the maximum power is determined and

$$FF \equiv \frac{J_{max}V_{max}}{J_{SC}V_{OC}} \leq 1 \quad (2.14)$$

is called **filling factor** (FF). The better the squareness of the I-V characteristics, the higher the FF. J_{SC} , V_{OC} , and FF are useful parameters for discussing phenomenology of solar cells, modeling equivalent circuits. In the ideal characteristics (2.13),

$$|J_{SC}| = eG(L_e + L_h), \quad V_{OC} = \frac{k_B T}{e} \ln \left[\frac{eG(\tau_e + \tau_h)}{j_0} + 1 \right]. \quad (2.15)$$

References

- [1] M. Lundstrom, "Fundamentals of Carrier Transport" (Cambridge, 2000).

Appendix A: Galvanomagnetic effect

We consider the response of drift current to magnetic flux \mathbf{B} . In the Boltzmann equation (1.3), \mathbf{F} is taken as $\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ and the relaxation approximation (1.4) is applied. With $f_1 \equiv f - f_0$,

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

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

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

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

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

This is from the concept that the Lorentz force shifts the Fermi sphere as in Fig.1.2 and the origin of the shift is represented as an electric field. Then the equation is

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

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

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

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

ω_c is the **cyclotron frequency**. Then f_1 is given as follows.

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

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.(A.7), f_1 is calculated as

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

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

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

The integrand in (A.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

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

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.(A.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 (A.9) and we obtain

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

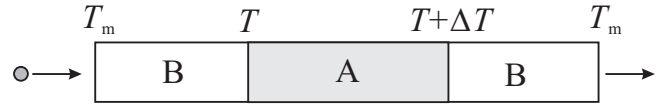
$$\equiv (ne^2/m^*)(A_l\mathcal{E}_x - A_t\mathcal{E}_y) \quad (\text{definitions of } A_l \text{ and } A_t). \quad (\text{A.11b})$$

$\langle \dots \rangle_E$ is defined in eq.(1.9). j_y is obtained in the same way and the conductivity tensor in xy -plane is expressed as

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

Appendix B: 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

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

with exchange of A and B.