CHAPTER II

ELECTRICAL CONDUCTIVITY AND RELAXATION TIME

2.1 INTRODUCTION

In this Chapter, we will give an elementary d.c. electrical conductivity theory generated from the Boltzmann transport equation by using the relaxation time approximation.

2.2 BOLTZMANN TRANSPORT EQUATION

To describe the electron system, we introduces the distribution function, $f_{\mathbf{k}}(\mathbf{r},t)$ in equilibrium state, the Fermi-Dirac distribution function, which gives the occupation probability of a state characterized by $\mathbf{k}$ -vector, and space vector $\mathbf{r}$. More precisely, the product of distribution function, density of states and volume element $d\mathbf{r}d\mathbf{k}$ of phase space gives the number of electrons in the volume element ($\mathbf{r},d\mathbf{r}$) of $\mathbf{r}$ -space and ($\mathbf{k},d\mathbf{k}$) of $\mathbf{k}$ -space at time t.

To calculate the distribution function $f_{\mathbf{k}}(\mathbf{r},t)$, in short $f_{\mathbf{k}}$, in given external fields, one considers a group of electrons in the volume element $d\mathbf{r}d\mathbf{k}$ in phase space. This group will move through phase space [11]. For the short time interval considered, let the form of the group remain essentially unchanged. Then the total differential quotient $df_{\mathbf{k}}/dt$ would be zero if electrons were not scattered from ($\mathbf{k},d\mathbf{k}$) to another ($\mathbf{k}',d\mathbf{k}'$) and vice versa, by electron-phonon interaction. Let the change in distribution function due to the scattering be $\left.\frac{df_{\mathbf{k}}}{dt}\right|_{scatt.}$. Then $\frac{df_{\mathbf{k}}}{dt}=\left.\frac{df_{\mathbf{k}}}{dt}\right|_{scatt.}$, or, if we replace the total differential quotient by the local one plus terms following from the implicit time dependence of $f_{\mathbf{k}}$ over $\mathbf{r}(t)$and $\mathbf{k}(t)$[12],

$$\frac{df_{\mathbf{k}}}{dt} = \frac{\partial f_{\mathbf{k}}}{\partial t} + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}} + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}} = \left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{scatt.} . \tag{2.2.1}$$

In the steady state the local differential quotient is zero and we are left with [12]

$$\dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}} + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}} = \left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{scatt.} . \tag{2.2.2}$$

The first term is the rate of change of distribution due to external fields and will change the $\mathbf{k}$ vector of each carrier, at the rate

$$\dot{\mathbf{k}} = \frac{e}{\hbar}\left(\mathbf{E} + \frac{1}{c}\left(\mathbf{v}_{\mathbf{k}} \times \mathbf{H}\right)\right) \tag{2.2.3}$$

where $\mathbf{E}$ is an applied electric field,

$\mathbf{H}$ an applied magnetic field,

e the electron charge,

$\hbar$ Planck's constant and

c speed of light.

The second term is the rate of change of the distribution due to diffusion.

The effect of scattering is more complicated but we will be confined mostly to elastic scattering. This gives rise to a rate of change of $f_{\mathbf{k}}$ [12]

$$\left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{scatt.} = \int \left\{ f_{\mathbf{k}'}\left(1 - f_{\mathbf{k}}\right) - f_{\mathbf{k}}\left(1 - f_{\mathbf{k}'}\right) \right\} Q(\mathbf{k},\mathbf{k}')\, d\mathbf{k}' \tag{2.2.4}$$

where $Q(\mathbf{k},\mathbf{k}')$ is the transition probability from state $\mathbf{k}$ to $\mathbf{k}'$ and vice versa.

The process of scattering from $\mathbf{k}$ to $\mathbf{k}'$ decreases $f_{\mathbf{k}}$. The probability of this process depends on $f_{\mathbf{k}}$ and $(1-f_{\mathbf{k}'})$, the distribution of vacancies available in the final states. There is also the inverse process, from $\mathbf{k}'$ into $\mathbf{k}$, which increases $f_{\mathbf{k}}$, and which is weighted with $f_{\mathbf{k}'}(1-f_{\mathbf{k}})$. The sum is over all other possible states $\mathbf{k}'$. For each value of $\mathbf{k}$ and $\mathbf{k}'$, however, there is a basic transition probability $Q(\mathbf{k},\mathbf{k}')$, which would measure the rate of transition if, say, $\mathbf{k}$ were known to be occupied and $\mathbf{k}'$ known to be empty.

2.3 ELECTRICAL CONDUCTIVITY

Suppose we have only an electric field $\mathbf{E}$ in an infinite medium kept at constant temperature. We uses Eq. (2.2.3) and the relation

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathrm{E}(\mathbf{k}),$$

where

$\mathrm{E}(\mathbf{k})$, in short E, the electronics energy of $\mathbf{k}$ th state,

$\mathbf{v}_{\mathbf{k}}$ electron velocity of $\mathbf{k}$ th state and

$\hbar = \frac{h}{2\pi}$, Planck's constant $h = 6.62620\times10^{-27}$ erg s ,

and then the Boltzmann transport equation (2.2.2) becomes

$$\left(\frac{\partial f^{0}{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)\mathbf{v}_{\mathbf{k}}\cdot e\mathbf{E} = -\left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{scatt.} \tag{2.3.1}$$

where the Fermi-Dirac distribution function in steady state is

$$f^0{}_{\mathbf{k}} = \frac{1}{1+exp[(\mathrm{E}(\mathbf{k})-\mu)/k_B T]} = f^0(\mathrm{E}(\mathbf{k})), \tag{2.3.2}$$

where μ is the chemical potential. We assume that the steady state distribution function does not depart very far from equilibrium $f^0{}_{\mathbf{k}}$. We therefore write

$$g_{\mathbf{k}} = f_{\mathbf{k}} - f^0{}_{\mathbf{k}}.$$

Thus from Eq. (2.2.4), Eq. (2.3.1) can be rewritten as [12]

$$\left(-\frac{\partial f^0{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)\mathbf{v}_{\mathbf{k}} \cdot e\mathbf{E} = \int (f_{\mathbf{k}} - f_{\mathbf{k}'})Q(\mathbf{k},\mathbf{k}')d\mathbf{k}'$$

$$= \int \left(g_{\mathbf{k}} + f^0_{\mathbf{k}} - (g_{\mathbf{k}'} + f^0_{\mathbf{k}'})\right)Q(\mathbf{k},\mathbf{k}')d\mathbf{k}'$$

$$= \int (g_{\mathbf{k}} - g_{\mathbf{k}'})Q(\mathbf{k},\mathbf{k}')d\mathbf{k}'. \tag{2.3.3}$$

Note that $f^0_{\mathbf{k}} = f^0_{\mathbf{k}'}$, momentum conserved principle is used.

Instead of solving this equation directly, let us make another phenomenological assumption

$$-\left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{scatt.} = \frac{1}{\tau} g_{\mathbf{k}} \,. \tag{2.3.4}$$

That is, we introduce a relaxation time τ. If the field is turned off, the any out of balance, $g_{\mathbf{k}}$ would decay to zero according to

$$-\frac{\partial g_{\mathbf{k}}}{\partial t} = \frac{g_{\mathbf{k}}}{\tau}, \tag{2.3.5}$$

so that

$$g_{\mathbf{k}} = g_{\mathbf{k}}(0)exp(-t/\tau) . \tag{2.3.6}$$

Substitution (2.3.4) into (2.3.1) gives

$$g_{\mathbf{k}} = -\left(\frac{\partial f^{0}{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)\tau \mathbf{v}_{\mathbf{k}} \cdot e\mathbf{E} . \tag{2.3.7}$$

To calculate the electrical conductivity, one needs the current density [13],

$$\mathbf{J} = \int e\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} d\mathbf{k}$$

$$= \int e\mathbf{v}_{\mathbf{k}} g_{\mathbf{k}} d\mathbf{k} \quad \left(\text{since } \int e\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}^{0} d\mathbf{k} \equiv \mathbf{0} \text{ in equilibrium state[13]}\right)$$

$$= \frac{1}{4\pi^{3}} \iint e^{2}\tau \mathbf{v}_{\mathbf{k}} \left(\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}\right)\left(-\frac{\partial f^{0}{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)\frac{dSd\mathrm{E}}{\hbar \upsilon_{\mathbf{k}}} \tag{2.3.8}$$

where $\upsilon_{\mathbf{k}} = |\mathbf{v}_{\mathbf{k}}|$, on the surface S of constant energy. Note that the concept of the density of state [14]

$$\mathrm{N}(\mathrm{E}) = \frac{1}{4\pi^{3}\hbar}\int \frac{dS}{\upsilon_{\mathbf{k}}}$$

and

$$\frac{d\mathbf{k}}{d\mathrm{E}}d\mathrm{E} = \mathrm{N}(\mathrm{E})d\mathrm{E}$$

has been used in Eq. (2.3.8). In a metal, the function $\left(-\frac{\partial f^0{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)$ behaves like a delta function at the Fermi level; one is left with an integral over the Fermi surface S_F. Thus

$$\mathbf{J} = \frac{1}{4\pi^3}\frac{e^2}{\hbar}\int \tau \mathbf{v}_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}\frac{dS_F}{\upsilon_{\mathbf{k}}}\cdot \mathbf{E}\ . \tag{2.3.9}$$

Comparing Eq. (2.3.9) with the standard macroscopic equation,

$$\mathbf{J} = \sigma\mathbf{E} \tag{2.3.10}$$

where σ is a tensor, we obtain (in dyadic notation) [12],

$$\sigma = \frac{1}{4\pi^3}\frac{e^2}{\hbar}\int \tau \frac{\mathbf{v}_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}}{\upsilon_{\mathbf{k}}}dS_F\ . \tag{2.3.11}$$

We usually deal with crystals having cubic symmetry, in which case the conductivity tensor reduces to a scalar. Thinking of the case where **E** and **J** are both in the x-direction, we find that the integrand

$$(\mathbf{v}_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}\cdot \mathbf{E})_{\mathbf{x}} = \upsilon_x{}^2 E \tag{2.3.12}$$

where $E = |\mathbf{E}|$,

which is one-third of the contribution from the square of the total velocity, $\upsilon_x{}^2 E$. Thus in an isotropic medium,

$$\sigma = \frac{1}{4\pi^3}\frac{e^2}{3\hbar}\int \tau\upsilon\, dS_F$$

$$= \frac{1}{4\pi}\frac{e^2}{3\hbar}\int \Lambda\, dS_F \qquad (2.3.13)$$

where we have introduced the mean free path

$$\Lambda = \tau\upsilon\,. \qquad (2.3.14)$$

This is the basic formula for the electrical conductivity.

Substituting $g_{\mathbf{k}}$ in our assumption for $g_{\mathbf{k}} = f_{\mathbf{k}} - f_{\mathbf{k}}^0$ we therefore have

$$f_{\mathbf{k}} = f_{\mathbf{k}}^0 - \frac{\partial f_{\mathbf{k}}^0}{\partial \mathrm{E}(\mathbf{k})}\frac{\partial \mathrm{E}(\mathbf{k})}{\partial \mathbf{k}} \cdot \frac{e\tau}{\hbar}\mathbf{E}$$

$$= f_{\mathbf{k}}^0\left(\mathbf{k} - \frac{e\tau}{\hbar}\mathbf{E}\right) \qquad (2.3.15)$$

by Taylor's theorem. Note that the relation $\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathrm{E}(\mathbf{k})$ is used. Another point to notice is that Eq. (2.3.15) can be rewritten

$$f_{\mathbf{k}} = f_{\mathbf{k}}^0\left(\mathrm{E} + e\tau\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}\right) \qquad (2.3.16)$$

as if the electron in state $\mathbf{k}$ has gained the energy of the amount

$$\delta \mathrm{E} = e\tau \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}. \qquad (2.3.17)$$

This extra energy acquired from the collision with the impurities, or phonons, is expressed in term of the drift velocity, $\delta \mathbf{v}_{\mathbf{k}}$, in the direction of the field, such that

$$\delta \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial \mathrm{E}}{\partial \mathbf{v}_{\mathbf{k}}} = \delta \mathrm{E} \qquad (2.3.18)$$

$$\delta \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial \mathrm{E}}{\partial \mathbf{v}_{\mathbf{k}}} = e\tau \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E} \qquad (2.3.19)$$

$$\delta \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{v}_{\mathbf{k}}} \left(\frac{1}{2} m \mathbf{v}_{\mathbf{k}}^2 \right) = e\tau \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}$$

so that

$$\delta \mathbf{v}_{\mathbf{k}} = \frac{e\tau}{m} \mathbf{E} \qquad (2.3.20)$$

for a classical particle of mass m. Note that the only kinetic part of an electronic energy E survives in Eq. (2.3.19).

If there are n particles per unit volume, then the current density due to an applied field $\mathbf{E}$ is

$$\mathbf{J} = ne\delta \mathbf{v}_{\mathbf{k}}. \qquad (2.3.21)$$

From Eqs. (2.3.20), (2.3.21) and (2.3.10), we get

$$\sigma = \frac{ne^2\tau}{m} . \qquad (2.3.22)$$

From Eqs. (2.3.13) and (2.3.22), we see that the conductivity depends only on the property of the electrons near the Fermi level, not on the total number of electrons in the metal. The high conductivity of metals is therefore to the high velocity of the few electrons at the top of the Fermi distribution rather than the total density of free electrons, which can be slowly drifting.

2.4 CALCULATION OF RELAXATION TIME [12]

We still have not solved the integral equation (2.3.3). The most general possible solution would be

$$g_{\mathbf{k}} = \left(\frac{-\partial f_{\mathbf{k}}^{0}}{\partial \mathrm{E}} \right) e\mathbf{E} \cdot \Lambda(\mathbf{k}) \ , \qquad (2.4.1)$$

where $\Lambda(\mathbf{k})$ is a vector defined at each point $\mathbf{k}$ of the Fermi surface. Our elementary solution (2.3.7) is equivalent to the identification

$$\Lambda(\mathbf{k}) = \tau \mathbf{v}_{\mathbf{k}} \qquad (2.4.2)$$

showing that $\Lambda(\mathbf{k})$ is the vector mean free path of the electrons. In general case one might have $\Lambda(\mathbf{k})$ varying in magnitude, and deviating from the direction of $\mathbf{v}_{\mathbf{k}}$ over the Fermi surface.

It is sometime assumed that

$$\Lambda(\mathbf{k}) = \tau(\mathbf{k}) \mathbf{v}_{\mathbf{k}} \qquad (2.4.3)$$

where $\tau(\mathbf{k})$ is an anisotropy relaxation time varying over the Fermi surface. It is easy to show, however, that Eq. (2.4.1) is not always a complete solution of the integral equation and there is no direct method for evaluating the function $\tau(\mathbf{k})$.

The only simple solution is, in fact, the elementary solution (2.3.7). Suppose one substitutes for $g_{\mathbf{k}}$ in (2.3.3), and also assumes that one has elastic scattering, i.e.

$$Q(\mathbf{k},\mathbf{k}')d\mathbf{k}' = \delta(\mathrm{E}-\mathrm{E}')\vartheta(\mathbf{k},\mathbf{k}')d\Omega' d\mathrm{E} \tag{2.4.4}$$

where $\delta(\mathrm{E}-\mathrm{E}')$ is Dirac's delta function, $\vartheta(\mathbf{k},\mathbf{k}')d\Omega'$ the differential transition probability subtended by element of solid angle $d\Omega'$ in the direction of $\mathbf{k}'$ after scattering (the magnitude of $\mathbf{k}'$ being fixed by the requirement that the energy is conserved during the collision).

Eliminating the delta function of energy on both sides of Eq. (2.3.3),

$$\left(-\frac{\partial f^0{}_{\mathbf{k}}}{\partial \mathrm{E}}\right)\mathbf{v}_{\mathbf{k}} \cdot e\mathbf{E} = \int (g_{\mathbf{k}} - g_{\mathbf{k}'})Q(\mathbf{k},\mathbf{k}')d\mathbf{k}', \tag{2.3.3}$$

we have

$$\int \left(-\frac{\partial f^0_{\mathbf{k}}}{\partial \mathrm{E}}\right) e\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}\, d\mathrm{E}' =$$

$$\iiint \left\{ \left[\left(-\frac{\partial f^0_{\mathbf{k}}}{\partial \mathrm{E}}\right) e\tau\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E} - \left(-\frac{\partial f^0_{\mathbf{k}'}}{\partial \mathrm{E}'}\right) e\tau\mathbf{v}_{\mathbf{k}'} \cdot \mathbf{E} \right] \delta(\mathrm{E}-\mathrm{E}')\vartheta(\mathbf{k},\mathbf{k}')d\Omega' d\mathrm{E} \right\} d\mathrm{E}'$$

where in equilibrium state $\left(-\frac{\partial f^0_{\mathbf{k}}}{\partial \mathrm{E}}\right) = \delta(\mathrm{E}-\mathrm{E}_F)$ is Dirac's delta function at the Fermi energy E_F. Then the left hand side becomes

$$\int \delta(\mathrm{E}-\mathrm{E}_F)e\mathbf{v}_\mathbf{k}\cdot\mathbf{E}\,d\mathrm{E}' = e\mathbf{v}_\mathbf{k}\cdot\mathbf{E}.$$

In the same manner, finally we have

$$\mathbf{v}_\mathrm{k}\cdot\mathbf{E} = \tau\int(\mathbf{v}_\mathrm{k}-\mathbf{v}_{\mathrm{k}'})\cdot\mathbf{E}\,\vartheta(\mathbf{k},\mathbf{k}')d\Omega'. \tag{2.4.5}$$

to be evaluated over the Fermi surface. This is a functional relation, which imposes conditions on the form of $\vartheta(\mathbf{k},\mathbf{k}')$. It is easy to show that it holds when we have a spherical Fermi surface, with $|\mathbf{v}_\mathbf{k}| = \upsilon = \frac{\hbar k}{m}$ constant, and when

$$\vartheta(\mathbf{k},\mathbf{k}') = \vartheta(\theta); \tag{2.4.6}$$

that is, the relation (2.4.5) can be satisfied when the scattering probability is a function of only the angle between the two wave vectors.

If these conditions, Eqs. (2.4.1) to (2.4.6) are satisfied, then we immediately have [13]

$$\frac{1}{\tau} = \int\left(1-\frac{\mathbf{v}_{\mathrm{k}'}\cdot\mathbf{E}}{\mathbf{v}_\mathrm{k}\cdot\mathbf{E}}\right)\vartheta(\theta)d\Omega'$$

or

$$\frac{1}{\tau} = \int(1-\cos\theta)\vartheta(\theta)d\Omega'. \tag{2.4.7}$$

This shows that the relaxation time is inversely proportional to an integral of the scattering probability $\vartheta(\theta)$ over all the process but weighted by a factor $(1-cos\,\theta)$, in favor of large scattering angles. This factor comes from $(\mathbf{v}_{\mathbf{k}}-\mathbf{v}_{\mathbf{k}'})\cdot\mathbf{E}$. The crucial point is not that the electron is scattered but the amount that the component of its velocity along the electric field is changed in the process.

We can express the scattering probability in term of the differential scattering cross section $\zeta(\theta)$ at a density N_i of impurities. The mean free path Λ is given by [12]

$$\frac{1}{\Lambda}=2\pi N_i\int_0^{\pi}(1-cos\,\theta)\zeta(\theta)sin\,\theta\,d\theta\,. \tag{2.4.8}$$

This formula will be applied to the Ziman theory in the next Chapter.