

A New Study on Calculation of Electron Transport Characteristics in Semiconductor Materials

¹H. Arabshahi and ²F. Sarlak

¹Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran

²Department of Physics, Payame Nour University of Fariman, Fariman, Iran

Abstract: We introduce a new calculation method to compute the electron transport properties in semiconductor devices. Using the relaxation-time approximation, the Boltzmann transport equation for electrons has been solved to calculate the thermal energy flux, electrical conductivity, seebeck coefficient and thermal conductivity.

Key words: Semiconductor device, Boltzmann transport equation, seebeck coefficient, flux, coefficient, electrons

INTRODUCTION

To carry out calculations of the electronic transport properties of in semiconductor material and devices it is necessary to solve the Boltzmann transport equation. There are many different techniques for the solution of the Boltzmann equation when the applied field is sufficiently low. The use of numerical calculation to solve the Boltzmann equation has been described and reviewed elsewhere (Rode and Gaskill, 1995; Moglestue, 1993; Tsen *et al.*, 1997). However, in more general cases the Boltzmann transport equation is often exceedingly difficult to solve directly.

By contrast, it is relatively easy although, computationally intensive, to simulate the trajectories of individual carriers as they move through a semiconductor under the influence of the applied field and the random scattering processes.

Indeed, much of the understanding of high field transport in bulk semiconductors and in devices has been obtained through the use of such a method, Monte Carlo simulation (Ridley, 1997; Brooks, 1951; Jacoboni and Lugli, 1989; Madelung, 1978). The Monte Carlo method allows the Boltzmann transport equation to be solved using a statistical numerical approach by following the transport history of one or more carriers (particles), subject to the action of external forces such as an applied electric field and the intrinsic scattering mechanisms. In this communication we present calculations of electron transport characteristics in low electric field application. We demonstrate the effect of low electric field on the electron transport properties in these materials.

CALCULATION METHOD

Consider the distribution function of electrons is f and the number of electrons with an energy between E and $E+dE$ is $fD(E)dE$. Since, the electric field, temperature gradient and concentration gradient are small, these electrons will have almost the same probability to move toward any direction. Also because the solid angle of a sphere is 4π , the probability for an electron to move in the (θ, ϕ) direction within a solid angle $d\Omega = \sin\theta d\theta d\phi$ will be $d\Omega/4\pi$. A charge q ($= -e$ for electrons and $+e$ for holes) moving in the (θ, ϕ) direction within a solid angle $d\Omega$ causes a charge flux of $qv\cos\theta$ and energy flux $Ev\cos\theta$ in the Z direction where $d\Omega$ is defined as the angle between the velocity vector and the positive Z direction with a range between $0-\pi$. Hence, the charge flux and energy flux in the Z direction carried by all electrons moving toward the entire sphere surrounding the point are, respectively:

$$J_z = \int \frac{d\Omega}{4\pi} \int_{E=0}^{\infty} (fD(E))(qv\cos\theta)dE \quad (1)$$

$$= \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta\cos\theta d\theta \int_{E=0}^{\infty} fD(E)qv dE$$

$$J_{Ez} = \int \frac{d\Omega}{4\pi} \int_{E=0}^{\infty} (fD(E))(Ev\cos\theta)dE \quad (2)$$

$$= \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta\cos\theta d\theta \int_{E=0}^{\infty} fD(E)Ev dE$$

With the relaxation-time approximation, the Boltzmann Transport Equation for electrons take the following form:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + q\vec{E} \cdot \frac{\partial f}{\partial \vec{p}} = \frac{f_0 - f}{\tau} \quad (3)$$

where, $q = -e$ for electrons and $+e$ for holes. For the steady state case with small temperature/concentration gradient and electric field in the Z direction only, the variation of the distribution function in time is much smaller than that in space or:

$$\frac{\partial f}{\partial t} \ll \vec{v} \cdot \nabla f$$

So that, we can assume:

$$\frac{\partial f}{\partial t} \sim 0$$

The temperature gradient and electric field is small so that the deviation from equilibrium distribution f_0 is small i.e., $f_0 - f \ll f_0$, $\nabla f \approx \nabla f_0$ and:

$$\frac{\partial f}{\partial \vec{p}} \approx \frac{\partial f_0}{\partial \vec{p}} = \frac{\partial f_0}{\partial E} \frac{dE}{d\vec{p}} = \vec{v} \frac{\partial f_0}{\partial E}$$

With these assumptions, Eq. 3 becomes:

$$\vec{v} \cdot [\nabla f_0 + q\vec{E} \frac{\partial f_0}{\partial E}] = \frac{f_0 - f}{\tau} \quad (4)$$

The equilibrium distribution of electrons is the Fermi-Dirac distribution:

$$f_0(\vec{k}) = \frac{1}{\exp(\frac{E(\vec{k}) - \mu}{k_B T}) + 1} \quad (5)$$

$$= \frac{1}{\exp(\eta) + 1}; \quad \eta \equiv \frac{E - \mu}{k_B T}$$

Where:

- μ = The chemical potential that depends strongly on carrier concentration and weakly on temperature
- E and μ = Measured from the band edge (e.g., E_c for conduction band)

This reference system essentially sets $E_c = 0$ at different locations although the absolute value of E_c measured from a global reference varies at different location. In this reference system the same quantum state $\vec{k} = (k_x, k_y, k_z)$ has the same energy:

$$E(\vec{k}) = E(\vec{k}) - E_c = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}$$

at different locations. Hence, this reference system yields the gradient:

$$\nabla E(\vec{k}) = 0$$

simplifying the following derivation. If we use a global reference level as the zero energy reference point, the same quantum state $\vec{k} = (k_x, k_y, k_z)$ has different energy:

$$E(\vec{k}) = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m} + E_c$$

because E_c changes with locations. In this case, $\nabla E(\vec{k}) = \nabla E_c \neq 0$, making the following derivation somewhat inconvenient. However, both reference systems will yield the same result. From Eq. 5:

$$\frac{\partial f_0}{\partial E} = \frac{df_0}{d\eta} \frac{\partial \eta}{\partial E} = \frac{df_0}{d\eta} \frac{1}{k_B T}$$

or

$$\frac{df_0}{d\eta} = k_B T \frac{\partial f_0}{\partial E} \quad (6)$$

From Eq. 6:

$$\nabla f_0 = \frac{df_0}{d\eta} \nabla \eta = k_B T \frac{\partial f_0}{\partial E} \nabla \eta \quad (7)$$

Also because $\nabla E(\vec{k}) = 0$ for the reference system that we are using:

$$\nabla \eta = \frac{1}{k_B T} (\nabla E(\vec{k}) - \nabla \mu) - \frac{E - \mu}{k_B T^2} \nabla T \quad (8)$$

$$= -\frac{1}{k_B T} \nabla \mu - \frac{E - \mu}{k_B T^2} \nabla T$$

From Eq. 7 and 8:

$$\nabla f_0 = -\frac{\partial f_0}{\partial E} (\nabla \mu + \frac{E - \mu}{T} \nabla T) \quad (9)$$

Combine Eq. 4 and 9, we obtain:

$$\vec{v} \cdot [-\nabla \mu - \frac{E - \mu}{T} \nabla T + q\vec{E}] \frac{\partial f_0}{\partial E} = \frac{f_0 - f}{\tau} \quad (10)$$

Note that:

$$\vec{E} = -\nabla \phi_e \quad (11)$$

where, ϕ_e is the electrostatic potential (also called electrical potential which is the potential energy per unit

of charge associated with a time-invariant electric field \vec{E}). From Eq. 10 and 11, we obtain:

$$\vec{v} \bullet [-\nabla\mu - \frac{E-\mu}{T} \nabla T - q\nabla\phi_e] \frac{\partial f_0}{\partial E} = \frac{f_0 - f}{\tau} \quad (12)$$

From Eq. 12, we obtain:

$$f = f_0 - \tau \vec{v} \bullet [-\nabla\Phi - \frac{E-\mu}{T} \nabla T] \frac{\partial f_0}{\partial E} \quad (13)$$

where, $\Phi = \mu + q\phi_e$ is the electrochemical potential that combines the chemical potential and electrostatic potential energy. This definition of the electrochemical potential is the definition in Chen's text multiplied by a factor of q . Both definitions are used in the literature with the definition here are used more widely. Electrochemical potential is the driving force for current flow which can be caused by the gradient in either chemical potential (e.g., due to the gradient in carrier concentration) or the gradient in electrostatic potential (i.e., electric field). When you measure voltage ΔV across a solid using a voltmeter, you actually measured the electrochemical potential difference $\Delta\Phi$ per unit charge between the two ends of the solid i.e., $\Delta V = \Delta\Phi/q$. If there is no temperature gradient or concentration gradient in the solid, the measured voltage equals $\Delta\phi_e$. In the current case all the gradients and \vec{E} are in the Z direction so from Eq. 13:

$$\begin{aligned} f &= f_0 - \tau v \cos\theta [-\frac{d\mu}{dZ} - \frac{E-\mu}{T} \frac{dT}{dZ} + qE_z] \frac{\partial f_0}{\partial E} \\ &= f_0 - \tau v \cos\theta [-\frac{d\Phi}{dZ} - \frac{E-\mu}{T} \frac{dT}{dZ}] \frac{\partial f_0}{\partial E} \end{aligned} \quad (14)$$

Combine Eq. 1 and 14, we obtain the charge flux and energy flux, respectively:

$$\begin{aligned} J_z &= \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta \cos\theta d\theta \int_{E=0}^{\infty} f_0 D(E) q v dE + \\ &\int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta \cos^2\theta d\theta \\ &\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) q v^2 \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \end{aligned} \quad (15)$$

And:

$$\begin{aligned} J_{Ez} &= \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta \cos\theta d\theta \int_{E=0}^{\infty} f_0 D(E) E v dE + \\ &\int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta \cos^2\theta d\theta \\ &\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E v^2 \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \end{aligned} \quad (16)$$

Note that the first term in the right hand of Eq. 15 side is zero and the second term yields:

$$\begin{aligned} J_z &= \frac{1}{3} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) q v^2 \tau \\ &(\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \end{aligned} \quad (17)$$

$$\begin{aligned} J_{Ez} &= \frac{1}{3} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E v^2 \tau \\ &(\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \end{aligned} \quad (18)$$

Note that:

$$E = \frac{1}{2} m v^2 \quad (19)$$

Use Eq. 17 to eliminate v in Eq. 19, we obtain:

$$\begin{aligned} J_z &= \frac{2q}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \\ &= \frac{2q}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau (\frac{d\Phi}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ}) dE \end{aligned} \quad (20)$$

$$\begin{aligned} J_{Ez} &= \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E^2 \tau \\ &(\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \end{aligned} \quad (21)$$

The energy flux from Eq. 21 can be broken up into two terms as following:

$$\begin{aligned} J_{Ez} &= \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E^2 \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \\ &= \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E-\mu) \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE + \\ &\mu \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau (\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE \\ &= \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E-\mu) \tau \\ &(\frac{d\mu}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ} - qE_z) dE + \frac{\mu J_z}{q} \\ &= \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E-\mu) \tau (\frac{d\Phi}{dZ} + \frac{E-\mu}{T} \frac{dT}{dZ}) dE + \frac{\mu J_z}{q} \end{aligned} \quad (22)$$

where, J_z is the current density or charge flux given by Eq. 22. At temperature $T = 0$ K, the 1st term in the right hand side of Eq. 21 is zero, so that the energy flux at $T = 0$ K is:

$$J_{E_z}(T = 0K) = \frac{\mu J_z}{q} \quad (23)$$

Because electrons do not carry any thermal energy at $T = 0$ K, the thermal energy flux or heat flux carried by the electrons at $T \neq 0$ is:

$$J_{q_z}(T) = J_{E_z}(T) - J_{E_z}(T = 0) \\ = \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau \left(\frac{d\Phi}{dZ} + \frac{E - \mu}{T} \frac{dT}{dZ} \right) dE \quad (24)$$

Equation 23 and 24 can be rearranged as:

$$J_z = L_{11} \left(-\frac{1}{q} \frac{d\Phi}{dZ} \right) + L_{12} \left(-\frac{dT}{dZ} \right) \quad (25)$$

$$J_{q_z} = L_{21} \left(-\frac{1}{q} \frac{d\Phi}{dZ} \right) + L_{22} \left(-\frac{dT}{dZ} \right) \quad (26)$$

Where:

$$L_{11} = -\frac{2q^2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE \quad (27)$$

$$L_{12} = -\frac{2q}{3mT} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau dE \quad (28)$$

$$L_{21} = -\frac{2q}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau dE \quad (29) \\ = TL_{12}$$

$$L_{22} = -\frac{2}{3mT} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu)^2 \tau dE \quad (30)$$

ELECTRICAL CONDUCTIVITY

In the case of zero temperature gradient and zero carrier concentration gradient:

$$\frac{dT}{dZ} = 0 \quad \text{and} \quad \frac{d\mu}{dZ} = 0$$

Equation 24 becomes:

$$J_z = L_{11} \left(-\frac{1}{q} \frac{d\Phi}{dZ} \right) = L_{11} \left(-\frac{1}{q} \frac{d\mu}{dZ} + E_z \right) = L_{11} E_z \quad (31)$$

The electrical conductivity is defined as:

$$\sigma \equiv \frac{J_z}{E_z} = L_{11} = -\frac{2q^2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE \quad (32)$$

SEEBECK COEFFICIENT

In the case of non-zero temperature gradient along the Z direction, a thermoelectric voltage can be measured between the two ends of the solid with an open loop electrometer i.e, $j_z = 0$. Hence from Eq. 30 we obtain:

$$J_z = L_{11} \left(-\frac{1}{q} \frac{d\Phi}{dZ} \right) + L_{12} \left(-\frac{dT}{dZ} \right) = 0 \quad (33)$$

Therefore:

$$\left(\frac{d\Phi}{dZ} \right) = -\frac{qL_{12}}{L_{11}} \left(\frac{dT}{dZ} \right) \quad (34)$$

As discussed earlier, the voltage that the electrometer measure between the two ends of the solid is $\Delta V = \Delta\Phi/q$. Similarly, $dV = d\Phi/q$.

The Seebeck coefficient is defined as the ratio between the voltage gradient and the temperature gradient for an open loop configuration with zero net current flow:

$$S = -\frac{\left(\frac{dV}{dZ} \right)}{\left(\frac{dT}{dZ} \right)} = -\frac{1}{q} \frac{\left(\frac{d\Phi}{dZ} \right)}{\left(\frac{dT}{dZ} \right)} = \frac{L_{12}}{L_{11}} \\ = \frac{1}{qT} \left(\frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE} \right) \quad (35) \\ = -\frac{1}{qT} \left(\mu - \frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E^2 \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE} \right)$$

Combine Eq. 33-35, we can write:

$$J_z = \sigma \left(-\frac{1}{q} \frac{d\Phi}{dZ} \right) + \sigma S \left(-\frac{dT}{dZ} \right)$$

The scattering mean free time depends on the energy and we can assume:

$$\tau = \tau_0 E^r \quad (36)$$

where, τ_0 is a constant independent of E. When E is measured from the band edge for either electrons or holes, the density of states:

$$D(E) = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2} \tag{37}$$

Combine Eq. 35 and 37:

$$S = -\frac{1}{qT} \left(\mu - \frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E^2 \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE} \right) \tag{38}$$

$$= -\frac{1}{qT} \left(\mu - \frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} E^{2+r+1/2} dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} E^{1+r+1/2} dE} \right)$$

The integrals in Eq. 38 can be simplified using the product rule:

$$\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} E^s dE = f_0 E^s \Big|_0^{\infty} - s \int_{E=0}^{\infty} f_0 E^{s-1} dE \tag{39}$$

$$= -s \int_{E=0}^{\infty} f_0 E^{s-1} dE$$

Using Eq. 38 to reduce Eq. 39 to:

$$S = -\frac{1}{qT} \left(\mu - \frac{(r+5/2) \int_{E=0}^{\infty} f_0 E^{r+3/2} dE}{(r+3/2) \int_{E=0}^{\infty} f_0 E^{r+1/2} dE} \right) \tag{40}$$

The two integrals in Eq. 40 can be simplified with the reduced energy $\xi = E/k_{BT}$

$$\int_{E=0}^{\infty} f_0(E, \mu) E^n dE = (k_B T)^{n+1} \int_0^{\infty} f_0(\xi, \eta) \xi^n d\xi \tag{41}$$

$$= (k_B T)^{n+1} F_n(\eta), \quad \eta = \mu / k_B T$$

Where the Fermi-Dirac integral is defined as:

$$F_n(\eta) = \int_0^{\infty} f_0(\xi, \eta) \xi^n d\xi \tag{42}$$

Use Eq. 42 to reduce Eq. 41 to:

$$S = -\frac{1}{qT} \left(\mu - k_B T \frac{\left(\frac{r+5}{2} \right) F_{r+3/2}(\eta)}{\left(\frac{r+3}{2} \right) F_{r+1/2}(\eta)} \right)$$

$$= -\frac{k_B}{q} \left(\eta - \frac{\left(\frac{r+5}{2} \right) F_{r+3/2}(\eta)}{\left(\frac{r+3}{2} \right) F_{r+1/2}(\eta)} \right) \tag{43}$$

Seebeck coefficient for metals: For metals with $\eta = \mu/k_B T \gg 0$, the Fermi-Dirac integral can be expressed in the form of a rapidly converging series:

$$F_n(\eta) = \int_0^{\infty} f_0 \xi^n d\xi = -\frac{1}{n+1} \int_0^{\infty} \frac{\partial f_0}{\partial \xi} \xi^{n+1} d\xi$$

$$= -\frac{1}{n+1} \int_0^{\infty} \frac{\partial f_0}{\partial \xi} \left(\eta^{n+1} + \sum_{m=1}^{\infty} \frac{d^m(\xi^{n+1})}{d\xi^m} \Big|_{\xi=\eta} \frac{(\xi-\eta)^m}{m!} \right) d\xi \tag{44}$$

$$= -\frac{1}{n+1} \int_0^{\infty} \frac{\partial f_0}{\partial \xi} \left(\eta^{n+1} + (n+1)\eta^n(\xi-\eta) + (n+1)n\eta^{n-1} \frac{(\xi-\eta)^2}{2} + \dots \right) d\xi$$

$$= \frac{\eta^{n+1}}{n+1} + n\eta^{n-1} \frac{\pi^2}{6} + \dots$$

If we use only the 1st two terms of Eq. 44 to express the two Fermi-Dirac integrals in Eq. 43, we obtain the following ($q = -e$ for electrons in metals):

$$S = -\frac{k_B}{q} \left(\eta - \frac{\left(\frac{r+5}{2} \right) F_{r+3/2}(\eta)}{\left(\frac{r+3}{2} \right) F_{r+1/2}(\eta)} \right)$$

$$= \frac{k_B}{e} \left(\frac{\eta \left(\frac{r+3}{2} \right) F_{r+1/2}(\eta) - \left(\frac{r+5}{2} \right) F_{r+3/2}(\eta)}{\left(\frac{r+3}{2} \right) F_{r+1/2}(\eta)} \right)$$

$$= \frac{k_B}{e} \left(\frac{\eta \left(\frac{r+3}{2} \right) \left(\frac{\eta^{r+3/2}}{\frac{r+3}{2}} + \left(\frac{r+1}{2} \right) \eta^{r-1/2} \frac{\pi^2}{6} \right) - \left(\frac{r+5}{2} \right) \left(\frac{\eta^{r+5/2}}{\frac{r+5}{2}} + \left(\frac{r+3}{2} \right) \eta^{r+1/2} \frac{\pi^2}{6} \right)}{\left(\frac{r+3}{2} \right) \frac{\eta^{r+3/2}}{\frac{r+3}{2}}} \right) \tag{45}$$

$$= -\frac{\pi^2 k_B}{3e} \left(\frac{k_B T}{\mu} \right) \left(\frac{3}{2} + r \right)$$

This value can be either positive or negative depending on r or how the scattering rate depends on electron energy. We can ignore the weak temperature dependence of μ and assume $\mu = E_F$, the Fermi level that is the highest energy occupied by electrons at 0 K in a metal.

SEEBECK COEFFICIENT FOR NONDEGENERATE SEMICONDUCTORS

In non-degenerate semiconductors, μ is located within the bandgap with a distance from the conduction or valence band edges larger than $3k_B T$ so that:

$$\frac{E - \mu}{k_B T} = \zeta - \eta > 3$$

This is true for both electrons in the conduction band and holes in valence band. For holes in valence band, the energy is higher at a position further down below the valence band edge. When:

$$\frac{E - \mu}{k_B T} = \zeta - \eta > 3$$

The Fermi-Dirac integrals become:

$$\begin{aligned} F_n(\eta) &= \int_0^\infty f_0(\zeta, \eta) \zeta^n d\zeta \\ &= \int_0^\infty \frac{1}{\exp(\zeta - \eta) + 1} \zeta^n d\zeta \approx \int_0^\infty \frac{1}{\exp(\zeta - \eta)} \zeta^n d\zeta \quad (46) \\ &= \exp(\eta) \int_0^\infty \exp(-\zeta) \zeta^n d\zeta = \exp(\eta) \Gamma(n + 1) \end{aligned}$$

Where the gamma (Γ) function has the property:

$$\Gamma(n + 1) = \int_0^\infty \exp(-\zeta) \zeta^n d\zeta = n\Gamma(n) \quad (47)$$

We can use Eq. 47 to reduce Eq. 42 to obtain:

$$\begin{aligned} S &= -\frac{k_B}{q} \left(\eta - \frac{\left(\frac{r+5}{2}\right) \exp(\eta) \Gamma\left(\frac{r+5}{2}\right)}{\left(\frac{r+3}{2}\right) \exp(\eta) \Gamma\left(\frac{r+3}{2}\right)} \right) \quad (48) \\ &= -\frac{k_B}{q} \left(\eta - \left(\frac{r+5}{2}\right) \right) = -\frac{1}{qT} \left(\mu - k_B T \left(\frac{r+5}{2}\right) \right) \end{aligned}$$

In this equation, μ is measured from the conduction band edge E_C for electrons and from the valence band edge E_V for holes. Located within the bandgap, μ is

negative for electrons and is also negative for holes because the hole energy is higher when the energy level is moved further down. Also $q = -e$ for electrons and $+e$ for holes so that, the Seebeck coefficient is negative for electrons in the conduction band and positive for holes in the valence band.

If μ is measured from a global reference instead of the band edge as the zero energy point, we can express Eq. 48 for electrons and holes separately; For electrons:

$$S_e = -\frac{1}{eT} (E_C - \mu + (r + 5/2)k_B T) < 0 \quad (49)$$

For holes:

$$S_h = \frac{1}{eT} (\mu - E_V + (r + 5/2)k_B T) > 0 \quad (50)$$

The effective Seebeck coefficient in a nondegenerate semiconductors have contribution from both electrons and holes i.e.,

$$S = \frac{n\mu_e S_e + p\mu_h S_h}{n\mu_e + p\mu_h} \quad (51)$$

Where:

- n and p = Electron and hole concentrations, respectively
- μ_e and μ_h = The mobility of electrons and holes, respectively

The mobility is defined in the following section on Wiedemann-Franx law.

THERMAL CONDUCTIVITY OF ELECTRONS

From Eq. 21:

$$-\frac{1}{q} \frac{d\Phi}{dZ} = -\frac{L_{12}}{L_{11}} \left(-\frac{dT}{dZ}\right) + \frac{1}{L_{11}} J_z \quad (52)$$

Use Eq. 52 to eliminate $\frac{d\Phi}{dZ}$ from Eq. 21 b to obtain:

$$\begin{aligned} J_{q_z} &= \frac{L_{21}}{L_{11}} J_z + \left(L_{22} - \frac{L_{12} L_{21}}{L_{11}} \right) \left(-\frac{dT}{dZ}\right) \quad (53) \\ &= \Pi J_z + k_e \left(-\frac{dT}{dZ}\right) \end{aligned}$$

The Peltier coefficient Π and thermal conductivity k_e are defined in the following. In the case of zero current $J_z = 0$ and non-zero temperature gradient along the Z direction:

$$J_{q_z} = \left(L_{22} - \frac{L_{12}L_{21}}{L_{11}} \right) \left(-\frac{dT}{dZ} \right) \quad (54)$$

The thermal conductivity of electrons:

$$k_e = -\frac{J_{q_z}}{dT/dZ} = \left(L_{22} - \frac{L_{12}L_{21}}{L_{11}} \right) = (L_{22} - L_{21}S) = \frac{2}{3mT} \left(\frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E(E-\mu)^2 \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E \tau dE} \right) \quad (55)$$

Equation 55 can be reduced to the following by expanding the (E-μ) term in the two integrals:

$$k_e = \frac{2}{3mT} \left(\frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E^2 \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E \tau dE} - \frac{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E^3 \tau dE}{\int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E \tau dE} \right) \quad (56)$$

For metals, S is usually very small so that from Eq. 56:

$$k_e = (L_{22} - L_{21}S) \approx L_{22} = -\frac{2}{3mT} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E(E-\mu)^2 \tau dE \quad (57)$$

Note that:

$$\frac{\partial f_0}{\partial T} = \frac{df_0}{d\eta} \frac{\partial \eta}{\partial T} = -\frac{df_0}{d\eta} \frac{E-\mu}{k_B T^2} \quad (58)$$

Compare Eq. 57 with Eq. 5, we can obtain:

$$\frac{\partial f_0}{\partial E} = -\frac{T}{E-\mu} \frac{\partial f_0}{\partial T} \quad (59)$$

Combine Eq. 59 and 56:

$$k_e = \frac{2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial T} D(E)E(E-\mu)\tau dE \quad (60)$$

We can use $E = mv^2/2$ to rewrite Eq. 60 as:

$$k_e = \frac{1}{3} \int_{E=0}^{\infty} \frac{\partial f_0(E)}{\partial T} D(E)v^2(E-\mu)\tau dE \quad (61)$$

When E is far away from μ, $f_0(E)$ remains to be either 0 or 1 as the temperature changes, so that:

$$\frac{\partial f_0(E)}{\partial T}$$

is non-zero only when E is close to μ. Therefore, Eq. 61 can be approximated by taking $v = v_F$ and $\tau = \tau_F$, i.e., the Fermi velocity and the scattering mean free time of Fermi electrons:

$$k_e = \frac{1}{3} v_F^2 \tau_F \int_{E=0}^{\infty} \frac{\partial f_0(E)}{\partial T} D(E)(E-\mu) dE = \frac{1}{3} v_F^2 \tau_F C_e = \frac{1}{3} C_e v_F l_F \quad (62)$$

This is essentially the Kinetic theory expression of the thermal conductivity.

WIEDEMANN-FRANZ LAW

From Eq. 24, the electrical conductivity is:

$$\sigma \equiv \frac{J_z}{E_z} = -\frac{2e^2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E)E \tau dE \quad (63)$$

$$\frac{\partial f_0(E)}{\partial E}$$

is non-zero only when E is close to μ and can be approximated to as a delta function:

$$\frac{\partial f_0(E)}{\partial E} \approx -\delta(E-\mu) \quad (64)$$

Combine Eq. 64 and 63:

$$\sigma \equiv \frac{J_z}{E_z} = \frac{2e^2}{3m} \int_{E=0}^{\infty} \delta(E-\mu) D(E)E \tau dE = \frac{2e^2}{3m} D_{E=\mu} \mu \tau_{E=\mu} = \frac{2e^2}{3m} D_F \mu \tau_F \quad (65)$$

We can use $\mu \approx E_F = mv_F^2/2$ to reduce Eq. 65 to:

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

Note that the electron concentration can be calculated as:

$$\begin{aligned}
 n &= \int_{E=0}^{\infty} f_0(E)D(E)dE \\
 &= \int_{E=0}^{\infty} f_0(E, T=0)D(E)dE = \int_{E=0}^{E_F} D(E)dE \\
 &= \int_{E=0}^{E_F} \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{2/3} E^{1/2} dE = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{2/3} E_F^{3/2} \\
 &= \frac{2}{3} D_F E_F \approx \frac{2}{3} D_F \mu
 \end{aligned} \tag{67}$$

Combine Eq. 67 and 65, we obtain:

$$\sigma = \frac{e^2}{m} n \tau_F \tag{68}$$

If we use the following definition of electron mobility:

$$\mu_e = \frac{e}{m} \tau_F \tag{69}$$

We obtain from Eq. 68:

$$\sigma = ne\mu_e \tag{70}$$

Note that μ_e is electron mobility and is different from μ that is chemical potential. We can use Eq. 68 and 62 to calculate the ratio between the electron thermal conductivity and electrical conductivity:

$$\frac{k_e}{\sigma} = \frac{\frac{1}{3} v_F^2 \tau_F C_e}{\frac{e^2}{m} n \tau_F} = \frac{m C_e v_F^2}{3 n e^2} \tag{71}$$

Here we have assumed that the τ_F is the same in the thermal conductivity and electrical conductivity expressions. As discussed in Chen, these two τ_F terms can be different.

Note that the electron specific heat of metals has been derived previously as:

$$C_e = \frac{1}{2} \pi^2 n k_B T / T_F = \frac{1}{2} \frac{\pi^2 n k_B T}{\frac{m v_F^2}{2 k_B}} = \frac{\pi^2 n k_B^2 T}{m v_F^2} \tag{72}$$

Combine Eq. 71 and 72, we obtain:

$$\frac{k_e}{\sigma} = \frac{m v_F^2}{3 n e^2} \frac{\pi^2 n k_B^2 T}{m v_F^2} = \frac{\pi^2 k_B^2 T}{3 e^2} \tag{73}$$

We define the Lorentz number:

$$L = \frac{\pi^2 k_B^2}{3 e^2} = 2.45 \times 10^{-8} (W \Omega K^{-2}) \tag{74}$$

So that, we obtain the Wiedemann-Franz law:

$$\frac{k_e}{\sigma} = L T \tag{75}$$

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