

The Wiedemann-Franz Law for Electrical and Thermal Conduction in Metals

V. Devanathan*

The Academy of Sciences, Chennai
Department of Nuclear Physics, University of Madras
Guindy Campus, Chennai - 600 025

Received 25 November 2020

Abstract: The Wiedemann-Franz law states that the ratio of the thermal conductivity to the electrical conductivity is the same for all metals at a given temperature. It has been explained on the basis of free valence electron theory of metals. In classical physics, the electrons are treated like molecules in a perfect gas, obeying kinetic theory of gases. It has given only qualitative agreement. In quantum physics, electrons are treated as Fermions, obeying both the Pauli exclusion principle and Fermi-Dirac statistics. As a consequence, not all the valence electrons but only those in the neighbourhood of the Fermi level contribute to the reaction. A simple elegant method of deriving the formulae for electrical and thermal conductivity in quantum theory is presented; which is not found in standard textbooks. The quantum theory yields results in quantitative agreement with experiments.

1 Introduction

The ratio of the thermal conductivity K and the electrical conductivity σ of a metal is proportional to temperature.

$$\frac{K}{\sigma} = LT$$

where L is a constant, known as the Lorenz number. The empirical law is named after Wiedemann and Franz who found in 1853 that K/σ is approximately the same for different metals at the same temperature. The proportionality constant was discovered by Lorenz in 1872.

Soon after the discovery of electron by J.J. Thomson in the year 1897, Paul Drude proposed that the electrical conductivity in metals is essentially due to the

*Email: vdevanathan@hotmail.com

flow of electrons. The Drude model of electrical conductivity was proposed in 1900 and extended by Lorentz in 1905. Sommerfeld applied quantum theory in 1928.

Now, we know that the electrical and thermal conductivities in a metal are due to valence electrons [1-3] that flow freely through a lattice structure of positive ions (nucleus + core electrons). In classical physics, the valence electrons can occupy a continuous series of energy levels and they are treated like molecules in a perfect gas as in kinetic theory of gases. All the valence electrons participate in the conduction phenomena and the mean energy of an electron depends on the temperature.

In quantum physics, the valence electrons occupy a set of closely packed discrete energy levels since they are confined within a volume and obey the Pauli exclusion principle that no two identical electrons can occupy the same energy level. At absolute zero temperature, all the electrons occupy the lowest possible energy levels below a certain energy level known as the Fermi energy level. So, as the temperature is raised, not all the electrons can jump to higher energy levels but only those just below the Fermi energy level can jump to the vacant energy levels above the Fermi level. This is due to the operation of Pauli Exclusion principle. Hence in quantum physics, only the valence electrons in the neighbourhood of Fermi energy level participate in the electrical and thermal conductivities.

In Sec. 2, we have deduced expressions for electrical and thermal conductivities in metals, using classical physics, assuming all valence electrons participate in the process. It is shown that the ratio of the electrical conductivity and the thermal conductivity is a constant at a given temperature but the proportionality constant is less than half the value found experimentally. So, there is only a qualitative agreement but not quantitative agreement.

In Sec. 3, the problem is addressed, using quantum physics. In quantum physics, electrons are treated as Fermions, occupying discrete energy states and obeying the Pauli exclusion principle that no two identical electrons can occupy the same state. Electrons obey the Fermi-Dirac statistics and the distribution of electrons at a given temperature is governed by the Fermi distribution function. In quantum physics, only the electrons in the neighbourhood of Fermi energy level participate in the reaction. It is a remarkable coincidence that the same expressions are obtained, both in classical and quantum physics, for electrical and thermal conductivity in terms of relaxation time τ and the electronic specific heat $[C_V]_{el}$, but they assume different values in quantum physics. The quantum physics yields values in quantitative agreement with experiments at normal temperatures.

In Sec. 4 and Sec. 5, the problem is treated ab-initio using Fermi distribution function [4-5] and expressions for electrical conductivity and thermal conductivity are derived in a simple elegant way. This is something new and not found in standard textbooks [1-3].

In Sec. 6, numerical results are presented, which will be useful to the reader for a deeper understanding of the subject.

2 Classical Physics

2.1 Electrical conductivity

According to Ohm's law, the resistance $r = V/I$, where V denotes the applied voltage and I the current that flows through the conductor. If l is the length of the conductor and A , its area of cross section and ρ , its specific resistance, then $r = \rho l/A$.

$$r = \frac{\rho l}{A} = \frac{V}{I} = \frac{\mathcal{E} l}{JA} \longrightarrow \rho = \frac{\mathcal{E}}{J}.$$

where \mathcal{E} is the electric field caused by the application of external potential V and J is the current density ($I = JA$). The electrical conductivity σ is the reciprocal of the specific resistance $\sigma = 1/\rho$

When an external electric field \mathcal{E} is applied to a metal, then there will be a flow of current \mathbf{I} in the direction of the field with current density \mathbf{J} .

$$\mathbf{J} = \sigma \mathcal{E}, \quad (1)$$

where σ denotes the electrical conductivity of the metal. The current flow is due to the flow of electrons due to the application of the electric field.

$$\mathbf{J} = -nev\mathbf{v},$$

where n denotes the electron density, $-e$ the electron charge and \mathbf{v} the electron velocity. In the absence of the electric field, electrons will be moving with random velocity in all directions and hence the net current will be zero. On the application of the electric field, electrons will undergo acceleration and due to the dissipating forces arising out of the collisions with lattice points, the electrons will attain a steady state with a drift velocity \mathbf{v}_d in the direction of the applied field, in time τ , known as the relaxation time. If m is the mass of the electron, then the acceleration \mathbf{a} that it will experience due to the application of electric field \mathcal{E} is

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{-e\mathcal{E}}{m}; \quad \mathbf{v}_d = \mathbf{a}\tau = \frac{-e\mathcal{E}\tau}{m} \quad (2)$$

$$\mathbf{J} = -nev_d = \frac{ne^2\tau}{m}\mathcal{E} = \sigma\mathcal{E}. \quad (3)$$

It follows that

$$\sigma = \frac{\mathbf{J}}{\mathcal{E}} = \frac{ne^2\tau}{m} = ne\mu; \quad \mu = \frac{e\tau}{m} = -\frac{\mathbf{v}_d}{\mathcal{E}}. \quad (4)$$

The quantity μ is known as the *mobility* and it is the drift velocity of electron along the field direction due to the application of unit intensity of electric field.

If λ is the mean free path, then λ is the average distance travelled by the electron in time τ . Then

$$v_d = \frac{\lambda}{\tau} \longrightarrow \tau = \frac{\lambda}{v_d}. \quad (5)$$

It follows that

$$\sigma = \frac{ne^2\tau}{m} = \frac{ne^2\lambda}{mv_d}. \quad (6)$$

It is assumed that the valence electrons move over the entire solid as free electrons like the molecules of a perfect gas in a container [1-3]. Accordingly, the electrons obey the laws of kinetic theory of gases,

$$\frac{1}{2}mv_d^2 = \frac{3}{2}k_B T; \quad v_d = \left(\frac{3k_B T}{m}\right)^{1/2}; \quad (7)$$

where k_B denotes the Boltzmann constant and T , the absolute temperature. . Thus,

$$\sigma = \frac{ne^2\lambda}{mv_d} = \frac{ne^2\lambda}{\sqrt{3mk_B T}}. \quad (8)$$

According to the above Eq. (8), the resistivity is proportional to the square root of temperature but we know in metals, the resistivity is directly proportional to temperature. So, the classical theory which uses the kinetic theory of gases for obtaining the temperature dependence is invalid.

2.2 Thermal conductivity

Generally heat is conducted in solids either by the free electrons or by lattice vibrations. In metals, conduction by free electrons dominate and so let us confine our consideration to free electron motion [1-3].

Consider a conductor with unit area of cross section, one end of which is kept at a higher temperature than the other. In the steady state, the three sections A, B, C, separated by a distance equal to the mean free path λ of the electron, will be at different temperatures, as shown in Fig. 1. Consider the net heat transfer and the net energy transfer across the section B. It is reasonable to assume that one-sixth of the total number of electrons move from left to right and similarly an equal number move from right to left and they contribute to the energy transfer. Let n be the electron density and v , its average velocity.

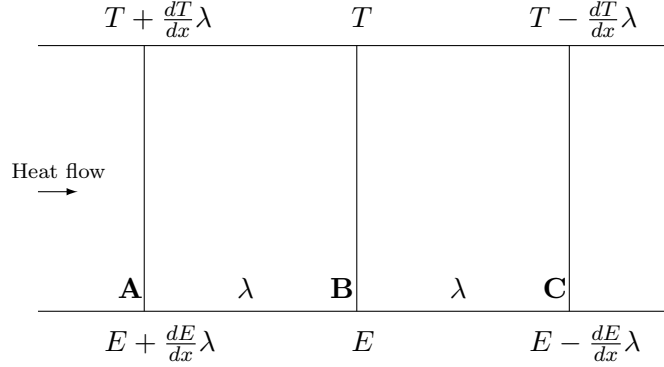


Figure 1: Heat conduction through a conductor

$$\text{Energy transfer from A to B} = \frac{1}{6}nv\lambda \frac{dE}{dx}$$

$$\text{Energy transfer from C to B} = -\frac{1}{6}nv\lambda \frac{dE}{dx}$$

$$\text{Net energy transfer across B} = \frac{1}{6}nv\lambda \frac{dE}{dx} - \left(-\frac{1}{6}nv\lambda \frac{dE}{dx} \right) = \frac{1}{3}nv\lambda \frac{dE}{dx}$$

This should be equal to the net heat transfer $Q = K(dT/dx)$ across B per unit time. The quantity K is known as the thermal conductivity.

$$K \frac{dT}{dx} = \frac{1}{3}nv\lambda \frac{dE}{dx} = \frac{1}{3}nv\lambda \frac{dE}{dT} \frac{dT}{dx}$$

Thus, we obtain an expression for the thermal conductivity K .

$$K = \frac{1}{3}nv\lambda \frac{dE}{dT} = \frac{1}{3}nv\lambda [C_V]_{\text{el}}, \quad (9)$$

where $[C_V]_{\text{el}} = dE/dT$ is the specific heat associated with each electron. In terms of the relaxation time $\tau = \frac{\lambda}{v}$,

$$K = \frac{1}{3}nv^2\tau [C_V]_{\text{el}}. \quad (10)$$

Using the principles of kinetic theory of gases,

$$E = \frac{1}{2}mv^2 = \frac{3}{2}k_B T,$$

we get expressions for electronic specific heat $[C_V]_{\text{el}}$ and mean velocity of electron v .

$$[C_V]_{\text{el}} = \frac{dE}{dT} = \frac{3}{2}k_B; \quad v = \sqrt{\frac{3k_B T}{m}} \quad (11)$$

Substituting these values in K , we obtain

$$K = \frac{n\lambda k_B}{2} \sqrt{\frac{3k_B T}{m}}. \quad (12)$$

2.3 Ratio of K/σ

From Eqs. (8) and (12), we obtain

$$\frac{K}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 \quad (13)$$

Substituting the values of Boltzmann constant $k_B = 1.381 \times 10^{-23}$ J/K and electronic charge $e = 1.602 \times 10^{-19}$ C, we get

$$\frac{K}{\sigma T} = 1.11 \times 10^{-8} \text{ Watt ohm/K}^2 \quad (14)$$

Eq. (13) expresses the validity of Wiedemann-Franz law that the ratio of the thermal conductivity to the electrical conductivity of a metal is proportional to Temperature but does not yield correctly the proportionality constant.

3 Quantum Physics

Hitherto, we discussed the electrical and thermal conductivity in metals using the concepts of classical physics and the kinetic theory of gases. We could arrive at only qualitative results but failed to reach any quantitative agreement.

Let us now revisit the problem using Quantum Physics. The electrical and thermal conduction in metals are due to the valence electrons which are confined within the conductor. Since they are confined, they can occupy only discrete energy levels and since they are fermions, they obey Pauli exclusion principle.

3.1 Concept of phase-space and discrete energy levels

As discussed in an earlier paper by Devanathan [6], let us use the concept of phase-space to enumerate the discrete energy states of valence electrons in a metal.

The phase-space is a six-dimensional space which is a combination of ordinary space and momentum space. In classical physics, the state of a particle can be represented by a point in the phase-space. In quantum physics, the position and momentum of a particle are conjugate variables and they cannot be simultaneously determined accurately due to the operation of Heisenberg's uncertainty principle

and so the state of a particle can be represented only by a cell of finite volume h^3 , where h is the Planck constant. Hence the number of discrete energy states $Z(p)$ with momentum lying between p and $p + dp$ is given by

$$Z(p)dp = \frac{V4\pi p^2 dp}{h^3}, \quad (15)$$

where V denotes the volume of the conductor and h , Planck's constant. Although the energy states are discrete, they are so closely spaced that, for all practical purposes, they can be considered continuous. Let us express the energy levels in terms of the kinetic energy of electron $E = p^2/(2m)$, where m denotes the mass of the electron. Substituting $p = \sqrt{2mE}$ and $pdp = mdE$ in the above expression, we get the number of states lying between energy E and $E + dE$.

$$Z(E)dE = \frac{4\pi V}{h^3}(2mE)^{1/2}mdE = \frac{4\sqrt{2}\pi Vm^{3/2}E^{1/2}}{h^3}dE. \quad (16)$$

Electrons are spin- $\frac{1}{2}$ particles and so each electron can have two spin states, one with spin-up and another with spin-down. So, the number of electrons $N(E)dE$ that can be accommodated in volume V with energy lying between E and $E + dE$ and their corresponding energy $U(E)dE$ are

$$N(E)dE = 2 Z(E)dE = \left(\frac{8\sqrt{2}\pi Vm^{3/2}}{h^3} \right) E^{1/2}dE = A E^{1/2}dE \quad (17)$$

$$U(E)dE = 2 Z(E)EdE = \left(\frac{8\sqrt{2}\pi Vm^{3/2}}{h^3} \right) E^{3/2}dE = A E^{3/2}dE \quad (18)$$

where A is a constant.

$$A = \frac{8\sqrt{2}\pi Vm^{3/2}}{h^3}. \quad (19)$$

3.2 Electron distribution at Temperature $T = 0^\circ$ K

At temperature $T = 0^\circ$ K, all the low-lying states up to the Fermi energy E_F will be filled. The valence electron distribution and the corresponding energy distribution are $N(E)$ and $U(E)$ as given by Eqs. (17) and (18). Now, one can calculate the total number N_{total} of valence electrons and their total energy U_{total} and find the

mean energy \bar{E}_0 of an electron at absolute temperature $T = 0^\circ$ K.

$$N_{total}(T = 0) = \int_0^{E_F} N(E)dE = A \int_0^{E_F} E^{1/2}dE = A \left(\frac{E_F^{3/2}}{3/2} \right). \quad (20)$$

$$U_{total}(T = 0) = \int_0^{E_F} U(E)dE = A \int_0^{E_F} E^{3/2}dE = A \left(\frac{E_F^{5/2}}{5/2} \right). \quad (21)$$

$$\bar{E}_0 = \frac{U_{total}(T = 0)}{N_{total}(T = 0)} = \frac{3}{5}E_F. \quad (22)$$

Also, one can find the mean electron density n and Fermi energy E_F from Eqs. (20) and (19).

$$n = \frac{N_{total}(T = 0)}{V} = \frac{2}{3} \frac{A}{V} E_F^{3/2} = \left(\frac{16\sqrt{2}\pi m^{3/2}}{3h^3} \right) E_F^{3/2}. \quad (23)$$

$$E_F = \left(\frac{3h^3 n}{16\sqrt{2}\pi m^{3/2}} \right)^{2/3} = \frac{h^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}, \quad (24)$$

where $\hbar = h/(2\pi)$.

3.3 Electron distribution at Temperature T

As the temperature rises, electrons below the Fermi level will gain energy and move to vacant states above the Fermi level and the distribution of electrons will follow the Fermi-Dirac statistics. Let $N(E, T)$ denote the number of particles with energy E and $U(E, T)$, their energy at temperature T° K. Then

$$N(E, T)dE = N(E)f(E, T)dE = AE^{1/2}f(E, T)dE \quad (25)$$

$$U(E, T)dE = EN(E)f(E, T)dE = AE^{3/2}f(E, T)dE \quad (26)$$

In the above Eqs.(25) and (26), A is a constant defined by Eq. (19) and $f(E, T)$ denotes the Fermi-Dirac distribution function.

$$f(E, T) = \frac{1}{e^{(E-E_F)/(k_B T)} + 1} \quad (27)$$

3.3.1 Fermi-Dirac Distribution Function

At $T = 0^\circ$ K,

$$f(E, T) = \begin{cases} 1, & \text{if } E \leq E_F \\ 0, & \text{if } E > E_F \end{cases}$$

As the temperature is raised, more and more electrons just below the Fermi level will gain energy and move to the vacant levels immediately above the Fermi energy,

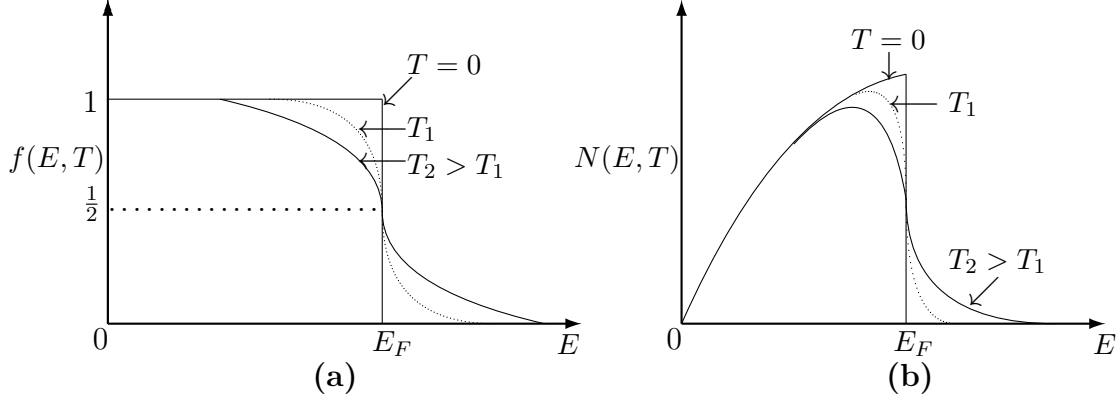


Figure 2: (a) Plot of $f(E, T)$ as a function of E and T ; (b) Plot of number of valence electrons as a function of E and T .

as illustrated in Fig. 2(a).

Electrons in energy states well below the Fermi level are not affected and only the electrons in the small energy range $k_B T$ immediately below the Fermi level are affected. Given the Boltzmann constant $k_B = 1.381 \times 10^{-23}$ J/K, the value of $k_B T$ at room temperature 300^0 K can be expressed either in terms of Joules or in terms of eV ($1 \text{ eV} = 1.602 \times 10^{-19}$ J).

$$\begin{aligned}
 k_B T &= 300 \times 1.381 \times 10^{-23} \text{ J} \\
 &= \frac{300 \times 1.381 \times 10^{-23}}{1.602 \times 10^{-19}} = 2.586 \times 10^{-2} \text{ eV}.
 \end{aligned} \tag{28}$$

The energy range $k_B T$ is of the order of 10^{-2} eV which is very small compared to the Fermi energy of most metals which is of the order of eV. For instance, the Fermi energy of Copper is 7.05 eV.

Fig. 2(a) represents the Fermi-Dirac distribution function at three temperatures $T = 0, T_1, T_2$. At the Fermi energy $E = E_F$, the function $f(E, T) = 1$ at temperature $T = 0$ and $f(E, T) = 1/2$ at higher temperatures $T = T_1$ and $T = T_2$.

Fig. 2(b) represents the distribution of electrons $N(E, T)$ given by Eq. (25) as a function of energy at different temperatures according to Fermi-Dirac distribution function. It is observed that only the electrons in the neighbourhood of Fermi level are disturbed, as the temperature is raised.

The Fermi distribution function at $T = 0$ is a step function at the Fermi energy and hence its derivative is a delta function at the Fermi energy.

3.3.2 To show that df/dE is similar to a delta function

In the above analysis, we have found that the change in the distribution of electrons occurs only near the Fermi level as the temperature is increased and it is found that the derivative of distribution function with respect to energy peaks at the Fermi level and consequently $\frac{df}{dE}$ takes the form of a delta function, as shown in Fig. 3.

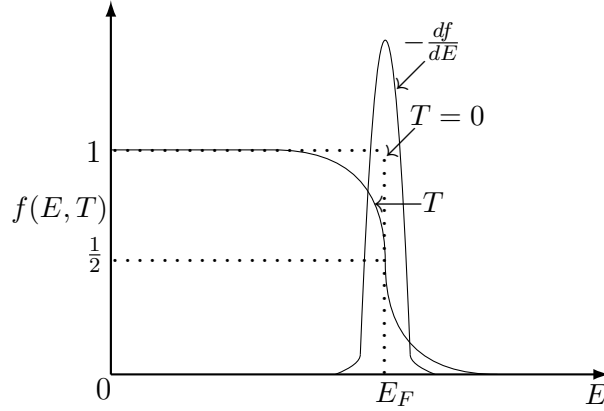


Figure 3: Plot of $f(E, T)$ and $-\frac{df}{dE}$ as a function of E .

Let us now re-write the Fermi-Dirac distribution function in terms of x

$$x = \frac{E - E_F}{k_B T} \longrightarrow dx = \frac{dE}{k_B T}$$

and find its derivative.

$$\begin{aligned} f(E, T) &= \frac{1}{e^{(E-E_F)/(k_B T)} + 1} = \frac{1}{e^x + 1}, \\ \frac{df}{dE} &= \frac{d}{dx} \left(\frac{1}{e^x + 1} \right) \frac{dx}{dE} \\ &= -\frac{e^x}{(e^x + 1)^2} \left(\frac{1}{k_B T} \right) \end{aligned} \quad (29)$$

It can be easily checked that df/dE is an even function of x , since

$$\begin{aligned} \frac{e^x}{(e^x + 1)^2} &= \frac{e^{-x}}{(e^{-x} + 1)^2} \\ \Downarrow & \qquad \qquad \Downarrow \\ \frac{1}{(e^{\frac{x}{2}} + e^{-\frac{x}{2}})^2} &= \frac{1}{(e^{-\frac{x}{2}} + e^{\frac{x}{2}})^2} \end{aligned}$$

The function $-(df/dE)$ behaves as a delta function with a peak at $E = E_F$ that corresponds to $x = 0$ and its integral yields unity. Since $df/dE = 0$ beyond a

narrow region around the Fermi energy, the integral can be extended from $-\infty$ to $+\infty$, without affecting the result.

$$-\int_{-\infty}^{\infty} \frac{df}{dE} dE = -|f(E, T)|_{-\infty}^{\infty} = \left| \frac{1}{e^x + 1} \right|_{x=-\infty}^{x=\infty} = 1 \quad (30)$$

Thus, we have shown that $-\frac{df}{dE}$ is similar to a delta function since it peaks at $E = E_F$ and the integral $\int -(df/dE)dE = 1$.

3.4 Total number and total energy of electrons at Temperature T

There will not be any change in the total number of electrons due to raise in temperature but only a change in the distribution of electrons in the energy states. Some of the electrons just below the Fermi energy will be lifted to vacant states above and consequently, only the total energy of electrons will increase with raise in temperature.

Since the total number of electrons is a constant, it is found that the Fermi energy decreases slightly with increase in temperature.

Let us now find N_{total} and also the total energy U_{total} at temperature T .

$$N_{\text{total}}(T) = \int_0^{\infty} N(E)f(E, T)dE = A \int_0^{\infty} E^{1/2}f(E, T)dE \quad (31)$$

$$U_{\text{total}}(T) = \int_0^{\infty} EN(E)f(E, T)dE = A \int_0^{\infty} E^{3/2}f(E, T)dE \quad (32)$$

To evaluate the above integrals, let us consider the following auxiliary integral I .

$$I = \int_0^{\infty} f(E, T) \frac{d}{dE} g(E) dE, \quad (33)$$

where $g(E)$ is some function of E which obeys the condition that $g(E) \rightarrow 0$ as $E \rightarrow 0$. By inspection, we find that $\frac{dg(E)}{dE}$ corresponds to $AE^{1/2}$ in the integral (31) for $N_{\text{total}}(T)$ and $AE^{3/2}$ in the integral (32) for $U_{\text{total}}(T)$. It is found that the condition $g(E) \rightarrow 0$ as $E \rightarrow 0$ is satisfied in both cases.

Integrating (33) by parts, we get

$$\begin{aligned} I &= [f(E, T)g(E)]_0^{\infty} - \int_0^{\infty} g(E)f'(E, T)dE \\ &= - \int_0^{\infty} g(E)f'(E, T)dE. \end{aligned} \quad (34)$$

The first term $[f(E, T)g(E)]_0^\infty$ in the integral I vanishes since $g(E) = 0$ at $E = 0$ and the Fermi-Dirac function $f(E, T) \rightarrow 0$ as $E \rightarrow \infty$. Since $f'(E, T)$ is similar to a delta function that peaks at the Fermi energy $E = E_f$, let us make a Taylor series expansion of $g(E)$ about the Fermi energy E_f . The Fermi energy E_f at temperature T may slightly differ from the Fermi energy E_F at temperature $T = 0$.

$$g(E) = g(E_f) + (E - E_f)g'(E_f) + \frac{1}{2}(E - E_f)^2g''(E_f) + \dots \quad (35)$$

Substituting this in Eq. (34), we get

$$\begin{aligned} I &= - \int_0^\infty f'(E, T) \left\{ g(E_f) + (E - E_f)g'(E_f) + \frac{1}{2}(E - E_f)^2g''(E_f) + \dots \right\} dE \\ &= L_0 g(E_f) + L_1 g'(E_f) + L_2 g''(E_f) + \dots \end{aligned} \quad (36)$$

where

$$L_0 = - \int_0^\infty f'(E, T) dE \quad (37)$$

$$L_1 = - \int_0^\infty (E - E_f) f'(E, T) dE \quad (38)$$

$$L_2 = - \frac{1}{2} \int_0^\infty (E - E_f)^2 f'(E, T) dE \quad (39)$$

It can be easily checked that the derivative function $f'(E, T)$ is large only near the Fermi energy E_f and negligible at other energies. So, one can replace the lower limit of integration 0 by $-\infty$ and solve the integrals. Let us now find the derivative function $f'(E, T)$.

$$f'(E, T) = \frac{df(E, T)}{dE} = \frac{d}{dE} \left(\frac{1}{e^{(E-E_f)/(k_B T)} + 1} \right) \quad (40)$$

For convenience, let us put

$$x = \frac{E - E_f}{k_B T}. \quad \text{Then } \frac{dx}{dE} = \frac{1}{k_B T} \quad \text{and } f(E, T) = \frac{1}{e^x + 1}. \quad (41)$$

$$\begin{aligned} f'(E, T) = \frac{df(E, T)}{dE} &= \frac{d}{dx} \left(\frac{1}{e^x + 1} \right) \frac{dx}{dE} = - \frac{e^x}{(e^x + 1)^2} \frac{dx}{dE} \\ &= - \frac{1}{k_B T} \frac{e^x}{(e^x + 1)^2} \end{aligned} \quad (42)$$

With this input, the integrals L_0 , L_1 and L_2 are found.

$$L_0 = - \int_{-\infty}^{\infty} f'(E, T) dE = - |f(E, T)|_{E=-\infty}^{E=\infty} = \left| \frac{1}{e^x + 1} \right|_{x=-\infty}^{x=\infty} = 1 \quad (43)$$

$$L_1 = - \int_{-\infty}^{\infty} (E - E_f) f'(E, T) dE = k_B T \int_{-\infty}^{\infty} \frac{x e^x}{(e^x + 1)^2} dx = 0 \quad (44)$$

$$L_2 = - \frac{1}{2} \int_{-\infty}^{\infty} (E - E_f)^2 f'(E, T) dE = \frac{1}{2} (k_B T)^2 \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{6} (k_B T)^2 \quad (45)$$

The integral L_0 yields 1, L_1 vanishes since the integral involves the odd function of x , whereas we obtain a value for L_2 .

$$L_2 = \frac{\pi^2}{6} (k_B T)^2, \quad (46)$$

using the value of the standard integral

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}.$$

Substituting the values of L_0 , L_1 , L_2 in Eq. (36), we get

$$I = g(E_f) + \frac{\pi^2}{6} (k_B T)^2 g''(E_f) + \dots \quad (47)$$

Eq. (47) gives the value of the auxiliary integral I , given in Eq. (33). This result can be directly used to evaluate the integrals (31) and (32) to obtain the total number of electrons and their total energy at a finite temperature T .

First let us find the total number of electrons at temperature T . For this, we need to evaluate the integral (31), which represents the total number of electrons at a finite temperature T , by making the following substitutions in Eq. (47):

$$\begin{aligned} \frac{d}{dE} g(E) = N(E) = AE^{1/2}; \quad g(E) = \int N(E) dE; \quad g(E_f) = \int_0^{E_f} N(E) dE, \\ g''(E) = N'(E); \quad g''(E_f) = N'(E)|_{E_f}. \end{aligned} \quad (48)$$

The total number of electrons will be the same at $T = 0^\circ$ K and at any finite temperature T , since we are considering the same number of valence electrons in a fixed volume V . There will be no change in the total number of electrons but only the distribution of electrons in the energy states will change with the change in temperature. At $T = 0^\circ$ K, the total number of electrons is given by

$$N_{\text{total}} = \int_0^{E_F} N(E) dE. \quad (49)$$

At a finite temperature T , the total number of electrons is given by

$$\begin{aligned} N_{\text{total}} &= \int_0^{\infty} N(E)f(E, T)dE \\ &= \int_0^{E_f} N(E)dE + \frac{\pi^2}{6}(k_B T)^2 |N'(E)|_{E_f}. \end{aligned} \quad (50)$$

Eq. (50) is obtained from Eq. (47) by substituting (48).

3.4.1 Fermi energy at temperature T

The Fermi energy may depend upon the temperature, if you define the Fermi energy as the energy at which $-\frac{df}{dE}$ peaks at a given temperature. Let the Fermi energy at $T = 0$ be E_F and the Fermi energy at temperature T be E_f . Equating the two expressions (49) and (50) for the total number of electrons, we get

$$\begin{aligned} \int_0^{E_F} N(E)dE &= \int_0^{E_f} N(E)dE + \frac{\pi^2}{6}(k_B T)^2 |N'(E)|_{E_f} \\ \int_{E_f}^{E_F} N(E)dE &= \frac{\pi^2}{6}(k_B T)^2 |N'(E)|_{E_f}. \end{aligned} \quad (51)$$

We note that $N(E)$ is independent of temperature and will not vary much in the small energy interval E_F and E_f . So, $N(E)$ can be pulled out of the integral.

$$\begin{aligned} N(E_f)(E_F - E_f) &= \frac{\pi^2}{6}(k_B T)^2 |N'(E)|_{E_f} \\ E_f &= E_F - \frac{\pi^2}{6}(k_B T)^2 \left| \frac{N'(E)}{N(E)} \right|_{E_f} \end{aligned} \quad (52)$$

Since $N(E) = AE^{1/2}$ and $N'(E) = \frac{1}{2}AE^{-1/2}$, we obtain $N'/N = 1/(2E)$. Substituting this value, we get

$$\begin{aligned} E_f &= E_F - \frac{\pi^2}{12}(k_B T)^2 \frac{1}{E_f} \\ &\approx E_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right\}. \end{aligned} \quad (53)$$

The above relation is obtained by replacing E_f by E_F on the right-hand side, since $E_f \approx E_F$. It may be observed that the Fermi energy E_f at temperature T is slightly less than the Fermi energy E_F at $T = 0$.

3.4.2 Mean electron energy at temperature T and Electronic specific heat

To find the total energy $U_{\text{total}}(T)$ of valence electrons at temperature T , we revert to Eq. (32) and the value of the integral is obtained by making the following substitution in Eq. (47):

$$\begin{aligned} \frac{d}{dE}g(E) &= EN(E) = AE^{3/2}; & g(E) &= \int EN(E)dE = A \int E^{3/2}dE = \frac{2}{5}AE^{5/2}; \\ g(E_f) &= \int_0^{E_f} N(E)dE; & g''(E) &= \frac{d}{dE}\{EN'(E)\}; & g''(E_f) &= N'(E)|_{E_f} \end{aligned} \quad (54)$$

This yields the total energy $U_{\text{total}}(T)$ of valence electrons at temperature T .

$$U_{\text{total}}(T) = \int_0^{E_F} N(E)EdE + \int_{E_F}^{E_f} N(E)EdE + \frac{\pi^2}{6}(k_B T)^2 \left| \frac{d}{dE}(EN(E)) \right|_{E_f}$$

The first term on the right hand side of the above equation is just the total energy of electrons at $T = 0$. In the second term, $N(E)$ can be pulled out of the integral, since it can be treated as a constant in the narrow energy interval E_F and E_f .

$$\begin{aligned} U_{\text{total}}(T) &= U_{\text{total}}(T = 0) + N(E_F)E_F(E_f - E_F) + \frac{\pi^2}{6}(k_B T)^2 \left| \frac{d}{dE}(EAE^{1/2}) \right|_{E_f} \\ &= U_{\text{total}}(T = 0) + N(E_F)E_F \left(-\frac{\pi^2}{12E_F}(k_B T)^2 \right) + \frac{\pi^2}{6}(k_B T)^2 \left| \frac{3}{2}AE^{1/2} \right|_{E_f} \\ &= U_{\text{total}}(T = 0) - \frac{\pi^2}{12}(k_B T)^2 N(E_F) + \frac{\pi^2}{4}(k_B T)^2 N(E_F) \\ &= U_{\text{total}}(T = 0) + \frac{\pi^2}{6}(k_B T)^2 N(E_F) \end{aligned} \quad (55)$$

Eq. (55) is obtained using the relation (53). To find the mean energy of the electron at temperature T , we divide the total energy $U_{\text{total}}(T)$ of electrons at temperature T by the total number of electrons N_{total} .

$$\begin{aligned} \bar{E} = \frac{U_{\text{total}}(T)}{N_{\text{total}}} &= \frac{U_{\text{total}}(T = 0)}{N_{\text{total}}} + \frac{\pi^2}{6}(k_B T)^2 \frac{N(E_F)}{N_{\text{total}}} \\ &= \bar{E}_0 + \frac{\pi^2}{6}(k_B T)^2 \frac{N(E_F)}{N_{\text{total}}} \end{aligned} \quad (56)$$

Since $N(E_F) = AE_F^{1/2}$ and $N_{\text{total}} = \frac{2}{3}AE_F^{3/2}$, it follows that

$$\frac{N(E_F)}{N_{\text{total}}} = \frac{3}{2E_F}.$$

Substituting this value in Eq. (56), we get

$$\begin{aligned}
\bar{E} &= \bar{E}_0 + \frac{\pi^2}{4} \left(\frac{k_B T}{E_F} \right)^2 E_F \\
&= \bar{E}_0 + \frac{\pi^2}{4} \left(\frac{k_B T}{E_F} \right)^2 \left(\frac{5}{3} \bar{E}_0 \right) \\
&= \bar{E}_0 \left\{ 1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right\}
\end{aligned} \tag{57}$$

Electronic specific heat is given by

$$\begin{aligned}
[C_V]_{\text{el}} = \frac{d\bar{E}}{dT} &= \frac{5}{6} \pi^2 \bar{E}_0 \left(\frac{k_B^2 T}{E_F^2} \right), \quad \bar{E}_0 = \frac{3}{5} E_F \\
&= \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right)
\end{aligned} \tag{58}$$

This is the value obtained from quantum theory for the electronic specific heat and this has to be substituted in the expression obtained for thermal conductivity K .

3.4.3 Ratio of K/σ

Using classical physics, we found earlier expressions (Eqs. (10) and (6)) for the thermal conductivity K and electrical conductivity σ . The same expressions hold in quantum physics also. In quantum physics, only the electrons near the Fermi level participate in the process and consequently we obtain a modified expression for the electronic specific heat $[C_V]_{\text{el}}$.

$$K = \frac{1}{3} n v_d \lambda [C_v]_{\text{el}}; \quad \sigma = \frac{n e^2 \lambda}{m v_d}.$$

$$\frac{K}{\sigma} = \frac{1}{3 e^2} m v_d^2 [C_V]_{\text{el}}; \quad [C_V]_{\text{el}} = \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right) \tag{59}$$

It is found that the electrons near the Fermi level only contribute to the electrical and thermal conductivity in metals. Then

$$E_F = \frac{1}{2} m v_d^2.$$

Substituting this value, we get

$$\frac{K}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2. \tag{60}$$

Substituting the values $k_B = 1.381 \times 10^{-23}$ J/K and $e = 1.602 \times 10^{-19}$ Coulomb, we find

$$\frac{K}{\sigma T} = 2.445 \times 10^{-8} \text{ Watt ohm/K}^2. \quad (61)$$

It is a remarkable result that $\frac{K}{\sigma T}$ is independent of the material and is the same for all good conductors. This value for the Lorenz number is in excellent agreement with experimental results.

In the above analysis, we have used expressions (6) and (10), obtained from classical physics, for the electrical conductivity σ and thermal conductivity K . In the following sections 4 & 5, let us derive expressions for σ and K , using quantum theory. It comes out explicitly that the changes in the Fermi-dirac distribution function [4,5] arises mainly due to the transport of electrons in the neighbourhood of Fermi energy level.

4 Quantum Theory of Electrical conductivity

When an electric field \mathcal{E} is applied to the conductor, electrons in the conductor will be accelerated but due to the collision of electrons with lattice points, the electrons will reach a steady state with a drift velocity. When the electric field is switched off, the electrons in the conductor will switch back to the original state in time τ , known as the relaxation time.

Let f_0 be the Fermi distribution function before the application of the electric field.

$$f_0 = \frac{1}{e^{(E-E_F)/(k_B T)} + 1}, \quad E = \frac{p^2}{2m},$$

where E denotes the electron energy, p , its momentum and m , its mass.

The application of the electric field will affect the initial Fermi distribution function f_0 and let f be the distribution function of the steady state that is reached after the application of electric field. The steady state is reached because of the retarding forces due to collision of electrons with lattice points. If the electric field is switched off, the distribution function will revert back to f_0 in time τ , known as the relaxation time, due to the collision of electrons.

$$\left(\frac{df}{dt} \right)_{\text{coll}} = \frac{f - f_0}{\tau}.$$

When the electric field is switched on, the system will reach a steady state with a distribution function f . This can be represented by the equation

$$\frac{df}{dt} = - \left(\frac{df}{dt} \right)_{\text{coll}} = - \frac{f - f_0}{\tau}. \quad (62)$$

The rate of change df/dt can be written as

$$\frac{df}{dt} = \frac{df}{dE} \frac{dE}{dt} \quad \text{and} \quad \frac{dE}{dt} = \frac{d}{dt} \left(\frac{p^2}{2m} \right) = \frac{p}{m} \frac{dp}{dt} = v \frac{dp}{dt}. \quad (63)$$

The rate of change of momentum is due to the application of the external electric field \mathcal{E} and $\frac{d\mathbf{p}}{dt} = -e\mathcal{E}$. Substituting this in Eqs. (62) and (63), we get

$$\frac{df}{dE} e\mathbf{v} \cdot \mathcal{E} = \frac{f - f_0}{\tau} \quad (64)$$

$$f = f_0 + e\mathbf{v} \cdot \mathcal{E} \tau \frac{df}{dE} \approx f_0 + e\mathbf{v} \cdot \mathcal{E} \tau \frac{df_0}{dE} \quad (65)$$

Eq. (65) is obtained by restricting the expansion of f to first order.

The current density $\mathbf{J} = \sigma \mathcal{E}$ depends on the number of electrons crossing unit area per second due to the application of the electric field and σ is defined as the electrical conductivity.

$$\begin{aligned} \mathbf{J} = \sigma \mathcal{E} &= - \int e\mathbf{v}n(E)f dE \\ &= - \int e\mathbf{v}n(E) \left(f_0 + e\mathbf{v} \cdot \mathcal{E} \tau \frac{df_0}{dE} \right) dE \end{aligned} \quad (66)$$

where $n(E)$ denotes the electron density with energy E . It can be observed that f_0 is an even function of v and so the first term of the integral which is an odd function of v involving f_0 vanishes. So, we need to evaluate only the second term in the integral. So, the conductivity σ due to the application of electric field \mathcal{E} along the x-direction is

$$\begin{aligned} \sigma &= \int e v_x n(E) e v_x \tau \left(-\frac{df_0}{dE} \right) dE \\ &= e^2 \tau \int v_x^2 n(E) \left(-\frac{df_0}{dE} \right) dE \end{aligned} \quad (67)$$

It has been found from Eq. (43) that $-(df_0/dE)$ is of the type of delta function² which peaks at the value $E = E_F$, the Fermi energy. The mean value of v_x^2 is

$$v_x^2 = \frac{1}{3} v^2 = \frac{2}{3} \frac{E}{m}.$$

²Since the Fermi distribution function f_0 is a step function in the energy scale, its differential is the delta function. For a step-up function, the differential will peak in the upward direction and for a step-down function, the differential will peak in the negative direction.

Thus, we find that the conductivity σ gets contribution only from the electrons at the Fermi surface.

$$\sigma = e^2 \tau \frac{2 E_F}{3 m} n(E_F) \quad (68)$$

$$= \frac{n e^2 \tau(E_F)}{m} \quad (69)$$

In the above Eqs., $n(E_F)$ denotes electron density of electrons at the Fermi level and n denotes the electron density of the valence electrons in the conductor. Eq. (68) expresses the electrical conductivity in terms of $n(E_F)$ and Eq. (69) expresses it in terms of n , since one can express $n(E_F)$ in terms of n and vice versa. According to Eq. (17),

$$n(E_F) = \frac{A}{V} E_F^{1/2}, \quad (70)$$

$$n = \frac{A}{V} \int_0^{E_F} E^{1/2} dE = \frac{2 A}{3 V} E_F^{3/2} = \frac{2}{3} E_F n(E_F), \quad (71)$$

where A is given by Eq. (19).

$$A = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3}.$$

Thus, we have shown that the expression (69), we have deduced for electrical conductivity using quantum physics is essentially the same as Eq. (6), obtained in classical physics, but only the relaxation time $\tau(E_F)$ corresponds to the electron at the Fermi level.

5 Quantum Theory of Thermal Conductivity

In the study of heat conduction, we need to supply heat at one end of the conductor and in the steady state, there will be a temperature gradient along the length of the conductor. As a consequence, the Fermi distribution function f of valence electrons will vary from point to point along the length of the conductor. The steady state can be represented by the equation

$$\frac{df}{dt} = \frac{df}{dx} \frac{dx}{dt} = -\frac{f - f_0}{\tau}, \quad (72)$$

where τ denotes the relaxation time for the electron. The flow of heat is due to the flow of electrons with drift velocity $v_x = \frac{dx}{dt}$. There will be a change in the Fermi distribution function along the x-axis.

$$f = f_0 - v_x \tau \frac{df}{dx} \approx f_0 - v_x \tau \frac{df_0}{dx}. \quad (73)$$

Since

$$\frac{df_0}{dx} = \frac{df_0}{dE} \frac{dE}{dT} \frac{dT}{dx} = \frac{df_0}{dE} [C_V]_{\text{el}} \frac{dT}{dx},$$

where $[C_V]_{\text{el}} = \frac{dE}{dT}$ is the electronic specific heat, for which we have already derived an expression in quantum physics.

$$[C_V]_{\text{el}} = \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right),$$

The Fermi distribution function f in the steady state can be written as

$$f = f_0 - v_x \tau [C_V]_{\text{el}} \frac{df_0}{dE} \frac{dT}{dx}. \quad (74)$$

From this, one can find the heat (energy) flow per second. To find the heat (energy) flow along the x-direction, we need to multiply f by $E v_x n(E)$ and integrate over all energies. The quantity $E v_x n(E)$ denotes the flow of energy per unit area per second due to the passage of $n(E)$ electrons, where $n(E)$ represents the valence electron density with energy E .

$$Q = \int E v_x f n(E) dE = \int E v_x \left(f_0 - v_x \tau [C_V]_{\text{el}} \frac{df_0}{dE} \frac{dT}{dx} \right) n(E) dE \quad (75)$$

The first term in the integral will vanish since f_0 is an even function of v and $v_x f_0$ is an odd function of v . So,

$$Q = - \int E v_x^2 \tau [C_V]_{\text{el}} \frac{df_0}{dE} \frac{dT}{dx} n(E) dE \quad (76)$$

Using the classical definition of thermal conductivity,

$$Q = K \frac{dT}{dx},$$

we find

$$K = \int E v_x^2 \tau [C_V]_{\text{el}} \left(-\frac{df_0}{dE} \right) n(E) dE \quad (77)$$

We are considering the heat flow in the x-direction. So, $v_x^2 = \frac{1}{3} v^2 = \frac{2E}{3m}$. At low temperatures, $-df_0/dE$ has a sharp maximum at $E = E_F$ as a delta function $\delta(E - E_F)$. So,

$$\begin{aligned} K &= \int \frac{2}{3} \frac{E^2 \tau [C_V]_{\text{el}}}{m} \delta(E - E_F) n(E) dE \\ &= \frac{2}{3} \frac{E_F^2 \tau (E_F) [C_V]_{\text{el}} n(E_F)}{m} \end{aligned} \quad (78)$$

The mean electron density (n) of valence electrons, the Fermi velocity of the electron v_F and the electronic specific heat $[C_V]_{\text{el}}$ are given by Eqs. (71) and (58).

$$n = \frac{2}{3}E_F n(E_F); \quad E_F = \frac{1}{2}mv_F^2; \quad [C_V]_{\text{el}} = \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right).$$

Using the above relations, the thermal conductivity K can be expressed in different ways

$$K = \frac{E_F \tau(E_F) n}{m} [C_V]_{\text{el}} = \frac{1}{2} v_F^2 \tau(E_F) n [C_V]_{\text{el}} = \frac{\pi^2}{3} \frac{n \tau(E_F)}{m} k_B^2 T. \quad (79)$$

This expression is similar to the one deduced from classical physics but the quantum physics attributes the entire phenomenon to the valence electrons in the neighbourhood of Fermi energy E_F .

6 Numerical Results

Let us now summarize the outcome of our theoretical studies and write down the expressions (6) and (10) for electrical conductivity σ and thermal conductivity K that we obtained from classical physics and later refined by quantum physics. They depend upon the mean density n of valence electrons and also the Fermi energy E_F of the metal, given by Eqs. (23) and (24).

$$\sigma = \frac{ne^2\tau(E_F)}{m}, \quad \text{where } n = \frac{2}{3}E_F n(E_F). \quad (80)$$

$$\begin{aligned} K &= \frac{1}{3}nv_F^2\tau(E_F)[C_V]_{\text{el}}, \quad \text{where } [C_V]_{\text{el}} = \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right) \\ &= \frac{\pi^2}{3} \frac{n\tau(E_F)}{m} k_B^2 T. \end{aligned} \quad (81)$$

$$\frac{K}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.445 \times 10^{-8} \text{ Watt ohm/K}^2. \quad (82)$$

$$n = \frac{2}{3} \frac{A}{V} E_F^{3/2} = \left(\frac{16\sqrt{2}\pi m^{3/2}}{3h^3} \right) E_F^{3/2}. \quad (83)$$

$$E_F = \frac{h^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}; \quad \hbar = \frac{h}{2\pi}. \quad (84)$$

In the above Eqs., n denotes the mean density of valence electron, $n(E_F)$, the valence electron density at the Fermi energy level $E_F = \frac{1}{2}mv_F^2$ and $\tau(E_F)$, the relaxation time for the electron at the Fermi level E_F . It is assumed that the relaxation time is the same for both the electrical and thermal conductivity at a given temperature.

The ratio $\frac{K}{\sigma T}$ is a constant known as the Lorenz number and it is the same for all metals. The greatest triumph of the quantum theory is that it yields the correct value for the Lorenz number, as determined from experiments.

The classical theory also predicted that $\frac{K}{\sigma T}$ is a constant but yielded a wrong value for Lorenz number, a value much less than half of what was found experimentally.

One cannot accept a theory if it yields the correct value for the ratio of two quantities, since the errors may mutually cancel away in taking the ratio. A more stringent test for the correctness of the theory is to calculate the electrical conductivity and thermal conductivity separately for each metal and compare them with the experimental values.

From Eqs. (80) and (81), we find that only two quantities n and $\tau(E_F)$ depend upon the sample.

How to find n , the number of valence electrons per unit volume? For this, we need to find the number of atoms per unit volume and the valency of the metal.

$$n = \text{Number of Valence electrons/m}^3 = \text{Number of atoms/m}^3 \times \text{valency}$$

There are two different ways of finding the number of atoms per unit volume. One method is by invoking Avagadro's hypothesis. If the atomic weight of a substance is M_A , then M_A Kgm of substance (known as one K-mole of substance) contains N_A number of atoms, where N_A is the Avagadro number ($N_A = 6.02 \times 10^{26}$ /K.mole). If ρ is the density of substance, then the volume of M_A Kgm of substance is $V = M_A/\rho$, then

$$\text{Number of atoms/m}^3 = \frac{N_A}{V} = \frac{\rho N_A}{M_A},$$

where M_A denotes M_A Kgm. The Fermi energy is given by Eq. (84)

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = \left(\frac{\hbar^2}{2m}(3\pi^2)^{2/3} \right) n^{2/3}.$$

In the above equation, we have separated the constant part from the only variable n which depends on the metal. Substituting the values

$$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ Js}$$

$$\text{Electron mass } m = 9.109 \times 10^{-31} \text{ Kg}$$

we can express E_F in terms of Joule or in terms of eV, using the conversion factor $1 \text{ eV} = 1.602 \times 10^{-19}$.

$$E_F = 58.473 \times 10^{-39} n^{2/3} \text{ J} = 36.50 \times 10^{-20} n^{2/3} \text{ eV},$$

where n denotes the number of valence electrons per cubic meter. The results are presented in Table 1 for a few metals.

Table 1: Density of metal ρ , atomic weight M_A , atomic density, valency, valence electron density and Fermi energy for some selected metals

Metal	Density of metal ρ (Kg/m ³)	Atomic weight M_A	No. of atoms per m ³ ($\rho N_A/M_A$)	Valency	Valence Electron density (n per m ³)	Fermi energy (E_F in eV)
Sodium	0.97×10^3	22.99	2.54×10^{28}	1	2.54×10^{28}	3.15
Copper	8.96×10^3	63.54	8.49×10^{28}	1	8.49×10^{28}	7.05
Silver	10.49×10^3	107.87	5.85×10^{28}	1	5.85×10^{28}	5.50
Gold	19.32×10^3	196.97	5.90×10^{28}	1	5.90×10^{28}	5.53
Magnesium	1.74×10^3	24.32	4.30×10^{28}	2	8.60×10^{28}	7.11
Aluminium	2.70×10^3	26.98	6.02×10^{28}	3	18.06×10^{28}	11.63

The other method is based on the lattice structure (*bcc*, *fcc*, *hcp*, ...) and the lattice parameters of the metals, which has been discussed at some length in an earlier paper of mine [6]. The reader is referred to this paper for details. The results are presented in Table 2 for comparison of the two methods. It is found that both methods yield nearly the same values for valence electron density n .

Table 2: Lattice structure, lattice constants, atomic density, valency, valence electron density and Fermi energy of some selected metals

Metal	Crystal structure	Lattice constant in n.m.	Atomic density per m ³	Valency	Valence Electron density per m ³	Fermi energy in eV
Sodium	<i>bcc</i>	$a = 0.4281$	2.65×10^{28}	1	2.65×10^{28}	3.23
Copper	<i>fcc</i>	$a = 0.3615$	8.50×10^{28}	1	8.50×10^{28}	7.05
Silver	<i>fcc</i>	$a = 0.4086$	5.85×10^{28}	1	5.85×10^{28}	5.50
Gold	<i>fcc</i>	$a = 0.4080$	5.89×10^{28}	1	5.89×10^{28}	5.52
Magnesium	<i>hcp</i>	$\begin{cases} a = 0.3209 \\ c = 0.5210 \end{cases}$	4.30×10^{28}	2	8.60×10^{28}	7.12
Aluminium	<i>fcc</i>	$a = 0.4049$	6.02×10^{28}	3	18.06×10^{28}	11.63

The other quantity that we need is the relaxation time $\tau(E_F)$ at the Fermi energy. $\tau(E_F) = \lambda/v_F$, where λ is the mean free path of electron and v_F is the velocity

of electron at the Fermi level. It is rather a difficult task to find it precisely. The redeeming feature is that the same $\tau(E_F)$ occurs in both the expressions for electrical conductivity and thermal conductivity and the electrical conductivity has been measured with great accuracy for all metals. So, let us use the experimental values for σ to determine $\tau(E_F)$ and use it to find the thermal conductivity K . The results are presented in Table 3.

Table 3: Valence electron density (n), relaxation time $\tau(E_F)$ at Fermi energy, electrical conductivity (σ) and thermal conductivity (K) of selected metals at temperature $T=293^\circ$ K and the Lorenz number $L = \frac{K}{\sigma T}$.

Metal	n (m^{-3})	$\tau(E_F)$ (10^{-14} sec)	$\sigma = \frac{ne^2\tau(E_F)}{m}$ ($\Omega^{-1} \text{m}^{-1}$)	$K = \frac{\pi^2 n\tau(E_F)k_B^2 T}{3m}$ ($\text{Wm}^{-1} \text{K}^{-1}$)	$L = \frac{K}{\sigma T}$
Sodium	2.54×10^{28}	3.10	2.22×10^7	158.93	2.44×10^{-8}
Copper	8.49×10^{28}	2.49	5.96×10^7	426.69	2.44×10^{-8}
Silver	5.85×10^{28}	3.82	6.30×10^7	451.06	2.44×10^{-8}
Gold	5.90×10^{28}	2.47	4.10×10^7	294.14	2.44×10^{-8}
Magnesium	8.60×10^{28}	0.98	2.38×10^7	170.11	2.44×10^{-8}
Aluminium	18.06×10^{28}	0.69	3.50×10^7	251.52	2.45×10^{-8}

Thus the results obtained using the free electron quantum theory are consistent and highly successful in reproducing the experimental results on the electrical and thermal conductivities of metals at normal temperatures.

The quantity $[C_V]_{\text{el}}$ represents the electronic specific heat for single electron. For comparison with the experimentally measured specific heat of metals, we need to calculate the electronic specific heat for one Kgm of metal. For this, we need to know the number of valence electrons n in unit volume of metal and the density ρ of metal.

$$\begin{aligned}
 \text{Electronic specific heat} &= \frac{[C_V]_{\text{el}} n}{\rho}, \quad \text{where } [C_V]_{\text{el}} = \frac{\pi^2}{2} \left(\frac{k_B^2 T}{E_F} \right) \\
 &= \frac{\pi^2 n}{2\rho} \left(\frac{k_B^2 T}{E_F} \right) \text{ Joules/Kgm.} \quad (85)
 \end{aligned}$$

For illustrative purpose, let us consider copper, for which the required data are obtained from Tables 1 & 2:

$$n = 8.49 \times 10^{28}/\text{m}^3; \quad \rho = 8.96 \times 10^3 \text{ Kg}/\text{m}^3; \quad E_F = 7.05 \text{ eV.}$$

Using the values $k_B = 1.381 \times 10^{-23}$ J/K, $1 \text{ eV} = 1.602 \times 10^{-19}$ J and $T = 293^\circ$ K, we get

$$\begin{aligned} \text{Electronic specific heat of copper} &= \frac{\pi^2 \times 8.49}{2 \times 8.96} \left(\frac{1.381^2 \times 293}{7.05 \times 1.602} \right) \times 10^{-2} \\ &= 2.31 \text{ J/KgmK}. \end{aligned}$$

Comparing this with the experimental value

$$\text{Specific heat of copper} = 3.85 \times 10^2 \text{ J/KgmK},$$

we find that the contribution of electrons to specific heat of metal is less than 1%. For metals, the specific heat arises mostly from the oscillations of atoms at the lattice points. Debye's theory of specific heat of solids which is the most successful theory takes into account only the molecular vibrations at lattice points.

From this, we conclude that electrons which play a dominant role in electrical conductivity and thermal conductivity of metals make insignificant contribution to the specific heat of metals.

7 Concluding Remarks

This article is devoted to the study of Weidemann-Franz law for electrical and thermal conductivities of metals and how they can be explained on the basis of Electron Theory of metals both in classical physics and quantum physics. Classical physics treats electrons in metals in the same way as molecules in kinetic theory of gases and yields only qualitative agreement with the experimental findings but fails miserably in quantitative agreement. Treating electrons as Fermions that obey both Pauli-exclusion principle and Fermi-Dirac statistics, quantitative agreement with experimental values are achieved. It is amazing that the expressions deduced for electrical conductivity and thermal conductivity for metals are essentially the same, both in classical and quantum physics except in minor details, regarding the relaxation time and the electronic specific heat. This article provides an alternative way of deducing expressions for electrical and thermal conductivities using Fermi statistical distribution function without resorting to classical physics. Instead of using the hand-waving arguments that only the electrons in the neighbourhood of Fermi level participate in the reaction, while using the mean density n of electrons in the expressions for conductivities, the quantum theory explicitly yields expressions in terms of $n(E_F)$, which when expressed in terms of n coincide with expressions obtained in classical physics. The direct method of obtaining expressions for the electrical and thermal conductivities in quantum theory is not found in many of the standard textbooks.

In quantum theory, the electrical conductivity and thermal conductivity depend on relaxation time τ and it is assumed that it is the same in both cases. The question arises whether τ is independent of temperature or temperature-dependent. Let us look into the two possibilities.

1. The relaxation time τ is a constant and independent of temperature. Then σ is a constant and independent of temperature and K is proportional to temperature. This follows from the expressions that we have derived for σ and K in terms of τ .
2. The relaxation time τ is inversely proportional to temperature. Then σ is inversely proportional to temperature and K is independent of temperature.

Experiments support the second possibility, since the electrical resistance is found to increase with increase of temperature, which means the electrical conductivity σ decreases with raise of temperature. Also, it is found that the thermal conductivity K is independent of temperature and depends only on the temperature gradient.

Every theory is based on certain postulates and its validity is restricted to situations where these postulates are applicable. Free electron quantum theory is applicable only for metals at normal temperatures but breaks down for semiconductors and insulators. In these cases, electrons cannot be treated as free but they should be considered to be propagated in a periodic potential due to the lattice structure of the solid. This results in the band theory of solids with energy bands inter-spaced by energy gaps.

References

1. S. O. Pillai, *Solid State Physics, 8th Edition*, New Age International, New Delhi (2018)
2. R. Asokamani, *Solid State Physics, 2nd Edition*, Eswar Press, Chennai (2015)
3. P. K. Palanisamy, *Material Science*, Scitech Publications (India) Pvt. Ltd. (2003)
4. B. K. Agarwal & M. Eisner, *Statistical Mechanics*, Wiley Eastern Limited, New Delhi (1988)
5. C. Kittel & H. Kroemer, *Thermal Physics*, W.H. Freeman & Company, New York (1980)
6. V. Devanathan, *The Concept of Phase-Space in Quantum Mechanics*, Journal of Chennai Academy of Sciences **2**, 26-42 (2020)