Notes on the Wiedemann-Franz Law
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Historically, “The Wiedemann-Franz Law states that for metals at not too low temperatures the ratio of the thermal conductivity to the electrical conductivity is directly proportional to the temperature with the value of the constant of proportionality independent of the particular metal.” [1]. Kittel writes the Wiedemann-Franz (WF) Law as [1]

\[
\frac{\kappa}{\sigma} = L_0 T = \frac{\pi^2}{3} \left( \frac{k_B}{q} \right)^2 T,
\]

where \( L_0 \) is the Lorenz number (which is actually a ratio, not a number). As Kittel notes, the fact that (1) can be derived from the electron gas theory of metals and that it applies to a wide range of metals under a wide range of conditions, was a major success in the early history of the theory of metals [1].

Both Kittel and Ziman [2] point out, however, that the Lorenz number (which Ziman calls the Lorenz ratio) can change for metals at low temperature. This is usually attributed to a breakdown of the Relaxation Time Approximation (RTA) – see Ashcroft and Merman [3], pp. 322, 323.) It is sometimes stated that the scattering times in the electrical and thermal conductivities may be different [1]. As summarized in eqns. (6), below, however, when solving the BTE in the RTA, there is only a single scattering time that determines the electrical and thermal conductivity (it appears in the mean-free-path, \( \lambda(E) \) in (6e)). As discussed by Ashcroft and Merman, the breakdown of the WF law at low temperatures is not the result of different scattering times for the electrical and thermal conductivities, but, rather, the due to the fact that the same scattering has different effects on the electrical and thermal conductivities ([3] footnote on p. 323).

More generally, we can always write

\[
\frac{\kappa}{\sigma} \equiv L T
\]

and simply regard it as the definition of the Lorenz number. According to Ziman, we should only refer to this relation as the Wiedemann-Franz Law when \( L = L_0 = \left( \frac{\pi^2}{3} \right) \left( \frac{k_B}{q} \right)^2 \) [3]. On the other hand, it is common to refer to (2) as the “Wiedemann-Franz Law” and apply it not only to metals but also to semiconductors for which \( L \) is rarely \( L_0 \). See, for example [4], which also points out that we should regard the Wiedemann-Franz Law to be a “rule of thumb” and not a law of nature. Even for metallic conditions, violations of the Wiedemann-Franz Law occur (see [5] for one example), and for semiconductors, \( L \) is rarely equal to \( L_0 \). The calculation of the Lorenz number requires an accurate band structure and knowledge
of the energy-dependent scattering processes [6]. In these notes, we discuss calculations for a simple, parabolic energy band with power-law scattering. We will consider (2) to be the definition of the Lorenz number, which can be written as ([7], p. 96)

\[
L = \left( \frac{k_B}{q} \right)^2 \left\{ \left[ \left( \frac{E - E_F}{k_B T_L} \right)^2 \right] - \left[ \left( \frac{E - E_F}{k_B T_L} \right)^2 \right] \right\},
\]

(3)

where the average, \(<\cdot>\), is defined by eqn. (5.51) in [7]. For a material with a single energy channel at \( E = E_i \), \( M(E) = M_0 \delta (E - E_i) \), and it is easy to show mathematically from eqn. (3) that \( L = 0 \). The physical reason is clear. If there is a single channel, then when we open-circuit it to measure \( \kappa_e \), no electrons flow. Since there is no flow of electrons, there can be no flow of heat.

In 3D, for a constant mean-free-path and parabolic energy bands, we find for a non-degenerate semiconductor

\[
L \approx 2 \left( \frac{k_B}{q} \right)^2
\]

(4)

and for a degenerate semiconductor,

\[
L \approx \frac{\pi^2}{3} \left( \frac{k_B}{q} \right)^2.
\]

(5)

What are the corresponding relations for 1D and 2D semiconductors with parabolic energy bands?

**Lorenz Number in 3D, 2D, and 1D**

To compute \( L \) from (2) we must calculate the thermoelectric coefficients:

\[
\sigma = \int \sigma'(E) dE
\]

(6a)

\[
S = -\frac{k_B}{q} \int \left( \frac{E - E_F}{k_B T} \right) \sigma'(E) dE \int \sigma'(E) dE
\]

(6b)

\[
\kappa_0 = T \left( \frac{k_B}{q} \right)^2 \int \left( \frac{E - E_F}{k_B T} \right)^2 \sigma'(E) dE
\]

(6c)

\[
\kappa_e = \kappa_0 - S^2 \sigma T
\]

(6d)
\[ \sigma'(E) = \frac{2q^2}{h} \lambda(E) \frac{M(E)}{A} \left( -\frac{\partial f_0}{\partial E} \right) = q^2 \Xi(E) \left( -\frac{\partial f_0}{\partial E} \right). \] 

(6e)

From (2) and (6d), we find

\[ L = \frac{\kappa_e}{\sigma T} = \frac{\kappa_0 - S^2 \sigma T}{\sigma T} = \frac{\kappa_0}{\sigma T} - S^2. \]

(7)

To find \( L \), we simply need to compute \( \kappa_e \) and \( \sigma \). In (6e), \( \Xi(E) \) is known as the “transport function” or “transport distribution” [8]. In general, the computation of \( L \) requires numerical calculations [6], but for parabolic energy bands with power law scattering, analytical results are possible (see the appendix of [7]).

1) Lorenz number in 3D for parabolic bands

From the Appendix of [7]:

\[ \kappa_e = T \left( \frac{k_B}{q} \right)^2 \frac{2q^2}{h} \lambda_0 \left( \frac{m^* k_B T}{2\pi h^2} \right)^r \Gamma(r+3) \left\{ (r+3) \frac{F_{r+2}(\eta_F)}{F_r(\eta_F)} \right\} \]

(8)

\[ \sigma = \frac{2q^2}{h} \lambda_0 \left( \frac{m^* k_B T}{2\pi h^2} \right)^r \Gamma(r+2) \frac{F_{r+1}(\eta_F)}{F_r(\eta_F)}, \]

(9)

where power law scattering has been assumed:

\[ \lambda(E) = \lambda_0 \left( \frac{E - E_c}{k_B T} \right)^r. \]

(10)

The resulting Lorenz number in 3D is

\[ L = \frac{\kappa_e}{\sigma T} = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma(r+3)}{\Gamma(r+2)} \left\{ (r+3) \frac{F_{r+2}(\eta_F)}{F_r(\eta_F)} \right\} \left( \frac{r+2}{F_{r+1}(\eta_F)} \right). \]

(11)
Case i) Maxwell-Boltzmann Statistics

\[ L = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma(r+3)}{\Gamma(r+2)} \left\{ \left( \frac{r+3}{r+2} \right) - 1 \right\} \]

For \( r = 0 \), we find

\[ L = 2 \left( \frac{k_B}{q} \right)^2 \]

Equation (13) is the WF law in 3D for parabolic energy bands, energy-independent scattering, and Maxwell-Boltzmann statistics.

Note that the mean-free-path is proportional to velocity times scattering time. For Acoustic Deformation Potential (ADP) scattering, the scattering rate (one over the scattering time) is proportional to the density-of-states, \( D(E) \). For parabolic bands, \( D(E) \propto (E - E_C)^{(d-2)/2} \), where \( d = 1, 2, \) or \( 3 \) for 1D, 2D, or 3D. For ADP scattering, we find

\[ \lambda(E) \propto v(E) \tau(E) \propto v(E)/D(E) \propto (E - E_C)^{(3-d)/2}. \]

For ADP scattering in 3D, \( r = 0 \), for ADP scattering in 2D, \( r = 1/2 \), and for ADP scattering in 1D, \( r = 1 \). The assumption of a constant mean-free-path in the 3D calculations above is equivalent to assuming ADP scattering.

Case ii) Strongly degenerate conditions

In this case, we must expand the Fermi-Dirac integrals for \( \eta_F \gg 0 \). From Jeong and Lundstrom, p. 101 [7]

\[ F_r(\eta_F) \rightarrow \frac{\eta_F^{r+1}}{\Gamma(r+2)} + \frac{\pi^2}{6} \frac{\eta_F^{r-1}}{\Gamma(r)} + \ldots \]

The rest is left as an exercise for the reader.
2) Lorenz number in 2D for parabolic bands

From the Appendix of [7]:

\[
\kappa_e = T \left( \frac{k_B}{q} \right)^2 \frac{2q^2}{h} \lambda_0 \left( \frac{\sqrt{2m^* k_B T}}{\pi \hbar} \right) \Gamma \left( r + \frac{5}{2} \right) \left[ \left( r + \frac{5}{2} \right) F_{r+3/2} (\eta_F) - \frac{r + \frac{3}{2}}{F_{r-1/2} (\eta_F)} \right]
\] (15)

and

\[
\sigma = \frac{2q^2}{h} \lambda_0 \left( \frac{\sqrt{2m^* k_B T}}{\pi \hbar} \right) \Gamma \left( r + \frac{3}{2} \right) F_{r-1/2} (\eta_F).
\] (16)

The Lorenz number in 2D is

\[
L = \frac{\kappa_e}{\sigma T} = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma \left( r + \frac{5}{2} \right)}{\Gamma \left( r + \frac{3}{2} \right)} \left[ \left( r + \frac{5}{2} \right) F_{r+3/2} (\eta_F) - \frac{r + \frac{3}{2}}{F_{r-1/2} (\eta_F)} \right].
\] (17)

Case i) Maxwell-Boltzmann Statistics

\[
L = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma \left( r + \frac{5}{2} \right)}{\Gamma \left( r + \frac{3}{2} \right)} \left[ \left( r + \frac{5}{2} \right) F_{r+3/2} (\eta_F) - \frac{r + \frac{3}{2}}{F_{r-1/2} (\eta_F)} \right].
\] (18)

For \( r = 0 \) (energy-independent mean-free-path), we find

\[
L = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma \left( 5/2 \right)}{\Gamma \left( 3/2 \right)} = \left( \frac{k_B}{q} \right)^2 \frac{3}{2} \frac{\Gamma \left( 3/2 \right)}{\Gamma \left( 3/2 \right)}
\]

\[
L = \frac{3}{2} \left( \frac{k_B}{q} \right)^2 \quad (2D \text{ constant MFP})
\] (19)
Equation (19) is the Lorenz number in 2D for parabolic energy bands, energy-independent scattering, and Maxwell-Boltzmann statistics. We see that the numerical factor of $3/2$ is different than the factor of 2 in the 3D case. If, however, we assume ADP scattering in 2D, then $r = 1/2$ and (18) gives

$$L = \left(\frac{k_B}{q}\right)^2 \frac{\Gamma(3)}{\Gamma(2)} = 2 \left(\frac{k_B}{q}\right)^2$$

(2D ADP scattering)

which is identical to the result for 3D ADP scattering.

**Case ii) Strongly degenerate conditions**

In this case, we must expand the Fermi-Dirac integrals for $\eta_F \gg 0$.

3) **Lorenz number in 1D for parabolic bands**

From the Appendix of [7]:

$$\kappa_e = T \left(\frac{k_B}{q}\right)^2 \frac{2q^2}{h} \lambda_0 \Gamma(r+2) \left\{ (r+2) F_{r+1}(\eta_F) - \frac{(r+1) F_r^2(\eta_F)}{F_{r-1}(\eta_F)} \right\}$$

$$\sigma = \frac{2q^2}{h} \lambda_0 \Gamma(r+1) F_{r-1}(\eta_F)$$

The Lorenz number in 1D is

$$L = \frac{\kappa_e}{\sigma T} \left(\frac{k_B}{q}\right)^2 \frac{\Gamma(r+2)}{\Gamma(r+1)} \left\{ (r+2) \frac{F_{r+1}(\eta_F)}{F_{r-1}(\eta_F)} - \frac{(r+1) F_r^2(\eta_F)}{F_{r-1}^2(\eta_F)} \right\}$$

(23)

**Case i) Maxwell-Boltzmann Statistics**

$$L = \left(\frac{k_B}{q}\right)^2 \frac{\Gamma(r+2)}{\Gamma(r+1)} \left\{ (r+2) - (r+1) \right\}$$

$$= \left(\frac{k_B}{q}\right)^2 \frac{\Gamma(r+2)}{\Gamma(r+1)}$$

(24)

For $r = 0$ (energy-independent mean-free-path), we find

$$L = \left(\frac{k_B}{q}\right)^2 \frac{\Gamma(2)}{\Gamma(1)} = \left(\frac{k_B}{q}\right)^2 \frac{(1)!}{(0)!}$$

$$L = 1 \left(\frac{k_B}{q}\right)^2$$  (1D constant MFP)  (25)
Equation (25) is the Lorenz number for 1D with parabolic energy bands, energy-independent scattering, and Maxwell-Boltzmann statistics. We see that the numerical factor of 1 is different than the factor of 2 in the 3D case and the factor of 3/2 in 2D. If, however, we assume ADP scattering in 1D, then $r = 1$ and (24) gives

$$L = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma(r+2)}{\Gamma(r+1)} = \left( \frac{k_B}{q} \right)^2 \frac{\Gamma(3)}{\Gamma(2)} = 2 \left( \frac{k_B}{q} \right)^2 \text{ (1D ADP scattering)}$$

which is identical to the result for 3D ADP scattering.

**Case ii) Strongly degenerate conditions**
In this case, we must expand the Fermi-Dirac integrals for $\eta_F >> 0$.

**Discussion:**
If we consider the Lorenz number in 3D as given by (11), in 2D as given by (17), and in 1D by (23) and assume ADP scattering in each case, so in 3D, $r = 0$, in 2D, $r = 1/2$, and 1D, $r = 1$ we find the same answer in 1D, 2D, 3D:

$$L = 2 \left\{ 3 \frac{F_2^2(\eta_F)}{F_0^2(\eta_F)} - 2 \frac{F_1^2(\eta_F)}{F_0^2(\eta_F)} \right\} \left( \frac{k_B}{q} \right)^2$$

For parabolic energy bands with ADP scattering, the Lorenz number is identical at any level of degeneracy. This result could have been anticipated. The transport distribution, $\Xi(E)$ in (6e) determines all of the transport coefficients. The transport distribution is proportional to $M(E)\lambda(E)$. The mean-free-path is proportional to velocity times scattering time, and the scattering time is inversely proportional to the DOS. The number of channels is proportional to velocity times the DOS [7], so for parabolic bands, we find

$$\Xi_{xx}(E) \propto \left( \frac{M(E)}{A} \right) \times \lambda(E) \propto v(E)D(E)\times v(E)/D(E) \propto v^2(E) \propto (E - E_C).$$

Since the transport function is independent of dimension for ADP scattering in parabolic bands, all thermoelectric transport coefficients are independent of dimension.
References


