Relation Between Electrical and Thermal Conductivities in Charged Condensed Phases

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Data and simple theory is brought into contact for the ratio $\lambda/\sigma T$ for some charged condensed phases, λ being the thermal conductivity and σ the electrical conductivity. The most extensive data presented is for liquid metals and deviations from the Weidmann – Franz law are discussed. But the paper is also concerned with metal nitrates (e.g., $NaNO_3$) and with ionized gases and dilute plasmas. Returning to metals, cases be cited where λ and σ separately vary markedly across the solid-liquid transition, while the ratio $\lambda/\sigma T$ remains substantially constant.

1 INTRODUCTION

The theoretical study of the relation between thermal and electrical conductivities has a long history, and the review by Chester and Thellung[1] plus the book by Ziman[2] discuss the background, with especial emphasis on metals. Since for simple metals, electrons remain essentially degenerate well above the melting point, one can write

$$\frac{\lambda_e}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = L, \tag{1.1}$$

where λ_e is electronic term in thermal conductivity while σ is the electrical conductivity. The right hand side constitutes the so called Lorenz number:

$$L = 2.45 \times 10^{-8} \, W\Omega K^{-2}. \tag{1.2}$$

Eq. (1.1) does not depend on such details as the shape of the Fermi surface, the density of electron states, the origin of the scattering etc, but it is based on the assumption of elastic scattering. In liquid metals, this is discussed, for example by Rice[3].

In relation to the measured thermal conductivity of metals, there is an excellent review by Powell[4]. We shall return to comment on some of the data he compiles in section 3 below.

Though the precise Lorenz number in Eq. (1.1) is obtained for degenerate electrons, we shall see in later sections that in classical charged condensed phases Eq. (1.1) is still useful in analyzing experimental measurements of thermal and electrical conductivity.

2   SOME THEORY FOR (CLASSICAL) CHARGED PHASES WITH OVERALL NEUTRALLITY

Let us start from the Green – Kubo expression for the thermal conductivity λ given as[5]

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty C(t)\,dt, \tag{2.1}$$

where $C(t)$ is the time correlation function of the heat current density, and $J(t)$ is given by

$$C(t) = \left\langle \sum_{i=1}^{N} J_i(t) \sum_{j=1}^{N} J_j(0) \right\rangle. \tag{2.2}$$

If the system consist of N^+ cations and N^- anions (electrons say) then we can write

$$C(t) \approx C^+(t) + C^-(t), \tag{2.3}$$

$C^+(t)$ and $C^-(t)$ being time correlation functions for cations and anions, respectively. In the first instance we consider cations and anions to be classical and write

$$C^{+(-)}(t) = C_0^{+(-)} - C_2^{+(-)}(t^2/2) + \ldots, \tag{2.4}$$

where C_0, and $-C_2$ are the zeroth and second frequency sum rules of the spectral function of $C(t)$. If the correlation functions decay with a relaxation time τ, we then write

$$C^{+(-)}(t) = C_0^{+(-)} F(t/\tau), \tag{2.5}$$

where $F(t/\tau)$ is some decaying function of time. Using Eqs. (2.1) and (2.5) we obtain

$$\lambda^+ = \frac{A}{Vk_B T^2} C_0^+ \tau^+, \tag{2.6a}$$

$$\lambda^- = \frac{A}{Vk_B T^2} C_0^- \tau^-, \tag{2.6b}$$

where $A = \int_0^\infty F(x)\,dx$. The relaxation time τ can be calculated in terms of the sum rules of $C(t)$ by assuming that $F(x)$ has a short-time expansion with coefficient of t^2 as $1/2\tau^2$. We then obtain

$$\tau^+ = (C_0^+/C_2^+)^{1/2} \tag{2.7a}$$

and

$$\tau^- = (C_0^- / C_2^-)^{1/2}. \tag{2.7b}$$

Thus by knowing the sum rules of the correlation functions one can calculate the contributions to the thermal conductivity from the two species, separately. These sum rules are known for the one component system[6] and we note from these that the mass dependence of thermal conductivity goes as the inverse square root of the mass. Following this we write for the two-component system:

$$\lambda = \lambda^+ + \lambda^- = \frac{B_1}{\sqrt{m_+}} + \frac{B_2}{\sqrt{m_-}}, \tag{2.8}$$

where B_1 and B_2 are functions independent of the masses. We shall test the above equation for the mass dependence of thermal conductivity using the known results for metal-nitrates in section 4. Here it may be noted that the cross contribution to the thermal conductivity is zero as the zero time value of the cross correlation function vanishes. In an appendix we shall extend the procedure for the calculation of thermal and electrical conductivities due to electrons (classical). It is also shown there that the value of L depends on the nature of the electrons and also on the treatment used for the evaluation of time correlation functions.

3 DATA ON CONDENSED METALLIC PHASES

Having given simple arguments as to the way deviations from constant Lorenz number might occur in classical charged liquids, we return to the degenerate electron system discussed already in section 1. It is in the area of pure metals, and intermetallic compounds, that the most systematic data is available. We therefore begin with pure metals, both solids and liquids, and then add some further data, especially on cerium compounds.

3.1 Deviation from Lorenz Number (Eq. (1.1)) in Pure Metals

Figure 1 shows data for $\lambda/\sigma T$, all taken from experiments[7–9], for some 33 different metals (see also Tab. 1). The dashed line shows the prediction of Eq. (1.1). Of course, the prediction is for $\lambda_e/\sigma T$, where λ_e is the purely electronic contribution to the thermal conductivity. However, in metals there has been little evidence that the ionic contribution to λ can be more than 1 or 2 percent of electronic contribution and this would always increase $\lambda/\sigma T$ plotted in Figure 1 above the theoretical dashed line. Clearly there are observed deviations about $(L \times 10^8)$ in Eq. (1.2) in both directions of approximately ± 0.7 at most.

3.2 Data on Cerium Compounds

The experimental ratio $\lambda/\sigma T$ is now temperature dependent as can be seen from Figure 5 of the work of Gratz et al[10] for $CeCu_2$ and $Y Cu_2$. It varies with temperature
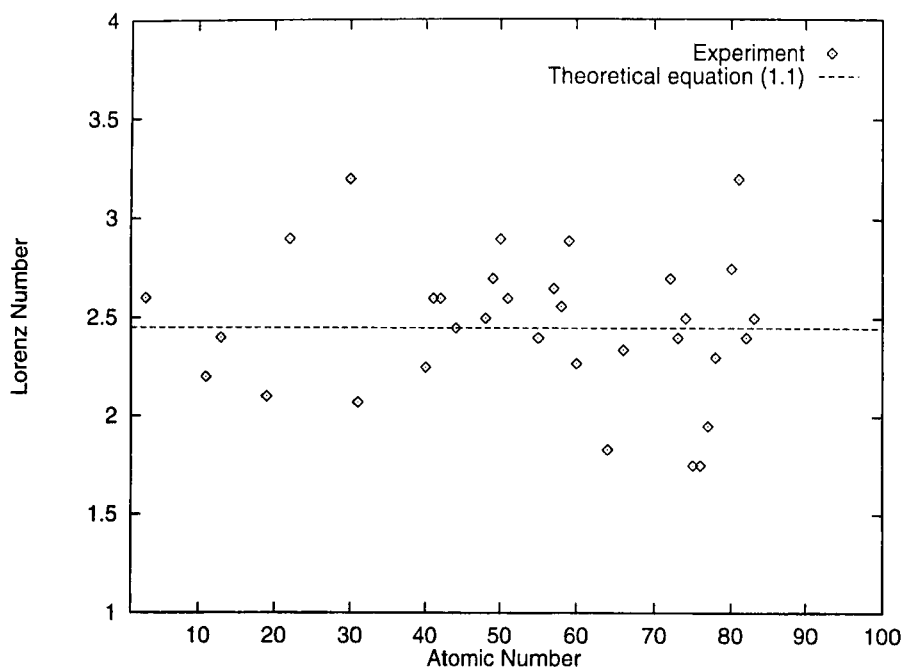
Figure 1 Variation of experimental Lorenz number $(10^{-8} W\Omega K^{-2})$ of metals with atomic number. Horizontal line represent Eq. (1.1).

Table 1 Lorenz numbers for some of the metals as obtained by experiments.

Metal	$L \times 10^8$	Metal	$L \times 10^8$	Metal	$L \times 10^8$
Li	2.6	Pb	2.4	Ta	2.4
Na	2.2	Sb	2.6	Re	1.75
K	2.1	Bi	2.5	Os	1.75
Cs	2.4	Ti	2.9	Pt	2.3
Cd	2.5	Zr	2.25	In	2.7
Hg	2.75	Hf	2.7	La	2.65
Zn	3.2	Mo	2.6	Ce	2.56
Al	2.4	W	2.5	Pr	2.89
Ga	2.07	Ru	2.45	Nd	2.27
Tl	3.2	Ir	1.95	Gd	1.83
Sn	2.9	Nb	2.6	Dy	2.34

from 1.5 to 3.5 $\times$ 10^{-8} $W\Omega K^{-2}$. The deviation in CeB_6 and $CeCu_6$ compounds[11] with large Kondo resistivity is markedly large and at low temperatures the Lorenz number is 5 times that of Eq. (1.2).

## 3.3   Effect of Solid-Liquid Transition on λ, σ and Lorenz Number

In Figures 2 and 3 we present the experimental data for thermal conductivity and Lorenz number of In due to Croldratt and Greenfield[12] on either side of the melting point. The vertical line separates the liquid and solid phases. The horizontal line represents Eq. (1.1). The conclusion seems clear: both λ and σ separately are sensitive to detailed changes in microscopic structure through the phase transition. The Lorenz number in the example exhibited is mainly, in contrast, insensitive to ionic structure.

4   CLASSICAL CHARGED FLUIDS

Though, we have not found extensive data such as presented in section 3 for metallic phases, it is of interest to mention, in the present context, data in some classical charged systems.

4.1   Metal Nitrates in Molten State

The conductivity in molten salts is due to the motion of cations and anions. Thermal conductivity values[13] of nitrates of Na, K and Ag are used to study the dependence on mass of the thermal conductivity of the two species in molten salts in analogy with two component state of metal (ions and electrons). Assuming that the anion contribution is
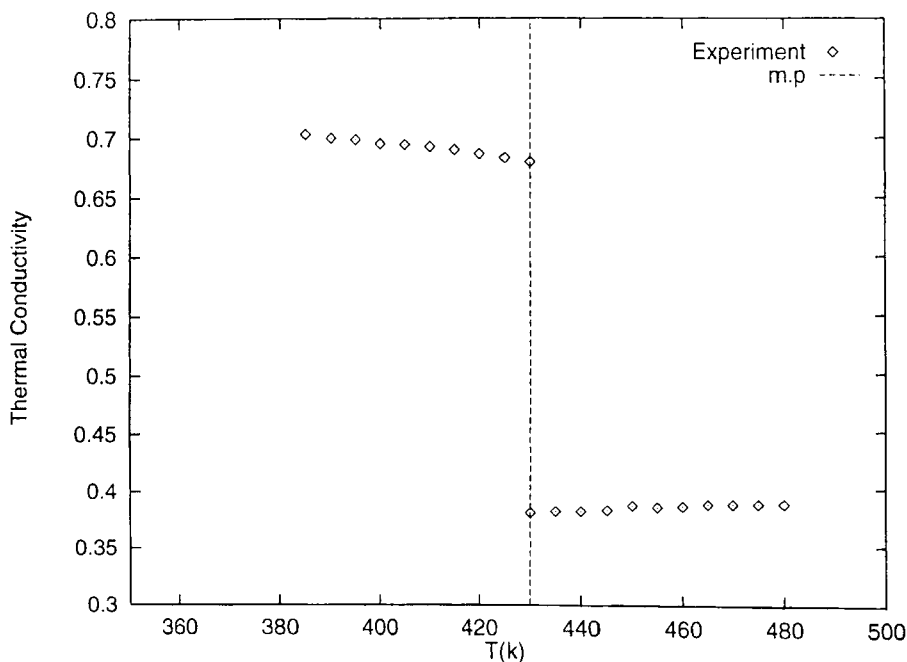
Figure 2   Variation of experimental thermal conductivity of Indium with temperature.
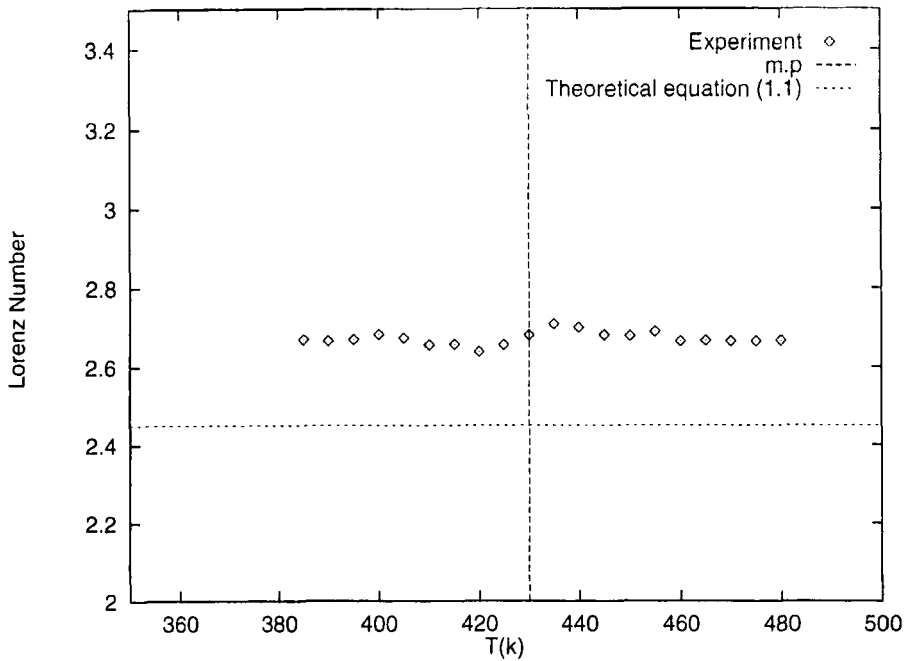
Figure 3   Variation of experimental Lorenz number of Indium with temperature.

same for three nitrates, the values obtained for the ratio of difference of thermal conductivity of metal nitrates are compared in Table 2 with the prediction of Eq. (2.8). (This leads us to conclude that the ionic contribution to the thermal conductivity of metals is very small as it varies as inverse square root of mass.)

4.2   Ionized Gases and Plasma

For the ionized gases the value of L is known[14] to depend on Z, the charge on the ions, and also on the degree of ionization. From classical theoretical work we note that for

Table 2   Values of ratio of difference in thermal conductivity of metal nitrates. $\Delta\lambda_{\alpha\beta} = \lambda_{\alpha NO_3} - \lambda_{\beta NO_3}, \Delta m_{\alpha\beta} = (1/\sqrt{m_\alpha} - 1/\sqrt{m_\beta})$ and 1, 2 and 3 represent Na, K and Ag respectively.

$\dfrac{\Delta\lambda_{23}}{\Delta\lambda_{12}} = 1.077$	$\dfrac{\Delta m_{23}}{\Delta m_{12}} = 1.32$
$\dfrac{\Delta\lambda_{13}}{\Delta\lambda_{23}} = 1.93$	$\dfrac{\Delta m_{13}}{\Delta m_{23}} = 1.77$
$\dfrac{\Delta\lambda_{13}}{\Delta\lambda_{12}} = 2.077$	$\dfrac{\Delta m_{13}}{\Delta m_{12}} = 2.33$

a fully ionized gas values of $L(10^8) = 1.208, 1.986$ and 2.546 for $Z = 1, 2, 4$ and 16, respectively. The value of the Lorenz number is 1.488 for classical metal electrons which is obtainable only for a weakly ionized gas. Returning to the non-classical case the value of L is close to that of Eq. (1.2) for dense fully ionized hydrogen[15], except at very high density and low temperature where the effect of inelastic scattering of electrons from ionic density fluctuation is around 30 percent.

5 SUMMARY AND CONCLUSION

The experimental data for the ratio $\lambda/\sigma T$ has been brought into contact with theoretical predictions for condensed phases of metals, both of simple sp character and for metals with d and with f electrons. Figure 1 shows that while the theoretically predicted Lorenz number for degenerate electrons represents a useful average of the data, considerable fluctuations arise about this constant value. It is clear therefore that one must relax the assumptions underlying the deviation of the Wiedmann–Franz law for degenerate electrons. In particular inelastic scattering processes must play a role and probably one must also consider the effect of electron-electron interactions as it may cause additional departure from the predicted constant Lorenz number.

A further point that is of interest, again for metals, is that the solid-liquid phase transition can markedly affect the behaviour of λ and σ separately. However, for the example of indium metal, there is barely any sign of the phase transition in the experimental ratio $\lambda/\sigma T$.

Finally, we have added a brief discussion on classical charged fluids, namely some metal nitrates and ionized gases. This time the ratio $\lambda/\sigma T$ must be compared with classical predictions. However for the ionized gases, this ratio depends on the charge state of the ion. Clearly further work, both experiment and theory, is required to explain quantitatively the microscopic mechanisms leading to departures from the Wiedmann–Franz law.

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APPENDIX

Transport processes involving electrons

For a classical system composed of free electrons and ions we can write

$$J^e(t) = \sum_i \left(\frac{1}{2} m_e v_i^2 - \frac{5}{2} k_B T \right) v_{ix} \tag{A.1}$$

The expressions for the first two sum rules are obtained as

$$C_0^- = \frac{5}{2} \left(\frac{k_B T}{m_e} \right) k_B^2 T^2 \tag{A.2}$$

and

$$C_2^- = \frac{15}{2} \left(\frac{k_B T)}{m_e} \right) \omega_E^2 \tag{A.3}$$

where

$$\omega_E^2 = \frac{n}{m} \int dr g(r) \frac{d^2 U(r)}{dx^2}. \tag{A.4}$$

Here $g(r)$ and $U(r)$ are the pair correlation function and pair potential for the ion-electron interaction. Using Eqs. (A.2), (A.3) (2.6b) and (2.7b) we obtain

$$\lambda = \frac{5}{2\sqrt{3}} A n k_B \left(\frac{k_B T}{m \omega_E} \right). \tag{A.5}$$

If we use a similar procedure for the calculation of electrical conductivity we obtain

$$\sigma = A \frac{n e^2}{m \omega_E}. \tag{A.6}$$

Substituting Eq. (A.6) in Eq. (A.5), we then find

$$\frac{\lambda}{\sigma T} = \frac{5}{2\sqrt{3}} \frac{k_B^2}{e^2} \tag{A.7}$$

On the other hand, if the time correlation function for heat current and electric current decay with the same relaxation time, say τ, then we obtain

$$\frac{\lambda}{\sigma T} = \frac{5}{2} \frac{k_B^2}{e^2}. \tag{A.8}$$

Here, it may be noted that Eqs. (A.7) and (A.8) do not depend on our choice of functional form for the time development of the time correlation functions. Further from Eqs. (A.5) and (A.6) we note that thermal and electrical conductivities both depend upon the ion-electron arrangement. But, the ratio $\lambda/\sigma T$ does not depend either on temperature or on ion-electron correlations. This implies that Lorenz number should cross the phase change continuously. As we have treated electrons as classical: our results may therefore be applied to ionized gases or to a classical plasma.