Some methods for predicting thermal conductivity of metallic melts

I Savchenko
Kutateladze Institute of Thermophysics of Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia
E-mail: savchenko@itp.nsc.ru

Abstract. The work is devoted to a search for regularities that allow predicting the heat transfer coefficients of metallic melts and their thorough testing.

1. Introduction
Liquid metals have a high potential in terms of future energy applications. First of all, nuclear power applications are widely discussed. Moreover, there are some technological solutions using metal melts for a broader range of tasks, for example heat pipes and direct-contact steam generators with liquid-metal coolants. Alkali and heavy metals with a low melting point, as well as a variety of their alloys, are traditionally considered as potential coolants for nuclear power plants (NPP). A recent review [1] states that the properties of metals and alloys that are promising for use in NPP remain poorly studied. The thermophysical properties of materials are of paramount importance for energy calculations. Thermal conductivity and thermal diffusivity are the most important characteristics of the coolant. Reliable information about these properties is necessary for any thermal engineering calculations. Unfortunately, these properties have not been studied in sufficient detail, experimental information for alloys is practically absent, and for some pure metals it is contradictory [2]. The situation is exacerbated by the fact that the reference books contain data on the properties of pure substances. However, in real coolants there are always impurities (dissolved gases, additives for reducing corrosion and others) that significantly affect the kinetic properties of melts. New horizon in this field may be opened by a large-scale experimental study of the coolant properties. Investigations are now underway, although rather slow and scaled down. The theory of the liquid state does not allow predicting the transport properties of liquid metals with the accuracy required for practice. In this situation, the only reasonable solution is the use of empirical regularities connecting the heat transfer coefficients with other properties of the melt. A good example of such a law is the Wiedemann-Franz-Lorentz law (WFL), which relates the heat and electrical conductivity to a simple dependence \( \lambda = L \sigma T \). Where \( \lambda \) is the thermal conductivity, \( \sigma \) is the electrical conductivity, \( L \) is the Lorentz number and \( T \) is the temperature. This law, which was experimentally found for solid metals, seems to be applicable to their melts. The law of WFL is perhaps the most popular regularity of its kind; it is mentioned in many books on solid state physics. In the literature there are other generalizations of experimental data on heat and thermal diffusivity, but few people know about them except for the authors.
2. Regularities in the variation of the thermal conductivity of melts

The present work is devoted to the search for regularities that allow predicting the heat transfer coefficients of metallic melts and their thorough testing. The verification was carried out by comparing the calculation results with specially selected, the most reliable literature data on the thermal conductivity and thermal diffusivity of various melts. The choice of the most reliable data is a very controversial issue. In the present work, in general, we relied on the data obtained by us as a result of experiments with Hg, Pb, Bi, In, Sn and their alloys [2–7]. These are the most recent results. They are obtained using the same modern measurement method, which is well-approved and certified as standard for studying molten metals [8].

2.1. Wiedemann–Franz law

First of all, the temperature dependences of the Lorentz number of the investigated metals and alloys in the liquid state were analyzed. The following literature data on electrical resistivity, namely for pure metals [9], for bismuth-lead eutectic alloy [10] and for eutectic alloys, tin-lead and tin-indium [11, 12], were used for calculations. The theoretical value of the Lorentz number for a gas of free electrons $L_0 = 2.445 \times 10^{-8}$ W Ohm/K$^2$ was taken from [13]. We considered the deviation of the experimental values of $L$ as a function of temperature. We denote it by $\delta L = (L - L_0)/L_0$, where $L$ is the Lorentz number calculated from the experimental data. As can be seen from figure 1, for all studied metals and alloys with the exception of bismuth the deviation from the theoretical value does not exceed or slightly exceeds the total error in the measurements of heat and electrical conductivity, which is approximately equal to 10%.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The deviation of the experimentally determined Lorentz number from the theoretical value 1 - indium, 2 - tin, 3 - bismuth, 4 - lead, 5 - indium-tin eutectic, 6 - tin-lead eutectic, 7 - bismuth-lead eutectic.
The anomalous behavior of bismuth is not surprising, since this element is a semimetal with a significant proportion of directed bonds. The localization of electrons leads to a smaller contribution of the electronic component to the processes of heat and charge transfer than in the other studied melts. Under these conditions, the relative contribution of the lattice thermal conductivity increases and, consequently, the experimentally determined value of the Lorentz number increases.

Indium and tin in a liquid state have a significant share of covalent bonds. This is confirmed by the results of diffraction studies of Bi, In, Sn, Hg, in which the complex structure of the first and the second intensity maxima of scattered X-ray radiation, namely the asymmetry of peaks and the appearance of spin-off maxima [14], was determined. When metals overheat above the equilibrium melting temperature, the anomalies gradually disappear, which indicates the metallization of the melts. This leads to an increase in electrical conductivity, which in turn explains the decrease in the Lorentz number of bismuth, indium and tin at a distance from the melting point (see figure 1).

Despite the different behavior of $L(T)$, the data of figure 1 show that the Wiedemann-Franz law can be used to calculate the thermal conductivity of melts based on indium, tin and lead with an error not exceeding 10-15%.

2.2. Estimation of the thermal conductivity of alloys by the additivity rule

The evaluation of the thermal conductivity of alloys according to the Wiedemann-Franz law can be difficult due to the lack of data on the electrical conductivity. Therefore, it is necessary to analyse the possibility of calculating $\lambda$ of alloys using data for pure metals. The most obvious and simple approach is to apply the additivity rule to these liquid metal systems. Figure 2 shows the results of such calculations using both mass and atomic concentrations for alloys of the indium-tin system. It should be taken into account that the atomic masses of these metals are insignificantly different from each other. For this reason, the results of both calculations of the thermal conductivity of alloys of these systems practically coincide. The data of figure 2 show that when the concentration of the high-conductivity component is less than 50 at. %, the thermal conductivity of the alloys practically coincides with $\lambda$ less than the heat-conducting component. Analysis of our results for alloys of tin-lead and bismuth-lead systems has shown that they have similar concentration dependence.

2.3. Rao's formula

In 1926 Peierls [15] put forward a hypothesis about the existence of a connection between the type of the crystal lattice of metals and the change in the electrical conductivity during melting, since atoms in the solid phase are strictly ordered and in the liquid phase are distributed chaotically. In 1934 Mott [16] obtained a theoretical dependence of the electrical conductivity ratio before and after melting $\sigma_S/\sigma_L$ on the ratio of the vibrational frequencies of atoms in the solid and liquid phases. This ratio is expressed by an exponential function with an exponent in the form of the ratio of enthalpy change upon melting $\Delta H_m$ to the melting temperature $T_m$:

$$\frac{\sigma_S}{\sigma_L} = \left(\frac{V_S}{V_L}\right)^2 = \exp\left[\frac{2}{3}\frac{\Delta H_m}{R T_m}\right]$$

(1)

here $R$ is the universal gas constant, and the indices $S$ and $L$ refer to the values for the solid and liquid states. Thus, Mott obtained a quantitative estimate of the jump in the electrical conductivity of metals upon melting, which comparatively well agrees with experiment [17].

In 1942 Rao [17] carried out a similar study of the ratio of thermal conductivities in the solid and liquid states $\lambda_S/\lambda_L$. Based on the results of Bidwell’s experiments [18], he showed that the thermal conductivity of metals in both phases is completely determined by the electrons. Assuming that the Lorentz function is the same for both phases at the melting point, the thermal conductivity ratio should be described by the Mott formula (1):
Figure 2. Comparison of results for thermal conductivity calculation on the additivity rule with experimental data for alloys of the indium-tin system. 1 - indium; 2 - tin; 3, 6, 9 - approximation of the experimental data for alloys with an indium content of 33%, 49%, 80%, respectively; 4, 7, 10 - calculation (atomic concentrations) for the same alloys; 5, 8, 11 - calculation (mass concentration) for the same alloys.

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\frac{\lambda_S}{\lambda_L} = \exp\left(\frac{2}{3} \frac{\Delta H_m}{R T_m}\right)
\]  

(2)

On the basis of the experimental data we have estimated the thermal conductivity jumps of lead and indium at the melting temperature and compared them with the values calculated from (2). The results of the calculations are given in the table 1. For lead the difference in the experimental \(\lambda_S/\lambda_L\) from the theoretical values is 1.7%, which is within the bounds of the estimated thermal conductivities of solid and liquid phases. For indium the difference is 16.6%. It may be assumed that the Rao formula is well satisfied for "true" metals, which include lead with a gcc structure in the solid state. Indium has a tetragonal crystal lattice with a small coordination number of 4 and belongs to the class of semimetals. To test the applicability of the Rao formula, we have estimated the thermal conductivity jumps from formula (2) for lithium, potassium and for such semimetals as bismuth, mercury, tin and their comparison with the literature data for \(\lambda_S/\lambda_L\). It is seen from the table 1 that for alkali metals the difference between the experimental and calculated values is less than the estimated errors of \(\lambda_S\), \(\lambda_L\). In semimetals deviations significantly exceed the total errors in measuring the thermal conductivity of phases, as well as in indium. It can be assumed that such a deviation is due to the metallization of these elements upon melting, which in the solid state have an appreciable fraction of covalent bonds and, consequently, loose crystalline structures. This is confirmed by densification of bismuth during melting and the presence of minima on the temperature dependence of the coefficient of thermal expansion of indium and tin melts due to the conservation of a certain proportion of directional bonds in the liquid state. Thus, the Rao formula predicts the change in the thermal conductivity during melting for "true" metals reliably enough and can hardly be applied to metals with a significant proportion of directed bonds.
Table 1. Estimation of thermal conductivity change at melting.

| Metal       | λS/λL | Experiment | Calculation (2) | Deviation, % |
|-------------|-------|------------|-----------------|--------------|
| Lead        | 1.93  | 1.90       |                 | 1.7          |
| Lithium     | 1.68  | 1.70       |                 | 1.2          |
| Potassium   | 1.73  | 1.74       |                 | 0.5          |
| Indium      | 2.15  | 1.85       |                 | 16.6         |
| Tin         | 2.04  | 3.14       |                 | 34.9         |
| Mercury     | 4.21  | 2.19       |                 | 92.1         |
| Bismuth     | 0.34  | 5.15       |                 | 93.3         |

3. Conclusion

It is shown that the Wiedemann-Frantz law is well-suited for prognostication of the heat transfer coefficients of liquid metals. The deviation of calculated values from the most reliable recommendations does not exceed 10–15%. The hypothesis on the calculation of the thermal conductivity of two-component liquid metal systems by additivity using mass concentrations has been verified. It turned out that such an approximation works satisfactorily for compositions with a fraction of the high-heat-conductive component of more than 50%. And at lower concentrations the thermal conductivity of the two-component liquid coincides with the thermal conductivity of the low-conductivity component. It is shown that the Rao formula is not applicable for predicting the change in thermal conductivity during the melting of semimetals. It is perfectly applicable to predict the change in thermal conductivity of true metals.

References

[1] Rachkov V I, Arnol’dov M N, Efanov A D, Kalyakin S G, Kozlov F A, Loginov N I, Orlov U I and Sorokin A P 2014 Therm. Eng. 61(5) 337
[2] Savchenko I V, Stankus S V, Agazhanov A S 2013 Atomic Energy 115(2) 83
[3] Stankus S V, Savchenko I V 2009 Thermophys. Aeromech. 16(4) 585
[4] Stankus S V, Savchenko I V, Agazhanov A S 2012 Int. J. Thermophys. 33(5) 774
[5] Savchenko I V, Stankus S V, Agadjanov A S 2011 High Temperature 49(4) 506
[6] Savchenko I V, Stankus S V, Agazhanov A S 2010 Thermophys. Aeromech. 17(1) 121
[7] Savchenko I V, Stankus S V, Agazhanov A S 2013 High Temperature 51(2) 281
[8] Savchenko I V, Stankus S V 2012 GSSSD ME 202-2012 A technique for the experimental determination of the thermal conductivity and temperature conductivity of metallic melts by the laser flash method (Moscow Publishing house of standards) p 43
[9] Pashaev B P, Palchaev D K, Pashuk E G and Revelis V G 1982 Density, ultrasound velocity, electric and thermal conductivity of low-melting multivalent metals in the liquid state Reviews of the Thermophysical Properties of Materials 3(35) (Moscow IVTAN) p 108
[10] Sobolev V 2007 Journal of Nuclear Materials 362(2) 235
[11] Li X, Zu F, Ding H, Yu J, Liu Q, Li Q, Xi Y 2005 Physica B: Condensed Matter. 358(1) 126
[12] Romanova A V 1977 Ukr. Fiz. Journal. 12(1) 73
[13] Ziman J M 1999 Principles of the theory of solids 2 (Cambridge: Cambridge Univ. Press) p 435
[14] Khruschev B I 1970 Structure of liquid metals (Tashkent FAN)
[15] Peierls R 1930 Annalen der Physik. 396(2) 121
[16] Mott N F 1934 Proc. Royal Society A 146(857) 465
[17] Missenard A 1965 Conductivité thermique des solides, liquides, gaz et de leurs mélanges (Éditions Eyrolles) p 588
[18] Powell R W 1948 J. App. Phys. 19 995