THERMAL CONDUCTIVITY OF MOLTEN MATERIALS. IS EXPERIMENT NECESSARY?

C. A. Nieto de Castro

Departamento de Química e Bioquímica, Centro de Ciências Moleculares e Materiais, Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

> *"It is extremely rare that physical properties themselves lead to a true competitive advantage. However, accurate thermophysical properties are essential in our quest to increase energy efficiency, reduce adverse environmental effects, and provide for a safer chemical process industry"*
> *James C. Holste,*
>
> *Forum 2000: Fluid Properties for New Technologies –*
> *Connecting Virtual Design with Physical Reality"*

ABSTRACT

The knowledge on the thermal conductivity of molten materials (salts, metals, semiconductors, polymers) is very scarce, both from the experimental and theoretical points of view. Knowing of the difficulty in obtaining accurate experimental data for most liquids, the task is uncouthly more difficult when the measurements are to be performed at medium and high temperatures with materials that are corrosive, easily reacting and good heat transfer media. Convective and radiative heat transfer effects affect in particular thermal conductivity measurements at high temperatures. These facts also make difficult theoretical calculations using molecular/ionic theories and drastic approximations, both from the phenomenological side, to the force field between particles, restrict the validity of the results obtained. Computer simulations are a possible alternative to overcome these problems and its development in recent years is noteworthy, induced by the improvements in theory, algorithms and computer hardware. Their applications to the study of molten materials have been very limited and with results of questionable validity. However, it was recently possible to apply equilibrium molecular dynamics simulations to the calculation molten salts thermal conductivity with a reasonable success. In this lecture a short review of the field will be presented, with especially emphasis in the actual situation, challenges faced and foreseen solutions, including microgravity experiments.

INTRODUCTION

Molten materials appear in the metallurgical industries, semiconductor industry, aerospace technology, glass manufacture, polymer technology and in nuclear power and solar energy plants and complex fluids recovery processes. In some of these industries the process of heat transfer accompanying solidification determines the quality of the product. For the metallurgical industry and aerospace technology, this process can determine the ultimate tensile, compressive or other features of strength and corrosion resistance of metals, alloys, ceramics, composites, etc. For the semiconductor industry, the process determines the degree of perfection achieved in crystal growth (and thereby the ultimate performance of semiconductor devices) and the heat dissipation in integrated circuits, following the operations of vapour deposition, sputtering or printing. Miniaturization and nanotechnology production also is also limited by an inadequate knowledge and control of these processes. In the glass industry the quality and uniformity of glass produced by the float-glass method is intimately linked to the same heat transfer operation. In all of these industries, therefore, attempts are made to control the quality of the product by a suitable mathematical model of the heat transfer process within the melt. The same heat transfer problems can determine the efficiency of nuclear and solar power plants.

In all of these industries, therefore, attempts are made to control the quality of the product by a suitable mathematical model of the heat transfer process within the melt. One of the most uncertain features of such models, arguably the most uncertain feature, is the thermal conductivity of the material in question, and its dependence on structure, chemical composition and manufacturing history. Viscosity, diffusion and heat capacity are also key data in the manufacturing process design.

The molten systems can be simple in theory from a structural point of view (metals, semiconductors, molten salts) or complex (glasses, binary and ternary mixtures of molten salts, polymers), but the fact that they can be obtained only at temperatures well above room temperature creates several problems from the point of measurement. The system melt/detector/environment is always a complex system, difficult to deal with high accuracy and to model molecularly.

The measurement of the thermal conductivity of molten materials at elevated temperatures has proved extremely difficult to perform with high accuracy. This fact can be revealed by the discrepancies among results discussed in several reports and workshops [1-7] and represents a tremendous challenge to all thermophysicists and materials engineers, as these materials have an enormous economical and environmental importance. Molten metals are a first example. Figure 1 illustrates this fact with indium, one of the metals used to define a fixed point of ITS90. The melting point of indium at 1 bar (429.7485 K) is a fixed point of the ITS 90 [8]. Until now only 3 sets of experimental data have been published up to 900 K, and 2 sets of recommended values [6]. It shows all data sets plotted as a function of temperature. From the three only available data sets, the measurements of Duggin [9] show a weak positive temperature, and the other two sets show somewhat stronger positive temperature dependence [10,11]. The deviations range between about 8 % at the lower temperatures till about 17 % at the higher temperatures. In this plot also the recommended values of Touloukian et al. [12] and Ho et al. [13] are given which extent till 1200 and 900 K, respectively. Recent measurements for indium by Peralta-Martinez and Wakeham using a transient hot-wire technique [14] seem to confirm within 5% the data of Goldratt and Greenfield [11]. The situation found for liquid mercury, in spite of the existence of many more sets of data, is rather similar [6].

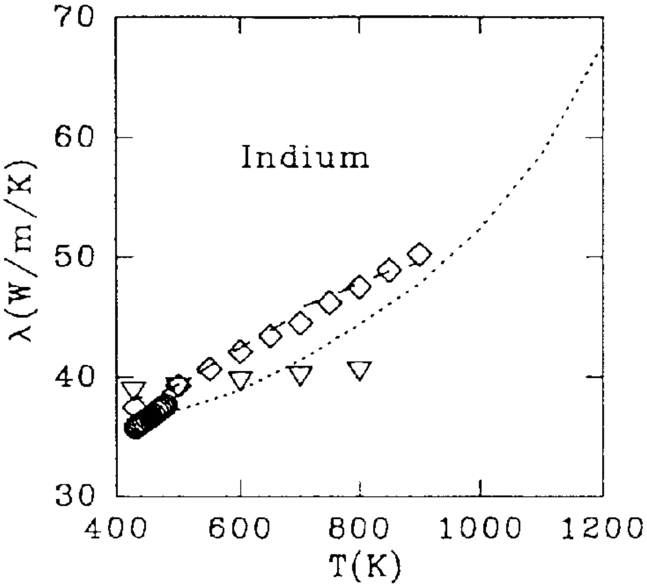

Figure 1: The thermal conductivity data of liquid indium. ▿ - Duggin [9]; ◇– Yurchak and Smirnov [10]; ○ - Goldratt and Greenfield [11]; ····· Touloukian *et al.* [12]; - - - Ho *et al.* [13].

The same happens with molten salts. Molten salts are liquids obtained by the fusion of a salt. The number of these systems is incredible high and range from relatively low temperatures (room temperature ionic liquids) until very high temperatures. Sodium chloride (NaCl) for instance melts at 801°C and boils at 1413°C, at atmospheric pressure. The general characteristics of molten salts are: (a) liquid state in a large range of temperature, (b) ability to dissolve many inorganic and organic compounds, attaining high concentrations, (c) low vapour pressure and stability at normal pressures, (d) low viscosity, as the ions are mutual independent, for most of the cases, (e) chemical inertness (no reaction with air or water), (f) high heat capacity per unit volume. These and other characteristics allow its utilisation in many processes not possible in normal solvents. When data is available, the differences among different laboratories are sometimes dramatic. Figure 2 shows the thermal conductivity of KNO_3 as a function of temperature [1,15-22]. The differences among different sets of data can go up to about 25 %. Also $d\lambda/dT$ is either positive or negative. For KCl the deviation between different sets of data reaches 300% at 1000 K [23].

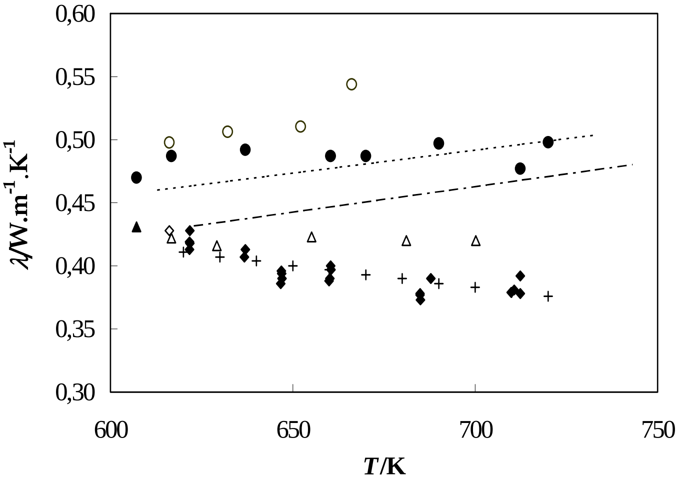

Figure 2: The thermal conductivity of molten potassium nitrate. △, Tufeu *et al.* [1]; ◆, Kitade *et al.* [15]; ○, Bloom *et al.* [16]; ▲, White and Davies [17]; +, Nagasaka *et al.* [18]; ●, Gustafsson *et al.* [19]; ◇, Turnbull [20]; •••••, McDonald and Davies [21]; - - • - -, Santini *et al.* [22].

THE PROBLEMS

The problems of obtaining a correct physical understanding of the molten systems an accurate experimental data for the thermal conductivity can be divided in three main areas: Experiment, theory and simulation. All these are areas will be dealt briefly.

Mardolcar and Nieto de Castro reviewed the different methods of measurement of this quantity at high temperatures up to 1991 [24,25]. The main conclusion of that work was that there was not a single method, contact or contactless with the melt, that could be used to measure thermal conductivity with an uncertainty smaller than 5%, and henceforth, the existing published data could not be used to define reference materials of high quality. Many of the experimental difficulties could be attributed to deficient use and conception of the methods of measurement, either by misapplication of methods that have proved to be reasonable at room temperature or by not taking into account different phenomena that are new to these systems and to the temperature ranges involved. The difficulties associated with accurate measurements are often due to the combined effect of a variety of factors: (i) sample purity and homogeneity, (ii) thermal stability of the sample, (iii) interaction between the sample and both the surrounding gaseous atmosphere and the container material, (iv) temperature measurement sensor and (v) other simultaneous heat transfer mechanisms such as convection and radiation. Especially when the sample is a metal extra difficulties rise from the high electrical and thermal conductivity and, moreover, oxidation problems are normally present. The difficulties with the materials compatibility are associated with the many complex interfaces present in the measuring system, the most important being the measuring sensor/melt/container/atmosphere. In addition, and for transient methods, the measuring sensor is always a complex structure, simplified as support/active element/insulating coatings.

The variety of materials involved is great. Molten materials are obtained at high temperatures and therefore it is necessary to understand completely the interaction (physical or chemical) of the different parts present and the properties of the different materials at high temperature. This discussion is the object of a companion paper in this conference [26], and it will not be dealt in detail here. However it is noteworthy to say that the design of an instrument to measure the thermal conductivity of molten materials for temperatures up to 1500 K is not an easy task and must be based con careful studies that involve thermodynamics of chemical reactions, chemical reactivity, and materials compatibility, in addition to a very good mathematical modelling of the measuring system. This philosophy has been followed by our group in Lisbon, where an instrument for the measurement of the thermal conductivity of molten materials has been designed, constructed and tested, based on the transient hot-strip principle [27-30]. The accuracy was found to be superior to any existing instrument for comparable high temperature measurements and the performance of the sensors developed as high temperature thermometers showed a total uncertainty of 0.6 K at high temperatures, better than the best industrial thermometers available with the best metrological quality. The use of the transient principle, the selection of materials, the geometric design and use of Self Adapting Finite Element Method (SAFEM) to solve the complex geometry non-linear heat transfer problem to extract the thermal conductivity with minimum sources of error has been dealt with success.

The presence of convection in these measurements also deserves a reference. In fact, liquids are the most sensitive to a gravitational force. This force causes an acceleration of all masses towards the centre of gravitation, and it makes bodies fall and fluids flow downwards. In an inhomogeneous fluid system at rest, sedimentation will result. In addition, gravity can also induce flows in combination with a temperature or concentration gradient. This is called buoyancy driven convection and can lead to fluid flow instabilities, like the famous Rayleigh-Bénard instability [31]. The problem of simultaneous conduction and convection in thermal conductivity measurements has been dealt carefully in reference [32]. Steady state methods of measurement have difficulties to eliminate convection and the transient methods cannot eliminate it completely but minimize its presence by performing measurements in a time frame prior to its effects in the conductive heat dissipation. Its presence possible explains many wrong results, by overestimating the reported thermal conductivity.

Convection can only be eliminated by the absence of gravity or reduced to a negligible effect in microgravity conditions [33, 34]. The advantages of these conditions are very important, although the measurements become only possible integrated in space programmes. A special mention to this will be made ahead.

The actual state of the molecular theories of transport phenomena in the liquid state, based in the first principles and with a strong basis of statistical mechanics, is far from being completely developed, even for simple systems like noble gases and molecular fluids [35]. The situation is even worse for complex systems like molten metals, molten salts or even molten semiconductors. In the case of the most complete book on the physical properties of liquid metals by Iida and Guthrie [36], for example, thermal conductivity is dealt in conjunction with electrical conductivity, and no reference at all is made to theoretical treatments, with the minor exception of the Wiedmann-Franz-Lorenz law, based on the electron gas theory of conduction in solids. However, this law, given by Equation (1), was tested with thermal conductivity data of molten metals with low accuracy (> 10%), the data available at the date of its establishment.

$$L_0 = \frac{\lambda}{\sigma\ T} = \frac{\pi^2\, k_B^2}{3e^2} = 2.445\times10^{-8}\ \mathrm{V}^2\ \mathrm{K}^{-2} \qquad \text{Eq. (1)}$$

In this equation, λ is the thermal conductivity of the molten metal, attributable to free electrons[1], σ its electrical conductivity, T the thermodynamic temperature, k_B the Boltzmann constant and e the charge of the electron. L_0 is the Lorenz number. As the electrical conductivity measurements are not affected by convection, the thermal conductivity (at least the contribution of the electron movement to the heat transfer) can be calculated. A recent discussion for tin and indium can be found in reference [14], whereby deviations of the order of +5-6% where found. Giordanego *et al.*, [37] have applied this concept to liquid metals (aluminum, tin, lead and copper) and metallic alloys (Cu-Al, Ag-Ga, Ag-Ge, Cu-Pb, In-Mn, Ga-Ge and Sn-Bi). The values obtained for the pure metals fall between the several experimental determinations available, claiming a total uncertainty in the thermal conductivity data

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[1] In fact it ignores any contribution to the thermal conductivity from phonons and it is strictly applicable to solids.

obtained from the electrical resistivity of 3%, a value probably too optimistic. Yamasue *et al.* [39] presented a complete discussion of the temperature dependence of the thermal conductivity of liquid tin and lead and the applicability of this law, arriving to the conclusion that the deviations found could be attributed to the existence of inelastic scattering processes in the electrons. However, the accuracy of their measurements is low (greater than 8%), which invalidates strong conclusions. This law has also been applied to semiconductors, like Si, Ge and InSb, at the Jet Propulsion Laboratory, California Institute of Technology, USA, but no publication is still available. In the absence of experimental data the application of the Wiedmann-Franz-Lorenz law is still a reasonable approach to calculate the thermal conductivity of molten metals, but a revision of all the theory of molten metals must be made.

The calculation of the thermal conductivity of molten materials is, therefore, an almost impossible task, not only because of the insolubility of the equations, but also because of our deficient knowledge of the interparticle (molecules, ions, atoms, etc.) interactions in the liquid state.

Computer simulations are a possible alternative to overcome these problems and its development in recent years is noteworthy, induced by the improvements in theory, algorithms and computer hardware [39]. However, their applications to the study of molten materials have been very limited and with results of questionable validity, mostly because the molecular dynamics techniques need the assumption of a given model for the interparticle interaction, and most of the studies have not been applied to thermal conductivity, the most difficult property to simulate.

However, it was recently possible to apply equilibrium molecular dynamics simulations to the calculation of molten alkali chlorides thermal conductivity [40], namely its temperature dependence. The thermal conductivity of molten alkali halides has been simulated by EMD before, but the results were inconclusive as to whether the temperature dependence predicted by the BMHTF[2] potential is positive or negative. Sindzingre and Gillan [41] performed EMD simulations using the Green–Kubo method in the canonical ensemble (N,V,T) of the thermal conductivity of solid NaCl and KCl, but only one state point was reported for the liquid state. Fuchiwaki and Nagasaka [42] reported EMD (N,V,E) simulations of the thermal conductivity for different molten alkali halides. The results of those simulations underpredict the thermal conductivity and were inconclusive regarding the temperature dependence of the thermal conductivity. In particular, the values reported from those simulations show positive and negative changes for the thermal conductivity of NaCl and KCl as the temperature is increased. Takase *et al.* [43,44] reported extensive EMD (N,V,E) calculations for the thermal conductivity of a number of molten alkali halides. Their results over predict the thermal conductivity and again for almost every substance, including NaCl and KCl, an alternating positive and negative temperature dependence of the thermal conductivity is observed within 100 K temperature intervals. A comparison of these results with the new simulations is presented in [40] and Lourenço *et al.* [26] presented a detailed analysis. The simulation results obtained in the work of Galamba *et al.* clearly show that the Born-Mayer-Huggins-Tosi-Fumi interionic potential over predicts the thermal conductivity of NaCl and KCl and well-defined negative temperature dependences are predicted. However these results support the statement previously stated that a closer inspection of the methodologies used in the experimental methods is necessary, namely the materials compatibility studies.

THE FRONTIERS OF MEASUREMENT

More than 15 years elapsed since Nagashima presented the famous paper on the thermophysical properties research on fluids at the technology frontier [45]. Since then the research community has tackled many of his suggestions. However, the field of molten materials, with special emphasis in the molten metals and molten salts, did not developed as some others, like the clean refrigerant research.

It is now time to select the most promising areas of research in the field of thermophysical properties, namely with thermal conductivity.

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[2] Born–Mayer–Huggins–Tosi–Fumi potential

From the discussion presented in the preceding sections, it is clear that the research in high temperatures still deserves our attention. By high temperatures we mean above 500 K, where the problems of temperature and heat flow measurement are very important. From new thermometers, miniaturized for many applications, to new and accurate methods of measurement, from theoretical to computer simulations, from material characterization to thin film technology, efforts are needed to support the technologies of processing of new materials in micro and nanotechnologies, which need accurate data on the thermal conductivity of molten materials.

Another important area is microgravity[3] research [33,34]. As already said the main difficulty in performing accurate measurements of thermal conductivity of liquids lies in the isolation of the conduction process from the other two mechanisms of heat transfer, as a temperature gradient has to be imposed on the sample, while preventing its motion. The imposition of this temperature gradient in the gravitational field of the earth creates natural convection, which is especially important in steady-state methods of measurement and in regions of the phase diagram closer to the critical point. The success of transient methods of measurement is based on the fact that the characteristic time for the acceleration of the fluid by buoyancy forces is much longer than the propagation time of the temperature wave originated by a strongly localised temperature gradient. Therefore, it is possible by a suitable choice of the experimental conditions and geometrical design of the measuring cells, to perform, in principle, convection free measurements [33]. Conversely, microgravity experiments can be used to show that convection is also present in thermal conductivity measurements and to demonstrate the best experimental conditions (temperature gradients, transient cells, duration of an experiment, etc.) to study a given system. If the measurements are performed at high temperatures, heat transfer by radiation becomes important, as its contribution increases as T^4 with temperature and most of the liquids with scientific or industrial relevance are strongly absorbent in the infrared region of the light spectrum. The experimental methods must therefore be designed also to minimise the effects of radiation. Although it is impossible to solve analytically the integro-differential equation of the coupled process, it has been shown by numerical simulation that the contributions to the heat flux vector have different weights. This made possible to design the cells to make the contribution arising from the liquid emission the most relevant, for a transient hot-wire system. This particular term is not represented by a spatial integral. However it is possible to obtain an approximate analytical solution which can correct the experimental temperature profile for the radiation effects, resulting in radiation free values for the thermal conductivity, namely in the transient hot-wire technique [32].

Hibiya *et al.* using InSb [46], a semiconductor presented the first measurements of the thermal conductivity of molten materials under microgravity. These measurements, made with the TCMF facility (developed by NEC, Japan) in the TEXUS-24 sounding rocket, showed that the thermal conductivity measured on Earth increased by a factor of two from 2 to 8 seconds (Figure 3) while the data obtained under microgravity appears to be almost constant, showing a good reproducibility. This might suggest that convection was partially, if not totally, suppressed. The existence of convection in transient hot-wire measurements for large experimental times has been demonstrated, as well as the non-existence of buoyancy forces in microgravity conditions. These results confirmed the theoretical predictions of the onset of natural convection in these measurements. It also confirms the recommendations of the Subcommittee of Transport Properties of IUPAC described in reference [32].

Further experiments on fluids with technological importance, including other molten semiconductors (e.g. GaAs and InP) and metals will no doubt confirm these studies and contribute to the necessary database for the thermophysical properties of these melts.

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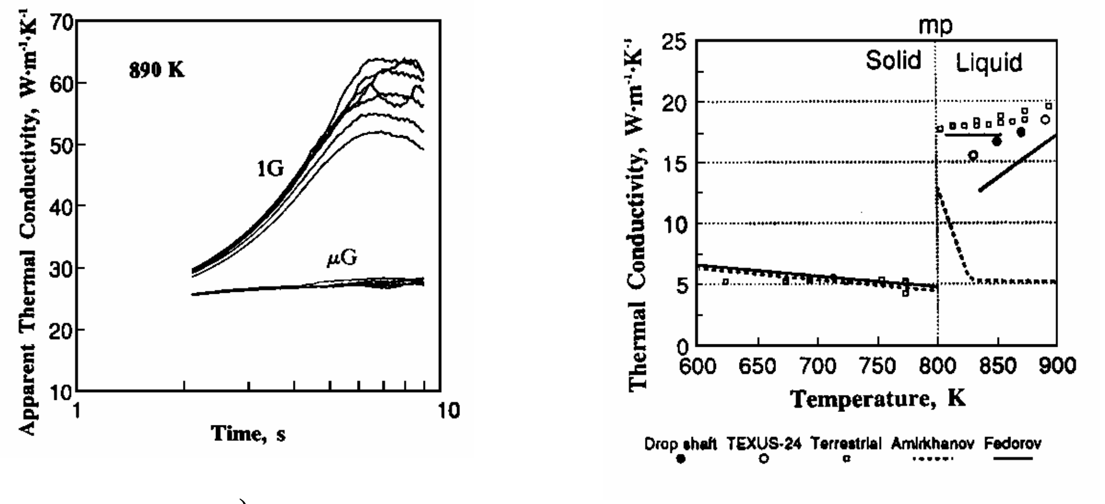
[3] The term microgravity (μg) has been introduced, because there are still residual accelerations on board a spacecraft of the order of 10^{-6} g_0, where g_0 is the gravitational acceleration on the earth's surface. While experiments under microgravity are still scarce today and have an exotic touch, they may become routine operations in the 21st century, when the International Space Station (ISS) is totally available.



a)

b)

Figure 3: a) Apparent thermal conductivity of molten InSb measured at 890 K under microgravity conditions on board of sounding rocket TEXUS 24 and on earth [46]; b) Comparison with other data: open and solid circles represent data obtained under microgravity conditions. Squares show data obtained on earth using the transient hot-wire method. Solid and dashed lines show data obtained on earth using steady-state methods.

IS EXPERIMENT NECESSARY?

The transport properties of molten materials at high temperatures are crucial for the efficient design of industrial equipment and chemical processes involving these materials. Their uncertainty has consequences on the design of heat exchangers and other equipment. Nunes et al. [47] presented recently an analysis of the effect, in recent applications of ionic liquids at high temperatures, both as heat-transfer and chemical-reaction media, concluding that the knowledge of thermophysical properties is important for proper and optimal technological design. Two examples were used (thermal storage in solar plants and molten salt oxidation of wastes). The results obtained support that the implementation of those applications needs a careful selection of experimental data; otherwise, equipment will be either under or over dimensioned, with the consequent poor operation and/or increased capital costs.

Considering the situation of the state of art in the theoretical modeling of molten materials and the inherent difficulties of the computer simulations, restricted to a given interparticle interaction potential, the experimental measurement of the thermal conductivity is always necessary. The data obtained, the correlations developed and the interpretations performed can be used for a better design and optimisation of industrial processes of the materials under study, for a better design of thermostats for the ITS90 reference points and for the development of reference materials, for equipment calibration and quality control in industry. However, and as in other areas, in thermal conductivity of molten materials,

to do or to do well is not enough! We must know how to do it well and rigorously!

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