Measurement of Thermal Conductivity of Liquids at High Temperature

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Abstract. The goal purchased in this paper is to implement a pulse method to measure the thermal conductivity of liquid silica glass above 1200°C until 1600°C. A heat flux stimulation controlled in energy and in time is generated on the front face of an experimental cell. The temperature rise is measured on the rear face of this cell face by using a fast cooled infrared camera. The choice of the measurement cell geometry is fundamental to be able to estimate at the same time the thermal diffusivity and the specific heat of the liquid by an inverse technique. The parameters estimation problem takes into account the optimization of the cell wall thickness. The theoretical model used for the inversion takes into account the coupled heat transfer modes (conduction, convection and radiation) that can occur during the experiment, particularly the thermal conductive short-cut through metallic lateral walls of the cell and radiative transfer within the semi-transparent and participating medium. First measurements are performed on a cell filled with water at ambient temperature in order to validate the parameters estimation procedure.

1. Introduction: measurement of the thermophysical properties of fluids at high temperature

The general problem of the measurement of thermophysical properties of fluids have already been presented in a previous paper [1]. The measurement method is based on a pulsed method (Flash method). A metallic cell containing the fluid (molten glass) is placed in a furnace and is stimulated by a laser beam on its front face. The mean rear-face temperature is measured by an infrared camera and allows the estimation of the liquid thermal properties by an inverse technique. The following study presents the methodology used for the characterization of molten glass at high temperature (1200-1600°C) by taking into account the coupling of conduction with convection and radiation. A particular attention is given to the design of the measurement cell. Its effect on the parameter estimation problem is studied. The challenge in this work is to perform estimations on different types of molten glass with various optical properties. As the temperature of the cell can be very sensitive to free convection, which is more difficult to model compared to radiation, it is important to know if such an effect can occur or not in our cell [4]. Another difficulty arises from the semi-transparent character of the molten glass in the near and mid-infrared wavelength range. Previous studies [2-3] were generally interested with the “apparent” conductivity of molten glass, which combines the conductive and radiative effects through the Rosseland approximation. The “apparent” thermal conductivity is a non-intrinsic value since it depends on the experimental configuration (type of stimulation, cell geometry and so on ...). As this quantity can be very different from the phonic (“true”) conductivity of the molten glass, thermal radiation must be taken into account through an adapted coupled thermal model. Even if radiation can be neglected in the present work (only validation tests at room temperature are
presented), the proposed coupled model is given here to evaluate the effects of radiation at high temperature in molten glass.

2. Heat transfer modelling

2.1. Conductive transfer

In a previous study [1], it has been shown that the best method to estimate the thermophysical properties by a pulse experiment is based on the geometry presented in Figure 1 where the liquid is confined between two walls. To simplify calculations, we assume \( L \gg e \) in order to consider the heat transfer as unidimensional. The implementation of the analytical model is simplified by the use of thermal quadrupoles. After a Laplace transform on the problem, our model is defined by a chain of quadrupoles. A diagram of the system is given in Figure 1. The inverse Laplace transform is implemented numerically with the De Hoog algorithm.

In the case of molten glass, the type of materials that can be used for the walls is limited since they are generally more conductive than the liquid itself (ceramic or noble metal).

The estimation problem allows us to identify four parameters:
- The thermal diffusivity of liquid \( a_l \)
- The thermal conductivity \( k_l \)
- The heat losses \( h \)
- The energy absorbed by the system per unit of area \( Q/S \)

A sensitivity study (See Figure 2 left) shows that we can estimate simultaneously these four parameters for a 4mm fluid layer thickness. By working with normalized thermograms, the number of unknown parameters is reduced to three \((a_l, k_l, h)\). By calculating the variance of thermophysical parameters (See [1] for more details) with a 4mm thick fluid layer, it appears an optimal wall thickness of 1mm for a platinum alloy cell. Finally, it is possible to improve the thermal conductivity estimation by fixing the fluid heat capacity to its nominal value that can be measured through a complementary experiment (e.g. calorimetry measurements) (See [1] for more details about this technique).

Figure 1. Simplified three-layer model (left) quadrupole representation (right)

![Figure 1](image1.png)

Figure 2. Sensitivity curves. Fluid (molten glass) \([e_f = 4 \text{ mm}, k_f = 1.5 \text{ W.m}^{-1}.\text{K}^{-1}, a_f = 1.43 \times 10^7 \text{ m}^2.\text{s}^{-1}]\); walls (Platinum) \([e_w = 1 \text{ mm}, k_w = 78 \text{ W.m}^{-1}.\text{K}^{-1}, a_w = 2.44 \times 10^7 \text{ m}^2.\text{s}^{-1}]\); \(h=10 \text{ W.m}^{-2}.\text{K}^{-1}\), \(Q/S = 10^4 \text{ J.m}^{-2}\).
2.2. Convective coupling

A previous study made in transient regime [4] shows that the extension $L/e$ of the cell and the characteristics of the contained fluid have an influence on the estimation of the thermal properties of the fluid by the pulsed method. Due to the diameter of our furnace ($\bar{O} 75$mm but only 40 mm are used) and the thickness of the fluid layer ($e=4$ mm), the cell extension of our cell is about 10. In this case, if the Prandtl and the Rayleigh number in the worst case with maximum free convection($\Delta T= 10\degree C$ and $L = 4$mm) are respectively very low and high, free convection must be included in the theoretical heat transfer model (see Table 1).

| $\Delta T= 10\degree C \: L = 4$mm | Rayleigh Number | Prandtl Number |
|----------------------------------|-----------------|----------------|
| Water (25°C)                     | 9000            | 7              |
| Oil (Alcatel 100) (25°C)         | 1000            | 720            |
| Molten glass (1200-1600°C)       | 0.04-0.18       | 8000-2000      |

Table 1. Prandtl and Rayleigh Numbers for different types of fluid

The cases presented in Table 1 show that water and oil at 25°C cannot be studied in our cell without taking into account the effects of free convection [4]. In contrast, molten glass presents a very low Rayleigh number. Consequently, this phenomenon of convection will not disturb the estimation of the thermophysical properties for materials exhibiting relative large viscosity values, even at high temperature.

2.3. 2D/3D effect

Due to a very narrow furnace ($\bar{O} 75$mm), the unidimensional three-layer model is not adapted to our case. The presence of lateral walls must therefore be included in the thermal model. As shown in Figure 3, there is a thermal shortcut through the lateral walls. To minimise these phenomena, the lateral walls must be chosen as thin as possible. Moreover, as the upper face is kept open and the cell is difficult to be entirely filled by the fluid, the conductive heat transfer is 3D. In this case, no analytical model exists. That is the reason why we decided to use a 3D numerical model implemented in FlexPDE® for the parameters estimation.

Figure 3. Visualisation of heat transfer (vector of heat flux) in the measurement cell with no lateral walls (left) and with lateral walls (right) - Simulations with a 2D Cartesian model on FlexPDE®

The thickness of the lateral wall is fixed to 1mm for commercial and experimental reasons (mechanical resistance of the cell at high temperature). However, a sensitivity study on 4 parameters with the 3D numerical model (see Figures 4) allows us to perform the simultaneous estimation of all parameters for water at room temperature.
2.4. Radiative transfer

Glass is a Semi-Transparent Material (STM) in the near and mid-infrared wavelength range. Thermal radiation plays a dominant role at high temperature, it is therefore necessary to take into account its effect in the thermal model used for inversion. The general transient heat transfer within an absorbing, emitting gray medium is obtained by solving the combined energy and Radiative Transfer Equations (R.T.E). The temperature field $T$ is coupled with the intensity $I(s, \Omega)$ through the divergence of the radiative flux that appears in the heat equation as a source term (see Eq. 1). The intensity is a function of the temperature field through the Blackbody emission term in the R.T.E (see Eq. 2).

- "Energy equation":

$$\nabla \cdot (k \nabla T) - \nabla \cdot [q_r(s)] = \rho C_p \frac{\partial T}{\partial t} \quad \text{with} \quad \nabla q_r(s) = 4 \pi \beta \left[ n^2 \frac{\sigma T^4(s)}{\pi} - I(s) \right]$$  \hspace{1cm} (1)

- "Radiative Transfer Equation" (R.T.E) in a gray absorbing-emitting semi-transparent medium:

$$\frac{dI(s, \Omega)}{ds} = -\beta I(s, \Omega) + \beta l_b[T(s)] \quad \text{or} \quad \sum_{i=1}^3 l_i \frac{\partial I(s, \Omega)}{\partial x_i} = -\beta I(s, \Omega) + \beta l_b[T(s)]$$  \hspace{1cm} (2)

$\beta$ is the absorption coefficient. $I_b[T(s)]$ is the blackbody radiative intensity at the local temperature of the medium, which is given by the Planck’s law: $I_b(s) = n^2 \frac{\sigma T^4}{\pi}$. $l_i$ represents the direction cosines $\{l_1, l_2, l_3\} = \{\cos \theta, \sin \theta \cos \varphi, \sin \theta \sin \varphi\}$ in the directions $x_1$, $x_2$ and $x_3$. The left-hand side term of the R.T.E represents the gradient of the intensity in the direction $\Omega$. The two right-hand side terms of the R.T.E describe the intensity variations due to absorption and emission phenomena respectively.
For solving the Radiative Transfer Equation, the modified PN method presented in [5] has been implemented in FlexPDE® FEM Software. The principle of the method consists in using the spherical harmonics approximation to describe the spatial and angular intensity variations. In a first order truncation, the radiative directional intensity can be written as the sum of its different moments:

\[ I'(s, \theta, \phi) = \frac{1}{4\pi} \left( I^{(0)} + 3I^{(1)} \cos \theta + 3I^{(2)} \sin \theta \cos \phi + 3I^{(3)} \sin \theta \sin \phi \right) \]  

(3)

The angular variations are given by Legendre polynomials and the unknowns of the problem \( I^{(0)}, I^{(1)}, I^{(2)} \) and \( I^{(3)} \) that respectively represent the average intensity (zeros order moment of the intensity) and the components of radiative flux in \( x_1, x_2 \) and \( x_3 \) (the first order moments) only depends of spatial coordinates \( x_i \).

\[ I^{(0)} = \int_{\Omega} I'(s, \Omega) d\Omega \quad \text{and} \quad I^{(i)} = \int_{\Omega} I'(s, \Omega) d\Omega \]  

(4)

The primary unknown corresponding to \( I^{(0)} \) (See [5]) can be obtained independently of first order moments \( I^{(1)}, I^{(2)}, I^{(3)} \) by solving the following 3D steady-state second order differential equation:

\[ \frac{1}{3\beta} \left( \frac{\partial^2 I^{(0)}}{\partial x_1^2} + \frac{\partial^2 I^{(0)}}{\partial x_2^2} + \frac{\partial^2 I^{(0)}}{\partial x_3^2} \right) = -(4\pi\beta \sigma_b(T) - k \delta^{(0)}) \]  

(5)

If needed, the secondary unknowns \( I^{(1)}, I^{(2)}, I^{(3)} \) (components of the radiative flux) can be obtained from \( I^{(0)} \) through the following first order equations:

\[ I^{(i)} = -\frac{1}{3\beta} \frac{\partial I^{(0)}}{\partial x_i} \quad (i = 1, 2 \text{ or } 3) \]  

(6)

The pure radiative conditions are given by the general Marshak’s boundary condition [6]. This simple but accurate model (See reference [5] for comparison with fine model in the case of the Flash method) has been applied for solving the coupled conductive-radiative heat transfer in a semi-transparent medium (molten glass) for three different optical thicknesses \( \tau_0 = \beta e \) and Planck numbers \( Npl = k\beta / 4n^2\sigma T_{ref}^3 \) (Conduction-Radiation interaction parameter). The different values used for the simulations are given in Table 2.

| Property | Value |
|----------|-------|
| \( k \) \( = 2.5 \text{ W/m.K} \) | \( \rho = 2500 \text{ Kg/m}^3 \) | \( C_p = 1000 \text{ J/Kg.K} \) | \( a = 10^{-6} \text{ m}^2/\text{s} \) |
| \( e = 4 \text{ mm} \) | | | |
| \( \beta (\text{m}^{-1}) \) | 25 | 250 | 1250 |
| \( \tau_0 = \beta e \) | 0.1 | 1 | 5 |
| \( Npl = k\beta / 4n^2\sigma T_{ref}^3 \) | 0.038 | 0.38 | 1.91 |

Table 2. Thermal and Optical Properties of molten glass used for the simulations

The results obtained in the case of the classical Flash Method are given in Figure 7a for a Semi-Transparent glass with opaque and emissive boundaries (black-painted) for three different optical thicknesses and Planck numbers.
The dashed black curve corresponds to the pure diffusion curve (no radiation) and the solid curves to the conducto-radiative thermograms. As explained in [5], thermograms with radiation are “faster” than purely conductive thermograms. We can also observe temperature “jumps” at the beginning of the conducto-radiative thermograms, especially for a medium with a low optical thickness. It can be explained by a direct and fast (speed of light) heat transfer by photons (radiative transfer) between the front and rear faces of the semi-transparent medium. The same simulations have been then carried out by taking into account the Platinum boundaries (Thicknes $e_p = 1\, mm$, $\epsilon = 1$ (worst case), $k_p = 34\, W/m.\,^{\circ}C$ and $a_p = 1.22.10^{-5}\, m^2/s$) in the front and rear faces of the molten glass (See dashed curves in Figure 7b). The response time is increasing. No temperature “jump” is observed because the temperature rise at the front face of the glass is reduced due to the capacitance effect of the walls. The simulations have been also performed with lateral Platinum walls (solid curves). These thermograms are “faster” because of the "thermal" shortcut through the lateral conductive walls. These simulations clearly show that the radiative effect must be taken into account at high temperature because the heat transfer strongly depends on the optical properties of the glass material.

3. Implementation

We have developed an optimised measurement cell, which takes into account different theoretical and experimental aspects specific to the material (molten glass at high temperature) and experimental constraints in connection with high temperature measurements (thermal shortcut with lateral conductive walls), coupled conducto-radiative transfer, tubular furnace with a reduced diameter.

3.1. Experimental bench

The measurement cell is build in a Pt/Rh(10%) alloy (see Figure 5), this material was chosen because of its good mechanical and chemical behaviours (no oxidation by the atmospheric environment until 1600°C) at high temperatures. Besides, the alloy does not chemically react with the type of fluid studied here and, as a metal, Platinum is quite a good flux absorber/ emitter and completely opaque in IR spectral ranges of the Laser beam and Infrared Camera. Moreover there no mass transfer with molten glass along the walls due to surface tension gradient. Concerning the geometry, the cell is a 40*40*6 mm$^3$ hollow rectangular box with 1 mm thick walls. The upper face is opened and its edges are overhung with a 1.5 mm wire in order to avoid the overflowing of molten glass at high temperature.
In order to validate the geometry of the cell and the heat transfer model for parameters estimation, measurements are performed at room temperature with a simplified experimental device and a reference fluid. Jellified water (with 0.15% in mass of Carbopol®) is chosen as a reference fluid, because of its high viscosity (with no shear stress) close to the glass viscosity at high temperature. This kind of fluid keeps the same thermal properties as water (well known at room temperature), with no perturbation due to convective effect during the measurement. Finally, water can be considered as an opaque fluid in the IR range. It is not necessary to take into account the radiative heat transfer within the fluid in this case because the Planck number is large, especially at room temperature.

Concerning the facility (see Figure 6), the larger face of the cell containing the fluids is heated through halogen lamps during 0.9s (crenel stimulation). A calibrated FLIR JADE III InSb Infrared camera [3.5µm-5.5µm] is placed and focused in front of the opposite face to measure the mean temperature of the entire surface of the rear face of the cell. After stimulation, a shutter plate is placed between the samples and the lamps to avoid residual heating of the sample by the light tubes. A borosicate glass, which strongly cut the infrared band after 2.5µm is put in front of the halogen system to isolate the IR camera from lamps emission. The cell is painted in black in order to maximise the signal/noise ratio. This device partially reproduces the condition of the high temperature experimentation. Four measurements have been performed with this facility at a room temperature of 25°C. Two parameters are estimated by inverse technique from reduced thermograms (thermal conductivity $k_l$ and heat losses $h$) by using the numerical 3D FlexPDE® conductive model coupled with a Levenberg Marquardt optimization algorithm implemented in Matlab (see Figure 7). Here, the specific heat $\rho C_p$ that is usually known (calorimetry measurements) is fixed to reduce estimation times and increase the accuracy on estimated thermal conductivity. These results are also presented in Table 

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**Figure 5.** Black painted measurement cell in Umicore FKS Pt/Rh(10%) for experiment at room temperature.

**Figure 6.** Schematic description of the experiment at room temperature.
3. The duration of the acquisition is 80s. The thermal properties can be considered as constant during the experiment (rear face maximum elevation temperature is 0.5°C).

![Graph](image)

**Figure 7.** Estimation on an experimental thermogram (jellified water) – Two-parameter model

The experiment appears to be very reproducible. The literature [7] gives a thermal conductivity of 0.607 W.m\(^{-1}\).K\(^{-1}\) at 25°C, so that a difference of 1.3% relative to the mean of the experimental results was found in our measurement.

| \(k_i\) (W.m\(^{-1}\).K\(^{-1}\)) | \(h\) (W.m\(^{-2}\) K\(^{-1}\)) |
|-------------------------------|-----------------|
| 0.629                         | 9.862           |
| 0.613                         | 12.642          |
| 0.623                         | 8.215           |
| 0.596                         | 8.541           |
| **Mean (± stand. dev.)**      | **9.815(±2.015)**|

**Table 3.** Results : Estimation with two parameters : thermal conductivity \(k_i\) and heat losses \(h\) (4 samples)

4. Conclusion

In this paper, the whole procedure for the estimation of the phonic conductivity of liquids by a pulse method at high temperature has been described. Thanks to a sensitivity study on experimental parameters, an optimal cell measurement allowing us to estimate thermal properties of liquids has been designed. First measurements have been successfully obtained with a fluid exhibiting a comparable rheology as molten glass and allow us to extend this experiment on semi-transparent materials at high temperature. As shown in this work, free convection can be neglected for molten glass but radiation must be taken into account using the proposed conducto-radiative model.

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