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Parameters estimation and measurement of thermophysical properties of liquids

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Abstract

The goal purchased in this paper is to implement an experimental bench allowing the measurement of the thermal diffusivity and conductivity of liquids. The principle of the measurement based on a pulsed method is presented. The entire problem is solved through the thermal quadrupoles method. Then, the parameters estimation problem that is specially difficult in this case due to the presence of the walls of the measurement cell is described and an optimal thickness for these walls is defined from a sensitivity study. Finally, we show how it is possible to take into account the radiative transfer within the fluid in the estimation problem, before presenting the set-up and some experimental results. 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

In a keynote lecture [\[1\]](#page-16-0), we have already presented the general problems for the measurement of the thermal conductivity and diffusivity of liquids. The problems related to the coupling of conduction with convective and radiative heat transfers have been specially investigated. First ones have been solved by a judicious choice of the measurement cell geometry. The others by taking into account the radiative heat transfer (when it cannot be neglected) in the fluid layer. In this paper, a particular attention will be given to the parameter estimation problem, first in a pure conductive regime and then by taking into account the conductive–radiative coupling, in a three-layer system where the properties of the intermediate layer are unknown.

2. Measurement of the thermophysical properties of liquids

2.1. Principle of the measurement

Contrary to the classical hot-wire method $[2-5]$, we have chosen to implement a pulsed method, which

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presents the advantage of allowing us to work in a pseudo-conduction regime where heat transfer within the fluid is not influenced by convection. The principle of this method is presented in Fig. 1. The liquid is confined between two metallic and coaxial cylindrical cylinders submitted to a heat pulsed stimulation on the inner face of the interior cylinder. The temperature is measured on the outer face of the external cylinder (technique known as a ''back-face'' measurement).

In this paper, we assume a purely conductive transfer.

To simplify calculations, we consider a cartesian coordinates system. Indeed, the thicknesses of the three layers being small compared to their radii, particularly for an aspect ratio lower than 0.1, it is possible to show that the differences between the temperatures calculated in cartesian and cylindrical coordinates are lower than 0.01%.

2.2. Direct model

The problem is described in [Fig. 2](#page-2-0).

The implementation of the analytical model is simplified by the use of thermal quadrupoles [\[6\]](#page-16-0).

After a Laplace transform on the problem, our model is given by a chain of quadrupoles. A diagram of the system is given in [Fig. 3](#page-2-0) with

• $1/hS$ being the convective resistance (heat losses with the surroundings),

 \cdot ¹)

Fig. 1. Principle of the measurement (cylindrical geometry).

• *A*, *B*, *C* and *D* being the coefficients of the inverse transfer matrices for the walls and the liquid.

Fig. 2. Model.

Their expressions are given by

$$
A_i = D_i = \cosh\left(\sqrt{\frac{pe_i^2}{a_i}}\right)
$$

$$
B_i = \frac{1}{\lambda_i S \sqrt{\frac{p}{a_i}}} \sinh\left(\sqrt{\frac{pe_i^2}{a_i}}\right)
$$
(1)

and

$$
C_i = \lambda_i S \sqrt{\frac{p}{a_i}} \sinh\left(\sqrt{\frac{pe_i^2}{a_i}}\right)
$$

(lowerscript i indifferently refers to the fluid or to the wall) and

 e_i thickness of the material

 a_i thermal diffusivity
 λ_i thermal conductiv thermal conductivity

The rear-face temperature $\theta(p)$ is then given by

$$
\theta(p) = \frac{\phi(p)}{C + 2\text{A}hS + \text{B}(hS)^2}
$$
 (2)

A, B and C represent the coefficients of the transfer matrix obtained by taking the product of the transfer matrices for the three materials:

$$
\begin{bmatrix} A & B \\ C & A \end{bmatrix} = \begin{bmatrix} A_w & B_w \\ C_w & A_w \end{bmatrix} \begin{bmatrix} A_l & B_l \\ C_l & A_l \end{bmatrix} \begin{bmatrix} A_w & B_w \\ C_w & A_w \end{bmatrix}
$$
 (3) with

$$
A = (A_w A_l + B_w C_l) A_w + (A_w B_l + B_w A_l) C_w
$$

$$
\mathsf{B}=(A_wA_l+B_wC_l)B_w+(A_wB_l+B_wA_l)A_w
$$

$$
C = (C_w A_l + A_w C_l)A_w + (C_w B_l + A_w A_l)C_w
$$

By assuming that the heat pulse $\varphi(t)$ received by the system is infinitely short in time (Dirac of flux), then $\phi(p)$ is a constant equal to the energy of the pulse.

For $h = 0$, the temperature at long times is obtained by

$$
T_{\infty} = \lim_{t \to \infty} T(t) = \lim_{p \to 0} p\theta(p)
$$
\n(4)

Thus,

$$
T_{\infty} = \lim_{p \to 0} \frac{p\phi(p)}{\mathsf{C}(p)}\tag{5}
$$

and

$$
T_{\infty} = \frac{Q}{S(2\rho c_w e_w + \rho c_l e_l)}
$$

(T is called the adiabatic temperature) (6)

 (T_{∞}) is called the adiabatic temperature) (6)

In general case (for any t), the inverse Laplace transform of relation (2) is implemented numerically. We use several algorithms that give the same results, either the Stehfest algorithm [\[7\],](#page-16-0) the De Hoog algorithm [\[8\]](#page-16-0) or a numerical Inverse Fast Fourier Transform (I.F.F.T.) [\[9\]](#page-16-0).

[Fig. 4](#page-3-0) gives an example of results obtained for two liquids (water and oil) and two different walls thicknesses (0.5 mm and 2mm). The thermophysical properties used for the simulations are

- $e_1 = 4.5$ mm, $h = 5$ W m⁻² K⁻¹
- Water: $\lambda_l = 0.597 \text{ W m}^{-1} \text{ K}^{-1}$, $a_l = 1.43 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
- Oil: $\lambda_l = 0.132 \text{ W m}^{-1} \text{ K}^{-1}$, $a_l = 7.33 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$
- Walls (copper): $\lambda_w = 395 \text{ W m}^{-1} \text{ K}^{-1}$, $a_w = 1.15 \times$ 10^{-4} m² s⁻¹
- $e_w = 0.5$ or 2 mm
- $Q/S = 4 \times 10^4$ J m⁻²

Fig. 3. Quadrupole representation.

Fig. 4. Simulation examples (pulsed responses).

3. Parameters estimation

3.1. Sensitivity study

The model depends on different parameters. Some of them are supposed to be exactly known and the others will be identified. The initial goal is to thermally characterize the fluid, i.e. to estimate two quantities, its thermal diffusivity and conductivity (or any other set of parameters as the effusivity or the specific heat). Assuming that the thermal properties of the walls and the geometry of the system are known, the model is a function of four unknown parameters:

$$
\bullet \hspace{1mm} e_l/\sqrt{a_l}
$$

$$
\bullet \hspace{0.1cm} e_{l}/\lambda_{l}
$$

- \bullet Q/S
- \bullet h

The question is to know if it is possible to estimate simultaneously from an experimental thermogram the four above mentioned parameters. The problem comes from the measurement noise, which involves errors in the estimated parameters that must be quantified. Beck and Arnold [\[10\]](#page-16-0) showed that one of the most powerful tools for that is the sensitivity study, associated with a stochastical approach.

Let $\beta = (\beta_1, \beta_2, \beta_3, \beta_4)$ be the vector of unknown parameters, the temperature field can be formally written as

$$
T = f(t, \beta_1, \beta_2, \beta_3, \beta_4) = f(t, \beta)
$$
\n(7)

The measured temperature being disturbed, one can write by assuming an additive noise:

$$
Y_i = T(t_i, \beta) + \varepsilon_i \tag{8}
$$

 ε_i being the random noise, associated with the measurement Y_i at the time t_i .

The sensitivity coefficient of the field T to parameter β_i at the time t is defined by

$$
X_j(t,\beta) = \frac{\partial T}{\partial \beta_j}(t,\beta)
$$
\n(9)

Thereafter, we will use the reduced sensitivity coefficients, which are easier to compare (they have the same dimension as the field T):

$$
X_j^*(t,\beta) = \beta_j \frac{\partial T}{\partial \beta_j}(t,\beta)
$$
\n(10)

The sensitivity curves give us informations in the estimation error (the error is small when the sensitivity coefficient is maximum) and in the possible correlations between parameters. The parameters are correlated if their sensitivity coefficients are proportional. In this case, it is not possible to estimate these parameters simultaneously.

The estimation problem is non-linear. Thus, the sensitivity curves and consequently the estimation will depend on the nominal values of the unknown parameters but also on the known parameters and on the geometry of the system. This is the reason why for instance, an optimum on the walls thicknesses exists.

As an example, [Fig. 5](#page-4-0) gives the sensitivity curves for water and oil with 0.5 mm and 2mm walls thicknesses respectively.

The whole curves seem to show that some parameters are more or less correlated, particularly $\beta_1(e_1/\sqrt{a_1})$ and $\beta_3(Q/S)$ or β_1 and $\beta_2(e_i/\lambda_i)$, which would not allow the simultaneous estimation of these parameters and consequently of the thermal diffusivity. In addition, one can notice that for time higher than twice of the maximum, the parameters are strongly correlated. Indeed, one is in the case of the cooling of a system with a quasi-uniform temperature. The thermogram is a pure decreasing exponential, which only depends on one parameter, the timeconstant of the system $h/(2\rho c_w e_w + \rho c_l e_l)$. This remark leads us to limit the estimation interval to short times. We have chosen to work between $t = 0$ and $t = 1.5t_{\text{max}}$.

The significant number of parameters [\(4\)](#page-2-0) and the cross correlations between them make difficult the reading and the interpretation of the sensitivity curves. The stochastical study and the simplified study in the following paragraphs will allow to specify the problem.

3.2. Stochastical approach

An efficient method to estimate the unknown parameters consists in using an inverse technique based on the previous analytical model. The method we use is based on the Nonlinear Gauss-Newton's Ordinary Least Squares method that consists in finding suitable values

Fig. 5. Sensitivity curves for water and oil (0.5 mm and 2mm).

for the unknown parameters introduced in the model to minimize by an iterative process the differences between the experimental and theoretical curves. Let S be the sum of the ordinary squared differences:

$$
S = \sum_{i} (Y_i - T(t_i, \beta))^2
$$
 (11)

 Y represents the experimental thermogram, T the theoretical thermogram as a function of the time t and unknown parameters β . The subscript *i* refers to the time t_i . Minimizing S with respect to β_i is equivalent to make its derivatives equal to zero:

$$
\frac{\partial S}{\partial \beta_j} = 0 \Rightarrow \sum_i \frac{\partial T(t, \beta)}{\partial \beta_j} (Y_i - T(t_i, \beta)) = 0 \quad (\forall j)
$$
\n(12)

The sensitivity coefficient $X_i(t, \beta)$ given by [\(9\)](#page-3-0) naturally appears in this minimization. Thus, the observation of the sensitivity curves allows us to know if the model we use is suitable or not to measure the parameter we seek. By a linear expansion of the model around the solution, one can obtain an analytical relation between the estimated values $\hat{\beta}$ of the parameters and their real values β that is given by

$$
\hat{\beta} = \beta + (X^t X)^{-1} X^t \varepsilon(t) \tag{13}
$$

 $\varepsilon(t)$ being the noise at time t.

From this relation, one shows that

 $E(\hat{\beta}) = \beta$

: expected values of parameters (unbiased estimator)

 (14)

Water -0.5 mm				$Water = 2 mm$			
0.3394	-2.3464	2.4913	1.4724	0.3218	-0.8419	0.7528	-0.5216
2.3464	16.5302	-17.4179	-9.4267	-0.8419	2.4531	-2.0146	2.5528
2.4913	-17.4179	184144	10.4120	0.7528	-2.0146	1 7770	-1.3092
1.4724	-9.4267	10.4120	9.7216	-0.5216	2.5528	-1.3092	8.7357
Oil -0.5 mm				$Oil - 2mm$			
0.0649	-0.2870	0.2533	0.1216	0.1920	-0.4540	0.1500	-0.2349
-0.2870	1 3529	-1.1408	-0.4388	-0.4540	1.3544	-0.2825	1 0 7 9 4
0.2533	-1.1408	0.9958	0.4599	0.1500	-0.2825	0.1413	-0.0219
0.1216	-0.4388	0.4599	0.3979	-0.2349	1.0794	-0.0219	1.4113

Table 2

Correlation matrices

$$
V(\hat{\beta}) = \sigma_n^2 (X'X)^{-1} = \sigma_n^2 \begin{bmatrix} \text{Var}(\beta_i) & \text{Cov}(\beta_i, \beta_j) \\ \text{Cov}(\beta_i, \beta_j) & \text{Var}(\beta_j) \end{bmatrix}
$$

: covariance matrix $(\sigma_n: \text{standard deviation of noise})$

 (15)

The previous relation is very important because it allows to evaluate the errors in the estimated parameters. It also clearly shows that if the signal is not corrupted by the measurement noise, then one can expect to estimate the unknown parameters with a high accuracy, even if their effects on the signal are strongly coupled. In contrast, in the case of a noised signal, errors in the estimated parameters values directly depend on the noise level, especially if they are strongly coupled. To know if the parameters that are estimated from the iterative process really correspond to the thermophysical properties of the material, it is also of a great interest to compute the correlation factors between parameters β_i and β_j that are defined by

$$
\rho(\beta_i, \beta_j) = \frac{\text{Cov}(\beta_i, \beta_j)}{\sqrt{\text{Var}(\beta_i) \cdot \text{Var}(\beta_j)}}
$$
(16)

The estimation will be as much accurate than the variances are small and the correlation coefficients far from

unity. The covariance and correlation matrices corresponding to the four preceding parameters are given in Tables 1 and 2. To be compared, the tables are calculated from the reduced sensitivities.

From the covariance matrices, one can notice that the variance on β_1 is the smallest one, which shows that the thermal diffusivity will be better identified than the thermal conductivity. In the same way, the estimation will be better for oil than for water. Later on, one will consider water as a test fluid because results are better for less conducting fluids. Finally, one can observe that the variances strongly vary with the thickness of the walls, which will thus have to be optimized.

From the correlation matrices, one can note that in most cases β_3 is correlated with β_1 and β_2 , particularly for water, which confirms the preceding results. In the case 4, one can notice that no parameter are correlated. Thus, it is possible to estimate a and λ at the same time, if the thickness of the walls is chosen in an optimal way.

One can also notice that the estimation problem is strongly nonlinear since the four studied cases exhibit some covariance and correlation matrices very different between each others.

3.3. Simplified study with two parameters

To simplify, let consider the case with no heat loss $(h = 0)$. The heat losses being uncorrelated at short times with the other parameters (until the maximum of the thermogram), the introduction of the heat exchanges will only have thereafter few effects in the estimation of the two parameters of interest.

To get rid of the influence of the parameter Q/S , we will work with the reduced thermogram defined by

$$
\theta(t, \beta_1, \beta_2) = \frac{T(t, \beta_1, \beta_2, \beta_3)}{T_{\text{max}}(\beta_2, \beta_3)}
$$
(17)

The four examples previously presented are given in Fig. 6 and [Table 3.](#page-7-0) In some cases, the correlation between the parameters β_1 and β_2 is large (greater than 0.99). The first idea is to seek a new couple of parameters, which would be less correlated and thus could be estimated in better conditions.

3.4. Parameters substitution

The model we developed makes appear a natural couple of parameters β_1 and β_2 . It is then possible, by a parameter substitution to introduce a new set of parameters β_a and β_b such as

$$
\theta = f(t, \beta_1, \beta_2) = g(t, \beta_a, \beta_b)
$$
\n(18)

The new parameters are functions of the old ones, that is

$$
\beta_a = f_a(\beta_1, \beta_2) \tag{19}
$$

Fig. 6. Reduced thermograms and sensitivity curves for water and oil (0.5 mm and 2mm).

$$
\beta_b = f_b(\beta_1, \beta_2) \tag{20}
$$

Sensitivities to the new parameters X_a and X_b can be written as a function of the old ones X_1 and X_2 (it is the same for reduced sensitivities, variances and covariances).

One obtains

• for the reduced sensitivities:

$$
X_{ab}^* = X_{12}^* J^{*-1} \tag{21}
$$

with

$$
J^* = \begin{bmatrix} \frac{\beta_1}{\beta_a} \frac{\partial f_a}{\partial \beta_1} & \frac{\beta_2}{\beta_a} \frac{\partial f_a}{\partial \beta_2} \\ \frac{\beta_1}{\beta_b} \frac{\partial f_b}{\partial \beta_1} & \frac{\beta_2}{\beta_b} \frac{\partial f_b}{\partial \beta_2} \end{bmatrix} \begin{array}{c} X_{ab}^* = \begin{bmatrix} X_a^* & X_b^* \end{bmatrix} \\ X_{12}^* = \begin{bmatrix} X_1^* & X_2^* \end{bmatrix} \end{array} \tag{22}
$$

• for the covariance matrix:

$$
\begin{bmatrix}\n\text{Var}(\beta_a) & \text{Cov}(\beta_a, \beta_b) \\
\text{Cov}(\beta_a, \beta_b) & \text{Var}(\beta_b)\n\end{bmatrix}\n= J^* \cdot\n\begin{bmatrix}\n\text{Var}(\beta_1) & \text{Cov}(\beta_1, \beta_2) \\
\text{Cov}(\beta_1, \beta_2) & \text{Var}(\beta_2)\n\end{bmatrix} \cdot J^{*t}
$$
\n(23)

It is then easy to show that if X_1 and X_2 are proportional in a given interval $(X_1 = K X_2)$ then X_a and X_b are also correlated in this same interval $(X_a = K'X_b)$.

The interest of introducing a new set of parameters is not to try to estimate the two parameters simultaneously but to find the more sensitive parameter of the system by nullify the sensitivity to the second parameter. Theoretically, it is possible to find a couple (β_a, β_b) , which allows to obtain this result. Nevertheless, in practice this parameter must keep a physical meaning and remain the same according to the nominal values of the parameters. In fact, the estimation problem being nonlinear, the optimum parameter is not unique and in our case varies with respect to the liquid we consider.

However, one can notice that the sensitivity to a parameter varies according to the choice of the second parameter, which would let think (if the parameters are not completely correlated) that it is possible to

improve the estimation of a given parameter by associating it with a particular parameter. In fact, the variance of a parameter and thus the error made in the estimated value of this parameter is independent of the choice of the second parameter.

More generally, one shows that the estimation of the new parameters from the model written with this new set of parameters is equivalent to calculate these new parameters from the estimated values of the old ones. That shows that the choice of the parameters to estimate has no effect on the quality of the estimation.

In fact, the parameters substitution allows to make appear a quantity, which can be measured independently in another experiment and that can be then fixed to its nominal value, which is equivalent to remove a parameter in the estimation.

3.5. Choice of a model and parameters

Let us apply the preceding remarks to the four thermograms in [Fig. 6](#page-6-0) and find a new set of parameters under the form:

$$
\begin{cases}\n\beta_a = \beta_1^m \beta_2^n \\
\beta_b = \beta_2\n\end{cases}
$$
\n(24)

One obtains (for the reduced sensitivities)

$$
J^* = \begin{bmatrix} m & n \\ 0 & 1 \end{bmatrix} \tag{25}
$$

The new sensitivities are given by

$$
\begin{cases} X_a^* = \frac{1}{m} X_1^* \\ X_b^* = X_2^* - \frac{n}{m} X_1^* \end{cases}
$$
 (26)

One has to choose n/m in such a way that $X_b^* \simeq 0$.

Minimizing X_b^* is equivalent to minimize the variance of β_a that is given by (see Appendix A for more details):

$$
Var(\beta_a) = m^2 Var(\beta_1) + n^2 Var(\beta_2) + 2nm Cov(\beta_1, \beta_2)
$$
\n(27)

Let fix *m* for example and take the derivative of $\text{Var}(\beta_a)$ with respect to nlm :

$$
\frac{\text{Var}(\beta_a)}{m^2} = \text{Var}(\beta_1) + \left(\frac{n}{m}\right)^2 \text{Var}(\beta_2) + 2\frac{n}{m} \text{Cov}(\beta_1, \beta_2)
$$
\n(28)

This yields

$$
\frac{\partial \operatorname{Var}(\beta_a)}{\partial (n/m)} = 2\frac{n}{m} \operatorname{Var}(\beta_2) + 2 \operatorname{Cov}(\beta_1, \beta_2) = 0 \tag{29}
$$

That is

$$
\frac{n}{m} = \frac{-\operatorname{Cov}(\beta_1, \beta_2)}{\operatorname{Var}(\beta_2)}\tag{30}
$$

Fig. 7. Sensitivity curves. Fluid (water) $[e_f = 4.5 \text{ mm}, \lambda_f =$ $0.597 \text{ W m}^{-1} \text{ K}^{-1}$, $a_l = 1.43 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\rho c_l = 4.17 \times 10^6 \text{ J m}^{-3}$ K^{-1} ; walls (copper) $[e_w = 1 \text{ mm}, \lambda_w = 395 \text{ W m}^{-1} \text{ K}^{-1},$ $a_w = 1.15 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $\rho c_w = 3.43 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$; $h = 5 \text{ W}$ $m^{-2} K^{-1}$, $Q/S = 4 \times 10^4$ J m^{-2} .

Table 4 Covariance and correlation matrices

• for a 0.5 mm wall thickness:

- Water
$$
\frac{n}{m} = \frac{1}{6.13} \approx \frac{1}{6}
$$

- Oil $\frac{n}{m} = \frac{1}{3.00} \approx -\frac{1}{3}$

• for a 2mm wall thickness:

- Water
$$
\frac{n}{m} = \frac{1}{1.97} \approx \frac{1}{2}
$$

- Oil $\frac{n}{m} = \frac{1}{1.07} \approx -\frac{1}{1}$

The values strongly depend on the nature of the fluid. Thus, it is not possible to find only one solution for β_a allowing to nullify X_b^* . In this case, the following procedure cannot be applied and no change of parameters allows us to improve the estimation. The only one solution in difficult cases, when the standard deviation of a parameter is too large, is to fix this parameter to its nominal value. This nominal value can be determined through another experiment. In our case, rather than to fix the thermal conductivity value (e/λ_i) , one prefers to work with the specific heat ($\rho c_l e_l$) that can be determined more easily by a calorimetric experiment:

$$
\beta_1 = e_l / \sqrt{a_l}
$$
 and $\beta_2 = \rho c_l e_l$

Fig. 7 gives an example of sensitivity curves obtained from the four parameters $(e_1/\sqrt{a_1}, \rho c_1e_1, Q/S$ and h) and the three parameters (β_2 being fixed in this case) models.

Table 4 gives the corresponding covariance and correlation matrices. One can observe that the variances and the correlations are strongly improved when β_2 is fixed.

4. Optimization of the walls thicknesses

The problem being non-linear, the estimation of β_1 and β_2 can be improved by an optimal choice of the walls thickness that minimizes the variances of the parameters. The deterioration of the signal/noise ratio when the walls thicknesses are increasing is taken into account in this optimization (the measurement noise remaining constant, the amplitude of the measured temperature is decreasing with the increasing of the thickness of the walls).

The study is made on the reduced thermograms with the three parameters model:

$$
\theta = f(t, \beta_1, \beta_2, h). \tag{31}
$$

The results are given in Fig. 8 for water and oil respectively.

At first sight, the results are quite surprising. Contrary to what one could imagine, the variances are larger for small walls thicknesses.

Indeed, in this case, we should find the behaviour of a monolayer material with a variance of 0.003 for β_1 . By fixing β_2 to its nominal value, one obtains this value.

Thus, contrary to what one could think, the use of thin walls does not improve the parameters estimation, except if those are sufficiently thin to be neglected (this case not being very useful in practice).

We are in the presence of three different behaviours according to the walls thickness:

Fig. 8. Optimization of the walls thicknesses (water and oil). Fluid (water) $[e_f = 4.5$ mm, $\lambda_f = 0.597$ W m⁻¹ K⁻¹, $a_l = 1.43 \times 10^{-7}$ m² s⁻¹, $\rho c_l = 4.17 \times 10^6$ J m⁻³ K⁻¹]; fluid (oil) $[\epsilon_f = 4.5$ mm, $\lambda_f = 0.132$ W m⁻¹ K⁻¹, $a_l = 7.33 \times 10^{-7}$ m² s⁻¹, $\rho c_l = 1.8 \times 10^6$ J m⁻³ K⁻¹]; walls
(copper) $[\lambda_w = 395$ W m⁻¹ K⁻¹, $a_w = 1.15 \times 10^{-4}$ m²

- 1. Lower than few microns, one is in presence of a monolayer of fluid.
- 2. Between few microns and hundreds of microns, one is in the presence of a homogeneous system, i.e. the response is that of a homogeneous medium but with an apparent diffusivity different from the diffusivity of the fluid:

$$
a_{\rm ap} = \frac{\lambda_{\rm ap}}{\rho c_{\rm ap}}\tag{32}
$$

with

$$
\lambda_{\rm ap} = (e_l + 2e_w) \bigg/ \bigg(\frac{e_l}{\lambda_l} + \frac{2e_w}{\lambda_w} \bigg)
$$

and

 $\rho c_{\rm ap} = (\rho c_l e_l + 2\rho c_w e_w)/(e_l + 2e_w).$

3. Above hundreds of microns, one is in the presence of a non-homogeneous three-layer material.

From this, two strategies can be defined:

- 1. In the case 2, one estimates an apparent diffusivity by the classical method (model with three parameters: a, h and Q) and knowing the characteristics of the wall and the specific heat of the fluid, one makes a correction.
- 2. In the case 3, it exists an optimum for walls thickness between 1 mm and 2mm. One uses a model with four parameters allowing to estimate a and ρc of the liquid, if the parameters β_1 and β_2 are uncorrelated (assuming the characteristics of the wall to be known).

For practical reasons, particularly the rigidity of the walls required to obtain a good centring of the cylinders, we made the choice to work in the case 3.

5. Inverse problem

Initially, we test the effectiveness of our approach on simulated thermograms. From the preceding model, one calculates the theoretical temperature response of the system and adds noise to obtain a simulated signal on which the estimation will be carried out. Let notice that the noise added to the signal presents a standard deviation of ± 0.005 °C, which corresponds to the experimental noise as we will see it in the last part.

The estimation program uses the Levenberg–Marquardt [\[11\]](#page-16-0) algorithm. The objective function depends on four parameters:

- $\beta_1 = e_1/\sqrt{a_1}$ (square root of the characteristic time of the fluid)
- $\beta_2 = \rho c_l e_l$ (heat capacity of the fluid)
- *O/S* (energy absorbed by the system per unit of area)
- h (convective heat transfer coefficient between the walls and the surroundings)

We plotted the simulated curves and the theoretical curves obtained from the estimated parameters, as well as the residuals (differences between theoretical and simulated curves).

We also calculated the covariance matrices as well as the standard deviations of the estimators. Fig. 9 and [Table 5](#page-11-0) give results for water and oil.

Fig. 9. Estimation on simulated thermograms by an Ordinary Least Squares method. Fluid (water) $[e_f = 4.5 \text{ mm}]$, $\lambda_f = 0.597 \text{ W m}^{-1} \text{ K}^{-1}$, $a_l = 1.43 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\rho c_l = 4.17 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$; fluid (oil) $\left[e_f = 4.5 \text{ mm}, \lambda_f = 0.132 \text{ W m}^{-1} \text{ K}^{-1} \right]$ $a_l = 7.33 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\rho c_l = 1.8 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$; walls (copper) $[e_w = 1 \text{ mm}$, $\lambda_w = 395 \text{ W m}^{-1} \text{ K}^{-1}$, $a_w = 1.15 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$,
 $\rho c_w = 3.43 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$; $h = 5 \text{ W m}^{-2} \text{ K$

Estimated values, covariance and correlation matrices (3 parameters)

If the value of the parameter β_2 is fixed, then the results given in Table 6 are obtained. One notes a much more precise estimation for β_1 and consequently for the thermal diffusivity (for water $a = 1.428 \times 10^{-7}$ m² s⁻¹ and $\sigma_a^* = \pm 0.08\%$, for oil $a = 7.323 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $\sigma_a^* = \pm 0.06\%$).

6. Taking into account the radiative heat transfer

In the case of a semi-transparent liquid with opaque boundaries, which is the case here, one can model the conducto-radiative coupling through a simple thermal resistance. The expression of this resistance can differ with the extinction coefficient of the material (or more precisely with its optical thickness). For instance, in the case of a high absorbing material, one shows that the effect of the boundaries can be neglected compared to the absorption within the material. In this case, the radiative transfer can be viewed like a diffusion process. In the literature, one talks about the diffusion approximation or the Rosseland approximation. The other case relates to low absorbing medium or thin film model, it is the opposite situation. In this case, one can also model the radiative heat transfer by a simple resistance. There is a complete decoupling between the conductive and

radiative transfers in the medium but these two transfers remain coupled through the boundary conditions.

h = 5 W m⁻² K⁻¹
 $h = 5.022$ W m⁻² K⁻¹
 $0/S = 4 \times 10^4$ J m⁻²
 $0/S = 4.005 \times 10^4$ J m

⁻¹ $a_l = 7.323 \times 10^{-7}$ m² s⁻¹

 $Q/S = 4.005 \times 10^4$ J m⁻²

In all cases, the quadrupole model can be set-up very quickly.

The heat flux ϕ within the medium being the sum of the conductive and radiative fluxes, the conducto-radiative transfer can be modelled by a conductive quadrupole and a radiative quadrupole in parallel. In our case, the radiative quadrupole is a pure resistive quadrupole:

$$
M_r = \begin{bmatrix} A_r = 1 & B_r = R_r \\ C_r = 0 & D_r = 1 \end{bmatrix} \tag{33}
$$

The equivalent quadrupole is given by

 $a_l = 7.33 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
 $h = 5 \text{ W m}^{-2} \text{ K}^{-1}$

Covariance

Correlation Correlation

$$
M' = \begin{bmatrix} A' = \frac{AR_r + B}{B + R_r} & B' = \frac{BR_r}{B + R_r} \\ C' = \frac{CR_r + D + A - 2}{B + R_r} & D' = \frac{B + R_r D}{B + R_r} \end{bmatrix}
$$
(34)

It is used strictly in the same way that the pure conductive quadrupole.

Many authors [\[12–16\]](#page-16-0) have proposed several expressions for R_r versus the optical thickness of the material. Here, R_r will be estimated and one will not try to reach

Fig. 10. Conducto-radiative quadrupole model.

optical quantities from this parameter. This parameter is only introduced to provide a correction on the thermogram allowing the estimation of ρc_l and a_l ([Fig. 10](#page-12-0)).

The response in temperature is then a function of five parameters:

$$
\beta_1 = e_1/\sqrt{a_1}, \quad \beta_2 = \rho c_1 e_1, \quad \beta_3 = Q/S
$$

\n $\beta_4 = h \quad \text{and} \quad \beta_5 = R_r$

Fig. 11 gives an example of thermograms versus R_r . One can observe that the effect of this parameter on the thermogram appears at small times, which allows us to think that this parameter is independent of the others.

Fig. 11. Thermograms for different values of $R_r^* =$ R_r/R_{cd} $(R_{cd} = e_l/\lambda_l)$. Fluid $[e_f = 4 \text{ mm}, \lambda_f = 0.2 \text{ W m}^{-1} \text{ K}^{-1},$ $a_l = 1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\rho c_l = 2 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$]; walls (copper)
[$e_w = 1 \text{ mm}$, $\lambda_w = 395 \text{ W m}^{-1} \text{ K}^{-1}$, $a_w = 1.15 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $\rho c_w =$ 3.43×10^6 J m⁻³ K⁻¹]; h = 5 W m⁻² K⁻¹, $Q/S = 4 \times 10^4$ J m⁻².

Table 7 Covariance and correlation matrices

Liquid

Fig. 12 gives an example of sensitivity curves obtained from the five parameters model. Table 7 gives the corresponding covariances and correlations matrices for the five parameters and the four parameters (β_2 being fixed in this case) models.

In this example, $R_r^* = R_r/R_{cd} = 10$ with $R_{cd} = e_l/\lambda_l$. It clearly appears that R_r is uncoupled with the others parameters and thus could be estimated without any difficulties.

It is possible to improve the radiative model and keep an analytical approach, by introducing two parameters (the optical thickness and the Planck number). For more details, the reader can refer to Refs. [\[17–19\].](#page-16-0)

Fig. 12. Sensitivity curves.

7. Implementation

7.1. Experimental bench

Following the preceding studies, one defines the characteristics of the measuring cell as follows:

- walls in copper or stainless steel (1 mm thick)
- thickness of the fluid (3 mm/4.5 mm)
- height of the cell (100 mm)
- inner diameter (24 mm)

The tubes constituting the walls are embedded in two pieces in Teflon allowing to ensure the concentricity and the sealing of the cell (see Fig. 13). The cell is placed on a frame surrounded by a metallic shield and an insulated bell to limit the heat exchange by convection and radiation with the surroundings.

The pulsed stimulation is produced by a moving Flashlamp, which is placed inside the measurement cell for the stimulation. The duration of the pulse is a few milliseconds and the power is about 1000 J. The temperature measurement is carried out via welded Chromel– Alumel thermocouples $(120 \mu m)$ diameter) with separated contacts. The acquisition system is composed either of a measurement amplifier and a numerical oscil-

Fig. 13. Measurement cell.

loscope, or of an Analog/Digital acquisition card and a conditioning module. A computer allows the automatic treatment of the thermogram.

7.2. Example of experimental results

As shown before, water has been chosen as a test fluid because it represents the most unfavourable case for this kind of measurement.

In practice, the magnification factor K of the experimental device (sensitivity of the thermocouples, amplifier, oscilloscope), which consists of multiplying the measured signal (a temperature) to obtain a potential that can be measured through an oscilloscope is illknown. Thus, the parameter Q/S is replaced by KQ/S in the theoretical model. For practical reasons (estimation with three parameters for instance), the experimental thermogram is normalised by its apparent maximum U_{max} . Thus, the estimated parameter in the four parameters method is: $KQ/S \cdot U_{\text{max}}$.

Fig. 14 gives the results we obtained by the four parameters model and the corresponding variances are given in [Table 8](#page-15-0). As planed by the theoretical study, one can observe that the estimation of the specific heat (ρc) is not good.

[Fig. 15](#page-15-0) gives the results obtained by the three parameters model (i.e. ρc being fixed to its nominal value 4.18×10^6 J m⁻³ K⁻¹) and in [Table 8](#page-15-0) the corresponding variances.

One can note that the variances are much smaller than in the case with four parameters, which characterizes a better parameters estimation, particularly for the thermal diffusivity.

Fig. 14. Estimation on an experimental thermogram (water)—4 parameters model.

Fig. 15. Estimation on an experimental thermogram (water)—3 parameters model.

8. Conclusion

We describe in this paper the whole steps allowing to set up a procedure for the estimation of the thermophysical properties of liquids by a flash method. A sensitivity study on the parameters enabled first to determine an optimum thickness for the walls of the cell. The complete study of the problem of parameters estimation shows that for most liquids, it is possible to measure by this method two main properties of the fluid $(a$ and ρc). We also showed that one could remove the effect of the natural convection by a judicious choice of the measuring cell extension and take into account the radiative effects in the case of semi-transparent liquids through an additional parameter, the radiative resistance. Finally, experimentation was implemented. The first measurements obtained on water showed the relevance of the theoretical study.

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Appendix A

Let us consider the following parameters substitution:

$$
\begin{cases}\n\beta_a = f_a(\beta_1, \beta_2) \\
\beta_b = f_b(\beta_1, \beta_2)\n\end{cases}
$$

The reduced sensitivities X_a^* and X_b^* to the new parameters β_a and β_b are function of the reduced sensitivities X_1^* and X_2^* to β_1 and β_2 through the following relations:

$$
\begin{bmatrix} X_1^* & X_2^* \end{bmatrix} = \begin{bmatrix} X_a^* & X_b^* \end{bmatrix} \begin{bmatrix} J \end{bmatrix}^*
$$

with

$$
\left[J\right]^* = \begin{bmatrix} a_1^* = \frac{\beta_1}{\beta_a} \frac{\partial f_a}{\partial \beta_1} & a_2^* = \frac{\beta_2}{\beta_a} \frac{\partial f_a}{\partial \beta_2} \\ b_1^* = \frac{\beta_1}{\beta_b} \frac{\partial f_b}{\partial \beta_1} & b_2^* = \frac{\beta_2}{\beta_b} \frac{\partial f_b}{\partial \beta_2} \end{bmatrix}
$$

That is

$$
\begin{cases}\nX_1^* = a_1^* X_a^* + b_1^* X_b^* \\
X_2^* = a_2^* X_a^* + b_2^* X_b^*\n\end{cases}
$$

The reduced covariance matrix for the parameters (β_1, β_2) is given by

$$
\begin{split} \text{Var}(\beta_1, \beta_2) &= \sigma_n^2 (X^{*t} X^*)^{-1} = \sigma_n^2 \Bigg[\frac{\sum X_1^{*2}}{\sum X_1^* X_2^*} \frac{\sum X_1^* X_2^*}{\sum X_2^{*2}} \Bigg]^{-1} \\ &= \frac{\sigma_n^2}{\Delta(X_1^* X_2^*)} \Bigg[\frac{\sum X_2^{*2}}{-\sum X_1^* X_2^*} \frac{-\sum X_1^* X_2^*}{\sum X_1^{*2}} \Bigg] \end{split}
$$

with

$$
\Delta(X_1, X_2) = \sum X_1^{*2} \cdot \sum X_2^{*2} - \left(\sum X_1^{*2} X_2^{*2}\right)^2
$$

and

$$
\sum X_j^* = \sum_i X_j^*(t_i, \beta_j)
$$

Thus,

$$
Var(\beta_1) = \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \sum X_2^{*2}
$$

$$
Var(\beta_2) = \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \sum X_1^{*2}
$$

and

$$
Cov(\beta_1, \beta_2) = -\frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \sum X_1^* X_2^*
$$

The variance of the parameter β_a is given by

$$
Var(\beta_a) = a_1^{*2} Var(\beta_1) + a_2^{*2} Var(\beta_2) + 2a_1^{*} a_2^{*} Cov(\beta_1, \beta_2)
$$

Substituting $\text{Var}(\beta_1)$, $\text{Var}(\beta_2)$ and $\text{Cov}(\beta_1, \beta_2)$ by their expressions:

$$
\begin{split} \text{Var}(\beta_a) &= \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \left(a_1^{*2} \sum X_2^{*2} + a_2^{*2} \sum X_1^{*2} \right. \\ &\quad \left. - 2a_1^* a_2^* \sum X_1^* X_2^* \right) \\ &= \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \sum (a_1^{*2} X_2^{*2} + a_1^{*2} X_1^{*2} - 2a_1^* a_2^* X_1^* X_2^*) \\ &= \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} \sum (a_1^* X_2^* - a_2^* X_1^*)^2 \end{split}
$$

As $a_1^* X_2^* - a_2^* X_1^* = (a_1^* b_2^* - a_2^* b_1^*) X_b^*$, we obtain

$$
Var(\beta_a) = \frac{\sigma_n^2}{\Delta(X_1^*, X_2^*)} (a_1^* b_2^* - a_2^* b_1^*)^2 \cdot \sum X_b^{*2}
$$

Minimizing X_b^* is thus equivalent to minimize $\text{Var}(\beta_a)$.

Application:
$$
\begin{cases} \beta_a = f_a(\beta_1, \beta_2) = \beta_1^m \beta_2^n \\ \beta_b = f_b(\beta_1, \beta_2) = \beta_2 \end{cases}
$$

In our particular case, the reduced Jacobian matrix is equal to

$$
[J]^* = \begin{bmatrix} a_1^* = m & a_2^* = n \\ b_1^* = 0 & b_2^* = 1 \end{bmatrix}
$$

and yields

$$
\text{Var}(\beta_a) = \frac{\sigma_n^2 \cdot m^2}{\Delta(X_1^*, X_2^*)} \cdot \sum X_b^{*2}
$$

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