

On the selection of the experimental parameters in a thermal-wave-resonator-cavity (TWRC) configuration

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The paper investigates the influence of the most important experimental parameters on the behaviour of the phase of the back-photopyroelectric signal, in a thermal-wave-resonator-cavity. The linear behaviour of the “phase versus thickness” curve is located in the $2 < Labs_m/\mu_m < 3$ range, being delimited by the thermal impedance at the interfaces of the detection cell in the thermally thin regime, and by the signal/noise ratio, in the thermally thick side. A proper choice of the experimental parameters, together with a small enough thickness variation step ($\leq 1\mu m$) lead to an accuracy of about $\pm 0.3\%$ for the values of thermal diffusivity of liquids.

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1. Introduction

During the last decades, the photopyroelectric (PPE) technique has been extensively applied to study thermal properties of condensed matter samples [1, 2].

In principle, in the PPE technique, the temperature variation of a sample, exposed to a modulated radiation, is measured with a pyroelectric sensor [3-5]. One of the most usual detection schemes consists in irradiating directly the sample and measuring its temperature rise with a pyroelectric sensor, situated in good thermal contact with sample's rear side. This configuration is called ‘back detection configuration’ (BPPE) and the information, contained in the phase of the PPE signal, refers to sample's thermal diffusivity [6].

If we restrict our area of interest to liquid samples, we note that the thermal diffusivity can be obtained by performing both a frequency and a (sample's) thickness scan. The recently developed PPE detection cells, with a variable sensor-to-source distance (thermal-wave-resonator-cavity (TWRC) method), introduced the sample thickness as a powerful control parameter and proposed the methods based on sample's thickness scan as alternatives to the usual frequency-scanned schemes [7-9].

In the TWRC technique, the information (the value of the thermal diffusivity) is usually extracted from the linear dependence of the phase of the complex BPPE signal as a function of sample's thickness [7-9]. This linear dependence was supposed to be valid in the thermally thick regime ($\mu < L$) for both sensor and sample. It was recently demonstrated that, due to some theoretical and experimental features, the linear behaviour of the phase vs. sample's thickness is valid only in a very limited region [10].

The equation obtained for the phase of the BPPE signal is the following [10]:

$$\Theta = -\arctan \left[\frac{\sin(x) - R \exp(-2x) [\sin(x) \cos(2x) - \cos(x) \sin(2x)]}{\cos(x) - R \exp(-2x) [\sin(x) \sin(2x) + \cos(x) \cos(2x)]} \right] \quad (1)$$

where:

$$x = a_m L_m, \quad R = R_{mw} R_{mp}, \quad R_{jk} = (b_{jk} - 1) / (b_{jk} + 1),$$

$$b_{jk} = e_j / e_k, \quad \mu = (\alpha / \pi f)^{1/2} \quad (2)$$

In Eq. (1) R_{jk} represents the reflection coefficient of the thermal wave at the ‘jk’ interface, e represents the thermal effusivity and a is the reciprocal of the thermal diffusion length ($a = 1/\mu$). Eq. (1) is valid with the following restrictions: (i) a one dimensional propagation of heat is considered (the diameter of the laser beam is larger than the thermal diffusion length in the sample); (ii) the heat transport is due only to the conduction (the heat transport by radiation and convection is neglected); (iii) the sensor is thermally thick; (iv) the sample is optically opaque. The symbols “w”, “m” and “p” refer to the main components of the detection cell (window, sample material and pyroelectric sensor, respectively) [7-8].

As stated above, an analysis of Eq. (1) indicates that, at a fixed chopping frequency, it is possible to obtain the thermal diffusivity of the sample from the slope of the linear behaviour of the ‘phase vs. thickness’ curve as:

$$\alpha_m = \frac{\pi f}{(\text{slope})^2} \quad (3)$$

providing some clear restrictions are imposed to the experimental parameters.

There are four experimental parameters that delimitate the linear region of the 'phase vs. thickness' curve: the scanning range (relative thickness), the starting position (absolute thickness), the combined reflection coefficient of the thermal wave at the sample-window and sample-pyroelectric sensor interfaces (R), and the chopping frequency (the thermal diffusion length). Other two parameters, the step of the thickness variation and the signal/noise ratio, also influence the accuracy of the results.

The present paper analyses the influence of each of the previously mentioned parameters on the behaviour of the phase of the BPPE signal. The purpose of the present study is to locate precisely the linear region of the 'phase vs. thickness' curve (necessary to calculate the thermal diffusivity through Eq. (3)) and to obtain a maximum accuracy in thermal diffusivity investigations.

2. Experimental

The experimental setup, used for thermal diffusivity investigations, and the geometry of the detection cell were largely presented before [9-13]. An Ar^+ laser (Spectra Physics) with stabilized power output at $\lambda = 514$ nm, modulated with an acousto-optical modulator (Intra Action), was used as radiation source. The pyroelectric sensor, a $510 \mu\text{m}$ thick LiTaO_3 single crystal, provided with Cr-Au electrodes on both faces, was glued on a micrometric table. The backing material for the sensor was air. The modulated radiation passed through a 1.2 mm thick quartz window (Hellma Co.) situated on a rotating table, and was absorbed by an opaque $0.1 \mu\text{m}$ thick titanium layer, deposited on the rear side of the window. The liquid sample accommodated the space between the sensor and the titanium layer. The sample's thickness variation was performed with a step of $0.1 \mu\text{m}$, and with a rate of $0.2 \mu\text{m/s}$ (ITL09 micro-controller). The PPE signal was processed with a digital lock-in amplifier (Stanford SR830). The sample's thickness control and data acquisition were carried out with adequate software. Two liquids with stable properties at room temperature, silicon oil and triton ($4-(\text{C}_8\text{H}_{17})\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n$, $n \approx 10$), were selected as testing materials.

3. Results and discussion

3.1. Influence of the experimental parameters

3.1.1. Influence of the reflection coefficient of the thermal wave at the window-sample and sample-sensor interfaces.

Eq. (1) indicates that " R " influences the behaviour of the phase of the signal only in the thermally thin regime for the sample: $x = a_m L_m = L_m/\mu_m \ll 1$. In the thermally thick regime for the sample, $x \gg 1$, $\exp(-2x) \rightarrow 0$, and the

phase of the signal depends linearly on the sample's thickness (the correction terms in Eq. (1) vanish). R represents the product of the reflection coefficients of the thermal wave at the interfaces sample-sensor R_{mp} and sample-window R_{mw} , respectively. In a typical TWRC experiment, if the pyroelectric sensor is a LiTaO_3 crystal ($\epsilon_p \approx 3900 \text{Ws}^{1/2} \text{m}^{-2} \text{K}^{-1}$) and the sample is an ordinary liquid ($\epsilon_m \approx 500 \div 2000 \text{Ws}^{1/2} \text{m}^{-2} \text{K}^{-1}$) [9, 13], then $-1 < R_{mp} < 0$. Concerning the sample-window interface, assuming that the usual windows in visible and near infrared are made from glass or quartz, R_{mw} is also smaller than 1 and negative, so that the resulted R belongs to $(0, 1)$ interval. A simulation of Eq. (1) for several values of R is presented in Fig. 1.

Fig. 1 indicates that for $x \geq 2$ the phase of the signal behaves linearly as a function of sample's thickness and, consequently, Eq. (3) can be applied. An interesting situation appears when $R = 0$ ($\epsilon_m \approx \epsilon_w$). In this case Eq. (3) is theoretically valid in the whole thickness range (including the thermally thin regime). Accidentally, such an experimental situation is possible in the case of water as sample ($\epsilon_{\text{water}} = 1582 \text{Ws}^{1/2} \text{m}^{-2} \text{K}^{-1}$) and quartz as window ($\epsilon_{\text{quartz}} = 1531 \text{Ws}^{1/2} \text{m}^{-2} \text{K}^{-1}$) [13].

Fig. 2 represents the value of the thermal diffusivity as a function of relative sample thickness, as calculated with Eq. (3), for water, silicon oil and triton, at the same chopping frequency (1 Hz). The graphs contain the thermally thin regime for the sample, (small relative thicknesses) where the value of the thermal diffusivity appears thickness dependent, indicating that Eq. (3) is not valid. Water, in combination with quartz as window, represents an exception; due to the fact that $R=0$, the linear dependence of the phase of the signal as a function of the thickness is respected in the thermally thin regime, too.

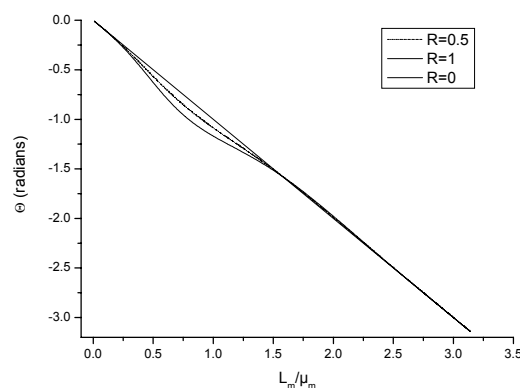


Fig. 1. Mathematical simulation of Eq.(1) for $R=0, 0.5$ and 1 .

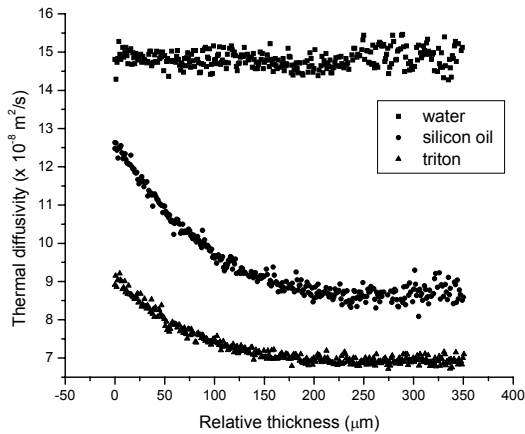


Fig. 2. Thermal diffusivity (calculated with Eq. (3)) as a function of relative thickness for water, silicon oil and triton, at 1 Hz chopping frequency.

3.1.2. Influence of the scanning range, starting position and chopping frequency.

These three parameters are interconnected, each of them acting in fact on the thermal thickness of the sample: the starting position of the scan and the scanning range act on the geometrical thickness of the sample, and the chopping frequency determines the thermal diffusion length (see Eq. (2)). With a proper choice of these parameters performed over a large thickness scanning range, the sample usually passes from a thermally thin regime ($L_m/\mu_m \ll 1$) to a thermally thick ($L_m/\mu_m > 1$), and then, to a thermally very thick one ($L_m/\mu_m \gg 1$).

Fig. 3 presents the behaviour of the thermal diffusivity as a function of sample's relative thickness (calculated with Eq. (3)) for triton, at three chopping frequencies.

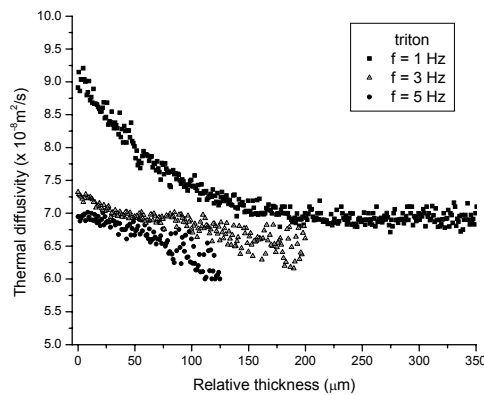


Fig. 3. Thermal diffusivity (calculated with Eq. (3)) as a function of relative thickness, for triton, at three different chopping frequencies.

One can see that, at 1 Hz the sample passes from thermally thin to thick regime (the thermally very thick region is not present in the graph), the graph at 3 Hz contains all the three regions, and at 5 Hz the sample is mainly thermally very thick (no linear behaviour can be detected). It is to be mentioned that the starting position for all the three scans is the same.

Fig. 4 presents the behaviour of the thermal diffusivity as a function of sample's relative thickness (calculated with Eq.(3)) for water and silicon oil at 3 Hz chopping frequency, and the same starting point for the thickness scan.

Two main conclusions can be extracted from Figs. 3 and 4: (i) in the thermally very thick regime for the sample, the measurement becomes very noisy – this is due to the strong attenuation of the amplitude of the thermal wave and to a degradation of the signal/noise ratio, and (ii) the linear, horizontal region of the scan is frequency dependent (it decreases with increasing chopping frequency).

Consequently, it appears as very important to find a quantity including all the above mentioned experimental parameters, to allow for comparison of different measurements. This parameter seems to be the ratio of the absolute sample's thickness and the thermal diffusion length, $Labs_m/\mu_m$. Unfortunately $Labs_m$ is not very easy to be precisely measured. We have to stress on the idea that the TWRC method was in fact introduced as an alternative for the frequency scanned techniques, due to the fact that, sometimes, the exact knowledge of $Labs_m$ was impossible.

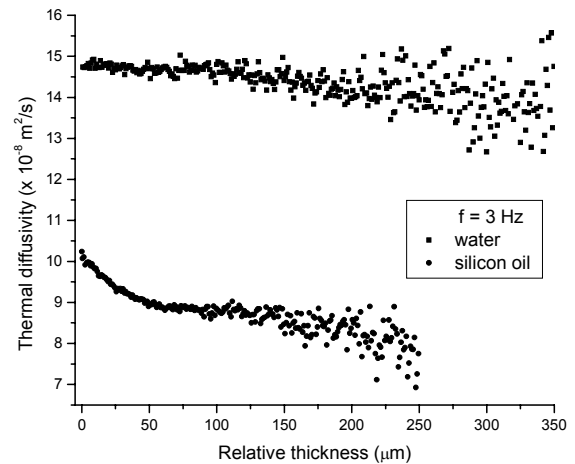


Fig. 4. Thermal diffusivity (calculated with Eq. (3)) as a function of relative thickness, for water and silicon oil at 3 Hz chopping frequency, over a large scanning range (including the thermally thin, thick and very thick regimes).

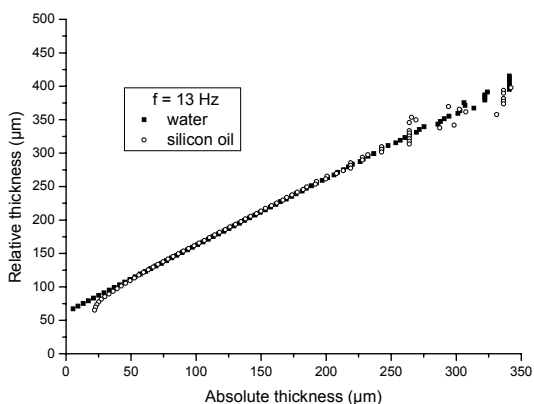


Fig. 5. Absolute sample thickness vs. relative thickness, as obtained from the scan of the phase of the PPE signal for water and silicon oil, at 13 Hz chopping frequency.

However, if we want to calculate $Labs_m$ a calibration of the set-up is always necessary, in order to find the absolute value of the phase of the signal. Such a calibration can be performed by measuring the phase of the signal with the sensor directly illuminated. Sometimes, it is more suitable to use for calibration another liquid with well known thermal diffusivity. Water as calibration liquid, together with quartz as window, is a suitable combination, because of the reasons mentioned before. A thickness scan of the phase of the BPPE signal for silicon oil and water, at the same chopping frequency, and in the same thickness interval is presented in Fig. 5. As expected from theory, the linear dependence of the phase of the BPPE signal as a function of thickness, in the case of water, extends in the thermally thin region too, leading to a more precise result for $Labs_m$.

3.1.3 The step of the thickness variation and the signal/noise ratio

Figs. 2-4 indicate that the linear behaviour of the thermal diffusivity as a function of thickness is limited in the thermally thin side by theory and in the thermally very thick regime by the signal/noise (S/N) ratio. The S/N ratio depends on the experimental parameters mentioned before (sample's thickness and chopping frequency) and it is thickness dependent: it decreases with increasing sample's thickness. For high quality investigations, the limit of a reasonable S/N ratio (of about 100) is reached at $Labs_m/\mu_m \leq 3 \div 4$, depending also on the quality of the experimental setup. Concerning the step of the thickness variation, it must be in principle as small as possible, in order to allow for an accurate fit. For ordinary liquids, at several Hz chopping frequency, the thermal diffusion length is around 100 μm (at 1 Hz for example, the thermal diffusion length for water is 210 μm , for triton 149 μm and for silicon oil 169 μm). In order to perform a good fit over one or two thermal diffusion lengths one needs a step of a few microns. For higher chopping frequencies, the thermal diffusion length decreases, requiring smaller thickness

variation steps. In our experiment the step was 0.1 μm , the smaller reported until now.

3.2. Data processing

The best way to find the correct value of the thermal diffusivity, by using the information contained in the phase of the BPPE signal in a TWRC experiment, is a combined experimental-theoretical iterative procedure.

The first step is to use the measured "relative phase vs. relative thickness" data in order to find an initial approach for the thermal diffusivity (see Eq. (3) from the slope of the curve (where the slope is defined by: $\text{slope} = \Theta/L_m$). With this "rough" value of the thermal diffusivity, one can calculate the thermal diffusion length. Using a calibration measurement for the initial offset of the phase of the signal (by directly irradiating the empty sensor [10, 13]), one can also obtain the absolute value of the phase of the signal, and a "rough" value of the absolute sample's thickness. The next step is to use the obtained data, to locate the linear (in general 2 μm -3 μm) region of the thickness scan, and to perform a fit of the experimental data in this region, in order to obtain improved values for the thermal diffusivity and $Labs_m$.

At this level of data processing there are two ways of obtaining the value of the thermal diffusivity.

The first one is to use the slope of the graph "absolute phase vs. thickness" in the linear region of the curve. This method was used in order to obtain the results presented in Figs. (2-4). We have to point out that the best way to obtain correct results is to calculate a "sliding slope" over a limited number of points; in such a way the linear region of the graph can be better located. In Figs. (2-4), the slope was calculated over 50 points (5 μm). As presented in Fig. (6), this method has an accuracy of about $\pm 3\%$.

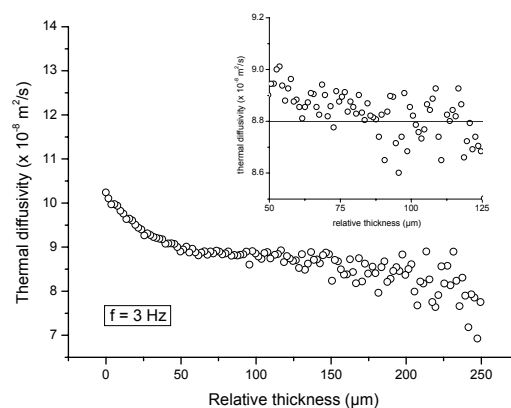


Fig. 6. Thermal diffusivity (calculated with Eq. (3)) as a function of relative thickness, for silicon oil at 3 Hz chopping frequency – inserted: detail of the linear part of the graph.

The second method uses the absolute values of the sample's thickness and the BPPE signal phase, and calculates the thermal diffusivity with the formula:

$$\alpha_m = \frac{\pi f Labs_m^2}{\Theta_{abs}^2} \quad (4)$$

The correct value of the thermal diffusivity will be obtained by using a fitting procedure: the best fit will be selected by minimizing the relative error of thermal diffusivity found with Eq. (4), as compared to the best fit value of the linear part of the curve, with $Labs_m$ as a fit parameter.

Some results are presented in Fig. 7. This method has an improved accuracy (about $\pm 0.3\%$). This improvement is connected with the fact that an error in $Labs_m$ influences, not only the value of the thermal diffusivity, but also the shape of the curve “thermal diffusivity vs. absolute thickness”; a correct choice of $Labs_m$ delimitates precisely the linear (horizontal) part of the graph.

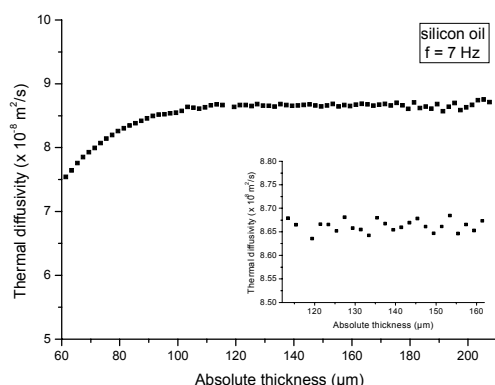


Fig. 7. Thermal diffusivity (calculated with Eq. (4)) as a function of absolute thickness, for silicon oil, at 7 Hz chopping frequency – inserted: detail of the linear part of the graph.

4. Conclusions

The accuracy of the result of a TWRC measurement (the value of the thermal diffusivity) is strongly influenced by several experimental parameters: the starting position, the step and the range of the thickness scan, the chopping frequency and the signal to noise ratio. The thermal impedance at the interfaces of the layers of the detection cell must be also taken into account, but only in the sample's thermally thin limit.

We have to mention first that the TWRC method is suitable only for liquids. The results of the investigation performed in this paper are useful for the methods based on the information contained in the phase of the PPE signal. There are two such methods: A first method is based on the calculation of the thermal diffusivity from the slope of the ‘phase vs. thickness’ curve - it is simple, it involves only one measurement and no calibrations [9]. A second method, that requires the absolute values of the phase and sample's thickness, is more accurate, but at least one calibration measurement (to find the absolute value of

the phase) is necessary [10]. The accuracy of the measurements is about $\pm 3\%$ in the first case and $\pm 0.3\%$ in the second one.

The main result of the study performed in this paper is the exact location of the linear behaviour of the “phase vs. thickness” curve and, consequently it is useful for both methods.

Independently on the method used for thermal diffusivity measurement, a good correlation between the sample's thickness scan range, absolute thickness of the sample and chopping frequency is necessary in order to find the correct linear region of the graph. It was demonstrated that all these three parameters are contained in only one, $Labs_m/\mu_m$, which must be optimized. Unfortunately, if the lower limit of this parameter is rather clear established by theory (see Fig. 1), the upper limit depends on parameters more difficult to estimate (the radiative contribution in the heat transport [8] and signal/noise ratio). The correct choice of the linear range of the ‘phase vs. thickness’ curve is responsible for the accuracy of the results. In our experiment $2 < Labs_m/\mu_m < 3$ was considered as a suitable scanning interval. Due to the fact that for high frequencies this thickness scan range is rather small, an accurate control of the sample's thickness variation is required.

Concerning the immediate applications of the method, we note that the processes of molecular association in liquids are accompanied by a non-linear dependence of the thermal diffusivity as a function of composition. Unfortunately, the deviation of the thermal diffusivity from additivity in interacting liquid mixtures is rather small (few percents) and difficult to be detected by usual calorimetric techniques. The high accuracy and reproducibility of the PPE methods based on the sample's thickness scan recommend these techniques for such type of investigations.

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