A systematic analysis of the influence of the surrounding media in the photothermal beam deflection signal

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Abstract: The photothermal beam deflection (PDS) technique was tested for low thermal diffusivity materials. The effect of using different liquids as surrounding media was studied in a systematic way. The fundamental experimental parameters, like the pump beam power and the modulation frequency were also studied in order to find out the best combination that still allows us to get good signals.

Due to the complexity of the optical alignment required, the usual mirage setup was adapted in order to allow the decoupling of the alignment of the cell containing the liquid and the sample holder.

Simple, straightforward methods (like e.g. the phase method) were used for the thermal diffusivity determination of solids once the thermal diffusivity of the liquids used is always much lower than that of solids.

The obtained values for the thermal diffusivity of test samples allow us to conclude that besides being possible to use any of the studied liquids as surrounding medium, ethanol is clearly the best choice, avoiding health problems related to CCl₄, which is the standard choice for PDS and PDS spectroscopy experiments, and technical/physical problems related to water and acetone. Modulation frequencies around 8 Hz combined with a pump beam power below 15 mW were proved to be the ideal conditions for this kind of experiment. The very low pump beam power required is also an important issue when talking about non-destructive analysis.

1. Introduction

Thermal characterization of materials, even of those usually not considered as good heat conductors, became more and more important during the last few years, mainly due to the increased research and demand for new materials with very specific functionalities. Those often require a very strict and trustable characterization.

The photothermal beam deflection technique is a very powerful one for a straight and rigorous determination of the thermal diffusivity of solids. However, for materials with low thermal diffusivity values, the simplest experimental procedure becomes useless. The complexity of the analysis of experimental data obtained by photothermal beam deflection when applied to low thermal diffusivity materials is usually related to the very low magnitude of the measured signals when the distance pump-probe beam increases.

In the most common configuration, the samples are just immersed in air. Being air a relatively good heat diffuser, it becomes competitive when the thermal diffusivity of the samples is lower than that of...
air. In this case, a multi-parameter fitting is necessary in order to calculate the thermal parameters from the experimental data. This makes the process much more complex and time consuming. To be able to apply simple methods (e.g. the “phase method”) to a straightforward thermal diffusivity determination, in any range of values, one has to guarantee that the thermal diffusivity of the material under study is higher than that of the surrounding medium [1]. For low diffusivity materials and using air as surrounding medium the mentioned condition is not fulfilled. To overcome this problem carbon tetrachloride \((\text{CCl}_4)\) is often chosen [2], once its properties are ideal for this application, but its use should be avoided due to health risks related.

The study of alternative surrounding media was carried out within this work. Although \(\text{CCl}_4\) was also studied, the main idea was to find alternatives to air rather than \(\text{CCl}_4\). Taking then \(\text{CCl}_4\) as a reference medium, ethanol, water and acetone were studied as potential alternatives. Reference materials with well known thermal properties, covering different ranges of thermal diffusivities, were used as test samples.

To achieve the desired results, as the thermal diffusion length becomes smaller, a very careful control of the experimental conditions, mainly the optical alignment, is needed. Other experimental parameters like the pump beam power and the modulation frequency were also controlled, to find the ideal set of experimental conditions for each range of thermal diffusivities [3]. As with any other liquid used as surrounding medium, the reactivity of the material under study related to liquid, must be evaluated before the experiment.

In section 2 brief details about the experimental setup are shown. In section 3 some of the main results obtained are presented. Conclusions are presented in section 4.

2. Experimental
The experimental setup used in this work (Fig. 1) uses an argon ion laser (Ar\(^+\) INNOVA90) as pump beam. An acousto-optic modulator (IntraAction Corp. ME-40) was used to modulate the pump beam. The modulation frequency was controlled directly by a two-phase Lock-in amplifier (SR830 DSP). The probe beam used is a low power He-Ne laser \((r_{\text{probe}} \approx 70 \ \mu m)\), and is part of a compact mirage cell [4] which includes also the focusing optics for the probe beam; the quadrant detector of photodiodes, allowing parallel and transverse measurements of the probe beam deflection; the sample holder mounted in a translation stage, which allows the rotation around the axis normal to the plane that contains the two laser beams and the control of the offset between the probe beam and the sample surface.

![Fig. 1 - Schematic view of the experimental setup when using liquid as surrounding medium](image-url)
The quadrant detector was connected to the lock-in amplifier. The whole process of scanning and data acquisition is controlled by software. The experimental data are fed to a computer for latter analysis. The experimental setup was mounted on a vibration-isolated table.

In this work four different surrounding fluids were tested - air, ethanol, water and carbon tetrachloride. Table 1 shows some of the most relevant parameters of those liquids, taking into account this specific application.

| fluid                        | \( \alpha_{\text{lit}} \) (\( \times 10^{-7} \text{ m}^2\text{s}^{-1} \)) | \( \frac{dn}{dT} \) (\( \times 10^{-4} \text{ K}^{-1} \)) | Boiling temperature (ºC) | Vapour pressure (25ºC) (kPa) |
|-----------------------------|-------------------------------------------------|-------------------------------------------------|-----------------|----------------------------|
| air                         | 220.9                                           | -0.0088                                         | ---             | ---                        |
| carbon tetrachloride (CCl\(_4\)) | 0.76                                           | -6.12                                          | 76.7            | 15.2                       |
| water (H\(_2\)O)            | 1.43                                            | -0.091                                         | 100.0           | 3.17                       |
| ethanol (C\(_2\)H\(_5\)OH)  | 0.88                                            | -4.0                                           | 78.3            | 7.89                       |
| Acetone (CH\(_3\)COCH\(_3\))| 0.11                                            | -5.42                                          | 56.1            | 30.8                       |

The use of liquids implied the use of a quartz cell (10 mm \( \times \) 10mm \( \times \) 40 mm). The sample was placed vertically and completely covered by the liquid. With the help of a screw, connected to a step motor it was possible to adjust the sample surface parallel to the probe beam. The measurement process is computer-controlled, with the amplitude and phase lag data registered as a function of the pump beam-probe beam distance (controlled by a step motor with a minimum step of 2.5 \( \mu\)m).

3. Results

The selection of results to be presented in this section is mainly focused on ethanol, once it is the obvious choice for future applications. The results will point out the role of the pump beam power and of the modulation frequency in the quality of the experimental results. An extensive and detailed report of all the experimental data obtained in this study can be found in reference [3]. In table 2 a summary of the values obtained for the thermal diffusivity of a reference sample of known low thermal diffusivity is presented.

| liquid                        | ethanol | acetone | water | carbon tetrachloride |
|-------------------------------|---------|---------|-------|----------------------|
| \( f_{\text{modulation}} \) (Hz) | 8.1     | 3.7     | 3.7   | 24.5                 |
| \( \alpha_{\text{exp}} \) \( \times 10^{-7} \text{m}^2\text{s}^{-1} \) | 2.12    | 1.52-2.16 | 2.14 | 2.28                 |
| \( \alpha_{\text{lit}} \) \( \times 10^{-7} \text{m}^2\text{s}^{-1} \) |         |         |       | 2.20                 |
| \( P_{\text{pump beam}} \) (mW) |         |         |       | 7.1                  |

Analysing the results presented in table 2 we are tempted to conclude that any of the liquids can be used as surrounding medium for thermal diffusivity measurements. Even if it is possible to get good...
results, the experimental care that has to be taken when using water or acetone makes the process too difficult and time consuming [3].

In Fig. 2 the phase of the tangential component of the deflection vector is represented as a function of the pump-probe distance. The data showed was obtained for the low thermal diffusivity reference sample immersed in ethanol, for different modulation frequencies (a) and pump-beam power (b).

![Fig. 2 Phase of the tangential component (Φ) as a function of the pump-probe offset (d).](image)
a) same pump laser power (14.3 mW) but different frequencies. b) Same frequency (8.1 Hz) but different pump laser power.

Note: phase values on Fig. 2 b) were shifted in order to allow a better visualization. The slope of each curve remains, obviously, the same.

The data were divided into two distinct parts (1 and 2) for which the measurement is considered either far enough from the intersection of the two beams (zone 1) or not (zone 2). For the first group the pump beam can be considered as a punctual heat source (d >> r) available when working with liquids with such low thermal diffusivity, simplifying the analysis.

Table 3 presents the thermal diffusivity values obtained from the data above.

| Ppump beam (mW) | 4.3 | 7.1 | 14.3 |
|----------------|-----|-----|------|
| αexp (x10^-7 m^2 s^-1) | 2.15 | 2.28 | 2.12 | 2.42 | 2.17 | 2.93 |
| αlit (x10^-7 m^2 s^-1) | 2.2 |
| f modulation (Hz) | 8.1 |

| f modulation (Hz) | 3.7 | 8.1 | 13.1 |
|------------------|-----|-----|------|
| Fit | 1 | 2 | 1 | 2 | 1 | 2 |
| αexp (x10^-7 m^2 s^-1) | 1.91 | 2.26 | 2.18 | 2.65 | 1.81 | 2.18 |
| αlit (x10^-7 m^2 s^-1) | 2.2 |
| Ppump beam (mW) | 14.3 |

From table 3a) it is worth pointing out that good results were obtained, even for an incident laser power around 4 mW. The choice for a higher pump beam power was tested in order to clarify the role of that parameter on the stability of the measured signals and on the coherence of the calculated values. The result was that the signal became unstable, much noisier and the values started to deviate from those obtained using a lower pump beam power.

Due to the very small thermal diffusion length (μ) available when working with liquids with such low thermal diffusivity, a special attention should be paid to the modulation frequency once μ ∝ f^{-1/2}. The
choice for very low modulation frequencies decreases the signal to noise ratio, and the measured signal becomes unstable. From table 3b) one can conclude that the best choice for modulation frequency for this particular system is around 8 Hz. Care should be taken and some basic calculations should be performed when dealing with samples with different thermal diffusivity.

4. Conclusions
Experimental results obtained in the four different media, for materials in all ranges of thermal diffusivities, were compared showing that the use of ethanol as surrounding medium is the only one that can be competitive with CCl₄.

The experimental data obtained, when using ethanol as surrounding medium, even for materials with very low values of thermal diffusivity, revealed that very stable signals can be measured using a pump beam power much lower when compared to the power needed when using air, allowing us to conclude that the use of ethanol leads to a very significant increase in the sensitivity of the technique, working as a “signal amplifier”. The numerical values obtained for the thermal diffusivity of the test samples clearly match the known values.

References
[1] Salazar, A. Sánchez-Lavega, Rev. Sci. Instrum. 65 (9), 2896 (1994).
[2] P. Prior, A. Gören, F Macedo, J. A. Ferreira and D. Soares, J. Phys. IV 125, 265 (2005).
[3] A. Gören, Master Thesis, “The influence of experimental parameters in the thermal characterization of solids using the photothermal beam deflection technique”, Universidade do Minho (2007).
[4] Phototherm Dr. Petry GmbH, Altenkesseler Strasse 17, 6600 Saarbrücken, Germany
[5] S. E. Bialkowsky, Photothermal Spectroscopy Methods For Chemical Analysis, John Wiley & Sons, New York (1996), Vol. 134 in Chemical Analysis.
[6] Y. Marcus, “The properties of solvents”, Wiley (1998).