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Novel Transmission Open Photoacoustic Cell Configuration for Thermal Diffusivity Measurements in Liquids

J. A. Balderas-López[1–3] and A. Mandelis[1]

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In this paper the photoacoustic technique in the thermal-wave transmission configuration is applied to thermal diffusivity measurements in liquids. The one-dimensional heat diffusion problem involving three layers, and assuming surface absorption only, is solved for this goal. Linear relations among the photoacoustic amplitude (on a semi-log scale) and phase, as functions of the liquid sample thickness, are shown in each case. An analytical procedure involving linear fits to the experimental data is developed to produce two independent values for thermal diffusivity. The thermal diffusivity of three homogeneous liquids (distilled water, ethylene-glycol, and olive oil) was measured, and excellent agreement was obtained between results from both the amplitude and phase, as well as with thermal-diffusivity values reported in the literature.

KEY WORDS: liquids; open photoacoustic cell; photoacoustic technique; thermal diffusivity.

1. INTRODUCTION

Among the main applications of photothermal (PT) techniques, those directed to the thermal characterization of materials are of substantial industrial and practical relevance [1, 2]. PT techniques involving photopyroelectric (PPE)

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[1] Photothermal and Optoelectronic Diagnostics Laboratories (PODL), Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5R 3G8, Canada.

[2] Permanent address: Unidad Profesional Interdisciplinaria de Biotecnología del IPN, Av. Acueducto S/N, Col. Barrio la Laguna, Del. Gustavo A. Madero, C.P. 07340, México, D.F., México.

[3] To whom correspondence should be addressed. E-mail: abrahambalderas@hotmail.com

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[3–10] and photoacoustic (PA) detection [10–15] have been reported in the literature for thermal diffusivity measurements of condensed matter and gases. This thermal property is important, since its value determines the ability of a material to transport heat under nonstationary conditions. With very few exceptions [15] it appears to be only solids, however, which have had the benefit of PA measurements of thermal diffusivity. This is due to the simplicity of the model on which the general methodology is based, which involves the one-dimensional heat-diffusion problem across one layer. Regarding the thermal diffusivity evaluation in liquids by means of the photoacoustic effect involving the open photoacoustic cell configuration (OPC), i.e., thermal-wave transmission across the sample, an experimental setup involving at least three material layers is required: the light-to-heat converter, the body of the liquid sample, and an extra material layer to seal and, at the same time, prevent the seepage of liquid into the photoacoustic chamber. Accordingly, in this article the one-dimensional model for harmonic heat diffusion across three layers is solved. The analytical solutions are shown to be useful for quantitative thermal diffusivity evaluations in liquids. Conventional PA methodologies for thermal diffusivity measurement purposes in solids rely on the scanning of the PA signal as a function of the laser modulation frequency. On the contrary, the PA methodology reported in this work makes use of the PA signal as a function of the liquid thickness. This technique results in fixed noise bandwidth of the instrumental system, which imparts a high degree of controllability and improvement of the signal-to-noise ratio (SNR), in addition to disposing with the requirement for instrumental transfer-function normalization. This method is very similar to the cavity-scanned PPE methodology recently reported in the literature for similar materials [8, 9] with the additional advantage that there is no limitation to the kind of liquid sample to be used, corrosive, reactive, and other aggressive fluids can be easily accommodated without compromising the integrity of the transducer itself, unlike cavity-scanned PPE detection, in which the liquid sample is in direct contact with the pyroelectric transducer. Linear relationships among the PA amplitude (on a semi-log scale) and phase, as functions of the sample thickness, hold in the thermally thick regime. Taking advantage of these facts, an analytical procedure for treating experimental data is developed, which involves linear fits. This analytical procedure yields two independent values for the thermal diffusivity of the liquid sample (one for the PA amplitude and the other for the PA phase). The thermal diffusivities of three liquids, distilled water, ethylene glycol, and olive oil, were thus measured resulting in excellent agreement with each other and with thermal-diffusivity values reported in the literature.

2. THEORETICAL CONSIDERATIONS

The geometry of the general model, depicted in Fig. 1, consists of three layers surrounded by two semi-infinite, optically nonabsorbing, media. Assuming that modulated light with intensity I_0 and angular modulation frequency $\omega = 2\pi f$ impinges on the upper surface of medium m (Fig. 1), and considering only surface absorption, the corresponding differential equations for the one-dimensional heat-diffusion problem are

$$\begin{aligned}
&\frac{\partial^2 T_w}{\partial x^2} - \frac{1}{\alpha_w}\frac{\partial T_w}{\partial t} = 0 && 0 \leqslant x \\
&\frac{\partial^2 T_m}{\partial x^2} - \frac{1}{\alpha_m}\frac{\partial T_m}{\partial t} = -\frac{\beta I \delta(x)}{2k_m}[1 + e^{i\omega t}] && -l \leqslant x \leqslant 0 \\
&\frac{\partial^2 T_s}{\partial x^2} - \frac{1}{\alpha_s}\frac{\partial T_s}{\partial t} = 0 && -L - l \leqslant x \leqslant -l \qquad (1) \\
&\frac{\partial^2 T_b}{\partial x^2} - \frac{1}{\alpha_b}\frac{\partial T_b}{\partial t} = 0 && -\Delta - L - l < x \leqslant -L - l \\
&\frac{\partial^2 T_g}{\partial x^2} - \frac{1}{\alpha_g}\frac{\partial T_g}{\partial t} = 0 && -\infty < x \leqslant -\Delta - L - l
\end{aligned}$$

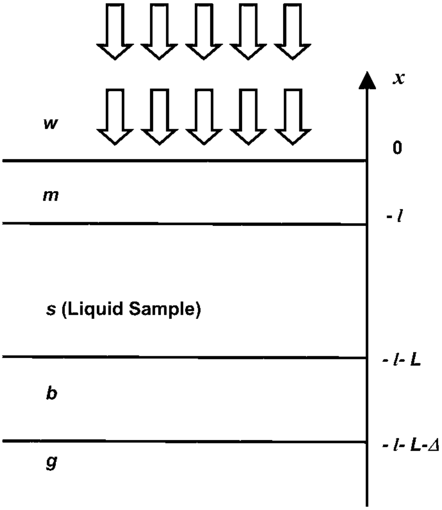

Fig. 1. Schematic representation of the one-dimensional multilayer photoacoustic model with surface absorption. w: glass; m: metal layer with surface absorption coefficient β at $x = 0$; s: liquid sample; b: glass slab; g: gas.

Here T_j and α_j, $j = w, m, s, b, g$, correspond to the oscillating temperature and thermal diffusivity of medium j, respectively. β is the surface absorption coefficient for the surface-absorbing medium m, and k_m is the corresponding thermal conductivity. Solving this system with the proper boundary conditions of heat flux and temperature continuity at all interfaces, and the physical requirement of finite solutions on $x \to \pm\infty$, the resulting nonstationary temperature fluctuation in medium g is

$$T_g(x, t) = \frac{\beta I d}{4 k_g \sigma_g} \frac{(1+\gamma_{wm})(1-\gamma_{ms})(1-\gamma_{sb})(1-\gamma_{bg})}{D} \times e^{-\sigma_m l} e^{-\sigma_s L} e^{-\sigma_b \Delta} e^{\sigma_g (x+l+L+\Delta)} e^{i\omega t} \tag{2}$$

where

$$\begin{aligned} D = {} & 1 + \gamma_{wm}\gamma_{ms} e^{-2\sigma_m l} + \gamma_{ms}\gamma_{sb} e^{-2\sigma_s L} + \gamma_{sb}\gamma_{bg} e^{-2\sigma_b \Delta} + \gamma_{wm}\gamma_{sb} e^{-2\sigma_m l} e^{-2\sigma_s L} \\ & + \gamma_{ms}\gamma_{bg} e^{-2\sigma_s L} e^{-2\sigma_b \Delta} + \gamma_{wm}\gamma_{ms}\gamma_{sb}\gamma_{bg} e^{-2\sigma_m l} e^{-2\sigma_b \Delta} + \gamma_{wm}\gamma_{bg} e^{-2\sigma_m l} e^{-2\sigma_s L} e^{-2\sigma_b \Delta} \end{aligned} \tag{3}$$

In these equations d is the thickness of the infinitesimal opaque layer in the material m where optical absorption takes place; $\sigma_j = (1+i)\, a_j$, $j = m, s, b$, where $a_j = (\pi f / \alpha_j)^{1/2}$ is the thermal diffusion coefficient; γ_{jk} are thermal coupling coefficients (the so-called thermal-wave reflection coefficients) defined as $\gamma_{jk} = (1 - e_j/e_k)/(1 + e_j/e_k)$, where e_l is the thermal effusivity of medium l. For the PA technique in the transmission configuration the medium g corresponds to the air inside the PA chamber. By using the Rosencwaig–Gersho [16] model, the corresponding pressure fluctuations can be shown to be

$$\delta P = \frac{\gamma P_0 \beta I d}{4\sqrt{2}\, l_g a_g T_0 k_m \sigma_m} \frac{(1+\gamma_{wm})(1-\gamma_{ms})(1-\gamma_{sb})(1-\gamma_{bg})}{D} e^{-\sigma_m l} e^{-\sigma_s L} e^{-\sigma_b \Delta} e^{i\omega t} \tag{4}$$

where T_0 and P_0 are, respectively, the ambient temperature and pressure. $\gamma = c_p / c_v$ is the ratio of the specific heats in air. Finally l_g is the thickness of medium g, which was assumed infinite in the analysis for simplicity. In terms of photothermal theory this is equivalent to assuming that this medium is thermally thick [16].

Under the assumption that sample s is thermally thick, we may write $|\sigma_s L| \gg 1$. As a consequence, $\exp(-\sigma_s L) = 0$ and the expression for D in Eq. (3) simplifies to

$$D = 1 + \gamma_{wm}\gamma_{ms} e^{-2\sigma_m l} + \gamma_{sb}\gamma_{bg} e^{-2\sigma_b \Delta} + \gamma_{wm}\gamma_{ms}\gamma_{sb}\gamma_{bg} e^{-2\sigma_m l} e^{-2\sigma_b \Delta} \tag{5}$$

It is clear that, by considering the liquid sample thickness L as the only variable, it is possible to write Eq. (4), in this thermally thick regime, in the very simple form

$$\delta P(L) = C \exp(-\sigma_s L) \tag{6}$$

where C is a constant containing thermal properties and geometrical parameters but, most importantly, C is independent of L. The logarithm of the amplitude, ln R, and phase, Φ, corresponding to this equation are linear functions of L and are given by

$$\ln R = \ln |C| - BL \tag{7}$$

$$\Phi = \Phi_0 - BL \tag{8}$$

Here the constant B is defined as $B = (\pi f / \alpha_s)^{1/2}$. Equations (7) and (8) provide two independent signal channels for thermal-diffusivity measurement purposes. The experimental procedure involves the scanning of the PA signal amplitude and phase as a function of the liquid sample thickness and the subsequent experimental data fits to a linear model (on a semilog scale for the amplitude). This procedure yields two independent values for the thermal diffusivity of the liquid by means of the fitted parameter B.

3. EXPERIMENTAL

The experimental PA setup is shown in Fig. 2. It consisted of an infrared (830 nm) semiconductor diode laser with a fiberoptic pigtail (Opto Power Corporation), delivering 60 mW of cw power. The intensity-modulated laser light was incident through a glass slab (120-μm thick), on a piece of aluminum foil (20-μm thick) attached to the glass slab with a small amount of silver paint. This set was mounted on a micrometer stage allowing the liquid sample thickness L to vary with 10-mm step resolution. Thermal waves, generated in the aluminum foil, traveling across the liquid sample and transmitted to another glass slab (120-μm thick) reached the PA chamber. This PA chamber consisted of a cylindrical cavity (3 mm diameter and 3 mm height), made of a brass body and communicating with an electret microphone and its built-in preamplifier through a hollow channel (Fig. 2). The PA signal due to the front-surface-generated thermal wave transmitted through the sample and the bottom glass slab was obtained as a function of the liquid sample thickness at the fixed modulation frequency of 2 Hz (at this modulation frequency the thermal diffusion

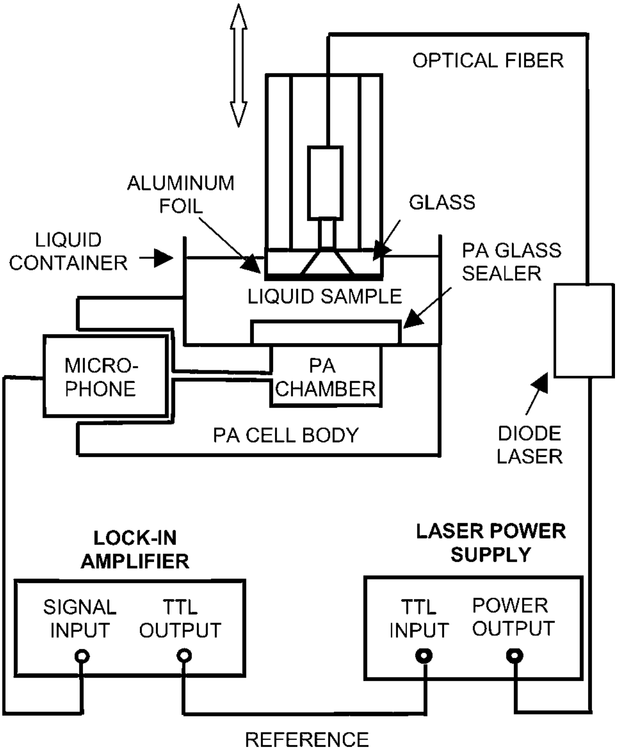

Fig. 2. Schematic cross section of the new transmission-mode open PA cell configuration experimental setup used for thermal diffusivity measurements of liquids.

length for the glass is about 200 μm [17], for which the glass slab was thermally thin). In terms of Fig. 1 the glass is represented by layer *b*. The signal was then fed to a lock-in amplifier (LIA) (Stanford Research Model SR830) for further amplification and demodulation. The laser intensity was modulated using the internal oscillator of the LIA to drive the laser power supply via a TTL communications port. Three liquid samples were used: distilled water, ethylene glycol, and extra virgin olive oil. In each case the sample container was filled with approximately 5 cm^3 of liquid sample. Five thickness scans were performed for each liquid sample. They consisted of varying the sample thickness from an initial value L_0 (approximately 300 μm) to $L_f = L_0 + 400$ μm in steps of 10 μm. All the measurements were made at room temperature (23°C) as measured by a thermocouple immersed in the liquid.

4. RESULTS AND DISCUSSION

Figure 3a shows typical PA signal amplitudes (on a semilog scale) as a function of the liquid layer thickness for two of the liquid samples used in this work. The linear relationship predicted by Eq. (7) is evident in each case. The continuous lines on the same graph are the best fits to this equation. The resulting thermal diffusivity values for all samples are summarized in Table I (column 2). Figure 3b shows the PA phases corresponding to the two amplitudes of Fig. 3a. The linear relationship predicted by Eq. (8) is, again, evident. The continuous lines on the same graph are the best fits to this equation. The phase-derived thermal diffusivity values are summarized in Table I (column 3). The thermal diffusivities reported in this table are averages over five measurements.

The simplicity and robustness of the present PA methodology lies in its ability to extract absolute thermophysical values from relative measurements, due to the simple PA phase dependence on the sample thickness, thus eliminating the need to know the absolute sample thickness, or

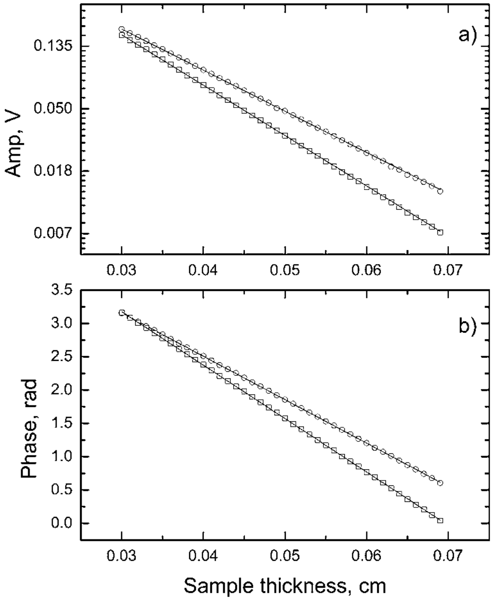

Fig. 3. Typical results of PA (a) signal amplitudes and (b) phases for the liquid samples used in this work. Circles (squares) correspond to distilled water (ethylene glycol). Continuous lines correspond to best fits to Eqs. (7) (amplitude) and (8) (phase).

Table I. Thermal Diffusivities for the Liquid Samples Used in This Work, Measured by Means of the Transmission Open Cell PA Configuration. (α_A refers to the thermal diffusivity values obtained from the PA amplitude. α_P refers to the corresponding values obtained from the PA phase. Thermal diffusivity values reported in the literature are also presented (α_{Ref}))

Liquid sample	α_A (10^{-2} cm^2 s^{-1})	α_P (10^{-2} cm^2 s^{-1})	α_{Ref} (10^{-2} cm^2 s^{-1})
Distilled water	0.1441 ± 0.0004	0.1464 ± 0.0003	0.1456 (Ref. 8)
Ethylene glycol	0.0954 ± 0.0005	0.0977 ± 0.0003	0.0939 (Ref. 8)
Virgin olive oil	0.0885 ± 0.0003	0.0899 ± 0.0004	0.0881 (Ref. 8)

to take into account difficult-to-quantify instrumental phase shifts. Additional advantages of the present PA methodology arise when it is compared to other similar photothermal techniques reported in the literature. The PA technique for thermal diffusivity measurements in liquids described in Ref. 15 involves the mechanical piston model proposed by McDonald and Wetzel [18] and makes use of a transverse light absorption configuration, which requires the use of liquid samples with weak optical absorption. This is not a requirement, however, of the present PA technique. With respect to the PPE methodology [8], it has already been mentioned that the PA technique allows similar-degree-of-precision thermal diffusivity measurements for all types of liquids, including reactive and corrosive fluids, which may potentially cause damage to the pyroelectric sensor.

Equation (6) exhibits the well-known exponential damping of the PA signal amplitude as a function of modulation frequency, a characteristic of the transmission configuration [19]. As the thermal-wave-generated transmission PA signal becomes weaker with increasing frequency, complicating thermoelastic signal contributions may appear [9]. This effect suggests the use of modulation frequencies as low as possible so that the sample will be well within the thermally thick range and, at the same time, there will be adequate signal strength to provide a satisfactory signal-to-noise ratio for the measurement. Obviously, there are limitations in using very low frequencies, such as sensor sensitivity, three-dimensional effects due to lateral conduction heat transfer pathways, $1/f$ noise, and longer LIA time constants. For a modulation frequency of 2 Hz, and a 1-s LIA time constant, these compromises were widely fulfilled, as is evident from Figs. 3a and 3b.

5. CONCLUSIONS

In conclusion, a new PA technique making use of the OPC configuration for high precision and accuracy thermal-diffusivity measurements in liquids has been presented. Precise and accurate measurements can be effected through a signal-generation procedure, which involves relative linear theoretical fits to PA amplitude and phase data, thus yielding two independent and self-consistent values for the thermal diffusivity of liquids without the requirement of accurate knowledge of instrumental or reference sample parameters. In principle, there is no limitation on the kind of liquid samples to be used for thermal characterization by means of the presented experimental transmission photoacoustic setup, independently of their thermal and optical properties. Moreover, since in the new open cell PA experimental setup there is no direct contact between the sample and the sensor (the microphone), as is the case with the various PPE setups reported in the literature [8], hostile fluids which could potentially interact with, or damage, the photothermal sensor can be used safely with essentially a similar degree of signal precision. This new photoacoustic methodology for thermal diffusivity measurements may become highly useful for carrying out photoacoustic thermal characterization of liquids in conjunction with other reported PA techniques, particularly those reported for measuring thermal effusivity [14].

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