Thermal diffusivity measurements in liquids using signal common-mode-rejection demodulation in a thermal-wave cavity

J. A. Balderas-López[a] and Andreas Mandelis
Photothermal and Optoelectronic Diagnostic Laboratories (PODL), Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, Canada M5R 3G8

A recently developed signal common-mode rejection demodulation signal methodology [Mandelis *et al.*, Rev. Sci. Instrum. **71**, 2440 (2000)] has been used to make direct absolute thermal diffusivity measurements in liquids using a thermal-wave cavity. This methodology combines the precision of the thermal-wave cavity scan and the flexibility of modulation-frequency scan modes, along with baseline suppression, yielding a high-resolution technique for thermal diffusivity measurements in liquids. The thermal diffusivity of two pure liquids (distilled water and ethylene glycol) has been measured and good agreement has been obtained with values reported in the literature. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1402136]

I. INTRODUCTION

The thermophysical characterization of liquids plays an important role in the control and improvement of physico-chemical processes, notably in heat exchangers and in their use as refrigerants and lubricants. Therefore the design of experimental methodologies to measure thermophysical properties of liquids becomes very relevant. Driven by these requirements, a wide variety of photothermal techniques has been developed for thermal characterization of liquids.[1–6] Ever since the introduction of the thermal-wave resonator cavity (TWRC),[7] this experimentally simple photothermal technique and its various modifications and variants are becoming increasingly popular for high precision thermal diffusivity measurements in fluids (gases and liquids).[4–10]

In this article the application of a recently developed general signal generation and modulation scheme[11,12] to the measurement of the thermal diffusivities of two liquids using a TWRC is reported. When combined with lock-in amplifier (LIA) detection and signal demodulation, this scheme, named common-mode rejection demodulation (CMRD), exhibits a major advantage over conventional sinusoidal and square-wave modulation methodologies due to its ability to suppress signal baselines generated by synchronous background modulation. This improves the dynamic range of the detection instrumentation substantially, thus increasing the overall measurement resolution. In the present work the major advantage of the CMRD method over other photothermal techniques was found to be its ability to perform absolute thermal-diffusivity measurements without the requirement of knowing the phase constant of the instrumental transfer function at any frequency and without the need for continuous mechanical scanning of the sample cavity length. Some analytical equations involving the thermal diffusivity of the fluid medium in terms of the two pulse widths of the bimodal wave form for a fixed thermal-wave cavity length are ob-

tained. These formulas are further used for measuring the thermal diffusivity of pure distilled water and ethylene glycol.

II. THEORY

The two-pulse configuration of the CMRD scheme is shown in Fig. 1. It has been shown[11,12] that the in-phase (Y_{ip}) and quadrature (Y_q) demodulated lock-in outputs from any experimental system driven by such a bimodal periodic pulse excitation with period T are given by

$$Y_{ip} = \text{Re}[Y(f)] = -\frac{2I_0}{\pi}\left\{\cos\left(\frac{\pi\Delta}{T}\right)\left[\sin\left(\frac{\pi\tau_1}{T}\right)\right.\right.$$
$$\left.+ \sin\left(\frac{\pi\tau_2}{T}\right)\right]\text{Re}[S(f)] + \sin\left(\frac{\pi\Delta}{T}\right)\left[\sin\left(\frac{\pi\tau_1}{T}\right)\right.$$
$$\left.\left.- \sin\left(\frac{\pi\tau_2}{T}\right)\right]\text{Im}[S(f)]\right\}, \tag{1a}$$

$$Y_q = \text{Im}[Y(f)] = +\frac{2I_0}{\pi}\left\{\sin\left(\frac{\pi\Delta}{T}\right)\left[\sin\left(\frac{\pi\tau_1}{T}\right)\right.\right.$$
$$\left.- \sin\left(\frac{\pi\tau_2}{T}\right)\right]\text{Re}[S(f)] - \cos\left(\frac{\pi\Delta}{T}\right)\left[\sin\left(\frac{\pi\tau_1}{T}\right)\right.$$
$$\left.\left.+ \sin\left(\frac{\pi\tau_2}{T}\right)\right]\text{Im}[S(f)]\right\}, \tag{1b}$$

where $f = 1/T$ is the CMRD wave-form repetition frequency, τ_1 and τ_2 are the two pulse widths, and $S(f)$ is the corresponding signal response of the experimental system to a single pulse excitation at the same frequency. When the CMRD method is applied to a TWRC system, such as the one shown in Fig. 2, it is easy to show that the analytical form of the real and imaginary parts of $S(f)$, when the sample m (the liquid filling the intracavity space) is in the thermally thick regime, can be written as[4,5]

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[a]Electronic mail: abraham@mie.utoronto.ca
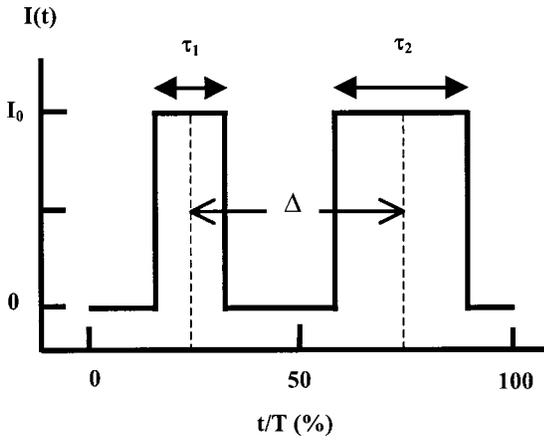
FIG. 1. Optical excitation wave form consisting of a bimodal pulse applied to a thermal wave resonator cavity (TWRC). The horizontal time units are expressed as a percentage of a full repetition period T, τ_1 and τ_2 are the corresponding square pulse widths, and Δ is the center-to-center time delay. Only one repetition period is presented for clarity.

$$\operatorname{Re}[S(f)] = \frac{C(f)}{f} \exp\left(-\sqrt{\frac{\pi f}{\alpha_m}} L\right) \sin\left(\Theta(f) + \sqrt{\frac{\pi f}{\alpha_m}} L\right),$$
(2a)

$$\operatorname{Im}[S(f)] = \frac{C(f)}{f} \exp\left(-\sqrt{\frac{\pi f}{\alpha_m}} L\right) \cos\left(\Theta(f) + \sqrt{\frac{\pi f}{\alpha_m}} L\right),$$
(2b)

where $C(f)$ is a complex constant involving instrumental factors and thermal coupling coefficients at the liquid boundaries, and $\Theta(f)$ is an instrumental phase shift largely due to system electronics [i.e., both $C(f)$ and $\Theta(f)$ involve components of the instrumental transfer function. These factors
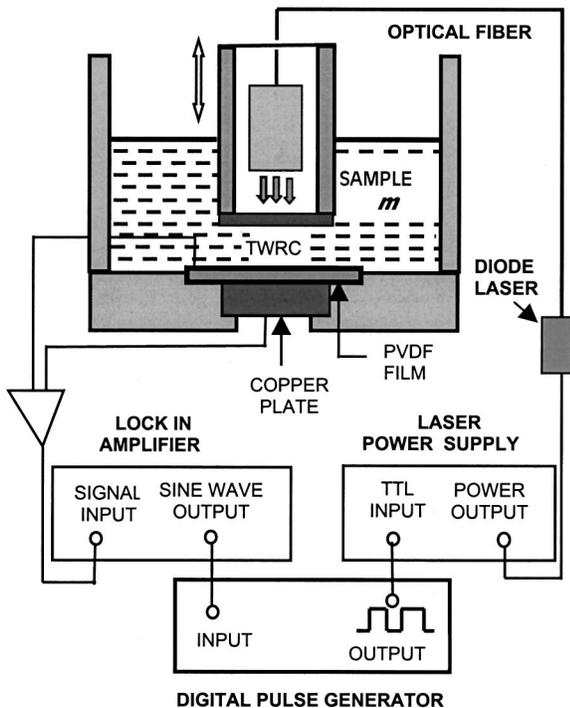
FIG. 2. Cross section of the experimental TWRC setup used in this work.

are, however, constant at fixed frequency]. Furthermore, L is the thickness of the intracavity layer and α_m is its thermal diffusivity.

Based on these equations, it is possible to develop two formulas (one for the in-phase and another one for the quadrature) for the evaluation of α_m for sample m. In these formulas only the general characteristics of the bimodal pulse and the cavity length L are involved.

In a bimodal pulse excitation at fixed repetition frequency $f = 1/T$ and pulse widths τ_1 and τ_2, with the center-to-center time delay Δ as the only variable, Fig. 1, it is evident that Eqs. (1a) and (1b) can be simplified in the form

$$Y_{ip}(\Delta) = P_1(f,\tau_1,\tau_2)\cos\left(\frac{\pi\Delta}{T}\right) + P_2(f,\tau_1,\tau_2)\sin\left(\frac{\pi\Delta}{T}\right),$$
(3a)

$$Y_q(\Delta) = P_3(f,\tau_1,\tau_2)\cos\left(\frac{\pi\Delta}{T}\right) - P_4(f,\tau_1,\tau_2)\sin\left(\frac{\pi\Delta}{T}\right),$$
(3b)

where coefficients $P_1(f,\tau_1,\tau_2)$ and $P_2(f,\tau_1,\tau_2)$, associated with the LIA in-phase signal, and coefficients $P_3(f,\tau_1,\tau_2)$ and $P_4(f,\tau_1,\tau_2)$, associated with the LIA quadrature signal, are given by

$$P_1(f,\tau_1,\tau_2) = -\frac{2I_0}{\pi}\left[\sin\left(\frac{\pi\tau_1}{T}\right) + \sin\left(\frac{\pi\tau_2}{T}\right)\right]\operatorname{Re}[S(f)],$$
(4a)

$$P_2(f,\tau_1,\tau_2) = -\frac{2I_0}{\pi}\left[\sin\left(\frac{\pi\tau_1}{T}\right) - \sin\left(\frac{\pi\tau_2}{T}\right)\right]\operatorname{Im}[S(f)],$$
(4b)

$$P_3(f,\tau_1,\tau_2) = -\frac{2I_0}{\pi}\left[\sin\left(\frac{\pi\tau_1}{T}\right) + \sin\left(\frac{\pi\tau_2}{T}\right)\right]\operatorname{Im}[S(f)],$$
(4c)

$$P_4(f,\tau_1,\tau_2) = -\frac{2I_0}{\pi}\left[\sin\left(\frac{\pi\tau_1}{T}\right) - \sin\left(\frac{\pi\tau_2}{T}\right)\right]\operatorname{Re}[S(f)].$$
(4d)

Upon taking the ratio $P_1(f,\tau_1,\tau_2)/P_2(f,\tau_1,\tau_2)$ and $P_3(f,\tau_1,\tau_2)/P_4(f,\tau_1,\tau_2)$ and taking into account the analytical expressions for $\operatorname{Re}[S(f)]$ and $\operatorname{Im}[S(f)]$, given in Eqs. (2a) and (2b), the following expressions can be obtained

$$\sqrt{\frac{\pi f}{\alpha_m}} L = \tan^{-1}\left(\frac{P_1}{P_2}\frac{R}{Q}\right) - \Theta(f),$$
(5a)

$$\sqrt{\frac{\pi f}{\alpha_m}} L = \tan^{-1}\left(\frac{P_4}{P_3}\frac{Q}{R}\right) - \Theta(f),$$
(5b)

where Q and R are constants defined by

$$Q = \sin\left(\frac{\pi\tau_1}{T}\right) + \sin\left(\frac{\pi\tau_2}{T}\right),$$
(6a)

$$R = \sin\left(\frac{\pi\tau_1}{T}\right) - \sin\left(\frac{\pi\tau_2}{T}\right).$$
(6b)

In principle, it is possible to evaluate the thermal diffusivity, α_m from Eqs. (5a) and (5b), if the values of the corresponding parameters are known. In practice, however, this is a

difficult task because the absolute sample thickness L and, moreover, the instrumental phase constant $\Theta(f)$ are involved. However, it is possible to extend Eqs. (5a) and (5b) in order to derive a relative expression for determining absolute values of thermal diffusivity using measurements at two cavity lengths. Under these conditions the offsetting influence of the transfer-function phase constant $\Theta(f)$ is also eliminated. Considering Eqs. (5a) and (5b) for the same bimodal pulse excitation, and for two different intracavity lengths (sample thicknesses) L_1 and L_2, we obtain the following results

$$\alpha_m = \frac{\pi f (L_2 - L_1)^2}{\left[\tan^{-1}\left(\frac{^2P_1}{^2P_2} \frac{R}{Q} \right) - \tan^{-1}\left(\frac{^1P_1}{^1P_2} \frac{R}{Q} \right) \right]^2}, \quad (7a)$$

$$\alpha_m = \frac{\pi f (L_2 - L_1)^2}{\left[\tan^{-1}\left(\frac{^2P_4}{^2P_3} \frac{Q}{R} \right) - \tan^{-1}\left(\frac{^1P_4}{^1P_3} \frac{Q}{R} \right) \right]^2}, \quad (7b)$$

where the back superscript i (=1, 2) refers to the in-phase parameters $P_1(f, \tau_1, \tau_2)$ and $P_2(f, \tau_1, \tau_2)$, and quadrature parameters $P_3(f, \tau_1, \tau_2)$ and $P_4(f, \tau_1, \tau_2)$ when the sample has thickness L_i.

Based on Eqs. (7a) and (7b) it is possible to develop an experimental procedure to carry out absolute measurements of the thermal diffusivity for a given liquid medium in the intracavity space of a TWRC instrument. As a first phase, this experimental procedure involves the scanning of the LIA in-phase and quadrature outputs for a given repetition frequency, f, as functions of the center-to-center time delay of the bimodal pulse widths (pulse separation) Δ (Fig. 1), for two cavity lengths with known difference $L_2 - L_1$. Following this procedure the fits of the in-phase and quadrature data to equations of the form (3a) and (3b) are required. In this manner the P_i parameters, needed for the evaluation of Eqs. (7a) and (7b), are obtained for each cavity length L_i. The remaining constants Q and R are determined from Eqs. (6a) and (6b) once the characteristics of the bimodal pulse distribution are chosen, i.e., when the pulse widths τ_1 and τ_2 are defined as fractions of the complete period T.

III. EXPERIMENT AND DISCUSSION

The experimental setup, shown in Fig. 2, consisted of an IR (830 nm) semiconductor laser (Opto Power Corporation), operating at 60 mW. The intensity-modulated laser light was driven by the bimodal square-wave signal generated by a four-channel digital signal pulse generator (Stanford Research Systems, model DG535). The bimodal optical power was incident on an aluminum foil (17 μm thick and 1 cm in diameter) attached to a glass support with a thin layer of highly conducting silver paint. Bimodal thermal waves generated in this metal foil largely retained the temporal shape of the incident optical wave form due to the considerable thermal thinness of the aluminum foil.[7] The thermal waves traveled (diffused) across the intracavity region, which was filled with the liquid under investigation, and were detected in transmission by a polyvinylidene fluoride (PVDF) pyro-electric thin-film sensor (Fig. 2). The aluminum foil was

TABLE I. Thermal diffusivity values for distilled water obtained by means of the CMRD method using a TWRC. Two combinations of wave-form repetition frequencies and pulse widths were used. α_{ip} refers to thermal diffusivity evaluated by the use of Eq. (7a). α_q refers to thermal diffusivity evaluated by the use of Eq. (7b). $\Delta L = 50$ μm throughout.

f (Hz)	Time square-pulse widths		α_{ip} ($\times 10^{-2}$) cm^2/s	α_q ($\times 10^{-2}$) cm^2/s
	τ_1	τ_2		
2	5	25	0.150	0.156
4	5	25	0.151	0.151
2	10	20	0.142	0.144
4	10	20	0.145	0.146

mounted on a micrometer stage to allow changing its relative distance from the PVDF surface with 10-μm resolution.[4,5] The in-phase and quadrature LIA signals (Stanford Research Systems, model SR 830) were obtained as a function of the temporal separation between the centers of the bimodal pulse wave form (Fig. 1). They were preamplified with a low-noise Ithaco preamplifier (Model 2001), and then stored for further analysis. Two pure liquids (distilled water and ethylene glycol) were used. All measurements were made at a temperature of 24 °C as determined by a thermocouple immersed in the liquid. This temperature varied at most within a few tenths of 1° during the experimental runs.

The experimental methodology consisted of applying a center-to-center separation, Δ, scan between two pulses with fixed pulse widths τ_1 and τ_2 (Fig. 1). Two different cavity lengths (sample thicknesses) were used with fixed $L_2 - L_1 \equiv \Delta L = 50$ μm. To test the reliability of this methodology, two combinations of bimodal thermal-wave source pulse widths and two repetition frequencies were applied (Tables I and II). Typical results from this procedure are shown for distilled water in Figs. 3(a) and 3(b) for a repetition frequency of 2 Hz and pulse widths of $\tau_1 = 5\%$ and $\tau_2 = 25\%$ (expressed as a percentage of the repetition period T). Similar experimental results are shown in Figs. 4(a) and 4(b) for the case of the ethylene glycol sample, with the same frequency and sample thicknesses, but with different pulse widths ($\tau_1 = 10\%$ and $\tau_2 = 20\%$). In each case continuous lines correspond to the best fit to Eqs. (3a) or (3b), as the case may be. The corresponding fitted parameters for each case were used to evaluate the thermal diffusivity from Eq. (7a) for the in-phase channel and from Eq. (7b) for the

TABLE II. Thermal diffusivity values for ethylene glycol obtained by means of the CMRD method using a TWRC. Two combinations of wave-form repetition frequencies and pulse widths were used. α_{ip} refers to thermal diffusivity evaluated by the use of Eq. (7a). α_q refers to thermal diffusivity evaluated by the use of Eq. (7b). $\Delta L = 50$ μm throughout.

f (Hz)	Time square-pulse widths		α_{ip} ($\times 10^{-2}$) cm^2/s	α_q ($\times 10^{-2}$) cm^2/s
	τ_1	τ_2		
2	5	25	0.090	0.099
4	5	25	0.097	0.098
2	10	20	0.099	0.095
4	10	20	0.096	0.097
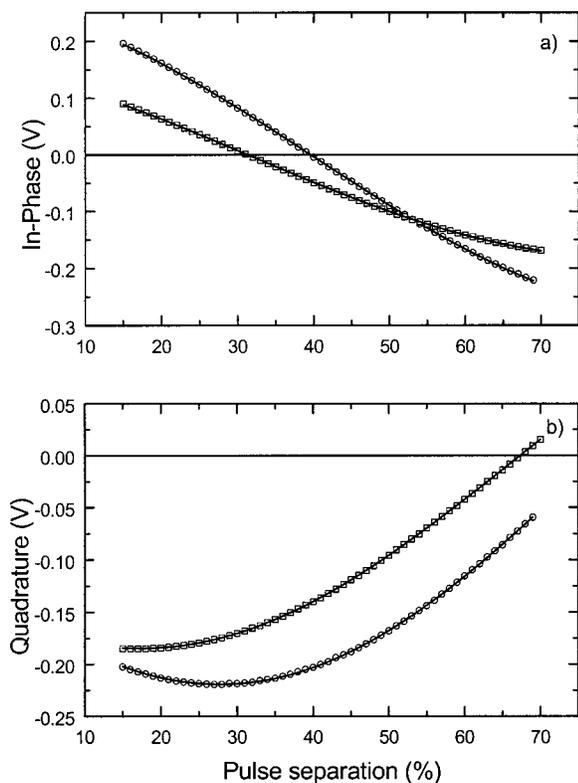
FIG. 3. Bimodal pulse center-to-center separation time scans of photothermal signals from distilled water at two different cavity lengths (50 μm relative cavity length difference). The initial cavity length was about 300 μm. A wave-form repetition frequency of 2 Hz and pulse widths of τ_1 =5% and τ_2=25% (as a percentage of a period T) were used. (a) LIA in-phase components: Circles ($\bigcirc$) correspond to the smaller cavity length (thinner liquid sample) and squares ($\square$) correspond to the thicker sample. (b) Quadrature components: Circles ($\bigcirc$) correspond to the thinner sample and squares ($\square$) correspond to the thicker sample.

FIG. 4. Bimodal pulse center-to-center separation time scans of photothermal signals from ethylene glycol at two different cavity lengths (50 μm relative cavity length difference). The initial cavity length was about 300 μm. A wave-form repetition frequency of 2 Hz and pulse widths of τ_1 =10% and τ_2=20% (as a percentage of a period T) were used. (a) LIA in-phase components: Circles ($\bigcirc$) correspond to the smaller cavity length (thinner liquid sample) and squares ($\square$) correspond to the thicker sample. (b) Quadrature components: Circles ($\bigcirc$) correspond to the thinner sample and squares ($\square$) correspond to the thicker sample.

quadrature channel. The results for the various combinations of frequency and pulse widths are summarized in columns 3 and 4 of Tables I and II.

For the case of distilled water the average thermal diffusivity values obtained from the in-phase and quadrature measurements are $\alpha_{ip}=(0.147\pm0.005)\times10^{-2}$ cm^2/s and α_q $=(0.149\pm0.005)\times10^{-2}$ cm^2/s, respectively. The corresponding values for ethylene glycol are $\alpha_{ip}=(0.096 \pm0.004)\times10^{-2}$ cm^2/s and $\alpha_q=(0.097\pm0.002)$ $\times10^{-2}$ cm^2/s. The in-phase and quadrature values are internally self-consistent and also compare very well with values reported in the literature for the same liquids.[13,14] These are $\alpha_{rep}=1.456\times10^{-3}$ cm^2/s for distilled water, and $\alpha_{rep}=9.39$ $\times10^{-4}$ cm^2/s for ethylene glycol.

From these measurements it can be seen that the CMRD signal generation methodology can be adapted to photothermal measurements using a TWRC and it yields absolute quantitative measurements of thermal diffusivity in liquids. The methodology is experimentally simple, involving only relative cavity lengths with no need for calibration on account of the instrumental transfer function considerations. In this sense, the CMRD methodology is similar to other photothermal techniques which involve the TWRC.[6,7] This technique, however, presents more flexibility because different

combinations of pulse widths and wave-form repetition frequencies are possible.

Using Eqs. (5a) and (5b) it is possible to measure fluid thermal diffusivities with fixed frequency and cavity length, provided a proper calibration measurement has been made with a reference liquid (such as distilled water) to account for the instrumental phase shift, $\Theta(f)$. This aspect of the CMRD method may be very useful in the design of photothermal sensors for absolute thermophysical measurements when the requirement for nonmobile parts is a limitation. Under this experimental limitation it is possible to take advantage of the baseline suppression characteristic of the CMRD method (zero-signal crossings in Figs. 3 and 4) to make a qualitative differentiation between different liquid substances. This can be done by monitoring the pulse separation at which the in-phase and/or the quadrature takes on the 0 value (the crossing point in Figs. 3 and 4). This depends strongly on the thermal properties of the liquid sample. In this manner it is possible to distinguish between two liquids with very similar thermal diffusivities. This fact can be especially useful in environmental science applications, specifically in the *in situ* evaluation, of the degree of contamination of a liquid sample by pollutants.

IV. CONCLUSIONS

Two formulas to carry out absolute thermal diffusivity measurements in liquids by means of thermal waves have been derived. The CMRD experimental methodology, to which these formulas pertain, combines the precision of the thermal-wave-cavity scans and the flexibility of modulation frequency scans, with the additional advantage of making absolute thermal diffusivity measurements in liquids. This CMRD methodology can be adapted for thermal diffusivity measurements when the requirement for nonmoving mechanical parts of the sensor is a limitation. Furthermore, it requires no signal normalization and features optimal measurement dynamic range based on complete baseline suppression. This ability renders thermal-wave CMRD into a very promising nonselective monitoring technique for high-resolution environmental liquid pollutant control.

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