Simple, accurate, and precise measurements of thermal diffusivity in liquids using a thermal-wave cavity

J. A. Balderas-López[a] and A. Mandelis[b]

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

A simple methodology for the direct measurement of the thermal wavelength using a thermal-wave cavity, and its application to the evaluation of the thermal diffusivity of liquids is described. The simplicity and robustness of this technique lie in its *relative* measurement features for both the thermal-wave phase and cavity length, thus eliminating the need for taking into account difficult-to-quantify and time-consuming instrumental phase shifts. Two liquid samples were used: distilled water and ethylene glycol. Excellent agreement was found with reported results in the literature. The *accuracy* of the thermal diffusivity measurements using the new methodology originates in the use of only difference measurements in the thermal-wave phase and cavity length. Measurement *precision* is directly related to the corresponding precision on the measurement of the thermal wavelength. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1372677]

I. INTRODUCTION

The development of the thermal-wave cavity (TWC) and its applications for measurements of thermophysical properties for gases and liquids[1–5] appears to be a significant instrumental advance in the field of photothermal techniques (PTs). The common principle of these techniques consists in measuring the temperature fluctuations in a sample as a result of nonradiative deexcitation processes, which take place following the absorption of intensity-modulated radiation. Unlike conventional PT techniques, which use variable modulation frequencies,[6–10] the TWC methodology allows the possibility of monitoring the spatial behavior of the thermal wave generated at a single modulation frequency with distinct noise-reduction advantages over multifrequency scans, due to the constant narrow detection bandwidth. In addition, the requirement of signal normalization by the instrumental transfer function is avoided. The final result is a measurable improvement in signal stability and signal-to-noise ratio.[2]

Various schemes for thermal diffusivity evaluation via the TWC theory are in use. Some of these schemes involve the fitting of the experimental cavity-scan data set as a function of cavity length.[3,5] Other TWC methods involve *indirect* evaluation of the thermal wavelength by (TW) measuring the cavity lengths at which the thermal wave has extrema.[2,4] In this article the feasibility of *directly* measuring the thermal wavelength is examined. The new methodology involves the direct determination of the relative cavity lengths where the thermal wave has its first two extrema. For this purpose, the thermal-wave phase in the TWC is used. Owing to the simple requirement of measuring only two points, the advan-

tages of this methodology in terms of measurement time and precision are evident. The precision of the technique is directly related to the precision with which the relevant cavity lengths can be measured. The methodology was applied to the measurement of the thermal diffusivity for two pure liquids: distilled water and ethylene glycol. The agreement with reported results was excellent, with the additional advantage of improved measurement precision.

II. THEORY

It has been shown that the pyroelectric signal $V(L, \alpha_l, \omega)$ in the TWC, Fig. 1, is given by the expression[1,2,5]

$$V(L, \alpha_l, \omega) = \text{Const}(\omega) \times \frac{e^{-\sigma_l L}}{1 - \gamma_{ls} \gamma_{lp} e^{-2\sigma_l L}}, \qquad (1)$$

where $\omega = 2\pi f$ is the angular modulation frequency, L is the cavity length, and σ_l is the complex thermal diffusion coefficient, defined by

$$\sigma_l = (1 + i) \sqrt{\omega / 2\alpha_l}. \qquad (2)$$

Here, α_l is the thermal diffusivity of the liquid sample. The interfacial thermal coefficients γ_{jk} are defined as

$$\gamma_{jk} = \frac{(1 - b_{jk})}{(1 + b_{jk})}, \qquad (3)$$

where $b_{jk} = e_j / e_k$ is a thermal coupling coefficient, the ratio of thermal effusivities of media j and k; the subscripts *s, p*, and *l* refer to the thermal-wave source (a plane metallic light absorber, such as a copper or aluminum strip; see Fig. 1), the pyroelectric material, and the liquid sample, respectively.

Considering that for typical cavity lengths in liquid media $|\exp(-2\sigma_l L)| \ll 1$ (a limiting condition easily obtained for liquids),[5] Eq. (1) can be written more simply as

$$V(L, \alpha_l, \omega) = \text{Const}(\omega) \times \exp(-\sigma_l L). \qquad (4)$$

[a]On leave from Centro de Investigación en Ciencia Aplicada y Tecnologia Avanzada del IPN, Av. Legaria 694, Col. Irrigación, C.P. 11500, México, D. F., Mexico.
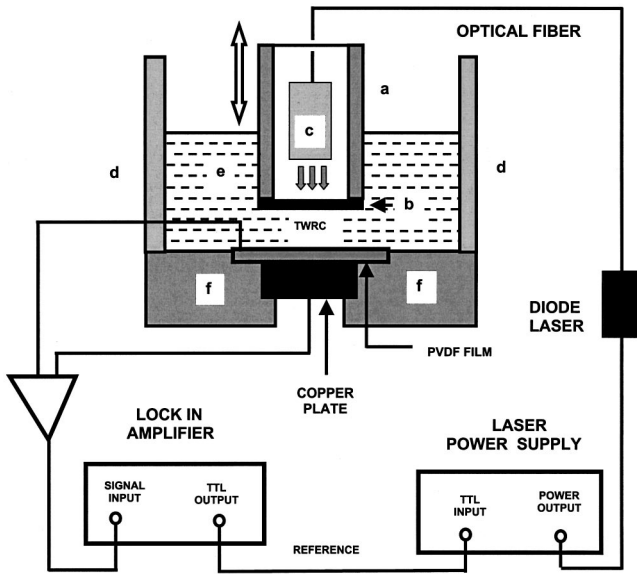[b]Electronic mail: mandelis@mie.utoronto.ca

FIG. 1. Schematic cross section of the TWC configuration experimental setup. (a) Cylindrical thermal-wave emitter head containing the aluminum foil optical absorber; (b) the photothermal chamber with the optical fiber; (c) and (d) container walls; (e) liquid sample filling the thermal-wave cavity; and (f) dielectric substrate. The bottom surface of the PVDF was attached to a copper plate, which acted as electric contact and support.

Equation (4) is the complex representation of an exponentially damped wave, the wavelength of which is defined as[1,2,4]

$$\lambda_{TW} = 2\sqrt{\frac{\pi \alpha_l}{f}}, \tag{5}$$

and can be used for thermal diffusivity measurements. From Eq. (5), the thermal diffusivity can be easily evaluated as

$$\alpha_l = \left(\frac{\lambda_{TW}}{2}\right)^2 \frac{f}{\pi}. \tag{6}$$

In fact, Eq. (6) shows that only partial cavity scans up to half a thermal wavelength are necessary for this purpose.

As is well known, the thermal-wave phase lag is a measure of the delay occurring between signal generation (photothermal excitation) and detection. Consequently, the experimental lock-in amplifier (LIA) demodulated output phase can be written as

$$\Delta \Phi_{LIA} = \sqrt{\frac{\pi f}{\alpha_l}} L + \Delta \Phi. \tag{7}$$

In this expression, $(\pi f/\alpha_l)^{1/2}L$ is the phase lag due to thermal-wave diffusion across the sample [obtained directly from Eq. (4)]; $\Delta \Phi$ is an instrumental phase lag due to system electronics (preamplifier, pyroelectric material, LIA circuitry, etc.). Equation (7) can be written more conveniently using the thermal wavelength definition, Eq. (5):

$$\Delta \Phi_{LIA} = \left(\frac{2\pi}{\lambda_{TW}}\right) L + \Delta \Phi. \tag{8}$$

Adjusting the reference phase in such a way that for two given cavity lengths L_1 and L_2, $\Delta \Phi_{LIA}$ assumes the values $-\pi$ and $+\pi$, Eq. (8) yields the following equations:

TABLE I. Thermal wavelengths and the corresponding thermal diffusivities for distilled water.

Modulation frequency (Hz)	$\lambda_{TW}/2$ (cm)	$\alpha \times 10^2$ (cm^2/s)
2.0	0.0480±0.0005	0.1466±0.0031
2.5	0.0420±0.0005	0.1404±0.0033
3.0	0.0390±0.0005	0.1452±0.0037
3.5	0.0360±0.0005	0.1444±0.0040
4.0	0.0330±0.0005	0.1387±0.0042
4.5	0.0310±0.0005	0.1376±0.0044
5.0	0.0300±0.0005	0.1432±0.0048

$$-\pi = \frac{2\pi}{\lambda_{TW}} L_1 + \Delta \Phi, \tag{9a}$$

$$+\pi = \frac{2\pi}{\lambda_{TW}} L_2 + \Delta \Phi. \tag{9b}$$

From Eqs. (9a) and (9b), it is easy to show that $\Delta L = L_2 - L_1 = \lambda_{TW}$. The practical idea behind Eqs. (9a) and (9b) is to take advantage of the apparent LIA phase discontinuity (an artifact of the multivaluedness of complex numbers), which occurs after the complex thermal-wave signal vector completes one full cycle (2π phase rotation) as a function of cavity length. It is clear that by measuring the TWC length difference between two adjacent phase "discontinuities," the thermal wavelength can be measured directly. Operationally, the one-half thermal wavelength required for the thermal diffusivity evaluation through Eq. (6) is obtained by measuring the cavity length difference between the points where the phase takes on the values $-\pi$ and 0. The simplicity and robustness of this technique lie in its relative measurement features for both the thermal-wave phase and cavity length, thus eliminating the need for taking into account difficult-to-quantify instrumental phase shifts.

III. EXPERIMENT

The experimental setup, shown in Fig. 1, consisted of an IR (806 μm) semiconductor laser (Opto Power Corporation), operated at 200 mW. The intensity-modulated laser light, electronically chopped by the internal oscillator of the lock-in amplifier (SR-830), was incident on an aluminum foil (80 μm thick and 1 cm in diameter). Thermal waves generated in this foil were measured by a pyroelectric PVDF detector, 150-μm-thick Kynar piezofilm, placed parallel to, and across from, the aluminum foil. The aluminum foil was mounted on a micrometer stage to allow changing its relative distance from the polyvinylidene difluoride (PVDF) surface with 10 μm resolution.[5] Amplitude and phase signals obtained as a function of cavity length were preamplified (ITHACO model 1201), then they were sent to the lock-in amplifier for further amplification and demodulation and stored for further analysis.

Two pure liquids (distilled water and ethylene glycol) were used. The TWC container was filled with the corresponding sample, as schematically shown in Fig. 1. Thermal waves of several wavelengths were generated inside the liquids by using various modulation frequencies (Tables I and II). The corresponding half thermal wavelengths were ob-

TABLE II. Thermal wavelengths and the corresponding thermal diffusivities for ethylene glycol.

Modulation frequency (Hz)	$\lambda_{TW}/2$ (cm)	$\alpha \times 10^2$ (cm^2/s)
2.0	0.0380 ± 0.0005	0.0919 ± 0.0024
2.5	0.0340 ± 0.0005	0.0920 ± 0.0027
3.0	0.0310 ± 0.0005	0.0918 ± 0.0030
3.5	0.0290 ± 0.0005	0.0937 ± 0.0032
4.0	0.0270 ± 0.0005	0.0928 ± 0.0034
4.5	0.0250 ± 0.0005	0.0895 ± 0.0036
5.0	0.0240 ± 0.0005	0.0917 ± 0.0038

tained *directly* by measuring the cavity-length increase between the onset of a phase ''jump'' from $-\pi$ and the attainment of the zero value.[5] The cavity-length scan was carried out in 10 μm steps. All measurements were made at 24 °C, as determined by a thermocouple immersed in the liquid. This temperature was only 1° higher than room temperature and represents the dc temperature rise inside the TWC during a complete experiment. The reported standard deviations in this work were calculated as the experimental error on the thermal wavelength by using the standard formula for error propagation[11] in Eq. (6).

IV. RESULTS AND DISCUSSION

In Fig. 2, typical behavior of the thermal-wave phase is shown for distilled water and three different reference phases $\Delta\Phi$ at 2 Hz. It is evident from Fig. 2 that the arbitrary reference phase can be conveniently chosen so as to scan exactly through two adjacent phase ''discontinuities,'' in order to keep the extent of the cavity scan to a minimum. These discontinuities are shown for the two studied samples at the same modulation frequency (2 Hz) in Figs. 3(a) and 3(b).

To investigate the fidelity of the technique, the thermal-wave phases resulting from cavity-length scans at two modulation frequencies (2 and 5 Hz) are shown in Fig. 4 for the
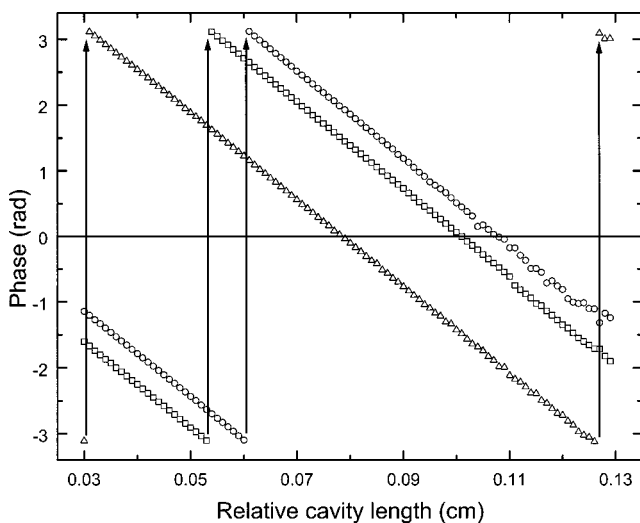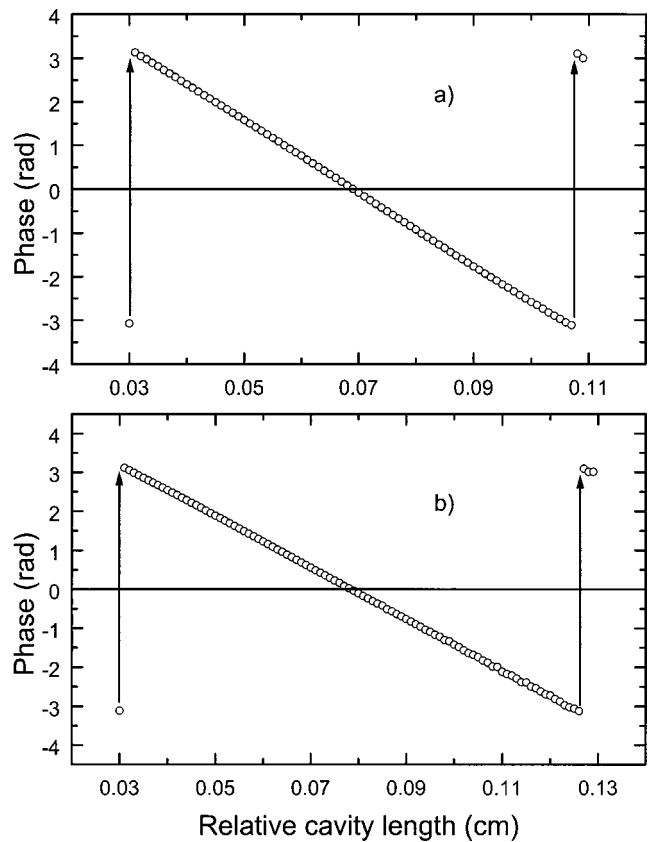

FIG. 3. TWC signal phases for ethylene glycol (a) and distilled water (b) at 2 Hz. The reference phases used were 110° and 114°, respectively.

ethylene glycol sample. For each case, the half thermal wavelength was directly obtained by measuring the distance between the first phase discontinuity (phase equals $-\pi$) and the phase curve's intersection with the X axis (phase equals 0), as the cavity length was varied. The results are summarized in each second column of Tables I and II. The corresponding thermal diffusivities obtained from these values were recorded in each third column of Tables I and II. For
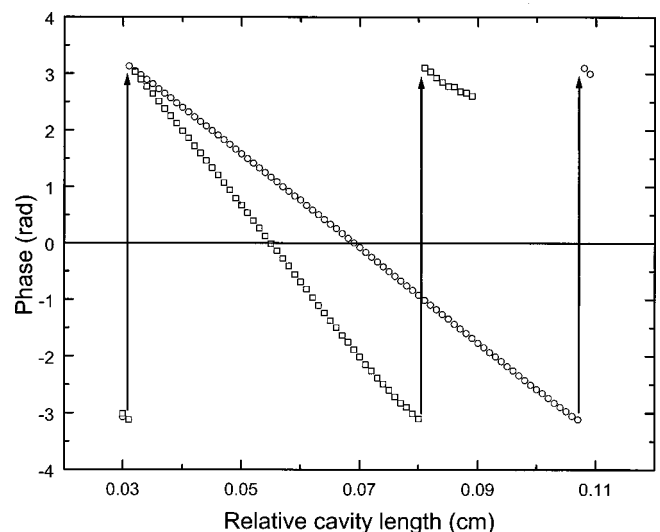

FIG. 2. TWC signal phases for distilled water at 2 Hz and three different reference phases: (○) 0°, (□) 27°, and (△) 114°. The jumps are deliberately shown as discontinuities between $-\pi$ and $-\pi+\varepsilon$ radians; and π and $\pi-\varepsilon$ rad.

FIG. 4. TWC signal phases for ethylene glycol at two modulation frequencies. (○) corresponds to 2 Hz and (□) corresponds to 5 Hz. The reference phases used were 110° and 65°, respectively.

comparison, the thermal diffusivity reported for distilled water[12] is 0.001 456 cm²/s (at 24 °C) and the corresponding value for ethylene glycol[13] is 0.000 939 cm²/s (at 20 °C).

It is evident from Fig. 4 that the phase deviates from the expected linear behavior at moderately high frequencies (5 Hz). This deviation is the result of the exponentially damped nature of the thermal-wave amplitude [Eq. (4)]. With the diminishing strength of the conductive thermal wave at long cavity lengths, other mechanisms start to emerge, specifically, radiative heat transfer.[3,14] Therefore, the measurement accuracy of higher-frequency TWC results may be somewhat compromised.

The precision in the thermal diffusivity values measured by the presented methodology is controlled by the ability to measure the corresponding thermal wavelength, as is evident from the results summarized in Tables I and II. At lower modulation frequencies the thermal wavelength is longer, resulting in an improvement in measurement resolution for a given total scan of the micrometer stage, even in the presence of the higher $1/f$ noise. This conclusion favors the use of low modulation frequencies for measurements of thermal wavelength by means of the present methodology. Obviously, there are limitations in using very low frequencies, such as sensor sensitivity and noise, three-dimensional thermal diffusion effects, and longer LIA time constants. For a modulation frequency of 2 Hz, a 1 s LIA time constant was adequate. Through Eq. (6) it is possible to calculate the standard deviation on the thermal diffusivity measured by means of this methodology by estimating the corresponding standard deviation on the measured thermal-wave length.

To our knowledge, this new measurement methodology has the virtue of being the simplest reported photothermal technique for *accurate and precise* measurements of the thermal diffusivity in liquids, as it involves only relative measurements to yield absolute diffusivity values. Adding to its high sensitivity, it exhibits excellent potential for applica-tions in diverse thermophysical and thermochemical studies of fluid substances, such as oxidation, dissolved gas concentration, and thermodynamic phase transitions. A major advantage of this new methodology is the minimum time required to make a thermal diffusivity measurement (about 3 min). This, in turn, is a consequence of the simple experimental requirement to determine only two relative cavity lengths and a very simple theoretical relation to the thermal wavelength given by Eqs. (9a) and (9b).

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