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Self-consistent photopyroelectric calorimetry for liquids

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ABSTRACT

The front photopyroelectric (FPPE) configuration, together with the thermal-wave resonator cavity (TWRC) method was applied in order to measure both thermal effusivity and diffusivity of liquids. The methodology is based on a 4-layer detection cell (pyroelectric sensor, coupling fluid, solid separator and liquid backing) in which the investigated liquid is inserted successively in backing and in coupling fluid's position, respectively. When inserted in the backing position a scan of the phase of the FPPE signal as a function of (a known) coupling fluid's thickness (TWRC method) leads to the direct measurement of liquid's thermal effusivity. Inserting then the investigated liquid in coupling fluid's position (with a known backing liquid), a similar thickness scan leads to the measurement of its thermal diffusivity. In such a way the FPPE-TWRC method becomes self-consistent; all static and dynamic thermal parameters can be derived with the same technique (two of them are directly measured and the remaining two, calculated). The suitability of the method was demonstrated with investigations on several liquids as water, ethylene glycol, glycerine, various oils.

1. Introduction and theoretical features

In the photopyroelectric (PPE) method, the temperature variation of a sample exposed to a modulated light is measured with a pyroelectric sensor, situated in intimate thermal contact with the sample [1–3]. From theoretical point of view, in the most general case, the complex PPE signal depends on all optical and thermal parameters of the layers of the detection cell. A large effort was dedicated in the last decades to simplify the mathematical expression of the PPE signal, by acting especially on the number of components of the detection cell and on the thermal and optical thickness of each layer. As a final result, several particular cases were obtained, in which the information is contained both in the amplitude and phase of the PPE signal; the amplitude and phase depend in these cases on one or, in a simple way, on two of the sample's related thermal parameters [1–3].

The thermal parameters resulting directly from PPE measurements are usually the "fundamental" ones (present in the thermal diffusion equation and its solution): the thermal diffusivity and effusivity. Concerning the PPE detection configurations, two of them, "back" and "front", respectively, have been mainly applied for calorimetric purposes.

In the back configuration, a modulated light impinges on the front surface of a sample, and a pyroelectric sensor, situated in good thermal contact with the sample's rear side, measures the heat developed in the sample due to the absorption of radiation. In the front configuration, the radiation impinges on the front surface of the sensor, and the sample, in good thermal contact with its rear side, acts as a heat sink [1–8].

Historically speaking, the PPE calorimetry developed many ways in order to obtain the values of the thermal parameters. Some of them are based on the measurement of single values; other alternatives make use of scanning procedures. The second type of investigations is proved to be more precise. When liquid samples are investigated, there are two parameters susceptible to be scanned: the chopping frequency of radiation and the sample's thickness.

In principle, any combination detection configuration (back or front) - source of information (PPE amplitude or phase) - scanning parameter (chopping frequency or sample's thickness scan) is possible in order to obtain one of the dynamic thermal parameters (thermal diffusivity or effusivity) of a condensed matter sample [1–8]. However, during the last decades, the PPE calorimetry focussed its interest mainly on liquid samples, due to the fact that the sample-sensor thermal contact is perfect in this case, and the investigations can lead to accurate quantitative results [7,9].

Going back to the way of obtaining the information, one of the most used combination is the front configuration, with the phase of the signal as source of information and with a liquid layer's thickness as scanning parameter (thermal-wave resonator cavity –TWRC- method) [10,11]. This FPPE-TWRC configuration was

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firstly used by the authors to measure the thermal effusivity of bulk solid materials situated in backing position in the PPE detection cell [12,13]. The main advantage of this configuration, compared to the classical frequency scanning methods, was connected with the possibility of controlling the type and thickness of the coupling fluid [12,13]. Additional advantages of the TWRC method are: (i) the absolute value of the liquid's thickness is not always necessary - its thickness variation is sometimes enough; (ii) the method gives the possibility of keeping a thermally thin/thick regime for different layers of the detection cell (sensor, backing, separator layer) and, in the mean time, changing the thermal regime of the scanned liquid from thermally thin to thermally thick; (iii) the normalization signal is contained in the same scanning run (thermally very thick regime for the scanned liquid) and consequently, no additional normalization measurement is necessary [9–13]. The very same method was applied later to investigate liquid samples inserted in backing position in the detection cell. Special cells were designed to accommodate the liquids under investigation, and the configuration proved to be very suitable especially for measuring the thermal effusivity of some liquid mixtures [14].

From theoretical point of view, the normalized FPPE complex signal is given by [14,15]:

$$V_n = \frac{1 - R_{21}e^{-2\sigma_1 L_1}}{1 - \rho_{21}e^{-2\sigma_1 L_1}} \times \frac{(e^{-\sigma_1 L_1} - 1) - \rho_{21}(e^{-\sigma_1 L_1} - e^{-2\sigma_1 L_1})}{(e^{-\sigma_1 L_1} - 1) - R_{21}(e^{-\sigma_1 L_1} - e^{-2\sigma_1 L_1})} \quad (1)$$

where standard notations have been used:

$$R_{21} = \frac{1 - b_{21}}{1 + b_{21}}$$

$$\rho_{21} = \frac{(1 - b_{21}) + \rho_{32}(1 + b_{21})e^{-2\sigma_2 L_2}}{(1 + b_{21}) + \rho_{32}(1 - b_{21})e^{-2\sigma_2 L_2}}$$

$$\rho_{32} = \frac{(1 - b_{32}) + \rho_{43}(1 + b_{32})e^{-2\sigma_3 L_3}}{(1 + b_{32}) + \rho_{43}(1 - b_{32})e^{-2\sigma_3 L_3}} \quad (2)$$

$$\rho_{43} = \frac{1 - b_{43}}{1 + b_{43}}$$

"Normalized signal" in Eq. (1) refers to the signal obtained with a 4-layers cell (directly irradiated sensor (1), coupling fluid (2), thin solid separator layer (3) and a semi-infinite liquid layer, in the backing position (4)), normalized with respect to the signal obtained with semi-infinite coupling fluid (see Fig. 1 for the schematic diagram of the detection cell).

In Eqs. (1) and (2) $\sigma_j = (1 + i)a_j$, $\mu = (2\alpha/\omega)^{1/2}$, $b_{ij} = e_i/e_j$, α and e are thermal diffusivity and effusivity, ω is the angular chopping frequency of radiation, σ and a are the complex thermal diffusion coefficient and the reciprocal of the thermal diffusion length ($a = 1/\mu$), respectively.

Eq. (1) indicates that the FPPE signal depends on the thermal diffusivity and effusivity of the first three layers of the detection cell (sensor, coupling fluid and separator layer) and on the thermal

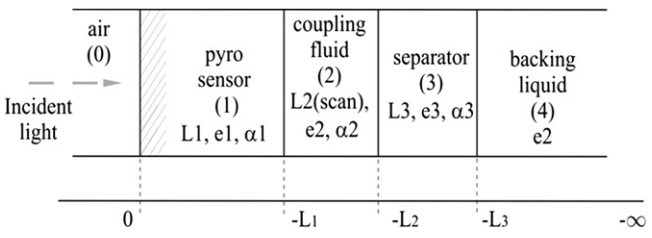

Fig. 1. Schematic diagram of the 4-layers detection cell.

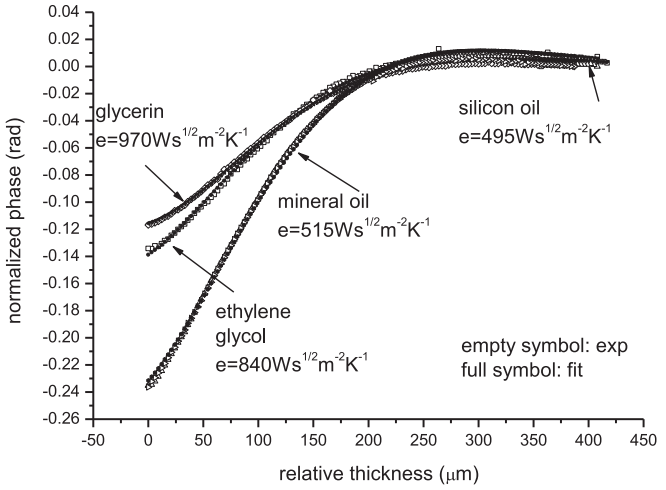

Fig. 2. Normalized phase of the complex FPPE signal as a function of the thickness of coupling fluid, for a cell containing water as coupling fluid and different liquids (glycerine, ethylene glycol, mineral and silicon oils) as backing liquids. Full points represent the best fit performed with Eq. (1).

effusivity of the backing. In conclusion, if the backing layer is liquid, one can obtain its thermal effusivity by performing a scan of the phase of the signal, as a function of the coupling fluid's thickness. The mathematical method developed to obtain the value of the thermal effusivity of the backing material is a fit of the phase of the FPPE signal with the coupling fluid's absolute thickness and backing's thermal effusivity as fitting parameters [12–14].

Unfortunately, for a complete thermal characterization (determination of all four thermal parameters) of a material, only the thermal effusivity is not enough; a second thermal parameter is necessary. It is well known that the four thermal parameters, the static volume specific heat, C, and the dynamic thermal diffusivity, α, conductivity, k, and effusivity, e, are connected by two relationships, $k = C\alpha$ and $e = (Ck)^{1/2}$ and, consequently, only two are independent. In order to measure a second thermal parameter one has to use, as mentioned before, a different PPE configuration (back detection configuration, for example) or frequency scanning procedures [16–19].

In this paper, we propose the use of the same FPPE-TWRC scheme, in a self-consistent way, in order to obtain both thermal

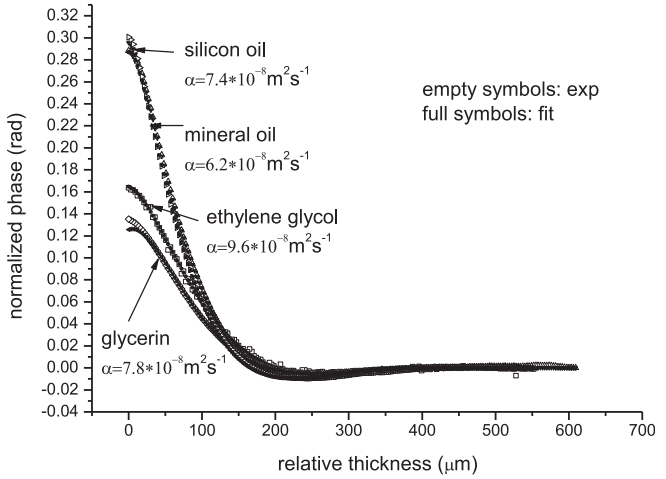

Fig. 3. Normalized phase of the complex FPPE signal as a function of the thickness of coupling fluid, for a cell containing the investigated liquids (glycerine, ethylene glycol, mineral and silicon oils) as coupling fluids and water as backing liquid. Full points represent the best fit performed with Eq. (1).