Photopyroelectric measurement of thermal properties: interpretation using the thermal wave interference model

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The photopyroelectric method has been recognized as a reliable and useful tool for the measurement of the thermal properties of condensed matter samples. Usually the signal dependence on these parameters is obtained by solving the heat diffusion equations. In this paper we will show how the so-called thermal wave interference model can lead to the same results. We show how typical patterns in the imaginary and real parts of the signal are characteristic of wave interference phenomena.

Keywords: Photopyroelectric technique; thermal diffusivity; thermal effusivity; thermal waves.

1. Introduction:

Among the photothermal (PT) techniques [1] the photopyroelectric (PPE) method [2] has been recognized as a reliable tool for the measurement of the thermal properties of condensed matter samples. The two most widely used experimental variants are the direct (or back) [3] and the inverse (or front) [4] detection configurations for thermal diffusivity, \( \alpha \) and thermal effusivity, \( \varepsilon \). Determination respectively Usually the PE signal dependence on these parameters is obtained by solving a complicated set of heat diffusion equations, in a way similar as in the well-known RG Model [5]. This can lead to a large mathematical expression in which particular cases are analyzed. In this paper we will show how the so-called thermal wave interference (TWI) model [6] can lead to the same results in a phenomenological but much straightforward way.

\[
\Gamma = \frac{\beta(1-R)I_0\eta}{2k_s(\beta^2 - q_s^2)} \frac{(r - 1)(g - 1)\exp(-[\beta + q_s]l) - (r + 1)(g + 1)\exp([q_s - \beta]l) + 2g + 2r}{(g + 1)(b + 1)\exp(q_s l) - (g - 1)(b - 1)\exp(-q_s l)}
\]

where

\[ T(l, t) = \Gamma \exp(i\omega t) \tag{1} \]

2. The analytical model

As the PE signal is proportional to the sample’s temperature oscillations its dependence on the thermal parameters is usually obtained by solving the heat diffusion equations with proper boundary conditions for the system schematically shown in Fig. 1a. Although for several PT methods the values of the temperature at the gas sample interface is of major importance, as given by the RG model [5], one may also choose to detect the rear temperature variation at the sample backing interface. Thoen and Glorieux [7] have obtained the following result:

\[ q_s = (1+i)/\mu_s, \text{ with } \mu_s = (\alpha_\beta \pi l)^{1/2} \text{ as the thermal diffusion length.} \]

This is a very complicated expression, whose analysis is often performed by considering different limiting cases taking into account three main characteristic lengths involved in the problem: The sample’s thickness \( l \), the thermal diffusion length \( \mu_s \) and the light penetration depth \( \mu_\beta = 1/\beta \). One can deal therefore with optically transparent \((\mu_\beta \gg l)\) or opaque samples \((\mu_\beta \ll l)\), and in each case with thermally thick \((\mu_s \ll l)\) or thin \((\mu_s \gg l)\) samples. For thermal properties assessment the important particular case is that in which the sample is optically opaque to the incident radiation. The results of simplifications of Eq. (2) can be found elsewhere [7], which lead to the following most important results:
2.1. Thermally thick sample, $\mu_s \ll l$, for $\mu > \mu_\beta$

$$\Gamma = \frac{(1 - R) I_0 \eta (1 - r) \exp(\beta l)}{2k_s \beta (b + 1)} \exp(-q_s l)$$

$$= \Gamma_0 \exp\left(-\sqrt{\frac{\pi^2 f}{\alpha}}\right) \exp\left(-i\sqrt{\frac{\pi^2 f}{\alpha}}\right) \exp\left(-i\eta \frac{\pi}{4}\right)$$

Then, if the backing material is substituted by a PE sensor this configuration, called the back or direct PPE method, can be used for measurement of thermal diffusivity.

2.2. Thermally thin sample, $\mu_s \gg l$ for $\mu \gg \mu_\beta$

If we interchange the role of backing and sample for a thermally thin and optically opaque pyroelectric detector, we have the so-called front or inverse detection configuration for which the signal will depend on the inverse of the sample’s thermal effusivity, $e_s$.

Consider the situation depicted in Fig. 1b, where a sample of thickness, $L$ sandwiched between the regions denoted as 1 and 2. The region 1, that we will suppose is the sample surface, is heated uniformly by a light source of periodically modulated intensity $I_0[1+\cos(\omega t)]/2$, where $I$ is the light source intensity and $\omega=2\pi f$ is the angular modulation frequency, acting as a thin superficial light absorbing layer. Following the periodical heating a thermal wave will be generated which can be described as [1]:

$$T(x, t) = \frac{I_0 (1 - R)}{2e_s \omega^{1/2}} \exp(-q_s x) \exp[i (\omega t - \pi/4)]$$

$$= T_0 \exp(-q_s x) \exp[i (\omega t - \pi/4)]$$

Consider now the propagation of a thermal wave described by Eq. (5) through the sample medium $s$. We are interested in the temperature at the surfaces 1 and 2 at $x=0$ and $x=L$ respectively. The TWI model shows us that the generated thermal waves will propagate towards the interface between the sample and region 2 and back towards the sample’s surface, 1, being partially reflected and transmitted occurring interference between the corresponding wave trains. The temperatures at both surfaces can be obtained by summing all the waves arriving at these points.

First, for the temperature at the surface at $x=L$ (for sake of simplicity, from now on we shall omit the time dependent exponential term), a straightforward calculation leads to:

$$T(L) = T_0 \frac{\exp(-q_s L)}{1 - \gamma \exp(-2q_s L)}$$

where $\gamma=R_{s1}R_{s2}$, $R_{ij}=(1-b)/(1+b)$ and $b=e_s/e_f$ [1]. The signal from a PE positioned in region 2 will be proportional to the temperature given by the above equation.

On the other hand, for the temperature at $x=0$ we obtain:

$$T(0) = T_0 \left[1 + R_{s2} \frac{\exp(-2q_s L)}{1 - \gamma \exp(-2q_s L)}\right]$$

It is worth to remember before continuing that the PE signal is often measured using a Lock-In amplifier, which allows simultaneous measurements in the amplitude and phase channels, as done by the majority of the authors. However, this detection technique also allows measurements in the In-Phase and Quadrature channels, corresponding to the real and imaginary parts of the signal respectively. Using the fact that often extreme appears in experimental data recorded in these channels we will show in what follows, on the basis of computational simulations, how the TWI model allows the simple understanding of several characteristic features underlying the PPE method and can provide us with easy methodologies for the determination of thermal properties of matter.
4. Results and discussion

Figure 2a shows the results of theoretical simulations for the back side detection configuration. Both the real and the imaginary part of Eq. (6) are represented as a function of the sample thickness for different values of the modulation frequency. As we can see a sequence of minima and maxima appears in both channels. Because the PPE signal is highly damped it is difficult to be measured for higher values of $L$. Therefore we will focus our attention on the first minima in the In-Phase channel and the first maxima in the Quadrature channel.

We see that as the frequency increases the extreme positions appear at lower positions and the signal goes more attenuated, as expected due to the damped nature of thermal waves. These positions are plotted in part (b) of the figure as a function of the inverse of the square root of the frequency at which they appear. A linear relationship can be seen. Similar relationships are obtained for other values of the thermal diffusivity of the region $s$. We determined the values of the corresponding slopes for both the real and imaginary parts. From these we see that the first minima in the In-Phase channel appear when the following relationships are fulfilled:

$$L_{\text{min, In-phase, back}} = \frac{\sqrt{\frac{\pi \alpha}{4f}}}{\sqrt{\pi \alpha}}$$  \hspace{1cm} (8)

Similarly, the first maxima in the Quadrature channel are at the positions:

$$L_{\text{min, quadrature, back}} = \frac{\sqrt{\frac{\pi \alpha}{4f}}}{\sqrt{\pi \alpha}}$$  \hspace{1cm} (9)

A similar analysis as above for the front side detection following Eq. (7) lead to the results:

![Figure 2](image-url)
\[ L_{\text{max, quadrature, front}} = \sqrt{\frac{\pi \alpha}{16f}} \] (10)

\[ L_{\text{min, In-phase, front}} = \sqrt{\frac{\pi \alpha}{4f}} \] (11)

Equations (8) to (11) can allow the measurement of thermal diffusivity in an easy way.

The same analysis can be made starting from the curves of the real and imaginary parts of the PPE signal as a function of \( f \) for a given \( L \), which also show maxima and minima.

5. Conclusions

In resume, we have shown that with the Thermal Wave Interference Model we can interpret easily and in a phenomenological way some photothermal results, in particular the results of PPE experiments. Expressions for the maxima and minima in the in-phase and quadrature channels were found for different detection configurations. As they involve sample’s diffusivity, they may be used for thermal characterisation purposes.

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