Investigation of layered systems and temperature-dependent thermophysical characterization by photothermal methods with periodic excitation

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Abstract. The salient features of periodically modulated photoacoustic (PA), photothermal radiometry (PTR) and photopyroelectric (PPE) methods are reviewed with emphasis on their use for characterization of layered samples. Using a general one-dimensional (1-D) heat diffusion model, explicit solutions for up to six layers are given in terms of thermal impedances. Two typical model configurations can be transformed and combined using symmetry properties in order to match a particular excitation/cell configuration couple. Different special cases allow for simultaneous measurement of two thermal parameters. For temperature-dependent investigations the direct temperature-conversion feature of the PPE method is advantageous. We show results on the temperature calibration of LiTaO$_3$ and PVDF pyroelectric sensors.

1. Introduction

The interest in photothermal (PT) investigations of layered samples [1-4] stems from their relevance for the broader field of materials science, in particular for non-destructive evaluation, thin films and interface characterization, and surface phenomena studies. Despite the fact that the thermal diffusion length $\mu$ is typically in the sub-mm range, in most solid materials it is still larger than the optical penetration depth $1/\beta$. Therefore, the PT signal carries information about the sample structure which is beyond the reach of pure optical methods. Moreover, $\mu$ can be adjusted simply by changing the modulation frequency, which is the basis of PT tomography. However, for a given frequency, the information contained in the signal is not related merely to the sample properties at a given depth, but rather to average properties over the whole layer thickness down to that depth. Direct models and inversion algorithms for time-dependent temperature fields in multilayers have been reported in the literature and for a large number of layers numerical computation is required. We restrict the discussion to the frequency domain modulation in a system with up to six layers, which still allows the manipulation of analytical solutions.

We present a synthetic overview on layered sample-cell configurations implemented in photoacoustic (PA) [5,6], photothermal radiometry (PTR) [7,8] and photopyroelectric (PPE) [9,10] techniques, selected out of several known PT methods [11-14]. Their specificities are taken into account by defining the respective transfer functions. The sample is described by its thermal impedance [15] which is independent on the detection method. This approach puts forward the similarities between the results obtained by the different PT methods, despite the fact that PA and PTR
signals depend on the surface temperature, while the PPE signal is given by the spatial average temperature in the pyroelectric (PE) layer.

2. 1-D thermal impedance of a layered system

If the detector integrates the ac temperature filed, the one dimensional (1-D) approach is justified even for small cross section Gaussian laser beams used in PT experiments [16]. We started from the 1-D model [17-19] developed for the PPE method with periodic excitation (angular frequency \( \omega = 2\pi f \)) and we identified two basic configurations with up to six layers depicted in Fig. 1(a,b). The sample (m) is semitransparent [absorption coefficient \( \beta (m^{-1}) \)] to the incident radiation flux density with amplitude \( H_1/2 \) [Wm\(^{-2}\)]. The opaque metallic electrode at (c/p) interface reflects a radiation fraction \( H_2/2 \) from the fraction \( H_3/2 \) which crossed the sample. Radiation-to-heat conversion efficiencies may be included as multiplicative factors. The depth-dependent temperature oscillations in layers \( j = g, m, c, p, s, b \) write:

\[
T_j(x) = A_j \exp(\sigma_j x) + A_j \exp(-\sigma_j x)
\]

For \( j = m \) the heat source term \( T_{H1} \exp(-\beta x) + T_{H2} \exp(-\beta(2L_m-x)) \) must be added. The boundary conditions on temperature and heat flux continuity between layers yield the matrix equation \( PA = Q \) with the solution \( A = P^{-1} Q \). Finally, the temperature amplitude averaged over the thickness \( L_p \) reads:

\[
\langle T_p \rangle = \left\{ A_j[\exp(\sigma_j L_p) - 1] - A_j[\exp(-\sigma_j L_p) - 1]\right\} / (\sigma_j L_p)
\]

The thermophysical parameters of the layers are the volume specific heat \( C_j \), conductivity \( k_j \), diffusivity \( \alpha_j = k_j / C_j \) and effusivity \( e_j = (C_j k_j)^{1/2} \). The 1-D complex thermal wave vector is \( \sigma_j = (i\omega \alpha_j)^{1/2} = (1+i) \mu_j \), with \( \mu_j = (\alpha_j / \pi f)^{1/2} \) being the thermal diffusion length in the material. The specific thermal impedance \( z_{p0} \) [m\(^2\)KW\(^{-1}\)] of the bare PE sensor suspended in air is defined as the ratio between its temperature and the heat flux density reaching it. Thus \( \langle T_p \rangle \) results from the superposition of three components [18]:

\[
\langle T_p \rangle = z_{p0}(H_1 \Gamma_1 + H_2 \Gamma_2 + H_3 \Gamma_3) / 2
\]

with:

\[
\Gamma_1 = \frac{2C^{-1}(1-P^{-1})(1+R_{gm} P^{-1})t}{(b_{mc} + 1)(b_{mp} + 1)(t^2 - 1)} e^{-\beta t} \left[-(t+1) + (t-1)R_{gm} M^{-2}\right] + 2M^{-1}(b_{gm} + t)/(b_{gm} + 1) (C_s - R_{gm} C_{P^{-2}} + (C_s - R_{gm} C_{P^{-2}})R_{gm} M^{-2})
\]

\[
\Gamma_2 = \frac{2C^{-1}(1-P^{-1})(1+R_{gm} P^{-1})t}{(b_{mc} + 1)(b_{mp} + 1)(t^2 - 1)} e^{-\beta t} \left[(t-1) - (t+1)R_{gm} M^{-2} + 2e^{-\beta t} M^{-1}(b_{gm} + t)/(b_{gm} + 1)\right] (C_s - R_{gm} C_{P^{-2}} + (C_s - R_{gm} C_{P^{-2}})R_{gm} M^{-2})
\]
Here $R_j = (b_j-1)/(b_j+1)$ is the thermal wave reflection coefficient with $b_j = e_j/e_s$ and $t = \beta / \sigma_m = \sigma / (2/1)\beta / \sigma_m$ is the complex thermo-optical thickness. Further notations are:

$$M = \exp(\sigma J), \quad j = m, c, p, s, \quad S_j = 1 + R_{m,s} R_{s,p} S^{-2}, \quad S_m = -(R_{m,s} + R_{s,p} S^{-2}) S,$$

$$C_j = 1 + R_{m,s} R_{s,p} C^{-2}, \quad C_m = -(R_{m,s} + R_{s,p} C^{-2}) C, \quad C' = R_{m,s} + R_{s,p} C^{-2}, \quad C' = -(R_{m,s} R_{s,p} C^{-2}) C$$

In order to match a particular cell design, the number of layers in Eqs. (3-5) needs to be reduced. This can be done in two ways, by assigning extreme values to the thickness of a layer (j); either $L_j \to 0$ and $\exp(\pm \sigma J L) = 1$ or $L_j \to \infty$ and $\exp(\pm \sigma J L) = 0$. Sometimes higher-order series development of the exponentials is necessary.

It is convenient to express PT signals in terms of a generalized specific thermal impedance $z = T(H/2) = z_{im}\Gamma$ as an average over the pyroelectric sensor layer (p) in the PPE method ($z_{im}$), or at the air-sample (g/m) interface in the PA and PTR methods ($z_{im}$). The respective interface temperature $T_{im}$ can be derived by setting $L_p \to 0$ in the expressions of $<T_p>$. The simple cases listed in Table 1 were derived from Eqs. (3-5). Their ideal frequency and phase features can serve as tests and/or as normalizing references in PT experiments [16].

| Sample (m) | PT Method, Configuration | Measured impedance | Approximations |
|------------|--------------------------|-------------------|---------------|
| No sample, bare pyro sensor | PPE, FD=BD (g→p/m) | $z_{im}=0$ | In $\Gamma_3$, $L_m=L_p=0$ (b) becomes (g) |
| Opaque, semi-infinite sample | PPE, FD=BD (p→m) transparent (p) | $z_{im}=0$ | In $\Gamma_3$, $L_m=L_p=0$ (b) becomes (m) |
| Opaque, thin layer on conducting backing | PA, PTR, PPE FD, (g→p/m) | $z_{im}=z_p=\frac{L_m}{k_m}=r_m$ | $L_m=L_p=0$ (s) becomes (m) |
| Opaque, thin layer on insulating backing | PA, PTR, PPE FD, (g→p/m/b) | $z_{im}=z_p=\frac{-i}{\omega L_m C_m}$ | $L_m=L_p=0$ (s) becomes (g) |
| Semitransparent, semi-infinite sample | PA, PTR, PPE FD, (m/e→p/m) transparent (p) | $z_{im}=z_p=\frac{-i\beta}{\omega C_m}$ | $L_m=L_p=0$ (b) becomes (g) |
| Opaque, thermally quasi-thick layer | PA, PTR, PPE BD, (g→p/m/g') | $z_{im}=z_p=\frac{2(1-i)}{\sqrt{2\omega e_m}} \times \exp(-(1+i)L_m / \alpha_m)$ | $L_m=L_p=0$ (b) becomes (g') |
In the front-detection (FD) configuration the excitation and the detection are situated at the same side of the sample. In the back-detection (BD) configuration, one measures the temperature at the opposite side relative to the excitation. From Table 1 it appears that FD is more appropriate for the characterization of shallow layers close to the surface (epsilon_m, C_m, thermal resistance L/theta_m, theta), while BD yields information on thermal parameters averaged over the sample thickness (epsilon_m and alpha_m). Contrary to PA and PTR which are remote techniques, the PPE one requires intimate thermal contact between sample and sensor. Nevertheless, non-contact PPE configuration was demonstrated as well and the (c) layer in Fig. 1 accounts for the coupling layer which can be an air gap.

3. PA, PTR and PPE signal generation

The complex amplitude V(f) of the PT signal can be expressed as the product of excitation heat flux, generalized specific impedance of the system, and the transfer function F of the PA, PTR or PPE method being used [16]: V(f) = (HS/2)F(z(f)). S is the area exposed to impinging radiation. We obtained the transfer functions of different PT methods by grouping the respective pre-factors in a way consistent with the above expression. As seen below, F has its own frequency and phase features.

The PA transfer function is: F_PA = (1-i)K_PA|p0(V_0T_0)^(-1)(alpha_p/2omega)^(1/2) with K_PA (V/Pa) the microphone sensitivity and gamma the ratio of the gas specific heats [20]. p0 and T0 are the equilibrium pressure and temperature in the cell volume V0. Note that F_PA has an f^(1/2) dependence and -45° phase.

The PTR transfer function is: F_PTR = 4K_PTR|epsilon_b|sigma_bT_a^3 where K_PTR (V/W) incorporates all instrumental and calibration factors of the detector, modulator and associated electronics [21, 22]. epsilon_b<1 is the integral emissivity of the sample surface, sigma_b is the Stefan-Boltzmann constant and T_a is the absolute temperature. F_PTR is frequency-independent and has 0 phase.

With a current preamplifier, the PPE transfer function in current mode is: F^c_PPE = iomega|p0|RE where p0 is the PE coefficient (which has negative sign) and R_E is the feed-back resistance of the preamplifier [23]. F^c_PPE has an f dependence and +90° phase. The combination of F^c_PPE with zeta_0 yields a flat amplitude response and 0 phase as a pre-factor for the Gamma factors which contain the effect of the sample.

4. Experimental examples

Fig. 2 shows experimental results for opaque and semitransparent, thermally thick materials [24]. In the intermediate frequency range the curves illustrate well the expected ideal behaviours resulting from the convolution of the method-specific transfer function with the impedance of the measured system (Eq. 7 and Table 1). At low frequency the deviations from linearity are due to the input ac filter of the lock-in amplifier and to the microphone bandwidth (for PA). In addition, at low frequency the condition for a thermally thick sample eventually breaks, and 2-D heat flow effects may influence the results as well. To the high frequency limit, one can notice the Helmholtz resonance of the PA cell at 2 kHz accompanied by a phase jump by -180° (not shown), while the PTR bandwidth is limited to about 100 kHz by the electronics. Most of these effects are efficiently cancelled out by normalization procedures [25]. The transfer functions and the laser power dependencies are also eliminated thereby, making possible direct comparison of normalized impedance spectra obtained by different PT methods. Glassy carbon as a normalizer behaves like a surface absorber at least up to 1 MHz. Better linearity can be obtained with polished, thick metallic samples (Ta, Zr).

The theoretical aspects discussed in Section 2 are supported by a series of experimental results obtained with the three methods, which covers the most representative situations encountered in layered systems, such as thermo-optical characterization of thin coatings, contact thermal resistances, subsurface damages, fluorescence efficiency, water and contaminants migration in (bio)polymers and wide dynamic range optical absorption coefficient of fluids ([16] and references therein).
5. Temperature-dependent PPE measurements

Among the different PT methods, the PPE one is based on direct conversion of temperature variations of the sample into electrical signals. For temperature-dependent investigations this feature considerably simplifies the calibration procedure, while the contact with the sample is easily achieved in a calorimetric set up. The $\Gamma$ factors contain the thermophysical parameters of the PE sensor in an intricate manner. Therefore, their absolute values and temperature dependencies have to be known in order to be extracted from temperature scans. Two PE materials are extensively being used in different laboratories for PPE investigations. The LiTaO$_3$ crystal is a displacement ferroelectric with rather stable properties up to about 670 K. For temperature-sensing applications it does not need poling. The polyvinylidene fluoride (PVDF or PVF$_2$) polymer has a Curie temperature of $T_C$=353 K. It exhibits deviations from linearity with temperature when approaching $T_C$, around the glass transition $T_g$$\approx$223 K and at $T_b$$\approx$293 K which is related to a change of the specific volume. Its properties are also frequency dependent around $T_g$. PVDF sheets need orientation by uni- or bi-axial stretching, followed by vacuum deposition of electrodes and polarization. The data gathered in Table 2 represent a compilation of the most accurate (to the best of our knowledge) parameters of the two materials [26].

We illustrate PPE measurements from cryogenic temperatures up to 400 K by studies of structural phase transitions in solids (magnetic and ferroelectric materials, high-$T_c$ superconductors and deuterated dielectric crystals), critical phenomena in liquid crystals, in binary liquid mixtures, in supercooled liquids near the glass transition (glycerol and propylene glycol), and by temperature-dependent behaviour of water in biopolymers (starch) ([26] and references therein). These results prove that the PPE technique assures high accuracy, high temperature resolution, low thermal perturbation of the sample and localized measurement capability which is required for the investigation of critical phenomena.

### Table 2. Typical values for thermal and electrical properties of LiTaO$_3$ and PVDF pyroelectric materials at room temperature and the respective temperature coefficients relative to 300 K. The temperature validity interval is given between parentheses.

| Parameter | Parameter value at 300 K | Temp. coefficient (%/K) | Parameter value at 300 K | Temp. coefficient (%/K) |
|-----------|-------------------------|--------------------------|-------------------------|--------------------------|
| $\alpha$ ($10^{-6}$ m$^2$s$^{-1}$) | 1.22-1.54 | -0.352 (230-360 K) | 0.0609 | -0.306 (100-340 K) |
| $\epsilon$ (Ws$^{1/2}$m$^{-2}$K$^{-1}$) | 3530-3700 | 0.085 (230-360 K) | 567 | 0.194 (100-340 K) |
| $\rho_{PE}$ (10$^{-4}$ Cm$^{-2}$K$^{-1}$) | 1.6-2.3 | 0.422 (200-400 K) | 0.2-0.3 | 0.681 (270-290 K) |
| $\varepsilon_r$ (diel. const.) | 41-47 | 0.0618 (130-400 K) | 9-11 | 0.342 (270-330 K) |

Figure 2. PA and PTR amplitude (a) and phase (b) for a surface optical absorber (glassy carbon) and for a volume optical absorber (grey glass filter).
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