THE THEORY OF PHOTOTHERMAL LENSING SPECTROSCOPY

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Abstract

A general theoretical description of dual-beam photothermal lensing spectroscopy is given. The results are valid for most general conditions, that is, for flowing as well as stationary media, for optically thick as well as optically thin media, and also for any transverse modes of incident pump beams.

Introduction

The Photothermal Lensing Spectroscopy (PTLS) has been discussed extensively in literature for trace detection of chemicals [1], and the use of PTLS in a flowing medium has been demonstrated for flow velocity measurements [2]. Although the thermal lensing effect may also be observed by monitoring the pump beam itself, in this paper we only consider the dual-beam technique in which the thermal lens is created by the pump beam and monitored by the probe beam.

The photothermal lensing effect was discovered accidentally by Gordon *et al.* [3] in 1964. In 1973, Hu and Whinnery [4] gave a detailed theoretical description of the effect for an extracavity sample and for a CW laser. Flynn and collaborators [5], on the other hand, used a pulsed laser and introduced the dual-beam technique, that is, a pump beam to create a change in the refractive index and a probe beam to monitor the change. Twarowski and Kliger [6] in 1977, gave a theoretical description of the pulsed PTLS in the impulse approximation, assuming that the excitation pulse is essentially a delta function. Swofford and collaborators [7,8], on the other hand, gave the theory of a repetitively pulsed excitation. All of the above authors considered only the collinear pump and probe beams since they were interested in maximizing the signal, and spatial resolution was not a consideration. Dovichi *et al.* [9], for the first time, considered transverse PTLS, that is a probe beam perpendicular to the pump beam for both single-pulse and repetitively pulsed excitation. Weimer and Dovichi [2,10] gave the theory of PTLS in a flowing medium for delta-function and repetitively pulsed excitations. Bialkowski [11] has considered the effect of the finite probe beam radius using a phase shift method. Excellent reviews on PTLS are given by Harris and Dovichi [12], by Fang and Swofford [1], and by Bialkowski [13]. A more general theoretical description of PTLS in a flowing as well as stationary media is given by R. Vyas and R. Gupta [14].

The basic idea underlying dual-beam PTLS is shown in Figure 1. A laser beam (pump beam) propagates through a medium, and is tuned to one of the absorption frequencies of the medium. The medium absorbs some of the optical energy from the laser beam. If the collision rate in the medium is sufficiently high compared to the radiative rates, most of the energy appears in the translational-rotational modes of the medium, within a short period of time. In effect, the laser-irradiated region gets slightly heated. The refractive index of the medium is thus modified. The refractive-index change can be monitored in several different ways [15]. We make use of the lensing effect of the medium to monitor the refractive-index change. A weak probe beam passes through the pump-irradiated region, as shown in Figure 1. Due to the curvature of the refractive index, the probe beam diverges; this can be detected as a change in the intensity of the probe beam passing through a pinhole. In other words, under the influence of the pump beam, the medium acts

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like a diverging lens. It is also possible that the medium behaves like a converging lens. If a pulsed pump laser is used, a transient lens is formed; the probe changes shape shortly after the pump beam is fired and returns to its original shape on the time scale of the diffusion of heat from a probe region.

In this paper, we present the theory of dual-beam PTLS in a fluid medium valid for most general conditions, that is, for flowing as well as stationary media in which the optical thickness of the media is considered. In this theory, the mode structure of the pump beam is not necessarily Gaussian. This is important because in practice, it is difficult to have a Gaussian beam. The calculation is done for different pump laser modes using the Green's function method where both the CW and pulsed excitation can be treated on the same footing. Also, both collinear and transversed PTLS can be treated in a unified way.

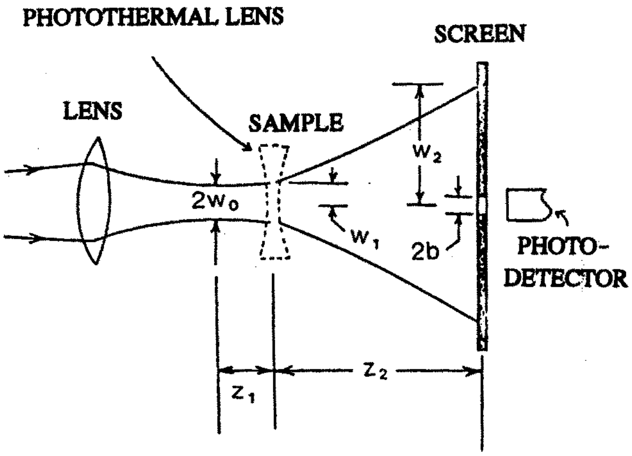


Figure 1. Schematic illustration of the photothermal lensing effect

Temperature Distribution

The absorption of the pump beam by the medium creates temperature distribution. This temperature distribution is given by the solution of the differential equation [14]:

$$\frac{\partial T(\vec{r},t)}{\partial t} = D\nabla^2 T(\vec{r},t) - V_x \frac{\partial T(\vec{r},t)}{\partial x} + \frac{1}{\rho C_p} Q(\vec{r},t) \tag{1}$$

where T ($\vec{r}$, t) is temperature above the ambient, D is the diffusivity, ρ is the density, C_p is the specific heat at constant pressure of the medium, and V_x is the flow velocity of the medium (assumed to be in the x-direction), and Q ($\vec{r}$, t) is the source term. The first, second and third terms on the right in Equation (1) represent, respectively, the effects of the thermal diffusion, flow, and the heat production due to the pump beam absorption. We assume that the pump beam propagates through the medium in the z-direction and is centered at the origin of the coordinate system. We further assume that the pump laser is a pulsed one. The procedure given here can be applied to CW cases. For discussion of a more general case refer to reference [16]. The heat produced per unit volume, per unit time by the absorption of laser energy is given by

$$Q(x,y,z) = \alpha I(x,y,z) =$$

$$\frac{2\alpha E_0}{\pi a^2 t_0} \frac{1}{2^{l+m}\, l!\, m!} H_l^2\left(\frac{\sqrt{2}x}{a}\right) H_m^2\left(\frac{\sqrt{2}y}{a}\right) e^{\frac{-2(x^2+y^2)}{a^2}} e^{-\alpha z}$$

$$\text{for } 0 \le t \le t_0 \tag{2}$$

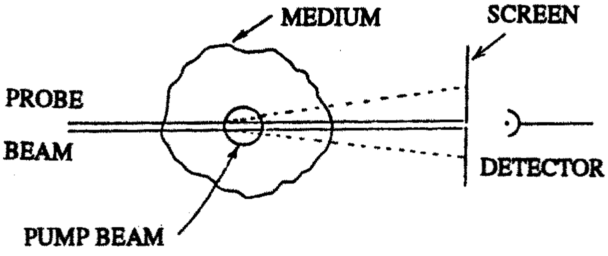


Figure 2. Detection of photothermal lens

where H's are Hermit polynomials to account for various transverse modes of the pump beam, the $e^{-\alpha z}$ accounts for absorption of optical thickness of the medium, E_0 the electric amplitude of laser, t_0 the time duration, and a the laser spot size [17].

To obtain the solution of Equation (1), one needs to apply appropriate boundary conditions. If T is the ambient temperature, then we have:

$$T(\vec{r},t)|_{t=0} = 0 \qquad T'(\vec{r},t)|_{t=0} = 0$$
$$T(\vec{r},t)|_{x=\pm\infty} = 0 \qquad T(\vec{r},t)|_{y=\pm\infty} = 0,$$
$$T(\vec{r},t)|_{z=\pm\infty} = 0 \tag{3}$$

where the laser is turned on at t = 0 and T' represents the gradient of the temperature. The solution of Equation (1) is given by

$$T(\vec{r},t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\zeta,\eta,\xi,\tau)\, G(x/\zeta, y/\eta, z/\xi, t/\tau)\, d\zeta\, d\eta\, d\xi\, d\tau \tag{4}$$

where G is the Green's function appropriate for Equation (1) and Q is given by Equation (2). The Green's function satisfies the differential equation

$$-Dv^2G + V_x\partial G/\partial x + \partial G/\partial t= \frac{1}{\rho C_p}\times$$
$$\delta(x-\zeta)\,\delta(y-\eta)\,\delta(z-\xi)\,\delta(t-\tau) \tag{5}$$

with appropriate boundary conditions. The solution of Equation (5) was derived by Zandi *et al.* [18] and found to be

$$G = \frac{H(t-\tau)}{8\pi\rho C_p[\pi D(t-\tau)]^{3/2}}\, e^{\frac{-[x-(\zeta+V_x(t-\tau))]^2}{4D(t-\tau)}}\, e^{\frac{-(y-\eta)^2}{4D(t-\tau)}}\, e^{\frac{-(z-\xi)^2}{4D(t-\tau)}} \tag{6}$$

where H(t-τ) is the unit step function. Substitution of Equations (2) and (6) into Equation (4) leads to the desired temperature distributions

$$T(x,y,t) = \frac{2\alpha E_0}{4\pi^2a^2t_0\rho C_p2^{1+m}1\,!m!}\int_0^{t_0}\frac{e\text{-}\alpha z+\alpha^2D(t-\tau)}{[D(t-\tau)]}\,d\tau$$
$$\int_{-\infty}^{+\infty} e^{\frac{-2\zeta^2}{a^2}+\frac{[\zeta+V_x(t-\tau)-x]^2}{4D(t-\tau)}}\,H_1^2\left(\frac{\sqrt{2}\zeta}{a}\right)$$
$$X\int_{-\infty}^{+\infty} e^{-2\frac{\eta^2}{a^2}+\frac{(\eta-y)^2}{4D(t-\tau)}}H_m^2\left(\frac{\sqrt{2}\eta}{a}\right)d\eta$$

$$\text{for } t>t_0 \tag{7}$$

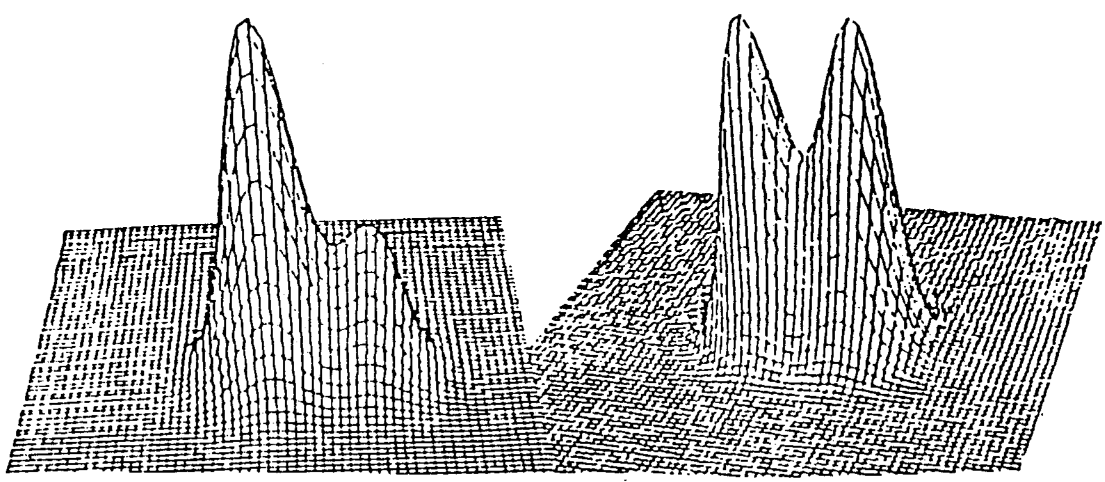
This equations must be evaluated numerically, except in certain special cases.

The expressions for the focal length of thermal lens have been taken from R. Vyas *et al.* [14] and M.H. Zandi [16] and will not be proved here, rather only explained briefly. The typical scheme for the detection of a thermal lens is shown in Figure (2). A thermal lens (sample with the pump beam passing through it) is placed at distance Z_1 in front of the probe beam waist. A screen with a pin-hole is placed at distance Z_2 in front of the thermal lens. Intensity of the probe beam passing through the pin-hole is observed by a photodetector. If the focal length of the thermal lens is $f >> Z_2$ (which is generally the case) and $Z_2 >> Z_1$, then the signal S(t), defined as the fractional change of the probe beam power at the photodetector is

$$S(t)= Z_1(1/f_x + 1/f_y) \tag{8}$$

where f_x and f_y are the focal lengths of the thermal lens in the x- and the y-directions, respectively. They are given by

$$1/f_x = -\partial n/\partial T\int_{path}\partial^2T(r,t)/\partial x^2\, ds \tag{9}$$



(b) (a)

Figure 3. The temperature distribution for TEM_{10} mode: a-stationary medium ($v_x= 0$), b-flowing medium with velocity of 0.1 m/s

$$1/f_y = -\partial n/\partial T \int_{path} \partial^2 T(r,t)/\partial y^2 \, ds \qquad (10)$$

The PTLS signal is then given by S(t), with the help of Equations (9) and (10), and T(r,t) given by Equation (7).

Figures (3) and (4) show a few typical pulsed PTLS temperatures and signals, respectively in a stationary as well as flowing medium for the transverse case. The medium is assumed to be N_2 at atmospheric pressure, seeded with 1000 ppm NO_2 to make the medium absorb in the visible region (absorption coefficient, $\alpha = 0.39 m^{-1}$ at 490 nm). In this medium, $\rho C_p = 1218 Jm^{-3}K^{-1}$, $D = 2.04\times10^{-5}\ m^2S^{-1}$, $n_0 = 1.000294$, and $\partial n/\partial T = 9.4\times10^{-7}K^{-1}$. The pump laser is assumed to give 1μs long pulses. The pump beam radius is assumed to be 0.5 mm. The probe beam radius does not enter into the calculation. The

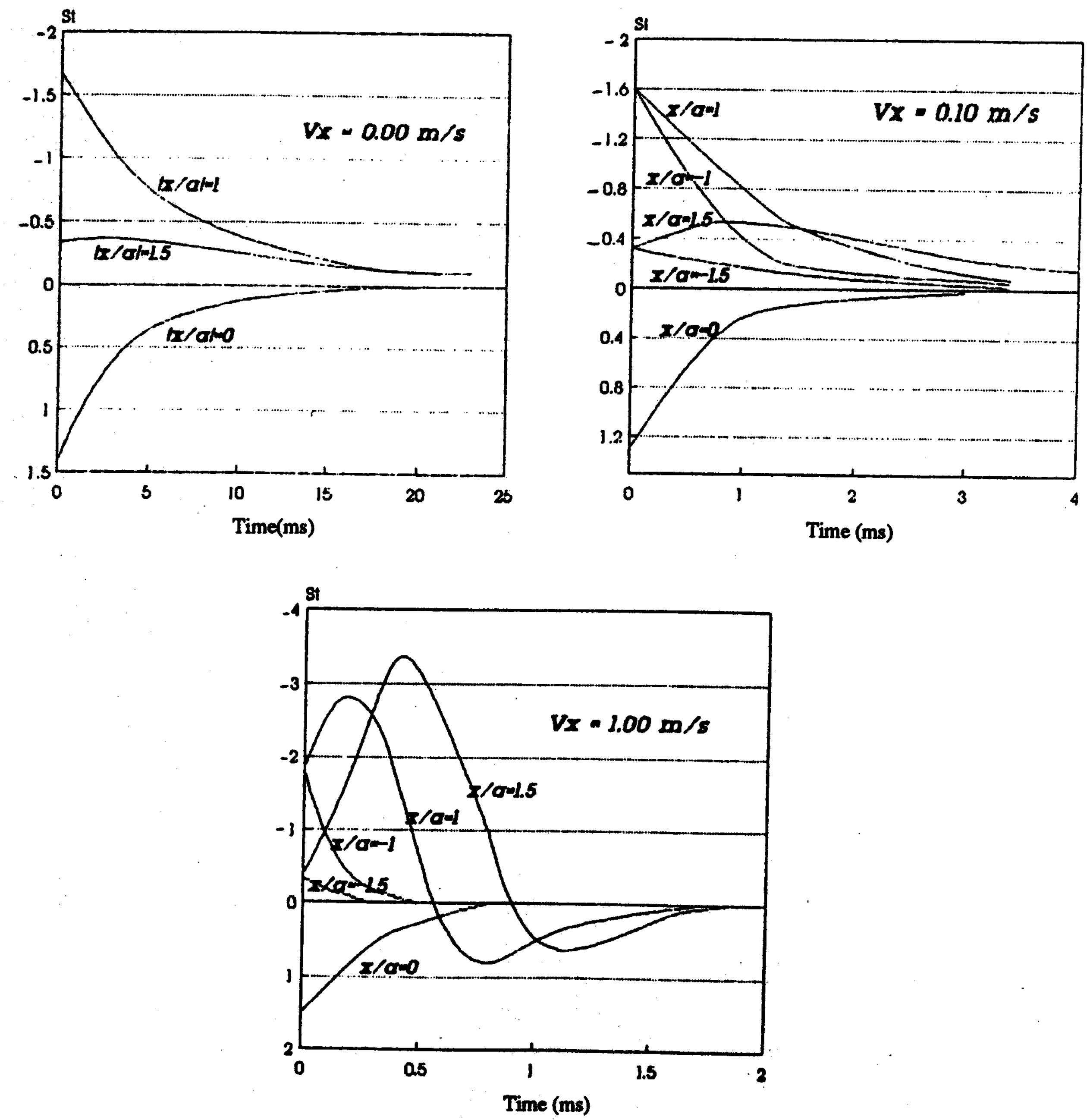


Figure 4. Photothermal lensing signal as a function of time for various pump-probe beam separations: a-stationary medium, b-flow velocity of 0.1 m/s, c-flow velocity of 1 m/s

fractional change in the intensity of the signal corresponds to a converging lens. The pumped laser mode is TEM_{10}. We have symmetric signal for $|x/a| = 0,1,1.5$. Figure (4-a) shows that the signals are smaller for $|x/a| = 1.5$ than for $|x/a| = 1$ and etc., as expected. Thus, as $|x/a|$ is increased, the power of the thermal lens is decreased until it is zero at certain values of $|x/a|$. S_L goes to zero at $t=t_0$ but regains a nonzero value for $t>t_0$ due to the diffusion of heat from the interior of the irradiated pump beam region. For certain values of x, the signal sign inverts, indicating that the thermal lens formed is a converging lens. In the case of a flowing medium, ($V_x = 0.1$ m/s), there is no symmetry in the signal. The left peak in temperature distribution is pulled toward the right as shown in Figure (3-b). If the flowing medium moves faster ($V_x=1$ m/s) for negative x, there is a small signal, but for positive x, the signal is more appreciable, as Figure (4-c) shows. Moreover, the thermal lens is a diverging lens in the center while it is a converging lens in the wings. The asymmetric wings result from thermal diffusion.

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