

Transworld Research Network 37/661 (2), Fort P.O. Trivandrum-695 023 Kerala, India

Thermal Wave Physics and Related Photothermal Techniques: Basic Principles and Recent Developments, 2009: 1-27 ISBN: 978-81-7895-401-1 Editor: Ernesto Marín Moares

# 1. Basic principles of thermal wave physics and related techniques

## E Marín

Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada Legaria 694, Colonia Irrigación, C.P. 11500, México D.F., México

**Abstract.** Fundamental and applied research have instigated and still require today the development of methods for studying phenomena and measurement of properties in several fields of science. In this introductory chapter we will examine the basic principles of a whole range of methods based on the common principle of heating the sample with intensity modulated or pulsed radiation beams and measuring the resulting dynamical sample's temperature (often denoted as thermal waves) or the fluctuations of some temperature dependent parameter, i.e., the so-called photothermal techniques.

# 1. Introduction

About hundred years ago, Fourier [1] showed that expanding temperature distributions as series of waves could be useful in solving heat conduction problems, anticipating the concept of thermal wave, widely used today for the explanation of the photothermal (PT) phenomena, on which several measurement techniques are based [2]. In these techniques, the periodic or transient absorption of energy without re-emission losses leads to sample heating, which at the same time induces changes in temperature-dependent

Correspondence/Reprint request: Dr. E Marín, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Legaria 694, Colonia Irrigación, C.P. 11500, México D.F., México. E. mail: emarinm@ipn.mx

parameters of the sample itself and/or of the surrounding medium, whose detection is the basis of the different experimental methods.

Fourier has used equations identical to those used today in describing thermal waves to propose a method for estimate the thermal properties at the earth crust, making use of the daily periodical temperature oscillations [3]. Today measurements of the soil's temperature as a function of time at different distances from the earth surface and interpretation of the results using the thermal wave solution of the heat diffusion equation in presence of periodical harmonic heat sources allow the determination of parameters like the soil's thermal diffusivity [4, 5], as proposed earlier by Fourier. This is probably one of the simplest experiments in thermal wave physics [6-8]. Although Ängström in 1861 proposed a similar temperature-wave method for measuring the thermal diffusivity of a solid in a form of a rod [9], it was not until the 1970's that practical applications of PT techniques appeared. This was motivated mainly by the works of Rosencwaig [10, 11] in the today well established field of Photoacoustic Spectroscopy (PAS), a technique based on the Photoacoustic (PA) effect, discovered approximately one century before by A. G. Bell [12], and investigated by relevant scientists of those times such as Röntgen [13], Tyndall [14] and Rayleigh [15]. It is worth to mention the early work of Viengerov in the 1930's [16] using the PA effect in gases, a field of active current investigation [17, 18].

Thermal waves can be generated using different kinds of radiation, but the most used form is by impinging a pulsed or intensity modulated electromagnetic light beam onto the sample to be investigated. Part of the light energy is then absorbed and transformed into heat by means of different non-radiative processes, which depend on the kind of the sample's material and the incident photons energy. The generated heat will diffuse through the sample and a temperature field will be created, which can be denoted as a thermal wave field. As a consequence of the temperature changes induced in a sample, its temperature dependent properties will also change, as well as those of its neighboring media. The measurement of these changes is the basis of the different measurement configurations, i.e., of the different PT techniques. Following the mentioned mechanisms the photothermal signal, whether in the time or modulation frequency domain depending if the thermal waves are excited by pulsed or periodical radiation respectively, will depend on the optical properties of the material, on those describing the electromagnetic energy into heat conversion mechanisms, and on the thermal properties responsible for the heat transfer process.

Although the physical aspects related to the mechanisms involved in the optical generation of thermal waves are well known, including the role played in the PT techniques by the thermal parameters governing the heat

transport, some peculiarities of this phenomenon are often not well known or they are misinterpreted. For example, the majority of people base their works using equations associated with the parabolic heat diffusion equation derived from the law of Fourier for stationary heat conduction and the law of energy conservation, or continuity equation. But this theoretical framework not always describes the heat transfer regimes on very small space and time scales [19] such as those that appears in the recent developed fields of nanoscience and nanotechnology and when thermal waves are excited using laser pulses of very short period when compared with the relaxation times of the heat carriers. Therefore, we will begin this chapter discussing the fundamental characteristics of the thermal transport in the case of time varying heat sources including aspects related to the so-called hyperbolic heat transport, trying to fill in part the lack of discussion in the field. Then we will briefly present the solution for the thermal wave fields in the case of pulsed and periodical heat sources, the so called thermal waves, making emphasis in their principal characteristics in the context of PT science and techniques. Although our general analysis here will be limited to the case of solid materials some special features concerning the work with liquids and gases will also be discussed.

## 2. Heat transfer mechanisms

It is well known that any temperature difference within a physical system causes a transfer of heat from the region of higher temperature to the one of lower. This transport process takes place until the system has reached a uniform temperature throughout. Thus, the quantity of heat, H, transferred per unit time, t, should be some function,  $\Phi$ , of the temperatures,  $T_1$  and  $T_2$ , of both the regions involved, i.e.,

$$\frac{\partial H}{\partial t} = \Phi(T_1, T_2) \tag{1}$$

It is denoted as the rate of heat flux (units of W) and its form depends on the nature of the transport mechanism, which can be convection, radiation or conduction (or a coupling of them) [20].

# 2.1. Convection

Heat convection takes place by means of macroscopic fluid motion. It can be caused by an external source (forced convection) or by temperature dependent density variations in the fluid (free or natural convection). In general, the mathematical analysis of convective heat transfer is extremely complex. These problems can often be solved only numerically or graphically. But convective heat flow in its most simple form, i.e. heat transfer from surface of wetted area A and temperature  $T_2$ , to a fluid with a temperature  $T_1 < T_2$ , and for small temperature differences  $\Delta T = T_2 - T_1$ , is given by Newton's law of cooling,

$$\Phi_{\rm conv} = h_{\rm conv} A (T_2 - T_1) = h_{\rm conv} A \Delta T$$
<sup>(2)</sup>

The convective heat transfer coefficient,  $h_{conv}$  (Wm<sup>-2</sup>K<sup>-1</sup>), is a function of several parameters of different kinds but independent of  $\Delta T$ .

## 2.2. Radiation

It is the continuous energy interchange between separated bodies by means of electromagnetic waves. In this mechanism the net rate of heat flow,  $q_{rad}$ , radiated by a body surrounded by a medium at a temperature  $T_1$  is given by the Stefan-Boltzmann Law

$$\boldsymbol{\Phi}_{\rm rad} = \sigma A \varepsilon \left( T_2^{\ 4} - T_1^4 \right) \tag{3}$$

where  $\sigma$  is the Stefan-Boltzmann constant, A is the surface area of the radiating object and  $\varepsilon$  is the emissivity of its surface having absolute temperature  $T_2$ . The non-linearity of Eq. (3) makes often difficult the solution of heat transfer problems. However a glance at Eq. (3) shows that if the temperature difference  $\Delta T = T_2 - T_1$  is small enough, then one could expand  $\Phi_{\rm rad}$  as Taylor series around  $T_1$  obtaining a linear relationship:

$$\boldsymbol{\Phi}_{\mathrm{rad}} = 4\sigma A \varepsilon T_1^3 \left( T_2 - T_1 \right) = h_{\mathrm{rad}} A \left( T_2 - T_1 \right) = h_{\mathrm{rad}} A \Delta T \tag{4}$$

Observing the analogy with Eq. (2) we will denote  $h_{rad} = 4\sigma \varepsilon T_1^3$  as a radiation heat transfer coefficient.

## 2.3. Conduction

#### 2.3.1. Fourier's law

Thermal conduction can be understood as a microscopic downtemperature diffusion process of heat within solids and stagnant fluids. It is a process where the thermal energy, in the case of solids, is mainly transported by phonons, the quanta of lattice vibrations, and/or free electrons. In the case of fluids (i.e. liquids and gases) this process occurs through the movement of atoms and molecules in a more complicated form due to the presence of other hydrodynamic effects, such as convection.

The local heat flow-rate in some direction, r, of homogeneous solid material is governed by Fourier's law:

$$\Phi_{\rm cond} = -kA\nabla T \tag{5}$$

The thermal conductivity, k, is expressed as the quantity of heat transmitted per unit time, t, per unit area, A, and per unit temperature gradient  $\nabla T = \partial T / \partial r$ . The negative sign indicate that heat flow will take place in the opposite direction of the temperature gradient. Thermal conductivity is a measure of the ability of a material to conduct heat. Although it depends on temperature as well as pressure and, beyond it, for solids it is highly structure sensitive parameter, over moderate ranges of temperature and pressure it can often be considered as constant. For one-dimensional steady state conduction in extended samples of homogeneous and isotropic material and for small temperature gradients Fourier's law can be integrated in each direction to its potential form. In one dimensional, rectangular coordinates it reads [20]:

$$\Phi_{\rm cond} = -kA \frac{T_2 - T_1}{x_2 - x_1} = -kA \frac{\Delta T}{\Delta x} = h_{\rm cond} A \Delta T$$
(6)

Here, k is called the mean thermal conductivity and  $h_{cond}$  is the conduction heat transfer coefficient.  $T_1$  and  $T_2$  represent two planar isotherms at positions  $x_1$  and  $x_2$ , respectively. Due to its analogy to electrical conduction, Eq. (6) is often defined as Ohm's law for thermal conduction. This analogy shows that temperature differences are equivalent to potential differences (voltage) and (continuous) heat flux plays the role of (DC) electrical current. Then, the term

$$R_T = \frac{\Delta x}{kA} \tag{7}$$

should be interpreted as a thermal resistance of the material, so that:

$$\Delta T = R_T \Phi_{\rm cond} \tag{8}$$

Fourier's law is often expressed in terms of the heat flux density,  $\phi = \Phi_{cond}/A$ , as:

$$\phi = -k\nabla T \tag{9}$$

#### 2.3.2. Cattaneo's equation

Something appears paradoxical in the description given above because Eq. (5) gives rise to infinite speeds of heat propagation. In other words, if we apply at a given instant a supply of heat to, for example, one face of a flat slab, according to Eq. (5) there is an instantaneous effect at the rear side, what of course is not physically reasonable. This paradox was resolved in the mid of the past century [21, 22] in the following way: If as a consequence of the temperature existing at each time instant, *t*, the heat flux appears only in a posterior instant,  $t + \tau$ , for one dimensional heat flux (the here achieved results are easy extensible to the three dimensional case) the Fourier's Law adopts the form:

$$\phi(x,t+\tau) = -k \frac{\partial T(x,t)}{\partial x}$$
(10)

The time  $\tau$  is the so-called relaxation time, i.e. the build-up time for the onset of the thermal flux after a temperature gradient is suddenly imposed on the sample. If  $\tau$  is small (otherwise Fourier's Law would not work for the description of daily phenomena. In condensed mater  $\tau$  is often related to the phonon relaxation time, which is in the picosecond range) then we can expand the heat flux density in a Taylor Series around  $\tau = 0$  obtaining:

$$\phi(x,t+\tau) = \phi(x,t) + \tau \frac{\partial \phi(x,t)}{\partial t}$$
(11)

,

where we have neglected higher order terms. Substituting Eq. (11) into Eq. (9) leads to:

$$\phi(x,t) + \tau \frac{\partial \phi(x,t)}{\partial t} = -k \frac{\partial T(x,t)}{\partial x}$$
(12)

This is the so-called modified Fourier's law, also known as Cattaneo's equation.

# **2.3.3.** Heat conduction under non-stationary conditions: Heat diffusion equation

When a material is subjected to non-steady heating or cooling, its inner temperature profile is given in terms of time and spatial coordinates. In the more general case the resulting heat conduction can be analyzed by combining Cattaneo's law with a heat flow balance or energy conservation

law. In each time instant, *t*, and for each point *x*, this law lauds (neglecting internal heat generation)

$$-div\phi(x,t) = \rho c \frac{\partial T(x,t)}{\partial t}$$
(13)

where  $\rho$  is the density and *c* is the specific heat. The product  $C = \rho c$  is called the specific heat capacity or heat capacity per unit volume.

From Eqs. (12) and (13) and assuming constant thermal conductivity we can obtain the homogeneous *hyperbolic* heat diffusion equation

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x,t)}{\partial t} - \frac{\tau}{\alpha} \frac{\partial^2 T(x,t)}{\partial t^2} = 0$$
(14)

where  $\alpha = k/\rho c$  is the thermal diffusivity, which can be considered as the ratio of heat conducted through the material to the heat stored per unit volume.

For  $\tau = 0$  we become the well known homogeneous *parabolic* heat diffusion equation, some times called Fourier's second law:

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x,t)}{\partial t} = 0$$
(15)

# 3. Thermal waves

## **3.1. Harmonic, periodic heat sources**

Consider an isotropic homogeneous semi-infinite solid, whose surface is heated uniformly (in such a way that the one-dimensional approach be valid) by radiation (typically a light beam in PT phenomena, as stated before) of periodically modulated intensity  $I_0(1+\cos(\omega t))/2$ , where  $I_0$  is the intensity of the source,  $\omega=2\pi f$  is the angular modulation frequency, and t is the time. The temperature distribution T(x,t) within the solid can be obtained by solving Eq. (14) with the boundary condition (BC)

$$-k\frac{\partial T(x,t)}{\partial x}\Big|_{x=0} = \operatorname{Re}\left[\frac{I_0}{2}\exp(i\omega t)\right]$$
(16)

which expresses that the thermal energy generated at the surface of the solid by the absorption of light is dissipated into its bulk by diffusion. In the above equation  $i=(-1)^{1/2}$  is the imaginary constant.

The solution of physical interest for applications in PT techniques is the one related to the time dependent component. If we separate this component from the spatial part, the temperature can be expressed as:

$$T(x,t) = \operatorname{Re}[\Theta(x)\exp(i\omega t)]$$
(17)

Substituting in Eq. (14) we obtain

$$\frac{d^2\Theta(x)}{dx^2} - q^2\Theta(x) = 0 \tag{18}$$

where

$$q = \frac{\omega}{u} \sqrt{i \frac{1}{\omega \tau} - 1} \tag{19}$$

can be considered a complex wave number and  $u = (\alpha/\tau)^{1/2}$  is a parameter having the dimension of a velocity [23, 24].

Two limiting cases can be examined.

First, for  $\omega \tau >> 1$ , i.e., for frequencies much higher than  $1/\tau$ , the wave number becomes  $q=i\omega/u$ , and the solution of Eq. (18) with the BC (16) has the form [25]

$$\theta(x) = \frac{I_0}{2\varepsilon\omega\tau} \exp\left[-i\left(\frac{x\omega}{u} + \frac{\pi}{2}\right)\right]$$
(20)

i.e.,  $T(x,t)=\Theta(x)\exp(i\omega t)$  represents a non-attenuated harmonic thermal wave traveling at a given frequency across any solid without attenuation and with velocity *u*. This case represents a form of the heat transfer taking place through a direct coupling of vibrational modes (i.e. the acoustic phonon spectrum) of the material [25].

On the other hand, for  $\omega \tau \ll 1$ ,

$$q = \sqrt{\frac{i\omega}{\alpha}} = (1+i)\sqrt{\frac{\omega}{2\alpha}} = \frac{(1+i)}{\mu}$$
(21)

where

$$\mu = \sqrt{\frac{2\alpha}{\omega}} \tag{22}$$

The general solution of Eq. (18) has yet the form

$$\Theta(x) = \frac{I_o}{2\varepsilon\sqrt{\omega}} \exp\left(-\frac{x}{\mu}\right) \exp\left[-i\left(\frac{x}{\mu} + \frac{\pi}{4}\right)\right]$$
(23)

where

$$\varepsilon = \sqrt{k\rho c} = \frac{k}{\sqrt{\alpha}}$$
(24)

is denoted as thermal effusivity.

This case represents a mode through which the heat generated in the sample is transferred to the surrounding media by diffusion at a rate determined by the thermal diffusivity. The parameter  $\mu$  gives the distance at which an appreciable energy transfer takes place. It is denoted as the damping or heat diffusion coefficient. As  $1/\tau$  is in the ps range, PT experiments, which are often performed at frequencies ranging from a few Hz up to several kHz, can be then modeled using the simplest parabolic approach.

# 3.2. The physical and mathematical properties of thermal waves

From Eqs. (17) and (23) we can obtain the temperature variations T(x,t) as:

$$T(x,t) = \frac{I_o}{2\varepsilon\sqrt{\omega}} \exp\left(-\frac{x}{\mu}\right) \operatorname{Re}\left\{\exp\left[-i\left(\frac{x}{\mu} + \omega t + \frac{\pi}{4}\right)\right]\right\}$$
(25)

This equation has a form similar to an attenuated plane wave. It is called, therefore, a *thermal wave*. Like other waves it has an oscillatory spatial dependence of the form exp (-ix / $\mu$ ), with a wave number q given by Eq. (21). Its wavelength is  $\lambda = 2\pi\mu$  and it propagates with the phase velocity given by

$$\mathbf{v}_f = \lambda \, f = \sqrt{2\alpha\omega} \tag{26}$$

The parameter  $\mu$  is called the thermal diffusion length of the thermal wave, i.e. the distance at which the wave amplitude decays *e* times from its value at the surface of the periodical heated body. Between the light excitation and the thermal response of the sample there is a phase lag given by the term  $(x/\mu+\pi/4)$  in the complex exponent.

Note that the thermal wave behaviour depends on the values of both, thermal effusivity, which determines the wave amplitude at x=0, and the

thermal diffusivity, describing the temporal and spatial behaviour of the temperature field.

As in other wave phenomena the phase velocity is defined as the velocity of points of constant amplitude in a wave. Since Eq. (18) is a linear ordinary differential equation describing the motion of a thermal wave, then the superposition of its solutions will be also a solution of it (we have approximated the temperature distribution by just the first harmonic of that superposition because the higher harmonics damp out more quickly due to the damping coefficient decrease with frequency). This superposition represents a group of waves with angular frequencies in the interval  $[\omega, \omega+d\omega]$  travelling in space as "packets" with a group velocity v<sub>g</sub>. This velocity is the phase velocity of the envelope, i.e., it is the velocity of points of constant amplitude in a group of waves and it is calculated from the dispersion relation as usually:

$$\mathbf{v}_{g} = \operatorname{Re}\left(\frac{1}{dq/d\omega}\right) = 2\sqrt{2\alpha\omega} = 2\mathbf{v}_{f}$$
<sup>(27)</sup>

On the other hand, as other kind of waves, thermal waves experiences reflection and refraction. Consider two regions, 1 and 2, separated by the plane x=0. Suppose that the incident, reflected and transmitted plane thermal waves make angles  $\theta_i$ ,  $\theta_r$  and  $\theta_t$  with the *x* axis respectively. One can show that after some straightforward calculations the reflection and transmission coefficients can be written as [2]:

$$R_{t} = \frac{\cos(\theta_{t}) - b\cos(\theta_{t})}{\cos(\theta_{t}) + b\cos(\theta_{t})}$$
(28)

and

$$T_{t} = \frac{2\cos(\theta_{t})}{\cos(\theta_{t}) + b\cos(\theta_{t})}$$
(29)

where

$$b = \frac{\varepsilon_1}{\varepsilon_2} \tag{30}$$

is the ratio of the media thermal effusivities.

It is important to note that for normal incidence ( $\theta_i = \theta_t = 0$ ) the above coefficients reduce to the more useful:

$$R_t = \frac{1-b}{1+b} \tag{31}$$

and

$$T_t = \frac{2}{1+b} \tag{32}$$

Thermal effusivity can be regarded, therefore, as a measure of the thermal mismatch between the two media.

Now suppose that we have a modulated, alternating, heat flux, related to a periodic oscillating temperature field. Following the definition of electrical impedance, Z, as a ratio of the potential difference between two points of a conductor and the flowing alternating electrical current (Z=V/I), the thermal impedance  $Z_t$  can be defined, in analogy, as the temperature difference between two faces of a thermal conductor divided by the heat flux crossing the conductor. Then the thermal impedance becomes the ratio between the change in thermal wave amplitude and the thermal wave flux. At the surface of the semi-infinite medium treated with above we get,

$$Z_{t} = \frac{\Theta(x=0,\omega) - \Theta_{0}}{-k \left. \frac{d\Theta(x,\omega)}{dx} \right|_{x=0}}$$
(33)

where  $\Theta_0$  is the ambient (constant) temperature (we will set it equal to zero for a seek of simplicity) and  $\Theta(x, \omega)$  the spatial part of the thermal wave field. Substituting Eq. (23) in Eq. (33) one obtains after a straightforward calculation:

$$Z_{t} = \frac{1-i}{\varepsilon \sqrt{\omega}} = \frac{1}{\varepsilon \sqrt{\omega}} \exp\left(-i\frac{\pi}{4}\right)$$
(34)

Note that, contrary to thermal resistance (see Eq. (7)), which depends on thermal conductivity, in the thermal impedance definition it is not only the thermal conductivity that come into play; the specific heat capacity (C) must be also considered through the thermal effusivity definition (Eq. (24)). Also in this case the thermal effusivity becomes the relevant parameter.

## **3.3. Pulsed heat sources**

Now we will analyze the case of pulsed excitation with very short duration (transient) and that of longer duration step-like excitation. We will limit here our discussion to the solution of the parabolic heat diffusion equation by supposing that the pulse period is in both cases much longer than the characteristic relaxation times. A discussion of the solution of the hyperbolic heat diffusion can be found elsewhere [26-28] and numerous works have been devoted in the last years to the peculiarities of the resulting temperature fields [29].

#### 3.3.1. Transient excitation

Consider that a light pulse of energy density  $I_0$  [J/m<sup>2</sup>] generates a heat source of density  $Q_0$  at t=0 and x=0 decaying very fast to zero. The parabolic heat diffusion equation (without loss of the generality we will assume the one dimensional case) can be written in its non-homogeneous form as:

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x,t)}{\partial t} = -\frac{Q_0 \delta(t) \delta(x)}{k}$$
(35)

where  $\delta$  is a Dirac delta function defined as:

$$\delta(z) = \begin{cases} 1 & z = 0\\ 0 & z \neq 0 \end{cases}$$
(36)

The solution of Eq. (35) is [30]

$$T(x,t) = \frac{I_0}{\varepsilon \sqrt{\pi t}} \exp\left(-\frac{x^2}{4\alpha t}\right)$$
(37)

We can see that the energy distribution is Gaussian, with a characteristic width

$$\mu_{\rm t} = 2(\alpha t)^{1/2} \tag{38}$$

After a time *t* has been elapsed the generated heat have been dissipated over a distance equal to  $\mu_{\rm t}$ . As in the case of harmonic thermal waves, this parameter called the effective thermal diffusion length, is the distance at which the wave amplitude decays *e* times from its value at the surface of the sample. The surface amplitude at *x*=0 is also determined by the inverse of the thermal effusivity. Note from Eq. (38) that the time required for the heat to diffuse throughout a distance *D* is of the order of  $D^2/\alpha$ . For typical distances in the nanometer range this time is of about 1ps, i.e., it has the order of magnitude of typical relaxation times. For these time scales the parabolic approach is no longer applicable [19].

#### **3.3.2.** Step heating

As in the former case, when a constant flux of energy  $I_0$  is applied (uniformly, i.e. in such a way that the one-dimensional approach used in what follows is valid) at a surface of a semi-infinite homogeneous solid medium the temperature distribution within the sample is given by [30, 31]

$$T(x,t) = \frac{I_0}{k} \left[ \sqrt{\frac{\alpha t}{\pi}} \exp\left(-\frac{x^2}{4\alpha t}\right) - \frac{x}{2} \operatorname{erfc}\left[\frac{x}{2\sqrt{\alpha t}}\right] \right]$$
(39)

Again, at a surface (x=0) the temperature is inversely proportional to the thermal effusivity  $\varepsilon = k/\alpha^{1/2}$  and an effective thermal diffusion length can be defined by Eq. (38).

Eqs. (37) and (39) are the basis of transient photothermal methods for thermal properties measurement, such as the well recognized Flash method, devised by Parker *et al* [32]. In this technique a sample is heated by a short duration light pulse and the temperature as a function of time is measured at its front or at its rear side, some times from the emitted black body radiation (see Eq. (4)) using an IR detector. Heat losses are minimised in these methods by making measurements in a time sufficiently small so that slightly cooling can occur.

Considering now that as a consequence of the energy absorption a sudden temperature variation from  $T_0$  to  $T_1$  takes place at the sample's surface. For the calculation of the temperature evolution in the medium one can solve the homogeneous parabolic heat diffusion equation (15) with the boundary conditions

$$T(x = 0, t \ge 0) = T_1$$
;  $T(x > 0, t=0) = T_0$  (40)

The solution of the problem for t > 0 can be expressed as [8, 33]:

$$T(x,t) = T_1 + (T_0 - T_1) \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha t}}\right)$$
(41)

From the temperature field given by the above equation one may deduce, by differentiation, the heat flow,  $q = \Phi/A$ , given by the Fourier's law. This would lead to

$$q = \frac{\varepsilon (T_1 - T_0)}{\sqrt{\pi t}} \exp\left(-\frac{x^2}{4\alpha t}\right)$$
(42)

This heat flow is not proportional to the thermal conductivity of the material, as under steady state conditions, but to its thermal effusivity. At x=0 we have:

$$q = \frac{\varepsilon (T_1 - T_0)}{\sqrt{\pi t}} \tag{43}$$

Suppose now that one brings two half infinite materials with temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ) into ideal thermal contact at t=0. The mutual contact interface acquires a contact temperature  $T_c$  in between. This means that the surface temperature of each material becomes  $T_c$ . This temperature follows from Eq. (43) by requiring that the flow out of the hotter surface equals that into the cooler one. One finds

$$\frac{\varepsilon_1(T_1 - T_c)}{\sqrt{\pi t}} = \frac{\varepsilon_2(T_c - T_2)}{\sqrt{\pi t}}$$
(44)

giving

$$T_c = \frac{\varepsilon_1 T_1 + \varepsilon_2 T_2}{\varepsilon_1 + \varepsilon_2} \tag{45}$$

According to this result, if  $\varepsilon_1 = \varepsilon_2$ ,  $T_c$  lies halfway between  $T_1$  and  $T_2$ , while if  $\varepsilon_1 > \varepsilon_2$ ,  $T_c$  will be closer to  $T_1$  and if  $\varepsilon_1 < \varepsilon_2$ ,  $T_c$  will be closer to  $T_2$ . This is the reason why when we touch bodies of equal temperature but of different effusivities, they do not seem to be equally hot or cold [17]. The contact temperature is a function of the effusivity of the body we touch [34, 35].

#### 3.3.3. The temperature relaxation method

We will analyze yet the important case of a sample heated with a step like heat pulse of very long duration so that thermodynamic equilibrium can be reached. Consider the following experimental situation. A thin slab of a solid sample of thickness L is heated with a light beam that is uniformly focused onto one of its surfaces. We will suppose that the thickness is small enough so that the effects of the temperature gradient across the sample could be ignored in the energy balance equation (see later), as has been demonstrated elsewhere [36]. On the opposite side of the sample, its temperature can be monitored as a function of time during and after the illumination is abruptly interrupted. The variation with time, t, of the generated heat in the sample, Q, due to the absorption of light of incident power  $P_i$ , is given by

$$\frac{\partial Q}{\partial t} = P_i - \Phi, \tag{46}$$

where  $\Phi$  is a term taking into account the power losses.

If we want to calculate the rise of temperature,  $\Delta T$ , of the back sample's surface, we must express the heat term of Eq. (46) as a function of that increase. It is given by the relationship

$$Q = \rho c V \Delta T \tag{47}$$

where V=AL the sample's volume. Differentiation of Eq. (47) with respect to time and substitution into Eq. (46) leads to:

$$\frac{\partial \Delta T}{\partial t} + \frac{\Phi}{\rho c V} - \frac{P_i}{\rho c V} = 0$$
(48)

Here, for small enough temperature differences, the parameter  $\Phi$  is specified by the sum of the convection, radiation and conduction linear terms given by Eqs. (2), (4) and (6) respectively. Substituting them into Eq. (48) leads to

$$\frac{\partial \Delta T}{\partial t} + \frac{h}{\rho c L} \Delta T - \frac{P_i}{\rho c V} = 0$$
(49)

where

$$h = h_{\rm conv} + h_{\rm cond} + h_{\rm rad} \tag{50}$$

The solution of Eq. (49) is well known [37]:

$$\Delta T_{\uparrow} = \frac{P_i}{Ah} \left( 1 - \exp(-\frac{t}{\tau}) \right)$$
(51)

If illumination is interrupted, then the temperature sinks exponentially to its initial value following the law

$$\Delta T_{\downarrow} = \frac{P_i}{Ah} \exp(-\frac{t}{\tau})$$
(52)

In the above equations

$$\tau = \frac{L\rho c}{2h} \tag{53}$$

This result has been used before in a technique known as the temperature relaxation method under continuous illumination for the measurement of the specific heat capacity of solids. In original variants, used with the aim of complement PT measurements of thermal properties, the sample was supported adiabatically using a poor heat conductor in a reservoir where vacuum was performed in order to neglect heat losses by conduction and convection [37]. Experiments in the presence of both, convection and radiation [36, 38] have been reported recently making use of the above presented linear relationships.

# 4. The photothermal techniques

# 4.1. Experimental

Photothermal methods can be defined as a group of highly sensitivity methods which were originally developed, and still are widely used, to measure optical absorption, but with the potential of giving access to a variety of thermodynamic and kinetic parameters of a given sample. As mentioned before the term *photothermal* comes from the detection of *thermal* relaxation of excess energy associated with *photo*excitation of the sample, although PT techniques can also detect processes and events that are not necessary of thermal origin [39].

When pulsed or periodic light energy is absorbed (Fig. 1) and subsequently totally or partially dissipated as heat, it results in sample heating, leading to temperature changes as well as changes in the thermodynamic parameters of the sample and its surroundings. Measurements of these changes are ultimately the basis for all photothermal methods that have been developed mainly in the last three decades and differ fundamentally by the kind of excitation and detection of the thermal waves. Fig. 2 synthesizes some of them.

The temperature variations could be detected directly using a pyroelectric transducer in the so called Photopyroelectric (PPE) method [40]. In the microphone based photoacoustic detection the sample is enclosed in a gas (example air) tight cell. The temperature variations in the sample following the absorption of modulated radiation induce pressure fluctuations in the gas, i.e. acoustic waves, that can be detected by a sensitive microphone already coupled to the cell [41]. The gas itself can be the sample under study [42].

Acoustic waves should be also induced in the sample itself and can be sensed by a piezoelectric sensor in contact with it in the Piezoelectric detection scheme, mainly applied in time domain, pulsed excitation experiments [43]. The sample's temperature oscillations can be also the cause



**Figure 1.** The photothermal effect schematically. The direct or indirect detection of the temperature changes in the sample or its surrounding is the basis of the PT techniques (After Ref. [2]).



Figure 2. Some photothermal detection schemes.

of periodical black body infrared electromagnetic waves that are radiated by the sample and that can be measured using an appropriate sensor in the PT radiometry method [44], in a way similar as in the Flash technique described before. The temperature changes induces variations in the sample's optical reflection coefficient, modulating the intensity of a probe laser beam in PT reflectance [45], and those induced in the refraction index of the sample or its surrounding media are detected also with a probe laser beam in the Mirage technique [46] and in the thermal lens technique [47]. Other detection schemes can be devised. Due to the frequency dependence of the thermal diffusion length and of the phase lag in experiments with intensity modulated light excitation, and the existence of a time delay between laser excitation and the detection of thermal waves in pulsed experiments, the monitoring of the time and spatial dependence of the oscillating temperature fields offers the possibility to obtain depth resolved information on optical and thermal parameters [48, 49].

The detection of the thermal response is performed in several ways, either in direct contact or without contact of the detector with the sample (see table I). Besides oscillatory temperature fields, which are analyzed in the frequency domain using a synchronous lock-in amplifier (Fig. 3 shows a



**Figure 3.** A typical experimental set-up for experiments performed in the modulation frequency domain. A PA cell was chosen for illustration of the PT sensor. In non-spectroscopic applications the lamp and the monochromator are often substituted by continuous laser sources. The whole apparatus is frequently computer controlled for data acquisition and processing.

typical experimental set-up), also pulse heating is frequently used, where data recording is performed using oscilloscopes, boxcar systems, or fast A/D converters. In modulated excitation schemes, radiation sources are employed whose intensities fluctuate periodically in the form of a square or a sine wave, resulting in a 50% duty cycle. This can be realized for example by mechanical chopping or by electronic modulation of the light source. In pulsed experiments lasers are also usually employed for excitation, in which short illumination intervals followed by a much longer dark period are available, i.e. a very low duty cycle.

The existence of superimposed signals of different nature can be a possible source of complexity in the data analysis. However, instead of being a drawback, this has turned out to be a feature which can, in principle, yield a wealth of information otherwise not obtainable. Although data analysis is often complicated requiring in many cases sophisticated approaches, in a number of situations of practical interest it can be simplified by making reasonable assumptions. In the following section we will briefly describe some features of the theory behind the PT methods which constitute the basic of the principal applications of the PT techniques.

## 4.2. Theoretical considerations

#### **4.2.1.** Photothermal experiments in condensed matter

Perhaps the simplest theory describing the generation of the PT signal in frequency domain is based in the well-known RG model for PA signal generation [10]. This constitutes the fundamental theoretical apparatus for the most applications in the field even neglecting important contributions such as those due to thermoelastic effects [50, 51], volatile components evaporation [52], and spatial and temporal distributed heat sources as occurs in doped substances [53] and semiconductors [54, 55], among others. On its basis we will discuss now what we can call the general model for the PT [56] signal generation in condensed matter under intensity modulated light excitation of thermal waves.

In Fig. 4 a schematic view of the experimental situation is given.

In the discussion of section 3 we assumed that the incident energy was absorbed at the sample surface. Now we will consider that the heat density generated at any point x in the sample due to the absorption of light of intensity  $I_0$  and wavelength  $\lambda$  modulated at a frequency  $\omega = 2\pi f$  is:

$$H(x) = \eta \beta I_0 (1 - R) \frac{\left[1 + \exp(i\omega t)\right]}{2} \exp(\beta x)$$
(54)



**Figure 4.** Schematic view of a typical experimental situation showing the relevant coordinates for the standard one-dimensional model.

where  $\beta$  and *R* are the sample absorption and reflection coefficients at the photon energy respectively and  $\eta$  is the light energy into heat conversion efficiency. We will assume that only the sample absorbs light, thus no heat generation takes place in the gas and the backing media. Note that, depending on the detection method, one can be interested in the temperature distribution in different regions of the Fig. 4. The temperature distribution in each region can be obtained by solving the heat diffusion equation for the gas, sample and backing with the BC given by the continuity of temperature and heat flux at the interfaces at x=0 and x=-l. For most of the PT methods the values of the temperature at the gas sample interface is of major importance. It is given by [10, 56]

$$T(0,t) = \Gamma \exp[i(\omega t)]$$
(55)

where

$$\Gamma = \frac{\beta(1-R)I_0\eta}{2k_s(\beta^2 - q_s^2)} \frac{(r-1)(b+1)\exp(q_s l) - (r+1)(b-1)\exp(-q_s l) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(q_s l) - (g-1)(b-1)\exp(-q_s l)}$$
(56)

Here  $b = \varepsilon_b/\varepsilon_s$ ,  $g = = \varepsilon_g/\varepsilon_s$ ,  $r = (1-i)\beta\mu_s/2$  and  $q_s = (1+i)/\mu_s$ . The subindexes g, s and b refer to the gas, sample and backing regions respectively.

Following Rosencwaig and Gersho [10], different limiting cases can be discussed by comparing the three main characteristic lengths involved in the

problem: The sample's thickness l, the thermal diffusion length  $\mu_s$  and the light penetration depth  $\mu_{\beta}=1/\beta$  (Fig. 5). One can deal therefore with optically transparent ( $\mu_{\rm B} >> l$ ) or opaque samples ( $\mu_{\rm B} << l$ ), and in each case with thermally thick ( $\mu_s \ll l$ ) or thin ( $\mu_s \gg l$ ) samples. Such an analysis can be found in the pioneer work of Rosencwaig and Gersho [10]<sup>1</sup>. For optically transparent samples (Case I of Fig. 5) the signal depends on the product  $\beta l$ when the sample is thermally thin and on  $\beta \mu_s$  if it is thermally thick. These products determine the distance from which useful information can be obtained and suggest the possibility of spectroscopic applications. In the second case only light absorbed within the thermal diffusion length contributes to the signal [10]. For thermally thin samples (cases IA and B) the thermal effusivity of the backing comes into play whereas the signal for thermally thick samples depends on both, thermal diffusivity and effusivity of the sample (IC). On the other hand, for optically opaque samples (case II) the signal can be determined by the thermal properties of both, the sample and/or the substrate backing material. This result is useful for applications involving thermal properties determination. Only the particular situation IIB, for which the sample becomes thermally thick with the thermal diffusion length smaller than the optical penetration depth, allows spectroscopic measurements.

For a given sample  $\mu_{\beta}(\lambda)$  can be varied by changing the wavelength whereas  $\mu_s(\omega)$  can be controlled by adjusting the modulation frequency, a fact that renders noticeable experimental possibilities. Note also that the role of backing and sample can be interchanged in a given experimental situation. It is also worth to notice that often one needs a calibration procedure because many parameters involved in Eq. (56) can be unknown for the experimenter and due to the fact that the relationships between the measured signals given by the used detectors and the temperature can be rather complicated. In spectroscopic measurements one often uses carbon black as the reference sample. Thin metal foils of well known thermal properties can be used in transport properties characterization experiments, among others.

One may also choose to detect the rear temperature variation at the sample-backing interface. Thoen and Glorieux [56] have obtained the following result:

 $T(l,t) = \Gamma \exp[i(\omega t)]$ 

(57)

<sup>&</sup>lt;sup>1</sup>Note that these authors have developed their work only for the special case of PA detection, where the whole arrangement displayed in Fig. 4 has been enclosed in a PA cell. They obtained an expression for the pressure in the PA gas chamber differing slightly (mainly in the frequency dependence) from our Eq. (57).

#### E Marin



**Figure 5.** Schematically representation of the particular cases mentioned in the text for the front side temperature. In the left hand side we show the results to which the approximations performed in Eq. (57) lead. Note that for optically transparent solids (Eq. 59) the frequency dependence of the front temperature amplitude is  $\omega^{1/2}$  for thermally thin samples and  $\omega^{-1}$  for thermally thick ones. For optically opaque and for both thermally thin and thermally thick samples the signal depends as  $\omega^{-1/2}$  (Eq. (60) whenever  $\mu > \mu_{\beta}$ . For thermally thick samples the signal scales with  $\omega^{-1}$  if  $\mu < \mu_{\beta}$ . The modulation frequency dependence can allow us the identification of the particular case at hand in a given experiment. where

$$\Gamma = \frac{\beta(1-R)I_0\eta}{2k_s(\beta^2 - q_s^2)} \frac{(r-1)(g-1)\exp[-(\beta + q_s)l] - (r+1)(g+1)\exp[(q_s - \beta)l] + 2g + 2r}{(g+1)(b+1)\exp(q_s l) - (g-1)(b-1)\exp(-q_s l)}$$
(58)

Note that the backing can be substituted by air, if remote detection is required such as in the mirage or radiometric detection schemes, by a pyroelectric sensor in a PPE method, or by a PA open cell detection in heat transmission configuration [57], among others. Particular cases of Eq. (57) can also be discussed, in a way similar as doing with Eq. (55). Spectroscopic applications are possible for optically transparent as well as for opaque samples, as discussed by Chirtoc *et al* [58], a result used in photopyroelectric and

photoacoustic spectroscopy of semiconductors by Christofides et al [59] and Vigil et al [60] respectively. If the sample is optically opaque for the radiation impinging on its front face, opposite to the sensor, and thermally thick, the PT signal will depends on its thermal diffusivity in a [61], allowing the straightforward manner, namely  $T(l,t) \sim \exp(-q_s l)$ determination of this parameter from both the amplitude or the signal phase. In other useful configurations, the backing can also play the role of a sample and the later can be substituted by a thermally thin and optically opaque pyroelectric detector in a so-called front detection configuration for which the signal will depends on the inverse of the sample's thermal effusivity [62]. The pyroelectric and similar detection schemes [63] in both, front and rear side configurations, have been widely used in the last years for thermal characterization [64] and in applications involving thermal properties variations such as phase transition studies [65] and study of dynamic processes in liquids [66, 67], among others.

When short duration laser pulses are used the light absorption leads to an instantaneous adiabatic expansion of the medium, generating pressure pulses that propagate through the sample at the speed of sound, c [68]. These ultrasonic pulses can be detected photoacoustically at the sample's boundary by piezoelectric transducers or by optical methods [69] such as thermal lens or mirage. As in modulated PT techniques the signal is proportional to the excitation energy and the absorption coefficient of the sample. For a useful discussion about pulsed experiments in condensed matter the earlier review of Patel and Tam [70] about PA spectroscopy is recommend.

## 4.2.2. Gas-phase experiments

In the case of gaseous samples the majority of the published work deal with PA spectroscopy for traces detection, whose basic principles can be found elsewhere [71]. A modulated light energy of suitable wavelength, selected so that the absorption spectrum of the molecules of the investigated substance can be accessed (often a thermal IR source, and a CO or a  $CO_2$  continuous wave IR laser are used), is absorbed by the molecules in a spectroscopically selective step. The absorbed energy is then transformed into sound following relaxation processes whose rates depend on the properties of the participating molecules. The generated sound can be detected by a sensitive microphone. There are some special requirements for the PA cells used for gas phase measurements: They must be mainly resonant cells and the gas volume has to be sufficiently small so that no dilution takes place when the produced trace gas is flowed through the cell volume. Siegrist [17] has considered detection schemes different from PA detection. Although

the author concludes that the PA technique appears to give the simplest and most sensitive solution, there are instances, however, where other approaches such as thermal lens are necessary.

Other applications of PT methods to gases characterization are still scarce, although recently Shen and Mandelis [72] and Lima et al [73] described about the potential use of the so-called thermal wave interferometry for thermal properties measurement and study of diffusion processes [74]. A thermal wave interferometer (TWI) consists of a cavity of variable length formed between a thin metallic foil and a pyroelectric temperature sensor. A modulated laser light beam impinges on the outer surface of the metallic foil, which acts as a light absorber, thus launching thermal waves into the gas filled cell. According to the wave model the thermal waves propagate back and forth between the foil and the sensor. On striking the gas-foil and gas-sensor boundaries, they are partially reflected, and interference between the reflected and incident wave trains will set in [73]. The temperature oscillations resulting from the superposition of all arriving waves can be measured with the sensor as a function of the gas laver thickness. The measured signal depends on the gas thermal diffusivity in a relative simple manner. The potential uses of TWI not only for gases but also for liquids [75] and solid samples coatings thermal characterization [76] have been recognized nowadays as well established applications of thermal wave physics.

# **5.** Conclusions

In this introductory chapter we have tried to give a brief overview about the basic principles behind thermal wave physics on which the different photothermal methods and applications can be constructed. We have shown how the spatial and temporal dynamic temperature fields created in a sample by time variable optical excitation are tightly linked to the boundary conditions imposed by the kind of excitation. Photothermal methods have become common and useful tools in many scientific and industrial laboratories. Their easy of use and versatility increase the fields of applications and new areas of research are emerging at a rapid rate. Very promising is the presence of these methods in multidisciplinary experiments involving people with expertise in dissimilar areas such as biology, chemistry, physics, material science, medicine, environmental science, food industry and so on. Much of these developments are possible because photothermal methods have several advantages over more conventional techniques such as the wide dynamic range, the possibility they offers to perform optical measurements in highly opaque samples, and in those in the form of powers, gels, etc. The lesser influence from light scattering when compared with optical techniques, the possibility of depth profiling in layered samples, the non necessity of electrical contacts for transport properties measurements, and the straightforward mathematical formalism behind them, are also advantages of the method. The most common PT techniques are based on modulated excitation of thermal waves in condensed matter samples, and in the pulsed excitation and direct generation of sound waves, mainly in gaseous samples. The availability of compact light sources of high intensity and with a wide range of available wavelengths, such as continuous and pulsed lasers of very short duration, as well as the development of new techniques for the detection of signals with low signal to noise ratio and the existence of strong computer capabilities will expand the field of applicability of these methods in the near future.

# Acknowledgements

The support of SIP-IPN projects 20080032 and 20090160, SEP-CONACyT grants 61-541 and 83-289 and COFAA-IPN is greatly acknowledged.

# References

- 1. Fourier, B. 1952, "Analytical theory of Heat", Encyclopedia Britannica, Inc., Chicago.
- 2. Almond, D. P. and Patel, P. M. 1996, "Photothermal Science and Techniques" in "Physics and its Applications, 10", E.R. Dobbsand and S.B. Palmer (Eds), Chapman and Hall, London.
- 3. Poisson, S. D. 1855, "Théorie Mathématique de la Chaleur", Bachelier, Imprimeur-Libraire, Paris.
- 4. Hanks, R. J. 1992, "Applied soil physics. Soil water and temperature applications", 2nd ed., Springer-Verlag, New York.
- Fuhrer, O. 2000, "Inverse Heat Conduction In Soils A New Approach Towards Recovering Soil Moisture From Temperature Records" Diploma Thesis Climate Research ETH, Zurich ETH Zurich, Dept. Physics. http://iacweb.ethz.ch/staff/ fuhrer/publ/dipl /
- 6. McIntosh, G. and Sharratt, B. S. 2001, The Phys. Teach., 39, 458.
- 7. Marín, E., Jean-Baptiste, E. y Hernández, M. 2006, Revista Mexicana de Física, E52, 21.
- 8. Marin, E. 2007, European Journal of Physics, 28, 429.
- 9. Ångström, A. J., 1861, Ann. Physik. Lpz. 114, 513.
- 10. Rosencwaig, A. and Gersho, A. 1976, J. of Appl. Phys., 47, 64.
- 11. Rosencwaig, A. 1975, Phys. Today 28, 23.
- 12. Bell, A. G. 1880, Am. J. of Sci. 20, 305.
- 13. Röntgen, W. K. 1881 Ann Phys Lpz., 12, 155.
- 14. Tyndall, J. 1881 J. Proc. R. Soc. London, 31, 308.

- 15. Lord Rayleigh 1881 Nature, 23, 274.
- 16. Viengerov M. L. 1938 Dokl. Akad. Nauk. SSSR, 19, 687.
- 17. Sigrist M.W. 1994 in "Air Monitoring by Spectroscopyc Techniques" M.W. Sigrist (Ed.) Wiley, New York, 163.
- 18. de Vries, H. S. M. 1995 "Non-intrusive fruit and plant analysis by laser photothermal measurements of ethylene emission" in "Modern methods of plant análisis" H.F. Linskend and J.F. Jackson (Eds) Springer-Verlag, Heidelberg.
- 19. Greffet, J. 2007 "Laws of Macroscopic Heat Transfer and Their Limits", in "Microscale and nanoscale Heat Transfer", S. Volz (Ed.), Topics in Applied Physics, 107 Springer, Paris, pp. 7-13.
- Landolt-Bornstein, 2005, "Thermal Transport" in "Numerical Data and Functional Relationships in Science and Technology: New Series III", O. Madelung and G. K. White (Eds.) 2.3.1.11. Springer, Berlin, pp 2-217.
- 21. Vernotte, P. 1958 C. R. Acad. Sci., 247, 2103.
- 22. Cattaneo, O. C. 1948 Atti del Semin. Mat. E Fis. UnIII. Modena 3, 3.
- 23. Joseph, D. D. and Preziosi, L. 1989 Rev. Mod. Phys., 61, 41.
- 24. Joseph, D. D. and Preziosi, L. 1990 Rev. Mod. Phys., 62, 375.
- 25. Marin, E., Marin, J. and Díaz, P. 2002 Eur. J. Phys., 23, 523.
- 26. Qiu, T. Q., Tien, C. L. 1993 J Heat Transfer, 115, 835.
- 27. Vick, B. and Ozisik, M. N. 1983 J. Heat Transfer, 105, 902.
- 28. Marin, E., Marin, J. and Hechavarría R. 2005 J. Phys. IV. 125, 365.
- 29. Haji-Sheikh, A., Minkowycz, W. J. and Sparrow, E. M. 2002 J. Heat Transfer, 124, 307.
- 30. Carlslaw, H. S. and J. C. Jaeger 1959 "Conduction of Heat in Solids" Oxford Univ. Press, London.
- 31. Lau, S. K., Almond, D. P. and Patel, P. M. 1991, J. Phys. D: Appl. Phys. 24, 428.
- 32. Parker, W. J., Jenkins, R. J., Butler, C. P. and Abbott, G. L. 1961 J. Appl. Phys. 32, 1679.
- 33. Boeker, E. and van Grondelle, R., 1999 "Environmental Physics" John Wiley and Sons, New York.
- 34. Marín, E. 2006 Phys. Teach., 44, 432.
- 35. Marín, E. 2008 LAJPE 2, 15.
- Valiente, H., Delgado-Vasallo, O., Galarraga, R., Calderón, A. and Marin, E. 2006 Int. J. Thermophys., 276, 1859.
- Mansanares, A. M., Bento, A. C., Vargas, H., Leite, N. F. and Miranda, L. C. M. 1990 Phys. Rev. B 42, 4477.
- 38. Marín, E., Delgado-Vasallo, O. and Valiente, H. 2003 Am. J. Phys., 71, 1032.
- 39. Gensch, T.and Viappiani, C. 2003 Photochem. Photobiol. Sci., 2, 699.
- 40. Mandelis, A. and Zver, M. M. 1985 J. Appl. Phys., 57, 4421.
- 41. Vargas, H. and Miranda, L.C.M. 1980 Physics Reports, 161, 43.
- 42. Pao, Y. H. 1977 "Optoacoustic Spectroscopy and Detection", Academic, N.Y.
- 43. Jackson, W. and Amer, N. 1980 J. Appl. Phys., 51, 3343.
- 44. Chen, Z. H., Bleiss, R. and Mandelis, A. 1993 J. Appl. Phys., 73, 5042.
- 45. Rosencwaig, A., Opsal, J., Smith, W. L. and Willenborg, D. L. 1985 Appl. Phys. Lett., 46, 1013.
- 46. Boccara, A. C., Fournier, D. and Badoz, J. 1980 Appl. Phys. Lett., 36, 130.

- 47. Bialkowski, S. E. 1996 "Photothermal Spectroscopic Methods for Chemical Analyses" J. D. Winedorfer (Ed) Wiley, New York.
- 48. Helander, P. and Lundström, I. 1983 J. Appl. Phys., 54, 5069.
- 49. Cesar, C. L., Vargas, H. and Miranda, L. C. M. 1985 J. Phys. D: Appl. Phys. 18, 599.
- 50. Mc. Donald, F. A. and Wetsel, G. C. Jr. 1978 J. of Appl. Phys., 49, 2313.
- 51. Rousset, G., Lepoutre, F. and Bertrand, L. 1983 J. of Appl. Phys., 54, 2383.
- 52. Korpiun, P. 1984 Appl. Phys. Lett., 44, 675.
- 53. Quimby, R. S. and Yen, W. M. 1980 J. Appl. Phys. 51, 4985.
- 54. Miranda, L. C. M. 1982 Appl. Opt. 21, 2923.
- 55. Marín, E., Vargas, H., Diaz, P. and Riech, I. 2000 Phys. Stat. Sol.(A), 179, 387.
- 56. Thoen, J. and Glorieux, C. 1997 Thermochim. Acta, 304/305,137.
- Marquezini, M. V., Cella, N., Manzanares, A. M., Vargas, H. and Miranda, L. C. M. 1991 Meas. Sc. and Techn., 2, 396.
- 58. Chirtoc, M., Chirtoc, I., Bicanic, D. and Pelzl, 1995 J. Ferroelectrics, 165, 27.
- 59. Christofides, C., Engel, A.and Mandelis, A. 1989 Rev. Sci. Instrum, 61, 2360.
- Vigil-Galán, O., Sánchez-Meza, E., Sastré-Hernández, J., Cruz-Gandarilla, F., Marín, E., Contreras-Puente, G., Saucedo, E., Ruiz, C. M., Tufiño-Velázquez, M. and Calderón, A. 2008 Thin solid films 516, 3818.
- 61. Christofides, C., Mandelis, A., Gandhi, K. and Wagner, R. E. 1990, Rev. Sci. Instrum. 61, 2360.
- 62. Dadarlat, D., Chirtoc, M., Neamtu, C., Condea, R. M., Bicanic, D. 1990 Phys. Status Solidi A, 121, K231.
- 63. Delgado-Vasallo, O. and Marín, E. 1999 J. of Phys. D: Appl. Phys. 32, 593.
- 64. Favier, J.P., Dadarlat, D., Gibkes, J., van den Berg, C. and Bicanic, D. 1998, Inst. Sc. and Technol. 26, 113.
- 65. Dadarlat, D., Bicanic, D., Visser, H., Mercuri, F. and Frandas, A. 1995 JAOCS 72, 281.
- 66. Miranda, L. C. M. and Cella, N. 1993 Phys. Rev. B, 47, 3896.
- 67. Landa, A., Alvarado-Gil, J. J., Gutiérrez-Juarez, G. and Vargas-Luna, M. 2003 Rev. Sc. Instrum. 74, 377.
- 68. Schmidt, T. 2006 Anal. Bioanal. Chem. 384, 1071.
- 69. Gusev, V. E., Karabutov, A. A. 1993 "Laser optoacoustics". AIP, NY.
- 70. Patel, C. K. N. and Tam, A. C. 1981 Rev. Mod. Phys. 53, 517.
- 71. Harren, F. and Reuss, J. 1997 in "Encyclopedia of Applied Physics 19", VCH Publishers, Inc., 413.
- 72. Shen, J., Mandelis, A. and Tsai, H. 1998, Rev. Sci. Instrum. 69, 198.
- Lima J. A. P., Marín E., Cardoso S. L., Takeuty D., da Silva M. G., Sthel M. S., Rezende C. E., Gatts C. N., Vargas H. and Miranda L.C.M. 2000, Rev. of Sci. Inst. 71, 2928.
- 74. Lima, J. A. P., da Silva, M. G., Massunaga, M. S. O., Marín, E., Vargas, H. and Miranda, L. C. M. 2002 Journal of Applied Physics 91, 5581.
- 75. Lima, J. A. P., Marin, E., Massunaga, M. S. O., Correa, O., Cardoso, S. L., Vargas, H. and Miranda, L. C. M. 2001, Appl. Phys. B: Lasers and Optics 73, 151.
- 76. Bennett, C. A. and Patty, R.R. 1982 Appl. Opt., 21, 49.