CHAPTER I
INTRODUCTION TO PHOTOTHERMAL EFFECTS

1.1 INTRODUCTION TO PHOTOTHERMAL SCIENCE

The ever growing interest in optical communication and the continuing progress in the development of high power lasers motivate the development of sensitive techniques to measure low absorption losses in highly transparent solids, thin films and optical coatings. Photothermal technique encompass a wide range of techniques and phenomena based upon the conversion of absorbed optical energy into heat. Optical energy is absorbed and eventually converted into thermal energy by solids, liquids and gases. Although the initial absorption processes in many materials is very selective, it is common for excited electronic states in atoms or molecules to loose their excitation energy by a series of non-radiative transitions that result in a general heating of the material.

Absorption of electromagnetic radiation by matter causes absorption, emission and inelastic scattering of light. Except for emission, absorbed energy results in production of several forms of energy like luminescence, photochemical energy, photoelectricity or heat. Heat can be produced promptly or at various time delays. This heating induces changes in the sample as well as in the surrounding medium. These changes are referred to as photothermal effects [1,2]. Although it may seem counterintuitive to pursue phenomena based on the transformation of energy to the most chaotic form, heat, these techniques have many advantages for applications in low
absorption environments and in the domain of materials characterization and nondestructive testing. PT material probing is the most important in making significant contribution to the field of science and technology. Photothermal material characterization relies on high sensitivity detection techniques to monitor the effects caused by PT material heating of a sample.

In recent years thermal wave physics emerged as effective research and analytical tool for the characterization of materials.[3,4] The nondestructive and nonintrusive photothermal methods are based on the detection by one means or the other, of a transient temperature change that characterises the thermal wave generated in the sample after illumination with a pulsed or chopped optical radiation.[5-19] The detected photothermal signal depends on the optical absorption coefficient as well as how heat diffuses through the sample [20-24]. Dependence of photothermal signal on how heat diffuses through the specimen allows the investigation of transport and structural properties such as thermal diffusivity, thermal effusivity, thermal conductivity, voids, etc [25-34]). Photothermal methods can be effectively used for the optical characterization of the sample due to its dependence on optical absorption coefficient [35-39]. The unique feature of photothermal methods is that the detected photothermal signal depends only on the absorbed light and it is independent of transmitted or scattered light. The two features that make photothermal methods superior to conventional methods is that it can directly monitor the nonradiative path of deexcitation in addition to being sensitive to very small optical absorption coefficient[38-39]. Apart from this, photothermal effects can amplify the measured optical signal which is referred to as enhancement factor and it is the ratio of the signal obtained using photothermal spectroscopy to that obtained using conventional transmission spectroscopy. Enhancement factors depend on thermal and optical properties of the sample, the power of energy of light source and the optical geometry used
to excite the sample[40]. As these parameters can vary externally, photothermal methods can be used even for specimens having relatively poor thermal and optical properties. The merit of these methods also lies in the extremely sensitive detection technique used here in comparison to conventional transmission methods. The various photothermal methods are depicted in Fig. 1. The magnitude of photothermal signal depends on the specific method used to detect the photothermal effect and on the type of the sample analysed.

Most of the photothermal effects occur simultaneously. The choice of a suitable PT source depends on the purpose of measurement. In short PT generation is an example of energy conversion and has in general three kinds of applications. a) PT material probing: do not cause any sample modification. b) PT material processing: causes the sample to change to another useful form. c) PT material destruction: makes the sample useless.
The different techniques that are employed in Photothermal methods are shown in Table I.

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The detecting parameter changes in all techniques even though all techniques are based on the same principle.

Temperature rise occurring in the sample can be directly measured using thermocouples, thermistors, or pyroelectric detectors and is called laser calorimetry or photothermal calorimetry [41,42]. In the photopyroelectric techniques [43-45] which can be used for the simultaneous measurement of different thermal parameters such as thermal diffusivity, effusivity etc a
thermally thick pyroelectric film (thickness of film greater than thermal diffusion length of the film) is attached to one side of the thermally thick backing medium. The other side of the specimen is illuminated by an intensity modulated optical radiation. When thermal waves reach the pyroelectric sensor sample interface, the pyroelectric sensor detects an electric current which contain information about the structure and thermal properties of the sample. A variant configuration of the standard photopyroelectric method, well suited for thermal effusivity measurements, is the so-called inverse photopyroelectric technique. In this method light is incident directly on the surface of pyroelectric transducer and the substrate is substituted for the sample. Application of IPPE technique for the thermal effusivity of margarines, cultured milk and pastry materials is a typical example of the potential application of this technique for the quality control of the food stuff. 

Direct determination of the thermal conductivity of solids and liquids was recently discussed by Thoen and co-workers. In photothermal radiometry, the temperature changes are measured indirectly by monitoring the infrared emission and it can be used in situations where a large temperature change has occurred. Although not very sensitive, this method has potential application in non-destructive materials analysis and testing. Using sensitive infrared cameras, it can be used for imaging the thermal properties of large samples. However, in photothermal radiometry, a more careful analysis of the spectral detectivity of detector, spectral absorption of the sample and the geometry of the optical equipment are essential. The inherent advantage of this technique is that signal can be obtained remotely. The shapes of the objects can be arbitrary. Nevertheless, it is better to make sure that the quality for imaging a sample spot
on the detector is constantly good. Signal evaluation may be complicated if the sample is transparent or reflective in the infrared spectral range.

Another temperature dependent parameter exploited is the pressure change. Pressure variations or modulations resulting from the absorption of modulated light by the sample are referred to as optoacoustic or photoacoustic generation [51,52,53]. The pressure wave generated after light excitation contains contributions from various sources such as radiation pressure, electrostriction, thermoelastic expansion (by non radiative transition or thermal energy of chemical reaction), photoinduced volume change, gas evolution, boiling, ablation and dielectric breakdown. The acoustic wave can be detected in the sample itself (i.e. direct photoacoustic detection) or it can be detected via coupling fluid medium adjacent to the sample.

The majority of studies addressing the use of photothermal spectroscopy for chemical analysis have been based on the refractive index measurements. The refractive index change produced upon light absorption may be induced by the pressure wave, density change, a temperature change (by radiationless transition or chemical reaction), molecular alignment, vibration excitation, rotational excitation, electronic excitation, concentration change, photoinduced volume change, creation of electric field (charge creation), clustering and so on. In transparent samples, the temperature dependent changes in refractive index of the sample itself are probed. For opaque samples, the temperature dependent changes in refractive index of the fluid that couples heat out of the sample are measured. Two types of refractive index gradient are produced- Thermal RIG and Acoustic RIG. The thermal RIG is produced by the decreased density of the medium caused by the local temperature rise, decays in time following the diffusional decay of the temperature profile and remains near the initially optically excited region. The
Acoustic RIG is associated with the density fluctuation of the medium caused by the propagation of PA wave, decays in propagation distance following attenuation of the PA wave and travels at acoustic velocity away from initially optically excited region. The thermal RIG generated by the excitation beam affects the propagation of an optical beam in its vicinity, including its own propagation resulting in a well-known effect of thermal blooming self-defocusing or [54] In other words, spatial dependent refractive index profiles can also result in focusing and defocusing of light. The thermally perturbed sample acts as lens. Light transmitted through an aperture placed beyond the photothermal lens will vary with the strength of the lens. Photothermal methods based on the measurement of the strength of the lens are known as Photothermal lensing spectroscopy [55,56] The thermal RIG also affects the propagation of another weak beam in the vicinity of the excitation beam. Thus, as light exits the medium, with a refractive index gradient, at an angle relative to the incident ray. The detection of bending of light path is utilized in Photothermal deflection method.[57-61] In some experimental measurements a signal that is due the combined effects of deflection and lensing is detected. These can be generally classified as Photothermal refraction methods [62] and take advantage of the effects of the temperature distribution on the probe beam propagation. The optical path length changes that occur due to the Photothermal induced refractive index change can be measured with interferometry. A periodic refractive index modulation results in a volume phase diffraction grating. The grating will diffract light at an angle that meets requirements from Bragg’s law. The amount of light diffracted is proportional to the refractive index change. The diffracted light is measured with a photoelectric detector. Methods used to measure spectroscopic signals based
on volume phase grating formed by the photothermal heating are called Photothermal diffraction spectroscopy.[63,64]

![Figure 2: Perpendicular probe beam deflection through the sample](image)

In steady state isobaric conditions, the temperature change due to non-radiative de-excitation can result in a variation in the volume expansion coefficient, and a consequent change in the density of the specimen. Though temperature dependent density changes are difficult to measure directly, these changes can affect the samples in several different ways. In solid samples, the density change alters the physical dimensions at sample surface. Sample dimension changes give rise to two optical methods for monitoring temperature changes based on surface deformation. A homogeneous deformation displaces the surface of the sample. Interferometry can be used on reflective samples. Since small displacements of the order of few parts per million of the wavelength of the probe beam light can be measured using interferometry, this method may be used for sensitive measurements. Spatially
heterogeneous expansion (contraction) can also cause the surface angle to change. A probe beam reflected from the surface will change angle when heterogeneous expansion occurs. Measurement of probe beam angle gives rise to the method of PT surface displacement technique [65,66,67].

Temperature changes can also be indirectly measured using methods, which monitor infrared emission since the thermal infrared emission is related to sample temperature. The method of photothermal radiometry [68] can be used to measure the infrared emission changes. Although not very sensitive, this method has great potential application in non-destructive material analysis and testing. Using infrared sensitive cameras, it can be used for imaging the thermal properties of large samples.

Modulated PT heating of many types of metal or semiconductor samples causes modulated reflectivity changes [69] or transmission and scattering changes [70] that can be due to density change or the photoacoustic carrier generation at the surface. Transient thermal reflectance can be used to monitor thermal properties. PT heating can cause changes in absorptivity of the sample. Zapka and Tam have used probe beam absorption measurements to detect the change in the Boltzmann molecular population distribution due to PT heating of a gaseous sample [71].

Temperature changes resulting from optical absorption are directly related to heat capacity and thermal conductivity. Photothermal signals depend on the thermodynamic and energy transfer properties of the sample. Since the thermal and optical properties are to be known to a high accuracy, absolute sample absorption measurements are difficult. Hence, the dependence on thermodynamic and energy transfer properties allows for the analysis of thermal structure of materials. Photothermal methods have been efficiently used for the measurement of acoustic velocities, thermal diffusion coefficients.
sample temperature, bulk flow rates, phase transition, volume expansion coefficients and heterogeneous thermal conductivities in the solids [72-79]. The advent of the coherent, monochromatic and highly unidirectional light source namely laser had led a major renaissance in this field. For an excitation of a sample with a given absorption coefficient, the temperature change will be proportional to the optical power, in the case of continuous excitation or pulsed excitation. The photothermal signal is generally proportional to the temperature change. Thus, the great power and high spectral purity, lasers can deliver high power or pulsed energies over very narrow optical bandwidths thereby enhancing the photothermal signals. The temperature change is proportional to the optical power or energy, but at the same time is inversely proportional to the volume over which light is absorbed since the heat capacity scales with the amount of substance. The spatial coherence properties of the laser light also allow the light to be focussed to small, diffraction-limited volumes. The small volumes enhance the signal magnitude and allow the photothermal spectroscopy to be used in small volume sample analysis and allow for microscopic analysis of heterogeneous samples.

1.2 Photoacoustic technique.[81]

The photoacoustic effect is the generation of acoustic waves in the specimen after illumination with a chopped or pulsed optical radiation. In the case of Photoacoustic technique the excitation beam is not focussed in order to minimize the lateral heat flow. Hence, the heat diffusion can be analysed by one-dimensional calculation of the periodic temperature field.[82]
Consider a simple cylindrical cell of length $L$ and diameter $D$ as shown in figure 4. Assume that the length $L$ is small compared to the wavelength of the acoustic signal. The sample is considered to be in the form of a disk having diameter $D$ and thickness $D$.

The sample is mounted so that its front surface is exposed to the gas (air) within the cell and its back surface is a poor thermal conductor of thickness $l_b$. The length $l_g$ of the gas column in the cell is then given by $l_g = L - l - l_b$. Further assumption is that the gas and backing materials are not light absorbing.

Let $k_i$, $\rho_i$, $C_i$, $\alpha_i$ represent the thermal conductivity, density, specific heat and thermal diffusivity respectively of the material $i$. Then $\alpha_i = (\omega/2\alpha_i)^{1/2}$ is the thermal diffusion co-efficient and $\mu_i = 1/a_i$ is the thermal diffusion length of the material. $i$ can take subscripts $s$, $g$ and $b$ for solid, gas and backing material respectively. $\omega$ denotes the chopping frequency of the incident light beam in radians per second.
When the sinusoidally chopped monochromatic light source with wavelength $\lambda$ is incident on the solid with intensity $I = (1/2) I_0 (1 + \cos \omega t)$

The thermal diffusion equation in the three regions can be written as

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_h} \frac{\partial \varphi}{\partial t}, \quad -l_b \leq x \leq -l \quad \text{Region III}$$

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_s} \frac{\partial \varphi}{\partial t}, \quad 0 \leq x \leq -l_g \quad \text{Region I}$$

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_s} \frac{\partial \varphi}{\partial t} - A \exp(\beta x) \left[ 1 + \exp(j \omega t) \right], \quad -l \leq x \leq 0 \quad \text{Region II}$$

with $A = \frac{\beta \eta}{2k_s}$

where $\varphi$ is the temperature and $\eta$ is the light conversion efficiency. The real part of the complex-valued solution $\varphi(x, t)$ of the above equations is the solution of physical interest and represents the temperature in the cell relative to the ambient temperature as a function of position and time. Thus, the actual temperature field in the cell is given by

$$T(x, t) = \text{Re}[\varphi(x, t)] + \phi$$

where $\text{Re}$ stands for "the real part of" and $\phi$ is the ambient (room) temperature.

The complex amplitude of the periodic temperature distribution, $\theta$ at the solid-gas boundary ($x=0$) is given by

$$\theta = \frac{\beta I_0}{2k_s \left( \beta^2 - \sigma_s^2 \right)} \left( \frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta 1)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)} \right)$$

\[ \text{............... (4)} \]

where $b = \frac{k_b a_b}{k_s a_s}$, $g = \frac{k_g a_g}{k_s a_s}$, $r = \left(1 - j \right) \frac{\beta}{2a_s}$ and $\sigma_s = \left(1 + j \right) a_s$. 
Due to the periodic heat flow from the solid to the surrounding gas acoustic signal arises. The periodic heating causes the boundary layer of gas to expand and contract periodically. This can be thought of as the action of an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. The displacement of the gas piston due to the periodic heating can be estimated using the ideal gas law,

\[
\delta x(t) = 2\pi \mu g \frac{\phi(t)}{T_0} = \frac{\theta \mu g}{\sqrt{2 T_o}} \exp \left[ j \left( \omega t - \frac{\pi}{4} \right) \right] \tag{5}
\]

where the average dc temperature of the gas boundary layer is set as dc temperature at the solid surface, \( T_0 = \phi + \theta_0 \), \( \phi \) being the ambient temperature at the cell walls. Assuming that the rest of the gas responds to the action of the piston adiabatically, the acoustic pressure in the cell due to the displacement of the gas piston can be obtained from the adiabatic gas law \( PV^\gamma = \text{constant} \), where \( P \) is the pressure, \( V \) is the gas volume in the cell, and \( \gamma \) ratio of the specific heats. Thus the incremental pressure is

\[
\delta P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{l g} \delta x(t) \tag{6}
\]

where \( P_0 \) and \( V_0 \) are the ambient pressure and volume respectively and \(-\delta V\) is the incremental volume. Then from equations (5) & (6)

\[
\delta P(t) = Q \exp \left[ j \left( \omega t - \frac{\pi}{4} \right) \right] \tag{7}
\]
where \[ Q = \frac{\gamma P_0 \theta}{\sqrt{2} l a g T_0} \]

The actual physical pressure variation is given by the real part of \( \delta P(t) \) and \( Q \) specifies the complex envelop of the sinusoidal pressure variation.

Substituting for \( \delta \theta \)
\[ Q = \frac{\beta_0 P_0}{2 \sqrt{2} k_s l a g T_0 \left( \beta^2 - \sigma^2 \right)} \times \]
\[ \left( \frac{(r - 1)(b + i) \exp(\sigma l) - (r + 1)(b - 1) \exp(-\sigma l) + 2(b - r) \exp(-\beta l)}{(g + 1)(b + i) \exp(\sigma l) - (g - 1)(b - 1) \exp(-\sigma l)} \right)^2 \] .............. (8)

Thus, equation (8) can be evaluated for obtaining the amplitude and phase of the acoustic pressure wave produced in the cell by photoacoustic effect. It can be observed that interpretation of the full expression for \( \delta P(t) \) is difficult because of the complex expression of \( Q \). Physical insight can be gained easily if certain special cases according to the optical opaqueness of solids are examined. For each category of optical opaqueness, three cases according to the relative magnitude of the thermal diffusion length \( \mu_s \), as compared to the physical length \( l \) and the optical absorption length \( \mu_\beta \).

Defining \( \gamma = \frac{\gamma P_0 l_0}{2 \sqrt{2} l a g T_0} \), ................ (9)

CASE I: Optically Transparent solids (\( \mu_\beta > 1 \))

1. Case Ia: Thermally Thin Solids (\( \mu_s > 1 ; \mu_s > \mu_\beta \))

We can set \( e^{-\beta l} \equiv 1 - \beta l \), \( e^{+\beta l} \equiv 1 \) and \( |r| > 1 \) in equation (8) and hence we obtain
\[ Q = \frac{(1-i)\beta l}{-2a g} \left( \frac{\mu_b}{k_b} \right) Y \] ........................ (10)

Thus the acoustic signal is proportional to \( \beta l \) and varies as \( r^l \). In addition, the thermal properties of the backing material come into play in the expression for \( Q \).

2. Case Ib: Thermally Thin Solids \( (\mu_s > 1 ; \mu_s < \mu_\beta) \)

Here we can set \( \exp(-\beta l) \equiv 1-\beta l \), \( e^{2\eta l} \equiv 1 \pm \sigma_s l \) and \( |r| < 1 \) in equation (8).

Then, \[ Q = \frac{(1-j)\beta l}{2a g} \left( \frac{\mu_b}{k_b} \right) Y \] ........................ (11)

This equation is identical with equation (10) and hence the acoustic signal behaves in the same fashion.

3. Case Ic: Thermally Thick Solids \( (\mu_s > 1 ; \mu_s \ll \mu_\beta) \)

In this case we set \( \exp(-\beta l) \equiv 1-\beta l \), \( e^{2\eta l} \equiv 0 \) and \( |r| \ll 1 \) in equation (8)

Now, \[ Q = -j \frac{\beta l}{2a g} \left( \frac{\mu_s}{k_s} \right) Y \] ........................ (12)

The acoustic signal is now proportional to \( \beta \mu_s \) rather than \( \beta l \). This means that light absorbed within the first thermal diffusion length contributes to the signal, although light is being absorbed throughout the length of the solid. Moreover, \( \mu_s \) being less than the thickness \( l \), thermal properties of the backing material will not influence the signal. Here the signal varies as \( r^{3/2} \).

CASE II: Optically Opaque Solids

1. Case II a: Thermally Thin Solids \( (\mu_s >> 1 ; \mu_s >> \mu_0) \)
In equation (8), we set $\exp(-\beta l) \equiv 0$, $e^{-\beta l} \equiv 1$ and $|r| >> 1$.

Then we obtain

$$Q = \frac{(1-j)(\mu_b)}{2a_g}(\frac{\mu_s}{k_s})^2.$$  \hspace{1cm} (13)

Here the photoacoustic signal is independent of $\beta$. The signal depends on the thermal properties of the backing material and varies as $1/f$.

2. Case II b: Thermally Thick Solids ($\mu_s < l$; $\mu_s > \mu_b$)

We set $\exp(-\beta l) \equiv 0$, $e^{-\beta l} \equiv 0$ and $|r| > 1$ in equation (8).

We obtain

$$Q = \frac{(1-j)(\mu_s)}{2a_g}(\frac{\mu_s}{k_s})^2.$$  \hspace{1cm} (14)

Though equations (13) & (14) are similar, in the present case there is no contribution from the thermal properties of the backing material.

3. Case II c: Thermally Thick Solids ($\mu_s << l$; $\mu_s < \mu_b$)

We set $\exp(-\beta l) \equiv 0$, $e^{-\beta l} \equiv 0$ and $|r| < 1$ in equation (8). Then we obtain

$$Q = \frac{-j\beta\mu_s}{2a_g}(\frac{\mu_s}{k_s})^2.$$  \hspace{1cm} (15)

The photoacoustic signal will be proportional to $\beta\mu_s$. The signal is independent of the thermal properties of the backing material and varies as $f^{-3/2}$.

The theoretical analysis of the photoacoustic effect applied to different cases discussed above can be suitably applied to the study of any kind of sample.
1.3 PHOTOTHERMAL PROBE BEAM DEFLECTION (PBD) OR MIRAGE EFFECT]

In the case of photothermal beam deflection technique, the pump beam or the excitation beam is focussed. Hence, instead of the above 1-D calculation of periodic distribution of temperature, we have to resort to 3D calculations.

The heat diffusion equation in cylindrical geometry[82] is given by

$$\frac{\partial T}{\partial t} = D \left( \frac{\partial^2 T}{\partial t^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (16)$$

When heat flow takes place in planes through z-axis then the heat diffusion equation becomes

$$\frac{\partial T}{\partial t} = D \left( \frac{\partial^2 T}{\partial t^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) \quad (17)$$

The assumption that the homogeneous sample is the absorbing medium and the fluid and the backing are transparent still holds. The heat diffusion equation in three regions can be written as
\[
\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} + \frac{\partial^2 T_g}{\partial z^2} = \frac{1}{D_g} \frac{\partial T_g}{\partial t}, \quad 0 \leq z \leq l_s \quad \text{......... (18)}
\]

\[
\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial z^2} = \frac{1}{D_s} \frac{\partial T_s}{\partial t} - A(r,t) \exp(\alpha z) \left( 1 + \exp(j\omega t) \right) - t \leq z \leq 0 \quad \text{......... (19)}
\]

\[
\frac{\partial^2 T_b}{\partial r^2} + \frac{1}{r} \frac{\partial T_b}{\partial r} + \frac{\partial^2 T_b}{\partial z^2} = \frac{1}{D_b} \frac{\partial T_b}{\partial t} - (l + l_b) \leq z \leq -l \quad \text{......... (20)}
\]

\[
A(r,t) = \eta P \alpha \left( \begin{array}{c}
\frac{-2r^2}{a^2} \\
\frac{1}{\kappa a^2} \\
\end{array} \right) \left( 1 + \cos(\omega t) \right) \text{ is the heat deposited per unit volume where}
\]

\[P \text{ is the exciting beam power, } \alpha \text{ is the optical absorption coefficient, } \eta \text{ is the light conversion efficiency, } 'a' \text{ is the beam radius defined at } 1/e^2 \text{ intensity.}
\]

The boundary conditions are

\[
\kappa_s \frac{\partial T_s}{\partial z}(z=0) = \kappa_g \frac{\partial T_g}{\partial z}(z=0) \quad \text{......... (21)}
\]

\[
\kappa_s \frac{\partial T_s}{\partial z}(z=-l) = \kappa_b \frac{\partial T_b}{\partial z}(z=-l) \quad \text{......... (22)}
\]

\[
T_s(z=-l,t) = T_b(z=-l,t) \quad \text{......... (23)}
\]

\[
T_s(z=0,t) = T_g(z=0,t) \quad \text{......... (23)}
\]

\[
T_g(z=\infty,t) = T_b(-\infty,t) = 0 \quad \text{with } l_g \sim \infty, l_b \sim \infty
\]

Assume that \( l_g \) and \( l_b \) are very large compared to the heated area and neglect the backward heat propagation in these two regions.
In order to obtain the periodic steady state temperature, the above differential equations are reduced to simpler partial differential equation by Hankel transformation and Laplace transformation is used to obtain ordinary differential equation from the partial differential equation. Furthermore, the modulated source is replaced by the unit source $A(t)\delta(t)$

\[-\lambda^2 T_0(\lambda, z, p) + \frac{\partial^2 T_0(\lambda, z, p)}{\partial z^2} = \frac{p}{D_g} T_0(\lambda, z, p) \quad \ldots \ldots \ldots (24)\]

\[-\lambda^2 T_0(\lambda, z, p) + \frac{\partial^2 T_0(\lambda, z, p)}{\partial z^2} = \frac{p}{D_s} T_0(\lambda, z, p) - A_0(\lambda) \exp(\alpha z) \quad \ldots \ldots \ldots (25)\]

\[\frac{\partial^2 T_0(\lambda, z, p)}{\partial z^2} = \frac{p}{D_b} T_0(\lambda, z, p) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots . (26)\]

where
\[= \frac{\alpha P \eta}{k_s z a^2} \int_0^\infty e^{\frac{-2r^2}{a^2}} J_0(\lambda r) r dr \]

\[= \frac{\alpha P \eta}{4 k_s \pi} e^{-\frac{\lambda^2 a^2}{8}}\]

1) Assuming solution of the form to eq (24)

\[T_0(\lambda, z, p) = e^{\sqrt{\lambda^2 + \frac{p}{D} z}}\]
The general solution is

\[ T_0(\lambda, z, p) = T_s(\lambda, p)e^{-\sqrt{\frac{\lambda^2 + p}{D} z}} + B(\lambda, p)e^{\sqrt{\frac{\lambda^2 + p}{D} z}} \]

\[ B(\lambda, p) = 0, \text{ since the fluid is supposed to be very thick.} \]

Equations (25) and (26) can be solved similarly.

Thus solution to equations (24), (25), and (26) are

\[ T_0(\lambda, z, p) = T_s(\lambda, p)e^{-\sqrt{\frac{\lambda^2 + p}{D} z}} \]

\[ T_0(\lambda, z, p) = U(\lambda, p)e^{\sqrt{\frac{\lambda^2 + p}{D} z}} + V(\lambda, p)e^{-\sqrt{\frac{\lambda^2 + p}{D} z}} - \frac{A_0(\lambda)e^{az}}{\alpha^2 - (\frac{\lambda^2 + p}{D})} \]

\[ T_0(\lambda, z, p) = W(\lambda, p)e^{\sqrt{\frac{\lambda^2 + p}{D} z}} \]

After applying the Hankel inversion, to the above three equations the steady periodic state solution obtained is of the form

\[ T(r, z, t) = T_0(r, z, p) \bigg|_{p = j\omega} \exp(ja\lambda) \]

Thus the expressions for the modulated temperature field in the three regions are

\[ T_g(r, z, t) = \int_{0}^{\infty} T_s(\lambda) \exp(-\beta_g z) \exp(ja\lambda) J_0(\sqrt{\lambda^2 + p} r) d\lambda \]

\[ T_b(r, z, t) = \int_{0}^{\infty} W(\lambda) \exp(\beta_b (z + l)) \exp(ja\lambda) J_0(\sqrt{\lambda^2 + p} r) d\lambda \]
\[ T_s(r, z, t) = \int_0^\infty [U(\lambda) \exp(\beta_s z) + V(\lambda) \exp(-\beta_s z) - E(\lambda) \exp(\alpha z)] x \exp(j \omega t) J_0(\lambda r) d\lambda \quad \ldots (33) \]

where

\[
E(\lambda) = \frac{\rho \eta}{\pi k_s} \exp \left( -\frac{-\lambda^2 a^2}{8} \right) \left\{ -\lambda^2 - j \frac{\omega}{D_s} + \alpha^2 \right\} \quad \ldots \ldots \ldots (34)
\]

The final temperature distribution is obtained by substituting the following expressions in the above equations.

\[ T_s(\lambda) = -E(\lambda) + U(\lambda) + V(\lambda) \quad \ldots \ldots \ldots (35) \]

\[ W(\lambda) = -E(\lambda) \exp(-\alpha t) + U(\lambda) \exp(-\beta_s t) + V(\lambda) \exp(\beta_s t) \quad \ldots \ldots \ldots (36) \]

\[ U(\lambda) = \left[ (1 - g)(b - r) \exp(-\alpha t) + (g + r)(1 + b) \exp(\beta_s t) \right] \frac{E(\lambda)}{H(\lambda)} \quad \ldots \ldots \ldots (37) \]

\[ V(\lambda) = \left[ (1 + g)(b - r) \exp(-\alpha t) + (g + r)(1 - b) \exp(-\beta_s t) \right] \frac{E(\lambda)}{H(\lambda)} \quad \ldots \ldots \ldots (38) \]

and

\[ H(\lambda) = (1 + g)(1 + b) \exp(\beta_s t) - (1 - g)(1 - b) \exp(-\beta_s t) \]

\ldots \ldots \ldots (39)

with \( g = \frac{k_s \beta_g}{k_s \beta_s} \), \( b = \frac{k_b \beta_b}{k_s \beta_s} \), \( r = \frac{\alpha}{\beta_s} \).
The surface temperature can be written as

\[ T_s(\lambda) = \frac{P}{4k_\lambda} \left( e^{-\lambda r} - e^{-\beta r} \right) \frac{r^2 - 1}{r^2 - 1} \left[ \frac{2(b - r)e^{-\lambda r} + (1 + b)(r - 1)e^{\beta r} + (1 - b)(r + 1)e^{-\beta r}}{(1 + g)(1 + b)e^{\beta r} - (1 - g)(1 - b)e^{-\beta r}} \right] \] \tag{40}

The surface temperature can be written as

\[ T_s(0,t) = \int_{\lambda} T_s(\lambda) \lambda d\lambda \exp(j\omega t) \] \tag{41}

The geometry for the mirage deflection is as shown in figure 5. The propagation of the beam through the spatially varying index of refraction is given by

\[ \frac{dn}{ds} + \frac{dr_0}{ds} = \nabla_r n(r,t) \] \tag{42}

where \( r_0 \) is the perpendicular displacement of the beam from its original direction, \( n \) is the uniform index of refraction and \( \nabla_r n(r,t) \) is the gradient of the index of refraction perpendicular to \( S \) (the ray path). This relation can be integrated over the ray path \( S \)

\[ \frac{dr_0}{ds} = \frac{1}{n} \int_{\text{path}} \nabla_r n(r,t) ds \] \tag{43}

Since the deviation is small, one can get the expression of the deflection

\[ \theta(t) = \frac{dr_0}{ds} = \frac{1}{n} \frac{\partial n}{\partial T} \int_{\text{path}} \nabla_r T(r,t) ds \] \tag{44}

In our case, the probe beam is propagating through the fluid along the \( x \)-direction. Hence, the probe deflects with components in \( x-y \) plane and \( z-x \) plane so that after calculating the vector product in the integrand of the above
expression, we get the transverse ($\theta_t$) and the normal ($\theta_n$) components of the
deflection, respectively.

$$\theta_n = -\frac{1}{n} \frac{dn}{dT} \int_{-\infty}^{\infty} \frac{\partial T}{\partial z} dx j$$

...............(45)

$$\theta_t = \frac{1}{n} \frac{dn}{dT} \int_{-\infty}^{\infty} \sin \alpha \frac{\partial T}{\partial \tau} dx \hat{k}$$

...............(46)

$\theta_n$ and $\theta_t$ are the deflections normal and parallel to the sample surface.

Using the standard result

Figure 5: Geometry for 'mirage' deflection. The probe beam is along $x$
direction and excitation beam or pump beam is along $z$ direction.
\[ \int_{-\infty}^{\infty} T_s(x)dx = 2 \int_{0}^{\infty} T_s(\lambda)\cos(\lambda y)d\lambda \] ......(47)

Hence substituting for the integral in eq (34)

\[ \theta_n = \frac{2}{n} \frac{dn}{dT} \exp\left( j \omega t \right) \int_{0}^{\infty} T_s(\lambda) \beta_0 \exp\left(-\beta_< z \right) \cos(\lambda y) d\lambda \] .......... (48)

Similar treatment of the integral in eq (35) results in

\[ \theta_t = \frac{2}{n} \frac{dn}{dT} e^{j \omega t} \int_{0}^{\infty} T_s(\lambda) \beta \exp\left(-\beta_> z \right) \sin(\lambda y) d\lambda \] ..........(49)

Substituting the value of \( T_s(\lambda) \) from eq. (30) in the above equation the general expression for \( \theta_t \) and \( \theta_n \) can be obtained. \( \theta_n \) is related to the heat diffusion process perpendicular to the surface whereas \( \theta_t \) represents the heat diffusion process parallel to the sample surface.

Depending upon the optical absorption co-efficient, sample can be divided into optically opaque and optically transparent. According to the thermal properties, each are subdivided into thermally thick and thermally thin. Equation (30) will be modified accordingly for each of these special cases [42]. The basic assumption is that the thermal diffusivity of the sample is greater than that of fluid as well as backing i.e. \( b = g \sim 0 \)

Case I: Optically Opaque \((\alpha l >> 1)\)

In these materials, the optical absorption length is much smaller than the sample thickness.

\[ \frac{r}{1+r} = \frac{\alpha}{\beta_> + \alpha} \approx 1 \]
\[
\frac{r}{1-r} = \frac{\alpha}{\beta - \alpha} \approx -1
\]

Then the expression for the tangential component of deflection
\[
\theta_t = -\frac{1}{n} \frac{\exp(j \omega t)}{2 \pi k_s} \int_0^\infty \frac{e^{-\beta g z}}{\lambda \sin(\lambda y)} e^{-\frac{\lambda^2 a^2}{4} \beta} \left( \frac{1}{\beta} \frac{1 + e^{-2 \beta l}}{1 - e^{-2 \beta l}} \right) d\lambda k
\]

and that of normal component is given by
\[
\theta_n = \frac{1}{n} \frac{\exp(j \omega t)}{2 \pi k_s} \int_0^\infty \frac{\beta \cos(\lambda y)}{\lambda \sin(\lambda y)} e^{-\frac{\lambda^2 a^2}{4} \beta} \left( \frac{1 + e^{-2 \beta l}}{1 - e^{-2 \beta l}} \right) \exp(-\beta g z) d\lambda k
\]

(50)

For thermally thick solids, \( l > \mu \). Hence \( \exp(-\beta l) \approx 0 \) and the integrands are further reduced. For thermally thin solids, \( l < \mu \). And the equations are suitably modified.

**Case II Optically Transparent solids \((a l << 1)\)**

\[
\frac{r}{1+r} \approx \frac{r}{1-r} \approx \frac{\alpha}{\beta}
\]

Now the tangential component and normal components are given by (52)

\[
\theta_t = -\frac{1}{n} \frac{\exp(j \omega t)}{2 \pi k_s} \int_0^\infty \frac{\beta \sin(\lambda y)}{\lambda \sin(\lambda y)} e^{\frac{-\lambda^2 a^2}{4} \beta} \left( \frac{\alpha}{\beta^2} \right) e^{-\beta g z} d\lambda k \quad \ldots (52)
\]

\[
\theta_n = -\frac{1}{n} \frac{\exp(j \omega t)}{2 \pi k_s} \int_0^\infty \frac{\beta \cos(\lambda y)}{\lambda \sin(\lambda y)} e^{\frac{-\lambda^2 a^2}{4} \beta} \left( \frac{\alpha}{\beta^2} \right) \exp(-\beta g z) d\lambda k \quad \ldots (53)
\]
According to their thermal properties for thermally thick solids, $l > \mu$. Hence $\exp(-\beta/l) \sim 0$ and the integrands are further reduced. For thermally thin solids, $l < \mu$, and the equations are suitably modified.

In conclusion, this opening chapter gives an account of various photothermal techniques that can be suitably applied to various materials for the optical as well as thermal characterisation non-destructively. A review on the applicability of these techniques, namely PA and PTD technique, on the class of materials under investigation is also presented.
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