Chapter 2

Photoacoustics and photothermal deflection: General theoretical approach

Photothermal methods are well developed from the experimental point of view and the theoretical foundations on which they rely are also substantially strong. Since the formulation of one-dimensional heat flow model by Rosencwaig and Gersho to explain the photoacoustic signal generation, a number of modifications and extended models have been reported in the literature. In the present chapter a brief discussion regarding the Rosencwaig-Gersho model and its extension to open photoacoustic cell configuration are presented. The three-dimensional heat flow model used to describe the photothermal deflection signal generation is also included in this chapter.
2.1. Historical developments

Among the different photothermal methods, the photoacoustic effect is credited with the first observed photothermal phenomena noticed in 1880 during Alexander Graham Bell's voyage for new inventions [1,2]. Though Bell has prophesised the scope of his novel observation, after the initial flurry of interest generated by his original work, experimentation with the photoacoustic effect is almost in a dormant state. After the advent of microphones, Viengerov is able to observe this effect in gaseous sample [3]. Still the growth of this new branch of spectroscopy is in a hopeless state due to many of the experimental limitations. The emergence of lasers in early sixties paved a new way in the photoacoustic spectroscopy of gaseous samples. But the applications of this technique have been efficiently extended to liquids and solids only after the successful formulation of a general theoretical model by Rosencwaig and Gersho in mid-seventies [4]. Subsequent developments in the theoretical aspects of photothermal phenomena are mere extensions or modifications of Rosencwaig-Gersho model. Though Bennett and Forman in 1976, and Aamodt et al. in 1977 have modified the basic theoretical model by treating the acoustic wave transport in the gas using Navier-Stokes equations, the basic results of Rosencwaig-Gersho model remains the same [5,6]. Modification to the R-G theory by McDonald and Wetsel in 1978 by taking into account the contributions from thermally induced vibrations in the sample is somewhat intriguing [7]. By this time, a new form of photoacoustic configuration, namely the open photoacoustic cell has emerged [9]. Nowadays, the open cell photoacoustic technique is in widespread use for the thermal characterisation of solid and even liquid samples [10-20].

In fact, the concept of light beam deflection by thermally induced changes in the index of refraction of a medium has been known for a long time. However, only in 1979 Boccara et al. demonstrated the use of photothermal beam deflection method in material characterization [21]. Subsequent theoretical and experimental developments made by Jackson et al. in 1981, Aamodt et al. in 1981 and Grice et al. in 1983 have formed a strong basis to this technique [22-24]. Initially, people used the one-dimensional heat flow model formulated by Rosencwaig and Gersho to give a quantitative explanation to this effect. But, in many experimental conditions, such as when a focused pump-beam is used, this approach failed. In such situations, a three-dimensional heat flow model is required to give a satisfactory explanation and the details of this approach are included in this chapter.
2.2. Photoacoustic effect in condensed media

The photoacoustic technique is essentially a closed cavity detection of energy liberated by atoms or molecules through nonradiative de-excitation mechanism, subsequent to light absorption by a sample. When a solid sample placed inside an airtight cavity is irradiated with a modulated optical radiation, the energy liberated through nonradiative channels will result in the generation of thermal waves within the sample. The thermal waves diffused through the sample to the gas in the cavity will produce a periodic pressure fluctuation inside the cavity. This pressure variation can be detected using a microphone kept inside the cavity. If the sample to be analyzed is in the gaseous form, then the sample itself can act as the source of signal generation and the acoustic coupler to the microphone. In order to investigate a liquid sample, a piezoelectric transducer is usually used. The piezoelectric transducer kept in contact with the liquid sample will detect the acoustic pulse propagated through the liquid. In 1976 Rosencwaig and Gersho formulated a complete theoretical explanation to this effect in condensed media [4].

2.2.1. Rosencwaig-Gersho theory

The Rosencwaig-Gersho (R-G) theory is essentially a one-dimensional heat flow model, which is sufficient to describe the photoacoustic (PA) signal generation in condensed matter [4,8]. According to R-G theory, with a gas-microphone detection of PA signal, the signal depends on the generation of an acoustic pressure disturbance at the sample-gas interface. The generation of the surface pressure disturbance, in turn, depends on the periodic temperature at the sample-gas interface. Exact expressions for this temperature are derived in R-G theoretical model, but the transport of the acoustic disturbance in the gas is treated in an approximate heuristic manner, which is, however, valid in most experimental conditions.

The formulation of R-G model is based on the light absorption and thermal-wave propagation in an experimental configuration as shown in figure 1. Here the sample is considered to be in the form of a disc of thickness \( l \). It is assumed that the back surface of the sample is in contact with a poor thermal conductor of thickness \( l_b \) and the front surface is in contact with a gas column of length \( l_g \). It is further assumed that both gas and backing material are not light absorbing. Following are the parameters used in the R-G model which is being discussed below.

- \( k \): the thermal conductivity (cal/cm-s-°C)
- \( \rho \): the density (g/cm\(^3\))
- \( C \): the specific heat capacity (cal/g-°C)
\[ \alpha = \frac{k}{\rho c} \text{: the thermal diffusivity (cm}^2/\text{s)} \]

\[ a = \sqrt{\frac{\omega}{2\alpha}} \text{ the thermal diffusion coefficient (cm}^{-1}) \]

\[ \mu = \frac{1}{a} \text{ the thermal diffusion length (cm)} \]

where \( \omega = 2\pi f \), with \( f \) the modulation frequency of the incident light beam.

**Figure 1**: Schematic representation of photoacoustic experimental configuration.

When a sinusoidally modulated light beam of intensity \( I_0 \) is incident on a solid sample having an absorption coefficient \( \beta \), the heat density generated at any point due to the light absorbed at this point can be represented by

\[ \frac{1}{2} \beta I_0 e^{\beta \xi} (1 + \cos \omega \xi) \]  

(1)

The thermal diffusion equation in the solid taking into account the distributed heat source, can be written as

\[ \frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} - \frac{\beta I_0 \eta}{2k} e^{\beta \xi} (1 + e^{i\omega \xi}) \quad \text{for} -l \leq x \leq 0 \]  

(2)

For the backing material and the gas, the heat diffusion equations are

\[ \frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \theta}{\partial t} \quad \text{for} -(l_b + l) \leq x \leq -l \]  

(3)

\[ \frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \theta}{\partial t} \quad \text{for} 0 \leq x \leq l_g \]  

(4)

where \( \theta \) is the temperature and \( \eta \) is the light to heat conversion efficiency. Here, the subscripts \( b \) and \( g \) represent the backing and gas respectively. The real part of the complex valued solution \( \theta(x, t) \) of equations (2)-(4) is the solution of physical interest and represents the temperature in the cell relative to ambient temperature as a function of position and time.
After imposing appropriate boundary conditions for the temperature and heat flux continuity, and neglecting convective heat flow in the gas at steady-state conditions, the explicit solution for the complex amplitude of the periodic temperature at the solid-gas boundary can be obtained as

$$\theta_o = \frac{\beta a_o}{2k(\beta^2 - \sigma^2)} \left[ \frac{(r - 1)(b + 1)e^{\sigma t} - (r + 1)(b - 1)e^{-\sigma t} + 2(b - r)e^{-\beta t}}{(g + 1)(b + 1)e^{\sigma t} - (g - 1)(b - 1)e^{-\sigma t}} \right]$$ (5)

where

$$b = \frac{k_b a_b}{ka}, \quad g = \frac{k_g a_g}{ka}, \quad r = (1 - i) \frac{\beta}{2a}, \quad \sigma = (1 + i)a$$ (6)

The periodic heat flow from the solid to the surrounding gas produces a periodic temperature variation in the gas. The time dependent component of the temperature in the gas attenuates rapidly to zero with increasing distance from the surface of the solid. At a distance of $2\pi \mu_g$, where $\mu_g$ is the thermal diffusion length in the gas, the periodic temperature variation in the gas is effectively fully damped out. Thus there is a boundary layer of gas, which is only capable of responding thermally to the periodic temperature at the surface of the sample. This layer of gas expands and contracts periodically and thus can be thought of as acting as an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. Assuming that the rest of the gas responds adiabatically to the action of the acoustic piston, the adiabatic gas law can be used to derive an expression for the complex envelope of the sinusoidal pressure variation $Q$ as

$$Q = \frac{\gamma P_o \theta_o}{\sqrt{2T_o l_g a_g}}$$ (7)

with $\theta_o$ given by equation (5). $\gamma$, $P_o$ and $T_o$ are the ratio of heat capacities of air, ambient pressure and temperature, respectively.

Equation (7) can be used to evaluate the magnitude and phase of the acoustic pressure wave produced in the cell due to photoacoustic effect. However, a useful interpretation of the above equation is rather difficult in the present form. Hence, some special cases, according to the experimental conditions, have to be considered to get a clear physical insight. In fact, three lengths related to the sample, namely, the physical length $l$, the thermal diffusion length $\mu$ and the optical absorption length $l_\beta$ ($= \frac{1}{\beta}$) can be made use of in arriving at different special cases.
Optically transparent solids \((l_\beta > l)\)

**Case 1(a): Thermally thin solids \((\mu >> l; \mu > l_\beta)\)**

We can set \(e^{-A} \approx 1 - A, e^{\pm \sigma l} \approx 1\) and \(|r| > 1\) in equation (7) and we obtain

\[
Q \approx \frac{(1 - i)\mu}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y
\]  
(8)

with

\[
Y = \frac{P_0 l_0}{2\sqrt{2\pi l_g T_0}}
\]  
(9)

Now the acoustic signal is proportional to \(A\) and varies as \(f^{-1}\). Moreover, the signal is now determined by thermal properties of the backing material.

**Case 1(b): Thermally thin solids \((\mu > l; \mu < l_\beta)\)**

We can set \(e^{-A} \equiv 1 - A, e^{\pm \sigma l} \equiv (1 \pm \sigma l)\) and \(|r| < 1\) in equation (7) and we obtain

\[
Q \approx \frac{(1 - i)\beta}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y
\]  
(10)

The acoustic signal now behaves in the same fashion as in the previous case.

**Case 1(c): Thermally thick solids \((\mu < l; \mu << l_\beta)\)**

We can set \(e^{-A} \equiv 1 - A, e^{-\sigma l} \equiv 0\) and \(|r| < 1\) in equation (7) and we obtain

\[
Q \approx -i \frac{\beta\mu}{2a_g} \left( \frac{\mu}{k} \right) Y
\]  
(11)

Now, only the light absorbed within the first thermal diffusion length contributes to the signal in spite of the fact that light is being absorbed throughout the length of the sample. Also since \((\mu < l)\), the backing material does not have any contribution to the signal. Interestingly, the signal now varies as \(f^{-1.5}\).

Optically opaque solids \((l_\beta << l)\)

**Case 2(a): Thermally thin solids \((\mu >> l; \mu >> l_\beta)\)**

We can set \(e^{-A} \approx 0, e^{\pm \sigma l} \approx 1\) and \(|r| >> 1\) in equation (7) and we obtain

\[
Q \approx \frac{(1 - i)\mu}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y
\]  
(12)
Now the signal is independent of $\beta$, which is valid for a perfect black absorber such as carbon black. The signal will be much stronger compared to case 1(a) and varies as $f^{-1}$, but still depends on the thermal properties of the backing material.

**Case 2(b): Thermally thick solids ($\mu < l; \mu > l|\beta|$)**

We can set $e^{-\beta l} \equiv 0$, $e^{-\alpha d} \equiv 0$ and $|r| > 1$ in equation (7) and we obtain

$$Q \approx \frac{(1 - i) \left( \frac{\mu}{k} \right)}{2a_g} Y$$

Equation (13) is analogous to (12), but the thermal parameters of the backing material are now replaced with those of the sample. Again the signal is independent of $\beta$ and varies as $f^{-1}$.

**Case 2(c): Thermally thick solids ($\mu << l; \mu < l|\beta|$)**

We can set $e^{-\beta l} \equiv 0$, $e^{-\alpha d} \equiv 0$ and $|r| < 1$ in equation (7) and we obtain

$$Q \approx -i \frac{\beta \mu}{2a_g} \left( \frac{\mu}{k} \right) Y$$

This is a very interesting and important case. Even though the solid is optically opaque, the photoacoustic signal is proportional to $\beta$ as long as $\beta \mu < 1$. As in case 1(c), the signal is independent of the thermal properties of the backing material and varies as $f^{-1.5}$.

The different cases discussed so far can be made use of in the photoacoustic study of any kind of sample. One of the important predictions of the R-G theory is that the photoacoustic signal is always linearly proportional to the incident light intensity, irrespective of the sample properties and cell geometry. In cases 2(a) and 2(b), we have seen that the PA signal is independent of the optical absorption coefficient of the sample. For these cases, therefore, the only term in (12) and (13) that depends on the wavelength of the incident radiation is the light source intensity $I_o$. Thus it is clear that the PA spectrum of an optically opaque sample ($\mu > l|\beta|$) is simply the power spectrum of the light source.
2.2.2 Open photoacoustic cell configuration

Open photoacoustic cell (OPC) configuration is a modified and more convenient form of conventional photoacoustic configuration. In OPC, usually, solid sample will be mounted directly on top of the microphone, leaving a small volume of air in between the sample and the microphone [9-20]. It is an open cell detection configuration in the sense that the sample is placed on top of the detection system itself, as in the case of piezoelectric and pyroelectric detection. Consequently, this configuration is a minimum volume PA detection scheme and hence the signal strength will be much greater than the conventional PA configurations. The major advantage of this configuration is that samples having large area can be studied, whereas in conventional PA cells sample size should be small enough to be contained inside the PA cavity. A schematic representation of a typical OPC is shown in figure 2.

![Figure 2: A general schematic representation of an open photoacoustic cell. Here S is the sample; O the o-ring; M the microphone and C the cell body.](image)

R-G theory can be used to derive an expression for the periodic pressure variation inside the air chamber. Consider the OPC geometry shown in figure 3. Assume that the sample is optically opaque and whole energy is absorbed at the sample surface itself. Then, for the arrangement shown in figure 3, according to R-G theory, we can show that the periodic pressure variation in the air chamber is given by,

\[
Q = \frac{\mathcal{P}_0 I_0 \left(\alpha_g / \alpha_s\right)^{1/2}}{2\pi \tau_I \alpha_s k_s f} \frac{e^{j(\omega t - \pi / 2)}}{\sinh(l_s \alpha_s)}
\]

Now, if the sample is thermally thin (i.e., \(l_s \alpha_s >> 1\)), equation 15 reduces to

\[
Q \approx \frac{\mathcal{P}_0 I_0 \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} \tau_I l_s k_s} \frac{e^{j(\omega t - 3\pi / 4)}}{f^{3/2}}
\]

That is, the amplitude of the PA signal decreases as \(f^{-1.5}\)
In contrary, at high modulation frequencies, such that the sample is thermally thick (i.e., $l_s \alpha_s \gg 1$), then

$$Q \approx \frac{\kappa P_o l_o \left( \alpha_g \alpha_s \right)^{1/2} e^{-l_s \sqrt{\pi f / \alpha_s}}}{\pi T_0 l_g k_s f} e^{j(\omega \pi / 2 - l_s \alpha_s)}$$

Equation (17) means that, for a thermally thick sample, the amplitude of the OPC signal decreases exponentially with the modulation frequency as $\left( \frac{1}{\sqrt{f}} \right) \exp(-b \sqrt{f})$, where $b = l_s \sqrt{\pi / \alpha_s}$, whereas its phase decreases linearly with $\sqrt{f}$ with a slope of $b$. Hence, the thermal diffusivity $\alpha_s$ of the sample can be easily evaluated from either signal amplitude plot or from the phase plot. However, a necessary condition to employ the OPC configuration is that the sample should be optically opaque at the incident wavelength. The OPC configuration can not only be used for the study of solid samples, but liquid samples can also be characterised using this configuration. Commonly used approach in the study of liquid samples using OPC configuration is by keeping the liquid in contact with a thermally thin solid sample, the thermal properties of which are known [18-20].
2.3. Photothermal deflection: Mirage effect

In 1979 Boccara et.al proposed and demonstrated the usefulness of photothermal beam deflection (mirage effect) method for monitoring the temperature gradient field close to a sample surface or within the bulk of a sample [21]. In subsequent years, many theoretical and experimental developments have been reported in [22-32]. The method is essentially based on the detection of refractive index gradient associated with the temperature gradient. As we have seen in the previous section, absorption of optical radiation results in the generation of thermal waves in the sample which heats up the gas or liquid above the surface. The heated gas deflects a probe laser passing through it. The probe-beam deflection can be monitored using a position-sensing detector. Figure 4 shows a schematic diagram of the passage of a probe-beam through a refractive index profile.

![Figure 4: A schematic diagram of the passage of a probe-beam through a refractive index profile and the resulting normal and transverse components of the PTD signal.](image-url)
For a Gaussian beam propagating through an inhomogeneous medium, most of the beam parameters can be deduced from the analysis of Casperson [33]. The propagation of a light beam through a spatially varying index of refraction is given by [34]

$$\frac{d}{ds} \left( n_0 \frac{dr_0}{ds} \right) = \nabla \perp n(r, t)$$  \hspace{1cm} (18)

where \(r_0\) is the perpendicular displacement of the beam from its original direction, \(n_0\) is the uniform index of refraction, and \(\nabla \perp n(r, t)\) is the gradient of index of refraction perpendicular to the ray path. The above relation can be integrated over the ray path:

$$\frac{dr_0}{ds} = \frac{1}{n_0} \int_{\text{path}} \nabla \perp n(r, t) ds$$ \hspace{1cm} (19)

where \(s\) is the optical path length. Since the deviation is small, one can get the expression for the deflection \(\theta(t)\) as

$$\frac{dr_0}{ds} = \theta(t) = \frac{1}{n_0} \frac{\partial n}{\partial T} \int_{\text{path}} \nabla \perp T(r, t) ds$$ \hspace{1cm} (20)

where \(\nabla \perp T(r, t)\) is the temperature gradient perpendicular to the ray path. The deflection \(\theta(t)\) can be resolved into two components \(\theta_n\) and \(\theta_t\). Where \(\theta_n\) and \(\theta_t\) are, respectively, the deflections normal and parallel to the sample surface and are given by

$$\theta_n = \frac{1}{n_0} \frac{dn}{dT} \int_{-\infty}^{+\infty} \frac{\partial T_f}{\partial x} dx$$ \hspace{1cm} (21)

and

$$\theta_t = \frac{1}{n_0} \frac{dn}{dT} \int_{-\infty}^{+\infty} \sin \alpha \frac{\partial T_f}{\partial x} dx$$ \hspace{1cm} (22)

Now, we have to evaluate the temperature field in the sample and in the surrounding fluid. Though initially people used a one-dimensional heat flow model to evaluate the temperature field, it is found to vanish in most of the experimental conditions, especially when the excitation beam is focused. Hence, to get a complete general solution, we have to depend on a three-dimensional model. Consider an experimental configuration as shown in figure 5. The 3-D model used to describe the photothermal deflection is more complicated than the 1-D model used to explain the photoacoustic signal generation, since the thermal conduction in the solid and fluid has to be taken into account in the former case.
Figure 5: Schematic representation of experimental geometry used in 3-D model

Assume that the homogeneous sample is the only absorbing medium whereas the fluid and backing material are transparent. For simplicity, it is assumed that all the three regions extend infinitely in the radial direction, with the irradiated area usually being limited and small compared to the radial size of the sample. The heat diffusion equations in the three regions are

\[
\frac{\partial^2 T_f}{\partial r^2} + \frac{1}{r} \frac{\partial T_f}{\partial r} + \frac{\partial^2 T_f}{\partial z^2} = \frac{1}{D_f} \frac{\partial T_f}{\partial t} \quad \text{for} \ 0 \leq z \leq l_f \tag{23}
\]

\[
\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial z^2} = \frac{1}{D_s} \frac{\partial T_s}{\partial t} - A(r, t) e^{\alpha z} \left(1 + e^{j \alpha x}\right) \quad \text{for} \ -l \leq z \leq 0 \tag{24}
\]

\[
\frac{\partial^2 T_b}{\partial r^2} + \frac{1}{r} \frac{\partial T_b}{\partial r} + \frac{\partial^2 T_b}{\partial z^2} = \frac{1}{D_b} \frac{\partial T_b}{\partial t} \quad \text{for} \ -(l + l_b) \leq z \leq -l \tag{25}
\]

Here, the suffixes \( f, s \) and \( b \) stands for fluid, sample and backing material, respectively. \( D \) is the thermal diffusivity and \( \alpha \) is the optical absorption coefficient of the sample.

After introducing appropriate boundary conditions and making use of Hankel transform, one can arrive at the expressions for the modulated temperature field in the three regions as

\[
T_f(r, z, t) = \int_0^\infty T_s(\lambda) \exp(-\beta_f z) \exp(j \alpha x) J_0(\lambda_r) \lambda d\lambda \tag{26}
\]

\[
T_b(r, z, t) = \int_0^\infty W(\lambda) \exp(\beta_b(z + l)) + j \alpha x) J_0(\lambda_r) \lambda d\lambda \tag{27}
\]

\[
T_s(r, z, t) = \int_0^\infty \left[U(\lambda) \exp(\beta_s z) + V(\lambda) \exp(-\beta_s z) - E(\lambda) \exp(\alpha z)\right] \times \exp(j \alpha x) J_0(\lambda_r) \lambda d\lambda \tag{28}
\]
where

\[ E(\lambda) = \frac{P \eta}{\pi k_s} \left( \frac{-\lambda^2 a^2}{8} \right) \exp \left( \frac{-\lambda^2 a^2}{8} \right) \left( -\lambda^2 - j \frac{a}{D_s} + a^2 \right) \]  \quad (29)

with \( a^2 \exp \left( \frac{-\lambda^2 a^2}{8} \right) = \int_0^\infty \exp \left( -\frac{2\lambda^2}{a^2} \right) J_0(\lambda r) r dr \) \quad (30)

\[ \beta_i^2 = \lambda^2 + \frac{j\omega}{D_i} \] \quad (31)

\[ T_s(\lambda) = -E(\lambda) + U(\lambda) + V(\lambda) \] \quad (32)

\[ W(\lambda) = -E(\lambda) \exp(-\alpha l) + U(\lambda) \exp(-\beta_s l) + V(\lambda) \exp(\beta_s l) \] \quad (33)

\[ U(\lambda) = \left[ (1 - g)(b - r) \exp(-\alpha l) + (g + r)(1 + b) \exp(\beta_s l) \right] \frac{E(\lambda)}{H(\lambda)} \] \quad (34)

\[ V(\lambda) = \left[ (1 + g)(b - r) \exp(-\alpha l) + (g + r)(1 - b) \exp(-\beta_s l) \right] \frac{E(\lambda)}{H(\lambda)} \] \quad (35)

with

\[ g = \frac{k_f \beta_f}{k_s \beta_s}, \quad b = \frac{k_b \beta_b}{k_s \beta_s}, \quad r = \frac{\alpha}{\beta_s} \]  \quad (36)

and

\[ H(\lambda) = (1 + g)(1 + b) \exp(\beta_s l) - (1 - g)(1 - b) \exp(-\beta_s l) \] \quad (37)

In photothermal deflection technique, measurements are carried out using a probe-beam propagating through a transparent fluid in contact with the sample surface. The temperature field along the probe-beam path is a function of both the surface temperature and the distance between sample-surface and the probe-beam.

The complex amplitude of the surface temperature can be obtained as

\[ T_s(0, t) = \int_0^\infty E(\lambda) \left[ \frac{-(1 + b)(1 - r) \exp(\beta_s l) + (1 - b)(1 + r) \exp(-\beta_s l)}{(1 + g)(1 + b) \exp(\beta_s l) - (1 - g)(1 - b) \exp(-\beta_s l)} \right] J_0(\lambda r) d\lambda \exp(j\omega t) \] \quad (38)

In the above expression, the term in the bracket describes the thermal response of the three media, namely, the sample, backing and the coupling fluid. Now, if the sample is thermally thick, then the surface temperature of the sample can be easily evaluated by replacing this term of the above expression by

\[ \frac{(r - 1)}{(g + 1)} \] \quad (39)
and for thermally thin sample the term in the bracket becomes

\[ \frac{(r - b)(1 - \exp(-\alpha l)) + \alpha l(rb - 1)}{b + g} \]  

Based on expression (38), many people have carried out photothermal deflection measurements for the thermal and optical characterisation of solids [30-32, 35-48]. Among these, the thermal diffusivity of solids is one of the most widely studied thermal parameter. Salazar et al. analysed various theoretical and experimental conditions and arrived at certain expressions which describe a linear relationship of PTD signal phase with various parameters such as pump-probe offset, height of the probe-beam above the sample surface etc [31]. For \( a = b = z = 0 \), where \( a, b \) and \( z \) are the pump-beam spot size, probe-beam spot size and the probe-beam height above the sample surface, there exist a linear relationship between the phase of the transverse component of the probe-beam deflection and the pump-probe offset. Slope of the plot connecting the phase of the PTD signal and the pump-probe offset is given by

\[ m = \frac{1}{\mu_s} = \sqrt{\frac{\pi^2}{\alpha_s}} \]  

Investigations discussed in the subsequent chapters are based on the theoretical models described in this chapter.
References