OPTOACOUSTIC EFFECT AND THE THERMAL DIFFUSIVITY OF SOLIDS

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An optoacoustic method for determining the thermal diffusivity is investigated theoretically. The results are confirmed by experimental data.

Since 1973, methods based on the application of the optoacoustic effect for investigating solid and liquid materials [1, 2] have been growing in popularity. This effect entails the conversion of radiant energy into acoustic oscillations and takes place as follows for solids:

When a sample is illuminated with a modulated beam of radiation, temperature oscillations are generated in it and propagate across the surface into the contiguous gas. If the sample is situated in a small closed chamber, the temperature oscillations induce pressure oscillations of the same frequency in the gas volume, where they can be measured by means of a sensitive microphone.

The magnitude of the acoustic signal depends on such properties of the sample as the absorption coefficient, the duration of the processes of conversion of absorbed radiation into heat, the thermophysical properties, and the geometry. The acoustic oscillations also acquire a certain phase shift relative to the incident modulated radiation, mainly because of a considerable time lag of heat-transfer processes in comparison with the propagation of radiation.

Data obtained under various experimental conditions on the magnitude and phase shift of the signal can be used to determine the optical and thermal properties and geometrical parameters of the investigated sample.

Inasmuch as the pahse shift of the acoustic signal is largely related to heat-transfer processes, phase-angle measurements are preferable for determining such a characteristic as the thermal diffusivity of the material. Here it is more practical to perform measurements with the absorption of radiation on the outer surface of the sample rather than in the volume, and with propagation of thermal pulses through the sample into a gas-filled chamber. In this case the phase shift of the signal will not depend on the optical properties of the sample, and it is simpler to extract information about the thermal diffusivity from the measurement results. This condition can be established on practice for any material by depositing a thin absorbing layer on one of its surfaces.

The details of the evolution of the signal phase shift in this measurement procedure have not been investigated to date. The following equation proposed in [3, 4] from a simplified analysis of the propagation of temperature waves in a semiinfinite body for specified temperature oscillations on the surface:

$$\Psi = -\frac{\pi}{2} - l_s\left(\frac{\omega}{2\alpha_s}\right)^{1/2}, \tag{1}$$

relating the thermal diffusivity to the phase shift of the acoustic signal, describes the attendant process only in the first approximation and cannot always be used for quantitative analysis.

In the present article, on the basis of a more rigorous model conforming to the true conditions, we analyze theoretically the evolution of the phase shift of the acoustic signal produced by the absorption of radiation incident on one surface of a sample. We derive general relations, in which Eq. (1) is assumed as a special case and which can be used to determine the optimal conditions for thermal diffusivity measurements. We also give some experimental results confirming the validity of the derived relations.

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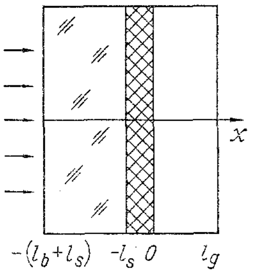

Fig. 1. One-dimensional model of a photoacoustic cell.

Figure 1 shows the investigated one-dimensional model of an optoacoustic, or so-called photoacoustic, cell. A sample of thickness l_s is placed on a transparent base of thickness l_b. The interior of the cell is filled with a gas and has a depth l_g. We assume that the transverse dimensions of all the components are much greater than the dimensions in the direction of the x axis and that heat-transmission processes in the transverse direction are negligible. This condition is readily created in experiment.

A beam of radiation modulated at an angular frequency ω propagates in the x direction and is absorbed at the surface of the sample at $x = -l_s$. The thermal pulses transmitted through the sample induce a periodic increase in the temperature and pressure of the gas in the cell.

The heat-conduction equations for the base, sample, and gas in this system have the same form:

$$\frac{\partial^2 T_i}{\partial x^2} = \frac{1}{\alpha_i} \frac{\partial T_i}{\partial t}, \tag{2}$$

where i = b, s, g. The indices refer quantities to the base, the sample, and the gas in the cell, respectively.

We now formulate the boundary conditions.

The heat fluxes used in optoacoustic techniques are of small magnitude, and the increase in the overall temperature level during the measurements is extremely slight. With this restriction, the radiation and convection components of the heat transfer are negligible, and it can be assumed that the conditions of continuity of the temperature and heat fluxes are satisfied at the boundaries:

$$T_s|_{x=0} = T_g|_{x=0}, \tag{3}$$

$$T_s|_{x=-l_s} = T_b|_{x=-l_s}, \tag{4}$$

$$\lambda_s \frac{\partial T_s}{\partial x}\bigg|_{x=0} = \lambda_g \frac{\partial T_g}{\partial x}\bigg|_{x=0}. \tag{5}$$

The absorption of modulated radiation on the surface of the sample is equivalent to the release of heat at the surface with a certain intensity I_0 according to the law $I_0[1 + \exp \times (j\omega t)]$. In the given problem we are concerned only with the periodic component of the heat source, and so the boundary condition can be written in the form

$$I_0 \exp(j\omega t) = -\lambda_s \frac{\partial T_s}{\partial x}\bigg|_{x=-l_s} + \lambda_b \frac{\partial T_b}{\partial x}\bigg|_{x=-l_s}. \tag{6}$$

We also assume that the thicknesses of the base and the gas in the chamber are greater than the thermal wavelengths in them at the investigated modulation frequencies, i.e., they are "thermally thick." In this case, heat losses through the base and the gas are absent for the periodic component of the solution, and we can write

$$T_b|_{x=-(l_b+l_s)} = 0, \tag{7}$$

$$T_g|_{x=l_g} = 0. \tag{8}$$

We solve the system (2)-(8) by separating variables and seeking the periodic components of the solution for each domain in the form

$$T_i = [U_i \,\mathrm{ch}(\sigma_i x) + V_i \,\mathrm{sh}(\sigma_i x)] \exp(j\omega t),$$
$$\sigma_i = (1 + j)/\mu_i, \quad \mu_i = \left(\frac{2\alpha_i}{\omega}\right)^{1/2}, \quad j = (-1)^{1/2}. \tag{9}$$

The quantity μ_i is called the thermal diffusion length. It corresponds to the length at which the thermal oscillations decay by 1/e for a given modulation frequency.

To determine the unknown coefficients U_i and V_i we substitute expressions (9) into the boundary conditions (3)-(8).

After appropriate transformations we obtain expressions for the temperature oscillations on the surfaces of the sample:

$$T|_{x=0} = \Theta \exp(j\omega t) = \lambda_s \sigma_s I_0 \{\lambda_s \sigma_s \,\mathrm{ch}(\sigma_s l_s)[\lambda_s \sigma_s \,\mathrm{th}(\sigma_s l_s) + \lambda_b \sigma_b] +$$
$$+ \lambda_g \sigma_g \,\mathrm{sh}(\sigma_s l_s)[\lambda_s \sigma_s \,\mathrm{cth}(\sigma_s l_s) + \lambda_b \sigma_b]\}^{-1} \exp(j\omega t), \tag{10}$$
$$T|_{x=-l_s} = W \exp(j\omega t) = \Theta \,\mathrm{ch}(\sigma_s l_s) \exp(j\omega t). \tag{11}$$

The temperature oscillations at the gas—sample boundary determine the magnitude of the pressure oscillations of the gas in the cell.

Under the condition that the gas obeys the ideal-gas laws and is "thermally thick," these pressure oscillations have the magnitude [5]

$$\Delta p = \frac{\Theta \gamma P_0 \mu_g}{\sqrt{2}\, l_g T_0} \exp\left[j\left(\omega t - \frac{\pi}{4}\right)\right]. \tag{12}$$

Expressions (10)-(11) are complex-valued and can be represented in the form

$$\Theta = \Theta_1 + j\Theta_2 = |\Theta| \exp \Psi(0), \quad W = W_1 + jW_2 = |W| \exp \Psi(-l_s),$$

where $|\Theta| = (\Theta_1^2 + \Theta_2^2)^{1/2}$; $|W| = (W_1^2 + W_2^2)^{1/2}$; $\mathrm{tg}\,\Psi(0) = \Theta_2/\Theta_1$; $\mathrm{tg}\,\Psi(-l_s) = W_2/W_1$.

Here $|\Theta|$ and $|W|$ are the real values of the temperature oscillations at the boundaries of the sample; $\psi(0)$ and $\psi(-l_s)$ are their phase shifts relative to the intensity oscillations of the incident radiation.

Separating real and imaginary parts in expressions (10)-(11), we obtain the values of the phase shifts of the temperature oscillations at the boundaries of the sample:

$$\mathrm{tg}\,\Psi(0) = -\left\{(1 + gb)\left[\mathrm{sh}\left(\frac{l_s}{\mu_s}\right)\cos\left(\frac{l_s}{\mu_s}\right) + \mathrm{ch}\left(\frac{l_s}{\mu_s}\right)\sin\left(\frac{l_s}{\mu_s}\right)\right] +\right.$$
$$\left. + (g + b)\left[\mathrm{ch}\left(\frac{l_s}{\mu_s}\right)\cos\left(\frac{l_s}{\mu_s}\right) + \mathrm{sh}\left(\frac{l_s}{\mu_s}\right)\sin\left(\frac{l_s}{\mu_s}\right)\right]\right\} \times \tag{13}$$
$$\times \left\{(1 + gb)\left[\mathrm{sh}\left(\frac{l_s}{\mu_s}\right)\cos\left(\frac{l_s}{\mu_s}\right) - \mathrm{ch}\left(\frac{l_s}{\mu_s}\right)\sin\left(\frac{l_s}{\mu_s}\right)\right] + (g + b)\left[\mathrm{ch}\left(\frac{l_s}{\mu_s}\right)\cos\left(\frac{l_s}{\mu_s}\right) - \mathrm{sh}\left(\frac{l_s}{\mu_s}\right)\sin\left(\frac{l_s}{\mu_s}\right)\right]\right\}^{-1},$$

$$\mathrm{tg}\,\Psi(-l_s) = -\left\{(1 + gb)\left(\mathrm{sh}\left(\frac{2l_s}{\mu_s}\right)\left[\mathrm{ch}\left(\frac{2l_s}{\mu_s}\right) + \cos\left(\frac{2l_s}{\mu_s}\right)\right]^{-1}\right.\right.$$
$$\left.\left. + \sin\left(\frac{2l_s}{\mu_s}\right)\left[\mathrm{ch}\left(\frac{2l_s}{\mu_s}\right) + \cos\left(\frac{2l_s}{\mu_s}\right)\right]^{-1}\right) + b + g\right\} \times \tag{14}$$
$$\times \left\{(1 + gb)\left(\mathrm{sh}\left(\frac{2l_s}{\mu_s}\right)\left[\mathrm{ch}\left(\frac{2l_s}{\mu_s}\right) + \cos\left(\frac{2l_s}{\mu_s}\right)\right]^{-1} - \sin\left(\frac{2l_s}{\mu_s}\right)\left[\mathrm{ch}\left(\frac{2l_s}{\mu_s}\right) + \cos\left(\frac{2l_s}{\mu_s}\right)\right]^{-1}\right) + b + g\right\}^{-1}$$

where $g = \lambda_g \mu_s/\lambda_s \mu_g$; $b = \lambda_b \mu_s/\lambda_s \mu_b$. We note that almost always the quantity $g < 10^{-2}$.

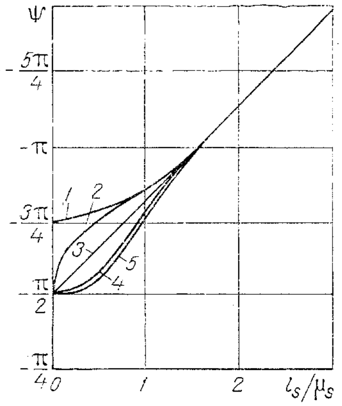

Fig. 2

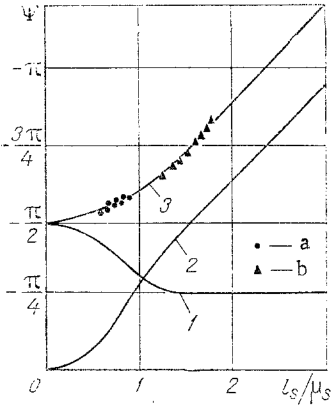

Fig. 3

Fig. 2. Phase shift Ψ, rad, of the acoustic signal dimensionless ratio l_s/μ_s for various values of the parameter b: 1) b = 0, b = 10^{-2}; 2) 10^{-1}; 3) 1; 4) 10; 5) 10^2.

Fig. 3. Various components of the total phase shift of the temperature oscillations l_s/μ_s: 1) phase shift between the temperature oscillations on the irradiated surface of the sample and the intensity oscillations of the incident radiation; 2) the same, on two surfaces of the sample; 3) the same, at the sample–gas boundary in the cell and between the intensity oscillations of the radiation; a) steel sample of thickness $0.1 \cdot 10^{-3}$ m; b) the same, $0.21 \cdot 10^{-3}$ m.

The ratios λ_i/μ_i have the units of a heat-transfer coefficient, and the parameters g and b therefore characterize the relative capacity of materials to transmit thermal waves.

On the basis of (12) the phase shift of the acoustic signal for a "thermally thick" cell is

$$\Psi = \Psi(0) - \frac{\pi}{4}. \tag{15}$$

For small gas thicknesses, such that the heat losses through it cannot be disregarded, the relationship is more complicated [6].

The phase shifts of the acoustic signal, calculated according to expression (13) with regard for (15), are shown in Fig. 2 as a function of the ratio of the sample thickness to the thermal diffusion length for various values of the parameter b.

It is seen that the functional relationship is linear in the interval $l_s/\mu_s \geqslant 1.5$. For smaller values of l_s/μ_s linearity is preserved only in the case b = 1, implying equality of the thermal characteristics of the base and the sample. When b < 1, corresponding to a thermally insulated base, the variation of the phase with decreasing l_s/μ_s slows down, and in the limit $b \to 0$ the phase shift approaches $3\pi/4$. When b > 1, i.e., when the sample is situated on a good thermally conducting base, the variation of the phase in this interval is more rapid.

Despite the fact that expression (13) describes the phase shift, it is difficult to use it in general form for determining the thermal diffusivity, because it is cumbersome and contains the parameter b, which cannot always be estimated beforehand.

Of practical importance is the situation in which the sample is placed in external contact with an insulator, i.e., $b \leqslant g < 10^{-2}$. The expressions for the phase shift in this case are greatly simplified and acquire the form

$$\Psi(-l_s) = -\operatorname{arctg}\left\{\left[\operatorname{sh}\left(\frac{2l_s}{\mu_s}\right) + \sin\left(\frac{2l_s}{\mu_s}\right)\right]\left[\operatorname{sh}\left(\frac{2l_s}{\mu_s}\right) - \sin\left(\frac{2l_s}{\mu_s}\right)\right]^{-1}\right\}, \tag{16}$$

$$\Psi(0) = \Psi(-l_s) - \operatorname{arctg}\left[\operatorname{tg}\left(\frac{l_s}{\mu_s}\right)\operatorname{th}\left(\frac{l_s}{\mu_s}\right)\right]. \tag{17}$$

Accordingly, the phase shift between the temperature oscillations on the two surfaces of the sample has the form

$$\Delta\Psi = -\operatorname{arctg}\left[\operatorname{tg}\left(\frac{l_s}{\mu_s}\right)\operatorname{th}\left(\frac{l_s}{\mu_s}\right)\right]. \tag{18}$$

Relations (16)-(18) provide a clearer picture of how the total phase shift of the acoustic signal evolves.

The first component of the phase shift is formed by the lagging of the temperature oscillations on the irridated surface behind the intensity oscillations of the incident radiation. This lag decreases as the ratio l_s/μ_s is increased, corresponding either to an increase in the thickness of the sample or an increase in the modulation frequency, and it attains a value of $\pi/4$ for $l_s/\mu_s \approx 1.5$. With a further increase in l_s/μ_s its value remains constant and equal to $\pi/4$.

The second component of the phase shift is formed as the temperature oscillations propagate through the sample. For small values of l_s/μ_s it is described by expression (18), and for $l_s/\mu_s \geqslant 1.5$ it is simply equal to l_s/μ_s. Finally, the third component is induced by the fact that the pressure oscillations of the gas in the cell lag the temperature oscillations on the sample surface facing the cell by $\pi/4$.

The values of the phase shifts as a function of l_s/μ_s, calculated according to relations (16)-(18), are shown in Fig. 3.

The experimental work was carried out on steel samples ($\alpha = 0.13 \cdot 10^{-4}$ m^2/sec) with a diameter of $1.5 \cdot 10^{-2}$ m and thicknesses of $0.1 \cdot 10^{-3}$ and $0.21 \cdot 10^{-3}$ m, which were placed with one surface in contact with the interior volume of a cell of diameter $0.6 \cdot 10^{-2}$ m and depth $1.5 \cdot 10^{-3}$ m. The second surface of the samples was placed in contact with a thermally thick transparent window to preclude the influence of convection and provide insulation against the surrounding medium.

The light from a 100-W incandescent lamp was focused through a mechanical light chopper in the form of a rotating slotted disk onto the surface of the sample away from the cell, creating a spot with a diameter of $\sim 3 \cdot 10^{-3}$ m. The acoustic signal was converted by an optical microphone into electrical pulses, which were amplified by a preamplifier and a narrowband amplifier with a tunable pass band. A comparison signal was generated by an LED—photodiode pair coupled optically through the copper disk. A frequency meter was used to measure the time shift between the pulses of the comparison signal and the signal generated by the microphone; the result was then converted into the phase shift by multiplying it by the angular modulation frequency. The modulation frequency was varied in the interval 140-280 Hz. The measurement error did not exceed ±0.05 rad. The experimental results are shown in Fig. 3. It is evident from the figure that the form of the theoretical curve has been correctly chosen.

The foregoing analysis indicates that the interval of the ratio $l_s/\mu_s \geqslant 1.5$ is the most suitable for thermal diffusivity measurements. It is readily estimated if at least the order of magnitude of the thermal diffusivity is known beforehand. It must be borne in mind that with an increase in the ratio l_s/μ_s the attenuation of the thermal waves in the sample increases, and the amplitude of the signal decays rapidly. In the general case the signal can acquire an appreciable contribution from elastic vibrations that are weaker but are only slightly attenuated in transmission through the sample. The influence of this effect on the acoustic signal has been studied in detail [7]. An estimation using the results of [7] shows that in connection with heat release at the surface of the solid sample the contribution of this effect to the signal is negligible if $l_s/\mu_s \leqslant 3.5$ and it can amount to several percent for $l_s/\mu_s \approx 5$.

In situations where the sample is so thin as to prevent attainment of the linear interval, it is possible to realize either the condition $b = 1$, in which case relation (1) is valid for any sample thickness, or $b \leqslant g$, in which case relations (16)-(18) are valid.

NOTATION

Ψ, phase shift; ω, angular frequency of modulation of radiation; α, thermal diffusivity; l, length; T, temperature; t, time; λ, thermal conductivity; U, V, coefficients of equations;

Θ, temperature at sample–gas boundary in photoacoustic cell; W, temperature at sample–base boundary; μ, thermal diffusion length; γ, ratio of specific heats at constant pressure and constant volume; P_0, pressure level of gas in photoacoustic cell; T_0, temperature level of gas in cell.

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METHOD OF MEASURING THE KINETIC AND THERMODYNAMIC PROPERTIES IN BINARY STRATIFIED SYSTEMS BY MEANS OF SCATTERED LIGHT SPECTRA

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A method and results of investigating the kinetic and thermodynamic parameters of the mutual diffusion coefficient in binary stratified liquid mixtures are described.

Diffusion in nonideal solutions has been investigated slightly. This refers especially to diffusion processes near the critical stratification point.

The possibilities of the combined utilization of optical mixing spectroscopy and the measurement of scattered radiation intensity to investigate the kinetic and thermodynamic properties of the mutual diffusion coefficient in a broad temperature range and in the neighborhood of the critical stratification point are described below.

From a consideration of the kinetics of concentration fluctuations, it follows that for the hydrodynamic approximation the unbiased component of the Rayleigh scattering spectrum is related to the thermodynamic force of the system $(\partial x/\partial \mu)_{P,T}$ and the mutual diffusion coefficient $D_{1,2}$ by the relationship [1]

$$J(q,\ \omega) \sim \left(\frac{\partial x_2}{\partial \mu_2}\right)_{P,T} \frac{x_1 T\cdot 2D_{1,2}q^2}{\omega^2+(D_{1,2}q^2)^2}, \tag{1}$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$. For the Lorentz form of the spectral line, $D_{1,2}$ is determined by the halfwidth of this line:

$$\Delta\omega_{1/2} = D_{1,2}q^2.$$

The integrated scattered light intensity for a given concentration x_i is determined entirely, as follows from (1), by the thermodynamic properties of the solution

$$J^{-1}(T) \sim x_j \left(\frac{\partial \mu_i}{\partial x_i}\right)_{P,T} T^{-1}, \tag{2}$$

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