OPTOACOUSTIC DETERMINATION OF THERMOPHYSICAL CHARACTERISTICS. II

S. A. Vinokurov

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Alternative techniques for the comprehensive determination of thermophysical characteristics by the optoacoustic method are discussed, and their domain of applicability is established.

The optoacoustic method makes it possible to perform comprehensive measurements of thermophysical characteristics when a two-layer system comprising a standard sample and the investigated sample is used, where radiation is absorbed on one of the surfaces and the relative thicknesses of the components of the system correspond to the condition $a_1 l_1 > 1.5$, $a_2 l_2 < 1.5$, where $a = (\omega/2\alpha)^{1/2}$ is the coefficient of thermal diffusion.

Thermal properties can be determined both from the amplitude or phase shift of the acoustic signal generated by absorption of the incoming radiation on the various surfaces of the system and also from the extremum of the phase shift associated with illumination of the outer surface of the investigated sample [1, 2].

The method is applicable if the thermal resistance between the samples is negligibly small. Its capabilities depend on the relative thicknesses and the relationship between the values of the thermophysical characteristics of the investigated and standard samples.

Below, on the basis of the theory presented earlier [2], we discuss certain alternative measurement techniques and determine their domains of applicability.

A schematic diagram of the two-layer system is shown in Fig. 1. Since the acoustic signal is related one-to-one with the amplitude and phase shift of the temperature oscillations on the sample surface connected to the optoacoustic chamber, we consider the behavior of these quantities at the boundaries of the two-layer system.

We assume at the outset, as in [2], that the surface $x = l_1 + l_2$ is illuminated and the sample 2 is opaque.

For quantitative measurements it is necessary that the thermal activity coefficient of the gas in the chamber be negligible in comparison with the value of this coefficient for samples 1 and 2. This condition is upheld for the majority of solid and liquid materials. Otherwise the result will depend on the relationship between the thermal properties of the sample and the gas, thereby introducing ambiguity into the determination of the thermophysical characteristics.

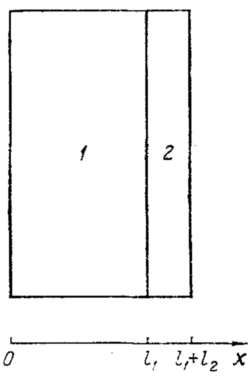

Fig. 1. Investigated two-sample system.

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In light of the foregoing, we simplify the expressions derived in [2] for the amplitude and phase shift of the temperature oscillations on the outer surfaces of the system under the conditions $a_1l_1 > 1.5$ and $a_2l_2 < 1.5$:

$$|\Delta T|\big|_{x=l_1+l_2} = |W| = \frac{I_0}{\sqrt{2}\,\lambda_1 a_1 s}\left(\frac{[s\,\mathrm{sh}\,(a_2l_2)+\mathrm{ch}\,(a_2l_2)]^2+\cos^2(a_2l_2)\,(s^2-1)}{[s\,\mathrm{sh}\,(a_2l_2)+\mathrm{ch}\,(a_2l_2)]^2+\sin^2(a_2l_2)\,(s^2-1)}\right)^{1/2}, \tag{1}$$

$$\Psi\big|_{x=l_1+l_2} = \Psi_W = -\frac{\pi}{4} + \mathrm{arctg}\left[\mathrm{tg}\,(a_2l_2)\,\frac{\mathrm{ch}\,(a_2l_2)+s\,\mathrm{sh}\,(a_2l_2)}{\mathrm{sh}\,(a_2l_2)+s\,\mathrm{ch}\,(a_2l_2)}\right] - \mathrm{arctg}\left[\mathrm{tg}\,(a_2l_2)\,\frac{\mathrm{sh}\,(a_2l_2)+s\,\mathrm{ch}\,(a_2l_2)}{\mathrm{ch}\,(a_2l_2)+s\,\mathrm{sh}\,(a_2l_2)}\right], \tag{2}$$

$$|\Delta T|\big|_{x=0} = |\Theta| = \frac{I_0}{\sqrt{2}\,\lambda_1 a_1\,\dfrac{\exp(a_1l_1)}{2}}\,\{[s\,\mathrm{sh}\,(a_2l_2)+\mathrm{ch}\,(a_2l_2)]^2+\sin^2(a_2l_2)\,(s^2-1)\}^{-1/2}, \tag{3}$$

$$\Psi\big|_{x=0} = \Psi_\Theta = -\frac{\pi}{4} - a_1l_1 - \mathrm{arctg}\left[\mathrm{tg}\,(a_2l_2)\,\frac{\mathrm{sh}\,(a_2l_2)+s\,\mathrm{ch}\,(a_2l_2)}{\mathrm{ch}\,(a_2l_2)+s\,\mathrm{sh}\,(a_2l_2)}\right], \tag{4}$$

where $s = (\lambda_2c_2\rho_2)^{1/2}/(\lambda_1c_1\rho_1)^{1/2}$ is the ratio of the thermal activity coefficients of the samples.

These relations are also valid for other positions of the heat source. If heat is released on the surface $x = 0$, the magnitude and phase shift of the temperature oscillations on the surface $x = l_1 + l_2$ are given by Eqs. (3) and (4). If the heat source is the surface $x = l_1$, these expressions are also valid for the surface $x = l_1 + l_2$, but now without the respective terms $\exp(a_1l_1)/2$ and a_1l_1.

When $l_2 \to 0$, i.e., when the system consists of sample 1 only, Eqs. (1)-(4) acquire the form

$$|W|_0 = \frac{I_0}{\sqrt{2}\,\lambda_1 a_1}, \quad \Psi_{W0} = -\frac{\pi}{4},$$

$$|\Theta|_0 = \frac{I_0}{\sqrt{2}\,\lambda_1 a_1\,\dfrac{\exp(a_1l_1)}{2}}, \quad \Psi_{\Theta 0} = -\frac{\pi}{4} - a_1l_1.$$

I. DETERMINATION OF THE THERMOPHYSICAL CHARACTERISTICS FROM THE PHASE SHIFT OF THE SIGNAL

We assume that sample 1 is the standard with known properties, and sample 2 is the investigated test sample. We introduce the notation

$$\Psi_1 = \Psi_W - \Psi_{W0} = \mathrm{arctg}\left[\frac{(1-s^2)\sin(2a_2l_2)}{(1+s^2)\,\mathrm{sh}\,(2a_2l_2)+2s\,\mathrm{ch}\,(2a_2l_2)}\right], \tag{5}$$

$$\Psi_2 = \Psi_\Theta - \Psi_{\Theta 0} = -\mathrm{arctg}\left[\mathrm{tg}\,(a_2l_2)\,\frac{\mathrm{sh}\,(a_2l_2)+s\,\mathrm{ch}\,(a_2l_2)}{\mathrm{ch}\,(a_2l_2)+s\,\mathrm{sh}\,(a_2l_2)}\right], \tag{6}$$

$$\Psi_3 = \mathrm{arctg}\left[\mathrm{tg}\,(a_2l_2)\,\frac{\mathrm{ch}\,(a_2l_2)+s\,\mathrm{sh}\,(a_2l_2)}{\mathrm{sh}\,(a_2l_2)+s\,\mathrm{ch}\,(a_2l_2)}\right]. \tag{7}$$

Here Ψ_1 and Ψ_2 are the relative phase shifts of the temperature and oscillations on the illuminated outer surface and the nonilluminated surface of sample 2; Ψ_3 is the phase shift be-

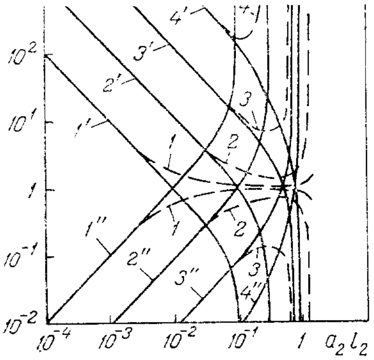

Fig. 2. Lines of constant values of the phase shift in coordinates s, $a_2 l_2$. 1) 0.01 rad; 2) 0.1; 3) 0.5; 4) 0.75; 1-4) values of Ψ_1 for s < 1 and ($-\Psi_1$) for s > 1; 1'-4') ($-\Psi_2$); 1"-4") Ψ_3; s and $a_2 l_2$ are dimensionless.

tween the temperature oscillations on the two surfaces of sample 2 with illumination of its outer surface or, alternatively, between the signals associated with illumination of its outer and inner surfaces.

The quantities Ψ_1 and Ψ_2 are determined relative to the constant phase shift of the temperature oscillations ($-\pi/4$) associated with, e.g., illumination of the outer surface of a thick opaque sample. The phase shift Ψ_2 is always negative, while Ψ_1 is negative for s > 1 and positive for s < 1.

The values of Ψ_1 and Ψ_2 are readily determined experimentally by directing radiation from opposite sides of the two-layer system. Of the three quantities Ψ_1, Ψ_2, and Ψ_3, the first two are independent, and $\Psi_3 = \Psi_1 - \Psi_2$.

Information about the thermophysical characteristics is contained in $s = (\lambda_2 c_2 \rho_2)^{1/2} / (\lambda_1 c_1 \rho_1)^{1/2}$ and $a = (\omega / 2\alpha)^{1/2}$.

Solving Eqs. (5)-(7) for s and equating the expressions so obtained, we obtain a relation between the relative sample thickness and the phase shifts Ψ_1, Ψ_2, and Ψ_3 for each specific sample—standard pair:

$$a_2 l_2 = \mathrm{arctg}\,[-\mathrm{tg}\,(\Psi_1 - \Psi_2)\,\mathrm{tg}\,\Psi_2]^{1/2} = \mathrm{arctg}\,[-\mathrm{tg}\,\Psi_3\,\mathrm{tg}\,\Psi_2]^{1/2}. \tag{8}$$

For the measured phase shifts Ψ_1 and Ψ_2, using (8) and one of the expressions (5)-(7), we can determine $a_2 l_2$ and s. The results are sufficient for determining the thermal activity coefficient, the thermal diffusivity, and the thermal conductivity of sample 2.

We now inquire how the capabilities of the method change with the relative thickness of sample 2 and the relationship between the thermal properties of the samples.

Curves 1, 1', and 1" in Fig. 2, which correspond to phase shifts of 0.01 radian, can be regarded as threshold curves separating the zones of sensitivity and insensitivity.

All the fundamental thermophysical characteristics can be determined only in the domain to the right of curves 1' and 1". Here the phase shifts Ψ_1, Ψ_2, and Ψ_3 are sufficient for the measurement of all characteristics. The measurement-suitable domain extends to values of $a_2 l_2 \approx 1$. When $a_2 l_2 > 1$, the influence of sample 1 diminishes rapidly, and for $a_2 l_2 > 1.5$ we have $\Psi_1 = 0$, $\Psi_2 = -a_2 l_2$, $\Psi_3 = a_2 l_2$.

In the zone bounded by curves 1, 1', and 1", neither the thermal properties of sample 2 nor the distribution of the absorbed radiation along its thickness has practically any influence on the phase shift of the signal. Sample 2, which corresponds to this domain, is suitable for use as a nondistorting absorber on a transparent test sample.

In the zone above curve 1' and to the left of curve 1" the phase shift of the signal is still not affected by the distribution of the heat sources in sample 2, but its thermal properties begin to have an effect. Since $\Psi_1 = \Psi_2$ here, the values of s or $a_2 l_2$ can only be obtained when one of these quantities is known beforehand.

In the domain below curve 1" and to the left of curve 1' it is also necessary to know one of the quantities s or $a_2 l_2$ beforehand for their determination. Here sample 2 does not contribution to the phase shift of the temperature oscillations on the surface x = 0.

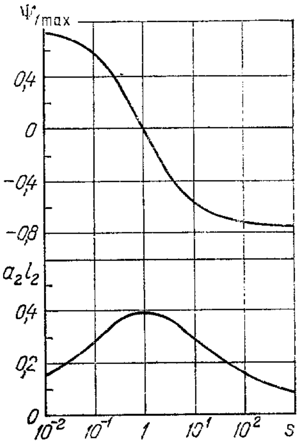

Fig. 3. External value of Ψ_1, rad, vs s, and corresponding curve of a_2l_2 vs s.

For $s < 10^{-2}$ the ratio of the thermal activity coefficients of the gas in the optoacoustic chamber and of sample 2 can become commensurate with s or even exceed it. The behavior of the curves is distorted in this domain; for small values of a_2l_2 they bend downward, and their form depends on the specific ratio of the thermal activity coefficients. It is a foregone conclusion that this situation must be avoided.

The variation of the phase shift Ψ_1 on the illuminated outer surface of the thin sample 2 as a function of a_2l_2 has an extremum, the value Ψ_{1max} of which depends on s, while its position depends on a_2l_2 (see Fig. 2 in [2]). By varying the modulation frequency, i.e., by varying a_2l_2 experimentally, it is possible to determine this extremal value of the phase shift and to acquire information at once about $(\lambda_2 c_2 \rho_2)^{1/2}$, α_2, and λ_2.

At the point of the extremum, the first derivative of Ψ_1 with respect to a_2l_2 is equal to zero. Carrying out the appropriate calculations, we obtain the following relations between s an a_2l_2 from expression (5) in this case:

$$s = \frac{1 - \mathrm{tg}\,(2a_2l_2)\,\mathrm{th}\,(2a_2l_2)}{\mathrm{tg}\,(2a_2l_2) - \mathrm{th}\,(2a_2l_2)} \pm \left[\left(\frac{1 - \mathrm{tg}\,(2a_2l_2)\,\mathrm{th}\,(2a_2l_2)}{\mathrm{tg}\,(2a_2l_2) - \mathrm{th}\,(2a_2l_2)}\right)^2 - 1\right]^{1/2}. \tag{9}$$

The plus and minus signs correspond to values of $\Psi_{1max} < 0$ and $\Psi_{1max} > 0$.

Figure 3 shows the functional relations between Ψ_{1max}, s, and a_2l_2, calculated according to (5) and (9). It follows from an analysis of these curves that such a measurement technique is applicable if $(2\text{-}3) < s < 10^2$ or $10^{-2} < s < (0.3\text{-}0.5)$. The values of a_2l_2 at which Ψ_1 passes through an extremum are restricted to the small domain $0.1 < a_2l_2 < 0.4$, and so the phase shift must be measured in a broad range of modulation frequencies in order to determine Ψ_{1max}.

We note that if the standard is sample 2 and the test sample is the thicker sample 1, the thermal activity coefficient of the latter can be determined from Ψ_1 or Ψ_2, and the thermal diffusivity can be determined from the phase shift of the signal on the side x = 0. The coefficient λ_1 is readily calculated from $(\lambda_1 c_1 \rho_1)^{1/2}$ and α_1.

II. DETERMINATION OF THE THERMOPHYSICAL CHARACTERISTICS FROM THE SIGNAL AMPLITUDE

As in Sec. I, we introduce the following notation for the relative temperatures:

$$T_1 = \frac{|W|}{|W|_0} = \frac{1}{s}\left\{\frac{[s\,\mathrm{sh}\,(a_2l_2) + \mathrm{ch}\,(a_2l_2)]^2 + \cos^2(a_2l_2)\,(s^2 - 1)}{[s\,\mathrm{sh}\,(a_2l_2) + \mathrm{ch}\,(a_2l_2)]^2 + \sin^2(a_2l_2)\,(s^2 - 1)}\right\}^{1/2}, \tag{10}$$

$$T_2 = \frac{|\Theta|}{|\Theta|_0} = \{[s\,\mathrm{sh}\,(a_2l_2) + \mathrm{ch}\,(a_2l_2)]^2 + \sin^2(a_2l_2)\,(s^2 - 1)\}^{-1/2}, \tag{11}$$

$$T_3 = \frac{T_1}{T_2} = \frac{1}{s}\,\{[s\,\mathrm{sh}\,(a_2l_2) + \mathrm{ch}\,(a_2l_2)]^2 + \cos^2(a_2l_2)\,(s^2 - 1)\}^{1/2}, \tag{12}$$

where T_1 is the ratio of the amplitudes of the temperature oscillations on the illuminated outer surface of sample 2 and on the open surface of the thick sample 1 for equal rates of heat release, T_2 is the ratio of the amplitudes of the temperature oscillations on the nonilluminated surface of sample 2 and on the open surface of sample 1 (T_2 does not depend on

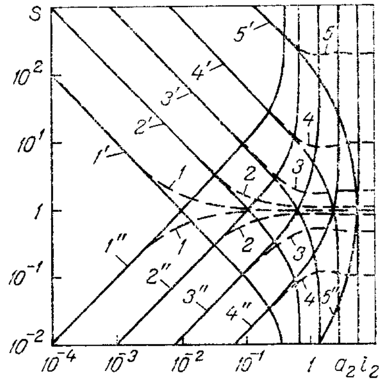

Fig. 4. Lines of constant values of the relative temperature in coordinates s, $a_2 l_2$. 1) 1.01; 2) 1.1; 3) 2.0; 4) 10.0; 5) 200; 1-5) values of T_1 for s < 1 and of $1/T_1$ for s > 1; 1'-5') $1/T_2$; 1"-5") T_3.

whether heat is released on the surface $x = l_2 + l_2$ or $x = l_1$), and T_3 is the ratio of the amplitudes of the temperature oscillations on the illuminated outer surface of sample 2 and on its opposite surface; $T_1 > 1$ for $s < 1$, and $T_1 < 1$ for $s > 1$; always $T_2 < 1$ and $T_3 > 1$.

Relations between the relative sample thickness and the temperature T_1, T_2, and T_3 can be obtained from (10)-(12) by a procedure analogous to that used for the phase shifts. The analytical expressions are cumbersome in this case, but a solution is readily obtained by numerical methods for every specific situation.

Curves 1, 1', and 1" in Fig. 4, which correspond to values of the relative temperatures deviating 1% from unity, are regarded as the threshold curves between different zones.

By analogy with the division of the sensitivity zones for the phase shifts, the thermal activity coefficient, thermal diffusivity, and thermal conductivity of sample 2 can only be determined here in the domain to the right of curves 1' and 1". The measurement-suitable domain is bounded by values of $a_2 l_2 = 0.6$-0.7.

In the zone between curves 1, 1', and 1" the signal amplitude is not affected either by the thermal properties of sample 2 or by the heat-release distribution in it. Its value depends only on the total quantity of heat released.

In the domain to the left of curve 1" the signal amplitude is not affected by the distribution of heat sources in the cross section of sample 2. This zone is broader than for the phase shift.

In amplitude measurements of the thermophysical characteristics, in contrast with phase measurements, it is necessary to establish heat sources of identical or known strengths on the different surfaces, but this requirement is not always practicable. We therefore judge phase measurements to be preferable.

We have discussed the capabilities of the method when either the phase or the amplitude of the signal is measured. For example, the quantity T_3 and one of the phase shifts are also sufficient for the comprehensive determination of thermal properties. The overall zone of sensitivity in this case is determined by amplitude measurements.

Reliable results are obtainable only with good thermal contact between the samples. For this purpose the thicker sample can be a liquid. Thin coatings with specially prepared substrates also have excellent contact qualities.

Firm contact between solid samples also helps to prevent the distorting signal associated with periodic mechanical bending of the thin sample as a result of one-sided heating [3]. The application of a liquid damping layer also eliminates this effect almost completely [4].

NOTATION

ω, angular modulation frequency; l, length; I_0, half-strength of heat source; ΔT, periodic component of temperature distribution; Ψ, phase shift; α, thermal diffusivity; λ, thermal conductivity; c, specific heat.

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BRIEF MEASUREMENTS OF THERMAL ACTIVITY IN THE MELTING RANGE OF A SUBSTANCE

G. G. Spirin, E. A. Nakashidze, and L. N. Kudryavtseva

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Methodological features of brief measurements in the phase transition region are examined.

It is known that the abrupt character of fusion, which is characterized by an infinitely small temperature range, is an idealization which corresponds only to perfect crystal structures. In actual polycrystalline systems — especially high-molecular-weight systems [1] — in real crystallization periods, complete thermodynamic equilibrium is not achieved, and the chemical potentials of the systems depend on other factors besides temperature and pressure. Among these factors are the degree of ordering and the size of the crystallite. This situation appreciably broadens the temperature range in which melting occurs; sometimes the range is quite large (about 10°C).

The interpretation of results of nonsteady thermophysical experiments conducted in this range is not always unambiguous.

The measurement process is significantly affected by absorption of heat of fusion during a change in the phase of a substance and the temperature dependence of its thermophysical characteristics. Also, for the brief measurements [2] we are discussing — when the measurement time is 10^{-4} sec — the kinetics of fusion should be taken into account.

The propagation of the temperature field in a substance undergoing a phase transition is connected with the appearance of heat sinks, the capacity of which is proportional to the fraction of melted substance and the heat of fusion h.

Let the content of the liquid phase in the melting range be given by the function u(T, t). In the general case, this function depends both on temperature and, explicitly, on time. The latter fact is related to the kinetics of fusion. In particular, a "lag" in the development of fusion relative to the melting point was noted in [3] for polyethylene glycol (PNG). The size of the "lag" depends on the molecular weight and in the case of PNG is on the order of 10^{-3}-10^{-2} sec. Without concerning ourselves with the mechanism of the lag, to describe it we naturally determine the concentration of the liquid phase in the form

$$u(T, t) = u_0(T)\left(1 - \exp\left(\frac{t}{\tau}\right)\right), \tag{1}$$

where τ is the relaxation time, a parameter which quantitatively determines the lag.

With allowance for (1), we will write the expression for the unit capacity of volumetrically distributed heat sinks as $\omega = h\frac{\partial u}{\partial T}\frac{\partial T}{\partial t}$. Accordingly, the model problem describing the measurement process takes the form

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