Laser dynamic optoacoustic diagnostics of condensed media

S. V. Egerev, L. M. Lyamshev, and O. V. Puchenkov

N. N. Andreev Acoustics Institute of the Academy of Sciences of the USSR

Usp. Fiz. Nauk **160**, 111–154 (September 1990)

Laser dynamic optoacoustic diagnostics is a method of studying materials that has rapidly developed in recent years, and which uses lasers to generate short-period acoustic perturbations and records these perturbations—responses of the material with high time resolution—for subsequent analysis of the fine structure of the response bearing information on the properties of the specimens. The fundamental concepts of the varieties of the method are given. The experience of applying it is generalized for analyzing inhomogeneous liquid and solid specimens, the process of crystallization from the melt, dielectrics, and films of surface-active materials.

INTRODUCTION

In the somewhat more than a hundred years that have passed since the discovery of the optoacoustic effect independently by Bell, Tyndall, and Roentgen, the studies of the interaction of a modulated light beam with a material leading to a specific acoustic response of the medium have taken shape as an independent field at the border between optics and acoustics. The interest in this effect, which has substantially grown with the development of laser technology, is explained in many ways by the rather unexpected potentialities that have been discovered for the creation of relatively inexpensive instruments for optoacoustic (OA) or laser-acoustic (LA) diagnostics with unique frequency properties unattainable for other analogous devices (an example is the measurement of the absorption spectra of powders). The mastery of the optoacoustic method is a considerable advance in laser spectroscopy at the border of the 70s and 80s,[1] along with the development of nonlinear optical methods,[2] the development of pico- and femtosecond diagnostics,[3] and other advances.

Let us briefly recall the essence of OA diagnostics. A pulsed or modulated optical radiation (as a rule, monochromatic), upon being absorbed in a specimen, excites elastic perturbations in the specimen or the media adjacent to it, as well as perturbations of its surface. The recording and analysis of these perturbations enables one to reconstruct the varied physical parameters of the material being studied and their distribution. Often absorption spectra are measured. For these purposes one uses wavelength-tunable laser sources (OA spectroscopy).

Optoacoustic measurement systems with a fixed wavelength of the light source are applicable for reconstructing the thermodynamic parameters of media, visualizing internal defects, layers, etc., which resemble the known technical solutions for ultrasonic introscopy. Therefore it is natural to consider these varieties of the method as OA introscopy.

The thermal OA effect was historically the first most widely studied. It involves the rapid optical heating and expansion of some region of the specimen. Correspondingly more popular and well mastered is the "unperturbing" thermooptical OA diagnostics, which constitutes a variant of calorimetric laser spectroscopy, which is performed by direct measurement of the power of optical radiation absorbed in the specimen by measuring the thermodynamic parameters of the specimen itself (temperature, pressure, etc.). An important feature of the calorimetric methods is the use of the channel of radiationless vibrational-translational relaxation and the nonresonance character of the process. As compared with the purely optical absorption methods of spectroscopy, the calorimetric methods, including the OA ones, possess an important advantage: they enable one to measure the absorbed power directly in the specimen on a "zero" background, rather than on the background of the far greater power of the light transmitted through the specimen. We note also that, from the standpoint of certain applications (e.g., spectral infrared analysis), the analytical potentialities of OA diagnostics are not inferior to those of the nonlinear resonance methods of light-scattering spectroscopy.[2]

With the development of methods and apparatus, OA diagnostics has become based on other, more effective mechanisms of optical sound generation (photochemical processes, evaporation, optical breakthrough, etc.), often associated with local phase transitions in the specimen. In these cases one must deal with "perturbing" OA diagnostics. The development of OA diagnostics has also followed the path of perfection and complication of the "source-specimen-receiver" measuring system.

One distinguishes two fundamental groups of methods: a) gas-microphonic (indirect) methods, b) methods of direct recording of the response signal. The former presuppose the measurement of pressure vibrations in the gas bordering the specimen heated by the modulated optical radiation. The latter are based on measuring the responses directly in the specimen. Below we shall mainly discuss the methods of the latter group.

At present OA diagnostics is applied for studying weakly absorbing media, for analysis of trace concentrations of impurities, for surface analysis, for profiling, and for studying turbid or porous media, powders, and biological tissues. There are also other applications. These methods are the basis of sensitive analytical devices for medicine, biology, technology of the elements of radioelectronic apparatus, and for environmental monitoring. A number of monographs and reviews are devoted to individual aspects of OA diagnostics.[4–7]

 0038-5670/90/090739-24$01.00

The further progress of OA diagnostics involves solving the problem of optimally exciting, recording, and analyzing the acoustic response so as to preserve fully the information on the specimen. It has proved possible to solve this problem by the methods of laser dynamic optoacoustic diagnostics (LDOA diagnostics).[8] This diagnostics presupposes the use of pulsed laser radiation to generate short-period surface or bulk perturbations in solid or liquid media (specimens). The recording of these perturbation responses with high time resolution and subsequent analysis of their forms, of the frequency-time and spatial characteristics of the signals enable one to increase the accuracy and sensitivity of the diagnostics, and to proceed from measuring the space-averaged characteristics to measuring their distributions. The latter is important in studying media having a complex structure (multiphase specimens, biological tissues, or layered inhomogeneous media).

The attention of specialists has also been attracted to the additional potentialities of LDOA diagnostics in the study of the behavior of materials in strong electromagnetic and acoustic fields.

The studies in the field of LDOA diagnostics already comprise an extensive bibliography and call for systematization.

The aim of this review is to present the fundamentals of laser dynamic OA diagnostics and the experience of applying it. We shall present also certain results of the studies of the present authors. Section 1 of the review describes the fundamentals of LDOA diagnostics and shows, in particular, how the development of amplitude OA methods led to the rise of the ideas of laser dynamic OA diagnostics. Section 2 discusses the problems of the apparatus used in LDOA diagnostics. Section 3 systematizes the measurement systems based on the dynamic analysis of short-period acoustic responses of thermooptical origin. Finally, Section 4 presents the results of LDOA diagnostics using nonlinear mechanisms of OA transformation.

1. FROM AMPLITUDE OA METHODS TO LASER DYNAMIC OA DIAGNOSTICS

The basic outline of diagnostic measurements in the different fields of studies includes as its fundamental components: the probe signal or external agent, the medium being studied (or specimen), and the informative signal (the response), the recording of which enables one to decide on certain properties of the medium (or specimen).

The methods of OA diagnostics are based on recording the acoustic response of the specimen under study to an external optical agent. In the general case the characteristics of the signal depend in a complex fashion on the parameters of the optical radiation and the properties of the medium. However, in most cases characterized by a moderate optical intensity J_0 and a moderate absorption α of the specimen, the amplitude depends linearly on the response

$$P_0 \sim \alpha J_0. \tag{1.1}$$

Thus, by measuring the signal for different wavelengths λ of radiation and determining the ratio $P_0/J_0(\lambda)$, one can find the optical absorption spectrum of the specimen being studied, $\alpha(\lambda)$. Thus we arrive at the idea of traditional OA spectroscopy. Its methods are substantially based on two assumptions. First, the specimen in the region of optical absorption, i.e., at distances $l \sim \alpha^{-1}$ must be optically homogeneous [in the opposite case, when we measure the absorption spectrum $\alpha(\lambda)$, we obtain a certain value of the absorption coefficient averaged over the volume of the specimen]. Second, the energy-release density in the medium $\sim \alpha J_0$ must not be too large so that, in the process of heating the medium with the optical radiation, its parameters do not vary and the linear relation (1.1) holds.

These conditions can be satisfied in a large number of practically important cases, which has predetermined the wide application of the methods of OA spectroscopy. In OA spectroscopy one uses both continuous modulated and pulsed optical radiation (not necessarily laser radiation), while measuring the signal either directly in the specimen or in the gas adjacent to it. We should note that it suffices to record the amplitude of the signals to measure the optical absorption spectra $\alpha(\lambda)$. This predetermines the preferential choice for measurements in OA spectroscopy of resonance-type (with respect to the frequency of modulation of the radiation) experimental instruments (spectrophones, resonance OA cells, etc.), which enable one substantially to increase the sensitivity of the measurements.

An important step in the development of OA spectroscopy was the study of absorption spectra using the algorithms of Fourier transforms for signal processing (not discussed in detail in this review). Without altering the amplitude character of the measurements, this enables one substantially to simplify the procedure of measuring the spectrum.[9]

It has been proposed for studying inhomogeneous media to add complications to the methodology of the amplitude measurements. Thus, e.g., Refs. 10 and 11 have proposed a scheme for determining the optical properties of the surface of strongly absorbing specimens in a direction transverse to the axis of the optical ray. The standard procedure for obtaining an "OA image" in such a situation requires transverse scanning of the surface of the specimen with a narrow beam. It is proposed to illuminate the specimen with a broad optical beam through specially prepared masks to measure the spatial optical spectrum. The spatial absorption spectrum is found by applying the procedure of inverse Hadamard (or Fourier) transformation to the function of the dependence of the amplitude response on the location of the receiver.

Another possibility for studying inhomogeneous media without going out of the framework of amplitude measurements appears when one uses the scheme of the so-called indirect measurement of the acoustic response. In this scheme one uses a microphone placed in the gas adjacent to the specimen to receive the acoustic perturbations caused by the heating of the specimen by modulated laser radiation. Here the sound vibrations in the gas can arise both from heating and expansion of the layers of the gas directly in contact with the surface of the specimen or from the thermal expansion of the specimen itself (the models of the "thermal" and "mechanical" pistons).[7] The amplitude of the signal received by the microphone depends on the depth of penetration of the temperature wave L_T. In turn, this is determined by the frequency ω of modulation of the continuous optical radiation absorbed in the medium. Here we have $L_T \sim \omega^{-1/2}$. Thus, by varying ω one can control the

depth of probing. This enables one purely qualitatively to draw inferences on changes in the properties of the specimen with depth. In particular, the stated method was used by the authors of Ref. 12 to distinguish the layers in a two-layer film structure. Under the condition that the thickness of the upper layer does not exceed half the thermodiffusion length at the given frequency of modulation of the laser radiation, one makes this distinction by comparing the spectra of the two-layer structure and the individual spectrum of the material of the upper layer. An analogous method of measurement in studying thin-film coatings was realized in Ref. 13.

Despite the extremely broad spread of the methods of amplitude OA diagnostics in physicochemical, biological, and medical studies, the amount of information on the specimen under study that these methods allow one to obtain is essentially rather limited. The desire to overcome the restrictions inherent in the traditional OA methods led the specialists to the independent introduction of the methods of laser dynamic optoacoustic diagnostics. In line with the definition given in the Introduction, LDOA diagnostics assumes the detailed resolution in time of signals of short duration and the extraction of the additional information offered by the moment of arrival of the acoustic response, its form, the profile of the rising front, the relationship among the amplitudes of the phases of its fine structure, the evolution of its profile upon propagating, etc. Of course, the method is not restricted to the merits of high time resolution.[1)]

A characteristic feature of the method being discussed is the possibility of using powerful laser radiation to change the initial state of the medium in the process of probing it. This is accompanied by a change in the characteristics of the acoustic signal that yields additional information on the character of the changes in the medium and its parameters. One can speak of a certain analogy with the process of recording and readout of a dynamic hologram. In this case one can be dealing with the nonlinear laser dynamic OA diagnostics of a material. Going over to LDOA diagnostics leads both to a quantitative gain, e.g., in sensitivity, and also to a qualitative expansion of the potentialities of measurement of the characteristics of the material.

Figure 1 shows a flow diagram that allows one to explain the fundamental principles of LDOA diagnostics.

In the absorption of laser radiation of intensity $J(t)$, the acoustic signal $P(t,\mu_i)$ arises, depending on the properties of the medium and the geometry of the OA interaction. Here μ_i denotes the parameters of the medium that directly determine the character of the OA interaction. As a rule, this signal is recorded at some distance from, rather than in, the interaction region so that one can distinguish the stage of propagation of the response to the receiver point, which can lie in the specimen being studied itself or in the adjacent medium (the indirect-recording scheme). The form of the signal being recorded $\tilde{P}(t;\mu_i;\gamma_i)$ differs from the form of the original signal owing to diffraction effects, the influence of nonlinear acoustic properties of the medium, and also various relaxation processes that lead in a number of cases to the appearance of a frequency dependence of the velocity of propagation of the signal and to a distortion of its spectrum. The parameters of the medium that influence the form of the signal in the propagation stage are denoted symbolically by γ_i. The process of receiving the signal is governed by the spectral sensitivity of the acoustic receiver and the parameters of the receiver electrical circuit.

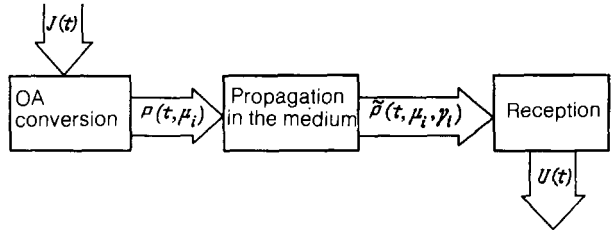

FIG. 1. Diagram of the signal formation in instruments for direct-recording OA diagnostics.

Let us point out two features of the OA interaction that enable one to apply signals excited by optical radiation for diagnostics:

1. The region of the OA interaction amounts to a sound source whose characteristics are subject to flexible control, and which give rise when needed to highly broad-band pulses of probing acoustic radiation. In this case the stage of OA transformation itself is auxiliary in character and is called on to give rise to the required characteristics of the signal $P(t,\mu_i)$ at the input to the part of the medium being studied. The central point becomes the stage of propagation of the signal. By distortion-free recording of the signal $\tilde{P}(t;\mu_i;\gamma_i)$ at the exit from the medium being studied and comparing its form with that of the original signal $P(t,\mu_i)$, we can infer the properties of the medium along the propagation track. This scheme is the basis of the methods of traditional acoustic spectroscopy. The use of laser sources to generate the acoustic probe pulse considerably expands the potentialities of acoustic spectroscopy in the high-frequency region. Moreover, the possibility arises of studying the nonlinear acoustic properties of media by optical generation of acoustic waves of finite amplitude, solitons, and shock waves, the production of which by another method often does not seem possible.

2. The parameters of the response are determined also by the properties of the medium directly in the region of the OA interaction, by the characteristics of the laser radiation, and the geometry of the OA conversion. Therefore, a knowledge of how to calculate the form of the response $P(t;\mu_i)$, as well as its transformation in the process of propagation

$$P(t;\ \mu_i)\rightarrow\tilde{P}(t;\ \mu_1;\ \gamma_1)$$

and reception

$$\tilde{P}(t;\ \mu_1;\ \gamma_1)\rightarrow U(t),$$

enables one to determine the distribution of optical and thermophysical characteristics in the interaction region:

$$\mu_1=\mu_1(\mathbf{r}).$$

Moreover, in situations in which light-induced chemical reactions occur in the medium or the heating of the medium is so great that it is accompanied by phase transitions, we gain the possibility of inferring from the form of the response the physical processes accompanying the interaction of the laser radiation with condensed media. In particular, in this review we shall discuss as a new field of LDOA diagnostics the diag-

nostics of light-induced chemical and phase transformations in matter.

2. EXPERIMENTAL TECHNIQUE IN LASER DYNAMIC OA DIAGNOSTICS

The features of the problems discussed above that can be solved by means of LDOA diagnostics define a set of specific requirements imposed on the experimental technique for recording OA signals.

As a rule, in problems of LDOA diagnostics one uses commercially produced pulsed laser sources that offer the experimenter a wide choice of energy parameters, wavelengths, and durations of radiation pulses. Among the most commonly used are CO_2, Nd^{3+} YAG, and N_2 lasers, as well as tunable dye lasers. The scheme for recording acoustic signals in experiments in LDOA diagnostics must be optimized with account taken of the properties of the specimen, the geometry of the OA conversion, and also the parameters of the response to be recorded. Therefore in each concrete case one must construct and set up special instruments for converting the acoustic into electric vibrations; from the output of these instruments the signal enters an electronic memory and processing apparatus.

A distinguishing feature of the signals used for LDOA diagnostics is their broad frequency range—from several kilohertz to tens of megahertz. In traditional acoustics, and also in the methods of ultrasonic nondestructive monitoring of materials, there are practically no instrumental means of measurement of acoustic pulses of nanosecond duration, since the very possibility of generating such brief acoustic pulses has arisen only with the development of laser technology. In this regard the need has arisen of developing special methods and apparatus for recording OA signals.

At present in laser optoacoustics two fundamental methods of direct measurement of acoustic signals are employed: using a probe laser beam that enables recording the thermal and acoustic modulation of the refractive index in the medium; and using pressure receivers (or OA cells) with sensitive elements made of piezoelectric materials of various types. Let us examine the potentialities of the stated recording methods to enable broadband reception of acoustic signals excited in a medium by laser radiation.

Contact-free methods of measurement in optoacoustics are widely used for direct recording of the displacement of the surface of a liquid or solid under the action of laser heating—the so-called photothermal-displacement spectroscopy;[14] for recording refractive-index gradients caused by heating of the medium by radiation,—thermal-lens methods, photothermal refraction;[5] and for direct measurement of the response from the variations in the refractive index caused by pressure.[15,16]

As an analysis of the experimental results shows, the latter of the listed methods is of greatest interest from the standpoint of LDOA diagnostics. An advantage of this method is the possibility of performing remote contact-free measurement of OA signals in media transparent to the probe laser radiation. An adequate reconstruction of the form of the signal in schemes with optical recording is possible in situations in which the parameters of the OA signal are invariant along the direction of propagation of the probe laser beam, as is realized, e.g., in the case of cylindrical geometry of the OA conversion[15] or in the case of quasiplanar wave fronts.[16]

A typical experimental scheme of optical recording is shown in Fig. 2. The deflection of the probe laser beam at the instant when its focal region is crossed by the plane wave front of the signal $p(t)$ leads to a modulation of the voltage at the output of the photodiode

$$\Delta V(t) = V_0 \operatorname{erf}\left(k_0 \frac{dp(t)}{dt}\right), \quad k_0 = \pi^{3/2} \frac{2b}{c\lambda} a \left.\frac{\partial n_0}{\partial p}\right|_{p=0}.$$

Here V_0 is the constant voltage at the output of the photodiode, $2b$ is the transverse dimension of the wave front of the signal, c is the velocity of light in the liquid, a is the radius of the focal region of the probe ray, whose wavelength is λ, and n_0 is the refractive index of the medium. For typical values of the derivative $dp/dt \lesssim 4\times 10^7$ Pa/s, we can write approximately

$$\Delta V(t) \propto k_0 \frac{dp(t)}{dt}. \tag{2.1}$$

This dependence reflects a common feature of schemes of optical recording of acoustic signals: the signal from the photoreceiver is not proportional to the signal itself, but to its time derivative. The time resolution is determined by the time of propagation of sound over the cross section of the focal region of the laser beam: $\Delta t \simeq 2a/c$. In the experiments of Ref. 16 a resolution was attained of ~ 30 ns.

We should include among the defects of schemes with

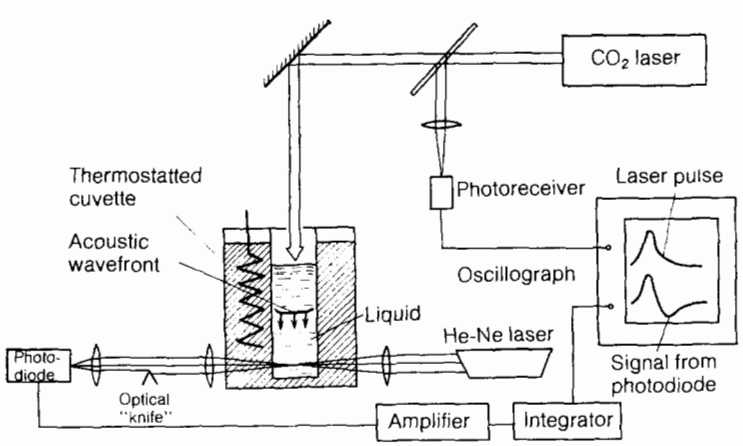

FIG. 2. Experimental scheme for optical shadow recording of the acoustic signal generated by a laser pulse in strongly absorbing liquids.[16]

optical recording that restrict their field of practical application: the rigid demands on the optical homogeneity of the media being studied; the need to determine the parameters $c(T)$ and $\partial n/\partial p$ for each medium to be studied in carrying out absolute pressure measurements; the decline in accuracy of reconstruction of the form of signals as their amplitude increases and their duration decreases.

Recording with use of broad-band pressure receivers is more widespread. As a rule, they are constructed on the basis of various piezoelectric materials. Along with the traditionally used ceramic and crystalline materials, such as lead zirconate-titanate (LZT), lithium metaniobate, quartz (transducers based on these materials have been described in detail in Ref. 17), at present new materials are widely used: various types of piezoelectric films(Mylar, polyvinylidene fluoride (PVDF), etc., and also oriented polycrystalline films of organic compounds (PFO). These materials have a number of advantages when used in the construction specifically of broad-band sound receivers: low Q-factor (as compared with a ceramic), simplicity of preparing micrometer-thick films, bending strength, and the possibility of good acoustic matching with liquids owing to low impedance. We should list among the defects of piezoelectric films a considerable pyroelectric effect, the dependence of the sensitivity on the technology of preparation and polarization, the influence of aging on the electroacoustic parameters, and also a lower absolute sensitivity than for most traditional piezoelectrics.

Despite the mentioned defects, piezopolymer films find wide application in various designs of receivers (see the review of Ref. 5 and also Refs. 18 and 19), which differ from one another mainly in the means of attaching the film, in its dimensions, and in the choice of the sensitive material. Figure 3 shows a simplified scheme of the design of a typical device for LDOA diagnostics.

The most important characteristics of pressure receivers from the standpoint of LDOA diagnostics are the spectral sensitivity and the dynamic range. In some cases one must also take account of the directional characteristics. The spectral sensitivity of a receiver operating in the thickness mode of vibrations is commonly calculated on the basis of a simplified theory (see Ref. 18 and the references given there), which enables one to calculate rigorously the frequency properties of the receiver as a layered inhomogeneous construction (in the direction of propagation of the

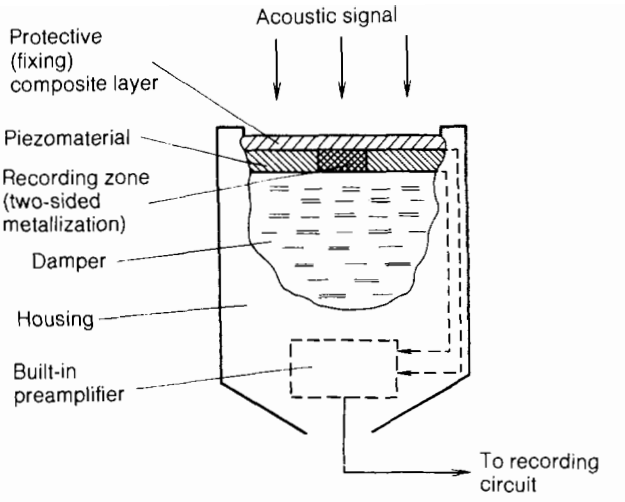

FIG. 3. Schematic diagram of a three-layer construction of a thin-film piezotransducer for distortion-free measurements of brief acoustic signals.

incident plane acoustic wave). For illustration Fig. 4 shows the dependences obtained on the basis of the formulas of Ref. 18 of the spectral sensitivity of three-layer piezoreceivers made of widespread construction materials for recording signals in water. Also the influence of the parameters of the electric loading on the frequency properties of the devices are modeled. Simple recommendations for the choice of parameters of the receiver for undistorted recording of the signal in the frequency band

$$f_н < f < f_в.$$

follow from the simplified theory. The thickness d of the piezomaterial must be $d < c_p/2f_h$ in the case of matching of the acoustic impedances of the film and the damper, and $d < c_p/4f_h$ in the case when one uses a damper with a high wave resistance (here c_p is the velocity of sound in the piezomaterial). To obtain a uniform frequency characteristic one should tend to choose maximally close values of the acoustic impedances of the material of the piezoelement and the damper, although it is possible in principle to use a value of the calculated sensitivity characteristic for subsequent correction of the form of the received signal in processing the results of the measurements on a computer. For an intrinsic

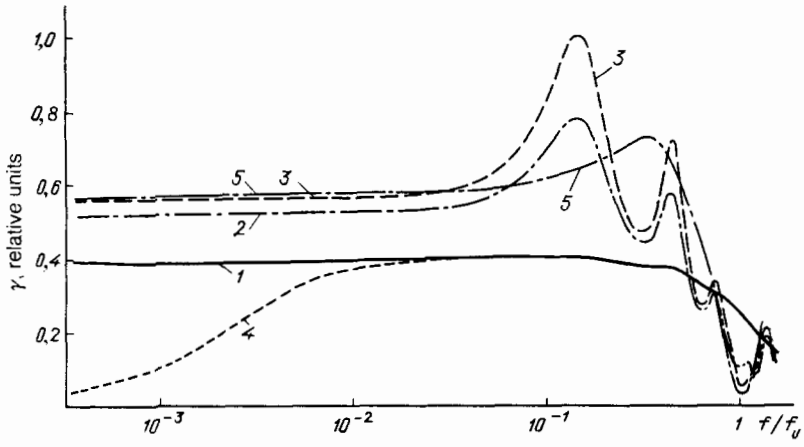

FIG. 4. Spectral sensitivity of three variants of piezotransducers based on PVDF film 25-μm thick (frequency of thickness resonance $f_0 = 32$ MHz). a–Composite-PVDF-polymethylmethacrylate (curve *1*). b–Composite-PVDF-quartz) (*2*) *c*–Composite-PVDF-brass (*3*). Thickness of the protective layer of the composite is 0.1 mm, which was taken for calculating the value of its acoustic impedance: $Z_1 = 3\times10^6$ kg/m^2 s. The input parameters of the electric scheme of the receiving circuit are: $R_E = 50$ MΩ, $C_E = 10$ pF. Curve *4* describes the sensitivity of a variant of design (*a*) with a small input resistance: $R_E = 0.1$ MΩ. Curve *5* differs from curve *3* in the choice of the impedance of the composite: $Z_1 = 1.5\times10^6$ kg/m^2 s.

TABLE I.

Material	Z, 10^6 kg/m^{2}s	d_{33}, 10^{11} C/N	ε	Use in pressure piezoreceivers			Reference
				Thickness of film, μm	Sensitivity, μV/Pa	Working range of frequencies, MHz	
PVDF*	3,5	35	12	25	0,06	1—10	[22]
				50	—	1—10	[67]
PVDF (F2-MÉ)	2,9	15	12	20	0,6	0,1—10	[18]
OPP	3,3	18	4	~1	0,05	—	[19]

*Material of the firm "Kureha Chemical Industry Company" (Japan).

static capacitance C_0 of the transducer, the parameters of the electric loading characterized by the input capacitance C_E and input resistance R_E are chosen by the conditions:

$$C_E < C_0$$

and

$$R_E > [2\pi f_H (C_0 + C_E)]^{-1}.$$

In the frequency region $[f_l, f_h]$, when the stated conditions are satisfied, the spectral sensitivity of the piezoreceiver practically does not depend on the frequency and is determined by the simple formula

$$Y_0 = d \frac{d_{33}^*}{\varepsilon} \frac{C_0}{C_0 + C_E} \frac{2}{1 + (Z_c/Z_2)}, \qquad (2.2)$$

Here d_{33}^* is the piezoelectric modulus for longitudinal vibrations [of dimensionality (C/N)]; ε is the relative permittivity, Z_c and Z_2 are the acoustic impedances of the piezomaterial and the damper, respectively. Table I gives the parameters of some types of piezoelectric films, as well as the characteristics of sound receivers based on them, most of which have been used for OA measurements. We note especially the piezoelectric converter based on OPP, which has been described in detail in Ref. 19. The authors note that OPP differs from its analogs in suitability for production in its preparation, cheapness, and accessibility. The process of preparing OPP consists in evaporating a low-molecular-weight polycyclic compound with polar substituents in vacuo with subsequent deposition on a substrate in the form of a film of thickness of some micrometers. One can use as the substrates-soundguides the most varied materials: metals, semiconductors, plastics, including flexible plastic bases, crystalline materials, etc. In a number of cases this allows one to apply transducers based on OPP directly to the objects of study and to avoid complications associated with acoustic matching.

The model discussed above of determining the parameters of broad-band receivers has a number of substantial restrictions. It is applicable for recording brief signals of duration $\lesssim 100$ ns, when undistorted measurements are ensured by the choice of an extended damper and rather large transverse dimensions of the receivers. Here the time of lag of the reflections from the boundaries of the construction elements considerably exceeds the duration of the signal. To reduce the influence of reflections one tries to use membrane sound receivers,[20] and also to use various multiphase composite materials to ensure effective damping in the material of the damper.[21]

In theoretical calculations one cannot take account of all the effects that exert an influence on the spectral sensitivity. Moreover, the values of the physical constants of the piezomaterial are not always known exactly, and can depend on the frequency in the high-frequency region (thus, in PVDF the permittivity at the frequency of 10 MHz is reduced by 20%).[22] Hence the need arises for a simple and reliable method of calibration of broad-band sound receivers. One of these calibration methods has been proposed in Refs. 18 and 19. It is based on the well-developed theory of laser thermooptical generation and propagation of sound in a liquid, which allows one to calculate the characteristics of acoustic pulses over a broad range of pressures. Thus, in Ref. 18 the spectral sensitivity of a broad-band transducer was determined from the results of comparing the spectrum of the electrical signal at the output of the receiver circuit with the theoretically calculated spectrum of the signal applied to the input of a transducer situated in the near field of the source where diffraction effects have no influence. The calculated spectral sensitivity, as was shown in the study, agrees well with the data of calibration by optoacoustic methods.

An analogous method of calibration was tested in Ref. 19. In this study the authors measured also the dynamic range of high-frequency transducers made of OPP in the high-pressure region. The signal was excited in distilled water with the radiation of a CO_2 laser. Upon taking account of the high absorption coefficient of optical radiation in water at this wavelength, this ensured close to optimal conditions for generation of brief acoustic pulses. The results of the measurements obtained upon averaging over 20 samples of OPP show that the sensitivity is invariant in the pressure range 10^4–10^8 Pa, and amounts to 5×10^{-8} V/Pa.

In a number of cases of LDOA diagnostics, it proves necessary to record broad-band signals of complex form. As an example, Fig. 5 shows a signal in water accompanying an evaporative OA interaction.[23]

This type of signals differ from the nanosecond signals discussed in the earlier reviews (e.g., Ref. 5) in that both the high-frequency (in the megahertz range) and the relatively low-frequency (in the range of tens and hundreds of kilohertz) components bear energy. Evidently the distortion-free recording of such signals poses a number of serious problems. First of all is the ensuring of a nonresonance character of the amplitude-frequency characteristics of the receiver, both in the high- and in the low-frequency regions. To solve the problem one must eliminate various sorts of reflections of the original signal from the design elements of the

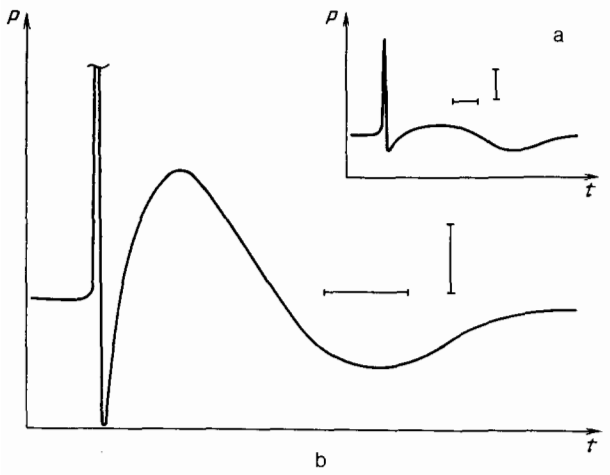

FIG. 5. Oscillogram of a broad-band acoustic signal accompanying the interaction of the intense radiation of a CO_2 laser with water (a) and a portion of it (b) at an emission energy $E = 500$ mJ.[23] Scale along the horizontal is 2 μs/division. Scale along the vertical is 5×10^4 Pa/division (a) and 10^4 Pa/division (b).

receiver and match its form and dimensions with the configuration of the field of acoustic perturbations to be recorded. Another problem is the low sensitivity of the measurements when one applies broad-band receiving instruments (in typical designs of receivers based on piezopolymer films, e.g., it amounts to 0.01–1 μV/Pa.[18] Hence high requirements must be imposed on the resistance to interference of the recording circuit with regard to acoustic and electrical noise. In this regard the cuvette containing the substance under study and the piezoelectric transducer are placed together in a single housing in a number of designs (see Ref. 5). Here in most cases one must make a transducer with an incorporated preamplifier to ensure an acceptable signal/noise ratio at the output of the receiver circuit.[5,18]

The assembly of measuring apparatus necessary for analyzing the form of a broad-band OA signal (or its spectrum) in experiments on dynamic diagnostics must include, together with the receiver and matching circuit, also an analog-digital converter (or specialized digital oscillographs with a high frequency of discretization) and a microcomputer, which controls the sequence of operations and enables express processing of the recorded signals.

3. NONPERTURBING LDOA DIAGNOSTICS

The *a priori* data used for reconstructing information on specimens include information on the features of shaping of the pulsed signals for OA conversion. To realize the methods of LDOA diagnostics such information becomes decisive.

Nonperturbing LDOA diagnostics is based on the thermal (or thermooptical) OA effect (for earlier results see the review of Ref. 24). The region of thermal OA conversion in the specimen has been named the thermooptical sound emitter or the thermoacoustic antenna. The more effective nonlinear mechanisms of OA conversion[25] have been applied relatively recently in diagnostics. Besides the nonlinear thermal regime of interaction of the optical radiation with the medium, they are based on processes of evaporation, optical breakthrough, and also photochemical transformations.

Below we shall briefly take up the description of the processes of generation of OA signals, staying within the framework of the linear thermoelastic mechanism, and we shall also treat the potentialities of laser thermooptical excitation of sound for solving problems of LDOA diagnostics. We shall combine the set of experimental methods based on the linear thermooptical excitation of sound as nonperturbing LDOA diagnostics.

3.1. The physics of the linear thermooptic excitation of sound

The problem of rigorous description of the physics of the interaction of optical radiation with condensed media is rather complex. However, for describing most of the situations of practical importance discussed in this review, a simplified phenomenological approach is fruitful that does not take account of quantum-mechanical effects. Within the framework of this approach the process of linear OA conversion in liquids is described by an inhomogeneous wave equation for the pressure P having a right-hand side describing the action of thermal sound sources:[26]

$$\Delta P - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}P = -\rho\frac{\partial \beta T}{\partial t}, \qquad (3.1)$$

Here ρ and c are the density and the velocity of sound in the liquid, and β is the volume thermal-expansion coefficient.

The concrete form of the temperature-field distribution $T(t, \mathbf{R})$ is found from the heat-conduction equation:

$$\rho C_P \frac{\partial T(t, \mathbf{R})}{\partial t} = \operatorname{div}(\varkappa_T \operatorname{grad} T(t, \mathbf{R})) - \operatorname{div} S_{\text{light}} \qquad (3.2)$$

Here S_{light} (α) is the flux density of optical (laser) radiation; C_p and $\varkappa_T$ are the specific heat and the thermal conductivity coefficient of the liquid. In the cases being discussed thermodiffusion processes are assumed to be slow, so that we can neglect the first term on the right-hand side of (3.2).

We note that for solids the linear equations of thermoelasticity are written for the scalar and vector potentials of the displacement vector. Their general form is given in Ref. 27. Under conditions in which we can neglect the change in β over the time of the laser pulse, Eqs. (3.1) and (3.2) imply that

$$\Delta P - \frac{1}{c^2}\frac{\partial^2 P}{\partial t^2} = -\frac{\beta}{C_P}\frac{\partial q}{\partial t}. \qquad (3.3)$$

Here q is the power density of heat release in the medium.

Thus for a complete description of the sonic response at the point of observation, we must solve the problem of the emission of sound by thermal sources distributed according to the law given by Eq. (3.2).

As Eqs. (3.1)–(3.2) imply, OA conversion is determined by the parameters of the medium: α, β, C_p, and c. Each of them can have an inhomogeneous space and time distribution. By measuring the signal $P(t; x,y,z)$, one can solve the problem of reconstructing the distributions of these parameters and of the temperature in the medium. In the case of short-term processes, the sonic responses amount to video pulses of specific profiles.

Further we discuss the fundamental groups of methods of unperturbing laser dynamic OA diagnostics.

3.2. Methods based on analyzing the time of arrival of the sonic response

Even the first experiments on pulsed optical generation of longitudinal acoustic waves in specimens showed the po-

tentiality of diagnostics of the internal structure of a specimen without using data on the amplitude of the signal, taking account only of the time of propagation of the response from the observation point to the recording point. In this setup the sonic response plays the role of a test signal, while the method resembles the methods of traditional ultrasonic defectoscopy. The advantages consist in contact-free excitation and reception of the OA signals and higher resolving power. With sufficiently small pulse durations and good resolving power of the receivers, the direct signal and the numerous echo signals corresponding to the boundaries of the specimen, to cracks, inner cavities, etc., are separately recorded. If the velocity of sound in the specimen is known, the pattern of time delays of pulses enables one to localize defects easily. Thus the only parameter to be measured is the time of arrival of the responses.

The energy densities to be released at the surface of the specimen are chosen to be small, of the order of hundredths of a J/cm^2, since here the thermal OA effect dominates and specimen breakdown does not occur.

The early articles on OA diagnostics of cavities and defects in solid specimens are numerous (see the monograph of Ref. 28). We especially note only Ref. 29, in which a completely remote principle of OA diagnostics was realized for the first time by using optical generation of an ultrasonic pulse at one surface of a specimen and optical readout of the echo pulses from the opposite side. The optical recording system enabled a receiving band of 5 kHz–150 MHz. The minimum thickness of the steel plate for diagnosis was 0.014 cm, or of lead–0.006 cm. This setup enabled solving also the inverse problems–determining, e.g., the velocity of longitudinal acoustic waves in rods of different materials.

The demands of modern microelectronic technology (in particular, thin-film) give rise to the need for using extremely short subnanosecond pulses.[30] In particular, analysis of the fine structure of subnanosecond acoustic reflections in layered structures has enabled distinguishing the contributions to the signal introduced by the thick substrate and the relatively thin film,[31] and to study defects in the layers separately. A demonstration experiment was performed by using a pulsed N_2 laser at atmospheric pressure. The receiver was a ZnO film 5-μm thick sputtered onto a

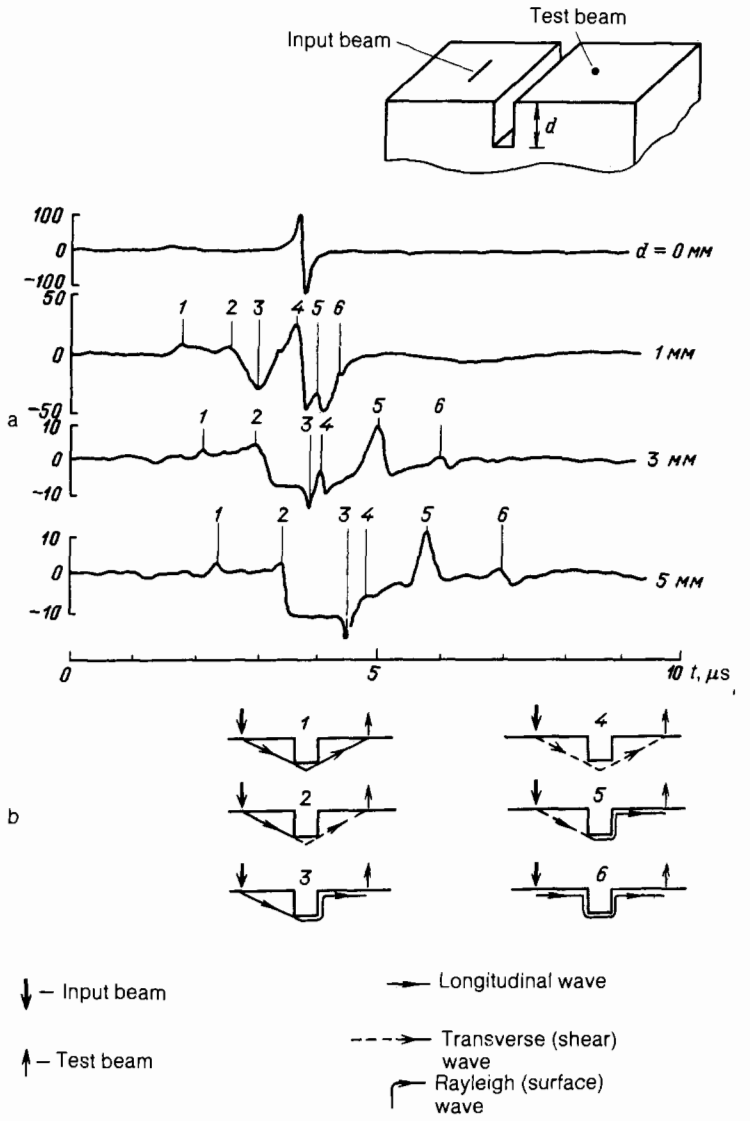

FIG. 6. Optoacoustic diagnostics of cracks in specimens.[6] a–Excitation and recording scheme and structure of the sonic response for different values of the depth of the test slit for a constant slit width of 1 mm. b–Six possible trajectories of perturbations corresponding to Fig. 6a. In the diagnostics process the radiation of a YAG:Nd^{3+} laser was focused on the line with cylindrical optics.

sapphire rod. A structure was studied that included a ceramic plate 0.4-cm thick and a film of Al_2O_3 sputtered onto it of thickness about 30 μm. The specimen was set up on a coordinate stage with feed in perpendicular directions. The recorded pattern of echo pulses shows repeated bundles. Processing on a computer of the data on the time of arrival of the bundles enables one to construct a spatial pattern of the roughnesses of the surface of the substrate. In turn, analysis of the fine structure of a bundle itself performed with subnanosecond resolution enables one to estimate the inhomogeneity of the coating.

Analysis of surface cracks and microinhomogeneities lying near the surface of a specimen is performed from the data on arrival times, not only of the longitudinal, but also of the transverse and surface waves accompanying OA conversion in solids.[32] All three forms of waves, while propagating at different velocities, interact with defects and create a detailed pattern of the near-surface layer of the specimen (Fig. 6).

As a special group the studies are distinguished that take the tomographic approach, using signals of optoacoustic origin to measure the spatially inhomogeneous distribution of the magnitude of the velocity of sound in the specimen. This enables one to monitor processes of crystallization from melts and to analyze temperature gradients in specimens in real time. Thus, to study the kinetics of crystallization of metallic-glass filaments, the time of passage of an acoustic pulse "of laser origin" was measured along a segment of filament of accurately measured length. This enabled monitoring the velocity of sound throughout the course of the entire process of heat treatment.[33] An increase in the velocity of sound indicated an increase in the degree of crystallization. At this stage of the experiment the results of the measurements were compared with the data of traditional measurements: x-ray diagnostics and metallography. The next stage of the experiment was marked by the quantitative results. The values of Young's modulus were measured with an accuracy of $\pm 0.2\%$ by using the values of the longitudinal velocity of sound. Thus it was first determined that, for filaments of composition $Pd_{0.775}Cu_{0.06}Si_{0.165}$ in the amorphous state (at the output from the melt) this value is 9.28 MPa, while in the established crystalline state (after heat treatment) it was 13.0 MPa. A more refined, yet also quite accessible, method was used for an OA study of the anisotropy of properties of specimens.[34]

3.3. Nonperturbing LDOA diagnostics with resolution of the form and spectrum of the sonic response[2)]

A feature of the group of methods under discussion is the high time resolution on reception, which enables one to distinguish the most information-rich elements of the profile of the signal.[37]

Most analytical instruments and methods are characterized by a one-dimensional geometry of the "source-specimen-receiver" system (opaque specimens). Here the condition is always satisfied that $\alpha a \gg 1$, $\alpha c\tau_1 \ll 1$. In agreement with the solution of (3.1) and (3.2), the profile of the signal in the near field of thermal OA sources represents either an N-wave, if the conversion region borders a gas, or a unipolar pulse if the OA conversion occurs at the boundary of the studied medium with an acoustically more rigid layer. Thus, in the former case the solution of Eqs. (3.1) and (3.2),

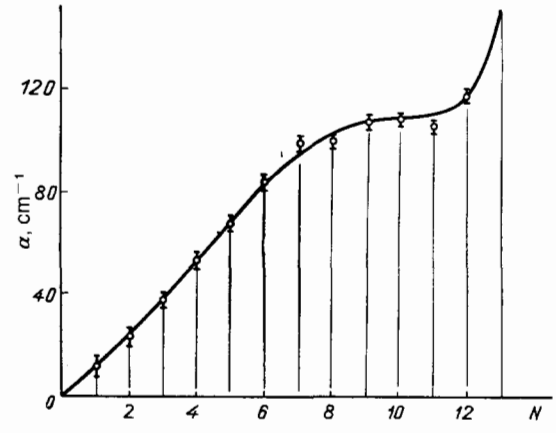

FIG. 7. Results of the diagnostics of the depth distribution of the absorption coefficient of a model layered, inhomogeneous structure using Eq. (3.3).[38] N is the number of the layer in order of depth.

which describes the leading front of the N-wave, has the form[38]

$$P(t) \sim \beta(|c\tilde{t}|)\,\alpha(|c\tilde{t}|)\exp\left(-\int_0^{|c\tilde{t}|}\alpha(\eta)\,d\eta\right), \quad \tilde{t}<0, \quad (3.4)$$

Here $\tilde{t} = t - (z/c)$ is the time in the traveling system of coordinates. We bear in mind the fact that the signal is recorded in the near (projector) zone on the projection of the laser beam. We can see from (3.4) that the leading front of the pulse is exponential: $P(\tilde{t}) \approx \exp \alpha|c\tilde{t}|$. This gives rise to an expression that is the basis of the experimental method of reconstructing the distribution of the optical absorption coefficient along the depth of the specimen, $\alpha(z)$ (Fig. 7) (here and below we assume that the z axis lies along the laser beam into the interior of the medium, while the xy plane coincides with the boundary of the specimen):

$$\alpha(|c\tilde{t}|) = P'(|c\tilde{t}|)\left(\int_{|c\tilde{t}|}^{\infty} P'(\eta)\,d\eta\right)^{-1}.$$

By using (3.4) one can perform an analogous reconstruction also in the case of diagnostics of temperature inhomogeneities, which in turn influence the distribution $\beta(z)$.

A model experiment has been performed[38] on OA introscopy of a thin, uniformly absorbing layer of an aqueous dye solution nonuniformly heated by an external source of radiant energy. The thickness of the layer was 2 mm. The radiation of a Nd^{3+} YAG laser was used to excite the probe pulse. The leading front of the pulse was recorded "in transmission" with a broad-band piezotransducer. Figure 8 shows the change in the leading front of the acoustic signal (a) and the corresponding dependence of the temperature on the depth of the absorbing layer (b) that was found. The original profile was the homogeneous profile (*1*). Curves *2* and *3* were obtained after heating for 8 and 15 min, respectively.

A one-dimensional geometry of conversion allows one to use the region of OA conversion as a standard thin-layer source of a very short-period probe signal that one can employ, e.g., to determine the nonlinear acoustic parameter of the medium. One can do this by observing the nonlinear evolution of the pulse as it propagates. The original pulse for a

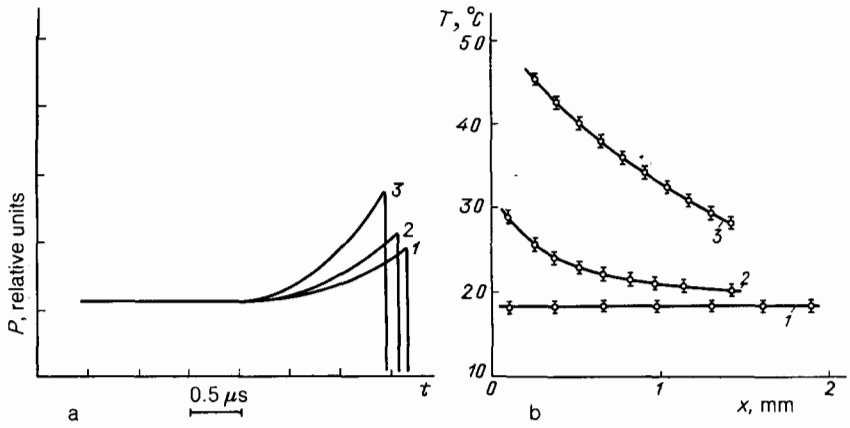

FIG. 8. Results of recording the leading front of a pressure pulse (a) and the reconstruction of the depth distribution of temperature (b) in water at room temperature (*1*) and with nonuniform heating (*2*,, *3*).[38]

rigid boundary surface is described by the expression[39]

$$P(\theta) \sim \xi_0 \left[\exp\left(\frac{\xi_0}{2}\right)^2\right]\left[e^{\xi_0\theta}\operatorname{erfc}\left(\frac{\xi_0}{2}+\theta\right)+e^{-\xi_0\theta}\operatorname{erfc}\left(\frac{\xi_0}{2}-\theta\right)\right].$$

Here we have $\xi_0 = \alpha c\tau_1$, $\theta = [t - (z/c)]\tau_1^{-1}$. It represents a symmetric pulse of positive polarity with a maximum at $\vartheta = 0$. Owing to the acoustic nonlinearity, upon propagation an increase occurs in the steepness of the leading front of the pulse. The pulse loses symmetry. The relative retardation of the peak with respect to the "trough" of the pulse measured at the two points z_1 and z_2 amounts to

$$(t_2 - t_1) = \frac{\varepsilon P_0 (z_1 - z_2)}{\rho c^3}.$$

Here P_0 is the maximum pressure, and ε is the acoustic nonlinearity parameter. Thus the determination of $(t_2 - t_1)$ enables one also to estimate ε. Values of ε were obtained[39] for a number of liquids. A defect of the method is the influence of diffraction effects on the form of the probe pulse.

A more refined method was applied in Ref. 16, where it was possible to obtain great accuracy in determining ε by measuring $t_2 - t_1$ at one point, but at two different energies of the laser pulse that correspond to the peak pressures P_{01} and P_{02}:

$$\varepsilon = 2\left[\frac{\rho c^3 (t_2 - t_1)}{z (P_{01} - P_{02})} - 1\right].$$

In the previous example a method was discussed that was based on the effect of nonlinear distortions accumulated upon propagation of a pulse.

However, cases are possible of local responses of a medium to the passage of a pulse of optoacoustic origin. This enables one to analyze various forms of distribution of the physical parameters of the medium outside the source.

Thus the complete form of the electric response was analyzed in Refs. 40 and 41, as taken from the plates of a condenser composed of electrodes holding the dielectric medium under study. Of interest was the spatial distribution of the charge in the dielectric, the distribution of the piezomodulus, and other parameters. A feature of these methods is that the probing elastic signal is converted into a current or voltage signal directly in the medium under study. A probe pulse excited in one of the plates with a defocused laser beam has the extent $c\tau_1$, which is much smaller than the spatial features of the charge distribution in the dielectric being studied. In the layer subjected to compression by the transmitted pulse a change occurs in the charge density. This leads to appearance of a voltage pulse on the plates of the condenser. Here, if the compression does not exceed the elastic limit, the form of the short-circuit current copies the profile of the charge-density distribution along the axis of the laser beam

$$i(t) \sim \chi P_0 c^2 \tau_n \rho_q(z) \frac{S}{d}.$$

Here P_0 is the peak pressure, $\rho_q(z)$ is the sought charge-density distribution, S and d are, respectively, the area and the thickness of the specimen; χ is the compressibility of the specimen. Thus the possibility is opened up of solving the currently pressing problem of analyzing the degree of inhomogeneity of charge implanted into a dielectric by various forms of ionizing radiation.

Certain problems of diagnostics of the electrical properties of media require a more detailed analysis of the physics of the process. The fundamentals of the method are given in the detailed theoretical paper of Ref. 42, whose authors used the Clausius-Mossotti equations to reconstruct the relation between the values of the charge and the deformation in a specimen. Application of the theory of Ref. 42 enables one to solve the problem of reconstructing the distribution of the piezomodulus of a specimen upon optoacoustic probing by recording the current signal and integrating its profile. As an example let us examine the OA probing of a thin piezoelectric film of PVDF, which finds ever increasing application in different fields of technology.[43] In the cited study a laser beam excited a signal in one of the electrodes compressing a specimen of the film. The diameter of the laser beam coincided with the diameter of the electrode, so that in this case a homogeneous geometry existed. The form of the response and the sought piezomodulus distribution $e_{33}^*(z)$ are connected by the relationship

$$i(t) = -\frac{S}{d}\frac{P_0\tau_n}{\rho}\frac{\mathrm{d}}{\mathrm{d}z}e_{33}^*(ct).$$

As before, here P_0 is the peak pressure in the pulse, and ρ is the density of the specimen. The integral

$$\int_0^{t_0} i(t)\,\mathrm{d}t$$

is proportional to the distribution $e_{33}^*(ct_0)$, which enables

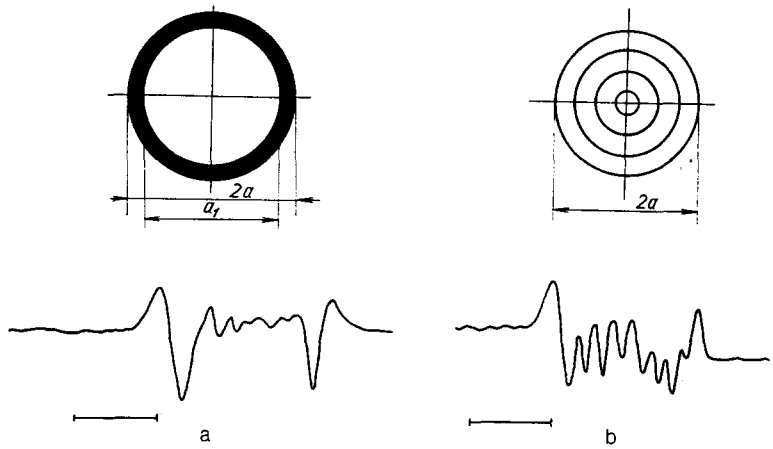

FIG. 9. Experimentally recorded profiles of the acoustic signal in the far field (aqueous solution of copper sulfate).[46] The signal was excited with a YAG-Nd^{3+} laser pulse at the free surface of the solution. a–Annular distribution of intensity, $a = 1.8$ cm, $a_1 = 0.5$ cm, $\alpha = 18$ cm^{-1}, $\varphi = 83°$. b–System of several rings, $a = 2.2$ cm, $\alpha = 18$ cm^{-1}, $\varphi = 52°$. Scale along the horizontal 10 μs/division.

one to reconstruct its spatial characteristics and determine the total charge that has passed. In the experiment of Ref. 43 a spatial resolving power of the method was attained of ~ 1.5 μm and lower.

In media having a moderate absorption the relationship $\alpha a \gg 1$ may not be satisfied. More characteristic is the situation $\alpha a \sim 1$; correspondingly, a one-dimensional geometry is not satisfied. Of interest are the characteristics of the responses in the far field.[44,45] The results of the studies of acoustic signals in the far field for cases of simple configurations of the OA conversion region are well known.[24]

For a pulsed regime the power density of heat release in formula (3.3) is written in the form

$$q(x, y, z, t) = \alpha I_0 g(t) f(x, y) e^{-\alpha z}.$$

Here I_0 is the peak intensity in the spot, and the functions $g(t)$ and $f(x,y)$, respectively, give the form of the optical pulse and the intensity distribution in the cross section of the beam. The solution of (3.3) in the practically important case of "long" laser pulses is

$$\tau_л \gg \frac{a \sin \varphi}{c}, \frac{\cos \varphi}{\alpha c}$$

(φ is the angle between the normal to the surface and the direction to the point of observation, and a is the radius of the cross section of the beam). This leads to an approximate expression for the pressure:[24]

$$p = \frac{1}{4\pi} \frac{\beta a^2 \cos \varphi}{\alpha c C_p} \frac{I_0}{r} g''\left(t - \frac{r}{c}\right).$$

In this case the characteristic form of the response amounts to an M-shaped pulse. Its characteristics do not depend on the transverse intensity distribution.

On the contrary, an influence of the transverse distribution of the optical intensity is manifested in the case of short enough pulses; moreover, the condition must be satisfied for the direction to the point of observation that

$$\sin \varphi \gg \frac{c\tau_л}{a}.$$

Under this condition the acoustic signal as though "reads out" the voltage pattern created in the region of the OA conversion. When the condition $\alpha a \gg 1$ is also satisfied (region of OA conversion in the form of a thin disk), the expression for $p(t)$ acquires the graphic form[46]

$$P(t) = \frac{E_0 \beta \cos \varphi \cdot c^2}{2\pi r \alpha c_p \sin^2 \varphi} F''_{yy}(y)\Big|_{y = \frac{ct - r}{\sin \varphi}}. \qquad (3.5)$$

Here E_0 is the energy in the pulse, $F(y) = \int f(x,y)dx$ is a function characterizing the effective distribution of elementary thermal sources of sound along the y axis, which is chosen in the direction of the projection of the point of observation on the phase boundary of the media.

Analysis of Eq. (3.5) indicates specific features of the sound emission by a spatially inhomogeneous OA source. Taking account of these features opens up the possibility of an additional control of the characteristics of the signal by spatial modulation of the transverse distribution of intensity in the laser beam. For example, one can form with a laser monopulse quasiharmonic elastic perturbations at certain points of the specimen for purposes of pure acoustic spectroscopy (Fig. 9). Moreover, the laws of emission of sound by a spatially inhomogeneous OA source are attracting attention owing to the prospects being discussed currently of using powerful multimode lasers for purposes of OA spectroscopy, OA microscopy, and also OA diagnostics of powerful laser beams.

Another example of diagnostics of media from the data of recording the form of the response is the analysis of gas-saturated media. In such media the character of thermooptical sound generation acquires specific features as compared with homogeneous media. It was shown[47] that this probing is most effectively done from the data of analysis of the change in the original acoustic-perturbation spectrum. The authors of Ref. 47 were able to reduce the problem of describing thermooptical sound generation in a two-phase medium (in a certain range of the volume concentration of free gas) to the ordinary theoretical scheme for homogeneous condensed media, whose formulas contain, instead of the ordinary wavenumber k of the sound, a certain effective wavenumber $\tilde{k}$:

$$\tilde{k} = \frac{\omega}{c - \Delta c(\omega)} + i\varkappa(\omega).$$

Here ω is the frequency of the sound wave being excited, while the frequency-dependent quantities Δc (which determines the dispersion of sound) and $\varkappa$ (the damping coefficient) are determined by the formulas[48]

$$\Delta c(\omega) = 2\pi c^3 \int \frac{n(R)(\zeta^2-1)R\,dR}{\omega^2[(\zeta^2-1)^2+\delta^2]}, \quad (3.6)$$

$$\varkappa(\omega) = 2\pi c \int \frac{\delta n(R) R dR}{\omega[(\zeta^2-1)^2+\delta^2]}. \quad (3.7)$$

Here $\zeta = \omega_0/\omega$, $\delta = \delta(\omega)$ is the damping constant of the pulsations; $\omega_0 = (3\gamma P_r)(\rho R^2)^{-1/2}$ is the frequency of the intrinsic pulsations of the bubble; γ is the index of the adiabat; P_r is the equilibrium pressure in the liquid; and R is the radius of the bubble. The integrals (3.6) and (3.7) contain the sought distribution of gas bubbles with respect to dimensions $n(R)$. Upon finding the latter, one can determine the free gas content u:

$$u = \frac{4}{3}\pi \int_{R_{min}}^{R_{max}} R^3 n(R)\,dR.$$

Analysis of the field of the pulsed thermooptical sound source in a two-phase media is conveniently performed in terms of the spectral density of pressure:

$$\tilde{P}(\omega) = -\frac{i\exp(i\tilde{k}\cdot r)\,\omega}{r} F(\omega) \frac{\alpha\beta}{C_p} I_0 \frac{\tilde{k}\cos\varphi}{\tilde{k}^2\cos^2\varphi+\alpha^2} \times \exp\left[-\left(\frac{\tilde{k}a\sin\varphi}{2}\right)^2\right]. \quad (3.8)$$

Here

$$F(\omega) = \int_{-\infty}^{+\infty} g(t)\,e^{-i\omega t}dt$$

is the spectrum of the envelope of the intensity of the laser pulse.

In Ref. 47 the authors made an experimental test of the theoretical model of a thermooptical emitter in a two-phase medium.

In Fig. 10 the calculated signal is compared with that recorded in the course of the experiment. The good agreement between the results of experiment and calculation enables us to conclude that the approach developed in Ref. 47 is applicable to the theoretical description of the process of optical sound generation in a two-phase system.

Analysis of Eq. (3.8) allows us to propose the following methodology of reconstructing the radius distribution of bubbles.[95] If the receiver of the acoustic signal lies on the continuation of the axis of the laser beam in the medium ($\varphi = 0$), then the expression for determining the $\varkappa(\omega)$ and $\Delta c(\omega)$ relationships has the following form:

$$\frac{\tilde{k}}{k}\frac{k^2+\alpha^2}{\tilde{k}^2+\alpha^2}\exp[i(k-\tilde{k})r] = \frac{\tilde{P}_n(\omega)}{\tilde{P}_0(\omega)}. \quad (3.9)$$

Here $\tilde{P}_0(\omega)$ is the spectrum of the acoustic signal excited by the radiation in the medium without bubbles, and $\tilde{P}_p(\omega)$ is the spectrum of the signal experimentally measured in the same geometry of the problem in the two-phase medium having an unknown gas content. If the content of free gas is small, so that $\Delta c/c_0 \ll 1$ and $\varkappa \ll \omega/c_0$, the preexponential factor on the left-hand side of (3.9) differs little from unity, and the fundamental influence on the form of the acoustic signal acquired in the two-phase medium is exerted by absorption and dispersion effects upon propagation from the region of OA conversion to the recording point. In this approximation one can independently find the quantities $\varkappa(\omega)$ and $\Delta c(\omega)$ by experimentally determining either the amplitude or the phase of the ratio $\tilde{P}_b(\omega)/\tilde{P}_0(\omega)$. Thus the formula for finding $\varkappa(\omega)$ has the form

$$\varkappa(\omega) = -\frac{1}{r}\ln\left|\frac{\tilde{P}_n(\omega)}{\tilde{P}_0(\omega)}\right|.$$

Correspondingly, the distribution law of the gas bubbles per unit volume with respect to radii $n(R)$ is related to $\varkappa(\omega)$ by Eq. (3.7). Usually, in studying the $n(R)$ law one assumes that it varies rather smoothly in comparison with the remainder of the integrand in (3.7), and one can remove it from the integral sign, which in this case is easily calculated:

$$n(R) = \frac{2A}{\pi c_0 R^3}\varkappa\left(\frac{A}{R}\right). \quad (3.10)$$

Here we have $A = (3\gamma P/\rho_0)^{1/2}$. In a number of experimental situations (e.g., in measuring the distribution of bubbles in the surface layer of the ocean),[51] when the distribution $n(R)$ is not smooth enough, or more exactly, the condition is not satisfied that

$$\left|\frac{R_0\delta}{n(R_0)}\left(\frac{\partial n}{\partial R}\right)_{R=R_0}\right| \ll 1,$$

the accuracy of the reconstruction of the function $n(R)$ by Eq. (3.10) is low. Increasing the accuracy of reconstruction enables one to use the original integral relationship (3.7). Here one must solve the inverse problem, whose mathematical expression is a Fredholm integral equation of the first kind. The methods of solving this type of problems are rather well described in Refs. 49, 50. The numerical simulation performed in Ref. 95 on a computer shows that, even with considerable errors that can arise in the course of a diagnostic experiment to measure $\varkappa(\omega)$, the application of regularizing algorithms for solving the stated integral equation enables one to find rather accurately the $n(R)$ relationship in the two-phase medium.

Another example of the spectral approach to nonperturbing LDOA diagnostics is the reconstruction of the frequency-dependent absorption of sound in porous media, which one can obtain as the ratio of the spectra of the responses in the porous medium and in a control aluminum plate.[6] Other studies are known. Thus, in Ref. 52 it was pro-

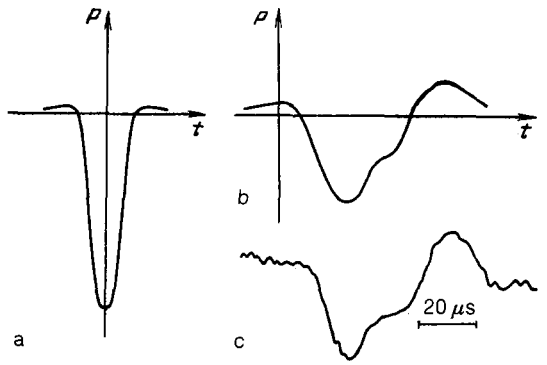

FIG. 10. Comparison of the acoustic signals excited by a pulse of a YAG-Nd^{3+} laser in water without bubbles (a) and in water with a specific gas content of $\sim 2\times10^{-5}$ (b,c).[47] a,b—Calculation. c—Experiment. The conditions of calculation and experiment are: $\alpha = 0.14\ cm^{-1}$, $\tau = 50$ ns, $\varphi = 27°$, $r = 25$ cm.

posed to use a spectral representation of the response to distinguish the contributions of bulk and surface sound sources, and hence, for separate reconstruction of the absorptive power of the surface and the bulk of the medium. Here one can eliminate the contribution from light scattering in the specimen, which distorts the indications of traditional optical spectroscopy.

The most important advantages of LDOA diagnostics are realized in the high sensitivity of analysis of weakly absorbing media and the possibility of measuring trace concentrations of substances in solution. Such problems are characterized by an extended cylindrical configuration of the OA conversion region, when the condition $\alpha a \ll 1$ is satisfied. It is assumed in the calculation that the region of release of optical energy amounts to an infinitely extended cylinder with a uniform distribution of heat sources along the axis of the cylinder (this implies that we neglect the exponential damping of the intensity of the laser radiation upon propagating in the medium, owing to the smallness of the absorption index α). The corresponding solution of Eq. (3.1) for the form of the signal outside the region of sources in the given case is obtained, e.g., in Refs. 53 and 54. The acoustic signal at some distance from the axis of the laser beam has the form of an N-wave and is shown in Fig. 11. The cylindrical geometry of the OA conversion is the basic experimental scheme of the OA spectroscopy of weakly absorbing media with direct recording of the signal. Here, in the amplitude variants of diagnostics, there is no need for distortion-free recording of the N-wave. It suffices to measure the amplitude of the vibrations in the transitional process that arises in the measuring OA cell under the action of such a signal.

An extended configuration of the region of absorption of the radiation can be convenient for observing certain physical features of the OA conversion. Interesting conclusions were drawn in Ref. 55 within the framework of a quantum-mechanical approach to the description of the process of laser sound generation in weakly absorbing media. In addition to the known expression that describes the ordinary cylindrical unloading N-wave, the author obtained two new terms describing the correction to the acoustic signal upon taking account of some additional arguments. One of them depends on the polarization of the laser radiation and cannot be derived in the phenomenological description. Since, unfortunately, the theory[55] introduces a set of parameters whose numerical values are not known even approximately, the author proposes for elucidating the magnitude of the predicted effect to conduct a painstaking comparison of the form of the recorded OA signals at two points, one of which would lie in the plane of polarization of the radiation, and the other on a straight line perpendicular to this plane. Although such an experiment has not yet been performed, insofar as we know, nevertheless this example shows the value of the dynamic approach to OA studies, which in a number of cases enables one to draw conclusions of fundamental type.

For purposes of LDOA diagnostics of weakly absorbing media, a scheme of recording the acoustic signal directly on the axis of the region of OA conversion has been developed. Here the z' coordinate of the point of observation satisfies the condition $z' \lesssim \alpha^{-1}$. The pattern of the character of the signals that arise enables one to obtain calculations performed for a half-space with a free boundary and two types of distribution of the intensity over the cross section of the laser beam, uniform and Gaussian. Thus, in the case of a Gaussian distribution the pressure everywhere on the axis of the region ($0 < z' < \infty$) has the form

$$P(t, z') = \frac{\alpha\beta c}{ac_P\tau_n} E_0 e^{-\left(\frac{\alpha a}{2}\right)^2} \left\{ e^{-\alpha z'} \int_{t-z'/c}^{t} \dot{f}(y)\, e^{(-\hat{y})^2} \left[\operatorname{erfi}\left(\hat{y} - \frac{\alpha a}{2}\right) - \operatorname{erfi}\left(-\hat{y} - \frac{\alpha a}{2}\right) \right] dy + \int_{-\infty}^{t-z'/c} \dot{f}(y)\, e^{-(\hat{y})^2} \left[-2\,\mathrm{sh}(\alpha z') \operatorname{erfi}\left(\hat{y} - \frac{\alpha a}{2}\right) + e^{\alpha z'} \operatorname{erfi} z_+ - e^{-\alpha z'} \operatorname{erfi} z_- \right] \right\} dy,$$

where we have

$$\operatorname{erfi} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{t^2} dt,$$

$$\hat{y} = \frac{c}{a}(t - y), \quad z_\pm = \pm \frac{z'}{a} - \frac{\alpha a}{2}.$$

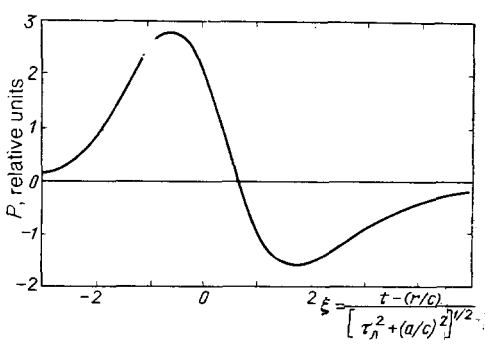

FIG. 11. Form of the OA signal in weakly absorbing media under conditions of cylindrical geometry of energy release.[54]

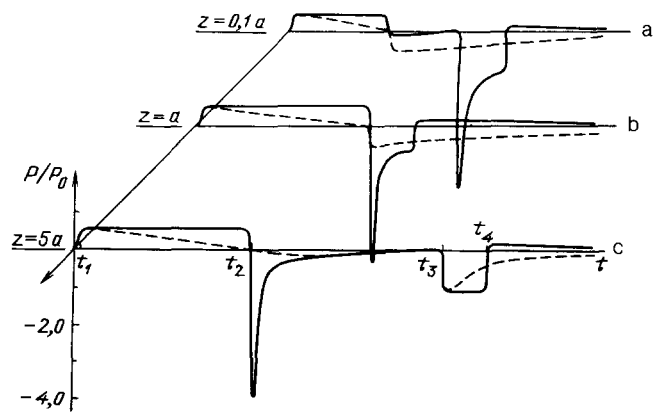

FIG. 12. OA signal at a point of observation situated on the axis of the region of release of laser energy for two forms of distribution of the radiation intensity in the cross section of the beam: $I(r) = I_0 (r \leqslant a)$, $0\ (r > a)$ (solid line); $I(r) = I_0 \exp(-r^2/a^2)$ (dotted line).[56] The z coordinate of the point of observation satisfies the condition $z < a$ (a), $z = a$ (b), and $z > a$ (c). In the graph $t_1 = a/c$, $t_2 = z/c$, $t_3 = (z^2 + a^2)^{1/2}/c$, $P_0 = (\alpha \cdot \beta / C_p) c^2 E_0 / \pi a^2$.

It is interesting to compare the unloading signal on the axis of the energy-release region for two types of transverse distribution of optical intensity (Fig. 12). The existence of sharp boundaries of the energy-release region in the case of a uniform intensity distribution leads to formation of a powerful rarefaction pulse on the axis of the region (in the case of a Gaussian distribution it is practically absent). Such pulses can be the reason for both breakdown of solid specimens and cavitation in liquid-medium specimens. According to the estimates made in Ref. 56 in water at room temperature, with $\alpha = 0.2\,\text{cm}^{-1}$ and $E_0 = 1$–$10\,\text{J}$, the values of the amplitudes of the rarefaction phase reach several MPa. The information-bearing component is the second pulse of the signal (Fig. 12), which is emitted from the thin near-surface layer of the medium of thickness $\sim c\tau_1$. Resolution of this pulse from the content of the entire signal enables one to increase the sensitivity of the method. The amplitude of this component is

$$P_2 = \frac{\alpha\beta c^3 E_0}{\pi a^2 C_p}. \tag{3.11}$$

Here E_0 is the total energy in the pulse. It is useful to compare the sensitivity with respect to α given by Eq. (3.11) with the sensitivity of traditional optoacoustic spectroscopy with piezoelectric recording of the signal outside the region at a distance r from its axis:[57]

$$P_0 = \frac{\alpha\beta c^3 E_0}{\pi r^{1/4} a^{5/4} C_p}.$$

For equal α we have $P_2/P_0 = (r/a)^{1/2} > 1$. Besides the gain in sensitivity, the recording of the second pulse in the region of energy release brings about a smaller dependence of the measurements on nonlinear heat effects and makes it possible to measure small absorption coefficients against the background of relatively strong scattering. As the authors of Ref. 57 acknowledge, the latter restricts the ultimate possibilities of traditional OA spectroscopy. Figure 13 shows the profile of such a pulse from the near-surface layer of a medium recorded in distortion-free fashion in the experiment of Ref. 18 for a Gaussian intensity distribution in the cross section of the laser beam. Analysis of the form of the received response is necessary also under certain specific conditions, e.g., in excitation of sound in water at temperatures close to $T_0 \approx 4\,^\circ\text{C}$.[25] The problem is that, according to the linear theory (Eq. 3.1), sound should not be excited, since the coefficient of thermal expansion of water vanishes:

$$\beta(T_0)|_{T_0 = 4^\circ\text{C}} = 0.$$

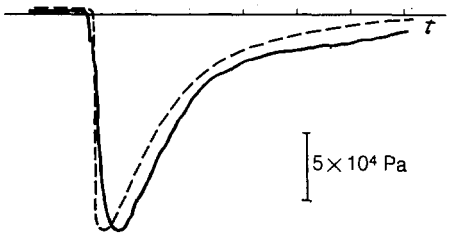

FIG. 13. Acoustic signal recorded on the axis of the OA conversion region in a liquid with a free boundary (the calculated form is shown by the dotted line).[18] The optical absorption coefficient is $\alpha = 5\ \text{cm}^{-1}$. The depth of the point of observation is 10 mm, and the radius of the cross section of the laser beam is 3 mm; the scale along the horizontal is 200 ns/division.

However, it was found experimentally[16,58] that complete disappearance of the acoustic signal does not occur. On the basis of the conditions of performance of concrete experiments (strong or weak absorption of the radiation in the medium), various theoretical models are proposed for this phenomenon. In the experiment of Ref. 16 the signals excited by the radiation of a CO_2 laser in light and heavy water were recorded (optical absorption coefficients 870 and 420 cm^{-1}). The receiver lay in the immediate vicinity of the surface of the water at a depth of 2 mm and received a plane acoustic wave not distorted by diffraction effects. The temperature dependence of the form and amplitude of the signals was carefully measured over the range from -2° to $+23\,^\circ\text{C}$ for different values of the intensity of the laser radiation. The author's estimates show that the laser energy released sufficed to heat the absorption region by the amount $\Delta T \sim 1$–$2\,^\circ\text{C}$. In this situation the minimum of the amplitude of the acoustic signal must shift from 4 °C toward lower temperatures by the amount ΔT, as was confirmed experimentally. The dependences of the amplitude of the signals on the power of the laser radiation given in Ref. 16 for different values of the equilibrium temperature offer grounds, as the author thinks, for explaining the evolution of the profile of the signal near 4 °C by a change in the coefficient $\beta(T)$ in the process of laser heating of the water. The theoretical estimates and additional measurements show that other possible mechanisms should not contribute appreciably to the acoustic signal at 4 °C under conditions of substantial heating of the region of interaction with water realized experimentally.[16] However, one can finally draw such a conclusion only by comparing the experimentally recorded transformation of the signal as the water temperature passes through 4 °C with the theoretical calculation of the thermal nonlinearity effect. Taking account of nonlinear thermal effects in the first-order approximation in the temperature increase yields a solution of the wave equation (3.1) with a right-hand side that takes account of the spatially inhomogeneous character of the heat release and the variation in β during the time of the laser pulse:

$$\Delta P - \frac{1}{c^2}\frac{\partial^2 P}{\partial t^2} = -\beta(T_0)\frac{\alpha}{C_p} f(x, y)\, e^{-\alpha z}\frac{\partial g(t)}{\partial t} + \frac{\partial \beta}{\partial T}\bigg|_{T=T_0} \frac{[(\alpha/C_p) f(x, y)]^2}{\rho} e^{-2\alpha z}\frac{\partial}{\partial t}\left(g(t)\int_0^t g(y)\,dy\right). \tag{3.12}$$

Here T_0 is the equilibrium temperature of the region of OA conversion.

An analysis of the solution of this equation for the far field has been performed in Ref. 59. It was shown[60] that the evolution of the form of the signal near 4 °C is not universal in character and is fully determined by the location of the point of observation and the parameters of the laser radiation. Under these conditions it is incorrect to compare the form of signals obtained in experiments with differing geometries of OA conversion and reception.[16,58]

As was noted in Ref. 61, thermal nonlinearity does not allow one to explain the results of the experiment of Ref. 58, where the radiation of a low-energy ruby laser ($\lambda = 695$ nm, $E_0 \sim 10^{-4}$ J) was used to excite sound in water at a temperature of 4 °C. An original theory was proposed in Ref. 61 that

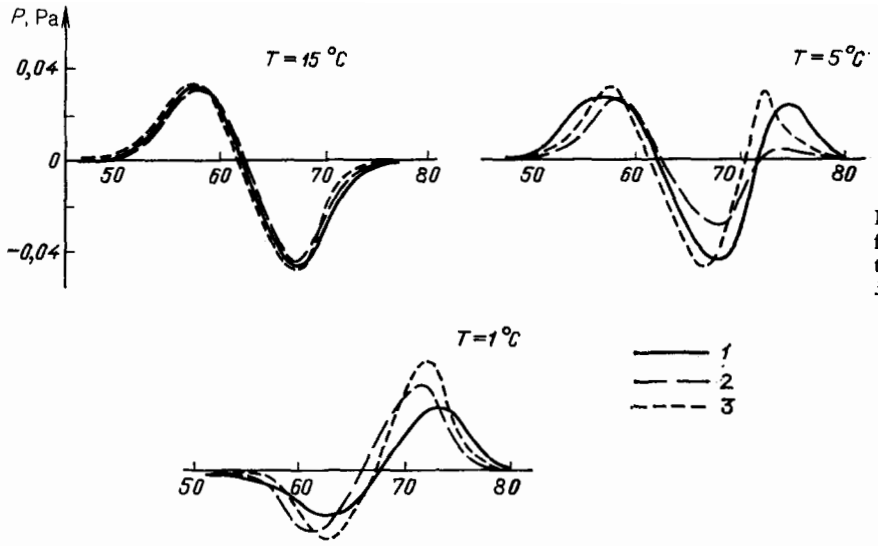

FIG. 14. Experimentally recorded evolution of the form of OA signals in water with decreasing temperature and theoretical models of it. *1*—experiment; *2*, *3*—theory: $\tau_\beta = 10^{-8}$ s (*2*) and 3×10^{-8} s (*3*).[61]

treats the OA interaction on the basis of the tenets of the thermodynamics of irreversible processes. The author assumes that one can explain the results of Ref. 58 satisfactorily by assuming the existence of a new mechanism of relaxation in water at 4 °C that can involve rearrangement of its cluster structure. In this case the right-hand side of (3.12) must have the form

$$-\frac{\alpha}{C_P}\left(\beta\frac{\partial}{\partial t}+\frac{\tau_\beta}{T_0}\frac{\partial^2}{\partial t^2}\right)g(t)f(x,y)e^{-\alpha z}.$$

Here τ_β is the characteristic time constant of the relaxation process. Figure 14 compares the results of the experiment of Ref. 58 and the theoretical calculation, in which the magnitude of τ_β was chosen so as to gain the best agreement. Unfortunately the existence of such a relaxation process has not yet been confirmed by other experimental data (e.g., the results of measuring sound absorption in water). Therefore the question of the source of the acoustic signal at the temperature 4 °C in the experiments[58] continues to be under discussion.

In addition to the variants of OA diagnostics with bulk acoustic waves that we have discussed, recently OA diagnostics with surface acoustic waves (SAWs) have found widespread application in OA diagnostics in studying solids. Various aspects of this have been discussed in detail in the review of Ref. 62. We note that, while possessing all the advantages of OA diagnostics with bulk waves (freedom from contact, local character, and high sensitivity to the energy being absorbed), OA diagnostics with SAWs can prove especially useful in studying the near-surface layers of condensed media. In particular, the existence of an unambiguous connection of the SAW spectrum with the spectrum of intensity distribution in depth allows one adequately to reconstruct the distribution of the light-absorption coefficient. According to the estimates made in Ref. 62, the resolving power of the method is restricted to the level of $\sim$0.3–1 μm. Therefore SAW diagnostics seems highly promising as a means for online monitoring of technological processes in microelectronics.

3.4. Features of the LDOA diagnostics of photoactive media

Above we have mainly been treating situations in which the interaction of the laser radiation with condensed media is accompanied by practically lag-free (in a time $t\sim10^{-12}$ s) transfer of energy of excited states to the translational degrees of freedom of molecules, i.e., practically instantaneous heat release. However, in the model of OA interaction in water at 4 °C presented in the previous section, the existence was proposed of a relaxation process involving rearrangement of the cluster structure of water, and possessing a time constant $\tau_\beta\sim10^{-8}$ s. The existence of this process, as we see from Fig. 16, substantially affects the form of the signal. This section is devoted to analyzing the possibility of diagnosing relaxation processes in *photoactive media* from the form of the received response.

Following Ref. 4, we shall term media photoactive in whose diagnosis we must consider expenditures of the absorbed optical energy in photoactivation (photoionization, photodissociation, chemical reactions of excited particles, etc.). The relaxation times in these media exceed the collisional relaxation time.

Relaxation processes in photoactive media are commonly associated with reversible (or irreversible) changes in structural organization, chemical composition, photoelectric effects, and also photoluminescence, that occur under the action of the laser radiation. In such media not all of the absorbed energy of the laser radiation is immediately converted into heat, or part of this energy is converted into other forms of energy and does not contribute to the process of sound formation. We can represent the magnitude of the acoustic signal in this case in the following form:[4]

$$P = KI\varkappa\left(1-\sum\frac{\eta_{pc}\Delta E_{\Phi p}}{N_A\hbar\omega}-\frac{\eta_L\omega_L}{\omega}-\eta_{PV}\right). \quad (3.13)$$

Here I is the intensity of the radiation at the entrance of the OA cell, $\varkappa$ is the fraction of the radiation energy absorbed in the specimen, K is a proportionality coefficient that depends on the properties of the specimen and the geometry of the experiment; the coefficients η_{PC}, η_L, and η_{PV} determine the

quantum yields of photochemical reactions, luminescence, and photovoltaic effects, respectively, ΔE_{PR} is the change in internal energy per mole associated with formation of products in photochemical reactions; N_A is Avogardo's number, $\hbar$ is Planck's constant, and ω, ω_1 are the frequencies of the exciting radiation and of the luminescence.

As Eq. (3.13) implies, laser excitation and the recording of the response in photoactive media enable one to obtain information on the magnitude of the quantum yield of some photoprocess, on the energy of photochemical reactions and their intermediate phases, while by analyzing the form (or spectrum) of the response one also obtains information on the kinetics of the photoprocesses that occur.

Optoacoustic methods in the study of the photoactive media have been applied relatively recently. Here the potentialities of OA diagnostics, especially its dynamical variants, as yet have not been realized sufficiently.

Let us examine some variants of OA diagnostics that have been developed to analyze photoactive media. Reference 63 modeled theoretically the complex photochemical processes that occur in photosynthesis. Photosynthesis amounts to a multistep sequence of reversible and irreversible processes, each of which is characterized by certain values of the energy of formation of intermediate (or final) chemical compounds, as well as by the rate constant of the reaction. Reference 63 proposed studying reactions by illuminating the specimen with laser radiation modulated according to a harmonic laws at frequency ω. The authors derived the corresponding analytic expressions for the frequency dependence of the heat release in the presence in the medium under study of photoreactions of three fundamental types. It was shown theoretically that, with an appropriate choice of the modulation frequency, one can measure both the energies of the intermediate states and the energy of formation of the stable reaction products. The choice of frequency is determined by the fact that, when photoprocesses exist in the medium having characteristic reaction rate constants k_i, the frequency dependence of the signal $\tilde{P}(\omega)$ must contain extrema at $\omega = k$.

The experimental measurement of the spectral dependences $\tilde{P}(\omega)$ enables one to solve the inverse problem of reconstructing the energy and kinetic characteristics of complex photochemical reactions. Such measurements have been performed, e.g., in Ref. 64, where the signal was recorded with a gas-microphonic scheme. The photocycle was studied of a suspension of fragments of the purple membrane extracted from the bacterium *Halobacterium halobium*. The modulation frequency of the radiation was varied in the range 5–500 Hz. Since the frequency dependence of the signal in the scheme with microphonic recording in the gas adjacent to the specimen is rather complicated (it is governed by processes of thermodiffusion, as well as by the frequency properties of the experimental OA cell), to reveal the information on the photochemical transformations it was necessary to normalize the signal. The reference used was the signal P_{REF} from a suspension of the same concentration in which the photoprocesses had been suppressed by adding NH_2OH. The obtained normalized signal as a function of the modulation frequency for different values of the pH of the suspension and different concentrations of NaCl in it are shown in Fig. 15. The noted jumps in the dependence at the frequencies 130, 60, and 35 Hz correspond to the constants

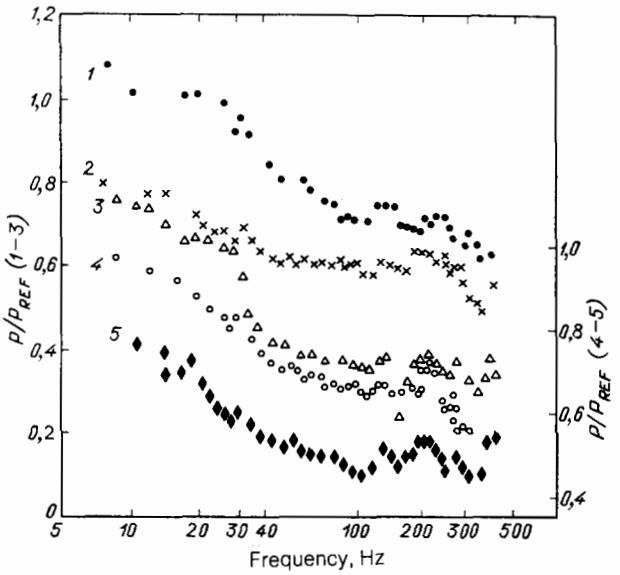

FIG. 15. Dependence of the amplitude of the normalized optoacoustic signal on the modulation frequency of continuous laser radiation in suspensions of membranes at different values of pH and the salt concentration (NaCl): *1*—pH = 7.7, 0 M; *2*—pH = 7.7, 1 M; *3*—pH = 7.0, 0 M; *4*—pH = 9.0, 0 M; *5*—pH = 9.0, 1 M.[64]

of known intermediate components of the photocycle. The jumps at the frequencies 185, 200, and 300 Hz, as the authors assume, can involve conformational changes in proteins that arise, respectively, at 2, 0.8, and 0.5 ms after the onset of irradiation.

In Ref. 65 the first attempt was made to apply a pulsed methodology of OA research to studying photoactive media. One of the best studied photochemical reactions was examined—the reaction of photolysis of triplet benzophenone under the action of aniline. The theory of photoacoustic calorimetry was treated in the approximation of a point OA source, while the law of entry into the medium of the energy of the laser radiation was approximated by a δ-function. Under these conditions the photoconversion occurring in the medium is governed by an exponential law for the bulk density of heat release:

$$q(t) \sim e^{-t/\tau_p}. \tag{3.14}$$

Here τ_p is the lifetime of the intermediate metastable products of the photolysis. The signal was recorded with a resonance piezoreceiver analogous to that described in Ref. 57, whose pulse characteristic has the form

$$s(t) = A \sin(\nu t)\, e^{-t/\tau_0}.$$

Here the values of the constants are $\beta = 10^5\ s^{-1}$, $\tau_0 \approx 1$ ms. It is proposed to use the resonance properties of the receiver to measure fast relaxation processes with $\tau_p < 1/\nu$. Thus the measurements are reduced to pure amplitude recording of the magnitude of the first negative peak of the vibrational process that arises upon excitation of the receiver by the brief signal. Comparison of the data obtained from recording the signal with the data of analogous measurements in solutions in which the photochemical processes do not occur enabled finding the quantum yield of the photolysis reaction of benzophenone to form a pair of stable radicals and determining

for the first time the heat of reaction: $\Delta H = 46 \pm 5$ kcal/mole. Later an analogous method was used to determine the energy of dissociation of a carbonyl group from the hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in solution in ethanol and cyclohexane.[66]

In the studies discussed above the simplest, information-poor variants of OA diagnostics were applied to analyze the photoactive media. At the same time, for the situation studied in Ref. 65, one can calculate the form of the signal without resorting to the point-source approximation. Such a calculation is contained in Ref. 67, where the situation was numerically modeled in which relaxation mechanisms exist in a medium whose time constants exceed the duration of the laser pulse and the propagation time of the sound over the cross section of the focused laser beam. In this case the dynamics of heat release is also determined by Eq. (3.14). Figure 16 shows the calculated evolution of the form of the recorded cylindrical wave upon increase in the relaxation time. Recording of the form of the response with use of broad-band receivers analogous to those described in Sec. 2 enables one to obtain information on the dynamics of some particular relaxation process. Since the response in a photoactive medium with long relaxation times is described as a convolution of the time dependence of the relaxation of photoexcitation and the "instrumental" response function (which coincides with the form of the signal in a medium with subnanosecond relaxation), the inverse transformation yields the dynamics of heat release in the photoactive medium. In the presence of a single relaxation process one can easily reconstruct also the lifetime of the excited state τ_p. The described reconstruction procedure has been performed[68] for a set of photochemical reactions. Here the experimental method allowed determining the τ_p constants in the range 60 ns–10 μs. The principles of calculation presented in Refs. 67 and 68 can be extended also to the case of complex, multistep photoconversions in photoactive media. Recording of the acoustic signals in such media with high time resolution enables one to study fast photoprocesses having unknown kinetics.

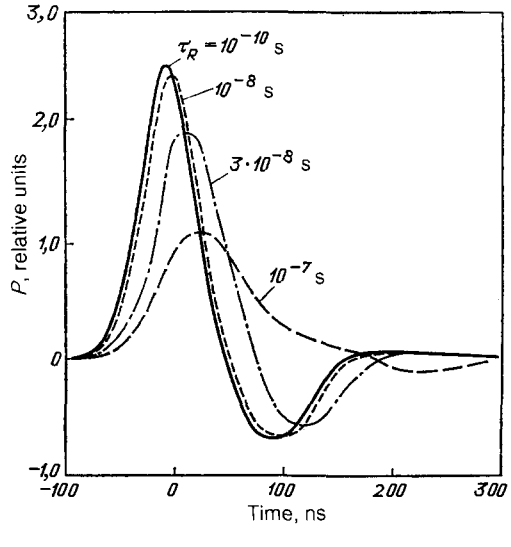

FIG. 16. Calculated forms of OA signals in a weakly absorbing liquid for different values of the relaxation time constant τ_R.[67]

This review is devoted to the diagnostics of condensed media. However, we should mention that also the specialists in gas OA diagnostics in recent years have found attractive the methods based not only on determining the amplitude of the response, but also on studying its form. For example, the form of the pulsed response has been studied in detail in gas-analytical instruments[69] for exciting sound with milli- and nanosecond ruby-laser pulses. The form of this response is associated in a complex way with the thermodynamic and relaxational characteristics of the gaseous medium and the parameters of the optical pulse. Indeed, the pattern is complicated by the numerous reflections from the walls of the chamber. The measured rise time of the envelope of the entire packet of the OA responses is used to determine the relaxation time and the dynamics of photosensitization.[70,71] Finally, Ref. 72 has paid attention to a more effective method of diagnostics of such media. It turns out that, in going from recording of the packet to distinguishing the individual responses with a broad-band receiver with a certain relationship of the amplitudes of the compression and rarefaction phases, the sensitivity of the method is substantially increased and the dynamic range of measurements is expanded.

4. HIGH-POWER LASER PULSES IN THE SERVICE OF LDOA DIAGNOSTICS

4.1. Preliminary information

With increasing laser intensity, the process of nonperturbing heating of the specimen gives way to phase transitions. From the standpoint of sound generation, these effects are substantially nonlinear owing to the strong perturbations of the equilibrium state of the medium[25] and they lead to a growth in the efficiency of OA conversion. Despite the extensive studies in the field of the physics of interaction of high-power laser radiation with matter, many problems remain unelucidated, e.g., there is little to be said on the regimes of interaction optimal from the standpoint of efficiency of conversion of optical energy into mechanical.

At present an approximate classification exists of the mechanisms of sound generation under conditions of optically stimulated fast phase transitions. In optically transparent condensed media, with increasing laser intensity the thermal mechanism is replaced by bulk optical breakthrough to form plasma microcavities that play the role of effective sources of shock waves. The intensity threshold for breakthrough depends on the existence in the medium of inhomogeneities, while in homogeneous media its value can be very large (10^9 W/cm^2 and higher in liquids subjected to special purification). The microcavities are distinguished by high initial velocities of expansion ($\sim 10^6$ m/s). At a distance of 10^{-2} cm from the cavity one records a shock wave with an amplitude of $\sim 10^4$ MPa.[73] In impure media the microcavities can combine into an extended laser spark. Here the efficiency of conversion of optical into acoustic energy reaches record-making values (10–30%). The presence in the medium of microparticles substantially lowers the value of the threshold (by several orders of magnitude). This enabled the authors of Ref. 74 to use high-power laser radiation to monitor the purity of media in microelectronics. When microparticles existing in the bulk of the medium under study lie in the focal region of the laser beam (the second harmonic of a pulsed YAG laser was used, the radiation of

which is weakly absorbed in the studied liquid), optical breakthrough occurs with its center at the site of the contaminating particle. Since the efficiency of sound formation in breakthrough greatly exceeds that corresponding to the thermal mechanism of sound generation, the acoustic signals from such "breakthrough" sources are distinctly visible on the background of the OA signal recorded in the absence of contamination. Thus, by using broad-band acoustic receivers, one can distinguish the signals corresponding to each of the microparticles existing in the focal region of the probe beam. In the course of such an experiment, the authors of Ref. 74 were able to detect a concentration of polystyrene microparticles in solutions at the level of 0.5 ppb. The acoustic signal thus excited is used not only for probing materials (see Sec. 4.2 below), but also for medical purposes (in promising problems of ophthalmology and lithotripsy; see, e.g., Ref. 75) and in technology.

In strongly light-absorbing media an increase in the density of released energy leads to melting, evaporation (surface and bulk) of matter, and plasma ignition on a surface. As the magnitude of the energy release approaches the corresponding magnitude of the heat of phase transition, the emitted acoustic signal of thermal origin undergoes changes and is combined in a complicated way with the contributions of "perturbing" nature caused by the recoil pulse of the droplet plume and the plasma flare, by the explosive expansion of the near-surface region of the medium, by nonlinear recombination effects (in semiconductors), etc. In these cases one can speak of a combination mechanism of optical sound generation. The acoustic response being excited proves to be very rich in information and is used in LDOA diagnostics, mainly for collecting data on the behavior of a material in strong light fields (see Sec. 4.2 below). Such studies should make it possible to determine the scope of regimes of programmed optical treatment (e.g., laser annealing of semiconductors) and the optimal regimes for generating sound pulses, including pulses of record-making amplitudes. In turn, such pulses are used for stimulating nonlinear effects,[76] remote probing of inhomogeneous media, e.g., seas and oceans,[77] and for solving problems of controlled thermonuclear fusion.[78]

Let us illustrate the features of the new field of LDOA diagnostics with concrete examples.

4.2. LDOA diagnostics of the behavior of condensed media in strong light fields

Contact-free monitoring of a number of technological processes (laser drilling and cutting) is performed by recording the acoustic signals that accompany these processes. Thus, in Ref. 79 the possibility was demonstrated of remote control of laser drilling. The drilling of an easily vaporized composite material fastened to a copper substrate was performed with two successive laser pulses. A cylindrical piezoreceiver lying in the air above the specimen measured the acoustic response, which was then integrated over the time of observation. Since the properties of the material were not sufficiently homogeneous in cross section (with respect to the drilling direction), the results of the measurements were processed statistically for a large number of drilling points. The hole never reached the substrate after action of the first laser pulse, as indicated by the practically constant integral acoustic response. Depending on whether the substrate was reached after action of the repeated laser pulse or not, the integral response either increased (as compared with the response to the first laser pulse), or it declined. On the basis of these measurements, the authors concluded that the depth of the aperture and the instant of reaching the substrate can be controlled by recording the acoustic signals accompanying the process of laser drilling.

In pointing out the prospects of applying laser vaporization of polymers and biological tissues in microtechnology and microsurgery, the authors of Refs. 80 and 81 studied by means of OA diagnostics the process itself of interaction of radiation with a medium. In Ref. 80 combined calorimetric and acoustic measurements were performed near the energy threshold of vaporization for three wavelengths of laser radiation. Exceeding the threshold was accompanied by sharp increase in the acoustic signal, which was caused by the additional action on the surface of the specimen of the recoil momentum of the vaporization products. The method that was used of recording the signal with a narrow-band piezotransducer at the frequency ~ 20 MHz permitted making only amplitude measurements.

For a more detailed study of the features of vaporization of organic polymers with the radiation of excimer lasers, a broad-band acoustic receiver based on PVDF was used in Ref. 81. This enabled obtaining information on the time evolution of the process of laser vaporization with high time resolution ($\leqslant 5$ ns). The form of the acoustic signals enabled one to infer some particular mechanism of interaction of radiation of different energies with polymer materials. Thus, in studying the interaction of pulses of an XeCl laser (wavelength 308 nm) and of an ArF laser (193 nm) with polyimide, unipolar acoustic signals were recorded that followed the laser-radiation pulse with a small time lag (4–6 ns). This indicates the onset of the vaporization process. In the studied range of radiation energy densities (40–300 mJ/cm^2 for the XeCl laser and 24–470 mJ/cm^2 for the ArF laser) no signal of pure thermoelastic origin was observed. Therefore the form of the acoustic response remained practically invariant as the energy of the radiation was increased. An important result of OA diagnostics is the fact that the recording of unipolar acoustic signals indicates the onset of laser vaporization long before the onset of the generally accepted threshold for photolysis for the given polymer. In a material with a smaller value of the optical absorption coefficient (polymethylmethacrylate, $\alpha \sim 4000$ cm^{-1}), an increase in the radiation energy is accompanied by transformation of the acoustic signal from an N-shaped form characteristic of a perturbation of thermoelastic origin to a unipolar one corresponding to action of the recoil pressure pulse of the products of laser vaporization escaping the surface. However, since the vaporization process begins with a small lag, at large radiation energies one can distinguish on the leading front of the acoustic pulse a contribution from the thermoelastic mechanism of sound generation (Fig. 17).

The authors of Ref. 82 used a broad-band PVDF receiver to study interaction processes of ultraviolet and visible laser radiation with normal and pathological tissues of the human aorta in the prethreshold (thermoelastic) and the vaporization regimes. The acoustic signal observed in the prethreshold regime agreed well in form with that theoretically calculated from the known formulas for the near field of a thermooptical sound emitter. This enabled determining

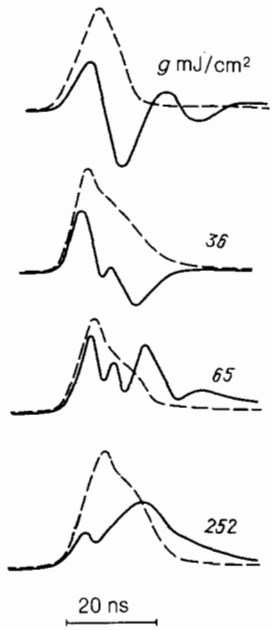

FIG. 17. Transformation of the signal excited by the radiation of an ArF laser in polymethylmethacrylate with increasing energy of the laser radiation.[81] The dotted line shows the form of the laser pulse.

the absorption coefficient α, in line with the procedure described in Ref. 38. It turned out that in a pathological tissue α is somewhat smaller, but this difference does not exceed the errors of measurement indicated by the authors. Upon increasing the energy of the laser radiation, as in the case of polymers, an additional compression pulse arises, caused by the action of the recoil pressure. One can distinguish on the leading front of the total acoustic signal a contribution from the thermal mechanism. For the given times of observation (tens of nanoseconds) we can consider the latter to be practically lag-free, whereas the vaporization process, in the opinion of the authors of Ref. 82, begins about 10 ns after the onset of the pulse of laser radiation (Fig. 18). Reaching the threshold is accompanied not only by a change in form, but also by a sharp increase in the amplitude of the acoustic signal. Therefore, by using a graph of the dependence of the amplitude of the acoustic signal on the energy density of the radiation, one can determine the magnitude of the energy

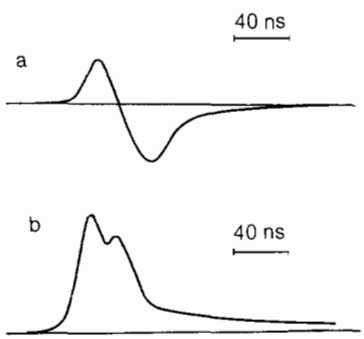

FIG. 18. Acoustic signal in aortic tissue irradiated with a KrF laser pulse ($\lambda = 248$ nm) of duration 10 ns. a–Prethreshold thermoelastic response–energy density 140 mJ/cm^2. b–Evaporative regime at 480 mJ/cm^2.[82]

corresponding to the onset of vaporization. The values thus found of the threshold energy contributions also proved to differ for the two types of tissues: normal and pathological.

For successful diagnosis of the behavior of media in strong light fields, one should analyze in detail the form of the acoustic signals, which is determined by the physical processes in the region of interaction of the radiation with the medium, and also by the rapidly varying thermophysical parameters of the medium.

A similar analysis was performed in Ref. 23, which investigated by LDOA diagnostics the non-steady-state interaction of the radiation of a CO_2 laser with water. The complexity of the phenomena that occur in the thin near-surface layer ($\sim 10^{-3}$ cm) does not allow one to give a complete theoretical description. Yet the experimental studies for a long time were restricted to analysis of the amplitudes of the pressure pulses and the values of the threshold optical intensity at which the nonlinear effects accompanying phase transition begin to be manifested. Specifying the relative roles of the contributions of various effects and establishing the time courses of the non-steady-state pressure in the near-surface layer enables one to analyze the form of the acoustic signal recorded in the far field of the OA source excited in water by a CO_2 laser pulse. The variant of acoustic diagnostics with recording in the far field has certain advantages; in particular, one can fully reconstruct the pressure profile in the near-surface layer and obtain additional information by recording the signal at an angle to the axis of the laser beam. In the cited study[23] only the first phase ($\sim$400 ns) of the total acoustic signal, whose duration equals the total duration of the laser pulse ($\sim$8–10 μs) was examined in detail. The summary table constructed in Ref. 23 of oscillograms of the first phase of the acoustic signal for different values of the angle φ of observation and of the measured values of the total energy E_0 of the laser pulse enables one to infer the relationship of the contributions of different mechanisms to the total signal (Fig. 19).

The theoretically predicted differing angular dependence of the contributions of the "vaporizing" and "thermal" sources has been confirmed in the course of an experiment that enabled establishing the nature of both peaks of the first phase of the signal (the middle row of oscillograms for $E_0 = 140$ mJ) and ascribing them respectively to the contributions of thermooptical and evaporative sources. The fact of the joint action of the sources was known even earlier, but the relationship of the contributions for a given E_0 was considered invariant. The graph of Fig. 19 pictorially demonstrates that the relationship of the contributions varies as a function of the angle φ. Thus, the signal observed at angles close to $\varphi = \pi/2$ involves only the evaporative sources, which possess a broader directional diagram of emission.[23] This fact has been applied in the course of diagnostics. The dependence of the amplitude of the acoustic signal on the energy E_0 for $\varphi = 75°$ was constructed (at these values of φ we can now neglect the contribution of thermooptical sources). The experimental points can be approximated by two intersecting lines. The intersection point corresponds to the threshold of the transition from surface vaporization to bulk phase transition, at which the specific density of the energy released in the medium is close to the value of the effective heat of vaporization for water.

The time course of the pressure in the near-surface layer

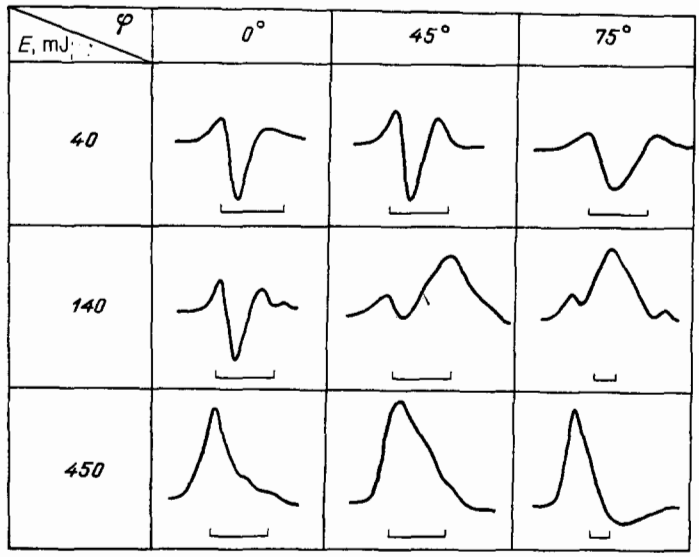

FIG. 19. Profiles of the acoustic signal in water for different energies of incident CO_2 laser radiation E_0 and angles of observation φ.[23] Scale along the horizontal 400 ns/division.

$\tilde{P}(t)$ was reconstructed from the data of recording the acoustic signals in the axial direction in the far field. The characteristic rise time of this pressure amounts to 300–350 ns, whereas the decline in intensity of the laser radiation begins at about 50 ns. Such a "delay" leads to the need of a cautious interpretation of the dependences of the amplitude of the pressure on the amplitude of the radiation intensity obtained in earlier studies.[25] The experimental results [23] indicate that, within the limits of accuracy of the measurements ($\pm$ 20%), the initial non-steady-state stage of the process is characterized by a constant ratio $\tilde{P}/E(t)$, where $E(t)$ is a certain value of the released energy characteristic of the initial stage of the process, while t_1 is the instant of time by which the stated energy is absorbed in water. The obtained results enabled proposing a series of uncomplicated theoretical estimates to describe the process of non-steady-state interaction of the optical radiation with the strongly absorbing dielectric liquid, which can be useful for further study of the phenomenon.

Study of the signals that arise upon interaction of laser radiation with matter can prove important for diagnostics of the behavior of semiconductors in a strong light field. This review does not claim to provide an exhaustive generalization of the results of the numerous studies of the physics of OA conversion in semiconductors. We shall restrict the discussion to information that reveals the features of LDOA diagnostics of semiconductor materials. Such a diagnostics is necessary in laser annealing, laser doping, and vaporization of thin films, and successfully supplements the new nonlinear-optical methods of diagnostics "in reflection".[83] Actually the information content of these signals is high, and it opens up new potentialities as compared with the examples of analysis of dielectrics discussed earlier. Here also the methods of distinguishing the contributions to the total signal of various processes stimulated by irradiation prove useful. However, we note that the diffraction methods of distinguishing the contributions discussed in the previous example do not "operate" in this case owing to the specific thin-layer configuration of the specimens.

The interaction of laser radiation with strongly absorbing semiconductors stimulates a chain of fast processes that have not been fully studied:[83–85] excitation and relaxation of the electronic subsystem, electron-phonon relaxation, phonon-phonon relaxation, and finally, thermal processes (heating, melting, vaporization). A characteristic thermal process in strongly absorbing semiconductors is the fast recrystallization of near-surface layers amorphized by ion implantation or by other agents. Here, as was shown recently,[86] the set of factors that stimulate these phase transitions include optical generation of a high-power ultrasonic field in the annealing region.

The process of optical sound generation in a semiconductor is distinguished by a number of specific features. For example, the density of the semiconductor material depends on the concentration of free carriers in the conduction band. Correspondingly, the ordinary wave equation (3.1) in describing the OA conversion in semiconductors (the one-dimensional case) must be supplemented also with at least one term and is modified:[84]

$$\frac{1}{c^2}\frac{\partial^2 P}{\partial t^2}-\frac{\partial^2 P}{\partial X^2}=\beta\rho\,\frac{\partial^2 T(x,t)}{\partial x^2}+\frac{1}{c^2}D\,\frac{\partial^2 n_a(x,t)}{\partial t^2}. \quad (4.1)$$

Here D is the constant of the deformation potential. The concentration of the nonequilibrium carriers $n_a(x, t)$ and the lattice temperature $T(x, t)$ are found from the corresponding diffusion equations.[87]

A number of studies (see, e.g., Ref. 84) are devoted to describing $T(x,t)$ and $n_a(x, t)$, i.e., the dynamics of the heating of semiconductors. In the calculations one should take account of the temperature dependence of the light-absorption coefficient, the width of the forbidden band (if it is close to the energy of a quantum of the radiation), the absorption by free carriers, and the energy expenditure in melting and vaporization of the surface layer. Thus the process of optical sound generation in semiconductors is substantially nonlinear in character, even at moderate intensities of laser radiation.

The experimental studies of OA conversion in semicon-

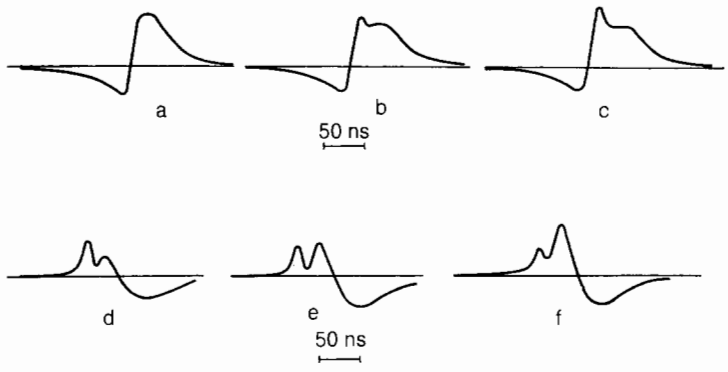

FIG. 20. Oscillograms of pressure pulses upon irradiating silicon with pulses from a neodymium laser with $E_s = 1.3$ (a), 1.7 (b), and 1.95 (c) J/cm^2, and oscillograms of the pressure pulses upon irradiating germanium with ruby-laser pulses with $E_s = 0.05$ (d), 0.07 (e), and 0.08 (f) J/cm^2.

ductors have aimed, first, to explain the problem of the influence of some particular dynamic process in the specimen on the form of the signal, and second, to learn to diagnose the behavior of semiconductors from the data of separate analysis of the phases of the signal.

In one of the first experiments on OA monitoring of the regimes of laser annealing,[88] the piezotransducer was placed on the unilluminated side of the silicon plate and was separated from it by a water layer. Subtle analysis of the sonic response of an acoustic signal of complex constitution enabled discriminating the contributions involving the photoexcitation of carriers and thermal processes, and also to reveal a negative OA effect in the range of intensities corresponding to optimal regimes of annealing. The negative OA effect is characterized by a declining dependence of the amplitude of the thermal phase of the signal on the intensity of the laser pulse. It is explained by the fact that the compression of the near-surface layer upon recrystallization compensates the thermal expansion of the layer. It was also shown that the form of the leading front of the response proves very sensitive to inadmissible phenomena of damage to the silicon by laser radiation of excessive intensity. The potentialities of OA diagnostics of laser melting and vaporization were studied in greater detail with the example of silicon and germanium specimens in Ref. 89. In silicon, pulses of wavelength 1.06 μm excite a bipolar signal (Fig. 20a–c) characteristic of relatively weak absorption. The first phase of the signal is negative (the deformation of the region of absorption involves an increase in the concentration of nonequilibrium carriers). Correspondingly, in describing the effect in Eq. (4.1), the second ("nonthermal") term on the right-hand side dominates. With increasing optical energy density E_s, one observes in the response a narrow pressure peak that indicates a sharp decrease in the depth of absorption and a transition to melting of the specimen.

The signal excited in germanium by laser pulses in the visible range (Fig. 20d–f) has a form typical of strongly absorbing media in which mechanisms that involve lattice heating dominate. The appearance of a narrow trough in the oscillogram indicates that the melting threshold has been reached, with a corresponding increase in the reflectivity of the surface. The onset of the rapid growth of the second pressure peak corresponds to reaching the vaporization threshold.

4.3. Hydrodynamic phenomena in LDOA diagnostics

The phase transitions that accompany the process of interaction of high-power laser radiation with condensed media can also lead to various hydrodynamic phenomena. For example, strong absorption of the radiation at the phase boundary causes intensive vaporization of the condensed medium, which in turn leads to deviation of the surface of the medium from the equilibrium position and even to spraying of the material in the form of separate drops or cumulative jets.[90,91] Optical breakthrough in the bulk of the liquid is accompanied by formation of a cavity and further pulsations in it.[92] Study of these processes enables one in a number of cases to supplement the information obtained in the course of acoustic diagnostics.

Reference 93 studied perturbations of the surface of various liquids under the action of the focused radiation of a pulsed electric-discharge CO_2 laser. In this case the heating of the medium leads to the appearance of a recoil pressure of the escaping vapor P_S acting on the surface of the liquid. For large values of the surface density of laser energy at which the magnitude of the total momentum transferred to the surface by the products of vaporization

$$\Pi = \int\int P_S \, dt \, dS,$$

satisfies the condition

$$\Pi \gg S\,(a\sigma\rho)^{1/2}$$

(σ is the surface tension, a is the characteristic radius of the region of application of the pressure, which is close to the radius of the laser spot on the surface, and S is the area of this region), the surface of the liquid in the region of application of the recoil pressure after the transition process acquires the form of a hemisphere that expands for some time inside the liquid. It was shown that the experimental study of the law of this expansion enables one to find the absolute magnitude of Π, whose determination by other methods is difficult in the case of a liquid. When $\Pi \sim S(a\sigma\rho)^{1/2}$, the surface deviates from the equilibrium position by an amount of the order of a. If $\Pi \ll S(a\sigma\rho)^{1/2}$, then the displacements of the surface are small, and their description, with some additional assumptions, is reduced to solving the initial problem for the acoustic potential distributed on the surface of the liquid.[94] The initial perturbation of the surface at the site of application of

the pulsed recoil pressure leads to formation of a train of diverging gravitational-capillary waves (GCWs). In the linear case of small deviations from the equilibrium position, one can calculate the profile of the GCWs analytically. Thus, at a sufficient distance from the site of excitation, the angles of deviation of the surface in the GCWs are described by the following expression obtained by an asymptotic estimate of the integrals of Ref. 93 by the stationary-phase method:

$$\varphi(r_0, t) \approx \sum_{i=1,2} \frac{2}{\rho} \frac{\Lambda(k_i)}{\Omega(k_i)} k_i^{5/2} \frac{\exp(-\beta(k_i)t)}{[(\partial^2\Omega/\partial k^2)_{k=k_i}]^{1/2}} \frac{\sin[\Omega(k_i)t - k_i r_0]}{(r_0 t)^{1/2}}, \quad (4.2)$$

Here the dispersion relationship for GCWs is: $\Omega(k) = (\sigma k^3/\rho) + gk$, r_0 is the distance to the point of observation in the plane of the boundary of the liquid, and the values of the wave numbers k are found as the points of stationary phase from the equation $d\Omega/dk = r_0/t$; $\beta(k)$ is the damping coefficient of the GCSs, $\Lambda(k)$ is the Hankel transform of the distribution of the recoil momentum over the region of application of pressure:

$$\Lambda(k) = \int_0^\infty\int P_S(t, R) R J_0(kR)\, dR\, dt.$$

(We assume that the distribution of recoil momentum depends only on the distance R from the center of the region of application of pressure.)

The use of GCWs excited by laser radiation on the surface of the liquid as the probe signal is based on the fact that the parameters of the GCW train and its damping coefficient $\beta(k)$ upon propagation are fully determined by the properties of the surface such as the surface tension σ, the surface elasticity modulus ε, and also the viscosity of the liquid.[96-98] Thus the experimental recording of the space-time characteristics of the GCWs enables one in principle to reconstruct the properties of the surface, and thus to solve a number of current problems of the physical chemistry of surfaces involving the study of the properties of films of surface-active materials and the dynamic relaxation processes that occur at such surfaces.[97]

Figure 21 shows the results of calculating the profiles of GCW packets, as well as the spectra both for a clean liquid surface ($\varepsilon = 0$) and for a surface covered with a film of a surface-active substance. We should note that, in a situation in which we can neglect relaxation processes at the surface, the modulus ε is a real quantity (the case of a "pure elastic" surface); yet if the times of occurrence of relaxation processes are comparable with the characteristic period of oscillation in the GCWs, then the modulus ε becomes a complex quantity. To illustrate this case, a process is chosen in Fig. 21 of diffusional exchange between the surface and the bulk of the liquid whose analytic description, together with the corresponding expressions for finding ε, are contained in Ref. 96.

The proposed method of surface diagnostics using remote excitation of GCWs by high-power laser radiation has a number of advantages over the traditional methods of surface probing in which, as a rule, an electromechanical vibrator generates standing capillary waves of fixed frequency. Diagnostics using a relatively broad-band packet of GCWs enables one directly to determine the spectrum of the damping coefficient $\beta(\omega)$. Actually, as we can show, when we record the GCW packet simultaneously at two points of observation r_1 and r_2, we can determine the spectrum $\beta(\omega)$

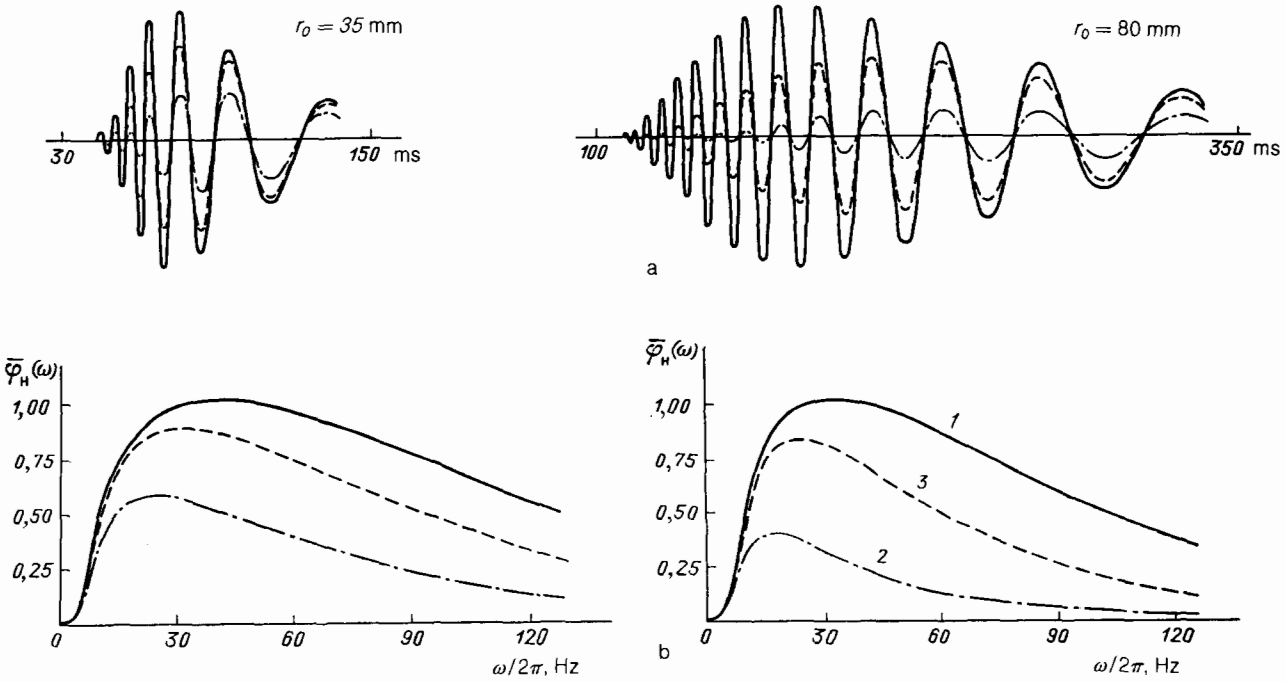

FIG. 21. Profiles of inclination angles in packets of GCWs induced by laser irradiation (a) and their normalized amplitude spectra (b) for two distances to the point of observation and various types of surfaces: clean surface (*1*), surface covered with a surface-active substance film for which $\varepsilon = 10^{-2}$ N/m and the influence of relaxation processes is small (*2*), and for the same value of ε with marked processes of diffusional exchange between the surface and the bulk of the liquid in the region of energy-bearing frequencies (*3*).[95]

even without having information on the distribution over the surface of the pulsed recoil pressure,

$$\beta(\omega) = \frac{v_r(\omega)}{r_2 - r_1} \ln \frac{\bar{\varphi}(\omega, r_1)\, r_1^{1/2}}{\bar{\varphi}(\omega, r_2)\, r_2^{1/2}}, \qquad (4.3)$$

Here $\bar{\varphi}(\omega, r)$ is the spectrum of the experimentally recorded GCW packet at the point r, $v_g(\omega)$ is the group velocity of the GCWs. A knowledge of the spectrum $\beta(\omega)$ makes it possible to find the spectrum of the modulus of surface elasticity $\varepsilon(\omega)$, which plays an important role in the physical chemistry of the surface. Comparison of the $\varepsilon(\omega)$ relationships for different values of the surface concentration of the surface-active substance enables one to study dynamic surface phenomena: diffusional exchange between the bulk of the liquid and the surface, breakdown and formation of micelles at the surface, reorientation of complex organic molecules, etc.[97,98]

CONCLUSION

The results presented above can serve as evidence that a new field is taking shape in laser OA diagnostics—laser dynamic OA diagnostics. We briefly recall that the fundamental results attained up to now can be classified into two groups.

1. The extension of the method of OA diagnostics to problems of analyzing the physicochemical characteristics (including their spatial distribution) of complex media: multiphase specimens, biological objects, thin films, layered and turbid media and structures. Increase in the resolving power and sensitivity of the method as compared with the amplitude variants of OA diagnostics.

2. New data on the behavior of matter in strong electromagnetic and acoustic fields obtained upon analyzing nonlinear-acoustic effects, light-induced chemical reactions, fast phase transitions under the action of laser radiation. Successful monitoring of technological processes in the electronics industry (crystallization, annealing, water treatment, etc.).

The results of the first group can be obtained by using relatively low-power laser pulses. On the contrary, the results of the second group are based on using pulses of high-power lasers, including state-of-the-art lasers.

Despite the evident advances, it will hardly be wrong to state that LDOA diagnostics is at the onset of its rise. Its further development involves a deeper study of the effects of OA conversion in the interaction of coherent optical radiation with matter. This interaction is nonlinear in nature. However, one could see that the nonlinear models and theories used to describe processes of OA conversion and substantiation of LDOA diagnostics "operate" quite satisfactorily at relatively moderate light intensities and bear important information on the parameters of the material.

Apparently further progress in LDOA diagnostics lies along the path of studying the role of nonequilibrium processes in laser OA conversion. Here the nontraditional "nonlinear-vibrational" approaches intrinsic to nonlinear wave dynamics may prove important. An example of such an approach that can have a direct relationship to progress in LDOA diagnostics can be the study of surface processes in laser macrokinetics. The latter includes the study of the thermal action of laser radiation on chemically active media. The beginning of these studies involves the discovery of *thermochemical instability* upon heating steels with the continuous radiation of a CO_2 laser and the corresponding theoretical calculations and models (see Ref. 99). The nontraditional nonlinear-vibrational approach characteristic of nonlinear wave dynamics has also proved very fruitful and most adequate for describing many varied phenomena in laser macrokinetics.[100] For example, it was found that a medium heated by laser radiation has a high tendency toward self-organization. Although in most cases the studies of self-organization phenomena were performed under conditions of action of continuous laser radiation on a chemically active, spatially inhomogeneous medium, while in this review we have spoken of LDOA diagnostics under conditions of action of laser pulses, nevertheless the information on the space-time characteristics of processes in laser macrokinetics and their association with processes of OA conversion are important ultimately from the standpoint of the progress of LDOA diagnostics. Study of this connection under various conditions of action of concrete optical radiation will allow creating new methods of LDOA diagnostics and using them for monitoring and further understanding of processes of laser macrokinetics, and this means, also for monitoring of varied laser technologies.

[1)] The narrower concept of OA diagnostics with high time resolution traditionally pertains to methods based on measuring the time of decay of the response in OA cells for gaseous specimens.

[2)] There is a group of studies whose authors characterize their field with the term "time-resolved LDOA diagnostics." However, in essence the topic is the stroboscopic observation of fast processes of OA interaction upon exciting sound with two successive nanosecond pulses and receiving the response with a relatively low-frequency piezoreceiver.[35,36]

[1]V. S. Letokhov, ed., *Laser Analytical Spectroscopy* (in Russian), Nauka, M., 1986.
[2]S. A. Akhmanov and N. I. Koroteev, *Methods of Nonlinear Optics in Light-scattering Spectroscopy* (in Russian), Nauka, M., 1981.
[3]S. A. Akhmanov, V. A. Vysloukh, and A. S. Chirkin, Usp. Fiz. Nauk **149**, 449 (1986) [Sov. Phys. Usp. **29**, 642 (1986)].
[4]V. P. Zharov and V. S. Letokhov, *Laser Optico-acoustic Spectroscopy* (in Russian), Nauka, M., 1984.
[5]A. C. Tam, Rev. Mod. Phys. **58**, 381 (1986).
[6]D. Hutchins and A. C. Tam, IEEE Trans. Ultrason. Ferroelectr. Frequency Control **33**, 429 (1986).
[7]A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy*, Wiley, New York, 1980.
[8]T. A. Dunina and S. V. Egerev, *Problems of Nonlinear Acoustodiagnostics* (in Russian), Valgus, Tallinn, 1986, p. 8
[9]B. S. H. Royce and J. B. Benziger, IEEE Trans. Ultrason. Ferroelectr. Frequency Control **33**, 561 (1986).
[10]H. Coufal, V. Möller, and S. Schnieder, Appl. Opt. **21**, 116 (1982).
[11]H. Coufal, V. Möller, and S. Schneider, *ibid.*, p. 2239.
[12]T. Zerlia, Appl. Spectrosc. **40**, 214 (1986).
[13]N. Teramae and S. Tanaka, *ibid.* **39**, 797 (1985).
[14]M. A. Olmstead, N. M. Amer, S. E. Kohn, D. Fournier, and C. Boccara, Appl. Phys. **32**, 141 (1983).
[15]B. Sullivan and A. C. Tam, J. Acoust. Soc. Am. **75**, 437 (1984).
[16]M. W. Sigrist, J. Appl. Phys. **60**, 83 (1986).
[17]W. P. Mason and R. N. Truston, Physical Acoustics, Vol. 14, ed. W. P. Mason, Academic Press, New York, 1979.
[18]O. B. Ovchinnokov, A. E. Pashin, O. V. Puchenkov, and D. A. Rastorguev, Akust. Zh. **33**, 312 (1987) [Sov. Phys. Acoust. **33**, 182 (1987)].
[19]I. A. Veselovskiĭ, L. M. Dorozhkin, *et al.*, *ibid.* p. 834 [Sov. Phys. Acoust. **33**, 483 (1987)].
[20]A. S. De Reggi, S. C. Roth, J. M. Kenney, S. Edelman, and G. R. Harris, J. Acoust. Soc. Am. **69**, 853 (1981).
[21]Y. Bar-Cohen, D. A. Stubbs, and W. C. Hoppe, *ibid.* **75**, 1034 (1984).
[22]P. A. Lewin, Ultrasonic. **19**, 213 (1981).
[23]V. N. Alekseev, S. V. Egerev, K. A. Naugol'nykh, O. B. Ovchinnikov, A. E. Pashin, O. V. Puchenkov, and V. N. Uchastnov, Akust. Zh. **33**, 961 (1987) [Sov. Phys. Acoust. **33**, 561 (1987)].

[24]L. M. Lyamshev and L. V. Sedov, *ibid.* **27**, 5 (1981) [Sov. Phys. Acoust. **27**, 4 (1981)].
[25]L. M. Lyamshev and K. A. Naugol'nykh, *ibid.*, p. 641 [Sov. Phys. Acoust. **27**, 357 (1981)].
[26]E. F. Carome, N. A. Clark, and C. E. Möeller, Appl. Phys. Lett. **4**, 95 (1964).
[27]L. M. Lyamshev and B. I. Chelnokov, Radiation Acoustics (in Russian), Nauka, M., 1987, p. 58.
[28]V. E. Chabanov, *Laser Ultrasonic Monitoring of Materials* (in Russian), Izd-vo Leningr. Un-ta. L., 1986.
[29]A. N. Bondarenko, Yu. B. Drobot, and S. V. Kruglov, Defektoskopiya, No. 6, 85 (1976) [Sov. J. Nondestr. Test. **12**, 655 (1976)].
[30]A. C. Tam, Appl. Phys. Lett. **45**, 510 (1984).
[31]A. C. Tam and G. Ayers, *Proc. of the 5th Intern. Topical Meeting on Photoacoustics and Photothermal Phenomena*, Heidelberg, FRG, 1987, p. 277.
[32]D. A. Hutchins, T. Nadeau, and P. Cielo, Can. J. Phys. **72**, 113 (1986).
[33]M. Rozen, H. N. G. Wadley, and K. Mehrabian, Scripta Metallurg. **15**, 1231 (1981).
[34]A. C. Tam and W. P. Leung, Appl. Phys. Lett. **45**, 1040 (1984).
[35]L. Rothberg, M. Bernstein, and K. Peters, J. Chem. Phys. **79**, 2569 (1983).
[36]J. M. Heritier and A. E. Siegman, IEEE J. Quantum Electron. **QE-19**, 821 (1983).
[37]S. V. Egerev, O. B. Ovchinnikov, A. E. Pashin, and O. V. Puchenkov, see Ref. 31, p. 331.
[38]A. A. Karabutov and O. B. Ovchinnikov, Sudostroit. Prom. Ser. "Akustika" **2**, 93 (1987).
[39]A. I. Vozhkov, F. V. Bunkin, A. M. Galstyan, and V. G. Mikhalevich, Akust. Zh. **28**, 321 (1982) [Sov. Phys. Acoust. **28**, 191 (1982)].
[40]G. M. Sessler and J. E. West, Phys. Rev. Lett. **48**, 563 (1982).
[41]A. Migliori and J. D. Thompson, J. Appl. Phys. **51**, 479 (1980).
[42]R. Gerhard-Multhaupt, Phys. Rev. B **27**, 2494 (1983).
[43]R. Gerhard-Multhaupt, G. M. Sessler, J. E. West, K. Holdik, M. Haardt, and W. Eisenmenger, J. Appl. Phys. **55**, 2769 (1984).
[44]A. A. Karabutov, O. V. Rudenko, and E. B. Cherepetskaya, Akust. Zh. **25**, 383 (1979) [Sov. Phys. Acoust. **25**, 218 (1979)].
[45]L. M. Lyamshev, Usp. Fiz. Nauk **135**, 637 (1981) [Sov. Phys. Usp. **24**, 977 (1981)].
[46]S. V. Egerev, K. A. Naugol'nykh, L. A. Ostrovskiĭ, A. E. Pashin, A. M. Sutin, and V. N. Uchastnov, Akust. Zh. **32**, 172 (1986) [Sov. Phys. Acoust. **32**, 103 (1986)].
[47]S. V. Egerev, K. A. Naugol'nykh, A. E. Pashin, and V. N. Uchastnov, *ibid.*, **30**, 310 (1984) [Sov. Phys. Acoust. **30**, 182 (1984)].
[48]L. R. Gavrilov, in *Physical Foundations of Ultrasonic Technology* (in Russian), ed. L. D. Rozenberg, Nauka, M., 1970.
[49]A. F. Verlan' and V. S. Sizikov, Integral Equations (in Russian), Naukova Dumka, Kiev, 1986.
[50]A. N. Tikhonov and V. Ya. Arsenin, *Solution of Ill-Posed Problems*, Winston, Washington, D.C., 1977 (Russ. transl., Nauka, M., 1979).
[51]V. P. Glotov, P. A. Kolobaev, and G. G. Neuĭmin, Akust. Zh. **7**, 421 (1961) [Sov. Phys. Acoust. **7**, 341 (1962)].
[52]M. Itoh and H. Saito, Opt. Commun. **44**, 229 (1983).
[53]H. M. Lai and K. Young, J. Acoust. Soc. Am. **72**, 2000 (1982).
[54]P. Heritier, Opt. Commun. **44**, 267 (1983).
[55]D. Ronis, Phys. Rev. A **29**, 2125 (1984).
[56]S. V. Egerev and O. V. Puchenkov, Akust. Zh. **32**, 50 (1986) [Sov. Phys. Acoust. **32**, 30 (1986)].
[57]A. C. Tam and C. K. N. Patel, Rev. Mod. Phys. **53**, 517 (1981).
[58]S. D. Hunter, W. V. Jones, and D. J. Malbrough, J. Acoust. Soc. Am. **69**, 1563 (1981).
[59]T. A. Dunina, S. V. Egerev, L. M. Lyamshev, and K. A. Naugol'nykh, Akust. Zh. **25**, 60 (1979) [Sov. Phys. Acoust. **25**, 32 (1979)].
[60]T. A. Dunina, S. V. Egerev, and K. A. Naugol'nykh, Pis'ma Zh. Tekh. Fiz. **9**, 410 (1983) [Sov. Tech. Phys. Lett. **9**, 176 (1983)].
[61]A. D. Pierce, J. Acoust. Soc. Am., Suppl. 1, **72**, 513 (1982).
[62]A. A. Karabutov, Usp. Fiz. Nauk **147**, 605 (1985) [Sov. Phys. Usp. **28**, 1042 (1985)].
[63]S. Malkin and D. Cahen, Photochem. Photobiol. **29**, 803 (1979).
[64]J. La Grande, D. Cahen, and S. Caplan, Biophys. J. **37**, 4 (1982).
[65]L. J. Rothberg, J. D. Simon, M. Bernstein, and K. Peters, J. Am. Chem. Soc. **105**, 3464 (1983).
[66]M. Bernstein, J. D. Simon, and K. S. Peters, Chem. Phys. Lett. **100**, 241 (1983).
[67]C.-Y. Kuo, M. M. F. Vieira, C. K. N. Patel, J. Appl. Phys. **55**, 3333 (1984).
[68]K. Heihoff and S. Braslavsky, in *Photoacoustic and Photothermal Phenomena*, eds. P. Hess and J. Pelzl, Springer-Verlag, Berlin a. o., 1988, p. 105.
[69]O. Yu. Nikiforov, Yu. N. Ponomarev, and B. A. Tikhomirov, Izv. Vyssh. Uchebn. Zaved. Fiz. **28**, (3), 37 (1985) [Sov. Phys. J. **28**, 208 (1985)].
[70]M. Yoshimura, see Ref. 31, p. 30.
[71]R. Redmond and S. Braslavsky, *ibid.*, p. 26.
[72]K. M. Beck, A. Ringlevsky, and R. J. Gordon, Chem. Phys. Lett. **121**, 529 (1985).
[73]C. E. Bell and J. A. Landt, Appl. Phys. Lett. **10**, 46 (1967).
[74]T. Kitamori and K. Suzuki, see Ref. 31, p. 180.
[75]A. Vogel and W. Lauterborn, J. Acoust. Soc. Am. **4**, 719 (1988).
[76]T. A. Dunina, S. V. Egerev, *et al.*, in *Problems of Nonlinear Acoustics*, Nauka, Novosibirsk, 1987, Part 1, p. 447.
[77]G. D. Hickman and J. R. Edmonds, J. Acoust. Soc. Am. **73**, 840 (1983).
[78]K. Brakner and S. Dzhorna, *Controlled Thermonuclear Fusion* (in Russian), Nauka, M., 1977.
[79]C. E. Yeack, Appl. Phys. Lett. **41**, 1043 (1982).
[80]G. Gorodetsky, T. G. Kazyaka, R. L. Melchev, and R. Srinivasan, *ibid.* **46**, 828 (1985).
[81]P. E. Dyer and R. Srinivasan, *ibid.* **48**, 445 (1986).
[82]F. W. Cross, R. K. Al-Dhahir, P. E. Dyer, and A. J. MacRobert, *ibid.* **50**, 1019 (1987).
[83]S. A. Akhmanov, V. I. Emel'yanov, N. I. Koroteev, and V. N. Seminogov, Usp. Fiz. Nauk. **147**, 675 (1985) [Sov. Phys. Usp. **28**, 1084 (1985)].
[84]S. N. Avanesyan and V. E. Gusev, Appl. Phys. Ser. A **40**, 163 (1986).
[85]Yu. V. Gulyaev, G. N. Shkerdin, and B. B. Elenkrig, Pis'ma Zh. Tekh. Fiz. **6**, 924 (1980) [Sov. Tech. Phys. Lett. **6**, 400 (1980)].
[86]A. P. Zdebskiĭ, Akust. Zh. **35**, 1116 (1989) [Sov. Phys. Acoust. **35**, 651 (1989)].
[87]A. Lietoila and J. F. Gibbons, Appl. Phys. Lett. **34**, 332 (1979).
[88]N. Baltzer, M. von Allmen, and M. W. Sigrist, *ibid.* **43**, 826 (1983).
[89]I. A. Veselovskiĭ, B. M. Zhiryakov, *et al.*, Kvantovaya Elektron. (Moscow) **12**, 381 (1985) [Sov. J. Quantum Electron. **15**, 246 (1985)].
[90]G. A. Askar'yan, A. M. Prokhorov, G. F. Chanturiya, and G. P. Shipulo, Zh. Eksp. Teor. Fiz. **44**, 2180 (1963) [Sov. Phys. JETP **17**, 1463 (1963)].
[91]D. C. Emmony and M. B. Geerken, Infrared Phys. **16**, No. 1/2, 87 (1976).
[92]S. V. Egerev and A. E. Pashin, Zh. Tekh. Fiz. **51**, 226 (1981) [Sov. Phys. Tech. Phys. **26**, 138 (1981)].
[93]V. V. Zosimov, M. Yu. Kukushkin, *et al.*, Zh. Prikl. Mekh. Tekh. Fiz. **5**, 33 (1989) [J. Appl. Mech. Tech. Fiz. (1989)].
[94]V. V. Zosimov, K. A. Naugol'nykh, and O. V. Puchenkov, *Abstracts of the 4th All-Union Symposium on the Physics of Acousto-Hydrodynamic Phenomena in Optoacoustics*, Izd-vo AN TSSR, Ashkhabad, 1985, p. 31.
[95]S. V. Egerev, L. M. Lyamshev, and O. V. Puchenkov, *Proc. 13th International Congress on Acoustics*, Beograd, 1989, p. 30.
[96]E. H. Lucassen-Reynders and J. Lucassen, Adv. Colloid Interface Sci. **2**, 347 (1970).
[97]M. Tempel and E. H. Lucassen-Reynders, *ibid.* **18**, 281 (1983).
[98]R. S. Hansen and I. Ahmad, in *Progress in Surface and Membrane Science*, Vol. 4, eds. I. F. Danielli, M. D. Rosenberg, and D. A. Cadenhead, Academic Press, N.Y., 1971.
[99]A. M. Bonch-Bruevich and M. I. Libenson, Izv. Akad. Nauk SSSR Ser. Fiz. **46**, 1104 (1982) [Bull. Acad. Sci. USSR Phys. Ser. **46**, (6), 82 (1982)].
[100]F. V. Bunkin, N. A. Kirichenko, and B. S. Lun'yanchuk, Kvantovaya Elektron. (Moscow) **7**, 2658 (1980) [Sov. J. Quantum Electron. **10**, 1560 (1980)].

Translated by M. V. King