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Theory of Second Harmonic Thermal-Wave Generation: One-Dimensional Geometry

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The analysis of the thermal-wave second harmonic generation induced by the time-modulated heating of the material with temperature-dependent heat capacity $C(T)$ and thermal conductivity $k(T)$ is presented. The developed theory describes nonmonotonic behavior of the second harmonic amplitude in a semi-infinite medium. An enhanced spatial resolution of nonlinear photothermal imaging in materials with dominant role of the $k(T)$ temperature dependence (i.e., for $|(1/k)(\partial k/\partial T)| \gg |(1/C)(\partial C/\partial T)|$ is predicted.

KEY WORDS: modulated heating; photothermal imaging; second-harmonic generation; thermal wave.

1. INTRODUCTION

Over the past few years, various detection techniques [1–3] have been applied to the investigation of nonlinear phenomena in photothermal imaging. The results of the experiments [1–3] revealed the possibility of obtaining higher contrast by second harmonic detection than with the image at the fundamental frequency. These experimental facts stimulated interest in the theoretical examination of the second harmonic generation processes in thermal wave physics.

The origin of the second harmonic excitations lies in the dependence of the thermophysical parameters of materials on temperature T [1]. Reference 1 gives, however, only a qualitative description of signal generation at 2ω, where ω is the fundamental thermal-wave angular frequency

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caused by thermal conductivity variations $k=k(T)$. In Ref. 2 a model of nonlinear boundary thermal resistance has been developed. An attempt has already been made [4] to take into account bulk thermal nonlinearities, that is, the dependences of thermal conductivity k and heat capacity C on temperature not only at the interfaces, but also in the semiinfinite domain in which thermal waves are generated and propagate. The main conclusion concerning the increased depth resolution of the nonlinear photothermal microscope [4] is physically right. Nevertheless, the inexact formulation of the basic heat conduction equation used for the theoretical analysis renders the results of Ref. 4 not very useful in practice. The formulas derived therein cannot be used for the exact evaluation at the amplitude and phase at 2ω or, most importantly, for deriving their spatial distributions.

In this paper, we reexamine the second harmonic generation problem in semiinfinite half-spaces, with emphasis on the physical fundamentals of frequency mixing of highly damped waves. In particular, we present in detail the description of the 2ω temperature field distribution in space.

2. MATHEMATICAL FORMALISM

We start from the conventional form of the heat conduction equation in a medium with nonconstant thermophysical parameters [5, 6]:

$$C\frac{\partial T}{\partial t}-\nabla\cdot(k\nabla T)=Q(\mathbf{r},t) \tag{1}$$

Here Q is the external heat source input per unit volume $C=\rho c_p$, where ρ is the material density and c_p is the heat capacity per unit mass at constant pressure. The particular form of Eq. (1) has neglected the coupling between thermal and acoustic waves, i.e., the thermal conductivity k is considered to be subsonic. Note that Eq. (1) differs from that used in Ref. 4, as we have considered the thermal energy per unit volume to be $\int^T C dT$ and not CT [4]. The boundary conditions at the interface S of adjacent materials are those of the continuity of heat flux and temperature:

$$k\frac{\partial T}{\partial n}\bigg|_{-0}^{+0}=0, \qquad T\,|_{-0}^{+0}=0 \tag{2}$$

where the coordinates ± 0 denote the values of physical quantities at opposite sides of the interface, while n is the unit normal to the interface.

Let us suppose that external heating initiates an increase in temperature T_1, relative to its initial value T_0,

$$T=T_0+T_1, \qquad T_0=\text{const.} \tag{3}$$

and that linear relationships

$$C(T) \simeq C(T_0) + \left[\frac{\partial C}{\partial T}(T_0)\right] T_1 \equiv C_0(1 + \delta_1 T_1) \tag{4a}$$

$$k(T) \simeq k(T_0) + \left[\frac{\partial k}{\partial T}(T_0)\right] T_1 \equiv k_0(1 + \delta_2 T_1) \tag{4b}$$

adequately describe the behavior of heat capacity and thermal conductivity in the temperature interval of interest. Under the conditions of Eqs. (3) and (4), the problem described by Eqs. (1) and (2) transforms to

$$\left(\nabla^2 - \frac{1}{D_0}\frac{\partial}{\partial t}\right) T_1 = -\frac{1}{k_0} Q(\mathbf{r}, t) - \frac{1}{2}\left(\delta_2 \nabla^2 - \frac{\delta_1}{D_0}\frac{\partial}{\partial t}\right) T_1^2 \tag{5a}$$

with

$$k_0 \frac{\partial}{\partial n}\left(T_1 + \frac{1}{2}\delta_2 T_1^2\right)\bigg|_{-0}^{+0} = 0, \qquad T_1|_{-0}^{+0} = 0 \tag{5b}$$

where $D_0 = k_0/C_0$ is the thermal diffusivity. Note that both dependences $C = C(T)$ and $k = k(T)$ contribute to nonlinear terms in the heat conduction equation, whereas only $k = k(T)$ contributes to the nonlinearity in the boundary conditions.

It can be readily seen that for

$$|\delta_1 T_1| \ll 1, \qquad |\delta_2 T_1| \ll 1 \tag{6}$$

the problem of Eq. (5) can be examined by a stepwise successive approximation method. As a first step one can neglect the nonlinear terms associated with T_1^2 in Eq. (5a):

$$\left(\nabla^2 - \frac{1}{D_0}\frac{\partial}{\partial t}\right) T_1 = -\frac{1}{k_0} Q(\mathbf{r}, t) \tag{7a}$$

with

$$k_0 \frac{\partial}{\partial n} T_1 \bigg|_{-0}^{+0} = 0, \qquad T_1|_{-0}^{+0} = 0 \tag{7b}$$

If the external forces are harmonicaly modulated at angular frequency ω,

$$Q(\mathbf{r}, t) = Q_0(\mathbf{r}) + Q_\omega(\mathbf{r}, t) \tag{8a}$$

$$Q(\mathbf{r}, t) = Q_0(\mathbf{r}) + Q_\omega(\mathbf{r}, t) \tag{8b}$$

then in the linear problem, Eq. (7), the contribution of the oscillating (T_ω) temperature field and of that averaged over the fundamental modulation period ($T_{01} < \langle T_1 \rangle$) may be separated out:

$$\left(\nabla^2 - \frac{1}{D_0}\frac{\partial}{\partial t}\right) T_{01} = -\frac{1}{k_0} Q_0(\mathbf{r}) \tag{9a}$$

with

$$k_0 \frac{\partial}{\partial n} T_{01}\bigg|_{-0}^{+0} = 0, \qquad T_{01}|_{-0}^{+0} = 0 \tag{9b}$$

and

$$\left(\nabla^2 - \frac{1}{D_0}\frac{\partial}{\partial t}\right) T_\omega = -\frac{1}{k_0} Q_\omega(\mathbf{r}, t) \tag{10a}$$

$$k_0 \frac{\partial}{\partial n} T_\omega\bigg|_{-0}^{+0} = 0, \qquad T_\omega|_{-0}^{+0} = 0 \tag{10b}$$

Note that $Q_0(\mathbf{r}) = \langle Q(\mathbf{r}, t) \rangle$. In the case of monochromatic optical excitation, the condition for thermal and acoustic decoupling is

$$\omega \ll \omega_D \equiv v^2/D_0 \tag{11}$$

where v is the velocity of sound and ω_D is the characteristic frequency at which the thermal and acoustic wavenumbers become equal.

As a second step, it is necessary to substitute the solution $T_1 = T_{01} + T_\omega$ of Eqs. (9) and (10) into the nonlinear terms of Eq. (5a), that is, to consider $T_1^2 = T_{01}^2 + 2T_{01}T_\omega + T_\omega^2$. In the first approximation, the temperature field consists of the quasi-stationary (dc) part ($\omega = 0$) and the part oscillating at angular frequency ω. The quadratic nonlinearity in Eq. (5a) will then be given by the frequency mixing contributions to the averaged field ($0 + 0 \to 0$, $\omega - \omega \to 0$) and to the fundamental frequency ($0 \pm \omega \to \pm\omega$). It will also induce the generation of the second harmonic ($\omega + \omega \to 2\omega$).[4] The description of the latter process may be separated out:

$$\left(\nabla^2 - \frac{1}{D_0}\frac{\partial}{\partial t}\right) T_{2\omega} = -\frac{1}{2}\left(\delta_2 \nabla^2 - \delta_1 \frac{1}{D_0}\frac{\partial}{\partial t}\right)(T_\omega^2 - \langle T_\omega^2 \rangle) \tag{12a}$$

[4] If the temperature dependences of $C(T)$ and/or $k(T)$ are considerably nonlinear around $T \simeq T_0$, then higher than second harmonics will appear in the system even in the second approximation. This can be illustrated in the case $(\partial C/\partial T)(T_0) = 0$ and/or $(\partial k/\partial T)(T_0) = 0$, where the $(\partial^2 C/\partial T^2)(T_0) \neq 0$ and/or $\partial^2 k/\partial T^2(T_0) \neq 0$ may introduce third harmonic generation.

with

$$k_0 \frac{\partial}{\partial n}\left[T_{2\omega} + \frac{1}{2}\ \delta_2(T_\omega^2 - \langle T_\omega^2 \rangle)\right]\Bigg|_{-0}^{+0} = 0, \qquad T_{2\omega}|_{-0}^{+0} = 0 \tag{12b}$$

Note that in the above approximations the second harmonic temperature field $T_{2\omega}$ is not related to the average field T_{01}. Therefore, the calculation of the averaged field T_{01} in Eq. (9) may be omitted. It should be solved only for the purpose of estimating the limits of validity of conditions (6) in the stepwise approximation for every concrete situation.

Without loss of generality, one can assume that $Q_\omega(\mathbf{r}, t)$ has the form $Q_\omega(\mathbf{r}) \cos \omega t$. Then the solutions of the linear problems of Eqs. (10) and (12) can be presented as

$$T_\omega = \mathrm{Re}(\tilde{T}_\omega e^{-i\omega t}) \tag{13a}$$

$$R_{2\omega} = \mathrm{Re}(\tilde{T}_{2\omega} e^{-2i\omega t}) \tag{13b}$$

The following equations are valid for the complex amplitudes $\tilde{T}_\omega$ and $\tilde{T}_{2\omega}$ of the harmonics:

$$(\nabla^2 - p^2)\tilde{T}_\omega = -\frac{1}{k_0} Q_\omega \tag{14a}$$

with

$$k_0 \frac{\partial}{\partial n} \tilde{T}_\omega \Bigg|_{-0}^{+0} = 0, \qquad \tilde{T}_\omega|_{-0}^{+0} = 0 \tag{14b}$$

and

$$(\nabla^2 - 2p^2)\tilde{T}_{2\omega} = -\tfrac{1}{4}(\delta_2 \nabla^2 - \delta_1 2p^2)\tilde{T}_\omega^2 \tag{15a}$$

with

$$k_0 \frac{\partial}{\partial n}\left(\tilde{T}_{2\omega} + \frac{1}{4}\delta_2 \tilde{T}_\omega^2\right)\Bigg|_{-0}^{+0} = 0, \qquad \tilde{T}_{2\omega}|_{-0}^{+0} = 0 \tag{15b}$$

where $\rho = \sqrt{-i(\omega/D_0)}$ $(\mathrm{Re}\, p > 0)$ is the complex wavenumber of the thermal wave at the fundamental frequency; $p = (1 - i)q$ with the real wavenumber $q = \sqrt{\omega/2D_0}$ being the inverse of the thermal wave penetration depth $\mu_q = 1/q$, otherwise known as the thermal diffusion length. The derived boundary value problem, Eq. (15), forms the theoretical basis for the description of the 2ω temperature field.

Let us examine a semiinfinite opaque sample ($z \geqslant 0$) heated by surface absorption of laser radiation. Then in the one-dimensional approximation, Eq. (14) transforms to

$$\left(\frac{d^2}{dz^2} - p^2\right) \tilde{T}_\omega = 0 \tag{16a}$$

with

$$k_0 \frac{d}{dz} \tilde{T}_\omega \bigg|_{z=0} = -I_\omega \tag{16b}$$

where I_ω is the magnitude of the modulated part of the absorbed laser intensity. With the additional condition $\tilde{T}_\omega(z \to \infty) \to 0$, Eq. (16) has the well-known solution:

$$\tilde{T}_\omega = \frac{I_\omega}{k_0} \frac{1}{p} e^{-pz} \tag{17}$$

Combining Eqs. (17) and (13a), one may obtain a complete description of the thermal wave, i.e., its amplitude A and phase ϕ at the fundamental frequency

$$T_\omega = \left(\frac{I_\omega}{k_0}\right) \frac{1}{\sqrt{2}q} e^{-qz} \cos\left(\omega t - qz - \frac{\pi}{4}\right) \tag{18a}$$

with

$$A_\omega = \left(\frac{I_\omega}{k_0}\right) \frac{1}{\sqrt{2}q} e^{-qz}, \qquad \phi_\omega = -\frac{\pi}{4} - qz \tag{18b}$$

Note that both A_ω and ϕ_ω vary monotonically with depth. Characteristic space scale for these variations is the thermal diffusion length μ_q.

Substitution of Eq. (17) into Eq. (15) leads to

$$\left(\frac{d^2}{dz^2} - 2p^2\right) \tilde{T}_{2\omega} = \frac{1}{2} (\delta_1 - 2\delta_2) \left(\frac{I_\omega}{K_0}\right)^2 e^{-2pz} \tag{19a}$$

subject to the boundary condition

$$\frac{d}{dz} \tilde{T}_{2\omega} \bigg|_{z=0} = \frac{1}{2} \delta_2 \left(\frac{I_\omega}{k_0}\right)^2 \frac{1}{p} \tag{19b}$$

It can be seen that bulk and surface sources of $\tilde{T}_{2\omega}$ on the right-hand side of Eqs. (19a) and (19b) depend on different combinations of δ_1 and δ_2. This fact initiates nontrivial interference phenomena in the second harmonic generation process. Before proceeding to the solution of Eqs. (19), we will briefly discuss one more potential mechanism for thermal wave second harmonic generation in the physical system under consideration. In the case of laser-induced heating, the sources $Q(\mathbf{r}, t)$ depend not only on the harmonically modulated laser intensity $I(\mathbf{r}, t)$ but also on material parameters characterizing the interaction of light with matter. In the simplest situation of linear absorption of laser radiation

$$Q(\mathbf{r}, t) = (1 - R)\, \alpha I(\mathbf{r}, t) \tag{20}$$

where R is the reflection coefficient of light at the irradiated surface and α is the optical absorption coefficient. If one takes into account the possible dependence of R and α on temperature

$$1 - R(T) \simeq 1 - R(T_0) + \left[\frac{\partial R}{\partial T}(T_0)\right] T_1 \equiv (1 - R_0)(1 + \delta_3 T_1),\ |\delta_3 T_1| \ll 1 \tag{21}$$

and

$$\alpha(T) \simeq \alpha(T_0) + \left[\frac{\partial \alpha}{\partial T}(T_0)\right] T_1 \equiv \alpha_0(1 - \delta_4 T_1),\ |\delta_4 T_1| \ll 1 \tag{22}$$

These dependences will induce the additional source of the thermal wave second harmonic:

$$-\frac{(1 - R_0)\alpha_0}{k_0}\{\delta_3[T_\omega(0)I - \langle T_\omega(0)I\rangle] + \delta_4[T_\omega I - \langle T_\omega I\rangle]\} \tag{23}$$

in the right-hand side of Eq. (12a). Here $T_\omega(0)$ denotes the fundamental frequency temperature component at the irradiated surface. Assuming $I = I_0(1 + \cos \omega t)$ one will also obtain the additional term

$$-[(1 - R_0)\alpha_0 I_0/2k_0][\delta_3 \tilde{T}_\omega(0) + \delta_4 \tilde{T}_\omega] \tag{24}$$

in the right-hand side of Eq. (15a). The action of the nonlinearity associated with the dependence of the optical absorption coefficient on temperature has been experimentally investigated [7]. In the case of surface absorption of the laser radiation, the corresponding second harmonic sources should be taken into account in the boundary conditions at the irradiated surface. The additional term in the right-hand side of Eq. (19b) may be presented in the form $(-\delta_3/2) \times (I_\omega/k_0)^2(1/p)$. For the sake of compactness, in the following, we neglect this nonlinearity assuming $\delta_3=0$. The role of the nonlinearity associated with the reflectivity dependence on temperature can be exactly described by the simple substitution $\delta_2 \to \delta_2-\delta_3$ and $\delta_1 \to \delta_1-2\delta_3$ in the solutions obtained below, starting from Eq. (25).

The solution of Eq. (19) diminishing to zero as $z \to \infty$ has the form

$$\tilde{T}_{2\omega}=\left(\frac{I_\omega}{k_0}\right)^2 \frac{1}{2\sqrt{2}\,p^2}\left[(\delta_2-\delta_1)e^{-\sqrt{2}pz}+\frac{1}{\sqrt{2}}(\delta_1-2\delta_2)e^{-2pz}\right] \quad (25)$$

According to Eq. (13b), the first term satisfies the dispersion relation of the thermal waves in the system considered: $p(2\omega)=\sqrt{-i(2\omega)/D_0}$. For this reason it has been denoted the "free-propagating wave." The second term in Eq. (25) is not subject to the dispersion relation, as $2p(\omega)\neq p(2\omega)$. Both the frequency and the spatial periodicity of this term are controlled by the field of the sources. Therefore, this component has been named the "forced wave." The solution, Eq. (25), consists of the free-propagating second harmonic thermal-wave term with a complex wavenumber, $p(2\omega)=\sqrt{2}\,p(\omega)$, and of the forced second harmonic wave with a wavenumber equal to $2p(\omega)$. The relative amplitudes of these contributions to $\tilde{T}_{2\omega}$ depend on the values of δ_1 and δ_2. For example, the forced mode disappears if $(\delta_1/\delta_2)=2$, when in accordance with Eq. (19a), there are no bulk sources of the second harmonic. The free-propagating mode disappears for $(\delta_1/\delta_2)=1$ as a result of compensation of the 2ω-waves excited in the bulk and at the surface of the material.

In the general case $(\delta_1/\delta_2)\neq 1, 2$ the solution, Eqs. (13) and (25), describes interference of free-propagating and forced 2ω-thermal waves:

$$T_{2\omega}(z,t)=A_{2\omega}(z)\cos(2\omega t+\phi_{2\omega}) \quad (26a)$$

where

$$A_{2\omega}(z)=\left(\frac{I_\omega}{k_0}\right)^2 \frac{1}{4\sqrt{2}q^2}\,e^{-\sqrt{2}qz}[(\delta_1-\delta_2)^2 - \sqrt{2}(\delta_1-\delta_2)(\delta_1-2\delta_2)e^{-\Delta qz}\cos(\Delta qz)+\frac{1}{2}(\delta_1-2\delta_2)^2 e^{-2\Delta qz}]^{1/2} \quad (26b)$$

and

$$\phi_{2\omega}=-\pi-\sqrt{2}qz-\frac{\pi}{2}\,\mathrm{sgn}\left[(\delta_1-\delta_2)-\frac{1}{\sqrt{2}}(\delta_1-2\delta_2)e^{-\Delta qz}\cos(\Delta qz)\right] + \tan^{-1}\left[\frac{(\delta_1-2\delta_2)e^{-\Delta qz}\sin(\Delta qz)}{\sqrt{2}(\delta_1-\delta_2)-(\delta_1-2\delta_2)e^{-\Delta qz}\cos(\Delta qz)}\right] \quad (26c)$$

In Eqs. (26b) and (26c) we have highlighted the dependence on Δq, which describes the influence of interference, caused by the difference in the wavenumbers of forced and free-propagating 2ω-waves:

$$\Delta q \equiv 2q(\omega) - q(2\omega) - q(2\omega) = \sqrt{2}(\sqrt{2} - 1)\, q(\omega) \tag{27}$$

3. DISCUSSION

The following important results may be obtained through the analysis of the second-harmonic thermal-wave field, Eq. (26).

1. The amplitude of the 2ω-wave at the irradiated surface can be expressed as

$$A_{2\omega}(0) = \frac{1}{8} \frac{|\delta_1 + \sqrt{2}\,\delta_2|}{1 + \sqrt{2}} \left(\frac{I_\omega}{k_0}\right)^2 \frac{1}{q^2} \tag{28}$$

Now one can introduce the nonlinear parameter N characterizing the efficiency of the 2ω-generation process at the surface, relative to the amplitude of the fundamental thermal wave,

$$N \equiv \frac{A_{2\omega}(0)}{A_\omega^2(0)} = \frac{1}{4} \frac{|\delta_1 + \sqrt{2}\delta_2|}{1 + \sqrt{2}} \tag{29}$$

which can be useful for estimates of nonlinear effects. From our very rough estimates at room temperature, $N \sim 10^{-5}\ \mathrm{K}^{-1}$ in such simple metals as Au, Ag, and Cu; $N \sim 10^{-4}$ in graphite and Fe; and $N \sim 5 \times 10^{-3}$ in Si and Ge [8]. In the above-mentioned materials $\delta_2 < 0$ while $\delta_1 > 0$. In some steels and alloys, $\delta_2 > 0$ even at room temperature [8]. For instance, note that $A_{2\omega} \propto I_\omega^2$, in agreement with earlier experimental evidence [1], and that in the 1-D geometry under consideration $A_{2\omega}$ $(z = 0) \propto 1/\omega$. It can also be shown that the 2ω-temperature field may vanish but only at the surface $z = 0$ and only for $\delta_1/\delta_2 = (\delta_1/\delta_2)_{\mathrm{cr}} \equiv -\sqrt{2}$.

2. It is evident that in the latter case $(\delta_1/\delta_2 = -\sqrt{2})$, the maximum of the 2ω-temperature distribution is localized under the surface. To examine the spatial distribution of the $A_{2\omega}(z)$ in the general case, it is convenient to examine the Taylor expansion of Eq. (26b) near the surface, i.e., for $qz \ll 1$.

$$\frac{A_{2\omega}(qz \ll 1)}{A_{2\omega}(z = 0)} \simeq \sqrt{\left[\frac{2\sqrt{2}(1 + \sqrt{2})\delta_2}{\delta_1 + \sqrt{2}\delta_2}(qz) - \frac{1}{\sqrt{2}}\right]^2 + \frac{1}{2}} \tag{30}$$

The requirement for positive slope of Eq. (30) yields the *sufficient* condition for achieving the $A_{2\omega}$ maximum under the surface $\{$with $(d/dz)[A_{2\omega}(z)]|_{z=0}$

$>0\}\,\delta_1/\delta_2<-\sqrt{2}$. This, however, is not a *necessary* condition for a subsurface second-harmonic temperature maximum, nor can it be used to locate its position. Equation (30) only describes a local (i.e., not absolute) 2ω-temperature minimum at

$$(qz)_{\min}=\frac{1}{4}\frac{(\delta_1/\delta_2)+\sqrt{2}}{1+\sqrt{2}} \tag{31}$$

The absolute minimum (i.e., zero) can be determined only from the exact equation, Eq. (26b), for the second-harmonic amplitude, as a result of its boundedness as $z\to\infty$. Therefore, if $0<(\delta_1/\delta_2)+\sqrt{2}\ll 1$, the present theory predicts the local temperature minimum $A_{2\omega}(z_{\min})=A_{2\omega}(0)/\sqrt{2}$ underneath the irradiated opaque surface and at a distance much smaller than the thermal diffusion length.

3. The phase of the 2ω-wave at the irradiated surface can be expressed as

$$\phi_{2\omega}(0)=\frac{\pi}{2}\,sgn(\delta_1+\sqrt{2}\,\delta_2) \tag{32}$$

$\phi_{2\omega}$ differs from the phase of the fundamental wave. This conclusion is also supported by the experimental results presented in Ref. 2. Note that in deriving Eq. (32) from Eq. (26c), we have taken into account the impossibility of distinguishing, in practice, between the phase $\phi_{2\omega}$ and the phase $\phi_{2\omega}\pm 2\pi$.

4. For the analysis of the phase spatial distribution of the second harmonic, it is convenient to separate out in the expression Eq. (26c) the phase of the free-propagating component

$$\phi_{2\omega}=\phi_{2\omega}\,|_{\delta_1/\delta_2=2}+\Delta\phi_{2\omega} \tag{33}$$

where $\phi_{2\omega}(\delta_1=2\delta_2)=(\pi/2)\,sgn(\delta_1-\delta_2)-\sqrt{2}qz$ is a linear function of the distance from the surface. The phase $\phi_{2\omega}$ $(\delta_1=2\delta_2)$ of the free-propagating mode varies significantly only at distances on the order of the diffusion length μ_q. All the effects caused by the interference of free and forced waves are contained in the remainder of Eq. (33), which depends on $(\Delta q)z$:

$$\begin{aligned}\Delta\phi_{2\omega}=&\frac{\pi}{2}-\frac{\pi}{2}\,sgn(1-ae^{-(\Delta q)z}\cos[(\Delta q)z])\\&+\tan^{-1}\left(\frac{ae^{-(\Delta q)z}\sin[(\Delta q)z]}{1-ae^{-(\Delta q)z}\cos[(\Delta q)z]}\right)\end{aligned} \tag{34}$$

with

$$a \equiv \frac{1}{\sqrt{2}} \frac{(\delta_1 - 2\delta_2)}{(\delta_1 - \delta_2)} \tag{35}$$

According to Eq. (34) in the quasi-critical regimes $(0 < \delta_1/\delta_2 + \sqrt{2} \ll 1)$, significant phase shifts of the order of $\pi/2$ take place just beneath the surface. This follows from the observation that, for these values of the parameter δ_1/δ_2, the argument of the $\tan^{-1}$ in Eq. (34) may be represented in the form $[(z/z_\phi) - 1]^{-1} \to \pm\infty$ as $z \to z_\phi \pm 0$, where

$$(qz)_\phi \simeq \frac{\sqrt{2}-1}{\sqrt{2}} \frac{(\delta_1/\delta_2 + \sqrt{2})}{1+\sqrt{2}} \ll 1 \tag{36}$$

Note that $(qz)_\phi \sim (qz)_{\min}$. So the proposed analytical description predicts steep phase variations at distances much shorter than the thermal wave penetration length in nonlinear materials.

All the above-mentioned peculiarities of the $A_{2\omega}$ and $\phi_{2\omega}$ spatial distribution are confirmed by the normalized plots of the amplitude $A_{2\omega}(qz)$ and the additional phase shift $\Delta\phi_{2\omega}(qz)$, presented in Figs. 1–3 for various values of the parameter δ_1/δ_2.

In Fig. 1a, curve 1 represents the spatial distribution of a second harmonic amplitude typical of simple metals. For simple metals $\delta_1/\delta_2 = -1$ over wide temperature ranges. For example, $\delta_1/\delta_2 = -1$ in Al for $0 \leqslant T \leqslant 500°C$; in Zn for $-50°C \leqslant T \leqslant 350°C$; in Cu for $0 \leqslant T \leqslant 10^3\,°C$, etc. [6]. One can readily see that there exists a local temperature minimum very close to the surface $(z_{\min} \simeq 5 \times 10^{-2} \mu_q \ll \mu_q)$, while the absolute 2ω-temperature maximum occurs much deeper into the bulk $(z_{\max} \simeq 0.6\mu_q \sim \mu_q)$. Correspondingly, curve 1 in Fig. 1b presents evidence of significant changes of the 2ω-temperature field phase in simple metals just beneath the irradiated surface.

Curve 2 in Fig. 1a represents the $A_{2\omega}$ distribution for materials with dominant nonlinearity associated with the temperature dependence of the thermal conductivity $(|\delta_2| \gg |\delta_1|)$. This situation is rather typical of semiconductors [8]. The amplitude decreases by a factor of two within a distance $\sim 0.2\,\mu_q$ from the surface, that is, even faster than the amplitude of the forced wave. This feature is shown upon comparison of curves 2 and 3 in Fig. 1a, the latter one representing the purely forced wave $(\delta_1/\delta_2 = 1)$. Therefore, in this special case, typical of semiconductors, one can expect even better spatial resolution of a nonlinear photothermal microscope than that predicted by the earlier theory [4]. This conclusion is further supported by steeper phase variations in the case $|\delta_1/\delta_2| \ll 1$ than in the forced wave $(\delta_1/\delta_2 = 1)$ as can be seen by comparison of the curves 2 and 3 in

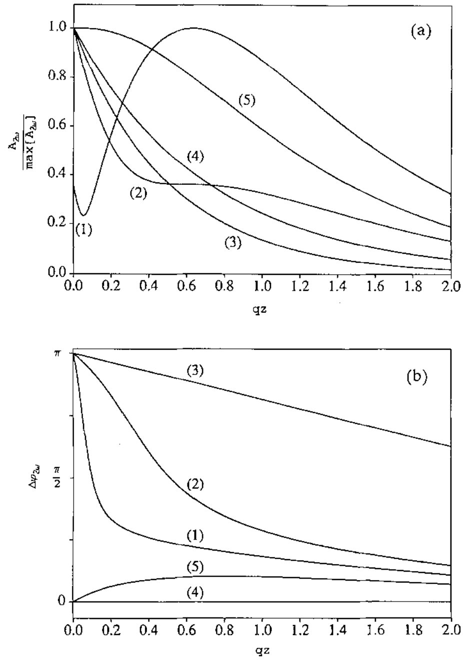

Fig. 1. Spatial distribution of (a) the normalized amplitude $A_{2\omega}(z)/A_{2\omega}^{\max}$ and (b) the phase shift of the forced propagating mode, $\Delta\phi_{2\omega}$, in Eq. (23), for the following values of the dimensionless nonlinear parameter $[(1/C)(\partial C/\partial T)]/[(1/K)(\partial K/\partial T)] \equiv \delta_1/\delta_2 = -1$ (curve 1), 0 (curve 2), 1 (curve 3), 2 (curve 4), and $\pm\infty$ (curve 5).

Fig. 1b. Another remarkable feature of curve 2, Fig. 1a, is the existence of a characteristic temperature plateau in the subsurface region $0.4\,\mu_q \leqslant z \leqslant 0.8\,\mu_q$.

Curves 4 in Figs. 1a and b represent the amplitude and phase in the free-propagating 2ω-wave. Finally, curves 5 are characteristic of materials dominated by the nonlinearity associated with the temperature dependence of the heat capacity ($|\delta_1| \gg |\delta_2|$). In this situation the characteristic spatial scale is of the order of the fundamental frequency penetration length. The 2ω-temperature field decays to its 50% level only at distances $z \sim \mu_q$ (Fig. 1a, curve 5). The phase is also nearly constant at these distances, as the phase increase shown in Fig. 1b (curve 5) is practically compensated by the diminution of phase in the free-propagating component, Eq. (33). The spatial resolution in this case is even lower than in the free propagating 2ω-wave; compare curves 4 and 5 in Fig. 1a.

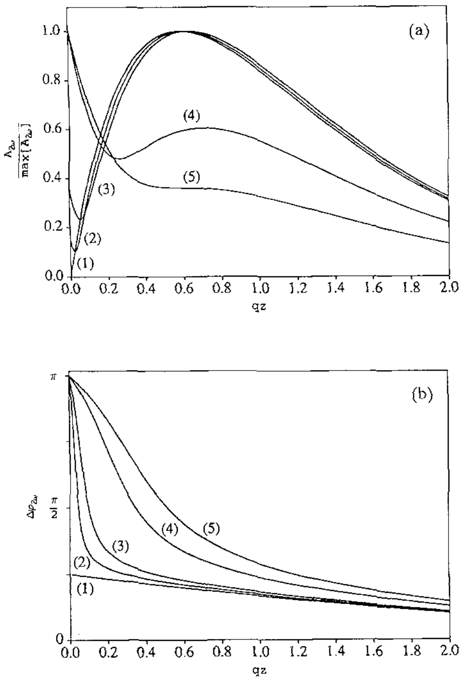

Fig. 2. Same as in Figs. 1a and 1b but for $\delta_1/\delta_2 = -\sqrt{2}$ (curve 1), $-\sqrt{2}+0.2$ (curve 2), -1 (curve 3), -0.3 (curve 4), and 0 (curve 5). For these values of the nonlinear parameters there exists a local temperature minimum under the surface, in addition to the one at $z \to \infty$.

Considering the curves 2 and 5, both amplitude and phase, one can predict higher spatial resolution of nonlinear photothermal imaging in materials with $|(1/k)(\partial k/\partial T)| \gg |(1/C)(\partial C/\partial T)|$. The physical explanation for this phenomenon comes from the analysis of the nonlinear sources in Eq. (12). In agreement with that equation, the $C = C(T)$ dependence always induces 2ω-generation under modulated laser heating of the material. The primary reason is, indeed, the qualitative relation $T_{2\omega} \sim T_\omega^2$, which efficiently increases spatial temperature gradients. At the same time, the $k = k(T)$ dependence "generates" a second harmonic only in the regions of the spatial gradients of the fundamental temperature field. This is the physical basis of this additional reason for which, in the 2ω-temperature field, the relative spatial gradients are higher than in the fundamental field. This provides additionally enhanced spatial resolution and may be achnieved only if $|(1/k)(\partial k/\partial T)| \gg |(1/C)(\partial C/\partial T)|$, as shown in Fig. 1. To be precise, we point out here that the spatial distribution represented by curve 2, Fig. 1a, is the result of the interference of the 2ω-thermal waves excited in

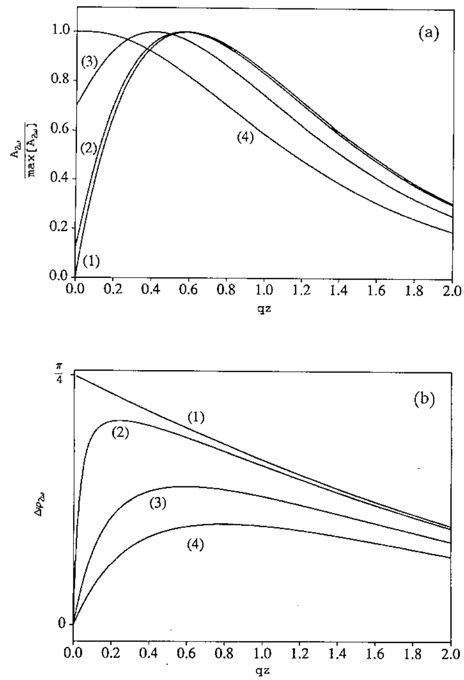

Fig. 3. Same as Figs. 1a and 1b but for $\delta_1/\delta_2 = -\sqrt{2}$ (curve 1), -4 (curve 2), -10 (curve 3), and $\pm\infty$ (curve 4). For these values of the nonlinear parameters the local 2ω-temperature minimum is localized at the irradiated surface, while the absolute temperature maximum occurs in the bulk of the material.

the bulk and at the surface of the material. Thus it is important for the enhanced spatial resolution that the $k(T)$ dependence contribute both to the bulk and to the surface sources, while $C(T)$ contribute only to the bulk.

Figure 2 presents some cases of $A_{2\omega}$ and $\Delta\phi_{2\omega}$ spatial distributions for $-\sqrt{2} \leqslant \delta_1/\delta_2 \leqslant 0$, when there exists a local temperature minimum in the 2ω-temperature field under the surface, in addition to the one at $z \to \infty$. Curve 1 describes the critical regime $\delta_1/\delta_2 = -\sqrt{2}$ in which the 2ω-temperature field vanishes at the surface of the sample. The maximum temperature in this case is attained at $z \simeq 0.6\mu_q$ (Fig. 2a, curve 1). The phase depends essentially linearly on distance:

$$\Delta\phi_{2\omega}(\delta_1 = -\sqrt{2}\delta_2) \simeq \frac{\pi}{4} + \left(1 - \frac{1}{\sqrt{2}}\right) qz \qquad \text{for} \quad qz \lesssim 1 \tag{37}$$

see Fig. 2b, curve 1.

Curves 1–4 in Fig. 2a demonstrate that the position of the temperature maximum beneath the surface does not vary considerably with deviation from the critical regime, i.e., with increasing δ_1/δ_2. However, for $\delta_1/\delta_2 \gtrsim -0.5$, this maximum becomes only local (i.e., not absolute), whereas the absolute maximum of the 2ω-temperature profile occurs at the irradiated surface (curve 4). The local temperature maximum inside the material disappears only for $|\delta_1/\delta_2| \ll 1$, Fig. 2a, curve 5. Curves 2–5 in Fig. 2b give evidence of the smoothing of the 2ω-phase spatial gradients with deviation from the critical regime. Figure 3 presents some cases of the $A_{2\omega}$ and $\Delta\phi_{2\omega}$ spatial distributions for $\delta_1/\delta_2 \leqslant -\sqrt{2}$. Curves 1–3 in Fig. 3a illustrate our theoretical predictions on the position of the absolute maximum of the second harmonic thermal-wave field profile beneath the surface in these regimes. In agreement with Fig. 3a, the position of the maximum approaches the surface when δ_1/δ_2 decreases. In the limit $\delta_1/\delta_2 \to -\infty$, the curve maximum intersects the material surface (Fig. 3a, curve 4). An important general feature of the regime $\delta_1/\delta_2 \leqslant -\sqrt{2}$ is the position of the local 2ω-temperature minimum on the surface of the material. Curves 2–4 in Fig. 3b ilustrate the smoothing of the phase spatial gradients with deviation from the critical combination of the parameters δ_1 and δ_2.

4. CRITIQUE OF THE STEPWISE APPROXIMATION METHOD

In this section we point out that the limits of validity of the obtained 1-D solutions Eqs. (18) and (26) are broader than the restriction indicated by inequalities (6). Experimentally, obtaining the 1-D response of the fundamental frequency thermal wave implies that the characteristic dimension r_0 of the laser spot at the irradiated surface is much larger than the thermal wave penetration length, $r_0 \gg \mu_q$. This leads to the requirement that spatial variations of the quasi-stationary (dc) temperature field T_{01} also take place at distances of the order of $r_0 \gg \mu_q$ in all directions. Consequently, the description of the fundamental and second harmonic thermal wave fields, Eqs. (10) and (12), respectively, as waves propagating in spatially homogeneous media is always valid under the 1-D approximation. The following consideration, however, must be taken into account: if T_{01} does not satisfy the condition (6), then (a) the characteristic averaged temperature in the irradiated region should be found from the solution of the nonlinearized but stationary Eq. (1), with time-averaged sources $Q(\mathbf{r}, t) \to \langle Q(\mathbf{r}, t)\rangle = Q_0(\mathbf{r})$, and (b) the values $C(T_0)$ and $k(T_0)$ of heat capacity and thermal conductivity, respectively, used in calculating the averaged field $T_{01} = \langle T_1 \rangle$, Eq. (9), should be replaced in Eqs. (5), (7), and (10) and subsequent equations by the laser-heating-enhanced values $C(T)$ and $k(T)$ in Eqs. (4) in calculations of the new increased averaged temperature field

$\langle T \rangle$. As a result, only the amplitude of the thermal wave at the fundamental frequency controls the limits of validity of the stepwise successive approximation method in the 1-D geometry. This is achieved through inequalities (6) with the values of δ_1 and δ_2 corrected, in agreement with the possible shift of the average temperature. Note that the dependence of the characteristic values of k and C on the new average temperature in the solutions Eqs. (18) and (26) induces an additional dependence of the second harmonic field, as well as the fundamental frequency temperature field, on laser intensity.

5. CONCLUSIONS

In developing the theoretical foundations of nonlinear photothermal imaging, we have proposed a mathematical formalism to describe second harmonic thermal-wave excitation, caused by the dependence of the material thermal conductivity and heat capacity on temperature. We have applied the stepwise successive approximation method for the evaluation of the spatial distribution of the second harmonic temperature field, generated by modulated laser action on the surface of a semiinfinite material. The analysis of the results obtained reveals the crucial dependence of the 2ω-thermal-wave spatial behavior on the value of the nonlinear parameter $\delta_1/\delta_2 = [(1/C)(\partial C/\partial T)]/[(1/k)(\partial k/\partial T)]$, which characterizes the relative role of the dependences of heat capacity $C = C(T)$ and thermal conductivity $k = k(T)$ on the 2ω-temperature field generation process.

It has been demonstrated that for some values of the parameter δ_1/δ_2 the shape of the 2ω-thermal-wave amplitude spatial distribution may be rather unusual. In particular, the absolute temperature maximum may be localized *beneath* the irradiated surface or there may exist a local temperature minimum besides the one at infinity. In other words, the distribution of the second harmonic amplitude may be nonmonotonic in space. The trends of the variations of the $T_{2\omega}$ field with the parameter δ_1/δ_2 in the entire region $-\infty < \delta_1/\delta_2 < \infty$ are described in Figs. 1–3. The present work describes phenomena for which there already exists some preliminary experimental evidence [1–3]. It is hoped that more of the predicted nonlinear features may be detected with some of the already existing experimental schemes, e.g., by the "mirage" effect in transparent materials [9].

In practice, the most important among our theoretical results is the prediction of the enhanced spatial resolution of nonlinear photothermal imaging in materials with $|(1/k)(\partial k/\partial T)| \gg |(1/C)(\partial C/\partial T)|$, particularly in semiconductors. The physical origin of this effect is related to the fact that any nonlinearity associated with the dependence of the thermal conductivity on temperature $k = k(T)$ acts only in the regions of temperature field gradients, both in the bulk and on the surface of the material. To confirm the experimental feasibility of our prediction of enhanced spatial resolution of nonlinear photothermal depth profiling, it will be necessary to derive the dependence of the 2ω-temperature field on the fundamental modulation frequency in spatially inhomogeneous media (for example, in a thin film on a substrate of a different material). Such an investigation of the second harmonic of the thermal-wave excitation in the simplest layered structures is now in progress. The final results will appear in a forthcoming publication.

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