

Boundary Conditions in Theory of Photothermal Processes

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The general boundary conditions for the thermal diffusion equation are obtained. It is shown that in the general case of a nonstationary photothermal process these boundary conditions must include both the surface thermal conductivity and surface thermal capacity. One more parameter, the surface capacity thermal impedance, appears in the boundary conditions when the photothermal process is the thermal wave propagation.

Keywords: Photothermal processes; Surface thermal conductivity; Surface thermal capacity; Surface thermal impedance

I. INTRODUCTION

The main idea of the photothermal experiments is the generation of nonstationary temperature in a sample due to absorption of the modulated laser beam [1]. The surface detection of temperature fluctuations by means of photothermal techniques enables to obtain various thermal, optic and relaxation parameters of a matter. These techniques are versatile, nondestructive and can be employed under different experimental conditions. The most techniques used in the harmonic photothermal processes (thermal waves), such as photoacoustic detection, photothermal beam deflection and others are described in [1,2].

In all cases, the photothermal signal depends on the material properties, features of the energy interaction between the quasiparticles as well as on the geometry of the sample.

The theoretical model of studying of photothermal phenomena is based on the equation of heat flow. In one-dimensional case and with taken into account the light absorption throughout the sample it can be written as following,

$$\rho c \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[\kappa(x) \frac{\partial T(x,t)}{\partial x} \right] + \beta e^{-\beta x} I(t). \quad (1)$$

Here $T(x,t)$ is nonequilibrium temperature; κ , ρ and c are the thermal conductivity, density and the bulk specific heat respectively; $I(t)$ is the intensity of the incident modulated light beam at the illuminated surface of the sample; β is the light absorption coefficient. The space coordinate is x , and t is time.

It is clear that the space temperature distribution depends strongly on the light absorption coefficient. One can consider two special cases according to correlation between the coefficient β and the sample length l [3]. One of them is the case of the weak light absorption, and it corresponds to $\beta l \leq 1$. In this case the intensity of the incident beam weakly changes with coordinates within the sample length.

The second one is the case of the strong light absorption, and it corresponds to $\beta l \gg 1$. If the last condition takes place the light intensity sharply decreases from the illuminated sam-

ple surface $x = 0$ deep into the sample. One may consider that the light is absorbed at the surface.

In both cases the main feature of all photothermal techniques is the detection of the temperature fluctuations created by the modulated light absorption on the sample surface. Frequently, two different ways of the sample heating are used in the photoacoustic experiments being the most popular of photothermal techniques [1,2]. First of them is the front surface illumination (the detecting photoacoustic cell is replaced at the irradiated sample surface, and it is called by the close photocoustic cell). The second one is the rear surface illumination (the photoacoustic cell is replaced at the back sample surface, and it is called by the open photoacoustic cell). In the first case the nonequilibrium temperature is detected at the same surface on which the modulated laser beam falls. The second method assumes the detection of this temperature at the opposite sample side.

Rosencwaig and Gersho [4] and many other scientists consider the temperature and heat flux continuity at the surface in order to describe thermal waves in photothermal experiments by Eq.(1). Opsal and Rosencwaig [5] have used a periodic heat source $Qe^{i\omega t}$ at the surface of a semi-infinite body as a boundary condition to study the thermal waves, ω is the light modulation frequency.

In Ref.[6] it was mentioned that in according with Opsal and Rosencwaig boundary conditions, only the periodically modulated part of the light beam generates heat diffusion process, and the contribution of the static carrier-light was ignored. Moreover, heat flux $Qe^{i\omega t}$ takes negative values, what has no physical sense.

In this connection in Refs. [7],[8] the incident modulated light beam at the illuminated surface $x = 0$ was written as

$$I(t) = I_0 + \Delta I e^{i\omega t}, \quad (2)$$

where I_0 is the average over time the total light intensity $I(t)$, ΔI is the intensity of the modulated light component, $I_0 \geq \Delta I$.

In this case the corresponding boundary conditions for the surface light absorption were represented by equation $Q(x=0,t) = [Q_0 + \Delta Q e^{i\omega t} - \eta(T - T_0)]_{x=0}$ [8], where Q_0 is the average over time the total thermal flux $Q(x=0,t)$ at the surface

$x = 0$, and it is proportional to I_0 . The thermal flux component ΔQ corresponds to the intensity ΔI . $\Delta Q \leq Q_0$, so the non-physical situation with negative values of the thermal flux is removed. T is the temperature of the sample on the boundary $x = 0$; T_0 is the ambient temperature; η is the surface thermal conductivity.

One need to note that practically in all cases boundary conditions are postulated and by this reason have no the properly argumentation. In the present paper we suggest the logical derivation of the boundary conditions for equations. From our point of view they have the most general form, and include all known special cases.

II. GENERAL BOUNDARY CONDITION

Let the modulated laser beam is incident onto the left surface $x = 0$ of an unipolar, isotropic semiconductor slab with the unit section. Let the beam intensity is given by Eq.(2). The right surface $x = l$ for simplicity is supposed to be kept up at the temperature T_0 . The lateral sides are to be supposed adiabatically insulated, so the problem is one-dimensional. We solve the linear problem, so the light intensity is to be so small that all kinetic coefficients do not depend on the nonequilibrium temperature, and the nonequilibrium temperature can be represented as $T(x, t) = T_0 + \Delta T(x, t)$ with $\Delta T(x, t) \ll T_0$.

Really the boundary between two arbitrary mediums is a transitional layer along which parameters describing the one matter's properties continually transfer to parameters of another matter.

Let us consider that layer $0 \leq x \leq \delta$ where δ is arbitrary small magnitude. Thus, the region $-\delta \leq x \leq 0$ applies to the ambient surrounding, which we suppose to be described by the temperature T_0 . Besides, we assume the light absorption is absent in this surrounding. This situation is closed to the photoacoustic spectroscopy when the sample is placed inside a cell containing a gas [4].

To obtain the boundary condition at the surface $x = 0$ for Eq.(1) in the case of the weak light absorption it is convenient to represent Eq.(1) in the following form,

$$\rho c \frac{\partial T(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[\kappa(x) \frac{\partial T(x, t)}{\partial x} \right] + \beta e^{-\beta x} I(t) \Theta(x), \quad (3)$$

where $\Theta(x) = \begin{cases} 0, & -\delta \leq x \leq 0, \\ 1, & 0 \leq x \leq \delta. \end{cases}$

Let us now integrate Eq.(1) over x from ξ to δ , where ξ is the arbitrary space point within the layer $-\delta \leq x \leq \delta$ and divide the obtained expression by $\kappa(\xi)$,

$$\frac{1}{\kappa(\xi)} \int_{\xi}^{\delta} \rho(x) c(x) \frac{\partial T(x, t)}{\partial t} dx =$$

$$= \frac{1}{\kappa(\xi)} \left(\kappa \frac{\partial T(x, t)}{\partial x} \right)_{x=\delta} - \frac{\partial T(\xi, t)}{\partial \xi} + \frac{\beta I(t)}{\kappa(\xi)} \int_{\xi}^{\delta} e^{-\beta x} \Theta(x) dx. \quad (4)$$

Integrating this equation over ζ from $-\delta$ to δ again and going to the limit $\delta \rightarrow 0$ (the approximation of the abrupt boundary) we obtain,

$$\begin{aligned} \eta \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \frac{1}{\kappa(\xi)} \left(\int_{\xi}^{\delta} \rho(x) c(x) \frac{\partial T(x, t)}{\partial t} dx \right) d\xi = \\ = \left(\kappa \frac{\partial T}{\partial x} \right)_{x=0} + \eta (T_0 - T(x=0, t)) + \\ + \eta \beta I(t) \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \frac{1}{\kappa(\xi)} \left[\int_{\xi}^{\delta} e^{-\beta x} \Theta(x) dx \right] d\xi, \end{aligned} \quad (5)$$

where $\eta^{-1} = \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}$.

The last term in Eq.(5) is equal to zero. Really,

$$\begin{aligned} \eta \beta I(t) \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \frac{1}{\kappa(\xi)} \left[\int_{\xi}^{\delta} e^{-\beta x} \Theta(x) dx \right] d\xi = \\ = \eta \beta I(t) \lim_{\delta \rightarrow 0} \int_0^{\delta} \frac{1}{\kappa(\xi)} \left[\int_{\xi}^{\delta} e^{-\beta x} dx \right] d\xi = \\ = \eta I(t) \lim_{\delta \rightarrow 0} \int_0^{\delta} \frac{1}{\kappa(\xi)} \left(e^{-\beta \xi} - e^{-\beta \delta} \right) d\xi. \end{aligned} \quad (6)$$

The expression between the brackets has no singularities and can be outside the integral. It tends to zero when $\delta \rightarrow 0$.

The comparison the value η with obtained earlier boundary conditions [8,9] allows to conclude that η is the surface thermal conductivity.

Generally, the thermal conductivity κ can depend on δ in the limit transition to zero. One can suppose that the following cases are possible:

- a) κ remains the finite value at δ tending to zero.
- b) κ tends to zero with the same speed as well as δ ;
- c) κ tends to zero with a higher speed than δ ;

In the first case the surface heat conductivity tends to infinity, so this situation describes the isothermal boundary condition. The boundary is defined by the finite surface heat conductivity in the second case, and this case is general. The

third case corresponds to an adiabatic insulation of the sample. Realization of the concrete situation can be understood only from the microscopic analysis of the surface energy relaxation mechanisms. The given question, however, demands separate research and does not enter into a subject of consideration of the present work.

The derivation $\frac{\partial T(x,t)}{\partial t}$ have no singularities and it can be outside the integral.

As a result we can write the founded boundary conditions by the following way,

$$c_s \frac{\partial T(x,t)}{\partial t} \Big|_{x=0} = \kappa \frac{\partial T(x,t)}{\partial x} \Big|_{x=0} + \eta (T_0 - T(x=0,t)). \quad (7)$$

Here the value $c_s = \eta \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \frac{1}{\kappa(\xi)} \left(\int_0^{\xi} \rho(x) c(x) dx \right) d\xi$ is the surface heat capacity by our definition.

The physical meaning of this value is the surface's ability to accumulate the heat energy at the surface. The surface heat capacity differs from the bulk heat capacity because of the different properties of the surface and volume as well as the surface thermal conductivity differs from the bulk thermal conductivity.

Let us now obtain the boundary conditions for the case of the very strong surface light absorption, i.e. for the case when all irradiation's energy is absorbed completely in the layer with the zero thickness at the surface $x = 0$.

To obtain these boundary conditions within the frame of the method described above let us write Eq(1) with the point source of heat at the surface $x = 0$,

$$\rho c \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[\kappa(x) \frac{\partial T(x,t)}{\partial x} \right] + I(t) \delta(x), \quad (8)$$

where $\delta(x)$ is the Dirac function.

Caring out the calculation similar to the previous case it is easy to obtain the following boundary conditions,

$$c_s \frac{\partial T(x,t)}{\partial t} \Big|_{x=0} - I(t) = \kappa \frac{\partial T(x,t)}{\partial x} \Big|_{x=0} + \eta (T_0 - T(x=0,t)). \quad (9)$$

Let us note that Eq.(8) was considered in the form (10) only for obtaining the boundary conditions. Really, one needs to use equation

$$\rho c \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[\kappa(x) \frac{\partial T(x,t)}{\partial x} \right] \quad (10)$$

for the case of the surface absorption and the boundary conditions (9) to it.

III. BOUNDARY CONDITIONS FOR THE STATIC AND DYNAMIC TEMPERATURE. SURFACE HEAT IMPEDANCE.

In this section we will restrict ourselves by analysis of the boundary conditions (6). Discussion of the boundary conditions is practically the same.

According to Eq.(3) the temperature distribution can be represented in the following general form,

$$T(x,t) = T^s(x) + T^d(x) \cdot e^{i\omega t}, \quad (11)$$

where $T^s(x)$ is the static temperature component originated due to the absorption of the intensity $I_0 e^{-\beta x}$ and $T^d(x) e^{i\omega t}$ is the dynamic temperature component arising due to absorption of the intensity $\Delta I e^{-\beta x} e^{i\omega t}$. Let us note that $T^d(x)$ is the complex function.

Substituting Eq.(11) to Eq.(6) we obtain the boundary conditions for the static and dynamic temperatures separately,

$$\kappa \frac{dT^s(x)}{dx} \Big|_{x=0} = \eta [T^s(x) - T_0] \Big|_{x=0} \quad (12)$$

$$\kappa \frac{dT^d(x)}{dx} \Big|_{x=0} = \eta \left(1 + i \frac{\omega}{\omega_s} \right) T^d(x) \Big|_{x=0}, \quad (13)$$

where $\omega_s = \eta / c_s$. To our opinion this frequency determines the relaxation rate of the accumulated heat at the surface into surrounding.

It is easy to see that the boundary conditions (12) and (13) are reduced to

$$T^s(x=0) = T_0 \quad (14)$$

and

$$T^d(x=0) = 0 \quad (15)$$

when $\eta \rightarrow \infty$. There are the isothermal boundary conditions.

Only one condition, $\eta \rightarrow 0$ is necessary for adiabatic insulation of the static thermal flux, while for the adiabatic insulation of the dynamic thermal flux it is necessary the same condition $\eta \rightarrow 0$, and one more, $c_s \rightarrow 0$. The last condition is clear because the dynamic thermal energy can accumulated on the boundary when $c_s \neq 0$, and, thus, thermal diffusion flux is different from zero even if $\eta \rightarrow 0$.

At the static case ($\Delta I = 0$) only boundary condition (11) occurs which is well known from the earliest papers (see, for example [8]).

The boundary condition (12) is quasistatic if the modulation frequency $\omega \ll \omega_s$. In this case the surface properties are characterized only by the surface thermal conductivity, like to Eq.(12),

$$\kappa \frac{dT^d(x)}{dx} \Big|_{x=0} = \eta T^d(x) \Big|_{x=0}. \quad (16)$$

In this case the surface energy accumulation is absent, and both static and dynamic heat components relax to the surrounding medium by means of the surface thermal conductivity.

We obtain another boundary condition when $\omega \gg \omega_s$,

$$\kappa \frac{dT^d(x)}{dx} \Big|_{x=0} = \frac{i}{Z_s} T^d(x) \Big|_{x=0}, \quad (17)$$

where $Z_s = (\omega c_s)^{-1}$. By analogy with electrics (see Ref.[10]) we call this value the surface heat capacity impedance or the surface thermal capacity resistance. This analogy can be justified if the electric current compare with the thermal flux ($I \rightarrow q = -\kappa \frac{dT^d}{dx}$), and the voltage compare with the temperature difference [$V \rightarrow \Delta T^d = (0 - T^d)$]. In this case we can write the boundary condition (16) at the surface $x = 0$ as

$$qZ_s \Big|_{x=0} = \Delta T^d \Big|_{x=0}. \quad (18)$$

In conclusion let us note that in electric circuits, containing the ohm resistance (R) and the electric capacity (c) we can introduce the total impedance [11],

$$Z = R + \frac{i}{\omega_e c}, \quad (19)$$

where ω_e is the frequency of electric oscillations.

In the considered case of the thermal fluxes we can not introduce the total heat impedance. Instead of it we can define the dynamic surface thermal conductivity

$$\eta^d = \eta + i\omega c_s. \quad (20)$$

Now the isothermal and adiabatic conditions for the dynamic thermal flux can be determined as $Re\eta^d \rightarrow \infty$ and $|\eta^d| \rightarrow 0$ respectively.

IV. CONCLUSIONS

In this work the general boundary conditions for the thermal diffusion equation are obtained when the photothermal phenomena are considered. Really, these boundary conditions represents only their structure and do not pretend to be the exact expressions. The later can be obtained only on the base of the microscopic analysis. By this reason, the surface parameters like surface thermal conductivity and surface thermal capacity have to be measured from experiments. Some calculation of the temperature distribution in the photothermal phenomena with taken into account the surface thermal capacity resistance can be found in Ref. [11]. The results of this paper can be useful and for analyses of two-layer samples like to the samples described in Ref. [12].

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