Nonlinear optical methods for researching of kinetic coefficients in binary mixtures

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Abstract. In two-component fluid (binary mixture) the heat flow can cause concentration stream arising from occurrence of thermodiffusion phenomenon (Soret effect). As a result these phenomenon changes the magnitude of the transport coefficients of the mixture. This paper analyzed nonlinear optical methods of diagnostics of the kinetic coefficients of binary mixtures - the thermal lens method and dynamical holography method. It was developed the theory of the light induced heat and mass transfer, taking into account the electrostrictive forces (for nanoliquids). The results are relevant to optical diagnostics of binary mixture and dispersed liquid materials.

1. Introduction
Investigations of the kinetic coefficients in liquid nanomaterials is a matter of theoretical and experimental works because transport processes in nanosuspensions and nanoliquids have their own characteristics1,2. Nonlinear optical diagnostics of materials involves methods based on different mechanisms of light induced modulation of optical constants of medium3,4. Light induced change in the concentration of polymer nanoparticles results in appropriate modulation of the optical properties of nanosuspension. This allows to implement various modifications of optical noncontact control parameters of nanoparticles in near real time. For example, a method is used in thermal lens spectrometry and thermo-optical diagnostics of materials5,6. A thermal lens response has its own peculiarities in two-component liquid, because in addition to normal thermal response associated with thermal expansion of the liquid, concentration flows can occur here arising from the phenomenon of thermal diffusion (Soret effect) and electrostriction7.

The purpose of this work is the theoretical analysis of the contribution of concentration mechanisms nonlinearity in the formation of light induced response in the nanosuspension.

2. Thermal lens method
Thermal lens technique is widely used for the optical diagnostics of materials. The light-induced thermal lens in a homogeneous fluid is formed as a result of thermal expansion of a medium. In two-component fluid the heat flow also can cause concentration stream arising from occurrence of thermodiffusion (Soret effect). Another mechanism of optical nonlinearity of the medium is due to the forces operating on the particles of the dispersed phase in gradient light field. A change in the concentration of dispersed components in the liquid as a result of these phenomena changes the magnitude of medium thermal lens response.
Let's take a two beam thermal lens scheme (see Figure 1). The reference (Gaussian) beam generates the thermal field in the optical cell with nanosuspension. The second (Gaussian) beam tests the thermal lens.

![Figure 1. A thermal lens scheme.](image)

Thermal lens signal $\vartheta(t)$ shows the change of the beam intensity on the optical axis behind the screen:

$$\vartheta(t) = \frac{I(t) - I(0)}{I(0)}.$$  \hspace{1cm} (1)

To calculate the thermal lens signal use the term for the lens transparency of the cell $^2$:

$$\vartheta_n = -\frac{2(z_1/l_0)\Phi_n(0)}{(1+z_1^2/l_1^2)(1+3z_2^2/l_2^2)}.$$  \hspace{1cm} (2)

where $Z_1, Z_2$ are the distance from the cell center to the Gaussian beam waist and to screen, respectively (fig. 1), $l_0 = \pi r_0^2/\lambda$, $r_0$ – the radius of the Gaussian beam waist, $\Phi_n(0)$ - nonlinear phases in optical cell on the beam axis. Nonlinear phase consists of two deposits: the first appears due to thermal expansion of the liquid phase and the second is associated with a change in the concentration of dispersed particles:

$$\Phi_n(0) = \Phi_r(0) + \Phi_c(0).$$ \hspace{1cm} (3)

$$\Phi_r(0) = k \int_0^d \left( \frac{\partial n}{\partial T} \right) \Delta T(z, r = 0) dz.$$ \hspace{1cm} (4)

$$\Phi_c(0) = k \int_0^d \left( \frac{\partial n}{\partial C} \right) \Delta C(z, r = 0) dz.$$ \hspace{1cm} (5)

where $k = 2\pi/\lambda$ is the wave vector of the probing beam, $d$ is the thickness of a layer of liquid.
To determine the value of thermal lens we should consider the thermal and mass transport processes. The next system of balanced equations describes the processes that occur when a binary mixture is exposed by light field:

\[
c_p \rho \frac{\partial T}{\partial t} = \chi \nabla^2 T + \alpha I_0. \tag{6}
\]

\[
\frac{\partial C}{\partial t} = -\text{div}(J_d + J_\text{el} + J_{thd}) . \tag{7}
\]

Here \(T\) is the liquid temperature, \(C(r,t)\) is mass concentration of the nanoparticles, \(\chi\) is coefficient of thermal conductivity; \(c_p, \rho\) are the specific heat capacity and density of the fluid, respectively; \(\alpha\) – radiation absorption coefficient, \(I_0\) is the beam intensity. We have three concentration flows: \(J_d = -D \nabla C\) is diffusion flow, \(J_\text{el} = \gamma C \nabla I\) is electrostrictive flow, \(J_{thd} = D_T C(1-C) \nabla T\) is thermal diffusion flow. \(D\) and \(D_T\) are the diffusion and thermal diffusion coefficients, respectively, \(\gamma = (2\beta b / c_n)\), (\(\beta\) and \(b\) are polarizability and mobility of nanoparticle, respectively), \(c\) is the light velocity. 

We will consider the case of low concentrations \((C \ll 1)\) and small changes, allowing you to provide the desired concentration in the form of sum of unperturbed parts \(C_0\) and perturbed \(C_N\):

\[
C(r,t) = C_0 + C_N(r,t) = C_0(1 + C'(r,t)), \quad C'(r,t) = \frac{C_N(r,t)}{C_0} \ll 1 . \tag{8}
\]

We have next initial conditions:

\[
C(R) = C_0, \quad T(R) = T_0, \tag{9}
\]

where \(R\) is the radius of the cylindrical cell, \(T_0\) is the temperature at the border cell.

After the necessary integration we obtain an exact solution:

\[
T(r,t) = T_0 + a I_0 \lambda^{-1} r_i^2 \sum_{n=1}^{\infty} J_0(\mu_n r/R) \exp\left(-\mu_n^2 r^2 / 4 R^2\right) \left[1 - \exp\left(-\mu_n^2 t / \tau_{thd}\right)\right], \tag{10}
\]

where \(\mu_n\) is the positive roots of the equation \(J_0(\mu_n) = 0\), \(\tau_{thd} = 4 R^2 c_p \rho (\mu_n \chi)^{-1}\).

Further it is assumed that the temperature field is set in the system faster than the particle concentration distribution. It allows solving the task in terms of stationary temperature\(^3\). Decision of the task (24)-(25) can be obtained by using the appropriate Green’s function:

\[
C'(r,t) = \delta D^{-1} r_i^2 \sum_{n=1}^{\infty} J_0(\mu_n r/R) \exp\left[-\mu_n^2 r^2 / 4 R^2\right] \left[1 - \exp\left(-\mu_n^2 t / \tau_{thd}\right)\right] \frac{\gamma a D^{-1} C_0 \exp\left[-r^2 / r_i^2\right] \left[1 - \exp\left(-t / \tau_d\right)\right]}{\mu_n^2 J_1(\mu_n)}, \tag{11}
\]

where \(\tau_{thd} = R^2 D^{-1}\), \(\tau_d = r_i^2 D^{-1}\). First and second terms describe the thermal diffusion and electrostrictive effects, respectively.

The obtained results allow us to calculate the summarized light induced lens response (for example, in stationary case):

\[
S_{st}^{oe} = \frac{z_i}{l_0} k I_0 d \frac{\alpha \chi^{-1} S_r C_0 r_i^2 \left(\frac{\partial n}{\partial C}\right) - \alpha \chi^{-1} r_i^2 \left(\frac{\partial n}{\partial T}\right) + \gamma C_0 D^{-1} \left(\frac{\partial n}{\partial C}\right)}{\left(1 + z_i^2 / l_0^2\right) \left(1 + 3 z_i^2 / l_0^2\right)}, \tag{11}
\]

Thus, the expression was achieved for the light induced lens response in nanosuspension.

3. Dynamic hologram method
Dynamic hologram method (Forced Raleigh Scattering) based on the record of the dynamic holograms in nonlinear material while reading it.

The next expression defines a diffraction efficiency of the hologram 4:

$$\eta = I_1/I_0,$$

where $I_0$ is the intensity of the incident beam; $I_1$ is the intensity of the diffracted beam. The diffraction efficiency of a thin phase hologram is:

$$\eta = t_0^2 J_1^2(\phi_1),$$

where $t_0$ is amplitude transmittance of the unlighting hologram; $\phi_1$ is amplitude modulation after light exposition; $J_n$ — Bessel function of the n-th order. If medium is transparent and the modulation amplitude is small ($\phi_1 \ll 1$), (3) we get:

$$\eta = (2\pi n J_n L \lambda^{-1})^2,$$

where $L$ is the thickness of a nanofluid layer.

The most universal non-resonant nonlinearity that exists in any absorbing medium is the heat mechanism. Let us find the value of such sensitivity for a single component material. A simplest mechanism of thermal non-linearity is due to the thermal expansion of the medium. The expression for the coefficient of effective cubic nonlinearity can be obtained by solving the one-dimensional heat equation:

$$c_r \rho \nu T/ \partial t = - \text{div} J_1 + \alpha I_0 (1 + \sin Kx),$$

where $J_1 = -\chi \text{grad} T$ - is a heat flow, $T$ is temperature of the material, $\chi$ is the thermal conductivity of the material, $c_r$ and $\rho$ are the specific heat capacity and density of the medium, $\alpha$ is the absorption coefficient of the medium, $I_1 = I_0 (1 + \sin Kx)$ is the intensity spatial distribution along the layer of the medium (x-axis), $K$ is the space wave vector of the elementary hologram. We have the solution (15) for the temperature amplitude $T_1$:

$$T_1 = \sigma T_r (c_r \rho)^{1/3} \left[1 - \exp(-t/\tau_r)\right],$$

$$\tau_r = \chi (c_r \rho)^{-1} K^2,$$

where $\tau_r$ is the thermal relaxation time.

Let’s consider an expression for the holographic sensitivity of the dispersion medium, taking into account both (thermodiffusion and electrostriction) concentration mechanisms. Assuming a one-dimensional problem, we seek the solution of equations (9-13) in the form of:

$$C(x, t) = C_0 + C_1(t) \sin Kx,$$

Here $C_0$ is the average particle concentration. Let’s the amplitudes of the concentration $C_1$ profiles is small $-(C_1/C_0) \ll 1$. The linearized system is easily solved and we have by taking into account (7) and (16-18):

$$C_1 = (\alpha x^{-1} c_r D_1 D^{-1} K^2 + \beta D^{-1} C_0) \left[1 - \exp(-K^2 D1t)\right],$$

The summarized expression for diffraction efficiency is the next (for simplicity in stationary case):

$$\eta = [2 \alpha D^2 (\alpha x^{-1} c_r D_1 D^{-1} K^2 + \beta D^{-1} C_0) \left(\partial n/\partial C\right)]^2,$$

This expression include thermal expansion (first term), the thermal diffusion (second term) and electrostrictive effect.

4. Conclusions

We have analyzed the two-dimensional diffusion in the nanosuspension with two concentration nonlinearities (thermodiffusion and electrostrictive) in a Gaussian beam radiation field. As a result the
exact expressions were achieved for the light induced lens response in nanosuspension. We get the exactly expression including thermal expansion, the thermal diffusion and electrostrictive effect for dynamic hologram method (Forced Raleigh Scattering)\textsuperscript{6,7}.

The analysis gives you the ability to determine not only characteristics of nanoparticles, but also the transport coefficients of nanosuspension. The results are relevant to optical diagnostics of dispersed liquid materials, including the thermo-optical spectroscopy\textsuperscript{9,10}.

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