

Analysis of Polydispersity of Macromolecular and Nanodisperse Systems by Electrooptical Methods

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Abstract—This work presents the general statement of the mathematical problem for estimating the distribution functions of particles with respect to their parameters from the data on electrooptical studies of dispersed systems. The most typical equations describing electrooptical effects in solutions of kinetically rigid macromolecules and nanoscale systems are given, and the method for their solution is proposed. Using model distribution functions, the proposed method is compared with the regularization method.

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INTRODUCTION

For more than a century, electrooptical methods have been used to study the electric characteristics of molecules in liquid systems, but they still have not lost their importance. The works of H. Benoit, A. Peterlin, V.N. Tsvetkov, N.A. Tolstoi, P.P. Feofilov, S. Stoylov, and B. Jennings have contributed significantly to the development of electrooptical methods for studying macromolecular solutions and disperse systems [1–8]. Nowadays, these studies are crucial for the study of complex nonequilibrium systems containing structures with dimensions varying from several nanometers to several thousands of nanometers [9–11]. These systems involve solutions of polyelectrolyte and polymer colloidal complexes, colloidal systems and suspensions of bacterial cells, viruses, bacteriophages, nanotubes, and fullerenes. From here on, the class of the above liquid systems will be referred to as nanodisperse systems, and the particles involved in these systems, as nanoparticles. Characteristics of nanodisperse systems strongly depend on electric charge, dipole moment, and polarizability of particles as well as on their dimensions and shape. In most macromolecular and nanodisperse systems, molecules and particles are not identical and the characteristics of the systems should be described by the distribution functions of particles with respect to their parameters. In other words, real systems should be described with allowance for their polydispersity because monodisperse approximations can lead to invalid conclusions on the characteristics of particles. In the electrooptical effects resulting from the ordered orientation of molecules or particles under the action of external electric field, the polydispersity of the systems strongly controls the dependence of induced optical anisotropy of the system on time and field parameters. Basic relationships for the theoretical description of the depen-

dence of induced anisotropy of the system on the parameters of the external action contain integrals that involve distribution functions of particles with respect to their parameters. When these dependences are experimentally estimated, we can find the distribution functions of particles with respect to their parameters if the above theoretical relationships are treated as integral equations. Such mathematical problems belong to the class of incorrect problems, and the methods for their solution require individual approaches. The development of methods for solving the above problems makes it possible to broaden the potential of electrooptical methods and use them in the combination with dynamic light scattering, chromatography, and certain other methods to estimate the distribution functions of particles with respect to their parameters.

This work focuses on the general statement of the mathematical problem for finding distribution functions from the data of electrooptical experiments, the typical equations describing electrooptical effects in the solutions of kinetically rigid macromolecules and nanodispersed systems, and the method for their solution.

Statement of the Problem for Estimating Distribution of Particles with Respect to Their Parameters in Dilute Systems

Distribution of particles with respect to their geometrical, electric, dynamic, and other parameters can be estimated from analysis of the static and transition processes induced in the system by the action of external fields. Below, we analyze the dependences of induced optical anisotropy on time, voltages, and frequency of the applied field. Consider the set of such external parameters as vector $\psi = (\psi_1, \dots, \psi_m)$. In a

similar manner, the set of such parameters of polarizability, dipole moment, constant of rotational diffusion, and other characteristics of molecules or particles is given by vector $\xi = (\xi_1, \dots, \xi_n)$.

In the dispersed system with a low concentration of particles in the absence of any interaction between them, experimentally observed electrooptical effect A induced by the action of the external field depends on some of the contributions from individual particles. Usually, parameter $A(\psi)$ is represented as the following integral [12, 13]:

$$A(\psi) = \int_{\Xi} (\kappa(\psi, \xi) \varphi(\xi)) d\xi, \quad (1)$$

where Ξ is the interval of changes in ξ , $\varphi(\xi)$ is the distribution functions of particles with respect to their parameters, $A(\psi)$ is the dependence of the induced anisotropy on time and/or on the parameters of electric field related to a given effect, which is controlled by the orientational ordering of the particles in the system. In the monodisperse system containing particles with a certain invariable $\kappa(\psi, \xi)$, $A(\psi)$ is equal to ξ .

For the polydisperse systems under study, $A(\psi)$ is estimated experimentally and Eq. (1) can be treated as the integral equation with respect to the distribution function $\varphi(\xi)$. In polydisperse systems, mathematical description of electrooptical effects is associated with the theoretical construction of the dependence $\kappa(\psi, \xi)$, which is the kernel of Eq. (1). The solution of the problem of polydispersity is reduced to measuring $A(\psi)$ by any methods and to finding $\varphi(\xi)$ from Eq. (1) at a given kernel $\kappa(\psi, \xi)$. In this case, $A(\psi)$ is the free term of this equation.

Difficulties in solving integral equation (1) strongly depend on the type of its kernel, on the number of the parameter of particles n , and on the number of external parameters m . It is noteworthy that, with increasing m , the experiments become more complicated; with increasing n , the physical model of a particle becomes more complex. In this work, we consider only cases when $n = 1, 2$ and $m = 1, 2$. Here, we assume that parameters that are not taken into account either do not influence the observed effect or they remain constant during experimental runs. In this case, $A(\psi) = A(\psi_1)$ or $A(\psi) = A(\psi_1, \psi_2)$ and $\varphi(\xi) = \varphi(\xi_1)$ or $\varphi(\xi) = \varphi(\xi_1, \xi_2)$ are the functions of one or two scalar arguments.

ELECTROOPTICAL EQUATIONS AND METHODS FOR THE STUDY OF POLYDISPERSE SYSTEMS

Consider electrooptical effects in the solutions of macromolecules and disperse systems. For monodisperse systems, induced anisotropy A and degree of orientational order Φ of particles are related by the following equation [14, 15]:

$$A = A_0 \Phi. \quad (2)$$

The value of A is controlled by the experimental conditions and optical characteristics of the particles, A_0 at complete orientation or, in other words, when $\Phi = 1$. In the high-frequency electric field with effective voltage Φ can be estimated as [16]

$$\Phi(E^2, \gamma) = \frac{3}{2} \int_0^1 \vartheta^2 \exp(\chi \vartheta^2) d\vartheta \bigg/ \int_0^1 \exp(\chi \vartheta^2) d\vartheta - \frac{1}{2} \quad (3)$$

Here, $\chi = \frac{\gamma E^2}{2k_B T}$, γ is the polarizability anisotropy of particles at a given frequency of the applied field; k_B is the Boltzmann constant, and T is temperature. When the degree of orientation of particles is low or at $\chi < 1$, Φ can be expanded into the following power-law series:

$$\Phi(E^2, \gamma) = \sum_{k=1}^{\infty} a_k \chi^k, \quad a_1 = \frac{2}{15}, \quad a_2 = \frac{4}{315}, \quad (4)$$

$$a_k = \frac{3}{2k+1} \left(\frac{a_{k-1}}{3} - \sum_{j=1}^{k-2} a_j a_{k-j-1} \right)$$

For nondipole particles, equality (3) is valid for a low-frequency field [3].

In the case of free relaxation of orientation of macromolecules or particles, the following relationship is used [1]:

$$\Phi(t, D) = \Phi(E^2, \gamma) e^{-6Dt}, \quad (5)$$

where D is the coefficient of rotational diffusion of the particles and t is time.

Electric Birefringence

The theory of birefringence deals with the rates of propagation of a plane front of monochromatic light waves, and this theory is strictly applicable only for optically homogeneous nonscattering media. In weakly light-scattering media, which include several macromolecular solutions, birefringence induced by the electric field can be approximately described when the dimensions of light-scattering macromolecules or particles are lower than the wavelength of light (typical dimensions of macromolecules vary from several nanometers to hundreds of nanometers, and this value is markedly lower than wavelength of light λ) or their dimensions are approximately equal to $\sim \lambda$ but the refractive index approaches the refractive index of the medium.

In media containing strongly light-scattering particles (the dimensions of particles are much higher than $\lambda/20$ but the refractive index differs appreciably from the refractive index of the solvent [16]), the plane wave front of incident light appears to be so distorted that

the refracted beam happens to be diffuse and, in this case, the refractive index concept cannot be applied. Observations performed on a two-beam interferometer show that when particles are added to a liquid through which one of the interference beams passes, interference bands are not shifted. This indicates that, in such systems, the speed of light propagation along the direction of the incident beam is equal to the speed of light propagation in a pure molecular medium around scattering particles. Therefore, orientational ordering of particles in such systems should lead to birefringence, and the phenomena associated with light propagation through crossed polarizers between which the system the field-oriented particles is located results from the specific character of light scattering rather than electric birefringence. W. Heller analyzed magneto-optical and electro-optical phenomena in disperse systems. His study [17] includes some comments on "conservative dichroism" (the difference in the extinction of light polarized along and perpendicular to the direction of the external field, which orients colloidal particles) as well as indications that this concept had been used earlier in works by Debye. Advantages of the use of birefringence for studying colloidal systems have been analyzed in [18], in which W. Heller revisited studies on electro-optical effects by crossed polarizers. H. Diesselhorst and H. Freundlich were the first to study the effects related to the anisotropy of light scattering by the system of oriented particles in colloidal systems [19, 20]. Heller mentioned that this effect was called the Diesselhorst–Freundlich effect.

Birefringence Δn is defined as the difference between refractive indices of the light polarized along and perpendicular to the direction of the applied field; according to Eq. (2), for particles or macromolecules with similar γ , birefringence appears as [12, 21]

$$\Delta n(E)/\Delta n_{\gamma}^{sat} = \Phi(E^2, \gamma), \quad (6)$$

Under complete orientation of particles along the field direction, Δn_{γ}^{sat} corresponds to the average Δn , and averaging is performed over all parameters of the particles, excluding those denoted in subscript (the same indexation will be used for the description of electro-optical effects). The Δn_{γ}^{sat} values are calculated using the theory of optical light polarizability by molecules and particles.

Electric birefringence can be studied only when orientation is low because macromolecules and small-sized particles cannot be fully oriented in actually attainable fields [22, 23]. The main types of electric fields used for studying relaxation processes are rectangular impulse and periodic (sinusoidal) fields [9, 24].

When distribution functions with weight $f(\gamma) = \Delta n_{\gamma}^{sat} \varphi(\gamma)$ and $f(\gamma, D) = \Delta n_{\gamma, D}^{sat} \varphi(\gamma, D)$ are introduced, Eq. (4) is used, and only two terms of expansions of Φ with respect to χ are considered, we can describe minor deviations from the Kerr law; then, the

stationary effect and its relaxation can be described by the following relationships:

$$\Delta n(E) = \int_{\gamma_c}^{\gamma_d} \left(\frac{\gamma E^2}{15k_B T} + \frac{2\gamma^2 E^4}{315(k_B T)^2} \right) f(\gamma) d\gamma, \quad (7)$$

$$\Delta n(E, t) = \int_{\gamma_c}^{\gamma_d} \int_{D_c}^{D_d} \left(\frac{\gamma E^2}{15k_B T} + \frac{2\gamma^2 E^4}{315(k_B T)^2} \right) \times e^{-6Dt} f(\gamma, D) d\gamma dD \quad (8)$$

It seems evident that Eq. (7) gives

$$\Delta n(E) = aE^2 + bE^4,$$

$$\int_{\gamma_c}^{\gamma_d} \left(\frac{\gamma}{15k_B T} \right) f(\gamma) d\gamma = a,$$

$$\int_{\gamma_c}^{\gamma_d} \left(\frac{2\gamma^2}{315(k_B T)^2} \right) f(\gamma) d\gamma = b,$$

and Eq. (8) leads to

$$\Delta n(E, t) = c(t)E^2 + d(t)E^4,$$

$$\int_{\gamma_c}^{\gamma_d} \int_{D_c}^{D_d} \frac{\gamma}{15k_B T} e^{-6Dt} f(\gamma, D) d\gamma dD = c(t),$$

$$\int_{\gamma_c}^{\gamma_d} \int_{D_c}^{D_d} \frac{2\gamma^2 E^4}{315(k_B T)^2} e^{-6Dt} f(\gamma, D) d\gamma dD = d(t),$$

Therefore, Eq. (7) cannot be treated as the equation for estimating $f(\gamma)$. For the same reason, relationship (8) cannot be used as the equation for estimating $f(\gamma, D)$. Nevertheless, the latter equalities show that Eq. (8) can be treated as the equation with respect to $f_1(\gamma) = f(\gamma, D(\gamma))$ or $f_2(D) = f(\gamma(D), D)$ when the dependence $D(\gamma)$ or $\gamma(D)$ is known.

H. Benoit analyzed the kinetics of development and relaxation of electric birefringence in a field of rectangular impulses when the Kerr law is applicable (Δn is proportional to E^2) [1, 2]. For a monodisperse system, relaxation of electric birefringence is described by the following relationship:

$$\Delta n(t) = \Delta n_0 e^{-6Dt} \quad (9)$$

(Δn_0 is the equilibrium electric birefringence). In the case of a polydisperse system for which the Kerr law holds, Eq. (9) takes the following form [25, 26]:

$$\Delta n(t) = \frac{E^2}{15k_B T} \int_{D_c}^{D_d} \gamma(D) e^{-6Dt} f(D) dD, \quad (10)$$

where $\gamma(D)$ is defined by the model of a macromolecule. This dependence can be analytically described for molecules in rodlike and coil configurations.

In a similar way, we can obtain the dependences for the description of the kinetics of electric birefringence.

(Let us recall that $f(D) = \Delta n_D^{sat} \varphi(D)$.)

In sinusoidal electric fields with intensity $E = E_0 \cos \omega t$, the distribution function with respect to orientations of dielectrically anisotropic and polar particles depends on time; hence, the observed birefringence Δn also changes with time. For dielectrically anisotropic particles, instant electric birefringence $\Delta n(\omega t)$ of the solution is defined by the following relationship [4]:

$$\Delta n(\omega t) = \Delta n_0 \left[1 + \frac{\cos(2\omega t - \phi)}{(1 + 4\omega^2 \tau_0^2)^{1/2}} \right], \quad (11)$$

Here, $\tan \phi = \omega/(3D)$, ω is the cyclic frequency, and ϕ is the phase shift between the applied electric field and optical response.

In the case of a polydisperse system, Eq. (11) with allowance for Eq. (4) appears as

$$\Delta n(\omega t) = \frac{E^2}{15k_B T} \int_{D_c}^{D_d} \gamma(D) \left[1 + \frac{\cos(2\omega t - \phi)}{(1 + 4\omega^2 \tau_0^2)^{1/2}} \right] f(D) dD \quad (12)$$

When dependences $\Delta n(t)$ and $\Delta n(\omega)$ are experimentally determined, Eqs. (10) and (12) can be treated as integral equations for estimating functions $f(D)$. To find function $\varphi(D)$, it is necessary to know the dependences of optical and dielectric polarizability on the dimensions of particles.

Electrooptical Effects in Scattering Systems

When the dimensions of particles are close to the wavelength of light, intense scattering is observed and this scattering markedly changes with varying orientation of particles with respect to the wave vector and polarization line of the beam of incident light. The optical characteristics of such systems can be characterized by the natural light attenuation factor (the product of turbidity and the length of the cuvette with me system under study), which is calculated by means of the following relationship $K = \ln(J_0/J)$, where J_0 and J are the intensity of incident and passed light beams, respectively. This parameter can be easily and correctly measured in experiments. In systems containing nonspherical light scattering particles, the electric field is able to induce the conservative dichroism, which is associated with the dependence of K on the polarization direction of incident light with respect to the direction of the applied field, which orients the particles. This value can be represented as the following relationship [12]:

$$N = (K_{\parallel} - K_{\perp}) / (K_{\parallel}^{sat} - K_{\perp}^{sat}), \quad (13)$$

where K_{\parallel} and K_{\perp} are the natural attenuation factors of light polarized along the field and perpendicular to it, respectively. The difference $K_{\parallel}^{sat} - K_{\perp}^{sat}$ is equal to

$K_{\parallel} - K_{\perp}$ when the orientation of particles is complete.

The values of K_{\parallel}^{sat} and K_{\perp}^{sat} cannot be calculated theoretically, but they can be measured experimentally because light-scattering particles are quite large and their complete orientation under the action of the applied field can be attained.

Experimental verification shows [27] that, in white light, N can be described by Eq. (2). According to Eq. (13), $0 \leq N < 1$ and, in this case, $A_0 = N^{sat} = 1$ in Eq. (2). Then,

$$N(E^2) = \Phi(E^2, \gamma), \quad N(t) = \Phi(t, D). \quad (14)$$

To describe the dependences of the stationary effect resulting from conservative dichroism on E and its relaxation from the state of saturated orientation of particles in the polydisperse system, it is necessary to use the distribution functions with dichroic weights ΔK_{γ} and ΔK_D :

$$f(\gamma) = \Delta K_{\gamma} \varphi(\gamma), \quad f(D) = \Delta K_D \varphi(D). \quad (15)$$

Parameters ΔK_{γ} and ΔK_D define the maximum contributions to N^{sat} from particles with given γ and D , respectively. In polydisperse systems, the dependence of N on the applied field and free relaxation from the state of saturated orientation of particles appears as

$$N(E^2) = \int_{\gamma_c}^{\gamma_d} \Phi(E^2, \gamma) f(\gamma) d\gamma. \quad (16)$$

$$N(t) = \int_{D_c}^{D_d} e^{-6Dt} f(D) dD \quad (17)$$

When the electric field does not result in complete orientation of particles, the profiles of relaxation curves in polydisperse colloidal systems depend on the field intensity, and relaxation N is described by the following relationship [12]:

$$N(E^2, t) = \int_{\gamma_c}^{\gamma_d} \int_{D_c}^{D_d} e^{-6Dt} \Phi(E^2, \gamma) f(D, \gamma) d\gamma dD, \quad (18)$$

where $f(\gamma, D) = \Delta K_{\gamma, D} \varphi(\gamma, D)$.

Equation (18) can be treated as the integral equation for the calculation of $f(\gamma, D)$.

In systems with high electric conductivity, only fields with low intensity resulting in poor orientation of particles can be used. In this case, it seems expedient to use only low fields as

$$E = E_0 \sin(\Omega t) \sin(\omega t) \quad (19)$$

and to study the dispersive dependence of electrooptical effect $N(\omega)$ when Ω is fixed. The particles are polarized by the electric field at frequencies $\Omega + \omega$ and $\Omega - \omega$; however, when $\Omega \gg \omega$, we can neglect the polarizability dispersion and assume that the orienta-

tion of particles results from polarizability anisotropy γ at frequency Ω . Ω is high, and a constant dipole moment of particles does not affect their orientation.

In the field given by Eq. (19), the dependence $N(\omega t)$ in the polydisperse colloidal system appears as [28]

$$N(\omega t) = N_0 + N_s(\omega)\sin 2\omega t - N_c(\omega)\cos 2\omega t \quad (20)$$

Here,

$$N_0 = \frac{E_0^2}{60k_B T} \int_{D_c}^{D_d} \gamma(D) f(D) dD \quad (21)$$

$$N_s(\omega) = \frac{E_0^2}{60k_B T} \int_{D_c}^{D_d} \gamma(D) \frac{\omega}{3D} \left(1 + \frac{\omega^2}{9D^2}\right)^{-1} f(D) dD \quad (22)$$

$$N_c(\omega) = \frac{E_0^2}{60k_B T} \int_{D_c}^{D_d} \gamma(D) \left(1 + \frac{\omega^2}{9D^2}\right)^{-1} f(D) dD \quad (23)$$

Dependences $N_s(\omega)$ and $N_c(\omega)$ are estimated experimentally with accuracy to a constant factor equal to the difference $K_{\parallel}^{sat} - K_{\perp}^{sat}$, because, in a low field, it cannot be estimated. Having solved Eqs. (20) or (21) and taking into account dependence $\gamma(D)$, we can calculate $f(D)$ with accuracy to a factor $K_{\parallel}^{sat} - K_{\perp}^{sat}$.

This method does not require the saturated orientation of particles; hence, it can be used for studying polydispersity of rigid-chain or other polymers with electric birefringence. In this case, it is sufficient to replace dependences $N(\omega t)$, $N_s(\omega)$, and $N_c(\omega)$ in Eqs. (20)–(23) by dependences $\Delta n(\omega t)$, $\Delta n_s(\omega)$, and $\Delta n_c(\omega)$, and $f(D) = \Delta K_D \varphi(D)$ by $f(D) = \Delta n_D^{sat} \varphi(D)$. The latter is also involved in Eqs. (10) and (12).

SOLUTION OF ELECTROOPTICAL INTEGRAL EQUATIONS

Statement of the Problem

Equations (8), (10), (12), (16), (17), (18), (22), and (23) are the integral Fredholm first-order equations with respect to the distribution functions of particles over γ and D with analytically described kernels and experimentally measured free terms. In general form, these equations can be written as

$$\int_a^b K(x, \xi) f(\xi) d\xi = A(x) \quad (24)$$

$$\int_a^b \int_c^d K_1(x, \xi) K_2(y, \eta) f(\xi, \eta) d\eta d\xi = A(x, y) \quad (25)$$

Here, K is the kernel of integral equation, f is the desired distribution functions of the particles with

respect to the parameters, A is the right-hand side of the integral equation. Since the right-hand side is experimentally estimated, it is given at points $A_i = A(x_i)$, $0 \leq i \leq I$ (or $A_{ij} = A(x_i, y_j)$, $0 \leq i \leq I$, $0 \leq j \leq J$ for the two-dimensional integral equation). We also assume that the integration limits are specified.

Equations (24) and (25) belong to the class of incorrect problems [29]. The methods for their solution are associated with the introduction of additional conditions, and the desired function should satisfy these conditions (see for example, [30–32]).

Critical Review of the Existing Approximate Methods of Solution

Consider the main methods for numerical solution of equations like (24). The regularization method proposed by Tikhonov [33, 34] involves the reduction of the problem on solving the initial integral equation to solving the problem on the search for the functional minimum as follows:

$$\|\hat{K}f - A\|^2 + \alpha \|\hat{\Gamma}f\|^2 \quad (26)$$

Here, \hat{K} is the operator of the kernel of the integral equation, f is the desired function, A is the experimentally estimated parameter, $\hat{\Gamma}$ is the regularizing operator, α is the regularization parameter, and $\|\cdot\|$ is the Euclidean norm. In many cases, the problem of finding f , at which functional (26) attains its minimum, reduces to solving the system of linear algebraic equations with respect to unknown values $f_i = f(x_i)$ by selecting the norm and regularizing operator. In applications, the sum of squares of the expression standing under the norm sign taken at a certain set of points is often used as the norm $\|\cdot\|^2$ (so $\|\hat{K}f - A\|^2$ will mean the residual between the left- and right-hand sides of the equation $\hat{K}f = A$). The regularizing operator is selected as either identical (in the search for solutions with the minimum norm) or differential (under the assumption that the solution is a smooth function). In numerical algorithms that give the solution of the integral Fredholm first-kind equation, a symmetrized equation rather than the initial integral equation is used. This approach makes it possible to solve the equations at higher errors in estimating A as compared with the initial method. In the method of truncated singular value decomposition, Eqs. (24) and (25) are solved in terms of least squares,

$$\|Kf - A\|^2 \rightarrow \min, \quad (27)$$

and solving problem (27) reduces to solving the system of linear algebraic equations by singular decomposition.

In both regularization and truncated singular value decomposition, specific parameters of the method exist (the regularization parameter, the rank of the

pseudoinverse matrix), and selection of their values strongly affects its solution. To estimate the above parameters, special numerical methods are used [33–35].

In addition to the methods for solving equations like (24) and (25), let us also mention the v method [36] and the method of maximum entropy [37].

The existing numerical realizations of the above methods for solving Eqs. (24) strongly depend on the selection of the method's parameters as well as on the error with which the free term of the equation is estimated.

Main Principles of the Proposed Solution Method

The main idea concerns application of the least-squares method, which is used to solve Eqs. (24) and (25). Namely, the functional is constructed; this functional is the function of parameters z of function f , and its minimum is associated with parameters \hat{z} , which correspond to the solution of the stated problem [38, 39]. As parametrization of the desired function f , the class of piecewise-smooth polynomial functions was chosen; the parameters are the coefficients of polynomials. Several conditions are imposed on the conditions of polynomials.

Assume that penalty function $\varphi_k(z)$ corresponds to a certain condition (constraints on z) if $\varphi_k(z) = 0$ when this condition holds; $\varphi_k(z) > 0$ in the opposite case. The functional corresponding to the constraints imposed on the solution can be written as

$$G(z) = \sum_{k=1}^m \varphi_k(z) \quad (28)$$

When all constraints imposed on the desired function are fulfilled simultaneously, the functional achieves its minimum (zero) value. The applied penalty functions are the residuals of the initial equation and other integral equations, which are derived from the initial equation as well as the penalty functions on the distortion of boundary conditions and smoothness of the solution. Generally, any additional information concerning the desired solution written as the penalty function takes into account all known features of the problem. From the manifold of the above-considered penalty functions, functions are selected such that nonuse of even one of the them leads to conflict between the model and reconstructed distribution function within a certain interval for Eqs. (8), (10), (12), (16)–(18), (22), and (23). However, depending on additional conditions of the stated problem, other conditions can be obtained and their addition to functional G as penalty functions can provide better agreement between the model and reconstructed distribution function.

Penalty Functions

All penalty functions on the distortion of residual of integral equations can be written as follows:

$$\varphi_f(z) = \sum_{v=1}^{r_j} R_j^2(x_v), \quad x_1, \dots, x_{r_j} \in \{\mathfrak{R}, \mathfrak{R}^2\} \quad (29)$$

Consider specific penalty functions that can be derived from Eqs. (24) and (25).

Penalty for residual of integral equations (24) and (25). As was mentioned above, Eqs. (24) and (25) are treated as one of the penalties on the desired function f . Using form (29), we consider these constraints assuming that

$$R_1(x) = \int_a^b K(x, \xi) f(\xi) d\xi - A(x) \quad (30)$$

$$R_1(x, y) = \int_a^b K_1(x, \xi) \int_a^b K_2(y, \eta) f(\xi, \eta) d\eta d\xi - A(x, y) \quad (31)$$

From initial Eqs. (24) and (25), some other integral equations can be derived and penalties on the corresponding residuals are defined.

Penalty for residual of integrated equation. By repeatedly integrating initial Eqs. (24) and (25) over interval $[x_0, x]$, we arrive at the following relationships at $k = 1, 2, \dots$:

$$\int_a^b I^k(x, \xi) f(\xi) d\xi = B^k(x) \quad \text{at } k = 1, 2, \dots \quad (32)$$

$$\int_a^b I_1^k(x, \xi) \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi = B_1^k(x, y) \quad (33)$$

at $k = 1, 2, \dots$,

where

$$I^1(x, \xi) = \int_{x_0}^x K(x, \xi) dx, \quad B^1(x) = \int_{x_0}^x A(x) dx,$$

$$I^k(x, \xi) = \int_{x_0}^x I^{k-1}(x, \xi) dx, \quad B^k(x) = \int_{x_0}^x B^{k-1}(x) dx,$$

$$I_1^1(x, \xi) = \int_{x_0}^x K_1(x, \xi) dx, \quad B_1^1(x, y) = \int_{x_0}^x A(x, y) dx,$$

$$I_1^k(x, \xi) = \int_{x_0}^x I_1^{k-1}(x, \xi) dx, \quad B_1^k(x, y) = \int_{x_0}^x B_1^{k-1}(x, y) dx$$

Using form (29), we take into account the above constraints by assuming that

$$R_{2,k}(x) = \int_a^b I^k(x, \xi) f(\xi) d\xi - B^k(x) \quad (34)$$

at $k = 1, 2, \dots$

$$R_{2,k}(x, y) = \int_a^b I^k(x, \xi) \times \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi - B^k(x, y) \quad (35)$$

at $k = 1, 2, \dots$

Penalty on the residual of symmetrized equations.

By multiplying initial equations (24) by kernel $K(x, \mu)$ and by integrating the derived relationship over x , we arrive at the following equation with symmetric kernel $\overline{K(\mu, \xi)}$:

$$\int_a^b \overline{K(\mu, \xi)} f(\xi) d\xi = \overline{A(\mu)} \quad (36)$$

In a similar manner, the following modified equation can be derived from Eq. (25):

$$\int_a^b \overline{K_1(\mu, \xi)} \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi = \overline{A(\mu, y)} \quad (37)$$

We take into account these additional relationships using form (29):

$$R_{3,k}(\mu) = \int_a^b \overline{K(\mu, \xi)} f(\xi) d\xi - \overline{A(\mu)} \quad (38)$$

at $k = 1, 2, \dots$

$$R_{3,k}(\mu, y) = \int_a^b \overline{K_1(\mu, \xi)} \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi - \overline{A(\mu, y)} \quad (39)$$

at $k = 1, 2, \dots$

Penalties on the residuals of differentiated equations. By differentiating Eqs. (24) and (25) k times, we arrive at

$$\int_a^b Y^k(x, \xi) f(\xi) d\xi = D^k(x) \quad \text{at } k = 1, 2, \dots, \quad (40)$$

$$\int_a^b Y_1^k(x, \xi) \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi = D^k(x, y) \quad (41)$$

at $k = 1, 2, \dots$,

where

$$Y^k(x, \xi) = \partial^k K(x, \xi) / \partial x^k, \quad D^k(x) = \partial^k A(x) / \partial x^k,$$

$$Y_1^k(x, \xi) = \partial^k K_1(x, \xi) / \partial x^k,$$

$$D^k(x, y) = \partial^k A(x, y) / \partial x^k.$$

To take into account constraints (40) and (41) through Eq. (29), we assume that

$$R_{4,k}(x) = \int_a^b Y^k(x, \xi) f(\xi) d\xi - D^k(x) \quad (42)$$

at $k = 1, 2, \dots$

$$R_{4,k}(x, y) = \int_a^b Y_1^k(x, \xi) \times \int_c^d K_2(y, \eta) f(\xi, \eta) d\eta d\xi - D^k(x, y) \quad (43)$$

at $k = 1, 2, \dots$

Penalties on the residuals of equations for moments

of derivatives. If $K(x, \xi)$ is the function of product $x\xi$, then it follows from Eq. (22) [40] that

$$\int_a^b K(x\xi) \xi^m f^{(m)}(\xi) d\xi = A_m(x) \quad \text{at } m = 1, 2, \dots$$

$$A_0(x) = A(x), \quad (44)$$

$$A_{m+1}(x) = (1 - m) A_m(x) - x \partial A_m(x) / \partial x.$$

To take into account constraints (44) through Eq. (29), we assume that

$$R_{5,k}(x) = \int_a^b K(x\xi) \xi^m f^{(m)}(\xi) d\xi - A_m(x) \quad (45)$$

at $m = 1, 2, \dots$

In a similar way, the residual for Eq. (25) can be derived:

$$R_{5,k}(x, y) = \int_a^b K_1(x\xi) \times \int_c^d K_{21}(y, \eta) \xi^m f^{(m)}(\xi, \eta) d\eta d\xi - A_m(x, y) \quad (46)$$

at $m = 1, 2, \dots$

From the above penalties for Eq. (25), here, we present the modified equations only with respect to the first argument A ; however, these equations can be also obtained using another argument, and their residuals are added to functional $G(z)$.

Penalty on the distortion of boundary conditions.

Consider boundary conditions with respect to f and its derivatives $f^{(i)}$ assuming for Eqs. (24) and (23), respectively,

$$\varphi_6(z) = \sum_{i=0}^s [(f^{(i)}(z, a) - f^{(i)}(a))^2 + (f^{(i)}(z, b) - f^{(i)}(b))^2], \quad (47)$$

$$\varphi_6(z) = \sum_{i=0}^s [(f^{(i)}(z, a, \eta) - f^{(i)}(a, \eta))^2 + (f^{(i)}(z, b, \eta) - f^{(i)}(b, \eta))^2 + (f^{(i)}(z, \xi, c) - f^{(i)}(\xi, c))^2 + (f^{(i)}(z, \xi, d) - f^{(i)}(\xi, d))^2] \quad (48)$$

For the above relationships in relation to the distribution functions according to their parameters, we have

$$f^{(i)}(a) = f^{(i)}(b) = f^{(i)}(c) = f^{(i)}(d) = 0.$$

Penalty on the distortion of the smoothness of solution. Let us consider the smoothness of order s of the solution f assuming, for each $i = 0, \dots, s$, that for Eqs. (24)

$$\varphi_{7,i} = \sum_{k=1}^{N-1} (f_k^{(i)}(\xi_k) - f_{k+1}^{(i)}(\xi_k))^2, \quad (49)$$

and for Eq. (25)

$$\varphi_{7,i} = \sum_{k=1}^{N-1} (f_k^{(i)}(\xi_k, \eta) - f_{k+1}^{(i)}(\xi_k, \eta))^2 + (f_k^{(i)}(\xi, \eta_k) - f_{k+1}^{(i)}(\xi, \eta_k))^2 \quad (50)$$

Here, f_k is the polynomial presentation of the desired function in the k th interval. Using Eqs. (49) and (50), at the junction points of piecewise-smooth polynomials, linear algebraic equations can be written and these equations are added to the initial functional as one of the penalty functions. In the case of functions with one variable, at the junction point between two intervals, the equality of s values of derivatives and the initial function is expressed simply by their equality at a point; as a result, we have equation s . For the function with two variables, this equality should exist on the straight line separating the above intervals. This equality occurs if the values of the k th derivative along this line are calculated; as a result, two polynomials of order P specified on this line are obtained; then, by equating coefficients at equal orders of polynomials, the system $s \times P$ of linear equations is obtained, and these equations are added to the initial functional as additional penalty functions.

Estimation of the Local Minimum

The necessary condition for the local minimum of the functional (28) is the following system of linear equations with respect to unknown values z :

$$\partial G(z)/\partial z_i = 0, \quad i = 1, \dots, n \quad (51)$$

For the numerical solution of linear system of equations (28), the DGESVD procedure from the LAPACK software [41] is used. This procedure makes

it possible to find the singular matrix decomposition in the system of linear algebraic equations.

Calculation of Modified Kernels

Many kernels of Eqs. (32)–(47) can be derived from each other in an iterative manner. To speed up calculations, they should be represented in a form that makes it possible to calculate the values of kernels at any points from the domain of definition without the use of iterative calculations. Therefore, each kernel of the modified equation [condition (2)–(6)] is represented as a piecewise-smooth polynomial like

$K(x, \xi) = \sum_{i,j \geq 0}^{i+j \leq P} x^i \xi^j$ on the set of rectangles, which represents the domain of its definition.

EVALUATION OF THE EFFICACY OF THE METHOD

Computer-Aided Simulation

One of the ways to estimate the correctness of the solution of the above problems is computer-aided simulation. As model functions representing the solution, we selected the functions with one or two maxima in order to evaluate the possibility of the resolution of several maxima if they exist in the systems under study. Moreover, this approach makes it possible to estimate the contribution from the measurement errors to the error of solution of the problem. The model function is defined as

$$f(\xi) = \exp(-a(\xi - b)^2) \quad (52)$$

or

$$f(\xi) = \exp(-a_1(\xi - b_1)^2) + \exp(-a_2(\xi - b_2)^2) \quad (53)$$

$$f(\xi, \xi_2) = \sum_i a_i \exp\left(-\frac{b_i(\xi_1 - c_i)^2}{c_i^2 - (\xi_1 - c_i)^2} - \frac{d_i(\xi_2 - f_i)^2}{f_i^2 - (\xi_2 - f_i)^2}\right) \quad (54)$$

in the case of Eqs. (24) and (25).

Kernels $K_{re}(x, \xi) = \exp(-6x\xi)$ and $K_s(x, y) = (x/3\xi)/(1 + (x/3\xi)^2)$ are selected for (24), and these kernels are similar to the kernels of Eqs. (17) and (22); this operation makes it possible to calculate the free term according to the model function and a given kernel. Then, to the free term, a certain random variable is added, and this term corresponds to the relative error $\varepsilon = 0-5\%$. For Eq. (25), kernel $K_{re}(x_1, x_2, \xi_1, \xi_2) = K_0(x_1, \xi_1)\exp(-6x_2\xi_2)$ is selected; in this kernel, $K_0(x_1, \xi_1)$ is defined by Eq. (3) if Φ , E^2 , and γ are substituted by K_0 , x_1 , and ξ_1 , respectively. This kernel is involved in eq. (18). The added random variable of free term in Eq. (25) calculated at given $K_{re}(x_1, x_2, \xi_1, \xi_2)$ and $f(\xi_1, \xi_2)$ specifies the relative error $\varepsilon = 1\%$. The derived dependences modeling relaxation and dispersion curves of electrooptical effect were

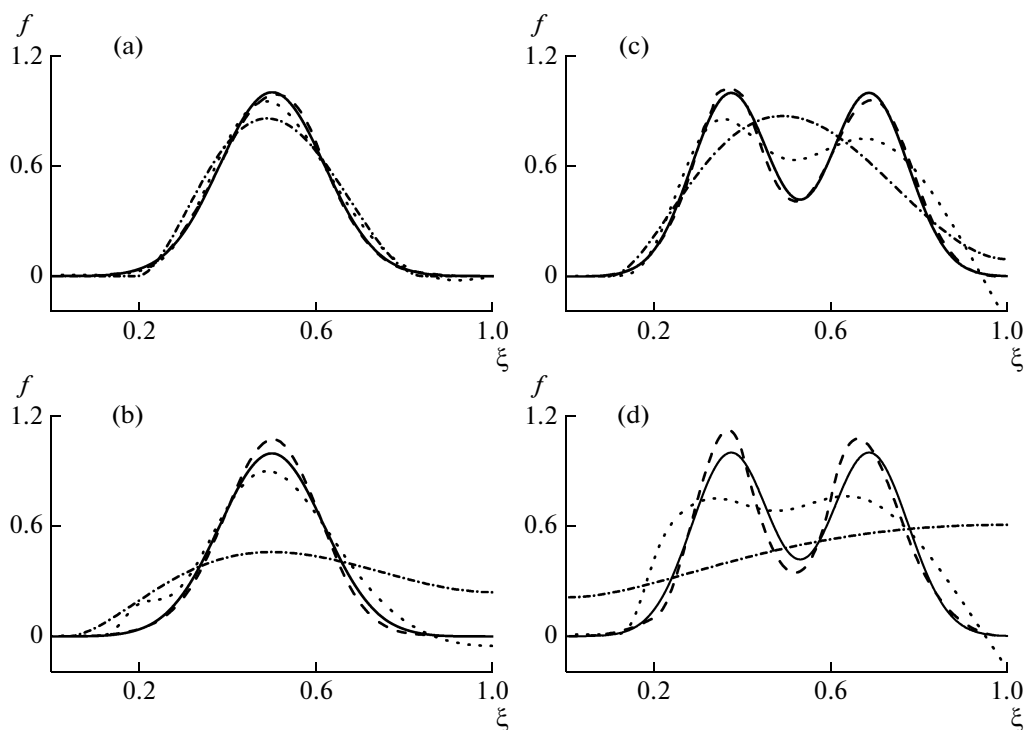


Fig. 1. Model function of the solution to Eq. (24) with kernel $K_{re}(x, \xi)$. Solid line—models (52) (a, b) and (53) (c, d). Solutions calculated by the programs: ICP (dashed line), Z (points); PTIPR (dot-and-dash line). $\varepsilon = 0$ (a, c) and 5% (b, d).

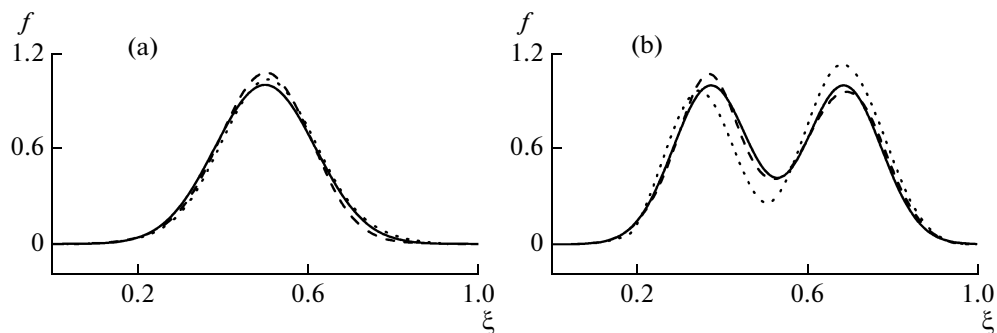


Fig. 2. Model function of the solution to Eq. (24) with kernel $K_s(x, \xi)$ at $\varepsilon = 5\%$. Solid line—model (52) (a) and (53) (b). Solutions calculated by the programs: ICP (dashed line), Z (points).

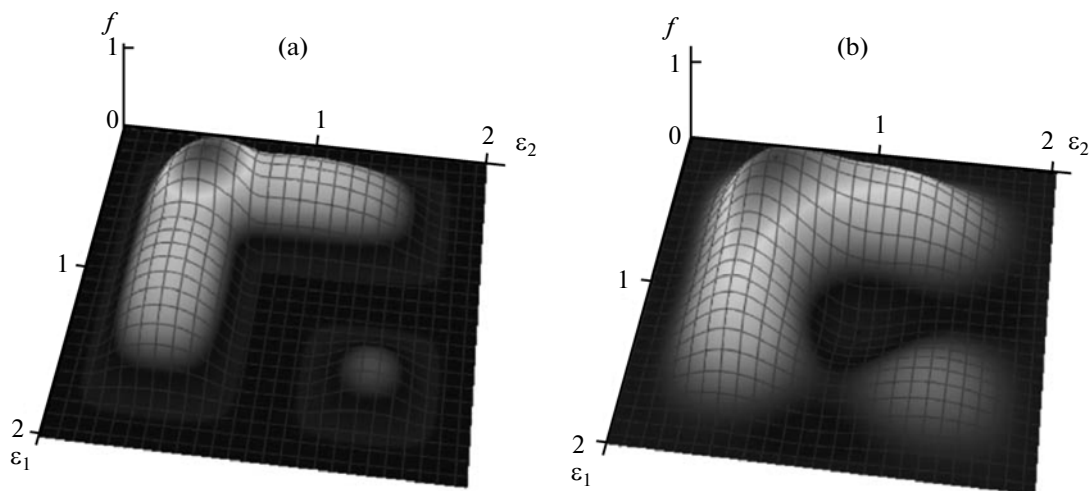


Fig. 3. Model function (53) (a) and solution of Eq. (25) (b).

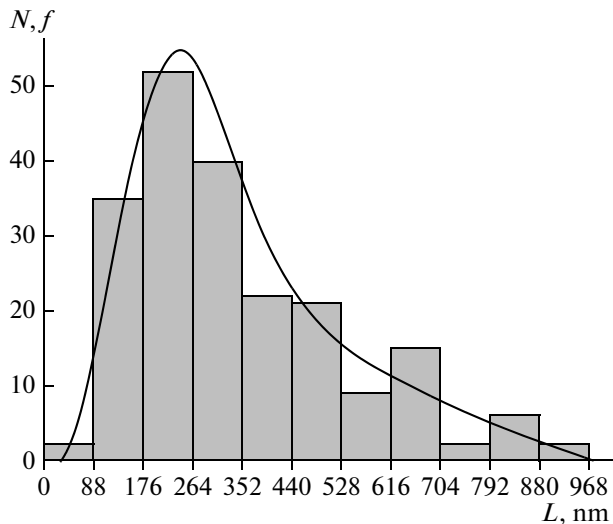


Fig. 4. Function (curve) and length distribution histogram for nanotubes based on magnesium hydroxysilicate.

used for the solution of the selected integral equations. Relationship (24) is solved according to the above-proposed algorithm and another two algorithms based on the regularization method. Equation (25) is solved only by the proposed method because, at the present time, no available regularization for Eq. (25) exists. The efficacy of the algorithms used is analyzed by comparing the solutions to Eqs. (24) and (25) with the initial model functions (52)–(54), which are adopted as exact solutions.

Herein, the computer programs based on the regularization method for solving the above equations are called Z and PTIPR. Z was developed for solving Eqs. (16), (17), (22), and (233). This program is based on the selection of the regularizing parameter α accord-

ing to the principle of the minimum residual of the symmetrized equation [42]. PTIPR [43] is based on the principle of minimization of the smoothing functional by the method of conjugated gradients. Herein, the program based on the proposed method is denoted ICP.

Simulation shows (Figs. 1–3) that the methods based on the regularization procedure appear to be less effective for functions with several extrema even though their use is quite admissible when the desired function has one extremum. Moreover, the proposed method is more stable as compared with Z and PTIR when the right-hand side of the integral equation is given with a high error. The fact that the solution cannot be obtained with a high error in the right-hand side triggered the development of a new method.

The comparison of model functions and solutions of the Fredholm equations used in electrooptics allows us to conclude that the proposed method of penalty functions appears to be very efficient for solving inverse problems of electrooptics and allows us to define the distribution functions of particles with respect to one and two parameters.

Application of the Method for Studying Polydisperse Systems

Various versions of the regularization method have been used earlier in electrooptical experiments for studying polarizability and estimating the dimensions in polydisperse systems [27, 32]. This method concerns the definition of distribution functions with respect to one of their parameters.

Figure 4 presents the length distribution function and histogram for nanotubes with composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ prepared by the hydrothermal method [44]. The distribution function was calculated

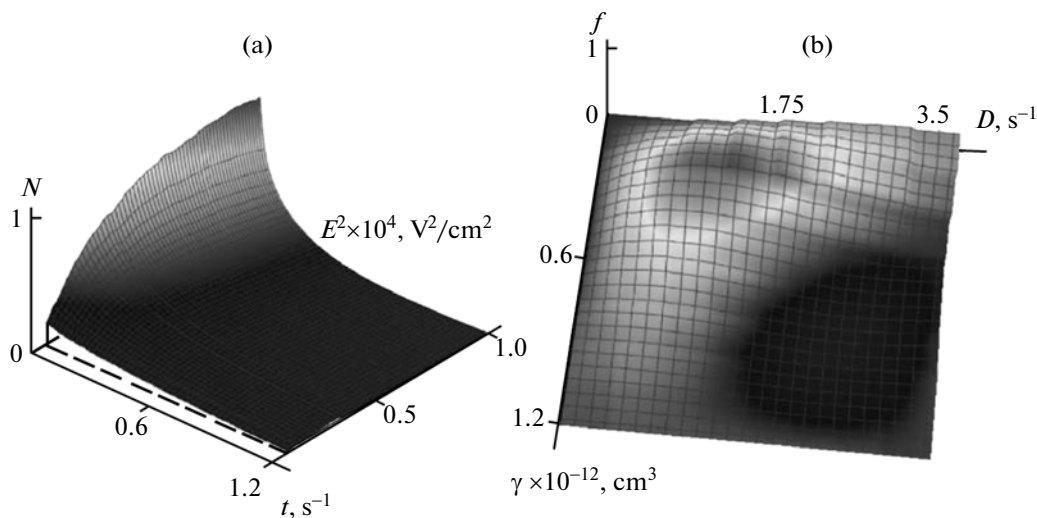


Fig. 5. Relaxation dependence $N(E^2, t)$ (a) and distribution function $f(\gamma, D)$ (b) of graphite particles.

according to the proposed method from the relaxation dependence of the electrooptical effect in an aqueous solution of nanotubes. A histogram illustrating the length distribution of nanotubes is constructed from electron microscopic analysis.

Attempts have been made to estimate experimentally the distribution function for particles with respect to two parameters, namely, $f(\gamma, D)$. This problem is solved by the proposed method and ICP. Figure 5 presents the experimental dependence $N(E^2, t)$ and the calculated distribution function $f(\gamma, D)$ for graphite particles in water. Analysis of function $f(\gamma, D)$ shows that this dependence does not conflict with the earlier results.

CONCLUSIONS

The proposed method of penalty functions can be used for the electrooptical study of colloidal systems. Analysis of the efficacy of this approach shows that it is possible to obtain more accurate solutions of inverse problems of electrooptics as compared with the regularization method and can be used to estimate the two-parameter distribution functions of the particles. The class of the systems under study can be widened and include the solutions of nanotubes, rigid-chain polymers as well as suspensions of structures based on nanotubes, macromolecules, and fullerenes. Experimental dependences, which can be represented as integral first-kind integral equations with other kernels and data from other physical experiments, for example, dynamic light scattering or small-angle scattering, can also be treated by this method.

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