



# Numerical methods for inverse problems in electrooptics of polydisperse colloids

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## Abstract

In this paper we propose a new method for the determination of the distribution of electrical and geometrical particle parameters based on electrooptical experimental data. The electrooptical method leads to the solution of inverse ill-posed problems. The main equations for the determination of the distribution of particles on these parameters are presented. To find out the distribution functions from the electrooptical experimental data one has to solve the first-kind Fredholm integral equation corresponding to the problem under study. The proposed method of its solution is based on the penalty functions method. The results of modelling that let us compare the various numerical methods are presented.

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## 1. Introduction

For the solution of the inverse problem, when the domain of parameter values is unknown or known approximately, it is desirable to have a unique algorithm for the determination of the kernels of integral equations with the desired precision, which has to correspond to the problem in hand. Such an algorithm that uses band matrices of infinite dimension and fulfilling the requirements of the inverse electrooptical problems was developed in this work. As well known, solution of the first-kind Fredholm integral equations used to be carried out using the regularization technique [1]. On the other hand this technique requires high skills from the researcher and does not always lead to reliable results. This makes the electrooptical study complex for a number of polydisperse systems. Here we propose a new algorithm for the solution of such equations. It uses the non-linear least-squares method together with the penalty functions that takes additional distribution functions properties into consideration. The computational algorithm proposed is stable and is weakly influenced by the errors in the experiment and lets us reliably determine the distribution functions on one, two, and three parameters that characterize particles. It is applicable to the

inverse problems of electrooptics, magnetooptics, and dynamic light scattering.

## 2. Physical problem statement

If the observed effect is proportional to the concentration of particles, then we get the following relation

$$A(\vec{\psi}) = \int_{\Xi} K(\vec{\psi}, \vec{\xi}) f(\vec{\xi}) d\vec{\xi}, \tag{1}$$

where  $(K(\vec{\psi}, \vec{\xi}))$  is the theoretical dependency of  $(A(\vec{\psi}))$  when all macromolecules have the same characteristic  $(\vec{\xi})$ . The dependency  $(A(\vec{\psi}))$  is the observed effect.

Here we will discuss the case of the application of external electric field to isotropic system, which makes it anisotropic, no matter whether this is macromolecular solution or any nano-disperse system. In this case the experimental data is the dependence of optical anisotropy on field characteristic or time. We consider below the case of determination of the particle distribution function of just one parameter. We also consider it being averaged on other parameters:  $f(\xi_i) = \int f(\vec{\xi}) d\xi^1 \dots d\xi^{i-1} d\xi^{i+1} \dots d\xi^n$ .  $(A(\psi^k))$  corresponds to fixed parameters  $(\psi^1, \dots, \psi^{k-1}, \psi^{k+1}, \dots, \psi^m)$ .

In electrooptical experiment  $(A(\psi))$  can be the dependence of birefringence, dichroism or dissipation of energy to a certain angle on time  $t$ , electric field strength  $E$  and frequency  $\omega$ .

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44 Then the distribution function is the one on sizes  $r$ , rotary dif-  
45 fusion coefficients  $D$ , values of polarizability anisotropy  $\Delta\gamma$   
46 and constant dipole moments of particles and macromolecules:  
47  $\psi^k = E, \omega, t, \xi^i = r, D, \Delta\gamma, \mu$ . Here we consider the following  
48 cases:

- 49 1. The stationary effect described by the following formulae in  
50 sine electric field of high frequency  $E = E_0 \sin(\Omega t)$ :

$$A(E^2) = \int_{\Delta\gamma_1}^{\Delta\gamma_2} K_{st}(E^2, \Delta\gamma) f(\Delta\gamma) d\Delta\gamma,$$

$$K_{st}(E^2, \Delta\gamma) = \frac{1.5 \int_0^1 x^2 e^{\Delta\gamma E^2 x^2} dx}{\int_0^1 e^{\Delta\gamma E^2 x^2} dx - 0.5}. \quad (2)$$

- 52 2. Relaxation from the state of complete orientation of particles  
53 and macromolecules after application of strong electric field  
54 is described as follows:

$$A(t) = \int_{D_1}^{D_2} K_{rel}(t, D) f_2(D) dD,$$

$$K_{rel}(t, D) = e^{-6Dt}. \quad (3)$$

- 55 3. Relaxation of the electrooptical effect. General case.

$$A(E^2) = \int_{\Delta\gamma_1}^{\Delta\gamma_2} \int_{D_1}^{D_2} K_{rel}(t, D) K_{st}(E^2, \Delta\gamma) f(\Delta\gamma) d\Delta\gamma dD. \quad (4)$$

- 56 4. In the case of weak field  $E = E_0 \sin(\Omega t) \sin(\omega t)$  we obtain:

$$A(\omega) = A_0 + A_s(\omega) \sin 2\omega t + A_c(\omega) \cos 2\omega t, \quad (5)$$

57 where one can get  $A_s$  and  $A_c$  from the experiment and use  
58 the following formulae:

$$A_s(\omega) = \int_{D_1}^{D_2} K_s(\omega, D) f_2(D) dD,$$

$$K_s(\omega, D) = \frac{E^2 a \Delta\gamma \tilde{\omega}}{60 kT(1 + \tilde{\omega}^2)}, \quad \tilde{\omega} \equiv \frac{\omega}{3D}.$$

59 An analogous equation can be obtained for  $A_c(\omega)$ , but we do  
60 not consider it here.

61 Furtheron we will only discuss the cases (2), (3), and (4). For  
62 details see [2].

### 62 3. Mathematical problem statement

63 We consider Fredholm equations of the first kind

$$64 \int_a^b K(\psi, \xi) f(\xi) d\xi = A(\psi) \quad (6)$$

$$65 \int_a^b K_1(\psi, \xi) K_2(\zeta, \eta) f(\xi, \eta) d\xi d\eta = A(\psi, \zeta) \quad (7)$$

66 with respect to distribution function  $f$ . One can find the  $L^2$  theory  
67 of this equation in standard textbooks on integral equations [3].  
68 The main result is the Picard's theorem on necessary and suffi-  
69 cient conditions for existence and uniqueness of solution. From  
70 a practical calculation's point of view, this theory is frustrating  
71 because this equation is an ill-conditioned one. It is unstable

with respect to small perturbations of  $A(\psi)$  which, as a rule, is  
approximately known from experiments [4].

### 74 4. Proposed method of solution

75 Despite the ill-conditioning of this problem, there are some  
76 algorithms to solve (6) and (7), for example, using Tikhonov  
77 regularization method. We can use one of the many exist-  
78 ing computer codes based on regularization techniques. Each  
79 of these codes has its own advantages and disadvantages.  
80 Note that all the codes we have tried give better results  
81 when the function  $f$  has just one extreme (is a unimodal  
82 function).

83 We offer the new version of the least-squares method  
84 which solves Fredholm Eqs. (6) and (7) more efficiently  
85 when  $f$  has several internal extremes (multimodal distribu-  
86 tion function  $f$ ). The idea of our method can be explained as  
87 follows:

- 88 1. We consider the  $n$  parameter family

$$\mathcal{F} = \begin{cases} \{f(c, \xi), & c = (c_1, \dots, c_n) \in R\}, & \text{in 1D} \\ \{f(c, \xi, \eta), & c = (c_{11}, \dots, c_{nm}) \in R\}, & \text{in 2D} \end{cases} \quad (8)$$

- 89 2. Instead of solving (6) or (7) directly, we construct the function  
90  $f(\xi) \in \mathcal{F}$  that satisfies the restrictions, which are the impli-  
91 cations of the Eqs. (6) and (7) and other a priori information,  
92 in the least-square sense.

93 To do this, we construct the penalty functions  
94  $\phi_1(c), \dots, \phi_m(c)$  which correspond to above restrictions as  
95 follows

$$96 \phi_k(c) = 0, \quad \text{if the restriction holds} \\ 97 \phi_k(c) > 0, \quad \text{otherwise} \quad (9)$$

- 98 3. We seek the point  $\hat{c}$  which minimizes locally

$$99 G(c) = \sum_{k=1}^m \alpha_k \phi_k(c), \quad (10)$$

100 where  $\alpha_1, \dots, \alpha_n$  are the weight coefficients. The function  
101  $\hat{f}(\xi) = f(\xi, \hat{c})$  (in 1D) or  $\hat{f}(\xi, \eta) = f(\xi, \eta, \hat{c})$  (in 2D) is the  
102 one we sought for. So, instead of solving Fredholm equa-  
103 tion, we consider the following formulation of the problem:  
104 minimize the object function which is the sum of penalty  
105 functions, corresponding to the restrictions which we take  
106 into account.

107 In this work, we do not state any theorems. We judge this method  
108 by the results obtained using the model examples only. To use  
109 this method for real-life problems, one has to consider some  
110 "similar" model problems to choose the suitable weight coef-  
111 ficients  $\alpha_k$ 's and select useful restrictions based on the set of  
112 restrictions we offer below.

4.1. Specification of  $\mathcal{F}$

We define  $\mathcal{F}$  as follows:

$$a = \xi_0 < \xi_1 < \dots < \xi_p = b, \quad c = \eta_0 < \eta_1 < \dots < \eta_q = d$$

$$\mathcal{J}_1 = [\xi_0, \xi_1], \mathcal{J}_2 = [\xi_1, \xi_2], \dots, \mathcal{J}_p = [\xi_{p-1}, \xi_p]$$

$$\mathcal{K}_1 = [\eta_0, \eta_1], \mathcal{K}_2 = [\eta_1, \eta_2], \dots, \mathcal{K}_q = [\eta_{q-1}, \eta_q]$$

$$\vartheta_k(\xi) = \sum_{0 \leq i \leq 3} a_{ki} \xi^i, \quad \vartheta_{kl}(\xi, \eta) = \sum_{0 \leq i \leq j \leq 3} a_{klij} \xi^i \eta^j \in R$$

$$\mathcal{F} = \begin{cases} \{f(c, \xi) : f(c, \xi)|_{\xi \in \mathcal{J}_k} = \vartheta_k(\xi), \quad 1 \leq k \leq p\}, & \text{in 1D} \\ \{f(c, \xi, \eta) : f(c, \xi, \eta)|_{\xi \in \mathcal{J}_k, \eta \in \mathcal{K}_l} = \vartheta_{kl}(\xi, \eta), \quad 0 \leq k \leq p, 0 \leq l \leq q\}, & \text{in 2D} \end{cases}$$

That is,  $\mathcal{F}$  is the class of piecewise polynomial functions with  $\xi_1, \dots, \xi_{p-1}$  (and  $\eta_1, \dots, \eta_{q-1}$  in 2D) being the jump points.

From this structure of the family  $\mathcal{F}$ , we see that functions  $f \in \mathcal{F}$  and their derivatives might have jump points. This implies that the family  $\mathcal{F}$  is wider than the family of Hermite's piecewise cubic polynomials.

On the other hand, we will include the penalty functions of the violation of the continuity of the solution and its derivatives in the object function. Therefore, although the function  $\hat{f}(\xi) = f_{\mathcal{A}}$  which is sought for will be discontinuous, the least-squares method should smooth out all its jumps.

4.2. Penalty functions

The object function in this method is the sum of the penalty functions corresponding to the restrictions we take into account.

We take the penalty functions on the residuals of the original Fredholm equation and other integral equations which we derive as the implications from the original one.

In addition, we use the penalty function on the violation of the boundary conditions and the penalty functions on the violations of the smoothness of the solution. Here we will first write the penalty functions in the case of 1D, and then note the differences in 2D.

We take the penalty functions on integral equation's residuals in the following form

$$\phi_j(c) = \sum_{\nu=1}^r R_j^2(\psi_\nu), \quad \psi_1, \dots, \psi_r \in R. \quad (12)$$

(PR1): The penalty on the residual of the original integral Eq. (6). As we mentioned above, we consider Eq. (6) as one of the restrictions on  $f(\xi)$ . Using the form (12), we take this restriction into account by letting

$$R_1(\psi) = \int_a^b K(\psi, \xi) f(\xi) d\xi - A(\psi) \quad (13)$$

From the original Eq. (6), we derive other integral equations and define the penalty functions corresponding to their residuals.

(PR2): The penalty on the residual of the symmetrized equation. By multiplying the original Eq. (6) by the same kernel  $K(\eta, \xi)$  and integrating the obtained equation by  $\eta$ , Schmidt has

derived the following equation with symmetric kernel  $\overline{K}(\psi, \xi)$ :

$$\int_a^b \overline{K}(\psi, \xi) f(\xi) d\xi = \overline{A}(\psi). \quad (14)$$

Using the form (12), we take this restriction into account by letting

$$R_2(\psi) = \int_a^b \overline{K}(\psi, \xi) f(\xi) d\xi - \overline{A}(\psi) \quad (15)$$

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$$\text{in 1D} \quad (11)$$

(PR3): The penalty on the residual of the differentiated equation. By differentiating the original Eq. (6) several times, we obtain for  $k = 1, 2, \dots$

$$\int_a^b Y^k(\psi, \xi) f(\xi) d\xi = D^k(\psi), \quad (16)$$

where

$$\frac{Y^k(\psi, \xi) = \partial^k K(\psi, \xi)}{\partial \psi^k}, \quad D^k(\psi) = \frac{\partial^k A(\psi)}{\partial \psi^k}. \quad (17)$$

Using the form (12), we take this restriction into account by letting

$$R_{3,k}(\psi) = \int_a^b Y^k(\psi, \xi) f(\xi) d\xi - D^k(\psi), \quad k = 1, 2, \dots \quad (18)$$

(PR4): The penalty on the residual of the integrated equation. By integrating the original Eq. (6) several times over the interval  $[a, \phi]$ , we obtain for  $k = 1, 2, \dots$

$$\int_a^b I^k(\psi, \xi) f(\xi) d\xi = B^k(\psi), \quad k = 1, 2, \dots, \quad (19)$$

where

$$\begin{aligned} I^1(\psi, \xi) &= \int_c^\psi K(\psi, \xi) d\psi, & B^1(\psi) &= \int_c^\psi A(\psi) d\psi, \\ I^k(\psi, \xi) &= \int_c^\psi I^{k-1}(\psi, \xi) d\psi, & B^k(\psi) &= \int_c^\psi B^{k-1}(\psi) d\psi \end{aligned} \quad (20)$$

Using the form (12), we take this restriction into account by letting

$$R_{4,k}(\psi) = \int_a^b I^k(\psi, \xi) f(\xi) d\xi - B^k(\psi), \quad k = 1, 2, \dots \quad (21)$$

(PR5): The penalty on the residual of the moments of the derivatives. Let the kernel  $K(\psi, \xi)$  of the original Eq. (6) be a function of  $\psi\xi$  and let

$$f^{(m)}(a) = f^{(m)}(b) = 0, \quad m = 0, 1, 2, \dots \quad (22)$$

Then, combining the procedures of differentiation and integration by parts, we derive the following formula

$$\int_a^b K(\psi\xi) \xi^m f^{(m)}(\xi) d\xi = A_m(\psi), \quad m = 1, 2, \dots \quad (23)$$

where

$$A_0(\psi) = A(\psi),$$

$$A_{m+1}(\psi) = \frac{(1 - m)A_m(\psi) - \psi \partial A_m(\psi)}{\partial \psi}. \quad (24)$$

Using the form (12), we take this restriction into account by letting

$$R_{5,m}(\psi) = \int_a^b K(\psi\xi)\xi^m f^{(m)}(\xi) d\xi - A_m(\psi), \quad m = 1, 2, \dots \quad (25)$$

(PB): The penalty on the violation of the boundary conditions. We take the boundary conditions into account by letting

$$\phi_6(c) = \sum_{i=0}^2 [(f^{(i)}(c, a) - f^{(i)}(a))^2 + (f^{(i)}(c, b) - f^{(i)}(b))^2]. \quad (26)$$

(PS): The penalty on the violation of the smoothness of the solution. We take the smoothness of the solution  $f(\xi)$  up to the order  $q$  into account by letting

$$\phi_{7,i}(c) = \sum_{k=1}^{p-1} (\vartheta_k^{(i)}(\xi_k) - \vartheta_{k+1}^{(i)}(\xi_k))^2, \quad (27)$$

for each  $i = 0, \dots, q$ .

In the 2D case the residuals (12) are sums on two variables  $(\psi, \zeta)$ , and integration in formulas (13)–(25) is carried out with respect to two internal variables  $(\xi, \eta)$ , just like in the case of

1D equations, since the kernel in (7) is a product:  $K(\psi, \zeta, \xi, \eta) = K_1(\psi, \xi)K_2(\zeta, \eta)$ .

### 4.3. Finding the local minimum

The necessary condition for local minimum is the following system of linear equations with respect to  $c = (c_1, \dots, c_n)$

$$\frac{\partial G(c)}{\partial c_j} = 0, \quad j = 1, \dots, n \quad (28)$$

In general, the standard linear equation solver from the FORTRAN IMSL library complains that this linear system is an ill-conditioned one but still solves this system in the least-square sense with acceptable accuracy.

In conclusion, it is very important to notice that the main idea of the method is that any additional restriction (penalty function) would not worsen the result but might only improve it. We chose them in such a way that discarding any of the restrictions used would deteriorate the agreement of the model and the recovered distribution functions on some part of the definition domain of  $f$ .

## 5. Numerical experiments

To implement the method, we developed the FORTRAN code **ICESolver**. We compared our code with the following two publicly available codes based on the regularization techniques:

**PTIPR**: The code from Tikhonov [4] devoted to the ill-posed problems.

**ZERT**: The code based on regularization technique specifically adapted to the problems of colloidal physics [5].

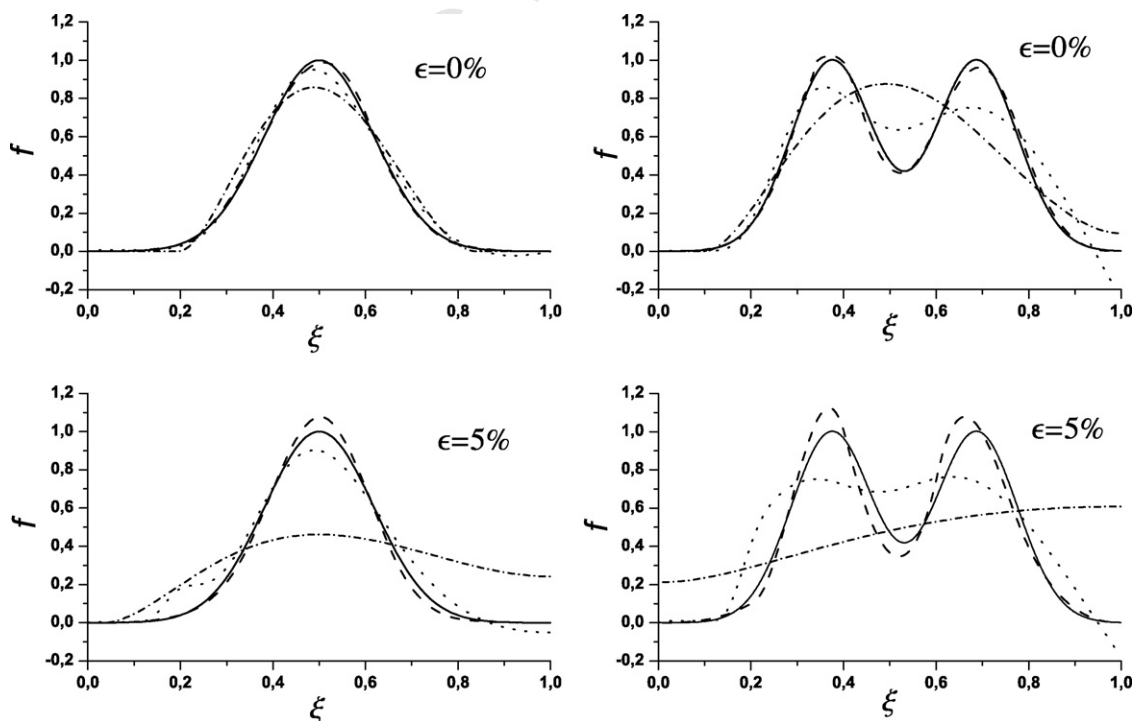


Fig. 1. Results of  $f(\xi)$  recovery modelling. Solid curve is the model function, dotted curve is the solution obtained by **ZERT**, dash-dotted curve is obtained by **PTIPR**, dashed curve is obtained by **ICESolver**.

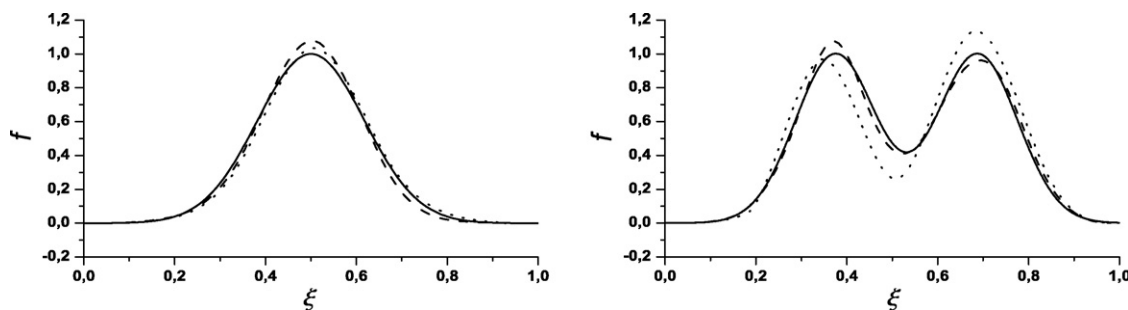


Fig. 2. Results of  $f(\xi)$  recovery modelling. Solid curve is the model function, the solutions obtained by ICESolver with  $\epsilon = 0\%$  (dotted curve),  $\epsilon = 5\%$  (dashed curve).

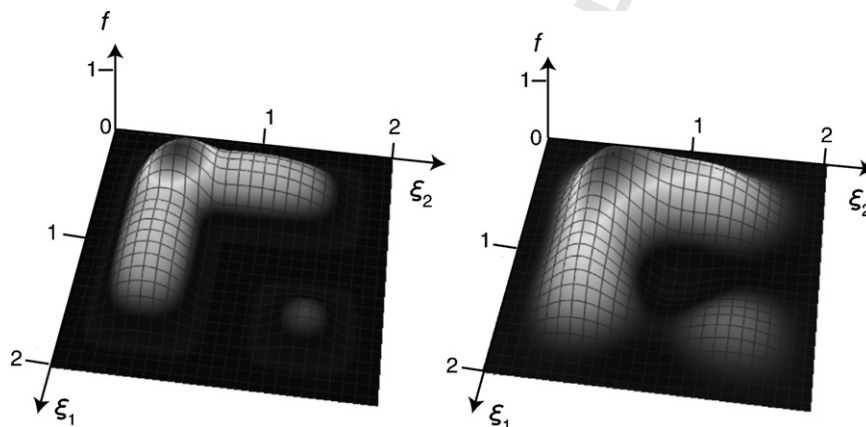


Fig. 3. Results of  $f(\xi_1, \xi_2)$  recovery modelling. Model function (left) and solution (right).

219 5.1. Explanation of figures

220 We used the following scheme in our calculations:

- 221 1. In 1D experiments we used the model functions

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$$f(\xi) = \sum_{k=1}^l e^{-(a_k \xi + b_k)^2}, \quad l = 1, 2, \quad (29)$$

while in 2D

$$f(\xi, \eta) = \sum_i a_i \exp \left( -\frac{b_i(\xi - c_i)^2}{c_i^2 - (\xi - c_i)^2} - \frac{d_i(\eta - f_i)^2}{f_i^2 - (\eta - f_i)^2} \right). \quad (30)$$

- 223 2. For various values of  $\psi$  (and  $\zeta$  in 2D case), the “experimental data” was obtained according to Eqs. (6) and (7). We also used, in some numerical experiments, the “measurements” corrupted with 5% multiplicative white noise in 1D case and 1% multiplicative white noise in 2D case.
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- 228 3. The three codes mentioned above were used to solve the 1D Fredholm equation of the first kind to recover  $f(\xi)$  from  $A(\psi)$ . The results obtained by these three programs are presented in Figs. 1–3.

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232 For the kernel  $K_s$  we give only the results obtained by our code ICESolver as the other two failed. In the 2D case the comparison with the other algorithms was not carried out due to their absence.

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236 6. Conclusions

237 As it is seen from the provided material this new method is quite suitable for the solution of inverse problems of electrooptics related with the determination of particle distribution on their parameters. This method allows to obtain more precise and stable solutions of Fredholm I kind integral equations than other numerical methods, such as the regularization method, as well as determine the distribution function on two parameters, which is important when studying many biological colloids.

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