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Determination of the Distribution of the Relaxation Times from Dielectric Spectra*

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Abstract. The dielectric susceptibility measurements are usually interpreted in terms of the relaxation times of various dynamical processes. Using the simple examples of the simulated spectra it is shown how the distribution of these relaxation times can be obtained by means of the integral equations solved with the Tikhonov regularization technique, and the criteria for the choice of the regularization parameter is discussed.

Keywords: dielectric spectroscopy, relaxation time, Tikhonov regularization.

1 Introduction

The dynamics of the dielectric response of ferroelectrics and related materials is of interest for applications in the high-frequency electronic devices, such as static memory (FRAM), sensors, microstrip lines, etc. Broadband dielectric spectroscopy is widely used to study molecular dynamics in complex systems such as glass-forming liquids and liquid crystalline materials (e.g., [1]). Sample polarization in an external electric field depends both on geometrical factors and on the mobility of molecular segments, molecules, or clusters of molecules. From the dielectric response one can obtain dipolar strengths, and correlation times of the relaxation processes present in the system.

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The most simple description of the dynamics in ferroelectrics is achieved by means of a single Debye process with the relaxation time τ or by a superposition of several such processes. Often some other phenomenological functions are used (see for instance [1]). The Debye model seams most natural due to the exponential decay of fluctuations. However the dielectric properties of condensed matter do not in general follow the Debye model. In order to meet the experimental needs some other predefined spectral functions – single-parameter Cole-Cole, Davidson-Cole, Williams-Wats, and two-parameter Havriliak-Negami, Jonsher, Dissado Hill, etc has been used [1]. Usually a superposition of several such functions provides a satisfactory multiparameter fit to the experimental data. However, relating obtained in such way parameters to the intrinsic physical properties of the material is not always straightforward. A further drawback of such an approach is the inherent difficulty of separating processes with comparable relaxation times. A proper choice of the number of processes used to fit the data is not always obvious, and additional $apriori$ assumptions have to be made.

An alternative way to describe a dielectric relaxation spectrum is to use an ensemble of Debye processes with a continuous relaxation time distribution, $w(\tau)$. Such method could be useful for the general handling of the sum of Debye processes what reduces to the sum of the corresponding δ functions in $w(\tau)$ distribution, as well as the symmetrically or asymmetrically broadened peaks in the materials with broad distribution of the relaxation times.

Unfortunately, the direct extraction of $w(\tau)$ from $\varepsilon^*(\omega)$ is a mathematically ill-posed problem [2]. This difficulty may be one of the reasons why up to now the superposition of a few parameterized functions were preferred in the description of the dielectric response spectra. Only few attempts were made to develop the numerical algorithm and to obtain the distribution of relaxation times [3, 4, 5]. This method so far has not been applied for the dipolar glasses, except in [4] where authors, however, used some empirical functions, what narrowed the problem. While the dipolar glasses, such as RADP or BP/BPI [6, 7, 8] or relaxor ceramics [9] have a broad distribution of relaxation times, and thus, are among the materials where the above time distribution $w(\tau)$ technique could be especially useful.

If a direct calculation of $w(\tau)$ from ε^* could reliably be performed, in a manner similar to the Fourier transformation between time and frequency domains, then several problems arising from the use of empirical functions could be avoided. Having obtained $w(\tau)$ one could then seek a physical interpretation in the τ domain rather than in the frequency domain.

Our purpose is to present some algorithm and program for solving the integral equations related to the calculation of the relaxation time distribution from the data of the dielectric spectra using the regularization technique and to discuss its application to the simple examples of the simulated spectra in order to demonstrate the main features of the proposed approach and the possible strategies in the choice of the regularization parameter. The paper is organized as follows. In Section 2 the problem is formulated and in Section 3 the description of algorithm and program is given. Next the illustrations follows. In Section 4 the results of the application of the program to the Cole-Cole, Havriliak-Negami and to some other simple models with fixed relaxation times distribution for various noise levels and various relaxation parameters are presented. The Section 5 is devoted to more detailed analysis of the regularization parameter choice, and in last Section 6 the conclusions are given.

2 Method

We assume that the real and imaginary parts of the dielectric spectrum $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ can be represented as a superposition of the independent individual Debye-like relaxation processes:

$$\varepsilon'(\omega) = \varepsilon_\infty + \int_{-\infty}^{\infty} \frac{w(\tau)d(\lg\tau)}{1+(\omega\tau)^2}, \tag{1a}$$

$$\varepsilon''(\nu) = \int_{-\infty}^{\infty} \frac{w(\tau)(\omega\tau)d(\lg\tau)}{1+(\omega\tau)^2}. \tag{1b}$$

These two expressions actually are the Fredholm integral equations of the first kind for the relaxation time distribution $w(\tau)$ definition. Such integral equations are known to be an ill-posed problem. The most general method of considering them is the Tikhonov regularization [2].

Treating integral equations (1) numerically one has to perform the discretization which leads to the linear non homogeneous algebraic equation set. In the matrix notation it can be represented as

$$\mathcal{A}\boldsymbol{X} = \boldsymbol{T}. \tag{2}$$

Here the components T_n ($1 \leq n \leq N$) of the vector $\boldsymbol{T}$ represent the dielectric spectrum $\{\varepsilon_i', \varepsilon_i''\}$ ($1 \leq i \leq N/2$) recorded at some frequencies ω_i. We used equidistant frequency intervals in the logarithmic scale ($\Delta \lg \omega_m = \mathrm{const}$). The vector $\boldsymbol{X}$ with components X_m ($1 \leq m \leq M$) stands for the relaxation time distribution $w(\tau_m)$ which we are looking for. We used equidistant time intervals in the logarithmic scale as well ($\Delta \lg \tau_m = \mathrm{const}$). The symbol $\mathcal{A}$ stands for the kernel of the above matrix equation. It represents the matrix with elements obtained by the direct substitution of ω_i and τ_m values into the kernels of integral equations (1).

In order to increase the accuracy in the case of noisy data, usually the number of frequency points ω_i exceeds the number of relaxation times τ_m at which the distribution is calculated. Thus, the number of equations in (2) exceeds the number of variables (the number of the vector $\boldsymbol{X}$ components). Due to that fact that equation (2) can not be solved directly, and it has to be replaced by the following minimization problem:

$$\Phi_0 = \|\boldsymbol{T} - \mathcal{A}\boldsymbol{X}\|^2 = \min. \tag{3}$$

Here and further we shall use the following vector norm notation $\|\boldsymbol{V}\|^2 = \boldsymbol{V}^T\boldsymbol{V}$ where the superscript ^{T} indicates the transposed vector or matrix.

Due to the ill-posed nature of the integral Fredholm equations the above minimization problem is ill-posed as well, namely, its solution is a rather sensitive to small changes of the vector $\boldsymbol{T}$ components (the dielectric spectrum $\epsilon(\omega)$) which are the input of the considered problem. That is why the above minimization problem can not be treated without some additional means. Following the Tikhonov regularization procedure we replace the functional Φ_0 by the following modified expression:

$$\Phi(\alpha) = \|\boldsymbol{T} - \mathcal{A}\boldsymbol{X}\|^2 + \alpha^2\|\mathcal{R}\boldsymbol{X}\|^2 = \min \tag{4}$$

where the additional regularization term is added. The symbol $\mathcal{R}$ stands for the regularization matrix, and α is the regularization parameter. It plays the same role as a filter bandwidth when smoothing noisy data.

The less is the value of the regularization parameter in minimization problem (4) the more solutions satisfy this equation within the experimentally recorded dielectric spectrum errors, and the more the solution becomes unstable itself. While increasing this parameter we deviate from the actual relaxation time distribution which we are looking for. Thus, in order to get the satisfactory result we have to add as many additional conditions as possible. First, we know that all relaxation time distribution components have to be positive ($X_n > 0$). Next, sometimes it is possible to obtain the rather reliable static permittivity $\varepsilon(0)$ or the limit high frequency dielectric permittivity ε_∞. In this case it is worth to restrict the above minimization problem fixing some of these values or both.

3 Debye program

Usually the minimization problem (4) is solved numerically by means of the least squares problem technique [10]. We developed the Debye program for the numerical solution of restricted minimization problem (4) and the calculation of the relaxation time distribution. In this section we give some details of this numerical program. Actually the program implements the simplified version of Provencher algorithm [11] adapted to integral equation (1) case.

As it was already mentioned in Section 2 the equidistant discretization in the logarithmic scale with steps

$$\Delta \lg(\omega/2\pi) = h_\nu, \quad \Delta \lg \tau = h_\tau \tag{5}$$

was used. The kernel matrix components are

$$A_{nm} = \begin{cases} h_\tau \big\{1 + (\omega_n \tau_m)^2\big\}^{-1}, & n \le N/2, \\ \omega_n \tau_m h_\tau \big\{1 + (\omega_n \tau_m)^2\big\}^{-1}, & n > N/2. \end{cases} \tag{6}$$

When the shift ε_∞ is known and fixed, it is subtracted from data vector replacing $\varepsilon'_i \to \varepsilon'_i - \varepsilon_\infty$. In the opposite case when the shift ε_∞ is not fixed, it is

added to the $\boldsymbol{X}$ vector as its first component. In this case the additional first $\{1, \cdots, 1, 0, \cdots, 0\}^T$ column is added to the kernel matrix.

The regularization matrix

$$\mathcal{R} = \mathcal{R}_0 = \begin{pmatrix} h_\tau^2 & 0 & 0 & 0 & \cdots & 0 \\ 1 & -2 & 1 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & 1 & -2 & 1 \\ 0 & \cdots & 0 & 0 & 0 & h_\tau^2 \end{pmatrix} \tag{7}$$

corresponding to the calculation of the second order derivative was used. The first and last components proportional to h_τ^2 were adjusted during the simulation. In the case with not fixed shift ε_∞ value the above regularization matrix was replaced by

$$\mathcal{R} = \begin{pmatrix} h_\tau^2 & 0 \\ 0 & \mathcal{R}_0 \end{pmatrix}. \tag{8}$$

When the static permittivity $\varepsilon(0)$ is fixed there is the additional equality condition

$$\varepsilon_\infty + \int w(\tau) d(\lg \tau) = \varepsilon(0) \tag{9}$$

which relaxation time distribution has to obey. The discrete version of this condition can be presented as $\boldsymbol{E}^T \boldsymbol{X} = e$ with

$$e = \varepsilon(0) - \varepsilon_\infty, \quad \boldsymbol{E}^T = h_\tau \{1/2, 1, \cdots, 1, 1/2\} \tag{10}$$

in the case with fixed ε_∞, and

$$e = \varepsilon(0), \quad \boldsymbol{E}^T = h_\tau \{1/h_\tau^{-1}, 1/2, 1, \cdots, 1, 1/2\} \tag{11}$$

in the opposite case.

Thus, we have to solve the minimization problem with linear equality and inequality constraints:

$$\Phi(\alpha) = \|\boldsymbol{T} - \mathcal{A}\boldsymbol{X}\|^2 + \alpha^2 \|\mathcal{R}\boldsymbol{X}\|^2 = \min, \tag{12a}$$

$$\boldsymbol{E}^T \boldsymbol{X} = e, \tag{12b}$$

$$X_n \geq 0. \tag{12c}$$

The standard way of treating such problem is the exclusion of the equality constraint, and reduction of the remaining minimization problem with inequality constraints to the LDP (*Least Distance Programming*) problem [10].

The exclusion of the equality constraint is performed as follows. First, the scalar constraint (12b) is formally replaced by its matrix analog

$$\mathcal{E}^T \boldsymbol{X} = \boldsymbol{e} \tag{13}$$

with $M \times M$ matrix $\mathcal{E} = (\boldsymbol{E}, 0)$ and M-component vector $\boldsymbol{e}^T = \{e, 0\}$. Next, the RQ-decomposition is performed:

$$\mathcal{E} = \begin{pmatrix} \boldsymbol{K}_1 & \mathcal{K}_2 \end{pmatrix} \begin{pmatrix} F & 0 \\ 0 & 0 \end{pmatrix}. \tag{14}$$

Here the symbol $\boldsymbol{K}_1$ stands for M-component vector, and $\mathcal{K}_2$ is the $M\times(M–1)$ matrix. Those two objects together form the unitary matrix

$$\begin{pmatrix} \boldsymbol{K}_1^T \\ \mathcal{K}_2^T \end{pmatrix} \begin{pmatrix} \boldsymbol{K}_1 & \mathcal{K}_2 \end{pmatrix} = \mathcal{I}. \tag{15}$$

Here $\mathcal{I}$ is the unity matrix.

Now inserting (14) into condition (13), and denoting

$$\boldsymbol{X} = \begin{pmatrix} \boldsymbol{K}_1 & \mathcal{K}_2 \end{pmatrix} \begin{pmatrix} X_1^E \\ \boldsymbol{X}_2^E \end{pmatrix} = \boldsymbol{K}_1 X_1^E + \mathcal{K}_2 \boldsymbol{X}_2^E, \tag{16}$$

we obtain

$$X_1^E = F^{-1} e, \tag{17}$$

and reduce the initial minimization problem to the problem with inequality constraints only

$$\begin{aligned} \Phi(\alpha) = {} & \|(\boldsymbol{T} - \mathcal{A}\boldsymbol{K}_1 F^{-1} e) - \mathcal{A}\mathcal{K}_2 \boldsymbol{X}_2^E\|^2 \\ & + \alpha^2 \|\mathcal{R}\boldsymbol{K}_1 F^{-1} e + \mathcal{R}\mathcal{K}_2 \boldsymbol{X}_2^E\|^2 = \min, \end{aligned} \tag{18a}$$

$$(\mathcal{K}_2 \boldsymbol{X}_2^E)_n \geq -(\boldsymbol{K}_1)_i F^{-1} e. \tag{18b}$$

for shorter vector $\boldsymbol{X}_2^E$ (with $(M-1)$ components).

The reduction of the above problem to LDP is based on the QR-decomposition

$$\mathcal{A}\mathcal{K}_2 = \mathcal{Q}_0\mathcal{C} \tag{19}$$

followed by twofold singular value decompositions (SVD)

$$\mathcal{R}\mathcal{K}_2 = \mathcal{U}\mathcal{H}\mathcal{Z}^T, \tag{20a}$$

$$\mathcal{C}\mathcal{Z}\mathcal{H}^{-1} = \mathcal{Q}\mathcal{S}\mathcal{W}^T. \tag{20b}$$

Here matrices $\mathcal{Q}_0, \mathcal{U}, \mathcal{Z}, \mathcal{Q}, \mathcal{W}$ are orthogonal ($\mathcal{Q}_0^T\mathcal{Q}_0 = \mathcal{I}$, etc.), matrices $\mathcal{H}$ and $\mathcal{S}$ are diagonal with diagonal matrix elements H_n and S_n, correspondingly, and the matrix $\mathcal{C}$ is upper triangular.

The substitution

$$\boldsymbol{X}_2^E = \mathcal{Z}\mathcal{H}^{-1}\left\{\mathcal{W}\boldsymbol{\lambda} - \mathcal{U}^T\mathcal{R}\boldsymbol{K}_1F^{-1}e\right\} \tag{21}$$

changes minimization problem (18) into the following one:

$$\Phi(\alpha) = \|\boldsymbol{\gamma} - \mathcal{S}\boldsymbol{\lambda}\| + \alpha^2\|\boldsymbol{\lambda}\| = \min, \tag{22a}$$

$$(\mathcal{D}\boldsymbol{\lambda})_n \geq -d_n, \tag{22b}$$

where

$$\mathcal{D} = \mathcal{K}_2\mathcal{Z}\mathcal{H}^{-1}\mathcal{W}, \tag{23a}$$

$$\boldsymbol{d} = \left\{\mathcal{K}_2\mathcal{Z}\mathcal{H}^{-1}\mathcal{U}^T - \mathcal{I}\right\}\boldsymbol{K}_1F^{-1}e, \tag{23b}$$

$$\boldsymbol{\gamma} = \mathcal{Q}^T\left\{\mathcal{Q}_0^T\boldsymbol{T} + (\mathcal{C}\mathcal{Z}\mathcal{H}^{-1}\mathcal{U}^T - \mathcal{Q}_0^T\mathcal{A})\boldsymbol{K}_1F^{-1}e\right\}. \tag{23c}$$

The main advantage of the obtained minimization problem is that both functional parts are composed of the diagonal components only. Thus, it can be easily rewritten in the single diagonal form:

$$\mathrm{Norm} = \|\boldsymbol{\xi}\| = \min, \tag{24a}$$

$$(\mathcal{D}\widetilde{\mathcal{S}}^{-1})_n \geq -(\boldsymbol{d} + \mathcal{D}\widetilde{\mathcal{S}}^{-1}\widetilde{\boldsymbol{\gamma}})_n, \tag{24b}$$

where the symbol $\widetilde{\mathcal{S}}$ stands for diagonal matrix with the components $\widetilde{S}_n = \sqrt{S_n^2 + \alpha^2}$, $\widetilde{\boldsymbol{\gamma}}$ is the vector with components $\widetilde{\gamma}_n = \gamma_n S_n/\widetilde{S}_n$, and

$$\boldsymbol{\lambda} = \widetilde{\mathcal{S}}^{-1}(\boldsymbol{\xi} + \widetilde{\boldsymbol{\gamma}}). \tag{25}$$

Final minimization problem (24) can be solved by LDP technique. When the vector $\boldsymbol{\xi}$ is found the vector $\boldsymbol{X}$ (actually the relaxation time distribution) is obtained by means of (25), (21), (17), and (16).

In the case when $\varepsilon(0)$ is not fixed there is no (12b), and the algorithm is more simple. It can be easily obtained from the previous one formally assuming that $\boldsymbol{K}_1 = 0$ and $\mathcal{K}_2 = \mathcal{I}$.

The Debye program is written in C^{++} as a `SDT` (*Single Document Interface*) program for the `Windows` environment. The LDP subroutine was rewritten from the fortran version given in [10], the matrix decomposition subroutines were taken from [12].

Up to now the we used to set the regularization parameter manually.

4 Simulation results

In order to illustrate the usefulness of proposed method we performed the following numerical experiment. We prepared some fixed distributions of the relaxation times, generated the corresponding dielectric spectra adding some noise to it, and then tried to reveal the relaxation time distribution using the Debye program with various regularization α parameters chosen. For this purpose we used rather popular distributions given by Cole-Cole

$$\epsilon(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau_{\rm cc})^\beta}, \tag{26a}$$

$$w(\tau) = \frac{\sin(\pi\beta)}{2\pi\Big\{ \cosh\big[\ln(\tau/\tau_{\rm cc})\big] + \sin(\pi\beta)\Big\}}, \tag{26b}$$

and Havriliak-Negami

$$\epsilon(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{\big\{1 + (i\omega\tau_{\rm hn})^\beta\big\}^\gamma}, \tag{27a}$$

$$w(\tau) = \frac{1}{\pi}(\tau/\tau_{\rm hn})^{\beta\gamma} \sin\Big(\gamma\big[1+2\cos(\pi\beta)(\tau/\tau_{\rm hn})^\beta+(\tau/\tau_{\rm hn})^{2\beta}\big]^{-\tau/2\tau_{\rm hn}}\Big) \times \arctan\left[\frac{\sin(\pi\beta)}{(\tau/\tau_{\rm hn})^\beta + \cos(\pi\beta)}\right] \tag{27b}$$

formulas. The main advantage of these expressions is that the exact analytical expressions for the corresponding dielectric spectrum are known. Besides, we

made the numerical experiments with simple distributions composed of single and multiple triangular and square shapes.

The results are presented in Figs. 1 and 2.

Inspecting Fig. 1 were the results obtained with Cole-Cole distribution are presented one may to conclude that in the absence of noise the relaxation time distributions can be revealed quite successfully either in the case of a single peak or double peak, although the regularization parameter cannot be chosen rather small in order to avoid the appearance of the artificial peaks. The addition of some noise doesn't change the situation drastically. The form

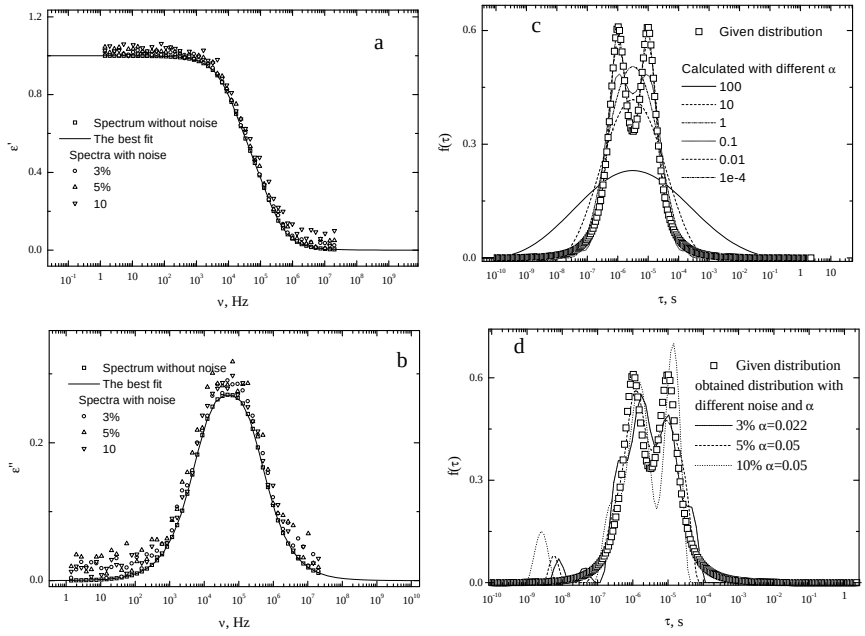

Fig. 1. The frequency dependence of real (a) and imaginary (b) parts of dielectric permittivity and the corresponding double-peaked Cole-Cole reference relaxation time distribution function (c, points), calculated distribution function with different α without noise (c, different lines) and calculated distribution function from the dielectric spectra with different noise (d).

of the distribution can be obtained successfully even with the noise levels up to 10%. It is also seen that the regularization parameter has to be increased in

the case of the larger noise levels.

The results of analogous experiments with the Havriliak-Negami distribution are presented in Fig. 2. The main idea of the Havriliak-Negami distri-

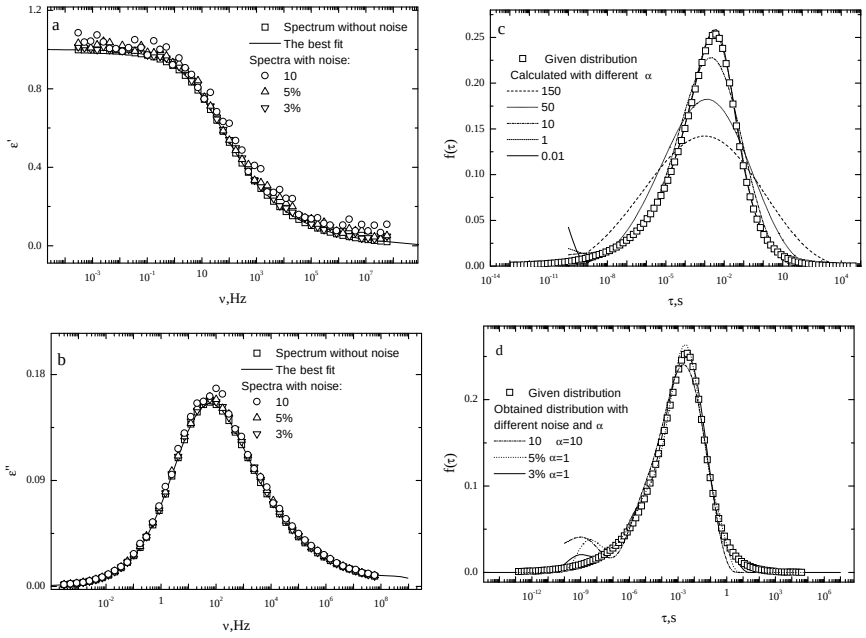

Fig. 2. The frequency dependence of real (a) and imaginary (b) parts of dielectric permittivity and the corresponding Havriliak-Negami reference relaxation time distribution function (c, points), calculated distribution function with different α without noise (c, different lines) and calculated distribution function from the dielectric spectra with different noise (d).

bution lays in the fact that it enables to model the non-symmetric relaxation time distributions. Comparison of these results with shown in Fig. (1) results indicates that distribution asymmetry does not affects its definition essentially.

Also, same calculations have been made for the simulated dielectric spectra with triangle and rectangular shapes of distributuion function. From these simmulations (see for example Fig. 3) we can conclude, that it is not possible to obtaine the exact shape of the disribution function, due to sharp edges, but general features of the spectra have been revealed.

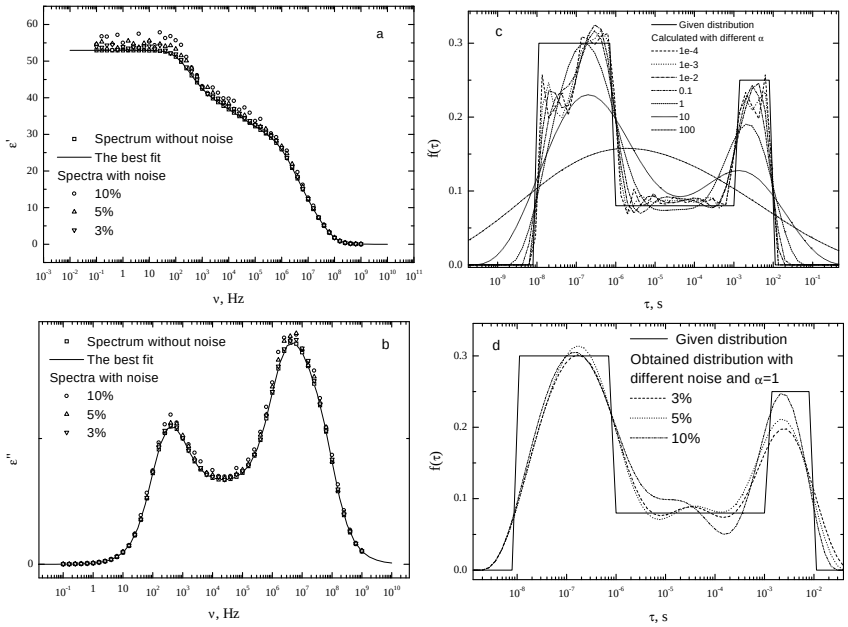

Fig. 3. The frequency dependence of real (a) and imaginary (b) parts of dielectric permittivity and the corresponding triple-rectangular reference relaxation time distribution function (c, points), calculated distribution function with different α without noise (c, different lines) and calculated distribution function from the dielectric spectra with different noise (d).

5 The regularization parameter

The results presented in the previous section show that the regularization parameter α is crucial for the shape of the distribution function of the relaxation times. Too small values for α result in artificial physically meaningless structures in $w(\tau)$, while too large α tends to oversmoth the shape of $w(\tau)$ and suppress information. When applying the Tikhonov regularization technique the proper choice of the regularization parameter α is the main problem.

To find out, how to chose proper α the following calculations have been performed. The following criteria for α have been chosen:

1. Deviation of the calculated spectra of dielectric permittivity from the given spectra of dielectric permittivity for the real and imaginary parts of dielectric permittivity;

2. Deviation of the calculated distribution function of the relaxation times from the given distribution of the relaxation times;
3. The NORM parameter.

From the 1st deviation we can see which dielectric spectra fits experimental results the best and is easiest to calculate (for routine calculations during fitting procedure). 2nd shows how close we are to the given distribution, but this parameter is not suitable for the experimental investigations, when we do not know initially the shape of the distribution function. 3rd or NORM parameter also gives information how close we are from the given distribution of the relaxation times.

Such calculations have been performed and results are presented in the Fig. 4.

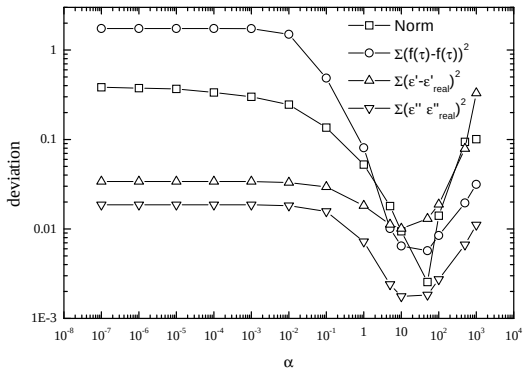

Fig. 4. The α dependence of various deviation values for single Cole-Cole process with gaussian noise.

We can see that all curves have clearly expressed minima, and what is the most important – NORM minima coincides with minima in deviation of the function of distribution of the relaxation times. The minima of the deviation of the real and imaginary parts of dielectric permittivity is not so clearly expressed. Because usually from the experimental data we do not know the shape of distribution function, most important is parameter NORM. Such calculations have been performed with different noise level and different distribution functions.

Thus, from all presented curves we can see that the best choice for regu-

larisation parameter is before it begins to increase. This happens for all three criteria.

6 Conclusions

We have presented the new approach to the dielectric spectra evaluation. Instead of using different models with given distribution of the relaxation times, the distribution of the relaxation times can be obtained. This was performed by solving integral equation with Tikhonov regularization technique. This method allows to resolve multiple dynamical processes. Crucial role in obtaining the distribution of relaxation times plays parameter α. We have shown, that all three parameters indicate the proper choise of parameter α. Thus it is possible to make the automatic choice of the regularisation parameter.

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