On the physical mechanisms of relaxation time distribution in disordered dielectrics.

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The distribution function of relaxation times in disordered dielectrics has been calculated in the random field theory framework. For this purpose, we first consider the dynamics of single two-orientable impurity electric dipole in a random electric field $E$ created by the rest of impurities in disordered ferroelectric. This dynamics is conveniently described by Langevin equation. Relaxation time $\tau$ is then a reciprocal probability (calculated on the base of Fokker-Planck equation) of the dipole transition through barrier in a double-well potential (corresponding to two possible dipole orientations), distorted by a random fields.

The obtained dependence $\tau(E)$ made it possible to obtain the expression for relaxation times distribution function $F(\tau)$ via random fields distribution function $f(E)$. Latter function has been calculated self-consistently in the random field theory framework. Nonlinear random field contribution and effects of spatial correlations between impurities have also been taken into account. It was shown that nonlinear contribution of random field gives asymmetric shape of $F(\tau)$, while in linear case it is symmetric.

Comparison of calculated $F(\tau)$ curves with those extracted from empirical Cole-Cole (CC), Davidson-Cole (DC), Kohlrausch-William-Watts (KWW) and Havriliak-Negami (HN) functions had shown, that they correspond to mixed ferro-glass phase with coexistence of short and long-range order. Different forms of $F(\tau)$ are determined by linear (CC) or nonlinear (DC, KWW, HN) contributions of random field.

I. INTRODUCTION

The anomalies of dynamic properties are the characteristic feature of the disordered ferroelectrics, polymers and composites. In particular, strong frequency dispersion of dielectric or magnetic susceptibility was observed in many dipole or spin glasses (see e.g. [1] and ref. therein). The dispersion is commonly attributed to existence in the disordered systems of broad spectrum of relaxation times which can be extracted from the observed frequency dependence of susceptibility [2]. The background of such phenomenological approach is the model of a superposition of Debye relaxors with different relaxation times $\tau$. In such a model the dynamic quantities like time or frequency dependence of polarization, system susceptibility etc. can be calculated by averaging of single relaxor characteristics with relaxation time distribution function $F(\tau)$ in supposition of parallel (independent) relaxation processes. The key point of such approach is the form of distribution function. Only a few simple empirical forms were proposed (rather than calculated in some physical model) for $F(\tau)$. One of them were considered by Fröchlich [3] who assumed that in arbitrary range $[\tau_0, \tau_1]$ $F(\tau)$ has constant positive value and outside this range it equals zero. But such form of $F(\tau)$ appeared unable to explain the experimental data for real systems with dielectric response described by Cole-Cole (CC), Davidson-Cole (DC), Havriliak-Negami (HN) and other more complex forms, than simple Debye equation [4]. Different and complex enough empirical forms of $F(\tau)$ were shown to be necessary to describe non-Debye dielectric response [5]. However the extraction of $F(\tau)$ from the experimental data makes it impossible to understand the physical reasons of these properties anomalies.

Recently the calculations of linear [6,7] and nonlinear [8] dynamic dielectric response were performed for ferroelectric relaxors like PMN, PST, PLZT. Random electric field produced by substitutional disorder and other lattice imperfections (which are known to be the characteristic features of all the disordered systems) was considered as the main reason of their properties peculiarities via its influence on the barriers between a dipole orientations. Vogel-Fulcher law in relaxation time temperature dependence, stretch-exponential behaviour of dynamic polarization [6] and several peculiarities of dc field non-linear susceptibility [8] were obtained.
In present work random field theory approach was applied for calculation of relaxation time distribution function. The influence of random electric field on the parabolic and rectangular barriers was considered. The relaxation time distribution function was calculated with the help of random fields distribution function allowing for linear [9] and non-linear random fields contribution as well as spatial correlation effects in the impurity subsystem [10].

II. CONNECTION BETWEEN DISTRIBUTION FUNCTIONS OF RELAXATION TIMES AND RANDOM FIELDS

Random field is known to be the characteristic feature of the disordered systems. The substitutional disorder, vacancies of ions, impurities and other imperfections are the sources of random electric and elastic field in the system. These random fields \( E \) make relaxation times \( \tau \) of the dipoles to vary from point to point in a sample, i.e. \( \tau = \tau(E) \). Possible forms of \( \tau(E) \) will be considered below. The distribution of random electric and elastic fields was calculated earlier in [9], [10] and [11] respectively in the statistical theory framework. The connection between \( \tau \) and \( E \) permits to calculate the distribution function of \( \tau \) for known distribution of \( E \) by means of theory of probability. In the case when \( \tau(E) \) is single-valued (monotonous) function of \( E \) the theory of probability gives [12]:

\[
F(\tau) = f(E(\tau)) \left| \frac{dE(\tau)}{d\tau} \right|
\]  

(1)

Here \( F(\tau) \) and \( f(E) \) are the relaxation time and random field distribution functions respectively, \( E(\tau) \) is inverse function to \( \tau(E) \). The Eq.(1) can be thought about as simple change of variables in normalization integrals

\[
\int_{\tau} F(\tau)d\tau = \int_{E} f(E)dE
\]  

(2)

where integration is performed over domains of \( \tau \) and \( E \) variation. The only difference is the modulus of the derivative because the distribution function has to be positive.

In more general case of non-monotonous behaviour of \( \tau(E) \), when one \( \tau \) value correspond to several \( E \)-values \((E_1, E_2, \ldots, E_n)\), the space of \( E \) values should be divided into \( n \) regions (containing \( E_1, E_2, \ldots, E_n \) points), where function \( \tau(E) \) is monotonous (see Fig.1). Now, for the entire \( E \)-domain, \( F(\tau) \) can be represented as a sum of expressions like Eq.(1) over regions \( E_i(\tau) \) of monotonous behaviour of \( \tau(E) \) [12]:

\[
F(\tau) = \sum_{i=1}^{n} f(E_i(\tau)) \left| \frac{dE_i(\tau)}{d\tau} \right|
\]  

(3)

Eq.(3) is general expression for the distribution function of one quantity via the distribution function of another one for a given connection between them. In particular, Eq.(3) can be used for the calculation of random field distribution function \( f(E) \) allowing for nonlinear and spatial correlation effects via that in the linear case. In general case internal random field \( E(r_i) \) can be written as:

\[
E_\gamma(\vec{r}_i) = \varepsilon_\gamma(\vec{r}_i) + \sum_{m=2}^{p} \alpha_m \varepsilon_m(\vec{r}_i)
\]  

(4)

\[
\varepsilon_\gamma(\vec{r}_i) = \sum_{k,j} (\varepsilon_k)_{\gamma j}(r_{ij})
\]  

(5)

where \((\varepsilon_k)_{\gamma} \) is \( \gamma \)-component of the field produced in the observation point \( \vec{r}_i \) by a source of \( k \)-th type (e.g. dipoles, point charges, dilatational centers) situated at the point \( \vec{r}_j \); \( \alpha_m \) are the coefficients of nonlinearity of \( m \)-th order of the host lattice, their dimension being the inverse electric field in \((m-1)\)-th power.

In the linear case \((\alpha_m = 0)\) the random field distribution function \( f_i \) can be calculated in the statistical theory framework, namely

\[
f_i(\varepsilon) = \delta(\varepsilon - \varepsilon'(r_{ij}))
\]  

(6)

where averaging (marked by bar) of \( \delta \)-function makes it possible to count all the spatial configurations of random field sources \( \varepsilon'(r_{ij}) \) leading to definite random field value \( \varepsilon_\gamma \equiv \varepsilon \). Averaging, neglecting the correlations between random field sources in Eq.(4), leads to well-known expression of statistical theory [13,14]:
\[ f_l(\varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\varepsilon t - \sum_k n_k F_k(t))dt \] (7)

\[ F_k(t) = \int_{-\infty}^{\infty} d^3r (1 - \exp(it\varepsilon_k(\vec{r}))) \] (8)

Here \( n_k \) and \( \varepsilon_k(\vec{r}) \) are respectively the concentration and electric field of \( k \)th random field source.

One can see, that the form of \( F_k(t) \) and thus \( f_l(\varepsilon) \) depends strongly on the form of \( \varepsilon_k(\vec{r}) \). So, \( f_l(\varepsilon) \) could not only be of Gaussian form (which is realized, e.g., for point charges with \( \varepsilon_k(\vec{r}) \sim 1/\vec{r}^2 \)), but also of Lorentzian form (this is the case for electric dipoles with \( \varepsilon_k(\vec{r}) \sim 1/\vec{r}^3 \)).

In the disordered dielectrics the main source of random fields is impurity electric dipole which can have several discrete orientations in a host dielectric lattice (see Ref. [9] for details). In this case, which is of interest for present consideration, the function \( f_l(\varepsilon) \) should be calculated with additional quantum statistical averaging over aforementioned discrete orientations. This was done self-consistently in Ref. [9] (see also [10]) for particular case of two-orientable dipoles, point charges and dilatational centers as the random field sources:

\[ f_l(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left[ it(E - E_0L) - n_1B_1 |t| - n_2B_2 |t|^{3/2} - n_3B_3t^2 \right] dt \] (9)

\[ B_1 = \frac{\Omega_0}{9} \frac{1 + \nu}{1 - \nu}, B_2 = \frac{32}{15} \left( \frac{\pi Ze}{\varepsilon_0} \right)^{3/2}, B_3 = \frac{16}{15} \frac{r^3}{\varepsilon_0 r_c^3}, L = \int_{-\infty}^{\infty} f_l(E) \tanh(\beta E) dE. \]

Here \( L = \langle (d^*)^2 \rangle / d^* \) is long-range order parameter (the number of coherently oriented impurity electric dipoles, see Ref. [9] for details), \( E_0 = 4\pi(n_3d^2)/\varepsilon_0 \) is the mean value of random electric field (in energy units), produced by the impurity dipoles, \( d^* = 1/3d\gamma(\varepsilon_0 - 1) \) is the electric dipole moment, \( \gamma \) and \( \varepsilon_0 \) are respectively the Lorentz factor and static dielectric permittivity of the host lattice, \( n_1, n_2 \) and \( n_3 \) are respectively the concentrations of dilatational centers, point charges and electric dipoles, \( Ze \) and \( \Omega_0 \) are the point defect charge and elastic moment, \( p \) and \( \nu \) are the host lattice piezoelectric component and Poisson coefficient respectively.

Thus Eqs. (6), (7), (8) give the possibility to calculate the distribution function of random field induced independently, i.e. without correlation, by any number of random field sources.

Spatial correlations and nonlinear effects can be taken into account on the base of Eq.(3) \((\alpha_n \neq 0)\). For such more general case the random field distribution function can be expressed through \( f_l(\varepsilon) \) with the help of expression like Eq.(2) [15]:

\[ f(E) = \sum_n f_l(\varepsilon_n(E)) \left| \frac{d\varepsilon_n(E)}{dE} \right| \] (10)

where \( \varepsilon_n \) are the real roots of the algebraic equation

\[ E - \varepsilon - \alpha_2\varepsilon^2 - ... - \alpha_n\varepsilon^n = 0 \] (11)

We have to emphasize that even for simple enough (e.g. Gaussian, Lorentzian) form of \( f_l(\varepsilon) \), coefficient \( \left| \frac{d\varepsilon_n(E)}{dE} \right| \) in Eq.(9) will be function of \( E \) by virtue of Eq [15]. So, the nonlinear distribution function \( f(E) \) will never be the simple algebraic sum of \( f_l(\varepsilon_n) \). The shape of \( f(E) \) was calculated recently with the help of Eqs. (10), (11) for the contribution of nonlinear terms of the second \((\alpha_2 \neq 0)\) and third \((\alpha_3 \neq 0)\) order [15,16].

III. INFLUENCE OF ELECTRIC FIELD ON RELAXATION TIME

The ordinary ferroelectric materials like PbTiO₃, BaTiO₃ with polar long-range order are known to have unique relaxation time characterizing the rate of macroscopic polarization restoration after external perturbation of the system.
Disordered systems like relaxors have a broad spectrum of relaxation times, because their most probable states are dipole glass (DG) with short-range order polar clusters of \( r_c \) size, imbeded into paraelectric phase and/or mixed ferro-glass phase (FG) with coexistence of short- and long-range order. Since an orientable electric dipole is usually the nucleation centre of a cluster, the random reorientation of the dipoles can be the main mechanism of the relaxation in the aforementioned disordered systems. It is commonly believed that the probability of a dipole reorientation temperature dependence is obeyed to Arrhenius law

\[
\frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( -\frac{U}{T} \right) \tag{12}
\]

where \( U \) is a height of a barrier between equivalent dipole orientations.

To obtain the connection between relaxation time \( \tau \) and random field \( E \), let us consider the relaxational dynamics of single impurity (for definiteness two-orientable) dipole in a random electric field, created by the rest of impurity dipoles. It is clear, that in such relaxation process the random field will be time dependent and will play a role of a random force, exerted on the given impurity dipole. For such motion we can write following Langevin equation (see, e.g. [17])

\[
\frac{dx}{dt} = -\frac{\partial U(x)}{\partial x} + f(t), \tag{13}
\]

where \( x \) is the displacement of impurity ion (so that impurity dipole moment \( d = ex, e \) is ion charge), \( U(x) \) determines the actual potential energy of dipole (e.g. for two-orientable dipole \( U(x) \) is a conventional double-well potential) and \( f(t) \) is a random force with known correlator. Without loss of generality we can put

\[
<f(t)> = 0, \quad <f(t)f(t')> = D\delta(t-t'), \tag{14}
\]

where \( D \) is diffusion coefficient (see below). Langevin equation (13) is nonlinear stochastic differential equation. It can be used, in particular, to determine the probability for impurity dipole to transit from shallower to deeper well of double-well potential (i.e. overbarrier "bounce"), deformed by a random field (Fig. 2a). This problem is equivalent to the problem of Brownian particles diffusion through barrier in the potential \( U(x) \) (see [18] and refs therein). For the probability \( n(x,t) \) that diffusing particle has coordinate \( x \) at time \( t \) the Fokker-Planck equation can be derived from (13). For two-orientable dipole (one-dimensional case) it reads

\[
\frac{\partial n}{\partial t} + \frac{\partial j}{\partial x} = 0, \tag{15}
\]

\[
j = -D\frac{\partial n}{\partial x} - bn\frac{\partial U(x)}{\partial x}.
\]

Here \( D \) is diffusion coefficient for particles from well \( A \) to well \( B \) of potential \( U(x) \) (Fig.2a). For it the Einstein relation holds

\[
D = bT,
\]

where \( b \) is particle mobility, \( j \) is diffusion flux. It is seen that \( \partial n/\partial t = 0 \) in Eq. (13) when

\[
n = n_{eq}(x) = A \exp \left( -\frac{U(x)}{T} \right), \tag{16}
\]

i.e. when \( n \) is equilibrium Maxwell-Boltzmann distribution.

It can be shown (see, e.g. [18] and refs therein) that probability of transition from well \( A \) to well \( B \) (i.e. reciprocal relaxation time) is ratio of stationary (at \( \partial n/\partial t = 0 \) flux \( j_0 \) and number of particles \( N_A \) in well \( A \)

\[
p = \tau^{-1} = \frac{j_0}{N_A}. \tag{17}
\]

Calculation with respect to boundary condition \( n(B) = 0 \) (reflecting the fact that at \( t = 0 \) all particles are in well \( A \)) yields

\[
j = \frac{Dn(A)}{\int_{A}^{B} \exp(U(x)/T)dx}, \quad N_A = \int_{A} n(A) \exp \left( \frac{U(x)}{T} \right) dx \tag{18}
\]
One can see from Eqs. (17), (18), that the relaxation time depends mainly on the form of potential $U(x)$. It can be shown that the main contribution to the integrals originates from potential $U(x)$ maximum region. So, we can approximate $U(x)$ by parabola near this point and integrate from $-\infty$ to $+\infty$ (this is standard steepest descent method). For zero random field ($E = 0$) $U(x) \equiv U_0(x)$ is symmetric with respect to $y$ axis and this procedure gives standard Arrhenius law (12) for relaxation time. For nonzero random local (i.e. in the given impurity location) electric field the symmetric form of $U_0(x)$ is distorted

$$U(x) = U_0(x) \pm eE_{loc}x, \quad U_0 = U - ax^2 + bx^4, \quad U = \frac{a^2}{4b}. \tag{19}$$

Here $U$ is barrier height and for undistorted potential we choose the simplest polynomial approximation. In subsequent calculations we will call this barrier shape "parabolic".

Consider now aforementioned potential $U_0(x) = U - ax^2 + bx^4$, which has maximum at $x_1 = 0$ and minima at $x_{2,3} = \pm \sqrt{a/2b}$. In the spirit of steepest descent method we considered the approximation of $U(x)$ (13) near its maximum at $x = 0$ for small fields $E$. This made it possible to carry out the integration in Eqs. (15), (16) by the steepest descent method, that yields

$$P = \frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( \frac{U + (eE_{loc})^2/4a}{T} \right) \tag{20}$$

where $1/\tau_0$ is temperature and field independent combination involving constant $b$ and $U_0(x)$ parameters. Note, that at $E = 0$ we once more obtain Arrhenius law from (20).

For rectangular potential of the form (see Fig.2b)

$$U_0(x) = \begin{cases} 0, & -x_0 - \Delta \leq x \leq -x_0 \\ U, & -x_0 \leq x \leq x_0 \\ 0, & x_0 \leq x \leq x_0 + \Delta \end{cases} \tag{21}$$

the integrals (17), (18) can be calculated exactly, which yields

$$P = \frac{\alpha^2 D \exp(-\alpha x_0)}{2/\alpha \exp(U/T) \sinh(\alpha x_0) + 4/\alpha \sinh(\alpha \Delta/2) \cosh(\alpha x_0 + \alpha \Delta/2) \exp(\alpha \Delta) - 1}. \tag{22}$$

$$\alpha = \frac{eE}{T}, \quad d = e x_0.$$

It is seen from the Fig. 2a that actually $\Delta \ll x_0$. In this case we can substantially simplify Eq (22) and obtain

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( -\frac{U \pm dE_{loc}}{T} \right) \tag{23}$$

It is seen that at $E_{loc} = 0$ we again arrive at Arrhenius law. Note that steepest descent method gives also Eq.(23).

One can see from Eqs. (21), (23), that electric field decreases the barrier for dipole orientation along field direction and increases it for opposite one. Thus, random electric field increases relaxation time.

The final form of relaxation time dependence on $E$ can be obtained after averaging Eq.(21) over possible orientations of electric dipole $d$. Quantum-statistical averaging with the energy in the form $\Re = -dE_{loc}$ gives

$$\langle \tau \rangle = \frac{\tau_0 s p \exp(d^* E/T - \Re/T)}{s p \exp(-\Re/T)} = \frac{\tau_0 \exp(ch(2d^* E/kT))}{\tau_0 \exp(ch(d^* E/kT))} = \tau_0 \exp \left( \frac{U}{T} \right) \tag{24}$$

In Eq. (24) we substituted product $dE_{loc}$ by $d^* E$ where effective dipole moment $d^* = (\varepsilon_0 - 1)\gamma d/3$ ($\varepsilon_0$ and $\gamma$ are respectively host lattice permittivity and Lorentz factor).

Note, that such type of electric field influence on the barrier height was supposed by us earlier (see e.g. [6-8] and ref. therein).

In what follows we will perform the calculations for rectangular barriers on the base Eq.(24), because the influence of electric field on parabolic barrier (13) is qualitatively the same.
IV. RELAXATION TIME DISTRIBUTION FUNCTION

A. General equations

Eq. (2) with respect to Eq. (22) makes it possible to calculate relaxation time distribution function. In particular, Eq. (22) leads to the following connection between electric field and relaxation time:

\[ E(t) = kT \arccosh \left( \frac{1}{4} \left( t + \sqrt{t^2 + 8} \right) \right) \equiv kT f_{0 \pm}(t); t \equiv \frac{\tau}{\tau_0}; t \geq 1 \]  

(25)

where signs "±" correspond to two branches of the function

\[ \arccosh(x) = \ln(x \pm \sqrt{x^2 - 1}) \]  

(26)

Allowing for these two branches as \( i = 1, 2 \) in Eq. (2) and substituting \( E(t) \) for \( E \) in Eq. (9) (linear case) or in Eqs. (10), (11) (nonlinear case) one can obtain general expressions for relaxation times distribution function. Since these expressions appeared to be quite cumbersome, we considered the case when only electric dipoles are the sources of random electric field i.e. \( n_1 = n_2 = 0 \) in Eq. (9). In this case Eq. (9) yields

\[ f_l(E) = \frac{1}{\sqrt{2\pi} \Delta} \exp \left( -\frac{(E - E_0 L)^2}{2\Delta^2} \right); \Delta = \sqrt{2n_3 B_3}, \]  

(27)

i.e. linear random field distribution function \( f_l(E) \) has Gaussian form. Eq. (25) with respect to Eqs. (3) and (25) leads to the following expression of relaxation time distribution function

\[ F(t) = \frac{b_1}{\sqrt{\pi}} \left\{ \left| \frac{df_{0+}}{dt} \right| \exp \left[ -b_2(v f_{0+}(t) - L(v, z))^2 \right] + \left| \frac{df_{0-}}{dt} \right| \exp \left[ -b_2(v f_{0-}(t) - L(v, z))^2 \right] \right\} \]  

(28a)

\[ \frac{df_{0\pm}}{dt} = \pm \frac{1}{\sqrt{2}} \frac{1 + t/\sqrt{t^2 + 8}}{\sqrt{t^2 + t/\sqrt{t^2 + 8} - 4}} \]  

(28b)

where we introduced the dimensionless parameters suitable for numerical calculations

\[ b_1 = \frac{kT}{2\sqrt{n_3 B_3}} = vb_2; b_2 = \frac{E_0}{2\sqrt{n_3 B_3}} = \frac{1}{2} \sqrt{15\pi z}; \]  

(29)

\[ z = n_3 r_c^3; v = \frac{kT}{E_0} \]

Let us check the normalization of \( F(t) \). The normalization condition for \( f(E) \)

\[ \int_{-\infty}^{\infty} f(E)dE = 1 \]  

(30)

transforms for \( F(t) \) into contour integral, where contour runs first from \( \infty \) to 1 over \( t \) axis and then back - from 1 to \( \infty \) (see Fig. 3).

To perform integration we should pass from integration over \( dt \) to the integration over \( df_0 \) (with respect to \( f_{0\pm}(t) = 0, f_{0+}(\infty) = \infty, f_{0-}(\infty) = -\infty \)). This yields

\[ \frac{b_1}{\sqrt{\pi}} \left[ \int_{0}^{\infty} \exp \left[ -(b_1 f_0 - b_2 L(v, z))^2 \right] df_0 + \int_{-\infty}^{0} \exp \left[ -(b_1 f_0 - b_2 L(v, z))^2 \right] df_0 \right] = \]  

(31)

\[ \frac{b_1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp \left[ -(b_1 f_0 - b_2 L(v, z))^2 \right] df_0 = 1 \]

Therefore Eqs. (28), (28b) represent normalized distribution function of relaxation time. Any other integral involving function \( F(t) \) may also be evaluated by this procedure.
One can see that $F(t)$ depends on random field sources concentration and temperature via dimensionless parameters $z, v$ and order parameter $L(z, v)$. The dependence $L(z, v)$ actually determines the phase diagram of the system under consideration. We calculated it earlier both for linear [9] and nonlinear [10] random field contributions. It was shown, that $L = 0$ for $n_3 < n_{3c}$, $T < T_g$, where $n_{3c}$ and $T_g$ are respectively critical concentration and freezing temperature for dipole glass (DG) state; $L = 1$ for $z \to \infty$ (mean field approximation) and $T \ll E_0 = kT_{cmf}$, where $T_{cmf}$ is ferroelectric (FE) phase transition temperature. In intermediate range of concentrations ($\infty > n_3 > n_{3c}$) only the part of dipoles is ordered, i.e. $0 < L < 1$ and ferro-glass (FG) phase with coexistence of long and short range order appears.

Thus, Eqs.(28a), (28b) permit to calculate the distribution function of relaxation times for DG, FG, FE and paraelectric phases via $L(z, v)$ dependence in these phases.

### B. Relaxation time distribution function in mean field approximation

In the ferroelectric and paraelectric phases all properties of disordered dielectrics, including distribution of relaxation times, can be calculated in mean field approximation. In this approximation random field distribution function has the form of $\delta$-function, i.e. $f_{mf}(E) = \delta(E - E_0L)$ (linear case) and $\delta(E - E_0L(1 + \alpha_3E_0^2L^2))$ (nonlinear case [10]) with $L \neq 0$ for FE phase and $L = 0$ for paraelectric phase. Substitution of these functions into Eq.(1) gives e.g. for linear case

$$F_{mf}(t) = \delta(E(t) - E_0L) \left| \frac{dE(t)}{dt} \right|$$

(32)

Taking into account that $f(x)\delta(x-a) = f(a)\delta(x-a)$ and $\delta(f(x)) = \sum_k \delta(x-x_k)/|f'(x_k)|$ (see, e.g.,[18]), where $x_k$ are the real roots of equation $f(x_k) = 0$, one can rewrite Eq.(32) in the form

$$F_{mf}(t) = \delta(t - t_{mf})$$

(33)

where $t_{mf}$ was shown to be the unique root of the equation $E(t) - E_0L = 0$ (linear case) or $E(t) - E_0L(1 + \alpha_3E_0^2L^2) = 0$ (nonlinear case), see Fig.3. One can see from Eq. (25) that in paraelectric phase ($L = 0$) $t_{mf} = 1$, i.e. $\tau_{mf} = \tau_0 \exp(U/kT)$, whereas in FE phase ($L \neq 0$) additional temperature dependence of relaxation time appears. In particular for $LE_0/kT \gg 1 \tau_{mf} = \tau_0 \exp((U + LE_0)/kT)$ (linear case) or $\tau_{mf} = \tau_0 \exp((U + LE_0(1 + \alpha_3E_0^2L^2))/kT)$ (nonlinear case), because of mean field influence on barrier height.

### C. Numerical calculations of relaxation time distribution function

The calculation of relaxation time distribution function beyond of mean field approximation were performed numerically on the base of Eq.(28a) (linear case) and on the base of Eqs. (8), (10), (11), (25) (nonlinear case). Since the spectrum of relaxation times in disordered systems is very broad ($1 \leq \tau/\tau_0 = t < \infty$), we, following literature on this subject, plotted $F(t)$ in logarithmic scale in $t$. By the same reason we did not include $d\tau_{0l}/dt \sim d(ln t)/dt$ into our plots. Also, $f_1(E)$ was always taken in Gaussian form [27].

The results of calculations of relaxation time distribution function in the linear case are represented in Fig.4. To exclude a paraelectric phase we choose $v = T/T_{cmf} < 1$ and considered two values of dipole concentrations $z = n_3c$ = 1 and 10 (curves 1 and 2 respectively). Due to the values of parameters chosen, curve 1 corresponds to $F(t)$ for FG phase whereas curve 2 illustrates the transformation of $F(t)$ into the form close to $\delta$-function, which is realized as $z$ increases (system approaches to FE phase). The shape of curve 1 reflects the Gaussian form (2) of $f_1(E)$ . For non-Gaussian shape of $f_1(E)$ (e.g. Lorentzian, Holtzmakian etc, corresponding to different random field sources), the shape of $F(t)$ in linear case will also reflect them. Since all aforementioned curves are known to be symmetric functions, the linear relaxation time distribution function also must be symmetric.

Let us proceed to calculation of $F(t)$ in nonlinear case. Since the solutions of Eq. (11) depend on the lattice symmetry we considered a host lattice with a centre of inversion in the paraelectric phase, that is characteristic for many disordered systems. In such a case only the terms with odd powers of $\varepsilon$ remain in Eq.(11). In our calculations we retained only the first nonlinear term in Eq.(11), i.e. $\alpha_3\varepsilon^2$. The sign and value of nonlinearity coefficient $\alpha_3 \equiv \alpha_0E_0^2$ appeared to influence strongly the shape of $F(t)$ (see Fig.5 for $\alpha_0 > 0$ and Fig.6 for $\alpha_0 < 0$). One can see that for $\alpha_0 > 0$ $F(t)$ broadens and shifts towards larger $t$ with $\alpha_0$ increase. Such behaviour can be the result of barrier increase due to nonlinear random field contribution. Shape of $F(t)$ transforms from almost symmetric to slightly asymmetric with $\alpha_0$ increase. For example, for $\alpha_0 = 1$ the right "wing" of the curve is just Gaussian while left one decays faster
then Gaussian. Strongly asymmetric shape of $F(t)$ is peculiar for $\alpha_0 < 0$, the line asymmetry being larger at larger $|\alpha_0|$ (see Fig.6). The narrowing of $F(t)$ and its maximum position shift to the smaller $t$ with $|\alpha_0|$ increase can be the result of the barrier decrease. More essential asymmetry of $F(t)$ for $\alpha_0 < 0$ in comparison with $\alpha_0 > 0$ is the result of presence of only one root of Eq. (11) (and symmetric shape of $f(E)$) for $\alpha_0 > 0$, whereas for $\alpha_0 < 0$ there are three different real roots of Eq. (11), which breaks $f(E)$ symmetric shape (see [15]). The curves depicted in Figs. 5 and 6 correspond to FG phase with coexistence of short- and long-range order. Calculations of $F(t)$ for DG state (where only short-range ordered clusters exist) lead to very broad curve with very slow decay even in $\ln(t)$ scale.

V. DISCUSSION

The distribution of relaxation times is usually extracted from observed frequency dependence of dielectric susceptibility. This dependence for ordered systems is known to be described by Debye law with the unique relaxation time. To describe the observed dynamic susceptibility of the disordered ferroelectrics, polymers and composites, several empirical functions were proposed as of Debye law generalizations (see e.g. [4]). Among them the most known are following:

$$
\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left\{ \begin{array}{ll}
(1 + (\omega\tau_{CC})^{1-\kappa})^{-1} & (a) \\
(1 + (\omega\tau_{DC})^{\kappa})^{-\beta} & (b) \\
(1 + (\omega\tau_{HN})^{\gamma})^{-\delta} & (c)
\end{array} \right.
$$

(34)

Eq. (34) (a), (b), (c) represent, respectively, Cole-Cole (CC) ($0 \leq \kappa < 1$), Davidson-Cole (DC) ($0 < \beta \leq 1$) and Havriliak-Negami (HN) ($\gamma \leq 1$, $\delta \leq 1$) functions.

All these functions are written in the frequency domain, whereas in time domain Debye relaxation is usually generalized to Kohlrausch-Williams-Watts (KWW) relaxation function, which is also currently called a "stretched exponential"

$$
\Phi(t) = \exp\left(-t/\tau_W\right)^\alpha, 0 < \alpha \leq 1
$$

(35)

Since there is no analytical expression for Eq. (35) in frequency domain, the numerical calculation of its Fourier transform was performed [4]. It was shown that at $\gamma \delta = \alpha^{1,2,3}$ the results are identical to those for H-N function.

Empirical laws (34), (33) were applied for many years for the description of slow relaxation processes in conventional glasses, polymers, composites, disordered ferroelectrics etc. The data obtained by several experimental techniques, including dielectric spectroscopy, nuclear magnetic resonance, quasielastic neutron scattering, kinetic reactions etc. were successfully fitted by these laws (see e.g. [4], [19]). It was supposed, that physical origin of the laws (34) and (33) was some distribution of relaxation times $F(\tau)$, so that

$$
\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{1}{1 + i\omega\tau} F(\tau) d(\ln \tau)
$$

(36a)

$$
\exp\left(-t/\tau_W\right)^\alpha = \int_0^\infty \exp\left(-t/\tau_W\right) F(\tau) d(\ln \tau)
$$

(36b)

The expressions (34), (36a), (36b) made it possible to extract relaxation time distribution function for all the empirical laws. The results of such extraction, obtained in Ref. [5] are represented in Fig.7 for Debye CC ($\kappa = 0.2$), DC ($\beta = 0.6$), KWW ($\alpha = 0.42$). Due to aforementioned relation between KWW and HN laws the shape of $F(\tau)$ for HN is similar to that for KWW function (see Fig.7). The obtained distribution functions are empirical ones with strongly different shapes. Namely, $F(\ln \tau)$ can be symmetric (CC), asymmetric (KWW, HN) and strongly asymmetric (DC) function. To the best of our knowledge, the physical mechanisms of such behaviour is not known out up to now.

To clarify the physical mechanisms let us compare the empirical curves from Fig.7 with the curves in Figs. 4, 5, 6, obtained on the base of random field distribution function. As it was shown in Section 4 the symmetric form of $F(\tau)$ is pertinent to linear approximation what is valid for small enough random field sources concentrations. With increase of random field sources concentration nonlinear and correlation effects become essential. They result in $F(\ln \tau/\tau_0)$ small asymmetry for $\alpha_0 > 0$ (Fig.5) and strong asymmetry for $\alpha_0 < 0$ (Fig.6). The comparison of the curves in Figs. 6 and 7 shows that the shape of the curves 2 and 3 in Fig.6 looks like that for KWW and DC laws respectively (Fig.7).
Relative position of their maxima is in conformity with that for curves 2 and 3 in Fig.6. The coincidence of $\tau_{CC}$ and Debye relaxation time $\tau_D$ (see Fig.7) can be expected also from calculated curves in Fig.4 because with increase of random electric dipoles concentration curve 2 has to be transformed into $\delta$-function (see Section 4). Since calculated curves in Figs. 4, 5, 6, correspond to FG phase with coexistence of short- and long-range order, we can conclude that this coexistence as well as small (CC law) or large nonlinear effect contribution with negative coefficient (KWW, DC laws) are the physical background of the considered empirical laws. Note, that nonlinear and correlation effects with negative nonlinearity coefficient decrease the system order, i.e. they makes it "more disordered", as it was shown recently [10]. Under such conditions the role of random fields and thus the distribution of relaxation times becomes more essential in the peculiarities of physical properties of disordered dielectrics.

VI. CONCLUSION

The coincidence between the relaxation time distribution function obtained from empirical laws and calculated on the base of random fields distribution function gives evidence that random fields are indeed the main physical reason for the distribution of relaxation times. Variety of distribution function forms is due to "degree of disorder" (i.e. presence of different amounts of different random field sources) in the systems under consideration.

Suggested general formalism for relaxation times distribution function calculation has pretty general nature (because of generality of statistical method, see [13,14]) within assumptions made. It can be easily generalized to other disordered systems like spin glasses.

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FIG. 1. Schematic plot of nonmonotonous behaviour of $\tau(E)$ function. One value $\tau_0$ corresponds to four $E$ values ($E_1 - E_4$). In the regions 1-4 function $\tau(E)$ is monotonous (it decreases in regions 1 and 3 and increases in 2 and 4).

FIG. 2. (a) - Parabolic barrier in the external electric field $E$. It is seen that barrier height at $E \neq 0$ is larger than that at $E = 0$. Parabolic approximation for steepest descent method is also shown.
(b) - Rectangular barrier at $E = 0$ (solid line), $E < 0$ (dashed line) and $E > 0$ (dotted line).
FIG. 3. Schematic plot of dependence $E(t)$ [25]. Arrows show the integration contour in (31). We also show the unique root $t_{mf}$ of equation $E(t) - E_{mf} = 0$ (see Eqs (34), (35)), $E_{mf} = E_0 L$ (linear case) or $E_{mf} = E_0 (1 + \alpha_0 L^2)$. For the sake of illustration $E_{mf}$ is plotted only for the case $L > 0$ and $\alpha_0 > 0$.

FIG. 4. Relaxation time distribution function for small random field contribution - linear case. Parameters of calculations: $v = 0, 3$, $z = 1$ (curve 1), $z = 10$ (curve 2).

FIG. 5. Relaxation time distribution function for large random field contribution - nonlinear case, with positive (a) and negative (b) coefficient of nonlinearity. Parameters of calculations: $v = 0, 5$; $z = 2$; $\alpha_0 = 1; 0, 5; 0, 1$ (curves 1, 2, 3 respectively in (a)); $v = 0, 3$; $z = 1$; $\alpha_0 = -0, 01; -0, 1; -0, 3$ (curves 1, 2, 3 respectively in (b)).

FIG. 6. Relaxation time distribution function for Debye (D), Cole-Cole (CC), Davidson-Cole (DC) and Kohlrausch-Williams-Watts (WW) laws [5].
Parabolic approximation for steepest descent method

Barrier height in a field $E$

$U$ - barrier height at $E=0$. 

Parabolic approximation for steepest descent method

$u(x)$
Fig. 2b
Fig. 3
$v = kT/E_0 = 0.3;$

$\alpha_0 = \alpha_3 E_0^2 = 0$

$1 - z = nr_c^3 = 1,$

$2 - z = 10.$
$\nu = 0.5, z = 2$, figures near curves - dimensionless nonlinearity coefficient of third order $\alpha_0$. 

$$F(\tau) = \ln(\frac{\tau}{\tau_0})$$

**Fig. 5.**
\[ F(\tau) = \ln\left(\frac{\tau}{\tau_0}\right) \]

\[ v=0.3, \ z=1, \]

Figures near curves - \( \alpha_0 \).
Fig. 7.

\[ \ln(\tau) \]

\[ F(\tau) \]

\[ \tau_D, \tau_{CC}, \tau_{WW}, \tau_{DC} \]