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Fluctuation theory of relaxation phenomena in disordered conductors: How fitting laws such as those of Kohlrausch and Jonscher are obtained from a consistent approach

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A theoretical approach to the description of temporal and frequency responses of glasslike conductors is developed and a detailed mathematical analysis of response functions is given. Being derived from general principles of Gaussian statistics of Coulomb fluctuations, which are produced by the random field of charged defects, these functions can be expressed in terms of the initial conductivity (without disorder) and a fluctuation exponent that reflects the sensitivity of mobile charges to disorder. In light of our present results, the Gaussian model of the distribution of activation barriers in glasslike systems is put on firm theoretical ground. The derived conductivity of the disordered medium reproduces all characteristic features of the empirical Jonscher law; also, the frequency range where it can be observed increases exponentially with the fluctuation exponent. The latter determines both the Jonscher exponent and the fractional exponent in the so-called Kohlrausch law. In this case, the non-Debye relaxation time takes the strict Arrhenius form with the effective activation energy carrying information about the disorder. The obtained results are compared with experimental data and possible ways to reconcile the discrepancy between theory and experiment are discussed. [S0163-1829(96)04629-2]

I. INTRODUCTION

The group of phenomena where universal (in both frequency and time) behavior of response functions of disordered systems is observed is rather wide. The first evidence of the deviation of the time response function from a simple exponential dependence became known as far back as the 19th century after the classic work of Rudolf Kohlrausch on the relaxation of a residual charge in the glass body of a Leyden jar (for a description of these experiments, see, for example, Ref. 1). In these experiments it was noticed that the dynamics of the process is described by the stretched exponent $\exp[-(t/\tau_K)^{\beta}]$, where τ_K and $0<\beta<1$ are the characteristic time and exponent (the so-called Kohlrausch-Williams-Watts law). At present one may consider it to be established that the difference of β from 1 is a reflection of the disorder of the system. The disorder leads to the existence of non-Debye behavior of the response functions of various materials: electronic conductors,[2,3] solid dielectrics,[4] liquid[5,6] and solid (including polymer) ionic conductors,[7–17] viscoelastic liquids,[18] protein molecule solutions,[19] and spin glasses.[20–22] The common feature of these disorder phenomena is that nonanalytical frequency dependences of the dynamic characteristics are observed in them. Thus, for example, the frequency-dependent parts of mechanical moduli and of the complex impedance of ion-conducting glasses are described by an expression of the type $\sim\omega^{s}, 0<s<1$, in a wide interval of frequencies ω (see, for example Refs. 5 and 7–11). Up to now the works where such regularities have been found are numbered, literally, in hundreds (we naturally cannot mention all of them). After Jonscher's work[23] the dependences have been united under the common name ''universal frequency response.''

Repeated attempts at derivation of the above mentioned dependences were made starting from different theoretical models. In Ref. 24, which was dedicated to the modeling of the electrical response of disordered semiconductors, it was noticed that at the base of the nonanalyticity of the low-frequency conductivity there lies a hierarchy of relaxation times of electrons. However, the approach applied in Ref. 24 did not allow an exhaustive interpretation of the peculiarities of the dynamic conductivity of disordered matter. One could not extend it to the case of glasslike systems with the classical—ionic—conductivity. Attempts to apply the ideology of Ref. 24 to ion-conducting systems had to use assumptions (like introducing truncating factors to provide the convergence of integrals[25]) which can hardly have a serious basis. One of the models, especially developed for analysis of the electric response of disordered ionic conductors, was suggested in Ref. 26, but the integro-differential equations for the electrical relaxation function of the conductor which occur in this model appear to be so cumbersome that one can analyze them only numerically.

One should mention the group of works (see, for example Refs. 27 and 28, and references therein) where the universal behavior of transport characteristics of disordered systems is considered from the position of fractal dynamics. In this case, as a rule, it is not possible to establish the dependence of the exponents β and s on physical characteristics of matter (for example, on temperature).

Lately, the approach based on the computer modeling of dynamical properties of disordered ionic conductors[29,30] was extended. The basis of this approach is a fundamental property of such systems, the Coulomb interaction between ions, but as in all computer experiments the transparent interpretation of the results appears to be difficult.

The fitting formulas for the processing of numerous experimental data on the non-Debye relaxation of glasslike systems were usually constructed by choosing some activation energy distributions for mobile particles; namely, in the most

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frequently discussed fitting formulas an exponential distribution is postulated (see, for example Refs. 4 and 10, and references therein), but then the obtained results crucially depend on the method of truncation of the integrals appearing in the model. On the other hand, there are some communications in the literature about the use of a Gaussian distribution function of energy barrier heights for processing the experimental data on disordered conductor relaxation dynamics.[31,32,12,13] Such a Gaussian form, naturally, is considerably less sensitive to the choice of the barrier height boundary values. In addition, with the help of this form it is possible to make the best fit of existing experimental dependences of the frequency response of ion-conducting glasses. This has been investigated by Macdonald,[33] who carried out the most complete investigation of the Gaussian model in application to disordered conductors. However, in Ref. 33 it was claimed without proof that the Gaussian distribution does not lead to forms reproducing the empirical laws of Jonscher and Kohlrausch.

Meanwhile, in our paper[34] it was found that such a Gaussian distribution is the natural consequence of an approach based on general ideas of statistical physics of Coulomb fluctuations. In this case, for the analytically derived function of the frequency response of a conducting glass we succeeded in obtaining a form which strictly reproduces the Jonscher one in a wide frequency interval.

The importance of the influence of Coulomb fluctuations on transport characteristics of ion-conducting matter was demonstrated earlier in the work of one of the authors and Kuskovskii.[35] In this work one of the variants of the theory of the universal electrical response of disodered conductors, with the use of the method applied earlier by Andreev[36] for calculation of frequency-dependent fluctuation corrections to hydrodynamic kinetic coefficients, has been proposed.

The present paper is the continuation of Ref. 34, in which the basis of the subsequent application of Coulomb fluctuation statistics for construction of a quantitative theory of non-Debye relaxation in disordered conductors has been laid. The ideas reported in the work of Bondarev and Zhukov[37] concerning the calculation of the dc conductivity of disordered ion-conducting systems were extended in Ref. 34 onto the dynamical case. But if in Ref. 37 (and in Ref. 34 as well) it has been assumed that the disorder is formed by the mobile ionic defect subsystem itself, then below, in Sec. II, the calculation of fluctuation additives to the activation energy of the dc conductivity of the disordered system is also performed for the case of frozen fluctuations. Sections III and IV are dedicated to the derivation and analysis of closed-form expressions for the response functions—temporal and frequency—of disordered conductors, and to the comparison of the theory with experimental data (the results of these sections have been partially published in Ref. 34). In the Summary we discuss the results obtained and outline methods for further investigation of the considered problem.

II. FLUCTUATION ADDITIVE TO THE dc CONDUCTIVITY ACTIVATION ENERGY

In order to understand the essence of the proposed approach, let us turn our attention to the method of calculation of the dc conductivity of glasslike conductors; this method was used in the paper of Bondarev and Zhukov.[37] For definiteness, we will start from the idea of a disordered conductor as an ionic crystal containing interstitial ionic defects—extrinsic or intrinsic—and a corresponding number of vacancies in sites of the host (ordered) lattice (for a similar picture in application to superionic glasses, see Ref. 38). The presence of such defects leads to a local violation of electroneutrality and to the appearance of long-ranged electric fields in the system. Under their influence the migration barriers for mobile defects will undergo fluctuation changes so that the conducting characteristics of the system must be obtained by averaging the corresponding local values over probabilities of the realization of these fluctuations. It is important that to obtain a concrete result one should average just the specific resistance (not the conductivity). Indeed, the resultant dissipation during ionic transport will be determined by the sum of local resistivities in each part of the sample. So, just the quantity which is reciprocal to the average specific resistivity can be identified with the experementally observable conductivity of such a disordered system.

Thus, the problem of finding the average (denoted below by the angular brackets) specific dc resistance of the disordered conductor $\langle z_{\mathrm{dc}}\rangle$, in fact, amounts to the averaging of the local value

$$z_{\mathrm{dc}}=z\,\exp\left\{\frac{D_0}{T}+\frac{q[\varphi(\vec{r}+\vec{a})-\varphi(\vec{r})]}{T}\right\}. \tag{1}$$

The product of ionic charge q and the random (fluctuation) potential difference of a mobile ion at points $\vec{r}$ and $\vec{r}+\vec{a}$ ($2|\vec{a}|$ is the length of an elementary hop) occurring in Eq. (1) must be considered as an additive to the initial (in the absence of disorder) activation energy D_0; T is the temperature and z is a preexponential factor.

The averaging in Eq. (1) should be made on random Coulomb potentials φ. Here the result of the averaging, in principle, will be dependent on how large or small is the decoupling index $R_\tau=\tau_s/\tau_\sigma$ for a given system, where τ_s and τ_σ are the relaxation times of shear stresses and conductivity, respectively. This parameter was introduced in Ref. 39 and in application to our problem one can consider that the limit $R_\tau\rightarrow\infty$ corresponds to the case of fluctuations φ frozen at the vitrification temperature T_g, when in an exceptionally slowly relaxing glass matrix (extremely nonergodic state of fluctuations) ionic transport with finite conductivity is possible. On the other hand, at finite ionic conductivity of the system the case of $R_\tau\sim 1$ can take place, when the conducting process will occur on the background of ergodic fluctuations φ which are created, in fact, by the subsystem of mobile ions themselves.

The latter case is realized in liquid electrolytes[39] and also in fast-ion-conducting glasses (see also Ref. 40). Then the distribution function of fluctuations depends on the actual temperature T and has the form

$$G_\varphi(T)=\exp[-F\{\varphi;T\}/T]. \tag{2}$$

Here

$$F\{\varphi;T\}=\frac{1}{2}\int dV\left[\rho\varphi+\frac{4\pi}{\varepsilon_\infty}R^2(T)\rho^2\right] \tag{3}$$

is the free energy of Coulomb fluctuations,[42,37] expressed through the local density of the fluctuation charge ρ. The latter is connected with φ by the Poisson equation

$$\vec{\nabla}^2\varphi=-4\pi\rho/\varepsilon_\infty\,, \tag{4}$$

where ε_∞ is the high-frequency dielectric constant of the ionic conductor, $R(T)$ is the Debye screening length in a plasma of mobile defects, and for simplicity we use the model of isotropic matter. Using $G_\varphi(T)$ at the averaging assumes the ergodicity of disorder, similarly to what takes place for superionics where fluctuations are created by mobile defects themselves and are not frozen.

In the other case, corresponding to glasslike solid solutions, a mobile particle experiences, mainly the fluctuation fields of charged defects, which at a given temperature T can be considered as frozen, i.e., extremely nonergodic. Here (i.e., neglecting the direct interaction between the mobile particles themselves) the role of the distribution function of the Coulomb fluctuations is played by the quantity $G_\varphi(T_g)$, corresponding to the vitrification temperature T_g of the material.

The average $\langle z_{\rm dc}\rangle$ at the frozen disorder (the case of ergodic disorder has been considered in Ref. 37),

$$\langle z_{\rm dc}\rangle=\int \mathcal{D}\varphi\, z_{\rm dc}G_\varphi(T_g)\bigg/\int \mathcal{D}\varphi\, G_\varphi(T_g), \tag{5}$$

can be presented as the normalized functional integral over fluctuations φ. The procedure of calculations, as in Ref. 37, consists in the transition to the Fourier representation

$$\varphi(\vec r)=\frac{1}{\sqrt{V}}\sum_{\vec k}\varphi_{\vec k}e^{i\vec k\cdot\vec r},\quad \varphi_{-\vec k}=\varphi^*_{\vec k}\,, \tag{6}$$

where V is the volume of the system, and in the functional integration of Eq. (5) over all variables

$$u_{\vec k}=\mathrm{Re}(\varphi_{\vec k}e^{i\vec k\cdot\vec r}),\quad v_{\vec k}=\mathrm{Im}(\varphi_{\vec k}e^{i\vec k\cdot\vec r}), \tag{7}$$

in the limits from $-\infty$ to ∞. Then because of the Gaussian character of the expressions the necessity for explicit integration drops out. Indeed, introducing new variables of integration in the numerator of Eq. (5)

$$u'_{\vec k}=u_{\vec k}+\frac{4\pi qT_g}{\varepsilon_\infty T\sqrt{V}}\frac{1-\cos(\vec k\cdot\vec a)}{k^2[1+R^2(T_g)k^2]},$$

$$v'_{\vec k}=v_{\vec k}+\frac{4\pi qT_g}{\varepsilon_\infty T\sqrt{V}}\frac{\sin(\vec k\vec a)}{k^2[1+R^2(T_g)k^2]}, \tag{8}$$

one can write

$$\begin{aligned}\frac{q}{T}[\varphi(\vec r+\vec a)-\varphi(\vec r)]-\frac{1}{2T_g}\int dV\left[\rho\varphi+\frac{4\pi}{\varepsilon_\infty}R^2(T_g)\rho^2\right]\\ =\frac{4\pi q^2T_g}{\varepsilon_\infty T^2V}\sum_{\vec k}\frac{1-\cos(\vec k\cdot\vec a)}{k^2[1+R^2(T_g)k^2]}\\ -\frac{\varepsilon_\infty}{8\pi T_g}\sum_{\vec k}k^2[1+R^2(T_g)k^2](u'^2_{\vec k}+v'^2_{\vec k}).\end{aligned} \tag{9}$$

Now it is easy to see that the multiplier

$$\prod_{\vec k}\int_{-\infty}^{\infty}du_{\vec k}\int_{-\infty}^{\infty}dv_{\vec k}\exp\left\{-\frac{\varepsilon_\infty}{8\pi T_g}k^2[1+R^2(T_g)k^2]\times(u_{\vec k}^2+v_{\vec k}^2)\right\} \tag{10}$$

is common for the numerator and the denominator of Eq. (5) and after reduction of it we obtain

$$\langle z_{\rm dc}\rangle=\sigma_0^{-1}\exp\left(\frac{\delta D}{T}\right). \tag{11}$$

Here

$$\sigma_0=z^{-1}\exp(-D_0/T) \tag{12}$$

is the initial conductivity of the system (in the absence of disorder), and the essentially positive quantity

$$\delta D^{(\rm fr)}=\frac{4\pi q^2T_g}{\varepsilon_\infty TV}\sum_{\vec k}\frac{1-\cos(\vec k\cdot\vec a)}{k^2[1+R^2(T_g)k^2]} \tag{13}$$

must be considered as the resulting addition to the activation energy of ionic conductivity due to Coulomb fluctuations frozen [indicated by the superscript (fr)] at the temperature of vitrification. Going over from summation to integration in Eq. (13) by the conventional rule

$$\begin{aligned}\sum_{\vec k}\frac{1-\cos(\vec k\cdot\vec a)}{k^2[1+R^2(T_g)k^2]}\to\frac{V}{(2\pi)^3}2\pi\int_0^\infty\frac{dk}{1+R^2(T_g)k^2}\\ \times\int_0^\pi d\theta\sin\theta[1-\cos(ka\cos\theta)]\end{aligned} \tag{14}$$

and calculating integrals, we find finally

$$\delta D^{(\rm fr)}=\frac{T_*^2}{T},T_*^2=\frac{q^2T_g}{\varepsilon_\infty a}\left\{\frac{a}{R(T_g)}-1+\exp\left[-\frac{a}{R(T_g)}\right]\right\}, \tag{15}$$

where the characteristic temperature T_* is introduced and $a=|\vec a|$. It is essential that the obtained addition $\delta D^{(\rm fr)}$ is inversely proportional to temperature.

In the case of ergodic disorder [denoted by the superscript (erg)] the expression for the fluctuation addition to the conductivity activation energy of the superionic system is derived from Eq. (15) by the replacement of T_g with T, and has the form

$$\delta D^{(\rm erg)}=\frac{q^2}{\varepsilon_\infty a}\left\{\frac{a}{R(T)}-1+\exp\left[-\frac{a}{R(T)}\right]\right\}. \tag{16}$$

Just Eq. (16) has been obtained in Ref. 37.

On the other hand, for a rarefied plasma of defects $[R(T)\gg a]$ we have from Eq. (16) with an accuracy to $[a/R(T)]^3$

$$\delta D^{(\rm erg)}=\frac{q^2a}{2\varepsilon_\infty R^2(T)}\left[1-\frac{a}{3R(T)}\right]. \tag{17}$$

Let us substitute the explicit expression for the Debye length[43] in Eq. (17):

$$R(T)=\sqrt{\varepsilon_\infty T/(8\pi n_0 x q^2)}, \tag{18}$$

where $n_0 x$ is the density of interstitial defects (and vacancies) creating Coulomb fluctuations and $n_0 \sim 10^{22}$ cm^{-3} is the density of interstitials on which the defect ions are distributed; the concentration x of defects in the disordered ionic conductor under investigation is determined by the composition and/or by the preparation (for instance, at the vitrification of the stoichiometric compound one should expect $x \ll 1$). As a result we get

$$\delta D^{(\mathrm{erg})}=\frac{T_0^2}{T}\left(1-\frac{\sqrt{2a}T_0}{3|q|\sqrt{T}}\right), \tag{19}$$

where we introduced another characteristic temperature

$$T_0=2q^2\sqrt{\pi a n_0 x}/\varepsilon_\infty . \tag{20}$$

Comparing Eq. (19) and Eq. (15) we note that the temperature dependences giving by them coincide only in the main approximation: in principle, by analyzing the details of the temperature behavior of the ionic conductivity of glass one can establish which type of disoder (ergodic or frozen) is realized in the system.

Here we have to make an important supplement clarifying the physical sense of the relation $\delta D^{(\mathrm{fr})}/T$ [see Eq. (11); an analogous equation, certainly, also occurs for the case of ergodic disorder] which will essentially determine the temperature dependences also of the averaged dynamic characteristics of disordered conductors. According to Eq. (15) one can write $\sqrt{\delta D^{(\mathrm{fr})}/T}=T_*/T$, where the characteristic temperature T_* is a function of the vitrification temperature and of fundamental characteristics of the ionic conductor. Hence it is seen that the quantity $\sqrt{\delta D^{(\mathrm{fr})}/T}$ is the ratio of the energetic amplitude of Coulomb fluctuations frozen at the vitrification temperature T_g, averaged in some way, to the average thermal energy of a mobile ion. Note that the parameter $1/\sqrt{\delta D^{(\mathrm{fr})}/T}$ in a definite sense is analogous to the one introduced in Ref. 41 for description of the properties of the spin-glass state, where the latter parameter corresponded to the number of replicas of the statistical sum of the glass. From our definition of $1/\sqrt{\delta D^{(\mathrm{fr})}/T}$ it follows that the manifestation of the disorder in transport properties of the ionic conductor will be greater the lower is the temperature. Therefore one can consider that the quantity $\delta D^{(\mathrm{fr})}/T$ determines how the conductive subsystem is sensitive to the structure disorder of the glass. Concerning Eqs. (16) and (18), which allow us to determine the sensitivity of the conducting subsystem to the ergodic disorder, they are applicable in the temperature range of existence of an electrolyte in a liquid state or in the state of a superionic conductor [just for the latter case Eq. (19), actually, has been obtained]. Naturally, the lower boundary of the range in the case of a liquid electrolyte is the temperature of its vitrification, T_g.

Let us pay attention to the following circumstance. The expressions obtained above were derived for the case of three-dimensional isotropic ion-conducting glasses which are most frequently investigated experimentally (see, for example, Ref. 14). However, systems are known like layered $\mathrm{Na_2O\text{-}K_2O}$ β-alumina[44] where the ionic disorder has quasi-two-dimensional character. To account for the specifics of such systems the fluctuation addition to the conductivity activation energy needs an additional—logarithmic in temperature—multiplier in comparison with Eqs. (15) and (20) (this result has been obtained in the work of one of the authors;[45] we shall not discuss this subject here in detail).

III. DYNAMICAL RESPONSE FUNCTIONS OF DISORDERED CONDUCTOR: RIGOROUS RESULTS

As a starting point for the derivation of observable transport characteristics of the disordered ionic conductor (the results obtained below, in principle, are applicable also to other systems with hopping conductivity) let us write down the expression for the local specific complex impedance $z(\omega)$ in the form (see, for example, Ref. 23)

$$z(\omega)=i\frac{4\pi}{\omega\varepsilon(\omega)}, \tag{21}$$

where

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{4\pi i}{\omega}\sigma \tag{22}$$

is the local complex dielectric function of the material and $\sigma=1/z_{\mathrm{dc}}$ is its local conductivity. Being measured experimentally, the complex impedance of the disordered conductor is derived by averaging of Eq. (21)

$$\langle z(\omega)\rangle=\left\langle\frac{z_{\mathrm{dc}}}{1-i\varepsilon_\infty z_{\mathrm{dc}}\omega/4\pi}\right\rangle, \tag{23}$$

so that at $\omega=0$ the result of the averaging is reduced to the result obtained above (see also Ref. 37) for the average specific resistance, $\langle z_{\mathrm{dc}}\rangle=\langle 1/\sigma\rangle$. Let us pay attention to the fact that the resulting expression for the impedance is obtained by averaging of random values of the specific resistance but not of the distribution of relaxation times as is accepted for models (see, for example Ref. 4) based on the Drude-Lorentz approximation. Note that the impedance introduced in this way [Eqs. (21) and (22)], having a single pole in the lower half plane of complex frequency, satisfies the conditions of the Kramers-Kronig theorem[43] and must be considered as a natural response function of the conductor. For this reason, also, the average quantity $\langle z(\omega)\rangle$ [Eq. (23)] will satisfy the Kramers-Kronig relations. Thus, the experimentally measured complex conductivity of the disodered system can be defined as (see, for example, Ref. 46)

$$\hat{\sigma}(\omega)=\frac{1}{\langle z(\omega)\rangle}, \tag{24}$$

so that the real part of the measurable conductivity is

$$\sigma(\omega)=\mathrm{Re}\hat{\sigma}(\omega). \tag{25}$$

For what follows it is convenient to turn to the temporal behavior of the impedance, having introduced the relaxation function by the equation

$$f(t)=\frac{\varepsilon_\infty}{4\pi}\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\exp(-i\omega t)\langle z(\omega)\rangle. \tag{26}$$

Substituting Eq. (23) in Eq. (26) and going over to integration on corresponding contours in the complex ω plane, we get

$$f(t)=\left\langle\exp\left[-\frac{4\pi t}{\varepsilon_\infty z_{dc}}\right]\right\rangle,\quad t\geqslant 0,$$

$$f(t)=0,\quad t<0. \tag{27}$$

For calculation of the relaxation function let us expand $f(t)$ at $t\geqslant 0$ into the series

$$f(t)=\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\left(\frac{4\pi t}{\varepsilon_\infty}\right)^m\langle z_{\mathrm{dc}}^{-m}\rangle,\quad t\geqslant 0. \tag{28}$$

The average $\langle z_{\mathrm{dc}}^{-m}\rangle$ at arbitrary m is derived in analogy with the $\langle z_{\mathrm{dc}}\rangle$ found above [see Eqs. (11)–(13)]. Omitting intermediate calculations we have

$$\langle z_{\mathrm{dc}}^{-m}\rangle=\int\mathcal{D}\varphi z_{\mathrm{dc}}^{-m}G_\varphi(T)\Bigg/\int\mathcal{D}\varphi G_\varphi(T)$$

$$=\sigma_0^m\exp\left(\frac{m^2\delta D}{T}\right), \tag{29}$$

so that the distribution function $G_\varphi(T)$ and the addition to the activation energy δD are written down in general form, i.e., without specification of the type of disorder which is realized in the system.

It is remarkable that series (28) taking into account Eq. (29) can be summed exactly. We do this as follows. Introduce dimensionless quantities

$$\Theta=\ln(4\pi\sigma_0 t/\varepsilon_\infty),\quad -\infty<\Theta<\infty,\quad \nu=\frac{4\delta D}{T}, \tag{30}$$

and consider them to be the arguments of the relaxation function. The introduced quantity ν has a fluctuation nature and we will call it *the fluctuation exponent* (its physical meaning as the sensitivity to the structural disorder of the conductor has already been mentioned at the end of Sec. II). Then the expansion of the relaxation function can be presented in the form

$$f(\Theta,\nu)=\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}e^{m^2\nu/4+m\Theta}. \tag{31}$$

Now one can notice that the function $f(\Theta,\nu)$ satisfies the linear one-dimensional equation of ''diffusion''

$$4\frac{\partial f(\Theta,\nu)}{\partial\nu}=\frac{\partial^2 f(\Theta,\nu)}{\partial\Theta^2}, \tag{32}$$

in which the role of the ''coordinate'' is played by the logarithmic time and the role of the ''time'' is played by the fluctuation exponent ν. As the initial condition to Eq. (32) one must take the equality

$$f(\Theta,0)=f_D(\Theta)=\exp(-\exp\Theta), \tag{33}$$

which indicates that in the absence of disorder, i.e., at $\nu=0$, the relaxation function of the conductor is transformed to the Debye function $f_D(\Theta)$, i.e., to $\exp(-4\pi\sigma_0 t/\varepsilon_\infty)$. The boundary conditions are

$$f(-\infty,\nu)=1,\quad f(\infty,\nu)=0. \tag{34}$$

The solution of the diffusion equation, which satisfies the conditions (33) and (34) can be presented as an integral (see, for example, Ref. 47):

$$f(\Theta,\nu)=\frac{1}{\sqrt{\pi\nu}}\int_{-\infty}^{\infty}\exp\left[-\frac{(\Theta'-\Theta)^2}{\nu}\right]\exp(-\exp\Theta')d\Theta', \tag{35}$$

which contains the convolution of the known Green function of Eq. (32) with the initial value of $f(\Theta,\nu)$. Returning to the presentation of the relaxation function through the real time t and changing the integration variable in Eq. (35), we have as a result the elegant expression

$$f(t)=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}du\exp[-u^2-(t/\tau)\exp(\sqrt{\nu}u)],\quad t\geqslant 0,$$

$$\tau=\frac{\varepsilon_\infty}{4\pi\sigma_0}, \tag{36}$$

where the Debye relaxation time τ is determined through the initial conductivity of the system and as in Eq. (26) we do not indicate the parameter ν as an argument of the relaxation function. It is easy to prove that series (28) is obtained by expanding the integrand in Eq. (36) in powers of t and by the termwise calculation of the resulting Gaussian integrals.

A brief derivation of Eq. (36), allowing one to analyze in detail the non-Debye relaxation in systems of superionic glass type, has been given in Ref. 34. In that paper, the expression for the averaged frequency-dependent impedance was also displayed. This is obtained from Eq. (36) by the Fourier transformation

$$\langle z(\omega)\rangle=\int_{-\infty}^{\infty}f(t)e^{i\omega t}dt=\frac{4\sqrt{\pi}\tau}{\varepsilon_\infty\sqrt{\nu}}\int_{-\infty}^{\infty}\frac{\exp(-u^2/\nu)}{-i\omega\tau+\exp u}du. \tag{37}$$

Considering this expression as a function of complex frequency, note that it does, like any physically correct response function, satisfy the requirement $\langle z(-\omega^*)\rangle=\langle z(\omega)\rangle^*$,[43] where the superscript * means complex conjugation.

To investigate the properties of the function $\langle z(\omega)\rangle$ at real positive ω it is convenient to introduce the variable $w=\nu^{-1}\ln(\omega\tau)$. Then the averaged impedance and the resulting complex conductivity as functions of the variable w take the forms

$$\langle z(w)\rangle=\frac{4\sqrt{\pi}\tau}{\varepsilon_\infty\sqrt{\nu}}\exp(-\nu w-\nu w^2)\times\int_{-\infty}^{\infty}\frac{dy\exp(-y^2/\nu-2wy)}{\exp y-i},$$

$$\hat{\sigma}(w)=\frac{1}{\langle z(w)\rangle},\tag{38}$$

following from Eqs. (37) and (24). Shifting now the argument in $\langle z(w)\rangle$, $w\rightarrow w-1/2$, and extracting from the obtained expression an exactly calculated Poisson integral, we come to the recurrence relation

$$\left\langle z\left(w-\frac{1}{2}\right)\right\rangle=\frac{1}{\sigma_0}\exp\left(\frac{\nu}{4}\right)+i\exp\left(\frac{\nu}{4}+\nu w\right)\langle z(w)\rangle\tag{39}$$

or to the equivalent one for the complex conductivity of a disordered system in terms of the variable w,

$$\hat{\sigma}(w)=\frac{\sigma_0\exp(-\nu/4)}{1+i\sigma_0\exp[\nu(w+1/2)]/\hat{\sigma}(w+1/2)}.\tag{40}$$

The last recurrence relation is the base for obtaining the representation of $\hat{\sigma}(w)$ in the form of continuous fractions. Indeed, from Eq. (40) one can get two equivalent forms:

$$\frac{\hat{\sigma}(w-1/2)}{\hat{\sigma}(w)}=\frac{1}{1+i\exp[\nu(w+1/4)]-i\exp[\nu(w+3/4)]\hat{\sigma}(w)/\hat{\sigma}(w+1/2)},\tag{41}$$

$$\frac{\hat{\sigma}(w+1/2)}{\hat{\sigma}(w)}=\frac{\exp(\nu/2)}{1-i\exp[-\nu(w+1/4)]+i\exp[-\nu(w+1/4)]\hat{\sigma}(w)/\hat{\sigma}(w-1/2)}.\tag{42}$$

Making in each of them sequential recursions, having taken into account Eq. (40), and returning to the frequency variable, we get two equivalent representations of $\hat{\sigma}(\omega)$ by the continuous fractions

$$\hat{\sigma}(\omega)=\sigma_0\exp(-\nu/4)\left(1-\frac{i\Omega}{1+i\Omega-}\,\frac{i\Omega\Lambda}{1+i\Omega\Lambda-}\,\frac{i\Omega\Lambda^2}{1+i\Omega\Lambda^2-}\cdots\right),\tag{43}$$

$$\hat{\sigma}(\omega)=\sigma_0\exp(\nu/4)\left(-\frac{i\Omega}{\Lambda^2}+\frac{1}{1-i\Omega^{-1}\Lambda^2+}\,\frac{i\Omega^{-1}\Lambda^3}{1-i\Omega^{-1}\Lambda^3+}\,\frac{i\Omega^{-1}\Lambda^4}{1-i\Omega^{-1}\Lambda^4+}\cdots\right),\tag{44}$$

where we introduced the dimensionless frequency $\Omega=\omega\tau\exp(3/4\nu)$ and the parameter $\Lambda=\exp(\nu/2)>1$.

Note that Eq. (43) corresponds to a ''low-frequency'' expansion and Eq. (44) corresponds to a ''high-frequency'' one. Thus from Eq. (43) it follows that at $\omega\rightarrow 0$ the experimentally measured conductivity of the disodered system $\sigma(\omega)$ [see Eq. (25)] tends to its low-frequency limit $\sigma_{\mathrm{dc}}=\sigma_0\exp(-\nu/4)$ and at large ω, as is seen from Eq. (44) it tends to the ''high-frequency'' limit $\sigma_\infty=\sigma_0\exp(\nu/4)$ (it is assumed, of course, that the approach to σ_∞ takes place at frequencies definitely lower than those at which the Drude-Lorentz regime or optical vibrations of the ionic conductor appear). However, the structure of both Eq. (43) and Eq. (44) is that the multiplier $\Lambda>1$ enters each of the subsequent elements of the fraction in increasing power, which means, in fact, that it is impossible to represent $\hat{\sigma}(\omega)$ by a convergent series in powers of ω or ω^{-1} [compare with the temporal expansion given above of the relaxation function through the formally divergent series (28) taking account of Eq. (29)]. Thus the absence of an analytical expansion of $\hat{\sigma}(\omega)$ at any finite value of argument leads to the conclusion that in a wide frequency range $\hat{\sigma}(\omega)$ can be approximated adequately by a suitable nonanalytical expression (see below), which proves the empirical Jonscher law.[23]

Note that the continuous fraction formalism has been used many times in modeling dynamic response functions of conducting systems (see, for example, Ref. 48). Often, however, the matter was restricted by choosing the approximation corresponding to taking into account only a few terms of the continuous fraction. Lately, in works of several authors (see Ref. 28) the Jonscher law has been discussed in connection with mathematical fractal models of disordered conductors as a hierarchical system of resistors and capacitors. Here the impedance of the conductor was obtained in the form of a continuous fraction for which one could find only scaling characteristics. On the other hand, the dynamical characteristics of one-dimensional disordered conductors[49] also could not be analyzed completely because a closed expression for the continuous fraction modeling the dynamical conductivity has not been found. In our case one succeeded in obtaining $\langle z(\omega)\rangle^{-1}$ in a closed form that is equivalent to the convolution of corresponding continuous fractions (43) and (44).

The expression for the dynamic conductivity of the disordered system, usually discussed on the base of experimental data, follows from Eqs. (37) and (38) which represent the main result of our paper:

$$\sigma(w)=\mathrm{Re}\,\hat{\sigma}(w)=\sigma_0\exp[\nu w(w+1)]\frac{B(w,\nu)}{B^2(w,\nu)+B^2(w+1/2,\nu)},\tag{45}$$

where the w function, which is symmetrical with respect to its argument,

$$B(w,\nu)=\frac{1}{2\sqrt{\pi\nu}}\int_{-\infty}^{\infty}\frac{dy\exp[-y^2/(4\nu)+(1/2-w)y]}{1+\exp y}$$
$$=B(-w,\nu) \tag{46}$$

has been introduced; as far as the authors know it was not investigated in the literature before Ref. 34. This function possesses several important properties. First, at values $w=m+1/2,\ m=0,\pm1,\pm2,\ldots$, it is calculated exactly and the recurrence formula[34]

$$B(w-\tfrac{1}{2},\nu)+B(w+\tfrac{1}{2},\nu)=\exp(\nu w^2) \tag{47}$$

occurs, which can be derived in analogy with the derivation of the recurrence formula (39) by changing the argument $w\rightarrow w-1/2$ in $B(w,\nu)$ and separating the Poisson integral in the result obtained. For example, it follows from Eq. (47) that $B(1/2,\nu)=1/2$. The existence of Eq. (47) means that it is enough to study the function $B(w,\nu)$, for instance, at $0\leqslant w<1/2$ to restore its values at all other w.

Equation (47) is the basis of the representation of the function $B(w,\nu)$ in the form of a continuous fraction. Again, by analogy with the derivation of Eqs. (43) and (44), we come to two equivalent representations:

$$B(w,\nu)=\frac{\exp[\nu(w-1/2)^2]}{1+}\,\frac{\exp[-2\nu(w-1)]}{1-\exp[-2\nu(w-1)]+}\,\frac{\exp[-2\nu(w-2)]}{1-\exp[-2\nu(w-2)]+}\cdots$$
$$=\frac{\exp[\nu(w+1/2)^2]}{1+}\,\frac{\exp[2\nu(w+1)]}{1-\exp[2\nu(w+1)]+}\,\frac{\exp[2\nu(w+2)]}{1-\exp[2\nu(w+2)]+}\cdots, \tag{48}$$

coinciding due to the symmetry properties of Eq. (46).

The function $B(w,\nu)$ allows two expansions into series:[34]

$$B(w,\nu)=\frac{\sqrt{\pi}}{2\sqrt{\nu}}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}\,\frac{1}{(4\nu)^k}\,\frac{d^{2k}}{dw^{2k}}\,\frac{1}{\cos\pi w},$$
$$-\frac{1}{2}<w<\frac{1}{2}, \tag{49}$$

$$B(w+\tfrac{1}{2},\nu)=\frac{1}{2}\sum_{k=0}^{\infty}(-1)^k\{\exp[\nu(k-w)^2]$$
$$\times[1-\Phi((\sqrt{\nu}(k-w))]+\exp[\nu(k+w+1)^2]$$
$$\times[1-\Phi(\sqrt{\nu}(k+w+1))]\}, \tag{50}$$

where $\Phi(x)=(2/\sqrt{\pi})\int_0^x\exp(-y^2)dy$ is the error integral. The first series is obtained by the expansion of $\exp[-y^2/(4\nu)]$ and by termwise integration in Eq. (46) with the use of the equation[50]

$$\int_{-\infty}^{\infty}\frac{\exp(\alpha x)}{1+\exp x}dx=\frac{\pi}{\sin(\pi\alpha)},\quad 0<\alpha<1. \tag{51}$$

To obtain the second expansion one should represent $B(w+1/2,\nu)$ in the form

$$B(w+\tfrac{1}{2},\nu)=\frac{1}{2\sqrt{\pi\nu}}\int_0^{\infty}\frac{dy\exp(-y^2/4\nu)}{1+\exp(-y)}$$
$$\times\{\exp[-(w+1)y]+\exp(wy)\}, \tag{52}$$

after which the expansion of the fraction $1/[1+\exp(-y)]$ in powers of $\exp(-y)<1$ and termwise integration lead to Eq. (50). Series (49) and (50) will be useful for us below while analyzing the frequency behavior of the function $\sigma(\omega)$ within the region of the realization of the Jonscher law.

Thus, for the integral in Eq. (37) determining the conducting characteristics of the disordered system in the frequency representation, it is possible to derive several rigorous relations. Now turn to the integral in Eq. (36) for the temporal relaxation function. For $f(t)$ one can point out an exact functional equation,

$$\frac{\partial f(t)}{\partial t}=-\frac{\exp(\nu/4)}{\tau}f(t\exp(\nu/2)). \tag{53}$$

It is derived by differentiation of Eq. (36) and by a simple transformation of the obtained integrand.

As we will see, for the function $f(t)$ itself one can write no elementary expansion. It is a little easier to deal with the derivative of the relaxation function (35) with respect to the first argument. Indeed, we have

$$\frac{\partial f(\Theta,\nu)}{\partial\Theta}=-\frac{1}{\sqrt{\pi\nu}}\int_{-\infty}^{\infty}dy\exp[y-\exp y-(y-\Theta)^2/\nu]$$
$$=-\frac{1}{\sqrt{\pi\nu}}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!\,\nu^k}\int_{-\infty}^{\infty}dy(y-\Theta)^{2k}$$
$$\times\exp(y-\exp y). \tag{54}$$

The integrals appearing in Eq. (54) are convergent and are expressed through the Γ function

$$\Gamma(\mu)=\int_{-\infty}^{\infty}dy\exp(\mu y-\exp y) \tag{55}$$

and its derivatives at $\mu=1$. (Here we should note that in the attempt to construct a similar expansion for the function $f(\Theta,\nu)$ itself we would obtain divergent integrals.) Replacing now $(y-\Theta)^{2k}$ by $(d/d\mu-\Theta)^{2k}$, where $d/d\mu$ is the differential operator, one can see that series (54) convolves into a symbolic exponential function and as a result we have

$$\frac{\partial f(\Theta,\nu)}{\partial\Theta}=-\frac{1}{\sqrt{\pi\nu}}\left\{\exp\left[-\frac{1}{\nu}\left(\frac{d}{d\mu}-\Theta\right)^2\right]\right\}\Gamma(\mu)\bigg|_{\mu=1}. \tag{56}$$

Taking into account the known property of the symbolic exponential function $\exp[(2\Theta/\nu)d/d\mu]$ as the operator of finite displacement (see, for instance, Ref. 51), one can reduce Eq. (56) to a simpler form,

$$\frac{\partial f(\Theta,\nu)}{\partial\Theta}=-\frac{1}{\sqrt{\pi\nu}}\exp\left(-\frac{\Theta^2}{\nu}-\frac{1}{\nu}\frac{d^2}{d\mu^2}\right)\Gamma\left(\mu+\frac{2\Theta}{\nu}\right)\bigg|_{\mu=1}. \tag{57}$$

We write down the symbolic form for the function $f(\Theta,\nu)$ in a final view. Being derived by a formal integration of Eq. (56) on Θ, it is reduced to the expression

$$f(\Theta,\nu)=\frac{1}{2}\left\{1+\Phi\left[\frac{1}{\sqrt{\nu}}\left(\frac{d}{d\mu}-\Theta\right)\right]\right\}\Gamma(\mu)\bigg|_{\mu=1}, \tag{58}$$

containing the error function as the series

$$\Phi\left[\frac{1}{\sqrt{\nu}}\left(\frac{d}{d\mu}-\Theta\right)\right]=\frac{2}{\sqrt{\pi}}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!(2k+1)}\times\left[\frac{1}{\sqrt{\nu}}\left(\frac{d}{d\mu}-\Theta\right)\right]^{2k+1} \tag{59}$$

in powers of the symbolic argument. From Eq. (58) it is seen that the limiting values $f(t=0)=1$ and $f(t\to\infty)\to 0$ are reached at $\Theta\to-\infty$ and $\Theta\to\infty$, respectively.

The rigorous relations obtained in this section will be used below for the derivation of expressions which are the theoretical alternative to the empirical laws of Jonscher and Kohlrausch.

IV. EMPIRICAL LAWS OF JONSCHER AND KOHLRAUSCH AS SEQUENCES OF THE OBTAINED RESPONSE FUNCTIONS

As mentioned above, experiments on the dynamical response of disordered conductors demonstrate the dependence $\sigma(\omega)\propto\omega^s(0<s<1)$ in a wide frequency range. Therefore of principal interest is the experimentally measured exponent (see, for example, Ref. 3)

$$s(\omega)=\frac{d\ln\sigma(\omega)}{d\ln\omega}, \tag{60}$$

or in terms of the variable w

$$s(w)=\frac{1}{\nu}\frac{d\ln\sigma(w)}{dw}. \tag{61}$$

Our aim in this section is to show that there exists a frequency region with a practically constant exponent s and that the width of the region sharply—exponentially—widens with the growth of the square root of the fluctuation exponent ν. As a result, the behavior of $\sigma(\omega)$ in this region will possess all the attributes of the Jonscher law.

According to definition (61) the exponent $s\to 0$ at $w\to-\infty$ and $w\to\infty$, as one can see from Eq. (45) with account of Eq. (48). This means that at some intermediate value $w=w_f$, determining the point of contrary flexure of the function $\ln\sigma(w)$, the function $s(w)$ reaches its maximum value $s(w_f)$. The quantity $s(w_f)$ can be consequently analyzed in the limits of ''weak'' (small values of the fluctuation exponent ν) and ''strong'' (large ν) disorder. In the case of $\nu\to 0$ we have

$$\ln\left[\frac{\sigma(w)}{\sigma_0}\right]=\frac{\nu}{4}\tanh(\nu w). \tag{62}$$

One can derive Eq. (62) directly from Eq. (38) by using the first terms of the expansion of the integral on ν and the definition $\sigma(w)=\mathrm{Re}\langle z(w)\rangle^{-1}$. Hence the expression

$$w_f=\frac{1}{8},\quad s=\frac{\nu}{4}=\frac{\delta D}{T}, \tag{63}$$

follows immediately, where for simplicity we have omitted the argument w_f in the Jonscher exponent s which in that case is one quarter of the fluctuation exponent. The corresponding frequency at which the function $\sigma(\omega)$ undergoes the contrary flexure is $\omega_f=\tau^{-1}$ and, as one can assure oneself, the frequency range in which $s(\omega)\approx s(\omega_f)$ is $\sim 1/\tau$.

The next term of the high-temperature expansion of s is obtained by a more cumbersome calculation. Omitting it, we give only the result

$$s=\frac{\nu}{4}-\frac{\nu^2}{4}. \tag{64}$$

Much more interesting is the case of the strong ($\nu\gg 1$) disorder and we shall study it in detail. In this limit, as one can see below, the value $w_f\to 0$, but $w_f\sqrt{\nu}\to$const. So, to understand the behavior of $\sigma(w)$ in the vicinity of w_f we can represent the functions $B(w,\nu)$ [Eq. (49)] and $B(w+1/2,\nu)$ [Eq. (50)] at small w in the forms

$$B(w,\nu)=\frac{\sqrt{\pi}}{2\sqrt{\nu}}, \tag{65}$$

$$B(w+\tfrac{1}{2},\nu)=\tfrac{1}{2}e^{\nu w^2}[1+\Phi(w\sqrt{\nu})], \tag{66}$$

where the finiteness of $w\sqrt{\nu}$ at $\nu\gg 1$ is taken into account. As a result we get from Eq. (45)

$$\ln\left[\frac{\sigma(w)}{\sigma_0}\right]=\ln\left(2\sqrt{\frac{\pi}{\nu}}\right)+\nu w(1-w)-2\ln[1+\Phi(w\sqrt{\nu})], \tag{67}$$

where we neglect $B^2(w,\nu)$ in comparison to $B^2(w+1/2,\nu)$.

Using the definition (61), we find in the case of $\nu\gg 1$ the following expression for the exponent s in the vicinity of the point $w=0$:

$$s(w)=1-\frac{2}{\sqrt{\nu}}P(w\sqrt{\nu}), \tag{68}$$

where the function

$$P(\xi)=\xi+\frac{2\exp(-\xi^2)}{\sqrt{\pi}[1+\Phi(\xi)]} \tag{69}$$

depending on the variable $\xi=w\sqrt{\nu}$ has been introduced. Now it is seen that the exponent s reaches its maximum value at the point ξ_f, determined from the equation

$$\frac{\sqrt{\pi}}{2}[1+\Phi(\xi_f)]e^{\xi_f^2}=\xi_f+\sqrt{1+\xi_f^2}, \tag{70}$$

which corresponds to zero of the derivative of the function $P(\xi)$. As the elementary numerical solution of Eq. (70) shows, $\xi_f\cong 0.389$ and $P(\xi_f)=\sqrt{1+\xi_f^2}\cong 1.073$. Thus the obtained conclusion about the finiteness of ξ_f at $\nu\gg 1$ proves the above made assumption of smallness of the value $w_f=\xi_f/\sqrt{\nu}$, which corresponds to the contrary flexure point of the function $\ln[\sigma(w)/\sigma_0]$. Substituting $w=w_f$ in Eq. (68) we find the exponent

$$s(w_f)=1-\frac{2.146}{\sqrt{\nu}} \tag{71}$$

at the maximum point of the function $s(w)$.

It is easy to prove that in the vicinity of the point ξ_f the first terms of the expansion of $P(\xi)$ in $\xi-\xi_f$ have the form

$$P(\xi)=\sqrt{1+\xi_f^2}+\xi_f(\xi-\xi_f)^2+\cdots. \tag{72}$$

Hence it follows that in the range

$$|\xi-\xi_f|\ll(1+\xi_f^{-2})^{1/4} \tag{73}$$

the exponent remains practically equal to $s(w_f)$. Returning to the frequency variable and using the numerical value of ξ_f, we find from Eq. (73) that in the frequency range

$$\tau^{-1}\exp(-1.27\sqrt{\nu})\ll\omega\ll\tau^{-1}\exp(2.05\sqrt{\nu}) \tag{74}$$

the exponent s is practically independent of the frequency and coincides with $s(w_f)$ from Eq. (71).

Therefore the function $\sigma(\omega)$ indeed has the form $\approx\omega^s$, which, in fact, is the empirical Jonscher law, experimentally observed for disordered systems (see, for instance, Refs. 23, 2, 15, 26, and 28). This form holds in a frequency range, which sharply—exponentially—widens with the growth of $\sqrt{\nu}$ (compare with the discussion at the end of Sec. II).

The knowledge of the limiting expressions (64) and (71) allows us to write the following interpolation formula for the exponent s at the point w_f at arbitrary ν:

$$s=1-\frac{5.333+2.146\nu}{(5.094+\nu)\sqrt{1.097+\nu}} \tag{75}$$

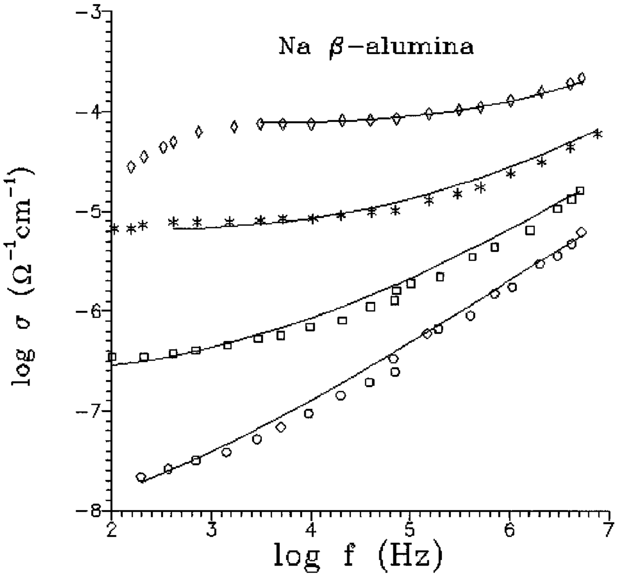

FIG. 1. Experimental frequency dependences of the conductivity of Na β-alumina (Refs. 8 and 52) at the temperatures 92 K (○), 113 K (□), 132 K (*), and 151 K (◇). The curves present the calculation according to our theory with the parameter values from Table I.

[compare with Eq. (18), obtained in our paper[34] by the steepest descent method in integrals (46) of the present paper for functions $B(w,\nu)$ and $B(w+1/2,\nu)$ and the following substitution of them into Eqs. (45) and (61)]. We emphasize that the obtained exponent depends only on the fluctuation exponent ν; in addition, the conductivity, being divided by σ_0, at a given ν is described by a universal function of the variable $\omega\tau$ (or w).

We transform Eq. (75) a little, using the explicit expression (30) for ν and substituting into it $\delta D^{(\mathrm{fr})}$ from Eq. (15). Then at temperatures $T\ll T_*$ we find

$$s\approx 1-1.073T/T_*. \tag{76}$$

Notice the formal analogy of Eq. (76) to those obtained in the framework of phenomenological models of ionic transport in systems with static disorder.[49,25] But at temperatures which considerably exceed the characteristic temperature T_*, the exponent s according to Eq. (75), decays by the law

$$s\approx T_*^2/T^2, \tag{77}$$

unlike the unphysical crossover of s to negative values that formally follows at $T>T_*$ from the models of Refs. 49 and 25.

We apply the above obtained results to the quantitative interpretation of experimental data on the dynamic conduc-

TABLE I. The values of parameters used for drawing the curves 1–4 in Fig. 1 according to the expression $\sigma(\omega)=\mathrm{Re}\langle z(\omega)\rangle^{-1}$ with $\langle z(\omega)\rangle$ from Eq. (37).

T (K)	92	113	132	151
ν	26.55	17.60	12.90	9.856
σ_{dc} (Ω^{-1} cm^{-1})	1.585×10^{-9}	1.995×10^{-7}	6.309×10^{-6}	7.727×10^{-5}
s	0.644	0.579	0.527	0.481

tivity of disordered ionic conductors. In Fig. 1, for example, there are displayed the experimental frequency dependences of the conductivity of superionic Na β-alumina at different temperatures[8,52] and those calculated according to our theory at fixed parameters $\varepsilon_\infty = 12$, $T_* = 237$ K; $\sigma_{\mathrm{dc}} = \sigma_0 \exp(-\nu/4)$ with σ_0 from Eq. (12) as well as the corresponding values of ν and s, calculated using Eqs. (15), (30), and (75), are given in Table I. All the curves can be fitted with a unique value of the preexponent $z^{-1} = 27.7$ $\Omega^{-1}\,\mathrm{cm}^{-1}$ and the initial activation energy of $D_0 \approx 1590$ K (with an accuracy $\pm 2.5\%$). Thus the analysis of isotherms of $\sigma(\omega)$ allows us to determine the fundamental parameters D_0 and T_* of the disordered ionic conductor, i.e., to separate, in principle, the short-range part of the activation energy from the Coulomb—long-range—part. As a result, our theory sustains much more severe experimental verification than if we exploited only a single isotherm $\sigma(\omega)$ as in our paper.[34]

Note the good agreement of our calculation with the experiment, at least within four orders of ω. The observed tendency to a discrepancy between the calculation and the experimental data, especially noticeable at low temperatures, can be explained by the fact that the conductivity mechanism turns out to be more sophisticated than that assumed above. Specifically, the ionic transport in glass can occur via a few nonequal parallel channels (in fact, on the empirical level such a possibility can be found in Ref. 5) and accounting for this circumstance is enough to eliminate the discrepancy between the theory and the experiment (the extension of the theory to the case of a few conductivity channels we leave as the subject of our next paper).

It is useful to give an estimation of the dimensionless concentration x of defects producing frozen fluctuations of activation barrier heights in ion-conducting glasses. Assuming $a/R(T_g) \ll 1$ and using the definition (18), we obtain from Eq. (15) in the main approximation an expression for T_*, which formally coincides with Eq. (20). Substituting the values of the parameters ε_∞ and T_* given above, used in the construction of the curves in Fig. 1, and choosing the mobile ion effective charge q equal to the Szigeti charge, which is a fraction of the elementary charge (according to Ref. 53, for a superionic conductor this fraction is ≈ 0.5), $a = 1$ Å , $n_0 = 10^{22}$ cm^{-3}, we find $x \approx 10^{-2}$. The last value is typical for the defect concentrations which destroy long-range crystalline order but retain short-range order in a glass.

Let us illustrate by experiment the theoretical temperature dependence obtained above for the exponent s. The results of processing[46] experimental data for crystals of the Hollandite type are depicted by circles in Fig. 2 and the solid line is calculated using Eq. (75) (the corresponding characteristic temperature $T_* =$ 281 K). Analogous experimental data[49] (denoted by circles and squares) for two samples of Hollandite and our calculation with $T_* = 209$ K (the solid line) are shown in Fig. 3.

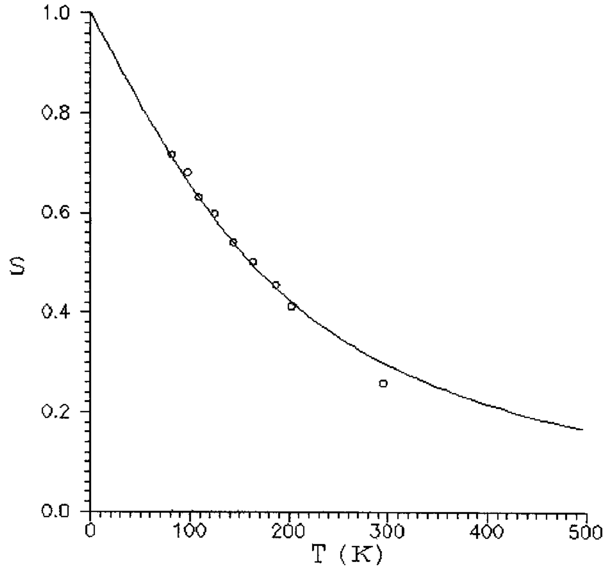

FIG. 2. The temperature dependence of the exponent s: circles denote the result of the processing (Ref. 46) of the experimental data for crystals of hollandite type; the solid curve corresponds to our calculation by Eq. (75) with the characteristic temperature $T_* =$ 281 K.

Let us turn now to Eq. (36) for the relaxation function of the disordered conductor and first of all obtain its asymptotics. Instead of directly analyzing this expression, consider its representation in the form of Eq. (58). Then in the limit $\Theta = \ln(t/\tau) \to \infty$ one can neglect the derivative $d/d\mu$ in the argument of the error function, and after that, using the known asymptotics of the latter (see, for instance, Ref. 50), we find the expression

$$f(t) \approx \frac{\sqrt{\nu}}{2\sqrt{\pi}} \ln^{-1}\left(\frac{t}{\tau}\right) \exp\left[-\frac{1}{\nu}\ln^{2}\left(\frac{t}{\tau}\right)\right], \qquad \frac{t}{\tau} \gg 1, \tag{78}$$

which is close to the log-normal distribution. But at small times our relaxation function is restored to the Debye form

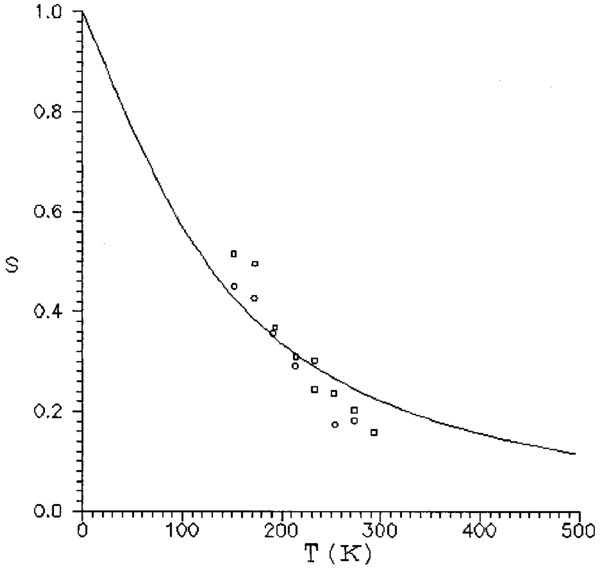

FIG. 3. The experimental temperature dependences of the exponent s for two samples of hollandite (Ref. 49) (denoted by circles and squares); the solid line corresponds to our calculation at $T_* =$ 209 K.

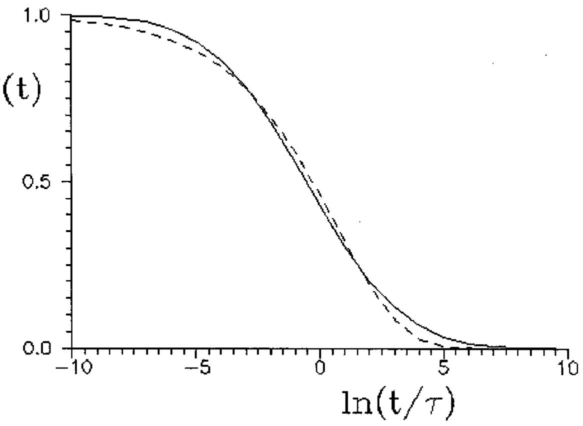

FIG. 4. An example of the relaxation function of the disordered system. The solid line is drawn according to our calculation of $f(t)$ for $\nu=16$. The Kohlrausch function $f_K(t)$ with the parameters $\tau_K=1.94\tau$ and $\beta=0.38$ which makes the best fit (by the least-squares method) to our $f(t)$ is shown by the dashed line.

[the necessity of a crossover to a pure exponential form of $f(t)$ at $t\rightarrow 0$ was remarked on the empirical level in Ref. 15; see also Ref. 26).

The experimental data for non-Debye relaxation are usually fitted by the empirical Kohlrausch law $f_K(t)=\exp[-(t/\tau_K)^{\beta}]$. For illustration in Fig. 4 the function (36) derived by us is displayed at $\nu=16$, and for comparison we show the fitting function $f_K(t)$ with $\tau_K=1.94\tau$ and $\beta=0.38$ (the results of corresponding calculations in the case of $\nu=4$, $\tau_K=1.33\tau$, and $\beta=0.58$ are shown in Fig. 4 of our paper[34]). The agreement demonstrated by this figure confirms the possibility of quantitative description of the experimental data on the relaxation dynamics of disordered conductors with the help of our theory.

In connection with such an opportunity there appears the natural problem of obtaining explicit expressions for β and τ_K through the physical parameters of the disordered conductor which are contained in ν and τ. Define the Kohlrausch exponent β by the expression

$$\beta=e\left[-\frac{\partial f(\Theta,\nu)}{\partial\Theta}\right]\Big|_{\Theta=0}, \tag{79}$$

which for the Kohlrausch function itself leads to the identity. Using Eq. (36) we find from Eq. (79)

$$\beta=\frac{e}{\sqrt{\pi\nu}}\int_{-\infty}^{\infty}\exp[-\psi(u)]du, \tag{80}$$

where the function

$$\psi(u)=\frac{u^2}{\nu}-u+e^u, \tag{81}$$

for which

$$\psi'(0)=0, \quad \psi(0)=1, \quad \psi''(0)=1+\frac{2}{\nu}. \tag{82}$$

The calculation of β by the standard saddle-point method (see, for example, Ref. 47) gives the following expression for β:

$$\beta=e\sqrt{\frac{2}{\nu}}\frac{e^{-\psi(0)}}{\psi''(0)}=\sqrt{\frac{2}{\nu+2}}. \tag{83}$$

In the limit $\nu\rightarrow\infty$ we obtain from Eq. (83)

$$\beta=\sqrt{\frac{2}{\nu}}, \tag{84}$$

and at $\nu\rightarrow 0$

$$\beta=1-\frac{\nu}{4}=1-\frac{T_*^2}{T^2}. \tag{85}$$

Therefore, the knowledge of the characteristic temperature T_* from experiments on the frequency-dependent conductivity of disordered conductors makes it possible to predict the temperature dependence of the Kohlrausch exponent β, which would be of major interest for experimental verification.

It is useful to note that at these limits the usually declared relation $\beta+s=1$ (see, for example, (Ref. 54) with substitution of our β and s [Eqs. (83) and (75)] holds exactly; but for intermediate ν the sum $\beta+s$ is less than 1 and reaches its minimum ≈ 0.875 at $\nu\approx 10.81$.

The most appropriate procedure for the approximation of our function (35) by fitting a Kohlrausch function consists in the minimization of the integral mean-square difference between these functions, i.e., in using the least-squares method for obtaining the dependences of β and τ_K/τ on ν. It is difficult to fulfill this procedure at arbitrary ν analytically, but the limiting cases of small and large values of ν yield to investigation (see the Appendix). In the most interesting case of $\nu\gg 1$ (strong sensitivity of the mobile ions to the disorder) the results of the numerical solution of Eq. (A8) give with accuracy up to main terms on $1/\sqrt{\nu}$

$$\beta=\frac{1.678}{\sqrt{\nu}} \tag{86}$$

[compare with Eq. (84)]. Now it follows directly from the Appendix and Eq. (86) that

$$\tau_K=0.5615\tau e^{0.2184\sqrt{\nu}}. \tag{87}$$

In the limit $\nu\rightarrow 0$ we obtain from Eq. (A15)

$$\beta=1-1.335\frac{\nu}{4}, \quad \tau_K=\tau e^{0.09018\nu}. \tag{88}$$

Thus, in the framework of our theory it is possible to find not only the temperature dependences of the exponents of Jonscher, s, and Kohlrausch, β, but, as it seems, to derive the dependence of the Kohlrausch relaxation time τ_K on the fluctuation exponent ν and, hence, on temperature. At high temperatures (where the relaxation becomes Debye-like) this dependence in ion-conducting glasses is described by the Arrhenius law,

$$\tau_K(T) = \frac{\varepsilon_\infty z}{4\pi} e^{D_0/T}, \tag{89}$$

with the activation energy D_0 [this follows from the connection between τ and σ_0; Eqs. (36) and (12)] However, it is remarkable that at low temperatures also (large ν, $T \ll T_*$) for $\tau_K(T)$ the Arrhenius law remains. Indeed, substituting in Eq. (87) the explicit expression of ν in terms of T_* [Eqs. (30) and (15)] we find

$$\tau_K(T) = 0.5615 \frac{\varepsilon_\infty z}{4\pi} e^{D_{\mathrm{eff}}/T}, \tag{90}$$

where the following effective—higher than D_0—activation energy appears:

$$D_{\mathrm{eff}} = D_0 + 0.4368 T_* . \tag{91}$$

The dependences obtained are the theoretical ground for the predicted behavior of $\tau_K(T)$ in real ion-conducting glasses and the experimental confirmation of Eqs. (89)–(91) is of principal interest.

We will discuss such dependences for the case of liquid electrolytes and analyze other related questions in a future publication.

V. SUMMARY

The theory developed in this paper (some of its results published in Ref. 34), which is based on the application of the fluctuation approach[37] to the investigation of relaxation phenomena, allowed us to obtain closed-form expressions for the response functions of disordered conductors from fundamental statistical principles. These expressions obviously possess the proper analytical behavior and correctly reproduce all the experimentally observable details of non-Debye relaxation. In this way, the non-Debye relaxation functions, discussed earlier on the purely phenomenological level, which are based on the Gaussian model of the activation barrier distribution in glasslike systems,[13,32,31,33] were put on a rigorous mathematical footing, which distinguishes the Gaussian model among the others. In this light, one can claim that the probable evolution of the non-Debye relaxation theory should follow the method of improvement of just the Gaussian approximation.

The possibility of the representation of the complex conductivity of glasslike systems with the help of the compact function $B(w,\nu)$ [Eq. (46)], which possesses rich properties, allows one to demonstrate the existence of the frequency interval in which the function $\sigma(\omega)$ derived by us reproduces the empirical Jonscher law; the interval widens sharply with the growth of the fluctuation exponent ν. So, without needing complicated models, i.e., on the quite general level, it has been shown how this fitting law is formed in any disordered system with hopping conductivity. Analogously, the function of the temporal relaxation of the disordered conductor reproduces with high accuracy the empirical Kohlrausch law, which allows us without introducing fitting parameters to give a quantitative interpretation of the experimental data with the help of our theory of the electrical response. Here the fundamental exponents appearing in the fitting laws of Jonscher (s) and Kohlrausch (β) turn out to be expressed through the single dimensionless combination ν, which contains only the experimentally measurable fundamental characteristics of the material and also the temperature. This allows one to give the explicit temperature dependences of s and β, which agree well with the experimental values for typical ion-conducting glasses, and, in addition, to prove the usually declared relation $s+\beta \approx 1$. Moreover, the explicit temperature dependence of the characteristic time of the non-Debye relaxation, τ_K, in the Kohlrausch law has been obtained. The most important thing is that the $\tau_K(T)$ introduced in glasslike materials yields to the Arrhenius law not only at high temperatures, which was assumed hitherto while constructing the theory, but also at low temperatures, which is the principal consequence of the concept considered. In the latter case the effective activation energy of the characteristic non-Debye relaxation time exceeds the initial—high-temperature—one. As to the dc conductivity of the glass, its temperature dependence according to our predictions must be of the substantially non-Arrhenius form $\sigma_{\mathrm{dc}}(T) \sim \exp(-D_0/T - T_*^2/T^2)$. In fact, such a form of $\sigma_{\mathrm{dc}}(T)$ can be considered as the theoretical alternative to the fitting Vogel-Tammann-Fulcher law in the approximation form of Bässler.[55] The detailed theoretical analysis of this and related questions is to be the content of our next paper.

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APPENDIX

In order to make the best fitting of our function (35) by the Kohlrausch function

$$f_K(\Theta) = \exp\{-\exp[\beta\Theta - g)]\}, \tag{A1}$$

where the notation $g = \beta \ln(\tau_K/\tau)$ has been introduced, let us use the least-squares method, having found the solution of the equations

$$\frac{\partial \mathcal{F}}{\partial g} = 0, \qquad \frac{\partial \mathcal{F}}{\partial \beta} = 0, \tag{A2}$$

which cause the extremum in the functional

$$\mathcal{F} = \int_{-\infty}^{\infty} d\Theta [f_K(\Theta) - f(\Theta,\nu)]^2 \tag{A3}$$

and, by that, determine the dependence of the Kohlrausch exponent β and time $\tau_K = \tau e^{g/\beta}$ on the fluctuation exponent ν of the medium. Equations (A2) are deduced by simple transformations to the form

$$\int_{-\infty}^{\infty} d\Theta f'(\Theta,\nu)\exp[-\exp(\beta\Theta-g)]=-\tfrac{1}{2}, \qquad \text{(A4)}$$

$$\int_{-\infty}^{\infty} d\Theta f(\Theta,\nu)\Theta\exp[-\exp(\beta\Theta-g)+\beta\Theta-g] = \frac{g-\ln 2-C}{2\beta^2}, \qquad \text{(A5)}$$

where $C\approx 0.5772$ is the Euler constant[47] and the prime denotes the derivative with respect to Θ.

Let us consider the most interesting case, $\nu\to\infty$, when $\beta\to 0$ [see the saddle-point formula (84)]. The direct substitution of the value $\beta=0$ into Eq. (A4) allows us to find for the quantity g at $\nu\to\infty$ the limiting value

$$g_\infty=-\ln\ln 2\approx 0.3665. \qquad \text{(A6)}$$

Moreover, at small but finite β the formula $g=g_\infty-C\beta$ follows from Eq. (A4).

In the same limit Eq. (A5) after changing integration variables and using the integral representation (36) can be rewritten in the form

$$\frac{1}{\sqrt{\pi\nu}\beta}\int_{-\infty}^{\infty} dx\int_{-\infty}^{\infty} dy x\exp\left[-\frac{y^2}{\nu\beta^2}-\exp(x-g)+x-g -\exp\left(\frac{x+y}{\beta}\right)\right]=\frac{g-\ln 2-C}{2}. \qquad \text{(A7)}$$

One can see that in the limit $\beta\to 0$ the function $\exp[-\exp(x+y/\beta)]$ becomes the step function, which at once allows one to fulfill the integration on y in Eq. (A7) and get the equation for $\beta\sqrt{\nu}$,

$$\int_{-\infty}^{\infty} dx x\Phi\left(\frac{x}{\beta\sqrt{\nu}}\right)\exp[-\exp(x-g_\infty)+x]=1, \qquad \text{(A8)}$$

where $\Phi(x)$ is the error function. The numerical solution of Eq. (A8) gives the value $\beta\sqrt{\nu}\approx 1.678$ [compare with the saddle-point value in Eq. (84)].

The case $\nu\ll 1$ we investigate by substituting into Eqs. (A4) and (A5) the expansion $f(\Theta,\nu)$ from Eq. (35) in the form which is convenient for further calculations,

$$f(\Theta,\nu)=f_D(\Theta)+\frac{\nu}{4}f_D{}'(\Theta), \qquad \text{(A9)}$$

where the definition (33) has been used. Representing

$$\beta=1-X\frac{\nu}{4}, \quad g=Y\frac{\nu}{4}, \qquad \text{(A10)}$$

we obtain for the unknown coefficients X and Y the equations

$$X\left[\int_{-\infty}^{\infty}\Theta f_D{}'(\Theta)f_D(\Theta)d\Theta-\frac{1}{2}\right]+Y\int_{-\infty}^{\infty}f_D{}'(\Theta)f_D(\Theta)d\Theta =0, \qquad \text{(A11)}$$

$$-\int_{-\infty}^{\infty}\Theta f_D{}'(\Theta)f_{D'}(\Theta)d\Theta+X\left[\int_{-\infty}^{\infty}\Theta^2 f_D{}'(\Theta)f_D(\Theta)d\Theta\right] +Y\int_{-\infty}^{\infty}\Theta f_D{}'(\Theta)f_D(\Theta)d\Theta=\frac{1}{2}[Y-2(\ln 2+C)X]. \qquad \text{(A12)}$$

After the calculation of the corresponding integrals we find from Eq. (A11) the relation

$$Y=(\ln 2+C-1)X, \qquad \text{(A13)}$$

and then from Eq. (A12) we get

$$X=\frac{1}{\pi^2/3-2C-2\ln 2}. \qquad \text{(A14)}$$

Finally, from Eq. (A10) and from the definition of g we derive for the Kohlrausch parameters the expressions

$$\beta=1-1.335\frac{\nu}{4}, \quad \tau_K=\tau\exp\left(0.3607\frac{\nu}{4}\right) \qquad \text{(A15)}$$

[compare with the saddle-point value β from Eq. (85)].

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[1] J. Jäckle, Philos. Mag. B **56**, 113 (1987).
[2] K. Pollak and T.H. Geballe, Phys. Rev. **122**, 1742 (1961).
[3] S. Summerfield, Philos. Mag. B **52**, 9 (1985).
[4] J.C. Wang and J.B. Bates, Solid State Ionics **50**, 75 (1992).
[5] P.G. Bruce, Solid State Ionics **15**, 247 (1985).
[6] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987).
[7] Ch. Liu and C.A. Angell, J. Non-Cryst. Solids **83**, 162 (1986).
[8] D.P. Almond, A.B. West, and R.J. Grant, Solid State Commun. **44**, 1277 (1982).
[9] D.P. Almond and A.R. West, J. Non-Cryst. Solids **88**, 222 (1986).
[10] J. Ross Macdonald and J.B. Cook, J. Electroanal. Chem. **193**, 57 (1985).
[11] Ch. Mai, A. Asseiro, G.P. Johari, S. Etienne, and K. Abbes, J. Non-Cryst. Solids **93**, 35 (1987).
[12] L. Börjesson, L.M. Torell, S.W. Martin, Ch. Liu, and C.A. Angell, Phys. Lett. A **125**, 330 (1987).
[13] G. Carini and G. Tripodo, J. Non-Cryst. Solids **131-133**, 1028 (1991).
[14] H. Jain and J.N. Mundy, J. Non-Cryst. Solids **91**, 315 (1987).
[15] K.I. Ngai and U. Strom, Phys. Rev. B **38**, 10 350 (1988).
[16] W. Rehwald, H. Kiess, and B. Binggeli, Z. Phys. B **68**, 143 (1987).
[17] W.K. Lee, J.F. Liu, and A.S. Nowick, Phys. Rev. Lett. **67**, 1559 (1991).
[18] P.J. Carroll and G.D. Patterson, J. Chem. Phys. **81**, 1666 (1984); **82**, 9 (1985).
[19] I.E.T. Iben, D. Braunstein, W. Doster, H. Frauenfelder, M.K. Hong, J.B. Johnson, S. Luck, P. Ormos, A. Schulte, P.J. Steinbach, A.H. Xie, and R.D. Young, Phys. Rev. Lett. **62**, 1916 (1989).
[20] R. Wendler, C. Pappa, C. Eckart, and K. Baberschke, J. Phys. C **20**, 2759 (1987).

[21] I.Ya. Korenblit and E.F. Shender, Usp. Fiz. Nauk **157**, 267 (1989) [Sov. Phys. Usp. **32**, 139 (1989)].

[22] C. von Borczyskowski and T. Kirski, Phys. Rev. B **40**, 11 335 (1989).

[23] A.K. Jonscher, Phys. Status Solidi A **32**, 665 (1975).

[24] H. Sher and M. Lax, Phys. Rev. B **7**, 4491 (1973).

[25] J.C. Dyre, J. Phys. C **19**, 5655 (1986).

[26] K. Funke and R. Hoppe, Solid State Ionics **40/41**, 200 (1990).

[27] S. Havlin and D. Ben-Avraham, Adv. Phys. **36**, 695 (1987).

[28] *Fractals in Physics*, Proceedings of the Sixth Trieste International Symposium on Fractals in Physics, ICTP, Trieste, Italy, 1985, edited by L. Pietronero and E. Tosatti (North-Holland, Amsterdam, 1986).

[29] W. Dieterich, D. Knödler, and J. Petersen, Ber. Bunsenges. Phys. Chem. **95**, 964 (1991).

[30] P. Maass, J. Petersen, A. Bunde, W. Dieterich, and H. E. Roman, Phys. Rev. Lett. **66**, 52 (1991).

[31] N.O. Birge, Y.H. Jeong, S.R. Nagel, S. Bhattacharya, and S. Susman, Phys. Rev. B **30**, 2306 (1984).

[32] G. Carini, M. Cutroni, M. Federico, G. Galli, and G. Tripodo, Phys. Rev. B **30**, 7219 (1984).

[33] J. Ross Macdonald, J. Appl. Phys. **61**, 700 (1987).

[34] V.N. Bondarev and P.V. Pikhitsa, Phys. Lett. A **196**, 247 (1994).

[35] V.N. Bondarev and I.L. Kuskovskii, Electrokhimiya **28**, 1531 (1992).

[36] A.F. Andreev, Zh. Exp. Teor. Fiz. **75**, 1132 (1978) [Sov. Phys. JETP **48**, 570 (1978)].

[37] V.N. Bondarev and V.M. Zhukov, Fiz. Tverd. Tela **33**, 846 (1991), [Sov. Phys. Solid State **33**, 481 (1991)].

[38] W. Müller and M. Torge, Solid State Ionics **36**, 201 (1989).

[39] C.T. Moynihan, N. Balitactac, L. Boone, and T.A. Litovitz, J. Chem. Phys. **55**, 3013 (1971).

[40] C.A. Angell, Annu. Rev. Phys. Chem. **43**, 693 (1992).

[41] V.S. Dotsenko, Usp. Fiz. Nauk **163**, 1 (1993) [Sov. Phys. Usp. **36**, 63 (1993)].

[42] I.H. Akopyan, V.N. Bondarev, D.N. Gromov, A.B. Kuklov, and B.V. Novikov, Fiz. Tverd. Tela **29**, 2263 (1987) [Sov. Phys. Solid State **29**, 1305 (1987)].

[43] L.D. Landau and E.M. Lifshitz, *Statistical Physics, Part 1* (Nauka, Moscow, 1976) (in Russian).

[44] J.A. Bruce and M.D. Ingram, Solid State Ionics **9–10**, 717 (1983).

[45] V.N. Bondarev, Solid State Ionics (to be published).

[46] S. Yoshikado, T. Ohachi, I. Taniguchi, Y. Onoda, M. Watanabe, and Y. Fujiki, Solid State Ionics **7**, 335 (1982).

[47] G.A. Korn and Th.M. Korn, *Mathematical Handbook for Scientists and Engineers* (McGraw-Hill, New York, 1961).

[48] *Physics of Superionic Conductors*, edited by M.B. Salamon (Springer-Verlag, Berlin, 1979).

[49] J. Bernasconi, H.U. Beyeler, S. Strässler, and S. Alexander, Phys. Rev. Lett. **42**, 819 (1979).

[50] I.S. Gradshtein and I.M. Ryzhik, *Tables of Integrals, Sums, Series, and Products* (Nauka, Moscow, 1971) (in Russian).

[51] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics. Non-Relativistic Theory* (Nauka, Moscow, 1989) (in Russian).

[52] D.P. Almond, G.K. Duncan, and A.R. West, Solid State Ionics **8**, 159 (1983).

[53] P. Brüesch, S. Strässler, and H.R. Zeller, Phys. Status Solidi A, **31**, 217 (1975).

[54] H. Sato, Prog. Theor. Phys. Suppl. No. 115, 317 (1994).

[55] H.Bässler, Phys. Rev. Lett. **58**, 767 (1987).