Cole–Davidson dielectric relaxation as a self-similar relaxation process

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An effort has been undertaken to understand the nature of one type of non-exponential relaxation, namely Cole–Davidson relaxation. Toward this end, a model of relaxation as a self-similar process is proposed. An equation containing operators of fractional integration and differentiation is obtained and solved, which the relaxation function obeys in this case. © *1997 American Institute of Physics.* [S1063-7834(97)02001-7]

INTRODUCTION

Problems associated with relaxation in insulators not obeying an exponential law have a long history. At present, in connection with significant extensions of the temporal and frequency ranges of the measurements[1] a significant amount of experimental data has been accumulated confirming the existence of non-exponential relaxation processes, and several empirical expressions have been proposed to describe them. In most cases these expressions are written in the frequency domain.

From the theoretical point of view, these dependences represent an attempt to understand the nature of these processes, on the conceptual basis of the temporal relaxation distribution (TRD), when the normalized macroscopic relaxation function $f(t)$ is represented as a sum of exponential functions with the appropriate amplitudes and relaxation times.

Such an approach to the description of non-exponential relaxation is obviously based on the assumption that the relaxing macroscopic system consists of the appropriate number of subsystems, each of which relaxes with its own relaxation time. Without a doubt, this assumption may be valid for many systems, but it is equally true that such a partitioning into subsystems has a real physical meaning only when the number of subsystems is finite and comparatively small.

As is well known,[1] three expressions for the complex susceptibility allow one to describe a wide range of experimental data. These are the Cole–Cole function

$$\chi(i\omega)=\frac{\chi_0}{1+(i\omega/\omega_p)^{\varepsilon}}, \tag{1}$$

the Cole–Davidson function

$$\chi(i\omega)=\frac{\chi_0}{(1+(i\omega/\omega_p))^{\nu}}, \tag{2}$$

and the Gavril'yak–Negami function

$$\chi(i\omega)=\frac{\chi_0}{(1+(i\omega/\omega_p)^{\varepsilon})^{\nu}}. \tag{3}$$

Here ω is the frequency, ω_p is the frequency of the peak of the dielectric losses, and ε and ν are parameters where $0<\varepsilon$ and $\nu\leqslant 1$.

If, as is usually done, we apply the TRD concept to explain these functional forms, then it becomes necessary to assume that the number of different relaxing subsystems making up the macroscopic system is infinite since in this case the TRD functions are continuous and do not have narrow peaks[1] which could be interpreted as a manifestation of separate subsystems. Therefore, in our opinion, the application of the TRD concept for such systems is invalid. Besides, the TRD concept does not allow one to clarify the physical nature of the parameters ε and ν entering into formulas (1)–(3), which is another indication of its incompleteness.

The present paper attempts to understand the possible mechanism of the appearance of one of these types of relaxation, namely Cole–Davidson relaxation, with the help of a model of a self-similar relaxation process.

At present, an effort is already underway[2] to understand the nature of non-exponential relaxation, based on the hypothesis of a self-similar relaxation process, but it is restricted to a consideration of processes describable in the frequency domain by the Cole–Cole expression.

The present paper attempts to answer the following questions.

1) What physical process can lead to the appearance of non-exponential relaxation of Cole–Davidson type and in what substances can such a process by detected?

2) What is the explicit form of the equation for the normalized macroscopic relaxation function $f(t)$ in this case?

3) What is the meaning of the parameter ν entering into the Cole–Davidson expression?

1. EQUATION OF SELF-SIMILAR RELAXATION

Before embarking upon a consideration of the model of self-similar relaxation, let us make a few remarks.

First, we agree that we will consider those physical systems in which relaxation on the macroscopic level is defined as relaxation of the elementary components of this system on the microlevel.

Second, following Fröhlich,[3] we assume as a first approximation that there is no indirect interaction at the microlevel between the elementary components of the physical system. Relaxation proceeds as a result of the interaction of the separate elements of this system with a thermostat.

In other words, applied to dielectric relaxation this means that the relaxation processes of individual electric dipoles do not affect each other. In addition, we assume that all elementary components of such a physical system find themselves under the same conditions. Then the equations describing relaxation of the system on the macrolevel will coincide with the equations describing relaxation of the individual electric dipoles on the microlevel. Therefore, in our discussion of the model of self-similar relaxation, from here on, we will use the equation for the total dipole moment of the insulator, bearing in mind that the motion of the individual elementary dipoles from which the insulator is composed in fact possess a self-similar character.

Let us consider the ordinary equation of exponential relaxation, which can be written in the form

$$\exp(-\Omega_0 t)\frac{d}{dt}\exp(\Omega_0 t)f(t)=0. \tag{4}$$

Here t is time, $f(t)$ is the normalized macroscopic relaxation function of some physical quantity, and Ω_0 is the relaxation rate constant.

For the case of dielectric relaxation $f(t)=P(t)/P(0)$, where $P(t)$ is the total dipole moment of the insulator, and Ω_0 is a constant describing the interaction of the macroscopic dipole with the thermostat.[3] In particular, Eq. (4) describes the behavior of systems whose relaxation on the microlevel can be described by the model of a deep potential well with two equilibrium positions (the Fröhlich relaxator).[1,3–5] In this model the relaxation process begins after a energy difference is created in the two equilibrium positions with the help of an external field (see Fig. 1). It is well known that the model of the Fröhlich relaxator is valid for a wide class of insulators, and works already exist whose authors have tried to modify this model using models of hopping charge transport and ionic conductivity [see, e.g., Refs. 1 and 6 (monographs), Ref. 4 (review), and Ref. 7 (a paper)] to describe non-exponential relaxation. However, in the final tally all such efforts are based on the TRD concept. In the present work, therefore, we have modified the model of the Fröhlich relaxator, departing from other considerations.

Toward this end, consider the function $G(t)=\exp(\Omega_0 t)f(t)$. If $f(t)$ solves Eq. (4), then $G(t)=f(0)$ is a constant and

$$\frac{d}{dt}G(t)=0. \tag{5}$$

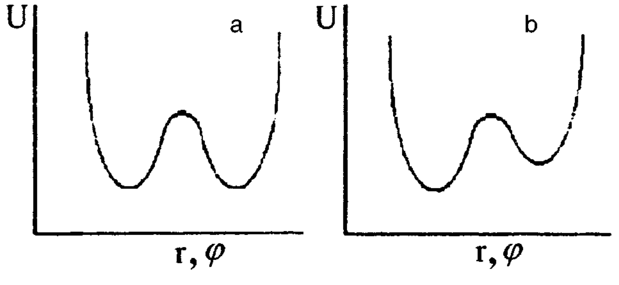

FIG. 1. Dependence of the potential energy U of a dielectric dipole on the rotation angle φ or the displacement r of the ion (electron). a, b—equilibrium positions, a—in an external electric field.

Suppose now that at certain times the system is found in the equilibrium state. In other words, at these times $G(t)$ is equal to zero and not to $f(0)$ and instead of the non-equilibrium picture (see Fig. 1b) the system is found in the equilibrium state (see Fig. 1a). The reason for this may be, for example, thermal fluctuations of the local fields in the insulator leading to screening of the external field.

In addition, suppose that the times when $G(t)=f(0)$ are distributed over a self-similar (fractal) set. The phrase ''self-similar object S'' means that the object S is invariant with respect to a scale transformation $S(\xi t)=bS(t)$, where the quantities ξ and b define the fractal dimension of this set. Thus, for example, the fractal Cantor set is invariant with respect to the transformation $S((1/3)t)=2S(t)$ and its fractal dimension is ln(2)/ln(3).

In other words, at times that coincide with the points of some self-similar set, $G(t)=f(0)$, and at times that coincide with the vacancies of this set $G(t)=0$. Thus, integrating the function $G(t)$ and averaging over the various realizations of the self-similar set, one obtains[8]

$$D^{-1}G(t)=AD^{-\nu}[f(0)]. \tag{6}$$

Here A is a constant determined by the structure of the fractal set on which $G(t)$ is distributed, ν is the dimension of this set $(0\leqslant\nu\leqslant1)$, and $D^{-\nu}$ is the Riemann–Liouville fractional integration operator, defined[9–11] as

$$D^{-\nu}[f(t)]=(1/\Gamma(\nu))\int_0^t(t-\tau)^{\nu-1}f(\tau)d\tau,$$

where $\Gamma(\nu)$ is the gamma function.

Employing the properties of the fractional integration and differentiation operators, we can rewrite Eq. (6) in the form

$$D^{\nu}[G(t)]=0. \tag{7}$$

Here D^{ν} is the fractional differentiation operator, defined[9–11] as

$$D^{\nu}[f(t)]=(1/\Gamma(1-\nu))\frac{d}{dt}\int_0^t(t-\tau)^{-\nu}f(\tau)d\tau.$$

In other words, if we are considering relaxation for which the interaction with the external field is of a discontinuous self-similar nature, then Eq. (5) for the function $G(t)$ must be replaced by Eq. (7).

Taking the nature of $G(t)$ into account, the equation for the relaxation function $f(t)$ can be written in the form

$$\exp(-\Omega_0 t)D^{\nu}[\exp(\Omega_0 t)f(t)]=0 \tag{8a}$$

or invoking the operator relation (see the Appendix)

$$\exp(-\Omega uD^{1-\varepsilon})D^{\alpha}\exp(\Omega uD^{1-\varepsilon})=(D^{\varepsilon}+\Omega\varepsilon)^{\alpha/\varepsilon},$$

$$0<\varepsilon\leqslant1,\quad \alpha\leqslant\varepsilon,$$

we can give it the more elegant form

$$(D^1+\Omega_0)^{\nu}[f(t)]=0. \tag{8b}$$

Here and below, expressions of the form $\exp(-\Omega uD^{1-\varepsilon})$ and $(D^{\varepsilon}+\Omega\varepsilon)^{\alpha\varepsilon}$ are understood in the customary sense as series of fractional integration and differentiation operators.

2. COMPLEX SUSCEPTIBILITY OF SYSTEMS DESCRIBED BY THE GENERALIZED RELAXATION EQUATION

As usual, to find the complex susceptibility $\chi(i\omega)$ of a system obeying the equation of self-similar relaxation, we consider the response of this system to a harmonic perturbation $B\exp(i\omega t)$. We seek the solution in the form $f(t)=\chi(i\omega)\exp(i\omega t)$. Then, substituting in Eq. (8b), we obtain

$$(D^1+\Omega_0)^\nu[\chi(i\omega)\exp(i\omega t)]=B\ \exp(i\omega t). \tag{9}$$

Taking into account the exceedingly precise nature of the operator $(D^1+\Omega_0)^\nu$ and assuming that the perturbation $B\exp(i\omega t)$ is switched on adiabatically at the time $t\rightarrow -\infty$, we arrive at the following expression for the complex susceptibility:

$$\chi(i\omega)=\frac{\chi_0}{(1+(i\omega/\Omega_0))^\nu}\ . \tag{10}$$

To obtain this result, we made use of the fact that, for the case in which the interaction in Eqs. (8) is switched on adiabatically, the fractional derivatives D^ν must be replaced by the alternative form $D^\nu_{-\infty}$ We also made use of the result

$$D^\nu_{-\infty}[\exp(t)]=(i\omega)^\nu\exp(i\omega t),$$

where

$$D^\nu_{-\infty}[f(t)]=(1/\Gamma(1-\nu))\frac{d}{dt}\int_{-\infty}^{t}(t-\tau)^{-\nu}f(\tau)d\tau.$$

It is easy to see that expression (10) coincides with empirical equation (2) describing Cole–Davidson relaxation in the frequency domain.

3. SOLUTION OF THE GENERALIZED RELAXATION EQUATION

The solution of Eq. (8b), equivalently Eq. (8a), can be obtained with the help of the Laplace transform.

Indeed, if we define the Laplace transform $F(p)$ of the function $f(t)$ as

$$F(p)=\int_0^\infty f(t)\exp(-pt)dt,$$

then, applying the Laplace transform to Eq. (8a) and invoking the properties of this transformation,[12] we obtain the following expression for the Laplace transform of $f(t)$:

$$F(p)=\frac{C}{(p+\Omega_0)^\nu}. \tag{11}$$

Here C is a constant determined by the initial conditions..

$$f(t)=C\,\frac{r^{\nu-1}}{\Gamma(\nu)}\,\exp(-\Omega_0 t). \tag{12}$$

This function is the solution of the equation describing self-similar relaxation

As $t\rightarrow 0$, the function $f(t)$ tends to infinity as $t^{\nu-1}$. The reason for such physically meaningless behavior is that in the derivation of the relaxation equation (8a), (8b), we assumed that self-similarity of the times when an interaction exists between the external field and the relaxing system holds over the entire time interval from zero to infinity. However, in real physical systems there always exist a lower and an upper bound on self-similarity, defined, for example, by the frequency $1/\tau$ of the interaction of the relaxing system with the ‘‘thermostat’’ and the time of formula (12). Self-similarity is possible, therefore, only at times greater than the lower bound ($t>\tau$).

As is clear from the above, it is not necessary to use the TRD concept, mentioned at the beginning of this paper, to describe non-exponential relaxation. We propose as an alternative the concept of self-similar relaxation. The main difference between this process and the usual relaxation process is that here the interaction with the external field causing the relaxation is of a discontinuous nature and that the times when this interaction exists are distributed over some self-similar (fractal) set.

We may take the modified Fröhlich relaxator as a possible physical model of such a process, in which the system relaxes only at times that coincide with the points of some fractal set and at these times the dependence of the potential energy of the interaction U of an individual electric dipole on the rotation angle φ has the form shown in Fig. 1a,b and at other times, as a result of screening of the external field by the local fields inside the insulator, the dependence of U on φ has the form shown in Fig. 1a. Note that this version of the dynamical Fröhlich relaxator is applicable not only when the variation of the total dipole moment of the insulator is due to rotations of the elementary dipoles, but also when the potential energy U depends on the displacement r of the ions of the crystal lattice[1,5] (see Fig. 1).

It is possible that such processes can be observed in ferroelectrics, for which the deep-potential-well model with two equilibrium positions is known to be applicable[1] and that experimental data exist confirming the presence in them of non-exponential relaxation processes.[1,6,7] It is also possible that such processes play a role in relaxation in liquid and plastic crystals.

It should be noted that when we averaged Eq. (5) over time by the method suggested in Ref. 8 we assumed that the fractal set over which the average was taken is a statistical fractal. In other words, the property of self-similarity is manifested in such an object only for its mean characteristics. Such are all actually existing fractal structures: the perimeters of coastlines, the shape of clouds, broken surfaces, etc. (see, e.g., Ref. 13).

Then the variation in time of the physical quantity f is described by Eq. (8a), equivalently (8b), whose solution is the function $f(t)$, given by Eq. (12).

Thus, we can give the following answers to the questions formulated at the beginning of this article.

1) The complex susceptibility described by the empirical Cole–Davidson relation can be observed in systems to which the generalized relaxation model is applicable, e.g., in those materials for which it is known, on the one hand, that the Fröhlich relaxator model is applicable and, on the other, that non-exponential relaxation processes are observed in them. It is possible that such processes take place in ferroelectrics,

crystals with ionic conductivity, and also in liquid and plastic crystals.

2) The relaxation function of such systems is the solution of Eq. (8a), equivalently (8b), and has the form (12).

3) The parameter ν is the fractal dimension of the set over which the times are statistically distributed at which the interaction between an elementary component of the physical system and the external field occurs.

APPENDIX A:

Before proving the operator relation about which we spoke in the main text, let us make two remarks.

First, recall the well-known operator identity

$$\exp(-\hat{B})\hat{A}\,\exp(\hat{B})=\frac{\hat{A}}{\Gamma(1)}+\frac{[\hat{A},\hat{B}]}{\Gamma(2)}+\frac{[[\hat{A},\hat{B}],\hat{B}]}{\Gamma(3)}+\cdots+\frac{[\ldots[\hat{A},\hat{B}],\ldots\hat{B}]}{\Gamma(n+1)}+\cdots\,. \tag{A1}$$

The brackets here denote the commutator of its operator arguments $\hat{A}$ and $\hat{B}$.

Second, we need to calculate the commutator $[D^{\alpha},\Omega uD^{1-\varepsilon}]$

$$[D^{\alpha},\Omega uD^{1-\varepsilon}]=\Omega\sum_{n=0}^{\infty}D^{n}[u]\binom{a}{n}D^{\alpha+1-\varepsilon-n}-\Omega uD^{\alpha+1-\varepsilon}=\Omega uD^{\alpha+1-\varepsilon}+\alpha\Omega D^{\alpha-\varepsilon}-\Omega uD^{\alpha+1-\varepsilon}=\alpha\Omega D^{\alpha-\varepsilon}. \tag{A2}$$

Here $\binom{a}{n}$ are the binomial coefficients. In the calculation of this commutator and in what follows we assume that $0<\varepsilon\leqslant 1$ and $\alpha\leqslant\varepsilon$.

Let us now consider the expression $\exp(-\Omega uD^{1-\varepsilon})D^{\alpha}\exp(\Omega uD^{1-\varepsilon})$. According to Eq. (A1)

$$\exp(-\Omega uD^{1-\varepsilon})D^{\alpha}\exp(\Omega uD^{1-\varepsilon})=\frac{D^{\alpha}}{\Gamma(1)}+\frac{[D^{\alpha},\Omega uD^{1-\varepsilon}]}{\Gamma(2)}+\frac{[[D^{\alpha},\Omega uD^{1-\varepsilon}],\Omega uD^{1-\varepsilon}]}{\Gamma(3)}+\ldots\,. \tag{A3}$$

Employing Eq. (A2), we easily obtain

$$[[D^{\alpha},\Omega uD^{1-\varepsilon}],\Omega uD^{1-\varepsilon}]=\Omega^{2}\alpha(\alpha-\varepsilon)D^{\alpha-2\varepsilon}. \tag{A4}$$

Therefore

$$\exp(-\Omega uD^{1-\varepsilon})D^{\alpha}\exp(\Omega uD^{1-\varepsilon})=\sum_{n=0}^{\infty}\frac{\Omega^{n}\alpha(\alpha-\varepsilon)\ldots(\alpha-(n-1)\varepsilon)}{\Gamma(n+1)}D^{\alpha-n\varepsilon}. \tag{A5}$$

Considered separately

$$\frac{\Omega^{n}\alpha(\alpha-\varepsilon)\ldots(\alpha-(n-1)\varepsilon)}{\Gamma(n+1)}=\frac{(-1)^{n}\Omega^{n}\varepsilon^{n}}{\Gamma(n+1)}\left(-\frac{\alpha}{\varepsilon}\right)\left(-\frac{\alpha}{\varepsilon}+1\right)\left(-\frac{\alpha}{\varepsilon}+n-1\right)=\frac{(-1)^{n}\Omega^{n}\varepsilon^{n}\Gamma(-\tfrac{\alpha}{\varepsilon}+n)}{\Gamma(n+1)\Gamma(-\alpha/\varepsilon)}=(\Omega\varepsilon)^{n}\binom{\alpha}{n} \tag{A6}$$

Substituting Eq. (A6) into Eq. (A5), we obtain

$$\exp(-\Omega uD^{1-\varepsilon})D^{\alpha}\exp(\Omega uD^{1-\varepsilon})=\sum_{n=0}^{\infty}(\Omega\varepsilon)^{n}\binom{\alpha/\varepsilon}{n}D^{\alpha-n\varepsilon}=\sum_{n=0}^{\infty}(\Omega\varepsilon)^{n}\binom{\alpha/\varepsilon}{n}\times[D^{\varepsilon}]^{\alpha/\varepsilon-n}=(D^{\varepsilon}+\Omega)^{\alpha/\epsilon},$$

$$0<\varepsilon\leqslant 1,\quad \alpha\leqslant\varepsilon, \tag{A7}$$

which was to be demonstrated.

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