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Anomalous relaxation in dielectrics. Equations with fractional derivatives

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It has been shown that anomalous relaxation in dielectrics can be described in terms of equations with fractional derivatives. The solutions of the resulting equation with fractional derivatives are expressed by the Mittag –Leffler function and the Fox function. The conditions of a change from the Debye relaxation to "slow" (anomalous) relaxation with a power time dependence have been examined in the limits $t \to 0$ and $t \to \infty$.

Key words: *relaxation; fractional derivative; dielectric*

1. Introduction

Anomalies of dynamic dielectric properties appear to be a characteristic feature of disordered ferroelectrics and polymers, as well as composites and other materials. In particular, strong dispersion of dynamic magnetic or dielectric susceptibility was observed in many spin or dipole glasses (see e.g., [1]). This dispersion is usually explained by the fact that the disordered systems have a wide spectrum of relaxation times, which may be extracted from the observed frequency dependence of susceptibility [2]. Examples include the dielectric response of ferroelectric relaxors of the following types: $PbMg_{1/3}Nb_{2/3}O_3$ $PbSc_{1/2}Nb_{1/2}O_3$, $Pb_{1-x}La_xZr_{0.35}Ti_{0.65}O_3$ (x = (0.7–0.9)) [3–6].

It has been shown [1–7] that it is necessary to have different complicated empirical formulae, such as the Cole–Cole, Cole–Davidson, Havriliak–Negami, and others in order to describe responses different from Debye.

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The empirical principles of Cole–Cole, Cole–Davidson, and Havriliak–Negami have been used for many years to describe relaxation processes in ordinary glasses, polymers, composites, disordered ferroelectrics, and other systems. Various data, obtained by means of methods including dielectric spectroscopy, nuclear magnetic resonance, quasi-elastic scattering of neutrons were successfully fitted with the Cole –Cole, Cole–Davidson, and Havriliak–Negami formulae. It is evident, however, that the application of distribution functions extracted from experimental dielectric responses, does not allow one to elucidate the physical nature of the anomalies in the responses of the disordered systems.

Relaxation characterizes the reaction of a thermodynamic system to outer changes. Based on the observation that the rate at which a system approaches equilibrium is proportional to the value of the deviation from equilibrium, the governing differential equation can be obtained, and its solution leads to an exponential (Debye) relaxation [7]:

$$f(t) \sim \mathrm{e}^{-t/\tau} \tag{1}$$

Many experimental investigations of relaxation processes in random media do not coincide, however, with the above exponential (Debye) law. There, Kohlrausch explored the phenomenon of charge decrease in the “Leiden jar” 150 years ago [8]. He experimentally determined that the decrease of charge with time, $q(t)$, occurred according to the law:

$$q(t) = q(0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{2}$$

In accordance with Kohlrausch’s experimental data, β = 0.43 (β – the Kohlrausch constant).

More recently, different dependences for the relaxation function have been obtained, such as Cole–Cole, Cole–Davidson, and Havriliak–Negami, all determined empirically. No results of the calculations of the distribution function of the relaxation times have been published in the case of a particular model, i.e. no models allowing one to describe dielectric responses more complicated than the simple Debye principle have been formulated. Below, we will construct a mathematical model that leads to an anomalous (non-Debyan) relaxation of the type described by Equation (2).

2. Anomalous relaxation

At present, there is no quantitative microscopic theory capable of explaining the experimental dependences of the Cole–Cole, Cole–Davidson, and Havriliak–Negami types [1–33]. Sometimes it is even stated that such a theory cannot be developed [22]. This is due to the fact that spatial heterogeneity connected, for instance, with the random positions of admixture molecules in a matrix or with the positions of atoms in an

amorphous semiconductors leads to a rather wide range of microscopic change rates. Such a spatial disorder will lead to a temporal and sometimes energetic disorder.

In a number of works, different models were shown to describe anomalous relaxation. These were based on fractal concepts about processes producing anomalous relaxation [9–35].

The mathematical language of a fractional derivative [36–39], based on the representation of the Riemann–Liouville operator of fractional differentiation, is used to describe and explore relaxation processes produced by fractal structures

$$D^{\alpha}\left[f(t)\right]=\frac{1}{\Gamma(1-\alpha)}\frac{d}{dt}\int_{c}^{t}(t-\tau)^{-\alpha}f(\tau)d\tau \tag{3}$$

Investigations in this field gave fruitful results [9–35]. Representing a fractional derivative by Equation (3), however, makes it difficult to interpret the operations of differentiation and their connection with the fractal set: for example, a fractional derivative of a constant is not equal to zero. The use of fractional derivatives has a phenomenological and formal character. Equations with fractional derivatives have made different attractive analogies. Foundations for the connection of a fractional derivative with a fractal set, which produces the anomalous behaviour of dielectric relaxation, has been given in [25–28, 34, 35].

To make calculations more convenient, one connects the fractional differentiation operator $D_{0+}^{\alpha}f(t)$ with the fractional integration operator $I^{\alpha}f(x)$ defined as [36–39]

$$I^{\alpha}f(x)=\Phi_{\alpha}(x) \tag{4}$$

where the function $\Phi_{\alpha}(x)$ is

$$\Phi_{\alpha}(t)=C\int_{0}^{t}\frac{\left[f(\tau)-f(0)\right]}{(t-\tau)^{\alpha}}d\tau \tag{5}$$

and

$$C=\frac{1}{\Gamma(1-\alpha)}$$

It can be shown that

$$D_{0+}^{\alpha}f(t)=\frac{d}{dt}\Phi_{\alpha}(t) \tag{6}$$

i.e., the function $\Phi_{\alpha}(x)$ can be thought of as a primitive function for $f(t)$. The Laplace transformation gives [36–39]

$$L\left[D_{0}^{\alpha}f(t)\right]=p^{\alpha}L\left[f(t)\right]-p^{\alpha-1}f(0) \tag{7}$$

Now we consider a medium whose non-equilibrium state is of a fractal nature. We will assume that the non-equilibrium state is defined by a set of time events, in which subsequent events occur some time after the previous event has finished. In this case, some segments are excluded from the continuous states of the system during evolution according to a certain law. Such a process can be characterized as a process formed by a fractal state with a certain fractal dimension d_f.

The relaxation equation will have the following operator form [35]:

$$\left(\tau^{-\alpha} + D_{0+}^{\alpha}\right) P(t) = \frac{\chi_0 E}{\tau^{\alpha}} \tag{8}$$

where D^{α} is the fractional differentiation operator

$$D^{\alpha}{}_{0+}\left[f(t)\right] = C\frac{d}{dx}\int_{0+}^{x}\frac{f(t)}{(x-t)^{\alpha}}dt \tag{9}$$

The initial condition of Equation (8) is $P(0) = 0$. In accordance with (8), the Laplace transform of the function $P(t)$ can be obtained as:

$$\bar{P}(p) = \frac{\chi_0 E}{p}\frac{1}{1+(\tau p)^{\alpha}} \tag{10}$$

According to Equation (10), the Laplace transform $\bar{P}(p) = L(P(t))$ can be expressed as the series

$$\begin{aligned}\bar{P}(p) &= \frac{\chi_0 E}{p}\frac{1}{1+(\tau p)^{\alpha}} = \chi_0 E\left(\frac{1}{p} - \frac{(\tau p)^{\alpha-1}}{1+(\tau p)^{\alpha}}\right)\\ &= \chi_0 E\left(\frac{1}{p} - \frac{(\tau p)^{-1}}{1+(\tau p)^{-\alpha}}\right) = \chi_0 E\left(\frac{1}{p} - \sum_{n=0}^{\infty}(-1)^n(\tau p)^{-\alpha n-1}\right)\end{aligned} \tag{11}$$

Thus, the solution of (8) in the space of originals is:

$$P(t) = \chi_0 E\left(1 - \sum_{n=0}^{\infty}\frac{(-1)^n\left(\frac{t}{\tau}\right)^{\alpha n}}{\Gamma(\alpha n+1)}\right) = \chi_0 E\left(1 - M_{\alpha,1}(z)\right) \tag{12}$$

where $M_{\alpha,1}(z)$ is the Mittag–Leffler function

$$M_{\alpha,\gamma}(z) = \sum_{n=0}^{\infty}\frac{z^n}{\Gamma(\alpha n+\gamma)}, \qquad z = -\left(\frac{t}{\tau}\right)^{\alpha} \tag{13}$$

In our case, $\gamma = 1$.

It is convenient to use the Fox functions (i.e., the generalized Mellin–Barnes integrals) when solving equations with fractional derivatives, since the Laplace and Fourier transforms for the Fox functions are expressed through the Fox functions with other parameters. The connection between the Mittag–Leffler functions and the Fox functions is the following [40, 41]:

$$M_{\alpha,\gamma}(-z) = H_{1,2}^{1,1}\left[z \left| \begin{matrix} (0,1) \\ (0,1),(1-\gamma,\alpha) \end{matrix} \right. \right] \tag{14}$$

Therefore, Equation (12) can be written as

$$P(t) = \chi_0 E\left(1 - H_{1,2}^{1,1}\left[\left(\frac{t}{\tau}\right)^{\alpha} \left| \begin{matrix} (0,1) \\ (0,1),(0,\alpha) \end{matrix} \right. \right] \right) \tag{15}$$

If $\alpha = 1$, we obtain from Equation (15):

$$P(t) = \chi_0 E\left(1 - \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{t}{\tau}\right)^n}{\Gamma(n+1)} \right) = E\chi_0\left(1 - \mathrm{e}^{-t/\tau}\right) \tag{16}$$

If $\alpha \neq 1$, according to Equation (15), it follows that

$$P(t) \approx 1 - \left(\frac{t}{\tau}\right)^{-\alpha}, \qquad \left(\frac{t}{\tau}\right) \to \infty \tag{17}$$

and

$$P(t) \approx \left(\frac{t}{\tau}\right)^{\alpha}, \qquad \left(\frac{t}{\tau}\right) \to 0 \tag{18}$$

Thus, the solution of the equation with the fractional derivative (Eq. (8)) describes relaxation in dielectrics having a power time dependence with the asymptotic approximations of Equations (17) and (18).

Now let us generalize the results obtained. Instead of Equation (8), another operator of fractional differentiation will be examined:

$$\left(\tau^{-\alpha} + D^{\alpha}\right)^{\nu} = \sum_{n=0}^{\infty} \left(\tau^{-\alpha}\right)^n \binom{\nu}{n} D^{\alpha(\nu-n)} \tag{19}$$

where $\binom{\nu}{n} = \frac{\nu!}{n!(\nu-n)!}$ is a binomial coefficient and D^{α} is the operator of fractional differentiation,

$$D^{\alpha}{}_{0+}\left[f(t)\right] = C\frac{d}{dx}\int_{0+}^{x}\frac{f(t)}{(x-t)^{\alpha}}dt$$

In this case, the equation describing relaxation processes in dielectrics can be written in the following way

$$\left(\tau^{-\alpha} + D^{\alpha}\right)^{\nu}\left[P(t)\right] = \frac{\chi_0 E_0}{\tau^{\alpha\nu}} \tag{20}$$

where the initial condition is $P(0) = 0$.

In accordance with Equation (5), the Laplace transform of the function $P(t)$ is:

$$\bar{P}(p) = \frac{\chi_0 E}{p}\frac{1}{(1+(\tau p)^{\alpha})^{\nu}} \tag{21}$$

where

$$\bar{P}(p) = \int_0^{\infty} e^{-pt}\frac{1}{2}(t)dt$$

By substituting $p \rightarrow i\omega$ and taking into account Equation (21), the complex susceptibility can be written in the form

$$\chi(i\omega) = \frac{\chi_0}{\left(1+(i\omega\tau)^{\alpha}\right)^{\gamma}} \tag{22}$$

Dependence (22) coincides with the experimental principle of Havriliak–Negami [7]. Hence it appears that the complex relative permittivity is equal to

$$\varepsilon^{*}(i\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{[1+(i\omega\tau)^{\alpha}]^{\gamma}} \tag{23}$$

Where

$$\varepsilon'(\omega) = \mathrm{Re}\left[\varepsilon^{*}(i\omega)\right] = \varepsilon_{\infty} + (\varepsilon_0 - \varepsilon_{\infty})\frac{\cos\left[\gamma\arctan\left(\dfrac{\sin\dfrac{\alpha\pi}{2}(\omega\tau)^{\alpha}}{1+\cos\dfrac{\alpha\pi}{2}(\omega\tau)^{\alpha}}\right)\right]}{\left(1+(\omega\tau)^{2\alpha}+2(\omega\tau)^{\alpha}\cos\dfrac{\alpha\pi}{2}\right)^{\gamma/2}} \tag{24}$$

$$\varepsilon''(\omega)=\mathrm{Im}\left[\varepsilon^*(i\omega)\right]=(\varepsilon_0-\varepsilon_\infty)\frac{\sin\left[\gamma\arctan\left(\dfrac{\sin\dfrac{\alpha\pi}{2}(\omega\tau)^\alpha}{1+\cos\dfrac{\alpha\pi}{2}(\omega\tau)^\alpha}\right)\right]}{\left(1+(\omega\tau)^{2\alpha}+2(\omega\tau)^\alpha\cos\dfrac{\alpha\pi}{2}\right)^{\gamma/2}} \tag{25}$$

Moving from the image in Equation (21) to the original, we get the solution of Equation (20), which describes a dielectric relaxation that coincides with the experimental principle of Havriliak–Negami:

$$P(t)=-\frac{1}{\Gamma(\gamma)}\sum_{k=0}^{\infty}\frac{(-1)^k\,\Gamma(k+\gamma)}{\Gamma(\alpha k+\alpha\gamma)\Gamma(k+1)}\left(\frac{t}{\tau}\right)^{\alpha(k+\gamma)},\quad 0<\alpha<1,\quad 0<\gamma<1 \tag{26}$$

Thus, the dependence of the dielectric polarization $P(t)$ on time has the form of Equation (26) for Havriliak–Negami relaxation.

When $\gamma = 1$, the dependence (26) turns into the relaxation principle of Cole–Cole, and when $\alpha = 1$, it turns into the principle of Cole–Davidson. Hence, one can conclude that the operator in (19) is a generalized operator of fractional differentiation.

Thus, a mathematical model, i.e. a differential equation with fractional derivatives, was constructed to describe the relaxations of the Cole–Cole, Cole–Davidson, and Havriliak–Negami types in dielectrics.

The obtained solution of the differential equation with fractional derivatives allows one to predict anomalous dynamic dielectric properties in disordered materials, such as ferroelectrics, polymers, and composites used in various fields of human activity, e.g. in electronics.

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References

[1] KORENBLIT I.YA., SHENDER E.F., Usp. Fiz. Nauk, 157 (1989), 267 (in Russian).
[2] COLLA E.V., KOROLEVA E.YU., OKUNEVA N.M., VAKHRUSHEV S.B., J. Phys.: Cond. Matter, 4, 3671 (1992).
[3] GLINCHUK M.D., STEPHANOVICH V.A., HILCZER B., WOLAK J., CARANONI C., J. Phys.: Cond. Matter, 11 (1999), 6263.
[4] GLINCHUK M.D., STEPHANOVICH V.A., J. Phys.: Cond. Matter, 10 (1998), 11081.
[5] GLINCHUK M.D., STEPHANOVICH V.A., J. Phys.: Cond. Matter, 6 (1994), 6317.
[6] GLINCHUK M.D., FARHI R., STEPHANOVICH V.A., J. Phys.: Cond. Matter, 9 (1997), 10 237.
[7] JONSCHER A.K., *Dielectric Relaxation in Solids*, Chelsea Dielectric, London, 1983.
[8] KOHLRAUSCH R., Ann. Phys. (Leipzig), 12 (1847), 393; Pogg. Ann. Phys. Chem., 91 (1854), 179.

[9] WILLIAMS G., WATTS D.C., Trans. Faraday Soc., 66 (1970), 80.
[10] INOKUTI M., HIRAYAMA F., J. Chem. Phys., 43 (1965), 1978.
[11] SCHER H., LAX M., Phys. Rev. B, 7 (1973), 4491.
[12] SCHER H., MONTROLL E.W., Phys. Rev. B, 12 (1975), 2245.
[13] NGAI K.L., JONSCHER A.K., WHITE C.T., Nature, 277, (1979), 185.
[14] BLUMEN A., KLAFTER J., WHITE B.S., ZUMOFEN G., Phys. Rev. Lett., 53 (1984), 1301.
[15] KLAFTER J., BLUMEN A., ZUMOFEN G., J. Stat. Phys., 36 (1984), 561.
[16] BLUMEN A., KLAFTER J., ZUMOFEN G., *Models for reaction dynamics in classes* [in:] *Optical Spectroscopy of Glasses*, I. Zschokke (Ed.), Kluwer, Dordrecht, 1986, pp. 199–265.
[17] SHLESINGER M.F., MONTROLL E.W., Proc. Natl. Acad. Sci. USA, 81 (1984),1280.
[18] GOETZE W., SJOGREN L., Rep. Prog. Phys., 55 (1992), 241.
[19] HARROWELL P., Phys. Rev. E, 48 (1993), 4359.
[20] PHILLIPS J.C J., Non-Cryst. Solids, 172 (1994), 98 ; Rep. Prog. Phys., 59 (1996), 1133.
[21] METZLER R., GLOCKLE W.G., NONNENMACHER T.F., Physica A, 211 (1994), 3; METZLER R., SCHICK W., KLIAN H-G., NONNENMACHER T.F., J. Chem. Phys., 103 (1995), 7180; METZLER R., NONNENMACHER T.F., J. Phys. A : Math. Gen., 30 (1997), 1089.
[22] FUJIWARA S., YONEZAWA F., J. Non-Cryst. Solids, 198–200 (1996), 507.
[23] GOMI S., YONEZAWA F., J. Non-Cryst. Solids, 198–200 (1996), 521.
[24] DOUGLAS J.F., J. Phys.: Cond. Matter, 11 (1999), A329.
[25] NIGMATULLIN R.R., Phys. Stat. Sol. (b), 124 (1984), 389.
[26] NIGMATULLIN R.R., Phys. Stat. Soli. (b), 133 (1986), 425.
[27] NIGMATULLIN R.R., Teor. Mat. Fiz., 90 (1992), 354.
[28] NIGMATULLIN R.R., RYABOV YA.E., Fiz. Tv. Tela, 39, 101 (1997).
[29] FELDMAN Y., KOZLOVICH N., ALEXANDROV Y., NIGMATULLIN R.R., RYABOV YA., Phys. Rev. E, 54 (1996), 5420.
[30] METZLER R., BARKAI E., KLAFTER J., Phys. Rev. Lett., 82 (1999), 3563.
[31] BARKAI E., METZLER R., KLAFTER J., Phys. Rev. E, 61 (2000), 132.
[32] KOLWANKAR K.H., GANGAL A.V., Phys. Rev. Lett., 80 (1998), 214.
[33] SCHIESSEL H., METZLER R., BLUMEN A., NONNENMACHER T.F., J. Phys. A : Math. Gen., 28 (1995), 6567.
[34] NOVIKOV V.V., WOJCIECHOWSKI K.W., J. Appl. Tech. Physics, 41, (2000), 149
[35] NOVIKOV V.V., PRIVALKO V.P., Phys. Rev. E, 64 (2001), 031504.
[36] OLDHAM K., SPANIER J., *The Fractional Calculus*, Academic Press, New York, 1974.
[37] SAMKO S.G., KILBAS A.A., MARYCHEV O.I., *Fractional Integrals and Derivatives. Theory and Applications*, Gordon and Breach, Amsterdam, 1993.
[38] PODLUBNY I., *Fractional Differential Equations*, Academic Press, New York, 1999.
[39] *Applications of Fractional Calculus in Physics*, R. Hilfer (Ed.), World Scientific, London, 2000.
[40] FOX C., Trans. Am. Math. Soc., 98 (1961), 395.
[41] PRUDNIKOV A.P., BRYCHKOV YU.A., MARICHEV O.I., *Integrals and Series*, Vol. 3, Gordon and Breach, New York, 1990.

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