Fractional dynamics and nonlinear harmonic responses in dielectric relaxation of disordered liquids

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The problem of the nonlinear dielectric response due to the application of a strong electric field is reconsidered in the context of fractional kinetic equations. To accomplish that, we start from a fractional noninertial Fokker-Planck equation and restrict ourselves to the case of anomalous subdiffusive processes characterized by the critical exponent α ranging from 0 to 1, the limit of normal diffusion. In particular, we evaluate the first- and third-order nonlinear harmonic components of the electric polarization in the case of either a pure ac field or a strong dc bias field superimposed on a weak ac field. The stationary regime is therefore calculated from an infinite set of differential recurrence relations by using a perturbation method. The results so obtained are illustrated by three-dimensional dispersion and absorption plots in order to show the influence of α. Cole-Cole diagrams are also presented, allowing one to see that the arcs become more and more flattened as $\alpha \rightarrow 0$, and corresponding to a broadening of the absorption peaks as effectively observed in complex liquids. The theoretical model is supported by comparison with experimental data of the third-order nonlinear dielectric permittivity of a ferroelectric liquid crystal.

I. INTRODUCTION

In the area of physics dealing with complex fluids like liquid crystals, glass-forming liquids, polymeric systems, to quote but a few, it is experimentally observed that the time evolution of the dielectric relaxation processes can no longer be described in the form of an exponential function as in the Debye model, but rather follows the Kohlrausch-Williams-Watt law corresponding to a stretched exponential function [1–6]. As a consequence, in the frequency domain, when the systems are acted on by ac electric fields, the absorption spectra are characterized by broadened relaxation peaks [7]. In view of reproducing such typical patterns, three different empirical expressions are generally used for fitting the corresponding experimental data. Expressed in normalized forms, and considering, for instance, the responses provided with the complex electric susceptibilities $\chi(\omega)$, ω being the angular frequency of the applied ac electric field, they are the Cole-Cole equation [8]

$$\chi(\omega) = \frac{1}{1 + (i\omega\tau_{CC})^\alpha}, \quad 0 < \alpha \leq 1, \tag{1}$$

the Davidson-Cole equation [9]

$$\chi(\omega) = \frac{1}{(1 + i\omega\tau_{DC})^\beta}, \quad 0 < \beta \leq 1, \tag{2}$$

and the combined Havriliak-Negami equation [10]

$$\chi(\omega) = \frac{1}{[1 + (i\omega\tau_{HN})^\alpha]^\beta}, \quad \alpha\beta \leq 1, \tag{3}$$

where τ_{CC}, τ_{DC}, and τ_{HN} are the characteristic relaxation times, and α,β are the stretching exponents. For $\alpha = \beta = 1$, the well-known formulas corresponding to normal diffusion

are recovered. As soon as α (or β) becomes different from unity, anomalous diffusion takes place, which is what effectively occurs in disordered media. In order to account for the dielectric relaxation of such systems, it is possible to use a fractional Fokker-Planck equation, based on the continuous-time random walk, as shown recently by many authors [11–13]. Moreover, solution of the fractional equations may be accomplished in the same manner as that well developed for the usual partial differential equations [12].

In this paper, we shall restrict ourselves to the case where the fractal exponent α ranges from 0 to 1, which corresponds to the subdiffusive regime characterized by a much slower decrease of the fractional relaxation function for long times than that observed with the exponential (superslow process) [14]. An attempt to give a demonstration of the Cole-Cole formula was recently derived by Novikov and Privalko [2], who used a phenomenological relaxation function to describe the electric polarization. The same result was also obtained by Coffey *et al.* [15] from the noninertial Fokker-Planck equation. Hence, we shall try to extend the usual theory (normal diffusion) of the nonlinear dielectric response to this context of fractional dynamics. To accomplish this, we consider a dilute solution consisting of an assembly of noninteracting, rigid, polar, and symmetric-top molecules. With such assumptions, we can consider the rotational motion of a single molecule having a permanent dipole moment μ under the application of an external electric field $E(t)$. In what follows, we shall seek results obtained for two different electric fields, namely, either a pure alternating field $E(t) = E_1 \cos(\omega t)$, or a strong dc constant bias field on which is superimposed a weak ac field in the same direction, $E(t) = E_0 + E_1 \cos(\omega t)$ with $E_1/E_0 \ll 1$, and we shall calculate for the stationary process (i.e., when the system has removed all the transient effects so that we consider its behavior a long time after the electric field has been switched on) the har-

monic components of the electric susceptibility valid up to the third order in the electric field strength.

II. THEORY

For one molecule whose symmetry axis makes the angle ϑ with the electric field, the orientational probability distribution function $W(\vartheta,t)$ in the framework of fractional dynamics obeys the following partial fractional differential equation written in configuration space only:

$$
\frac{\partial W(\vartheta,t)}{\partial t} = (2D_R)^\alpha \, _0D_t^{1-\alpha} \frac{1}{2\sin\vartheta} \frac{\partial}{\partial\vartheta} \left[\sin\vartheta \left(\frac{\partial W(\vartheta,t)}{\partial\vartheta} \right) \right.
$$
$$
\left. + \frac{W(\vartheta,t)}{kT} \frac{\partial V(\vartheta,t)}{\partial\vartheta} \right], \tag{4}
$$

where $V(\vartheta)$ is the orientational potential energy given by

$$
V(\vartheta) = -\mu E(t)\cos\vartheta, \tag{5}
$$

D_R is the rotational diffusion constant equal to $(2\tau)^{-1}$, τ being the Debye relaxation time, and $_0D_t^{1-\alpha}$ is the Riemann-Liouville operator defined by [16]

$$
_0D_t^{1-\alpha} = \frac{\partial}{\partial t} \, _0D_t^{-\alpha}, \tag{6}
$$

with

$$
_0D_t^{-\alpha}W(\vartheta,t) = \frac{1}{\Gamma(\alpha)} \int_0^t (t-t')^{-(1-\alpha)} W(\vartheta,t')dt'. \tag{7}
$$

We note that Eq. (4) is valid if inertial effects are completely ignored and reduces to the well-known Smoluchowski equation if $\alpha = 1$. From Eq. (7), which has the form of a convolution product, one notes the presence of a memory kernel indicating the non-Markovian nature of the subdiffusive process. It is also important to note that the Laplace transform of Eq. (7) is simply given by [16,17]

$$
\mathcal{L}[_0D_t^{-\alpha}W(\vartheta,t)] = p^{-\alpha}\widetilde{W}(\vartheta,p), \tag{8}
$$

where

$$
\widetilde{W}(\vartheta,p) = \mathcal{L}[W(\vartheta,t)] = \int_0^{+\infty} e^{-pt} W(\vartheta,t)dt. \tag{9}
$$

Since the Riemann-Liouville operator acts only on the time variable and not on the angular (space) variable, we can use classical methods for solving Eq. (4). By setting $u = \cos\vartheta$, multiplying both sides of Eq. (4) by $P_n(u)$, the nth Legendre polynomial, and integrating from -1 to $+1$ over the variable u, we arrive at

$$
\frac{d}{dt}\langle P_n(u)\rangle(t) = (2D_R)^\alpha \, _0D_t^{1-\alpha} \left\{ -[n(n+1)/2]\langle P_n(u)\rangle(t) \right.
$$
$$
+ (\gamma_0 + \gamma_1\cos\omega t)\frac{n(n+1)}{2(2n+1)}
$$
$$
\left. \times [\langle P_{n-1}(u)\rangle(t) - \langle P_{n+1}(u)\rangle(t)] \right\}, \tag{10}
$$

where the angular brackets stand for ensemble averages such that

$$
\langle P_n(u)\rangle(t) = \int_{-1}^{+1} P_n(u)W(u,t)du
$$
$$
= \int_0^\pi P_n(\cos\vartheta)W(\vartheta,t)\sin\vartheta \, d\vartheta, \tag{11}
$$

and

$$
\gamma_0 = \frac{\mu E_0}{kT}, \quad \gamma_1 = \frac{\mu E_1}{kT} \tag{12}
$$

are two dimensionless parameters giving the importance of the orientational potential energy due to the electric field with respect to the thermal energy (k is the Boltzmann constant and T is the absolute temperature). Now, considering again the Riemann-Liouville operator (fractional derivative) and using the properties

$$
(_0D_t^{1-\alpha})^{-1}(\partial/\partial t) = (\partial/\partial t)^{-1}(D_t^{-\alpha})^{-1}(\partial/\partial t) = _0D_t^\alpha \tag{13}
$$

and

$$
(_0D_t^{1-\alpha})^{-1} \, _0D_t^{1-\alpha} = \mathbf{1} \quad \text{(identity operator)}, \tag{14}
$$

Eq. (10) becomes

$$
_0D_t^\alpha\langle P_n(u)\rangle(t) = (2D_R)^\alpha \left\{ -[n(n+1)/2]\langle P_n(u)\rangle(t) \right.
$$
$$
+ (\gamma_0 + \gamma_1\cos\omega t)\frac{n(n+1)}{2(2n+1)}
$$
$$
\left. \times [\langle P_{n-1}(u)\rangle(t) - \langle P_{n+1}(u)\rangle(t)] \right\}. \tag{15}
$$

Since we are solely interested in the determination of the stationary ac response, which is obviously independent of the initial conditions, we can seek the solution of Eq. (15) in the form [18–20]

$$
f_n(t) = \langle P_n(u)\rangle(t) = \sum_{k=-\infty}^{+\infty} F_k^n(\omega)e^{ik\omega t}, \tag{16}
$$

where the Fourier amplitudes $F_k^n(\omega)$ satisfy the following condition (the asterisk stands for the complex conjugate):

$$F_{-k}^n(\omega)=[F_k^n(\omega)]^*, \tag{17}$$

because the expectation values of the Legendre polynomials, f_n, are real functions of the time variable t.

The physical quantity that is interesting from an experimental point of view and characteristic of dielectric relaxation is the electric polarization defined by

$$\mathcal{P}(t)=N\mu\langle P_1(u)\rangle(t)=N\mu f_1(t), \tag{18}$$

where N represents the number of molecules per unit volume. It is this quantity that we shall now evaluate for both types of electric field we mentioned at the end of the Introduction.

III. DIELECTRIC RESPONSE IN THE CASE OF SUPERIMPOSED ELECTRIC FIELDS

In the situation where a strong dc bias field is superimposed at the same time on a weak ac electric field, the solution for $f_1(t)$ can be presented in the form

$$f_1(t)=F_0^1(\omega)+2\sum_{k=1}^{+\infty}\text{Re}[F_k^1(\omega)e^{ik\omega t}]. \tag{19}$$

The first term $F_0^1(\omega)$ in the right-hand side of Eq. (19) is a time-independent but frequency-dependent term due to the presence of the dc field E_0. In order to calculate the Fourier coefficients of Eq. (19), it suffices to substitute the expression for $f_n(t)$ of Eq. (16) into Eq. (15), which yields

$$\left[\left(\frac{i\omega k}{2D_R}\right)^\alpha+\frac{n(n+1)}{2}\right]F_k^n(\omega)$$

$$=\gamma_0\frac{n(n+1)}{2(2n+1)}[F_k^{n-1}(\omega)-F_k^{n+1}(\omega)]+\gamma_1\frac{n(n+1)}{4(2n+1)}$$

$$\times[F_{k-1}^{n-1}(\omega)+F_{k+1}^{n-1}(\omega)-F_{k-1}^{n+1}(\omega)-F_{k+1}^{n+1}(\omega)], \tag{20}$$

or in condensed form

$$F_k^n(\omega)x_{k,n}(\omega)-2\gamma_0[F_k^{n-1}(\omega)-F_k^{n+1}(\omega)]$$

$$-\gamma_1[F_{k-1}^{n-1}(\omega)+F_{k+1}^{n-1}(\omega)-F_{k-1}^{n+1}(\omega)-F_{k+1}^{n+1}(\omega)]=0, \tag{21}$$

where

$$x_{k,n}(\omega)=2(2n+1)\left[1+\frac{2}{n(n+1)}\left(\frac{i\omega k}{2D_R}\right)^\alpha\right]. \tag{22}$$

If we restrict ourselves to the third order in the electric field strength, the time-independent term $F_0^1(\omega)$ will contain quantities proportional to γ_0, γ_0^3, and $\gamma_0\gamma_1^2$ only. By using a perturbation procedure on the set of differential recurrence relations Eq. (21), we obtain for $k=0$, $n=1$

$$F_0^1(\omega)=\frac{\gamma_0}{3}\left(1-\frac{\gamma_0^2}{15}\right)$$

$$-\frac{\gamma_0\gamma_1^2}{3}\text{Re}\left(\frac{1}{5x_{-1,1}}+\frac{2}{x_{-1,1}x_{-1,2}}+\frac{1}{3x_{-1,2}}\right), \tag{23}$$

where the notation "Re" stands for the "real part of," and setting $\omega'=\omega/(2D_R)$ as reduced variable

$$x_{-1,1}(\omega')=6[1+(-i\omega')^\alpha],$$

$$x_{-1,2}(\omega')=10[1+(-i\omega')^\alpha/3]. \tag{24}$$

After some calculation, it is found that the explicit expression for $F_0^1(\omega')$ is

$$F_0^1(\omega')=\frac{\gamma_0}{3}\left(1-\frac{\gamma_0^2}{15}\right)-\frac{\gamma_0\gamma_1^2}{90}\frac{27+(23/2)\omega'^{2\alpha}+4\omega'^\alpha(12+\omega'^{2\alpha})\cos(\pi\alpha/2)+9\omega'^{2\alpha}\cos^2(\pi\alpha/2)+(9/2)\omega'^{2\alpha}\cos(\pi\alpha)}{[1+2\omega'^\alpha\cos(\pi\alpha/2)+\omega'^{2\alpha}][9+6\omega'^\alpha\cos(\pi\alpha/2)+\omega'^{2\alpha}]}. \tag{25}$$

For $\alpha=1$, this equation yields the result already obtained in [21,22].

We can proceed in the same manner as that used above for determining the first-harmonic component of the electric polarization. By again keeping the third-order terms only, this quantity is proportional to γ_1 and $\gamma_0^2\gamma_1$, and so provides the nonlinear response in the ac electric field. Written in complex form, one has for $k=-1$, $n=1$

$$F_{-1}^1(\omega')=-\frac{2\gamma_0}{x_{-1,1}}F_{-1}^2(\omega')+\frac{\gamma_1}{x_{-1,1}}[1-F_0^2(\omega')]$$

$$=-\frac{2\gamma_0}{x_{-1,1}}\left(\frac{2\gamma_0\gamma_1}{x_{-1,1}x_{-1,2}}+\frac{\gamma_0\gamma_1}{3x_{-1,2}}\right)+\frac{\gamma_1}{x_{-1,1}}\left(1-\frac{\gamma_0^2}{15}\right). \tag{26}$$

In Eq. (26), we recognize the linear contribution given by

$(x_{-1,1})^{-1}$. Hence, by substituting the expressions given by Eq. (24) in Eq. (26), we have

$$F^1_{-1}(\omega') = \frac{\gamma_1}{6[1+(-i\omega')^\alpha]}$$
$$-\frac{\gamma_0^2\gamma_1}{90}\frac{1+[1+(-i\omega')^\alpha][2+(-i\omega')^\alpha/3]}{[1+(-i\omega')^\alpha]^2[1+(-i\omega')^\alpha/3]},$$
$$(27)$$

The second term in Eq. (27) is characteristic of the Langevin saturation with a negative contribution. We can therefore as in normal diffusion define a complex nonlinear dielectric increment such that

$$\Delta\varepsilon_{NL}(\omega') = \frac{2F^1_{-1}(\omega')}{\gamma_1} - \frac{1}{3[1+(-i\omega')^\alpha]}$$
$$= -\frac{\gamma_0^2}{45}\frac{1+[1+(-i\omega')^\alpha][2+(-i\omega')^\alpha/3]}{[1+(-i\omega')^\alpha]^2[1+(-i\omega')^\alpha/3]},$$
$$(28)$$

where the subscript "NL" stands for nonlinear, and the factor of 2 before $F^1_{-1}(\omega')$ arises from the definition given in Eq. (17). For $\alpha = 1$, Eq. (28) coincides exactly with the results previously obtained by Coffey and Paranjape [23] (see also Ref. [22]). It is interesting to make a partial fraction decomposition of Eq. (28) with the aim of extending this expression to the time domain, which is also of importance if one refers to some experimental work, namely,

$$\Delta\varepsilon_{NL}(\omega') = -\frac{\gamma_0^2}{45}\left[\frac{3/2}{[1+(-i\omega')^\alpha]^2} + \frac{7/4}{1+(-i\omega')^\alpha}\right.$$
$$\left.-\frac{3/4}{3+(-i\omega')^\alpha}\right].$$
$$(29)$$

In order to show the temporal evolution of each term in Eq. (29), it is convenient to introduce the following function:

$$g(t) = \frac{t^{\alpha-1}}{\tau}E_{\alpha,\alpha}\left(-\frac{t^\alpha}{\tau}\right), \quad 0<\alpha\leq 1, \qquad (30)$$

whose Laplace transform is

$$G(p) = \int_0^{+\infty} e^{-pt}g(t)dt = \frac{1}{1+\tau p^\alpha}, \qquad (31)$$

where

$$E_{\alpha,\alpha}(-z) = \sum_{k=0}^{+\infty}\frac{(-z)^k}{\Gamma(\alpha k+\alpha)} \qquad (32)$$

is the generalized Mittag-Leffler function [24], which reduces to the exponential one for $\alpha = 1$, and τ is the relaxation time equal to $(2D_R)^{-1}$. Applying this definition to Eq. (29), one obtains
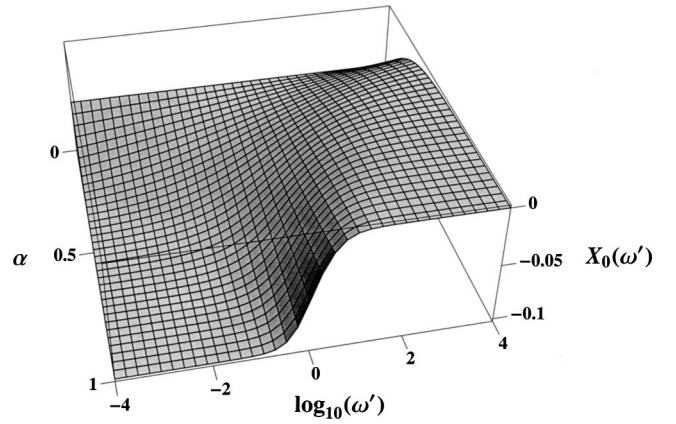

FIG. 1. Three-dimensional (3D) plot of the steady-state component X_0 as a function of the reduced angular frequency ω' and the fractional parameter α.

$$\Delta\varepsilon_{NL}(t) = -\frac{\gamma_0^2}{45}\left\{\frac{3}{2}\frac{t^{\alpha-1}}{\tau^\alpha}E_{\alpha,\alpha}\left[-\left(\frac{t}{\tau}\right)^\alpha\right]\otimes\frac{t^{\alpha-1}}{\tau^\alpha}E_{\alpha,\alpha}\right.$$
$$\left[-\left(\frac{t}{\tau}\right)^\alpha\right]+\frac{7}{4}\frac{t^{\alpha-1}}{\tau^\alpha}E_{\alpha,\alpha}\left[-\left(\frac{t}{\tau}\right)^\alpha\right]$$
$$\left.-\frac{3}{4}\frac{t^{\alpha-1}}{\tau^\alpha}E_{\alpha,\alpha}\left[-3\left(\frac{t}{\tau}\right)^\alpha\right]\right\}, \qquad (33)$$

where the symbol $\otimes$ represents a convolution product such as

$$h(t)\otimes l(t) = \int_0^t h(t-t')l(t')dt' = \int_0^t l(t-t')h(t')dt', \qquad (34)$$

with the important property of the Laplace transform

$$\mathcal{L}[h(t)\otimes l(t)] = \mathcal{L}[h(t)]\mathcal{L}[l(t)]. \qquad (35)$$

In order to simplify the presentation of the above results, we shall use the following reduced quantities:

$$X_0(\omega') = \left[F^1_0(\omega') - \frac{\gamma_0}{3}\left(1-\frac{\gamma_0^2}{45}\right)\right]\frac{90}{\gamma_0\gamma_1^2}, \qquad (36)$$

$$\Delta X_1(\omega') = \Delta X_1'(\omega') - i\Delta X_1''(\omega') = 45\frac{\Delta\varepsilon_{NL}(\omega')}{\gamma_0^2}, \qquad (37)$$

where $X_0(\omega')$ describes in fact the variations of the second term in the right-hand side of Eq. (25) since only this term is frequency-dependent. The dc component $X_0(\omega')$ of the electric polarization is presented in Fig. 1 for α values ranging from 0 to 1 (subdiffusive process). One can remark that the asymptotic value $X_0(\infty)=0$ is more rapidly attained when $\alpha\to 1$. Everywhere else, $X_0(\omega')$ takes on negative values. In Figs. 2 and 3 are pictured the real $\Delta X_1'$ and imaginary $\Delta X_1''$ parts of the complex nonlinear dielectric increment $\Delta X_1(\omega')$ as a function of ω' and α ($0<\alpha\leq 1$) corresponding to the contribution of the first-harmonic component to the linear
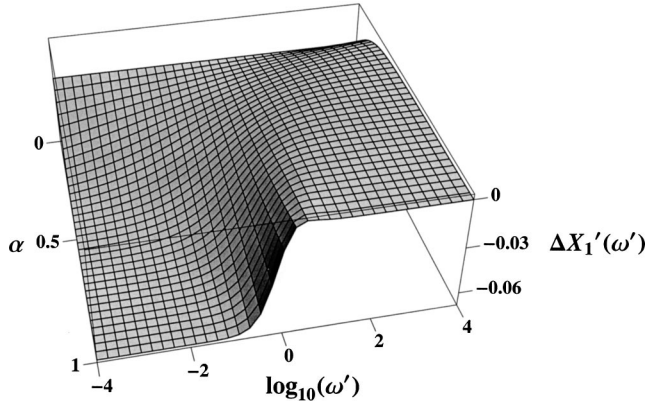
FIG. 2. 3D plot of the real part of the nonlinear dielectric increment $\Delta X_1'$ (first-harmonic component of the electric polarization) as a function of ω' and α.

response in the ac electric field. The higher α is, the steeper is the slope in the increase of the dispersion plot $[\Delta X_1'(\omega')]$. Regarding the absorption curves $\Delta X_1''(\omega')$, the height of the peaks increases in proportion to α while their maxima shift to the lowest frequencies as α decreases. The Cole-Cole diagrams (Fig. 4) demonstrate the influence of the anomalous exponent α, with decreasing amplitudes of the arcs as α diminishes. It is worth noting from these plots that $\Delta X_1'(\omega')$ and $\Delta X_1''(\omega')$ are always negative, with the exception of $\Delta X_1'(\omega')$ for $\alpha=1$ (normal diffusion), which becomes positive in the high-frequency region.

IV. NONLINEAR DIELECTRIC RESPONSE IN PRESENCE OF A PURE ac ELECTRIC FIELD

In the absence of the dc bias field ($\gamma_0=0$), there are no longer constant terms in the dielectric response. Hence, by limiting ourselves again to the third order of the external electric perturbation, we shall evaluate the analytic expressions for the harmonic components of the electric polarization varying at the fundamental frequency ω (first harmonic) and at 3ω (third harmonic). From Eq. (21) in which we put $\gamma_0=0$, we have now to solve the following set of differential recurrence relations:
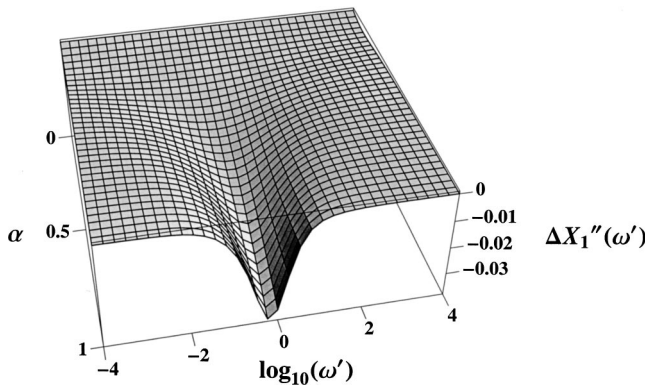

FIG. 3. 3D plot of the imaginary part of the nonlinear dielectric increment $\Delta X_1''$ (first-harmonic component of the electric polarization) as a function of ω' and α.
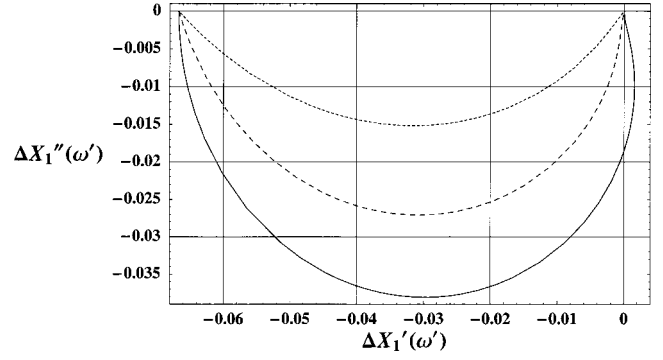

FIG. 4. Cole-Cole plots of the nonlinear complex dielectric increment $\Delta X_1(\omega')$ for three different values of α. Full line, $\alpha=1$ (Brownian limit); dashed line, $\alpha=0.8$; dotted line, $\alpha=0.5$.

$$F_k^n(\omega')x_{k,n}(\omega')=\gamma_1[F_{k-1}^{n-1}(\omega')+F_{k+1}^{n-1}(\omega')-F_{k-1}^{n+1}(\omega')$$
$$-F_{k+1}^{n+1}(\omega')], \qquad (38)$$

where

$$x_{k,n}(\omega')=2(2n+1)\left[1+\frac{2(i\omega'k)^\alpha}{n(n+1)}\right], \quad \omega'=\frac{\omega}{2D_R}=\omega\tau. \qquad (39)$$

For $k=-1$, $n=1$, we have

$$F_{-1}^1(\omega')=\frac{\gamma_1}{x_{-1,1}}[1-F_{-2}^2(\omega')-F_0^2(\omega')], \qquad (40)$$

where it suffices for our problem to evaluate F_{-2}^2 and F_0^2 up to the second order in the ac field only, which yields

$$F_{-2}^2(\omega')=\frac{1}{x_{-2,2}(\omega')}[\gamma_1 F_{-1}^1(\omega')]=\frac{\gamma_1^2}{x_{-1,1}(\omega')x_{-2,2}(\omega')},$$
$$x_{-2,2}(\omega')=10[1+(-2i\omega')^\alpha/3], \qquad (41)$$

and

$$F_0^2(\omega')=\frac{\gamma_1}{10}[F_{-1}^1(\omega')+F_1^1(\omega')]$$

$$=\frac{\gamma_1}{5}\operatorname{Re}[F_{-1}^1(\omega')]$$

$$=\frac{\gamma_1^2}{5}\operatorname{Re}\left[\frac{1}{x_{-1,1}(\omega')}\right], \qquad (42)$$

so that

$$F_{-1}^1(\omega')=\frac{\gamma_1}{6[1+(-i\omega')^\alpha]}-\frac{\gamma_1^3}{360}\frac{1}{[1+(-i\omega')^\alpha]^2}$$
$$\times\left[\frac{2[1+\omega'^\alpha\cos(\pi\alpha/2)]}{1+(i\omega')^\alpha}+\frac{1}{1+(-2i\omega')^\alpha/3}\right]. \qquad (43)$$

This expansion gives correct results as long as $\gamma_1 < 1$. In terms of the nonlinear electric susceptibility $\chi_1(\omega')$, Eq. (43) can be rewritten as

$$\chi_1(\omega') = \frac{2F_{-1}^1(\omega')}{\gamma_1}$$

$$= \frac{1}{3[1+(-i\omega')^\alpha]} - \frac{\gamma_1^2}{180} \frac{1}{[1+(-i\omega')^\alpha]^2}$$

$$\times \left[\frac{2[1+\omega'^\alpha \cos(\pi\alpha/2)]}{1+(i\omega')^\alpha} + \frac{3}{3+(-2i\omega')^\alpha} \right].$$

$$(44)$$

For $\alpha = 1$, we get

$$\chi_1(\omega')_{\alpha=1} = \frac{1}{3(1-i\omega')}$$

$$- \frac{\gamma_1^2}{180(1+\omega'^2)} \frac{9-i\omega'}{(1-i\omega')(3-2i\omega')},$$

$$(45)$$

which is in agreement with previously derived results [22,23]. More interesting experimentally in the application of a pure ac electric field only is the calculation of the third nonlinear harmonic component of the electric polarization given by the evaluation of $F_{-3}^1(\omega')$. Many data related to the study of disordered media are now available, and the interest in an interpretation of their behavior is still growing. It is important to understand the typical features of such systems, essentially characterized by their nonexponential relaxation patterns giving rise to slow diffusion. Among all these materials, ferroelectric liquid crystals in the chiral smectic-C phase [25–28] have caught the attention of many researchers. In particular, the third order of the nonlinear dielectric response for such liquids in the Goldstone mode yields negative values in the same manner as those observed for an equivalent study of free rotating dipoles in ordinary fluids (Langevin saturation effect). Setting $k = -3$ and $n = 1$ in Eq. (38) in order to calculate the third-harmonic component in 3ω proportional to γ_1^3, one obtains

$$x_{-3,1}(\omega')F_{-3}^1(\omega') = \gamma_1 F_{-2}^2(\omega'),$$

$$(46)$$

and using Eq. (41)

$$F_{-3}^1(\omega') = -\frac{\gamma_1^3}{x_{-1,1}(\omega')x_{-2,2}(\omega')x_{-3,3}(\omega')},$$

$$(47)$$

where

$$x_{-3,1}(\omega') = 6[1+(-3i\omega')^\alpha].$$

$$(48)$$

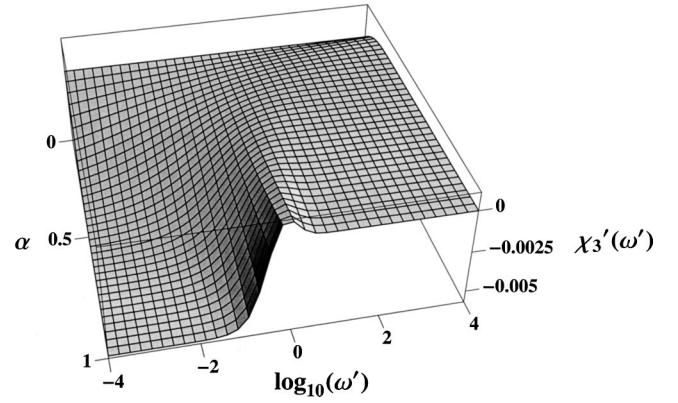Therefore, the explicit form for the electric susceptibility $\chi_3(\omega')$ is

FIG. 5. 3D plot of the real part of the third-harmonic component $\chi_3'(\omega')$ of the electric polarization as a function of ω' and α.

$$\chi_3(\omega') = \frac{2F_{-3}^1(\omega')}{\gamma_1^3}$$

$$= -\frac{1}{60}$$

$$\times \frac{1}{[1+(-i\omega')^\alpha][3+(-2i\omega')^\alpha][1+(-3i\omega')^\alpha]}$$

$$= -\frac{1}{60} \left[\frac{1}{(-3+2^\alpha)(-1+3^\alpha)} \frac{1}{1+(-i\omega')^\alpha} \right.$$

$$+ \frac{2^{2\alpha}}{(-3+2^\alpha)(2^\alpha-3^{1+\alpha})} \frac{1}{3+(-2i\omega')^\alpha}$$

$$\left. + \frac{3^{2\alpha}}{(-1+3^\alpha)(-2^\alpha+3^{1+\alpha})} \frac{1}{1+(-3i\omega')^\alpha} \right], \quad (49)$$

again in accord with the results of Refs. [21–23] for $\alpha = 1$. In Figs. 5 and 6 are shown the frequency evolution of the relaxation spectra of $\chi_3(\omega')$ as a function of α. The general pattern of all these plots is comparable to that already exhibited by the first-harmonic component [nonlinear dielectric increment $\Delta X_1(\omega')$], with, however, smaller amplitudes by
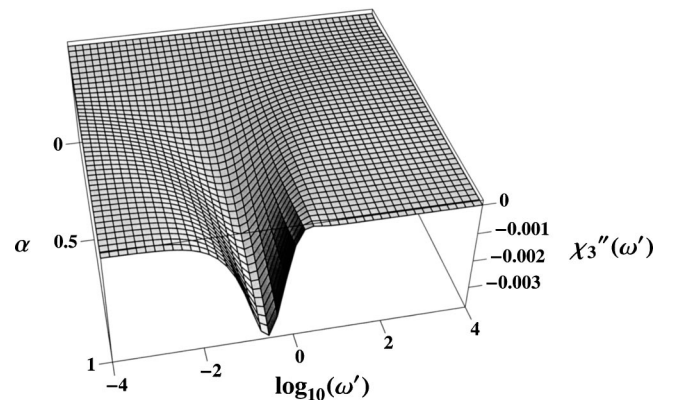

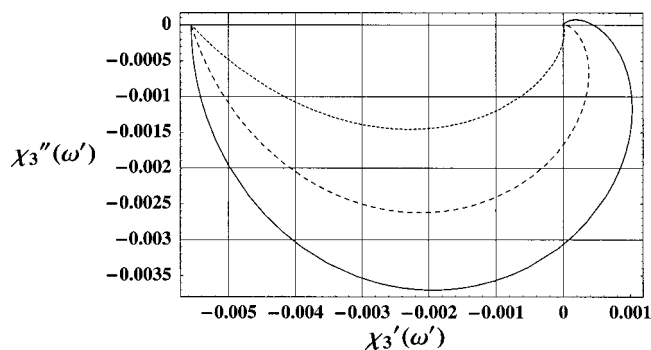FIG. 6. 3D plot of the imaginary part of the third-harmonic component $\chi_3''(\omega')$ of the electric polarization as a function of ω' and α.

FIG. 7. Cole-Cole plots of the third-harmonic component $\chi_3(\omega')$ for three different values of α. Full line, $\alpha=1$ (Brownian limit); dashed line, $\alpha=0.8$; dotted line, $\alpha=0.5$.

FIG. 8. Third-order nonlinear dispersion (ε_3') and absorption (ε_3'') spectra for CS 1017 (ferroelectric liquid crystal) at 50 °C. Filled circles are experimental data taken from Kimura *et al.* [29]. The full and dashed lines represent our best fit procedure from Eq. (49) for the real (ε_3') and imaginary (ε_3'') parts of the complex dielectric permittivity ε_3, respectively.

a factor of almost two orders of magnitude. Some slight differences are nevertheless visible by looking at the Cole-Cole diagrams (Fig. 7) where the skewed arcs are more flattened due, especially, to the positive values of the real part $\chi_3'(\omega')$ in the high-frequency region. We have checked our theoretical expression for the third-order nonlinear electric susceptibility $\chi_3(\omega')$ given by Eq. (49) by using experimental data recently obtained by Kimura *et al.* [29] on the ferroelectric liquid crystal CS 1017 (Chisso): these measurements were made at 50 °C with an ac electric field of angular frequency varying from 15 to 2.5×10^6 rad/s. This comparison between theory and experiment is illustrated by the nonlinear relaxation spectra in Fig. 8 where a quite good agreement can be observed with the exception of a few points (within the limits of accuracy) at low frequencies due to conductivity and electrode polarization effects which are not taken into account in our analytical formulation. A least mean square fit leads to the numerical determination of α and τ, namely, $\alpha=0.89$ and $\tau=0.58\times10^{-3}$ s.

V. CONCLUSION

In this paper, we have tried to introduce the fractional approach to the orientational motion of polar molecules acted on by an external perturbation, such as a time-dependent electric field. This problem is treated in the context of noninertial rotational diffusion (configuration space only) which leads to solving a fractional Smoluchowski equation. Hence, we consider a physical model corresponding to a slow relaxation process (subdiffusion) characterized by an anomalous exponent α ranging in the interval $(0,1)$ ($\alpha=1$ for normal diffusion). The generalization of this diffusion equation including a fractional order rests on the model of the continuous-time random walk. Here, because we are dealing with rotations rather than translations, it is preferable to speak of randomly distributed torques having
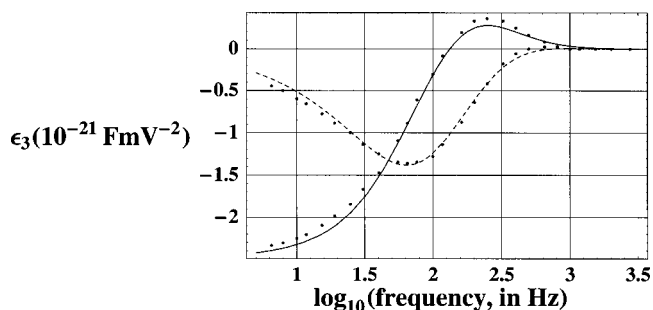
an anomalous waiting time distribution function. We have derived in the frequency domain analytical expressions for the electric susceptibilities corresponding to nonlinear ac stationary responses and valid up to the third order in the electric field strength. To illustrate these results, dispersion and absorption spectra for the first- and the third-harmonic components have been plotted in order to show the significant departure from the classical Brownian behavior as $\alpha\rightarrow0$. Moreover, a comparison of our theoretical model with experimental data for the third-order nonlinear dielectric relaxation spectra of a ferroelectric liquid crystal led to a quite good agreement in fitting these dispersion and absorption plots. To conclude, we indicate that our approach can be extended to the case of anisotropically polarizable molecules. In future studies, we intend to take into account dipolar interactions also [30], with the aim of deriving nonlinear responses in molecular systems where concentration effects can no longer be neglected, and to compare them to available computer simulations [31]. In such a case, even the simplest interaction potential gives rise to a coupling of the longitudinal and transverse components of the polarization. Moreover, higher-order responses can also be evaluated using the matrix continued fraction procedure in the manner developed for normal diffusion in our previous papers [18–20]. In addition, we mention that the present theory could be applied with minute modifications to the case of ferrofluids subjected to time-dependent magnetic fields.

[1] R. Hilfer, Phys. Rev. E **65**, 061510 (2002).

[2] V. V. Novikov and V. P. Privalko, Phys. Rev. E **64**, 031504 (2001).

[3] R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1847).

[4] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[5] R. Metzler and J. Klafter, J. Non-Cryst. Solids **305**, 81 (2002).

[6] R. Hilfer, *Applications of Fractional Calculus in Physics*

(World Scientific, Singapore, 2000).

[7] F. Alvarez, A. Alegria, and J. Colmenero, Phys. Rev. B **44**, 7306 (1991).

[8] K. Cole and R. Cole, J. Chem. Phys. **9**, 341 (1941).

[9] D. Davidson and R. Cole, J. Chem. Phys. **19**, 1484 (1951).

[10] S. Havriliak and S. Negami, J. Polym. Sci. C **14**, 99 (1966).

[11] R. Metzler, E. Barkai, and J. Klafter, Phys. Rev. Lett. **82**, 3563 (1999).

[12] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).

[13] R. Metzler and J. Klafter, Adv. Chem. Phys. **116**, 223 (2001).

[14] F. Mainardi, Chaos, Solitons Fractals **7**, 1461 (1996).

[15] W. T. Coffey, Y. P. Kalmykov, and S. V. Titov, J. Chem. Phys. **116**, 6422 (2002).

[16] K. B. Oldham and J. Spanier, *The Fractional Calculus* (Academic, New York, 1974).

[17] R. Metzler and J. Klafter, J. Mol. Liq. **86**, 219 (2000).

[18] J. L. Déjardin and Y. P. Kalmykov, Phys. Rev. E **61**, 1211 (2000).

[19] J. L. Déjardin and Y. P. Kalmykov, J. Chem. Phys. **112**, 2916 (2000).

[20] J. L. Déjardin, Y. P. Kalmykov, and P. M. Déjardin, Adv.

Chem. Phys. **117**, 275 (2001).

[21] J. L. Déjardin, J. Chem. Phys. **98**, 3191 (1993).

[22] J. L. Déjardin, *Dynamic Kerr Effect* (World Scientific, Singapore, 1995).

[23] W. T. Coffey and B. V. Paranjape, Proc. R. Ir. Acad. A, Math. Phys. Sci. **78A**, 17 (1978).

[24] A. Erdelyi *et al.*, *Higher Transcendental Functions*, Vol. III (Krieger, Malabar, 1981).

[25] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (France) Lett. **36**, L69 (1975).

[26] B. Zeks and R. Blinc, *Ferroelectric Liquid Crystals, Principles, Properties and Applications* (Gordon and Breach, Philadelphia, 1991), Chap. 5.

[27] P. G. Costello, Y. P. Kalmykov, and J. K. Vij, Phys. Rev. A **46**, 4852 (1992).

[28] A. E. Glazounov and A. K. Tagantsev, Phys. Rev. Lett. **85**, 2192 (2000).

[29] Y. Kimura, S. Hara, and R. Hayakawa, Phys. Rev. E **62**, R5907 (2000).

[30] B. Bagchi and A. Chandra, Phys. Rev. Lett. **64**, 455 (1990).

[31] E. L. Pollock and B. J. Alder, Phys. Rev. Lett. **46**, 950 (1981).