Anomalous nonlinear dielectric and Kerr effect relaxation steady state responses in superimposed ac and dc electric fields

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It is shown how the rotational diffusion model of polar molecules (which may be described in microscopic fashion as the diffusion limit of a discrete time random walk on the surface of the unit sphere) may be extended to anomalous nonlinear dielectric relaxation and the dynamic Kerr effect by using a fractional kinetic equation. This fractional kinetic equation (obtained via a generalization of the noninertial kinetic equation of conventional rotational diffusion to fractional kinetics to include anomalous relaxation) is solved using matrix continued fractions yielding the complex nonlinear dielectric susceptibility and the Kerr function of an assembly of rigid dipolar particles acted on by external superimposed dc $\mathbf{E}_0$ and ac $\mathbf{E}_1(t) = \mathbf{E}_1 \cos \omega t$ electric fields of arbitrary strengths. In the weak field limit, analytic equations for nonlinear response functions are also derived. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2463694]

I. INTRODUCTION

One of the most striking features of the dielectric relaxation of disordered materials such as complex liquids and amorphous polymers is the failure of the Debye[1] theory of dielectric relaxation to adequately describe the low-frequency spectrum, where the relaxation behavior may deviate considerably from the exponential (Debye) pattern and exhibits a broad distribution of relaxation times. The relaxation process in such disordered systems is characterized by the temporally nonlocal behavior arising from the energetic disorder which produces obstacles or traps simultaneously delaying the motion of the particle and producing memory effects. It appears that a significant amount of experimental data on anomalous relaxation of disordered systems and complex liquids supports the following empirical expressions for the dielectric susceptibility spectra, namely, the Cole-Cole equation,[2]

$$\chi_{CC}(\omega) = \frac{\chi_0}{1 + (i\omega\tau)^\sigma}, \tag{1}$$

the Cole-Davidson equation,[3]

$$\chi_{CD}(\omega) = \frac{\chi_0}{(1 + i\omega\tau)^\nu}, \tag{2}$$

and the Havriliak-Negami equation,[4]

$$\chi_{HN}(\omega) = \frac{\chi_0}{[1 + (i\omega\tau)^\sigma]^\nu}, \tag{3}$$

which is a combination of the Cole-Cole and Cole-Davidson equations. Here τ is a characteristic relaxation time known as the Debye relaxation time, χ_0 is the static susceptibility, and $\sigma(0 < \sigma \leq 1)$ and $\nu(0 < \nu \leq 1)$ are parameters with values usually obtained by fitting experimental data. In the context of the linear susceptibility, Eqs. (1)–(3), the Cole-Cole parameter σ is a *broadening* parameter because the curve of $\chi''(\omega)$ versus ω broadens as σ is reduced while the Cole-Davidson parameter ν in Eqs. (2) and (3) is a *skewing* parameter. This is so because the circular arc characteristic of the Debye equation $\chi''(\omega)$ versus ω is shifted toward the low-frequency end of the spectrum in the Cole-Cole plot of $\chi''(\omega)$ versus $\chi'(\omega)$.

The above results have been formulated using *linear* response theory. Nonlinear dielectric relaxation and the dynamic Kerr effect of permanent dipoles are naturally occurring examples of nonlinear ac responses and will be treated here. Unlike its linear counterpart, nonlinear response theory is much less developed because of its inherent mathematical and physical complexity. The calculation of the nonlinear stationary (ac) response even for systems of noninteracting particles described by a single coordinate is a difficult task because no connection between the transient and the ac responses exists, i.e., a *unique* response function valid for all stimuli unlike linear response does not exist. In this context we remark that the orientational electric polarization of noninteracting permanent dipoles in ac fields $\mathbf{E}(t)$ treated by Debye[1] depends in the linear approximation in $\mathbf{E}(t)$ on the

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average over orientations of the first Legendre polynomial $\langle P_1(\cos\vartheta)\rangle(t)$, ϑ being the polar angle of the electric dipole moment vector μ. Subsequently Debye's calculation was generalized[5–11] to nonlinear responses described by the averages of higher order Legendre polynomials $\langle P_n\rangle(t)$. We mention $\langle P_2\rangle(t)$ governing the Kerr effect.[9,11] The Kerr effect in complex systems may deviate considerably from the normal relaxation behavior and may also exhibit a broad distribution of relaxation times. Such anomalous relaxation behavior has been observed, e.g., for amorphous polymers, polymer, and supercooled liquid solutions.[12–14]

For the Debye model, theoretical treatments of various nonlinear response problems have been given recently via matrix continued fractions without using perturbation theory.[9,11] Here the calculation of the nonlinear response functions can be reduced to solving an infinite hierarchy of differential-recurrence equations for the statistical averages $\langle P_n\rangle(t)$. In the present paper, we extend this approach to the anomalous nonlinear relaxation behavior via a fractional generalization of the Debye kinetic equation for normal relaxation. Our analysis will essentially concern nonlinear dielectric and Kerr effect relaxation in superimposed ac and dc external electric fields.

II. FRACTIONAL KINETIC EQUATIONS

The normal Debye relaxation process is characterized by the single exponential after effect relaxation function $f_D(t)$ following the removal of a small constant electric field,[15]

$$f_D(t) = e^{-t/\tau}. \tag{4}$$

In the frequency domain, the corresponding quantity is the dynamic susceptibility $\chi_D(\omega)$ which is according to linear response theory[15]

$$\chi_D(\omega) = -\chi_0 \int_0^\infty e^{-i\omega t}\frac{d}{dt}f_D(t)dt = \frac{\chi_0}{1+i\omega\tau}. \tag{5}$$

Equations (4) and (5) may be derived using a variety of microscopic models of the relaxation process.[15] For example, Debye[1] extended Einstein's treatment[16] of the translational Brownian motion to the rotational Brownian motion of noninteracting permanent dipoles subjected to an external time-varying field. It might also happen that the motion which prevails is different for different kinds of dipoles. Moreover, both large and small jump transitions may exist simultaneously. The above observations lead us to the second microscopic (relaxator) model considered by Debye[1] (and much extended by Fröhlich[15]), which is a Poisson-type process, where relaxation occurs due to the crossing by large jumps of rare members of an assembly of dipoles over a potential barrier due to the shuttling action of thermal agitation. This model also produces a relaxation spectrum of the form of Eq. (4); however, the overbarrier relaxation time has an Arrhenius-type behavior as it depends exponentially on the height of the potential barrier. The advantage of a formulation in terms of the microscopic mechanisms is that the normal (Debye) relaxation behavior may be clearly understood as the diffusion limit of a discrete time random walk on the surface of the unit sphere. Here the random walker executes a jump of a fixed mean square length in a fixed time, so that the only random variable is the *direction* of the walker. As far as the physical mechanism underlying the Cole-Cole equation (1) is concerned, we first remark that Eq. (1) arises[11] from the diffusion limit of a *continuous* time random walk (CTRW). The CTRW was introduced by Montroll and Weiss[17] to render time continuous in a random walk without necessarily appealing to the diffusion limit. In the most general CTRW, the random walker may jump an *arbitrary length* in an *arbitrary time*. A simple case of the CTRW arises by assuming that the jump length and jump time random variables are decoupled and that the jump length variances are always *finite* (so that the central limit theorem applies in the limit of a large sequence of jump lengths[11]); however, the jump times may be arbitrarily long so that they obey a Lévy distribution with its characteristic long tail.[17–19] Such walks possessing a discrete hierarchy of time scales[20] are known as *fractal time random walks*.[21] In the limit of a large sequence of jump times, they yield a fractional Fokker-Planck equation in configuration space.[18,19] If this equation is now adapted to the fractional rotational diffusion, then Eqs. (1)–(3) can be readily obtained.[22,23] Furthermore, the after-effect function corresponding to the Havriliak-Negami equation [Eq. (3)] may be written[24] as a Fox H function[25] extrapolating between the stretched exponential (Kohlrausch-Williams-Watts) law at short times and an inverse long time tail power law at long times. The Debye relaxation time τ now plays the role of a time scale demarcating the transition from a *stretched exponential* law to a *power* law.[18]

The fractional kinetic equations incorporating the Cole-Cole, Cole-Davidson, and Havriliak-Negami relaxation processes can be written[22,23] by extending a hypothesis of Nigmatullin and Ryabov.[26] They noted that the conventional kinetic equation describing the ac stationary response of a system characterized by the single exponential relaxation function to a forcing function $F(t)=Fe^{i\omega t}$, namely,

$$\left(\tau\frac{d}{dt}+1\right)f(t) = F(t) \tag{6}$$

may be generalized to a fractional kinetic equation of fractional order ν so describing a system with Cole-Davidson anomalous relaxation behavior as

$$(\tau_{-\infty}D_t^1 + 1)^\nu f(t) = F(t). \tag{7}$$

From now on operator equations of the type $(\tau_{-\infty}D_t^1+1)^\nu$ are to be understood as series of fractional operators via the binomial expansion

$$(a+b)^\nu = \sum_{n=0}^\infty \frac{(-1)^n(-\nu)_n}{n!}a^{\nu-n}b^n, \tag{8}$$

where $(a)_n = \Gamma(n+a)/\Gamma(a)$ is a Pochhammer symbol,[27] the fractional derivative $_{-\infty}D_t^\alpha$ is given by the Riemann-Liouville definition,[18,19]

$$_{-\infty}D_t^\alpha[f(t)] = \frac{1}{\Gamma(1-\alpha)}\frac{d}{dt}\int_{-\infty}^t \frac{f(t')dt'}{(t-t')^\alpha}, \tag{9}$$

and $\Gamma(z)$ is the gamma function.[27] Assuming adiabatic switching on of the ac field $F(t)=Fe^{i\omega t}$, the solution of Eq.

(7) yields the Cole-Davidson Eq. (2).[26] According to Nigmatullin and Ryabov,[26] the fractional exponent ν reflects the discontinuous character of the anomalous relaxation process and represents the fractal dimension of the set over which the relaxation times are statistically distributed.[26] The Fröhlich relaxator model[15] modified to the fractional diffusion by Nigmatullin and Ryabov[26] may serve as an example of such a process. For the Cole-Cole relaxation, the underlying kinetic equation is given by[20]

$$(\tau_{-\infty}^{\sigma} D_t^{\sigma} + 1)f(t) = F(t). \qquad (10)$$

The physical meaning of the parameter σ is the order of the fractional derivative in the fractional differential equation describing the continuum limit of a random walk with a chaotic set of waiting times.[23] However, a more physically useful definition of σ is as the *fractal dimension* of the set of waiting times which is the scaling of the waiting time segments in the random walk with magnification. The fractional exponent σ measures the statistical self-similarity (or how the whole looks similar to its parts) of the waiting time segments.[20]

In like manner, combining the fractional diffusion equation [Eq. (10)] describing Cole-Cole relaxation and Eq. (7) describing Cole-Davidson relaxation, one may also introduce the fractional kinetic equation[14]

$$(\tau_{-\infty}^{\sigma} D_t^{\sigma} + 1)^{\nu} f(t) = F(t). \qquad (11)$$

Equation (11) represents a fractional generalization of the normal kinetic Eq. (6) to incorporate the Havriliak-Negami relaxation. For the two particular cases $\nu = 1$ and $0 < \sigma < 1$ and $\sigma = 1$ and $0 < \nu < 1$, Eq. (11) reduces to Eqs. (10) and (7), respectively. The fractional derivatives in Eqs. (7), (10), and (11) are memory functions with a slowly decaying power law kernel in time. Such behavior arises from random torques with an anomalous waiting time distribution, that is, from a fractal time random walk with τ as the intertrapping time.

III. FRACTIONAL KINETIC EQUATION FOR NONLINEAR RESPONSE FUNCTIONS

Here we shall generalize the Debye noninertial rotational diffusion model[1] to the anomalous nonlinear dielectric relaxation and dynamic Kerr effect responses of an assembly of rigid dipolar particles acted on by external superimposed dc $\mathbf{E}_0$ and ac $\mathbf{E}_1(t) = \mathbf{E}_1 \cos \omega t$ electric fields of arbitrary strengths. Each particle contains a rigid electric dipole μ. We also suppose for simplicity that both $\mathbf{E}_0$ and $\mathbf{E}_1$ are directed along the Z axis of the laboratory coordinate system and that effects due to the anisotropy of the polarizability of the particles can be neglected. Thus the orientational potential energy of the particle is

$$V(\vartheta, t) = -\mu[E_0 + E_1(t)]\cos \vartheta. \qquad (12)$$

The problem we wish to solve is intrinsically nonlinear because we assume that the magnitudes of both ac and dc fields are so large that the energy of a particle in these fields may be comparable to or larger than kT (k is the Boltzmann constant and T is the temperature). The physical quantities which are interesting from an experimental point of view are

the electric polarization $P(t)$ and the electric birefringence function $K(t)$ defined by[7,9]

$$P(t) = B_1 \langle P_1(\cos \vartheta) \rangle (t), \qquad (13)$$

$$K(t) = B_2 \langle P_2(\cos \vartheta) \rangle (t). \qquad (14)$$

The coefficients B_1 and B_2 depend on the number of particles per unit volume, the dipole moment, particle depolarization factors, etc. Here we shall assume that these coefficients are independent of the frequency of the electric field (in dielectric relaxation) and of the light frequency (in Kerr effect relaxation). Thus the effects of long-range torques due to the interaction between the average moments and the Maxwell fields are ignored. These effects are largely irrelevant for dilute systems in first approximation. Hence, the theory developed here pertains to situations where dipole-dipole interactions have been eliminated via suitable extrapolation of data to infinite dilution.

For the normal rotational diffusion model, the recurrence equation for the response functions $f_n(t) = \langle P_n(\cos \vartheta) \rangle (t)$ (expectation values of the Legendre polynomial of order n) is (see, e.g., Refs. 7, 9, and 11)

$$\left(\tau_n \frac{d}{dt} + 1 \right) f_n(t) = \frac{\xi_0 + \xi \cos \omega t}{2n+1} [f_{n-1}(t) - f_{n+1}(t)], \qquad (15)$$

where $\tau_n = 2\tau/n(n+1)$ is a characteristic relaxation time of $f_n(t)$ and $\xi_0 = \mu E_0/(kT)$ and $\xi = \mu E_1/(kT)$ are the dimensionless field parameters. In strong fields, all the $f_n(t)$ contribute to the dielectric relaxation and dynamic Kerr effect response functions $f_1(t)$ and $f_2(t)$. Noting Eq. (11), the fractional analogue of Eq. (15) is

$$(\tau_{n-\infty}^{\sigma} D_t^{\sigma} + 1)^{\nu} f_n(t) = \frac{\xi_0 + \xi \cos \omega t}{2n+1} [f_{n-1}(t) - f_{n+1}(t)]. \qquad (16)$$

The Cole-Cole and Cole-Davidson relaxation processes may be treated as particular cases of Eq. (16). It will become apparent that under linear response conditions, $\xi \ll 1$, and $\xi_0 = 0$, Eq. (16) yields the linear susceptibility from Eq. (3); moreover, that equation also allows one to evaluate the nonlinear ac stationary responses.

Equation (16) is *similar* but not *identical* to the fractional kinetic equation proposed by Déjardin and Jadzyn[28] (in Ref. 28 the authors calculated the nonlinear dielectric response for the Cole-Davidson relaxation $\sigma = 1, 0 < \nu < 1$). Their equation reads in our notation

$$(\tau_{n-\infty}^{\sigma} D_t^{\sigma} + 1)^{\nu} f_n(t) = [n(n+1)/2]^{1-\sigma\nu}$$

$$\times \frac{\xi_0 + \xi \cos \omega t}{(2n+1)} [f_{n-1}(t) - f_{n+1}(t)]. \qquad (17)$$

Equation (17) differs from Eq. (16) by the factor $[n(n+1)/2]^{1-\sigma\nu}$. However, this difference is of paramount importance, because response functions $f_n(t)$ calculated from these two equations will differ by this factor (which may be substantial). Furthermore, in the absence of the ac field, Eq. (17) reduces to the following recurrence equation for the equilibrium averages $\langle P_n \rangle_0$:

$$\langle P_n \rangle_0 = [n(n+1)/2]^{1-\sigma \nu} \frac{\xi_0}{(2n+1)} [\langle P_{n-1} \rangle_0 - \langle P_{n+1} \rangle_0]. \quad (18)$$

However, the values of $\langle P_n \rangle_0$ predicted by Eq. (18) are not equal to the correct equilibrium values $\langle P_n \rangle_0$. They can be calculated independently as $\langle P_n \rangle_0 = \int_{-1}^{1} P_n(z) e^{\xi_0 z} dz / \int_{-1}^{1} e^{\xi_0 z} dz$. These averages satisfy the recurrence relation[7,9,11]

$$\langle P_n \rangle_0 = \frac{\xi_0}{2n+1} [\langle P_{n-1} \rangle_0 - \langle P_{n+1} \rangle_0] \quad (19)$$

and not Eq. (18). Consequently Eq. (17) yields unphysical results for nonlinear response functions, in particular, for their static values (e.g., the Kerr constant and nonlinear static susceptibility at $\omega = 0$), which are all expressed in terms of $\langle P_n \rangle_0$. These static values as calculated from Eq. (18) depend on the (non equilibrium) fractional parameters ν and σ that contradicts general principles of statistical mechanics. Furthermore, as a result, the behavior of the spectra of nonlinear response functions as evaluated from Eq. (17) is also incorrect. In contrast, the fractional kinetic equation [Eq. (16)] predicts correct values of the equilibrium averages $\langle P_n \rangle_0$ and thus allows us to calculate correctly the nonlinear response functions.

IV. SOLUTION OF EQ. (16)

As we are solely concerned with the ac response corresponding to the stationary state, we may seek the $f_n(t)$ as a Fourier series just as normal diffusion (Ref. 11, Chapter 8),

$$f_n(t) = \sum_{k=-\infty}^{\infty} F_k^n e^{ik\omega t}. \quad (20)$$

Since all the $f_n(t)$ are real, the Fourier amplitudes F_k^n must satisfy the condition $F_{-k}^n = (F_k^n)^*$, where the asterisk denotes the complex conjugate. The term F_0^n in the right-hand side of Eq. (20) is a *time independent*, but *frequency dependent* term. In the absence of the dc bias field, i.e., for $\xi_0 = 0$, the series (20) contains only the odd components of F_k^1 and the even components of F_k^2. By substituting Eq. (20) into Eq. (16), we have the recurrence relations for the Fourier amplitudes F_k^n:

$$(4n+2)\{1 + 2(ki\omega\tau)^\sigma / [n(n+1)]\}^\nu F_k^n$$
$$= 2\xi_0 (F_k^{n-1} - F_k^{n+1}) + \xi (F_{k-1}^{n-1} + F_{k+1}^{n-1} - F_{k-1}^{n+1} - F_{k+1}^{n+1}). \quad (21)$$

Here we have used Eq. (8) and the known relation from fractional calculus $_{-\infty} D_t^\alpha [e^{izt}] = (iz)^\alpha e^{izt}$.[26]

Equation (21) can be solved using matrix continued fractions as described in the Appendix. This matrix continued fraction solution is valid for arbitrary values of ξ and ξ_0. For small fields ($\xi, \xi_0 \leq 0.1$), the solution can be obtained via perturbation theory.[9,11] Moreover, one may readily carry out such calculations using the MATHEMATICA program which allows one to extract the analytical perturbation solutions from the matrix Eqs. (A2) and (A3). For example, the Fourier amplitudes F_1^1, F_3^1, F_0^2, and F_2^2 (these quantities are usually observed experimentally) are given by
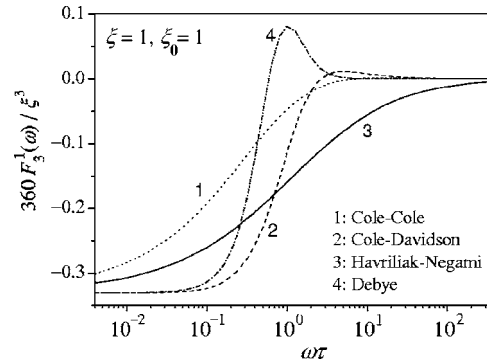

FIG. 1. The normalized third harmonic components of the electric polarization $360 F_3^1 / \xi^3$ vs $\omega\tau$ for the Cole-Cole (dotted line 1: $\sigma = 0.5$, $\nu = 1$), Cole-Davidson (dashed line 2: $\sigma = 1$, $\nu = 0.5$), and Havriliak-Negami (solid line 3: $\sigma = \nu = 0.5$) relaxations compared with normal (Debye) relaxation (dashed-dotted line 4: $\sigma = \nu = 1$). Results are presented for $\xi = \xi_0 = 1$ (nonlinear regime).

$$F_1^1 = \frac{\xi}{6} \left\{ \frac{1}{[1+(i\omega\tau)^\sigma]^\nu} - \frac{\xi_0^2}{15[1+(i\omega\tau)^\sigma]^\nu} \right.$$
$$\times \left[1 + \frac{1}{[1+(i\omega\tau)^\sigma/3]^\nu} \left(1 + \frac{1}{[1+(i\omega\tau)^\sigma]^\nu} \right) \right] \right\}$$
$$- \frac{\xi^3}{360[1+(i\omega\tau)^\sigma]^{2\nu}} \left\{ 1 + \frac{[1+(i\omega\tau)^\sigma]^\nu}{[1+(-i\omega\tau)^\sigma]^\nu} \right.$$
$$\left. + \frac{1}{[1+(2i\omega\tau)^\sigma/3]^\nu} \right\} + o(\xi^3, \xi\xi_0^2), \quad (22)$$

$$F_3^1 = - \frac{\xi^3}{360[1+(3i\omega\tau)^\sigma]^\nu [1+(2i\omega\tau)^\sigma/3]^\nu [1+(i\omega\tau)^\sigma]^\nu}$$
$$+ o(\xi^3), \quad (23)$$

$$F_0^2 = \frac{\xi_0^2}{15} + \frac{\xi^2}{30} \mathrm{Re} \left\{ \frac{1}{[1+(i\omega\tau)^\sigma]^\nu} \right\} + o(\xi^2, \xi_0^2), \quad (24)$$

$$F_2^2 = \frac{\xi^2}{60} \frac{1}{[1+(i\omega\tau)^\sigma]^\nu [1+(2i\omega\tau)^\sigma/3]^\nu} + o(\xi^2, \xi_0^2). \quad (25)$$

By evaluating the limit $\chi(\omega)/\chi_0 = \lim_{\xi, \xi_0 \to 0} 6 F_1^1 / \xi$, one can readily derive Eq. (3) for the linear susceptibility from Eq. (22). For normal diffusion ($\sigma = 1$, $\nu = 1$), Eqs. (22)–(25) are in full agreement with the known perturbation solutions for the ac stationary responses.[9,11] For the Cole-Cole relaxation ($\nu = 1, 0 < \sigma < 1$), Eqs. (22)–(25) reduce to the solutions given by Déjardin and Jadzyn.[29] However, for the Cole-Davidson relaxation ($0 < \nu < 1, \sigma = 1$), our perturbation solutions for F_1^1 and F_3^1 from Eqs. (22) and (23) differ from theirs given in Ref. 28 for the reason described above [cf. Eqs. (16) and (17)].

V. RESULTS AND DISCUSSION

The real parts of the normalized third harmonic component ($360 F_3^1 / \xi^3$) of the electric polarization and the dc ($30 F_0^2 / \xi^2$) and second ($60 F_2^2 / \xi^2$) harmonic components of the Kerr effect versus. $\omega\tau$ are presented in Figs. 1–3 for the
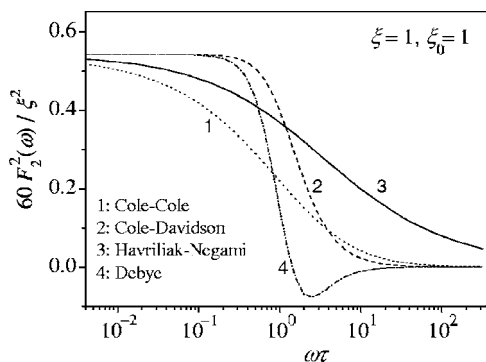
FIG. 2. The same as in Fig. 1 for the second harmonic components of the dynamic Kerr effect $60F_2^2/\xi^2$.

normal (Debye), Cole-Cole, Cole-Davidson, and Havriliak-Negami relaxations. The normalization was chosen to satisfy the condition

$$360F_3^1/\xi^3 = -1, \quad 30F_0^2/\xi^2 = 1, \quad \text{and} \quad 60F_2^2/\xi^2 = 1$$
$$\text{at} \quad \xi \to 0 \quad \text{and} \quad \xi_0 = 0.$$

In these figures, it is clearly seen how the nonlinear response relaxation spectra for normal diffusion are transformed for different anomalous relaxation models. As ξ increases the dispersion curves are shifted to higher frequencies and the amplitude decreases due to saturation. In anomalous relaxation, broader spectra in comparison to that of normal relaxation are predicted. The shape of the spectra calculated for various anomalous relaxation processes differs considerably so that the Cole-Cole, Cole-Davidson, and Havriliak-Negami relaxations can be distinguished from each other by a comparison with experimental data.

The theory we have developed may be used to interpret experimental data on nonlinear ac stationary responses in dielectric and Kerr effect relaxation. Although in actual experiments the applied electric fields are high enough ($\geqslant 10^6$ V/m) to observe nonlinear effects, for particles (molecules) with dipole moment ~ 1–5 D, the energy rendered by Eq. (12) is still sufficiently small compared to the thermal energy, to allow one to use the nonlinear response equations
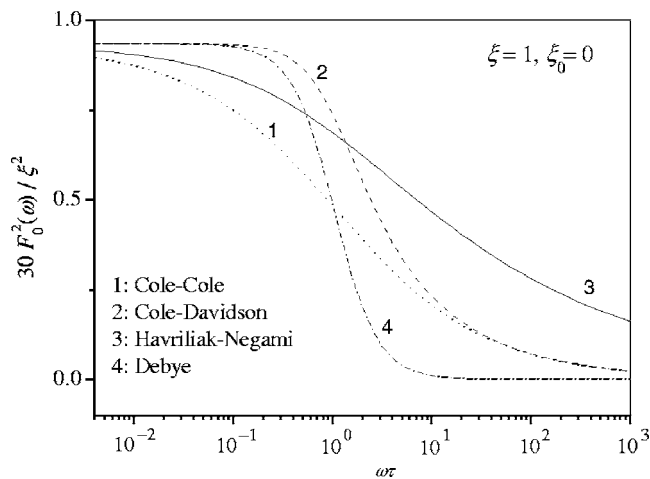
obtained via perturbation theory (see, e.g., Ref. 30). Thus Eqs. (22)–(25) may be very useful for practical comparison with experimental data. However, as the theory developed is applicable to ac fields of arbitrary strength, it also provides a rigorous method of comparison with experiments on nonlinear response in high ac fields, where perturbation solutions are no longer applicable. Furthermore, it will be possible to carry out a quantitative comparison of the theory with available molecular dynamics simulation data for relaxation processes in strong ac fields. Such data is preferable for testing the theory, as in computer simulations it is much easier (than in real experiments) to achieve values of the nonlinear parameters ξ and ξ_0 in excess of unity. We remark that experiments on the polarization induced by a weak ac field superimposed on a strong dc field may be realized in practice in a ferrofluid as large values of ξ and ξ_0 can be achieved with moderate constant magnetic fields due to the large value of the magnetic dipole moment m (10^4–10^5 bohr magnetons) of single domain ferromagnetic particles.[11]

Thus we have demonstrated how the anomalous nonlinear dielectric relaxation and dynamic Kerr effect can be treated by using fractional kinetic equations. The results obtained can explain the anomalous nonlinear relaxation of complex dipolar systems, where the anomalous exponents σ and ν differ from unity (corresponding to the classical theory of dielectric relaxation and the dynamic Kerr effect), i.e., the relaxation process is characterized by a broad distribution of relaxation times (see, e.g., Refs. 12–14). The advantage of having a kinetic equation incorporating the anomalous relaxation then becomes apparent as it is now possible to study the effect of the nonlinear anomalous behavior on fundamental parameters associated with the fractional diffusion. We finally remark that the method of the calculation of nonlinear ac responses based on matrix continued fractions presented is quite general. For example, the method can also be applied to the calculation of the dynamic Kerr effect ac response of *polar* and *anisotropically polarizable* molecules as well as to nonlinear dielectric and Kerr effect relaxation of molecules under the influence of a mean-field potential.[31,32]

APPENDIX: MATRIX CONTINUED FRACTION SOLUTION OF EQ. (21)

Equation (21) can be solved exactly using matrix continued fractions as described in Sec. 8.6 of Ref. 11. The *seven-term* recurrence Eq. (21) can be transformed into the *matrix three-term* recurrence equations,

$$\mathbf{Q}_n\mathbf{C}_n + \mathbf{q}(\mathbf{C}_{n+1} - \mathbf{C}_{n-1}) = \mathbf{R}\delta_{n,1} \quad (n \geqslant 1). \tag{A1}$$

Here the column vectors $\mathbf{C}_n$ and $\mathbf{R}$ are defined as

FIG. 3. The same as in Fig. 1 for the dc component of the dynamic Kerr effect $30F_0^2/\xi^2$. Here $\xi = 1$ and $\xi_0 = 0$.

$$\mathbf{C}_n = \begin{pmatrix} \vdots \\ F^n_{-2} \\ F^n_{-1} \\ F^n_0 \\ F^n_1 \\ F^n_2 \\ \vdots \end{pmatrix} \text{ and } \mathbf{R} = \begin{pmatrix} \vdots \\ 0 \\ \xi \\ 2\xi_0 \\ \xi \\ 0 \\ \vdots \end{pmatrix},$$

the matrices $\mathbf{q}$ and $\mathbf{Q}_n$ are tridiagonal and diagonal infinite matrices, respectively, with elements defined as

$$(\mathbf{q})_{l,m} = \xi\delta_{m,l-1} + 2\xi_0\delta_{m,l} + \xi\delta_{m,l+1},$$

$$(\mathbf{Q}_n)_{l,m} = (4n+2)\{1 + 2(li\omega\tau)^\sigma/[n(n+1)]\}^\nu \delta_{l,m},$$

where $-\infty < l,m < \infty$ and $\delta_{m,l}$ is Kronecker's delta. A solution of Eq. (A1) for $\mathbf{C}_1$ and $\mathbf{C}_2$ is

$$\mathbf{C}_1 = \mathbf{SR}, \tag{A2}$$

$$\mathbf{C}_2 = \mathbf{q}^{-1}[\mathbf{I} - \mathbf{Q}_1\mathbf{S}]\mathbf{R}, \tag{A3}$$

where the infinite matrix continued fraction $\mathbf{S}$ is

$$\mathbf{S} = \cfrac{\mathbf{I}}{\mathbf{Q}_1 + \mathbf{q}\cfrac{\mathbf{I}}{\mathbf{Q}_2 + \mathbf{q}\cfrac{\mathbf{I}}{\mathbf{Q}_3 + \dots}\mathbf{q}}\mathbf{q}}.$$

Here $\mathbf{I}$ is the unit matrix and the fraction lines mean matrix inversion.

Having determined the column vectors $\mathbf{C}_1$ and $\mathbf{C}_2$ from Eqs. (A2) and (A3), which contain all the Fourier amplitudes of $f_1(t)$ and $f_2(t)$, one can calculate the stationary ac dielectric and Kerr effect responses from Eqs. (13) and (14). The exact matrix continued fraction solution [Eqs. (A2) and (A3)] is easy to compute. We approximate the infinite matrix continued fraction $\mathbf{S}$ by some matrix continued fraction of finite order (by putting $\mathbf{Q}_n = \mathbf{0}$ at some $n=N$). Simultaneously, we confine the dimensions of the matrices $\mathbf{Q}_n$ and $\mathbf{q}$ to some finite number M. The values of N and M must be chosen taking account of the desired degree of accuracy of the calculation.

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