Transient nonlinear dielectric relaxation and dynamic Kerr effect from sudden changes of a strong dc electric field: Polar and polarizable molecules

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The nonlinear transient response of polar and polarizable particles (macromolecules) diluted in a nonpolar solvent to a sudden change both in magnitude and in direction of a strong external dc field is considered. By averaging the underlying Langevin equation, the infinite hierarchy of differential-recurrence equations for ensemble averages of the spherical harmonics is derived for an assembly of polar and anisotropically polarizable molecules pertaining to the noninertial rotational Brownian motion. On solving this hierarchy, the relaxation functions and relaxation times appropriate to the transient dynamic Kerr effect and nonlinear dielectric relaxation are calculated. The calculations are accomplished using the matrix continued fraction method, which allows us to express exactly the solution of the infinite hierarchy of differential-recurrence relations for the first- and second-order transient responses of the ensemble averages of the spherical harmonics (relaxation functions). The results are then compared with available experimental data and solutions previously obtained for various particular cases. [S1063-651X(99)09808-6]

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I. INTRODUCTION

Nonlinear dielectric and Kerr effect relaxation of polar fluids springs from the rotational motion of molecules in the presence of external electric fields and thermal agitation (see, e.g., [1–4]). Interpretation of these phenomena is usually based on the rotational diffusion model in the noninertial limit that relies on the solution of the appropriate Langevin or Fokker-Planck equation and has usually been confined to the linear response or the nonlinear response in low order of perturbation theory (see, for example, Refs. [1, 5–8]), where the energy of a molecule in the electric field is far less than the thermal energy. However, a few exact analytical solutions of particular nonlinear response problems exist (e.g., [2,9–13]). Also, Morita [14] and Morita and Watanabe [15] proposed a general formal theory of nonlinear response arising from the transient and stationary processes (in particular, the theory is valid for systems of polar molecules, the dynamics of which in the noninertial limit is governed by the Smoluchowski equation). In order to accomplish this they expanded the Green's function for the unperturbed state in terms of appropriate orthogonal functions. They showed that this Green's function is sufficient to calculate the nonlinear behavior of the distribution function perturbed by a strong external field. They found also that in the stationary state the nonlinear response function can be expressed in terms of integrals of products of infinite matrices whose elements are composed of correlation functions in the absence of the perturbation. However, this formalism is very difficult to apply to the calculation of transient responses in nonlinear dielectric and Kerr effect relaxation in high dc fields due to mathematical difficulties encountered. Indeed, the only expression for the birefringence function obtained in Ref. [15] was derived for a weak ac superimposed on a weak dc bias field.

The goal of the present paper is to present a theory for the transient dynamic birefringence and nonlinear dielectric relaxation response of polar and anisotropically polarizable particles (macromolecules) dissolved in nonpolar solvents when both magnitude and direction of the dc field may suddenly be changed. This problem is truly nonlinear; therefore, there is no longer any connection between the step-on and step-off responses and the stationary ac response as in linear-response theory. The theory is based on an analytical method recently developed for the calculation of the linear and nonlinear responses of systems of Brownian particles compelled to rotate in three-dimensional space [12,16,17]. This method consists in the transformation of the angular variables in the underlying Langevin equation for the three-dimensional rotational Brownian motion and in the subsequent direct averaging of the stochastic differential equation so obtained. This allows us to derive the infinite hierarchy of the differential-recurrence equations for the moments (averaged spherical harmonics) without recourse to the corresponding Fokker-Planck equation [18]. (This has been accomplished by Coffey [19] who derived such a hierarchy by direct averaging of the one-dimensional Langevin equation for a planar rotator in a constant field). Then, the modified Risken's matrix continued fraction approach [18] is applied to the solution of this hierarchy [17]. As we shall show in the present paper, the above method can also be used in the calculation of the transient nonlinear dielectric relaxation and dynamic Kerr effect response of polar and anisotropically polarizable symmetric-top molecules. We shall demonstrate that the theory developed contains as particular cases all the results previously obtained for various particular transient relaxation problems

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caused by sudden changes of external fields and is in agreement with available experimental data.

II. ROTATIONAL DIFFUSION IN A STRONG ELECTRIC FIELD: THE LANGEVIN EQUATION APPROACH

We study the three-dimensional rotational Brownian motion of a symmetric top polar and polarizable particle in a strong external electric field $\mathbf{E}$. Let us take a unit vector $\mathbf{u}(t)$ through the center of mass of the particle in the direction of the axis of symmetry. Then the rate of change of $\mathbf{u}(t)$ is

$$\frac{d\mathbf{u}(t)}{dt}=\boldsymbol{\omega}(t)\times\mathbf{u}(t), \tag{1}$$

where $\boldsymbol{\omega}(t)$ is the angular velocity of the particle. We remark that Eq. (1) is a purely kinematic relation with no particular reference either to the Brownian movement or to the shape of the particle. Further, in the presence of an electric field $\mathbf{E}(t)$ we suppose that the angular velocity $\omega(t)$ obeys the Euler-Langevin equation [17],

$$\hat{I}\frac{d\boldsymbol{\omega}(t)}{dt}+\zeta\boldsymbol{\omega}(t)=\mathbf{m}(t)\times\mathbf{E}(t)+\boldsymbol{\lambda}(t), \tag{2}$$

where $\hat{I}$ is the inertia tensor of the particle, $\zeta\boldsymbol{\omega}(t)$ is the damping torque due to Brownian movement (for simplicity we assume that the friction coefficient ζ is a scalar), and $\boldsymbol{\lambda}(t)$ is the white-noise driving torque, again due to Brownian movement so that $\boldsymbol{\lambda}(t)$ has the following properties:

$$\overline{\lambda_i(t)}=0,$$

$$\overline{\lambda_i(t_1)\lambda_j(t_2)}=2kT\zeta\delta_{ij}\delta(t_1-t_2). \tag{3}$$

Here the overbar means a statistical average over an ensemble of Brownian particles which *all* start at time t with the *same* angular velocity $\boldsymbol{\omega}$ and orientation $\mathbf{u}$ [17,18]; δ_{ij} is Kronecker's delta, indexes $i,j=1,2,3$ correspond to the Cartesian axes X,Y,Z of the coordinate system $OXYZ$, and $\delta(t)$ is the Dirac delta function; $\mathbf{m}$ is the total dipole moment of the particle in the field $\mathbf{E}(t)$. The term $\mathbf{m}(t)\times\mathbf{E}(t)$ in Eq. (2) is the torque due to the electric field acting on the particle. This torque can be expressed in terms of the potential energy $V(\mathbf{u},t)$ of the particle in the field $\mathbf{E}$ as a function of the components of the vector $\mathbf{u}$, viz.,

$$\mathbf{m}\times\mathbf{E}=-\mathbf{u}\times\frac{\partial}{\partial\mathbf{u}}V.$$

Equation (2) includes the inertia of the particle. The noninertial limit (or the Debye approximation) occurs when the inertial term in Eq. (2) is neglected. In this limit one obtains from Eqs. (1) and (2) [16,17]

$$\zeta\frac{d\mathbf{u}(t)}{dt}=-\frac{\partial}{\partial\mathbf{u}}V+\mathbf{u}(t)\left(\mathbf{u}(t)\cdot\frac{\partial}{\partial\mathbf{u}}V\right)+\boldsymbol{\lambda}(t)\times\mathbf{u}(t). \tag{4}$$

This is the vector Langevin equation for the motion of the vector $\mathbf{u}$ in the noninertial limit.

In Refs. [12, 16, 17] a method has been suggested of the derivation of the infinite hierarchy of the differential-recurrence equations for the averaged spherical harmonics (moments) by means of the direct averaging of the Langevin equation (4) for particular potentials V. Here we extend this method and derive the infinite hierarchy for an arbitrary potential.

This is conveniently accomplished by using the spherical coordinate system. In its basis $\{\mathbf{e}_r,\mathbf{e}_\vartheta,\mathbf{e}_\varphi\}$:

$$\mathbf{u}=\{1,0,0\},\quad \dot{\mathbf{u}}=\{0,\dot{\vartheta},\sin\vartheta\dot{\varphi}\},\quad \frac{\partial V}{\partial\mathbf{u}}=\left(0,\frac{\partial V}{\partial\vartheta},\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\right),$$

where ϑ and φ are the polar and azimuthal angles, respectively. Thus, Eq. (4) is equivalent to two stochastic equations for ϑ and φ:

$$\dot{\vartheta}(t)=-\zeta^{-1}\frac{\partial}{\partial\vartheta}V(\vartheta(t),\varphi(t),t)+g_{\vartheta i}(\vartheta(t),\varphi(t))\lambda_i(t), \tag{5}$$

$$\dot{\varphi}(t)=-\zeta^{-1}\frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}V(\vartheta(t),\varphi(t),t)+g_{\varphi i}(\vartheta(t),\varphi(t))\lambda_i(t), \tag{6}$$

where

$$g_{\vartheta X}=-\zeta^{-1}\sin\varphi,\quad g_{\vartheta Y}=\zeta^{-1}\cos\varphi,\quad g_{\vartheta Z}=0,$$

$$g_{\varphi X}=-\zeta^{-1}\cot\vartheta\cos\varphi,\quad g_{\varphi Y}=-\zeta^{-1}\cot\vartheta\sin\varphi,$$

$$g_{\varphi Z}=\zeta^{-1}, \tag{7}$$

and the summation over $i=X,Y,Z$ is understood (Einstein's notation).

Here we shall use the Stratonovich definition [17,20] of the stochastic differential equations (5) and (6) with the multiplicative noise terms $g_{ki}\lambda_j(t)$, as that definition always constitutes the mathematical idealization of the physical stochastic process of orientational relaxation in the noninertial limit. Therefore, it is unnecessary to transform the Langevin equations (5) and (6) to Itô equations (e.g., [21]). Moreover, one can apply the methods of ordinary analysis [18,21]. Thus, one can obtain the stochastic differential equation for any function $f(\vartheta,\varphi)$ of the angles ϑ and φ:

$$\frac{d}{dt}f(\vartheta(t),\varphi(t))=\dot{\vartheta}(t)\frac{\partial}{\partial\vartheta}f(\vartheta(t),\varphi(t))+\dot{\varphi}(t)\frac{\partial}{\partial\varphi}f(\vartheta(t),\varphi(t)). \tag{8}$$

As has been described in detail in Refs. [16, 17], on averaging Eq. (8) over an ensemble of Brownian particles, which all start at time t with the same orientation $\mathbf{u}$, we obtain

$$2\tau_D\dot{f}(\vartheta,\varphi)=\Delta f(\vartheta,\varphi)+\frac{1}{2kT}[V(\vartheta,\varphi,t)\Delta f(\vartheta,\varphi)+f(\vartheta,\varphi)\Delta V(\vartheta,\varphi,t)-\Delta(V(\vartheta,\varphi,t)f(\vartheta,\varphi))], \tag{9}$$

where

$$\Delta = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

is the Laplace operator and ϑ and φ are the sharp values of the stochastic variables $\vartheta(t)$ and $\varphi(t)$ at the moment of averaging t. Here we have used that

$$\overline{g_{\vartheta i}\lambda_i(t)\frac{\partial}{\partial\vartheta}f(\vartheta(t),\varphi(t))+g_{\varphi i}\lambda_i(t)\frac{\partial}{\partial\varphi}f(\vartheta(t),\varphi(t))} = \frac{1}{2\tau_D}\Delta f(\vartheta,\varphi)$$

and

$$\overline{-\zeta^{-1}\left(\frac{\partial}{\partial\vartheta}V\frac{\partial}{\partial\vartheta}f(\theta(t),\varphi(t))+\frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}V\frac{\partial}{\partial\varphi}f(\vartheta(t),\varphi(t))\right)}$$
$$=\frac{1}{4\tau_D kT}[V(\vartheta,\varphi,t)\Delta f(\vartheta,\varphi)+f(\vartheta,\varphi)\Delta V(\vartheta,\varphi,t)-\Delta(V(\vartheta,\varphi,t)f(\vartheta,\varphi))].$$

Let us now specify the problem of the calculation of the nonlinear transient relaxation. Let us suppose that both magnitude and direction of the dc field are suddenly changed at time $t=0$ from $\mathbf{E}_{\mathrm{I}}$ to $\mathbf{E}_{\mathrm{II}}$. We are interested in the relaxation of the system of particles (macromolecules) diluted in a nonpolar solvent starting from an equilibrium state I with the distribution function W_{I} $(t\leqslant 0)$ to another equilibrium state II with the distribution function W_{II} $(t\to\infty)$. The distribution functions in the equilibrium states I and II are the Boltzmann ones, viz.,

$$W_N = e^{-V_N/kT}/Z_N \quad (N=\mathrm{I,II}), \tag{10}$$

where Z_N $(N=\mathrm{I,II})$ are the partition functions. On neglecting effects due to the hyperpolarizability of the molecule, the potential energy V_N is given by [3]

$$V_N = -\mu E_N\cos\Xi_N-\tfrac{1}{2}(\alpha_1-\alpha_2)E_N^2\cos^2\Xi_N \quad (N=\mathrm{I,II}). \tag{11}$$

Here μ is the dipole moment of the molecule, α_1 and α_2 are the components of the electric polarizability parallel and perpendicular to the axis of symmetry of the molecule, and Ξ_N is the angle between the vectors $\mathbf{u}$ and $\mathbf{E}_N$. This problem is intrinsically nonlinear because it is assumed that changes both in the magnitude and in the direction of the dc field are significant.

Our goal is to evaluate the transient relaxation of the electric polarization $P(t)$ and the birefringence function $K(t)$ in the direction of the field $\mathbf{E}_{\mathrm{II}}$, viz.,

$$P(t)=\mu N_0\langle P_1(\cos\Xi_{\mathrm{II}})\rangle(t) \tag{12}$$

and

$$K(t)=K_s\langle P_2(\cos\Xi_{\mathrm{II}})\rangle(t), \tag{13}$$

where N_0 is the concentration of molecules, $K_s=2\pi N_0(\alpha_1^0-\alpha_2^0)/\bar{n}$, α_1^0 and α_2^0 are the components of the optical polarizability due to the electric field of the light beam, $\bar{n}$ is the mean refractive index, $P_n(z)$ is the Legendre polynomial of order n, and the angular brackets $\langle\,\rangle$ mean the usual statistical averaging.

Both $P(t)$ and $K(t)$ may be expressed in terms of averages involving the spherical harmonics $Y_{l,m}(\vartheta,\varphi)$ [see Eqs. (34) and (35) below], which are defined as [22]

$$Y_{l,m}=(-1)^m\sqrt{[(2l+1)(l-m)!/4\pi(l+m)!]}\times e^{im\varphi}P_l^m(\cos\vartheta), \tag{14}$$

$$Y_{l,-m}=(-1)^m Y_{l,m}^*, \tag{15}$$

where $P_l^m(\cos\vartheta)$ is the associated Legendre function, the asterisk denotes the complex conjugate.

Thus Eq. (9) yields

$$2\tau_D\dot{Y}_{l,m}=\frac{1}{2kT}[V\Delta Y_{l,m}+Y_{l,m}\Delta V-\Delta(VY_{l,m})]+\Delta Y_{l,m}. \tag{16}$$

On using the known relationships [23]

$$\Delta Y_{l,m}=-l(l+1)Y_{l,m}, \tag{17}$$

$$Y_{n,m}Y_{N,M}=\sum_{\substack{j=|n-N|\\ \Delta j=2}}^{n+N}\sum_{k=-j}^{j}\sqrt{[(2n+1)(2N+1)/4\pi(2j+1)]}\times\langle n,0,N,0|j,0\rangle\langle n,m,N,M|j,k\rangle Y_{j,k} \tag{18}$$

($\langle l_1,m_1,l_2,m_2|l,m\rangle$ are the Clebsch-Gordan coefficients [22,23]), one can show that for any potential V, which can be expanded in a series as

$$\frac{V}{kT}=\sum_{R,S}\nu_{R,S}Y_{R,S}, \tag{19}$$

Eq. (16) can be presented as

$$\tau_D\frac{d}{dt}Y_{l,m}=\sum_{r,s}d_{l,m,l+r,m+s}Y_{l+r,m+s}, \tag{20}$$

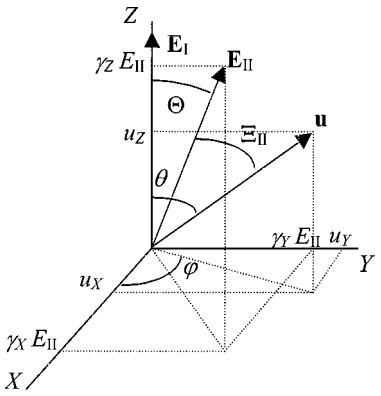

FIG. 1. The geometry of the problem.

where

$$d_{l,m,l+r,m+s}=-\frac{l(l+1)}{2}\delta_{r,0}\delta_{s,0}+(-1)^m \times\frac{\sqrt{(2l+1)(2l+2r+1)}}{8} \times\sum_{R=s}^{\infty}\nu_{R,s}\frac{r(2l+r+1)-R(R+1)}{\sqrt{\pi(2R+1)}} \times\langle l,0,l+r,0|R,0\rangle\langle l,m,l+r,-m-s|R,-s\rangle. \tag{21}$$

In order to obtain the equations for the moments, which govern the relaxation dynamics of the system, one also has to average Eq. (20) over the probability density function $W(\vartheta,\varphi,t)$ [17]. Thus, one obtains the infinite hierarchy of differential-recurrence relations,

$$\tau_D\frac{d}{dt}\langle Y_{l,m}\rangle(t)=\sum_{r,s}d_{l,m,l+r,m+s}\langle Y_{l+r,m+s}\rangle(t), \tag{22}$$

where the symbol $\langle\ \rangle$ denotes the averaging over W.

For the potential given by Eq. (11), we have

$$\frac{V_N}{kT}=\sum_{R=1}^{2}\sum_{S=-R}^{R}\nu_{R,S}^{N}Y_{R,S}-\frac{\sigma_N}{3}, \tag{23}$$

where

$$\nu_{1,0}^{N}=-\sqrt{(4\pi/3)}\,\xi_N\gamma_Z^N, \tag{24}$$

$$\nu_{1,1}^{N}=-(\nu_{1,-1}^{N})^*=\sqrt{(2\pi/3)}\,\xi_N(\gamma_X^N-i\gamma_Y^N), \tag{25}$$

$$\nu_{2,0}^{N}=-\sqrt{(4\pi/45)}\,\sigma_N[3(\gamma_Z^N)^2-1], \tag{26}$$

$$\nu_{2,1}^{N}=-(\nu_{2,-1}^{N})^*=\sqrt{(8\pi/15)}\,\sigma_N\gamma_Z^N(\gamma_X^N-i\gamma_Y^N), \tag{27}$$

$$\nu_{2,2}^{N}=(\nu_{2,-2}^{N})^*=-\sqrt{(2\pi/15)}\,\sigma_N(\gamma_X^N-i\gamma_Y^N)^2. \tag{28}$$

Here $\gamma_X^N=\sin\Theta_N\cos\Phi_N$, $\gamma_Y^N=\sin\Theta_N\sin\Phi_N$, and $\gamma_Z^N=\cos\Theta_N$ are the direction cosines of $\mathbf{E}_N$ in the coordinate system $OXYZ$ (see Fig. 1) and

$$\xi_N=\frac{\mu E_N}{kT},\quad \sigma_N=\frac{(\sigma_1-\alpha_2)E_N^2}{2kT}. \tag{29}$$

Without loss of generality it will be supposed that the field $\mathbf{E}_{\mathrm{I}}$ is directed along the Z axis. Thus, below we will use that $\Theta_{\mathrm{I}}=0$ and $\Theta_{\mathrm{II}}=\Theta$.

For the problem in question, it is convenient to introduce the relaxation functions $c_{n,m}(t)$ defined as

$$c_{n,m}(t)=\langle Y_{n,m}\rangle(t)-\langle Y_{n,m}\rangle_{\mathrm{II}}, \tag{30}$$

where $\langle\rangle_{\mathrm{II}}$ designates the equilibrium average in the state II. Thus, we can derive the following 21 term differential-recurrence equations:

$$\tau_D\frac{d}{dt}c_{n,m}(t)=\sum_{r=-2}^{2}\sum_{s=-2}^{2}d_{n,m,n+r,m+s}c_{n+r,m+s}(t), \tag{31}$$

where the coefficients $d_{n,m,n+r,m+s}$ are given by

$$d_{n,m,n+r,m+s}=-\frac{n(n+1)}{2}\delta_{s,0}\delta_{r,0} +\frac{(-1)^m\sqrt{(2n+1)(2n+2r+1)}}{8} \times\left\{\nu_{1,s}\left[\frac{r(2n+r+1)-2}{\sqrt{3\pi}}\right]\langle n,0,n+r,0|1,0\rangle \times\langle n,m,n+r,-m-s|1,-s\rangle +\nu_{2,s}\left[\frac{r(2n+r+1)-6}{\sqrt{5\pi}}\right]\langle n,0,n+r,0|2,0\rangle \times\langle n,m,n+r,-m-s|2,-s\rangle\right\}, \tag{32}$$

with $d_{n,m,n\pm1,m\pm2}\equiv0$. In order to derive Eq. (31) we have used that the equilibrium averages $\langle Y_{n,m}\rangle_{\mathrm{II}}$ ($N=\mathrm{I,II}$) satisfy the recurrence relation:

$$\sum_{r=-2}^{2}\sum_{s=-2}^{2}d_{n,m,n+r,m+s}\langle Y_{n+r,m+s}\rangle_N=0. \tag{33}$$

Thus, on solving Eq. (31) one is able to evaluate the transient responses of the polarization $\langle P\rangle(t)$ and the birefringence function $\langle K\rangle(t)$, which are conveniently described by the normalized relaxation functions,

$$f_1(t)=\frac{\langle P\rangle(t)-\langle P\rangle_{\mathrm{II}}}{\langle P\rangle_{\mathrm{I}}-\langle P\rangle_{\mathrm{II}}} =\frac{\gamma_Z^{\mathrm{II}}c_{1,0}(t)-\sqrt{2}\,\mathrm{Re}\{(\gamma_X^{\mathrm{II}}-i\gamma_Y^{\mathrm{II}})c_{1,1}(t)\}}{\gamma_Z^{\mathrm{II}}c_{1,0}(0)-\sqrt{2}\,\mathrm{Re}\{(\gamma_X^{\mathrm{II}}-i\gamma_Y^{\mathrm{II}})c_{1,1}(0)\}} \tag{34}$$

and

$$f_2(t)=\frac{\langle K\rangle(t)-\langle K\rangle_{\rm II}}{\langle K\rangle_{\rm I}-\langle K\rangle_{\rm II}}=\frac{[3(\gamma_Z^{\rm II})^2-1]c_{2,0}(t)+\sqrt{6}\,{\rm Re}\{(\gamma_X^{\rm II}-i\gamma_Y^{\rm II})^2c_{2,2}(t)\}-2\sqrt{6}\gamma_3^{\rm II}\,{\rm Re}\{(\gamma_X^{\rm II}-i\gamma_Y^{\rm II})c_{2,1}(t)\}}{[3(\gamma_Z^{\rm II})^2-1]c_{2,0}(0)+\sqrt{6}\,{\rm Re}\{(\gamma_X^{\rm II}-i\gamma_Y^{\rm II})^2c_{2,2}(0)\}-2\sqrt{6}\gamma_3^{\rm II}\,{\rm Re}\{(\gamma_X^{\rm II}-i\gamma_Y^{\rm II})c_{2,1}(0)\}},\quad(35)$$

respectively. Another quantities of interest are the integral relaxation times τ_n, which are defined as the area under the curve of $f_n(t)$:

$$\tau_n=\int_0^\infty f_n(t)dt=\tilde{f}_n(0),\quad(36)$$

where the tilde denotes the Laplace transform

$$\tilde{f}_n(s)=\int_0^\infty f_n(t)e^{-st}dt.\quad(37)$$

It should be noted that the system of Eqs. (31) can be also be derived starting from the underlying Smoluchowski equation for the probability distribution function $W(\mathbf{u},t)$ of orientations of the vector $\mathbf{u}$ in configuration space, namely,

$$2\tau_D\frac{\partial}{\partial t}W=\Delta W+\frac{1}{kT}{\rm div}(W\,{\rm grad}\,V_N).\quad(38)$$

The formal matrix-continued fraction method to the solution of the recurrence equations, such as Eq. (31), where two indexes vary, was suggested in Ref. [18]. However, in practice it is rather inconvenient, as one must use matrices of infinite dimension. We shall use below a more refined approach to the solution of Eq. (31) recently suggested in Refs. [24,25] for the solution of similar recurrence equations, so that it is possible to reduce the computational task to operations involving matrices of finite dimensions.

III. SOLUTION OF DIFFERENTIAL-RECURRENCE EQUATIONS (31)

Let us introduce a vector $\mathbf{C}_n(t)$, consisting of $8n$ elements:

$$\mathbf{C}_n(t)=\begin{pmatrix} c_{2n,-2n}(t)\\ c_{2n,-2n+1}(t)\\ \vdots\\ c_{2n,2n}(t)\\ c_{2n-1,-2n+1}(t)\\ c_{2n-1,-2n+2}(t)\\ \vdots\\ c_{2n-1,2n-1}(t)\end{pmatrix}.$$

Then, Eq. (31) can be transformed in a matrix three-term differential-recurrence equation,

$$\tau_D\frac{d}{dt}\mathbf{C}_n(t)=\mathbf{Q}_n^-\mathbf{C}_{n-1}(t)+\mathbf{Q}_n\mathbf{C}_n(t)+\mathbf{Q}_n^+\mathbf{C}_{n+1}(t),$$

$$n=1,2,3,\ldots\quad(39)$$

with

$$\mathbf{C}_0(t)=\mathbf{0}\ \text{ and }\ \mathbf{C}_1(t)=\begin{pmatrix} c_{2,-2}(t)\\ c_{2,-1}(t)\\ c_{2,0}(t)\\ c_{2,1}(t)\\ c_{2,2}(t)\\ c_{1,-1}(t)\\ c_{1,0}(t)\\ c_{1,1}(t)\end{pmatrix}.\quad(40)$$

The matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n^-$ in Eq. (39) are given by

$$\mathbf{Q}_n=\begin{pmatrix}\mathbf{X}_{2n} & \mathbf{W}_{2n}\\ \mathbf{Y}_{2n-1} & \mathbf{X}_{2n-1}\end{pmatrix},\quad \mathbf{Q}_n^+=\begin{pmatrix}\mathbf{Z}_{2n} & \mathbf{Y}_{2n}\\ \mathbf{0} & \mathbf{Z}_{2n-1}\end{pmatrix},$$

$$\mathbf{Q}_n^-=\begin{pmatrix}\mathbf{V}_{2n} & \mathbf{0}\\ \mathbf{W}_{2n-1} & \mathbf{V}_{2n-1}\end{pmatrix},$$

with

$$\mathbf{Y}_n=-\frac{n}{n+2}\mathbf{W}_{n+1}^\dagger,\quad \mathbf{Z}_n=-\frac{n}{n+3}\mathbf{V}_{n+2}^\dagger.$$

Here the symbol † denotes the Hermitian conjugation (transposition and complex conjugation). Thus the matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n^-$ can be expressed in terms of the submatrices $\mathbf{X}_n$, $\mathbf{W}_n$, and $\mathbf{V}_n$, which are described in details in the Appendix. The dimensions of the matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n^-$ are accordingly equal to $8n\times 8n$, $8n\times 8(n+1)$, and $8n\times 8(n-1)$. The exception is

$$\mathbf{Q}_1^-=\begin{pmatrix}\mathbf{V}_2\\ \mathbf{W}_1\end{pmatrix},$$

which degenerates to a column vector of dimension 8.

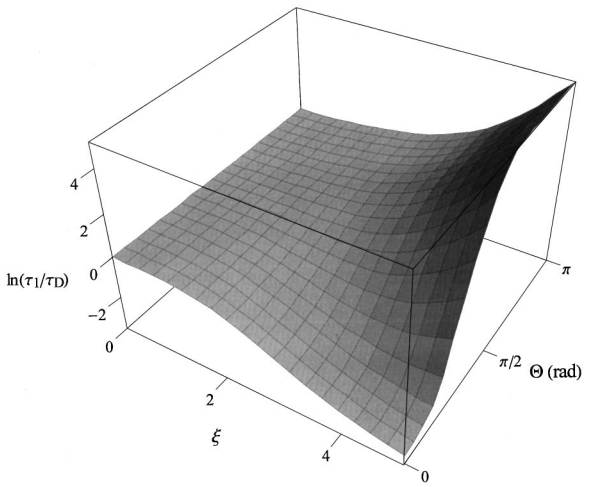

FIG. 2. $\ln(\tau_1/\tau_D)$ as a function of ξ and Θ for $R=1$ (a rapidly rotating field $\xi_{\rm I}=\xi_{\rm II}=\xi$, $0.01\leqslant\xi\leqslant 5$).

The column vector $\mathbf{C}_1(t)$ [Eq. (40)] contains all the $c_{l,m}(t)$, which are necessary for the calculation of the relaxation functions $f_1(t)$ and $f_2(t)$ from Eqs. (34) and (35).

On taking the Laplace transform of Eq. (39) we have

$$\mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(s) + [\mathbf{Q}_n - s\tau_D \mathbf{I}]\tilde{\mathbf{C}}_n(s) + \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(s) = -\tau_D \mathbf{C}_n(0), \tag{41}$$

where $\mathbf{I}$ is the unit matrix, which has the same dimension as the matrix $\mathbf{Q}_n$, and

$$\tilde{\mathbf{C}}_n(s) = \int_0^\infty \mathbf{C}_n(t) e^{-st} dt.$$

On applying the general method of solution of the matrix three-term differential-recurrence Eq. (41), suggested in Refs. [17,18], we obtain the *exact* solution for the Laplace transform $\tilde{\mathbf{C}}_1(s)$ in terms of *matrix continued fractions*, viz.,

$$\tilde{\mathbf{C}}_1(s) = \tau_D [\tau_D s\mathbf{I} - \mathbf{Q}_1 - \mathbf{Q}_1^+ \mathbf{S}_2^{\mathrm{II}}(s)]^{-1} \times \left\{ \mathbf{C}_1(0) + \sum_{n=2}^{\infty} \left(\prod_{k=2}^{n} \mathbf{Q}_{k-1}^+ [\tau_D s\mathbf{I} - \mathbf{Q}_k - \mathbf{Q}_k^+ \mathbf{S}_{k+1}^{\mathrm{II}}(s)]^{-1} \right) \mathbf{C}_n(0) \right\}, \tag{42}$$

where $\mathbf{S}_n^{\mathrm{II}}(s)$ is the infinite matrix continued fraction defined as

$$\mathbf{S}_n^{\mathrm{II}}(s) = [\tau_D s\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1}^{\mathrm{II}}(s)]^{-1} \mathbf{Q}_n^-$$

or

$$\mathbf{S}_n^{\mathrm{II}}(s) = \cfrac{\mathbf{I}}{\tau_D s\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \cfrac{\mathbf{I}}{\tau_D s\mathbf{I} - \mathbf{Q}_{n+1} - \mathbf{Q}_{n+1}^+ \cfrac{\mathbf{I}}{\tau_D s\mathbf{I} - \mathbf{Q}_{n+2} \ddots} \mathbf{Q}_{n+2}^-} \mathbf{Q}_{n+1}^-} \mathbf{Q}_n^- . \tag{43}$$

The initial conditions $\mathbf{C}_n(0)$ are vectors that can also be calculated with the help of the matrix continued fractions $\mathbf{S}_n^N(0)$ (see Appendix). On putting $s = i\omega$ in Eqs. (42) and (43), we are now able to calculate from Eqs. (34) and (35) the one-sided Fourier transforms of the relaxation functions $f_1(t)$ and $f_2(t)$. Moreover, on using Eq. (36), one can also calculate the relaxation times τ_1 and τ_2.

IV. RESULTS AND DISCUSSION

The matrix-continued fraction solution [Eq. (42)] we have obtained is very convenient for the purpose of computation. All the matrix-continued fractions and series involved converge very rapidly, thus 8–10 downward iterations in calculating these continued fractions and 8–10 terms in the series are enough to estimate the spectrum $\tilde{\mathbf{C}}_1(i\omega)$ at an accuracy not less than 6 significant digits in the majority of cases. Having determined $\tilde{\mathbf{C}}_1(i\omega)$, we are now able to calculate from Eqs. (34)–(37) all the quantities of interest. It should be noted that for a given value of ξ the two angles Θ (polar) and Φ (azimuthal) define the direction cosines of the applied field $\mathbf{E}_{\mathrm{II}}$ in general. However, due to the symmetry properties the solution is independent on the angle Φ, so that we may set $\Phi = 0$ in the calculations.

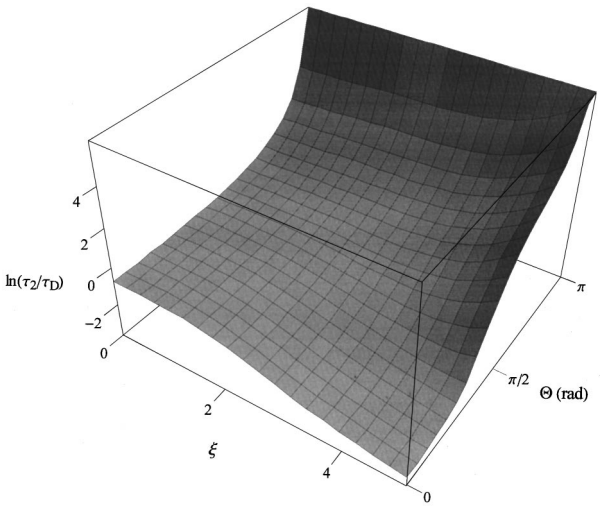

FIG. 3. $\ln(\tau_1/\tau_D)$ as a function of ξ and Θ for $R=1$ (a rapidly rotating field $\xi_{\mathrm{I}} = \xi_{\mathrm{II}} = \xi$, $0.01 \leqslant \xi \leqslant 5$).

Let us first calculate the transient responses when a strong dc field $\mathbf{E}$ is suddenly rotated at an angle Θ, which leads one to consider that only the direction of the field is changed, i.e., $\xi_{\mathrm{I}} = \xi_{\mathrm{II}}$. The rapidly rotating field method was introduced by Morita and Watanabe [26]. This method has the advantage in comparison with other methods (such as rise transient or rapidly reversing field methods) of obtaining a larger value for the birefringence. Previously, the theory of this method was developed only for *nonpolarizable* molecules [2,26]. The approach developed in the present paper allows us to calculate the relaxation time and spectra of the relaxation functions for *polar and polarizable molecules* as well. Some results of these calculations are shown in Figs. 2–7. The calculations were carried out for

$$\sigma_N = \frac{\xi_N^2}{2R} \quad \text{with} \quad R = \frac{\mu^2}{kT(\alpha_1 - \alpha_2)} = 1$$

(the ratio R characterizes the relative effect of the permanent dipole moment with respect to the induced one and can vary from $-\infty$ to $+\infty$ [2]).

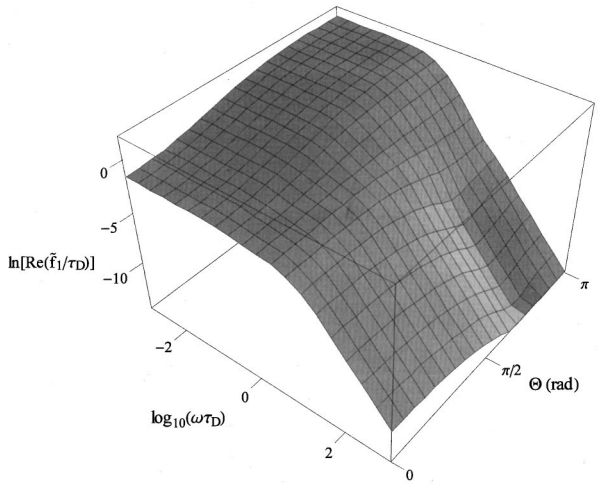

FIG. 4. $\ln[\mathrm{Re}(\tilde{f}_1/\tau_D)]$ as a function of $\log_{10}(\omega\tau_D)$ and Θ for a rapidly rotating field ($\xi_{\mathrm{I}}=\xi_{\mathrm{II}}=3$ and $R=1$).

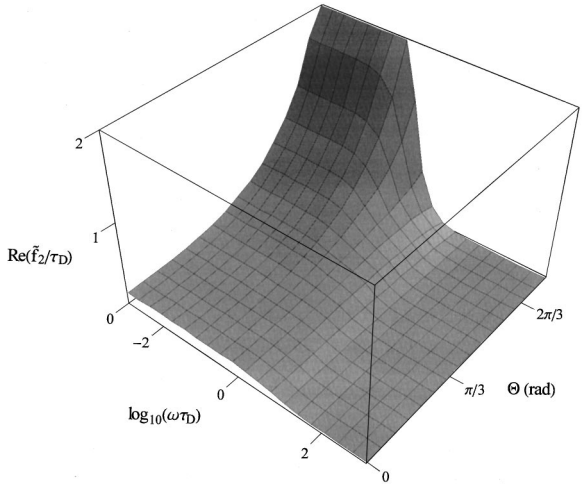

FIG. 6. $\mathrm{Re}(\tilde{f}_2/\tau_D)$ as a function of $\log_{10}(\omega\tau_D)$ and Θ.

The evolution of the relaxation time $\tau_1=\tilde{f}_1(0)$ of the electric polarization as a function of the angle Θ and the dimensionless parameter $\xi=\xi_{\mathrm{I}}=\xi_{\mathrm{II}}$ (which characterizes the strength of the dc field) is illustrated by a surface plot in Fig. 2. For $\Theta\approx 0$, the relaxation time $\tau_1\approx\tau_D$ for $\xi\ll 1$ (small fields), while $\tau_1\sim\tau_D/\xi$ for high values of ξ. For small values of Θ, τ_1 decreases monotonically to zero with increasing ξ. However, as $\Theta\to\pi$ (reversing field) one may notice that τ_1 increases with increasing ξ. A similar plot of the Kerr effect relaxation time $\tau_2=\tilde{f}_2(0)$ is shown in Fig. 3. For $\Theta\approx 0$, $\tau_2\approx\tau_D/3$ for $\xi\ll 1$ and $\tau_2\sim\tau_D/\xi$ for $\xi\gg 1$. Just as for τ_1, for a fixed value of $\Theta\approx 0$ the relaxation time τ_2 decreases monotonically to zero with increasing ξ. For a reversing field ($\Theta\to\pi$) the relaxation time τ_2 tends to infinity. However, such a behavior is only due to the definition of the relaxation time τ_2 given by Eq. (36), as in this case ($\xi_{\mathrm{I}}=\xi_{\mathrm{II}}$) $\langle P_2\rangle_{\mathrm{I}}=\langle P_2\rangle_{\mathrm{II}}$ for $\Theta=\pi$. Thus, a more suitable quantity characterizing this particular case would be the area under the unnormalized birefringence relaxation function, which is not equal to zero at $\Theta=\pi$.

The real and imaginary parts of the spectra of the one-sided Fourier transform of the relaxation functions $f_1(t)$ and $f_2(t)$, are illustrated in Figs. 4–7. As one can see in these figures, the dispersion curves have a very complicated behavior. It is clearly seen (Figs. 5 and 7) that in the vicinity of $\Theta=0$ corresponding to the step-on (or step-off) field response, two relaxation processes appear in these spectra. One (slow) Arrhenius-like process describes the overbarrier reversal of the molecule in the potential (23), while the second one describes the fast relaxation inside the wells located at the minima of the potential energy, namely, at $\vartheta=0$ and $\vartheta=\pi$. On increasing Θ, although both processes continue to exist, the amplitude of the slow process enhances and masks progressively the high-frequency relaxation. Such a behavior implies that for the rapidly rotating field the relaxation functions $f_1(t)$ and $f_2(t)$ appropriate to polar and anisotropically polarizable molecules may not be approximated by a single exponential in contrast to the Debye-like behavior encountered when only permanent moments are taken into account [27]. This difference arises mainly from the double-well structure of the potential energy (23) considered in this paper.

We considered above the transient behavior for a rapidly rotating field assuming that there is no change in the strength of the field. Similar calculations can also be carried out when the strength of the field may vary as well. The last case covers all possible situations for transient relaxation at sud-

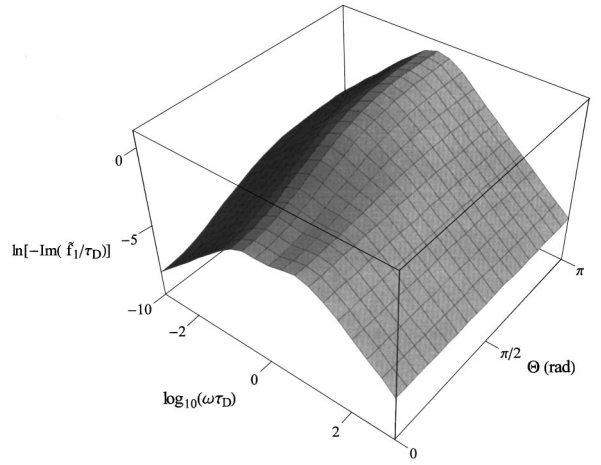

FIG. 5. $\ln[-\mathrm{Im}(\tilde{f}_1/\tau_D)]$ as a function of $\log_{10}(\omega\tau_D)$ and Θ.

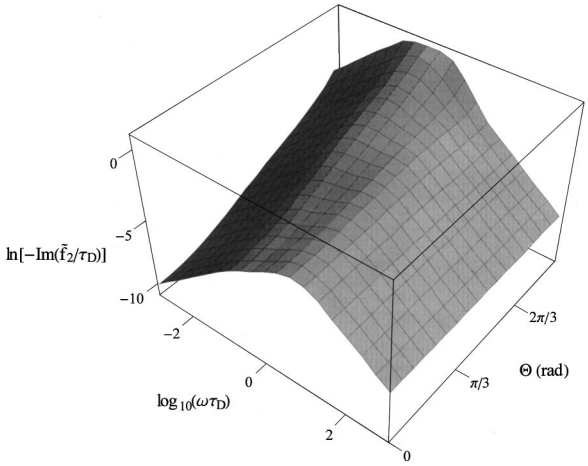

FIG. 7. $\ln[-\mathrm{Im}(\tilde{f}_2/\tau_D)]$ as a function of $\log_{10}(\omega\tau_D)$ and Θ.

den changes of the external field. If we suppose that only the strength but not the direction of the external field does change, then the calculations can be considerably simplified as in this case the dynamics of the system is governed by a five term differential-recurrence equation. This corresponds to $\Theta=0$ (step-on and/or step-off response) and $\Theta=\pi$ (suddenly reversing field response) for arbitrary values of E_{I} and E_{II}. The details of the matrix-continued fraction approach to the solution of all these problems can be found elsewhere [12]. Moreover, for step-on and/or step-off ($\Theta=0$) and suddenly reversing fields ($\Theta=\pi$) the relaxation times τ_1 and τ_2 can be calculated from an analytical equation [13,28]:

$$\tau_n=\frac{2\tau_D}{\langle P_n\rangle_{\mathrm{II}}-\langle P_n\rangle_{\mathrm{I}}}\int_{-1}^{1}\frac{\Phi(z)\Psi_n(z)e^{-\sigma_{\mathrm{II}}z^2-\xi_{\mathrm{II}}z}dz}{1-z^2}\quad(n=1,2), \tag{44}$$

where

$$\Phi(z)=\int_{-1}^{z}[W_{\mathrm{II}}(z')-W_{\mathrm{I}}(z')]dz', \tag{45}$$

$$\Psi_1(z)=\int_{-1}^{z}[P_1(z')-\langle P_1\rangle_{\mathrm{II}}]e^{\sigma_{\mathrm{II}}z'^2+\xi_{\mathrm{II}}z'}dz', \tag{46}$$

$$\Psi_2(z)=\int_{-1}^{z}[P_2(z')-\langle P_2\rangle_{\mathrm{II}}]e^{\sigma_{\mathrm{II}}z'^2+\xi_{\mathrm{II}}z'}dz'. \tag{47}$$

Equation (44) is a direct consequence of the nonlinear transient response theory developed in Ref. [28] for systems whose dynamics is governed by a one-dimensional Fokker-Planck equation (for $\Theta=0$ and $\Theta=\pi$ the relaxational dynamics of Brownian particles is governed by a one-dimensional Smoluchowski equation [2]). Equation (44) provides us with an independent check of the matrix-continued fraction solution as well as it allows one to evaluate readily the relaxation times τ_1 and τ_2 for various particular cases. For example, when a strong constant field is suddenly applied at $t=0$ (step-on response) to a system of nonpolar polarizable molecules that corresponds in Eqs. (44)–(47) to the following values of parameters:

$$\xi_{\mathrm{I}}=\xi_{\mathrm{II}}=0,\quad \sigma_{\mathrm{I}}=0,\quad \sigma_{\mathrm{II}}=\sigma. \tag{48}$$

Both the birefringence and the polarization are expressed in terms of $\langle P_2\rangle(t)$. Therefore, it is sufficient to calculate only τ_2, for which Eq. (44) takes the form [13,28]

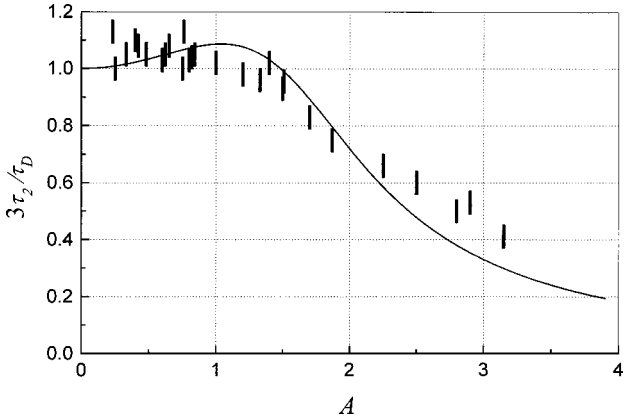

FIG. 8. Step-on response transient relaxation time (solid line) as a function of A given by Eq. (52). Bars are the experimental data from [30].

$$\tau_2=\frac{3\tau_D}{4\sigma\langle P_2\rangle_{\mathrm{II}}}\int_{-1}^{1}\left\{z\frac{\mathrm{erf}\,i(\sqrt{\sigma}z)}{\mathrm{erf}\,i(\sqrt{\sigma})}\left[1+e^{\sigma(1-z^2)}\right]-e^{\sigma(1-z^2)}\frac{\mathrm{erf}\,i^2(\sqrt{\sigma}z)}{\mathrm{erf}\,i^2(\sqrt{\sigma})}-z^2\right\}\frac{dz}{1-z^2}, \tag{49}$$

where

$$\langle P_2\rangle_{\mathrm{II}}=\frac{3e^{\sigma}}{2\sqrt{\pi\sigma}\,\mathrm{erf}\,i(\sqrt{\sigma})}-\frac{3}{4\sigma}-\frac{1}{2} \tag{50}$$

and

$$\mathrm{erf}\,i(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{t^2}dt \tag{51}$$

is the error function of imaginary argument.

We could find in the literature only a few experimental data [29–32], which can be used for checking the nonlinear theory. Tolles and co-workers [29,30] presented experimental results for the step-on nonlinear relaxation time τ_2 of *nonpolar polarizable* zinc oxide particles as a function of an applied electric field. The comparison of the theory with these data is given in Fig. 8. Here τ_2 [Eq. (49)] is plotted as a function of

$$A=2.4E_{\mathrm{II}}\sqrt{(\varepsilon_0\tau_D/\eta)[\ln(2l/d)-1.57-7\{[\ln(2l/d)]^{-1}-0.28\}^2]/[3.49\ln(2l/d)-1.84]}, \tag{52}$$

where ε_0 is the permittivity of free space, η is the viscosity of the fluid, and l/d is the length-to-diameter ratio, taken to be 15 for these experiments. The agreement of the theory with the experimental data [29,30] is good. The theory also agrees in all respects with the numerical solutions of the Smoluchowski equation obtained in Ref. [30].

Some measurements of transient and steady-state electric birefringence of rodlike macromolecules [helical $(\mathrm{Lys}\cdot\mathrm{HBr})_n$] in a methanol-water mixture were made by Kikuchi [31]. For this system the electro-optical response exhibits the characteristics of a pure-induced dipole orientation mechanism (the contribution from the permanent dipole moment is less than 5%). The theoretical prediction for the steady-state birefringence,

$$K(\infty)=K_s\langle P_2\rangle_{\mathrm{II}},$$

where $\langle P_2\rangle_{\mathrm{II}}$ is given by Eq. (50), is in accordance with clearly noticed experimental observations of upward deviations from Kerr's law [31]. Unfortunately, the author did not present experimental results for the field dependence of the transient relaxation time. Therefore, the detailed comparison with this experiment cannot be carried out.

Thus, in the context of the noninertial rotational diffusion model, the transient nonlinear dielectric relaxation and dynamic Kerr effect responses of an ensemble of noninteracting polar and polarizable molecules in a strong dc field, when both the magnitude and the direction of the dc field may suddenly be changed, can be evaluated from Eq. (42) in terms of matrix-continued fractions. The theory contains as particular cases all the results previously obtained for various particular transient relaxation problems such as transient responses on step-on, step-off, suddenly reversing or suddenly rotating fields [2,9–13]. Another advantage is that the nonlinear dielectric and Kerr effect relaxation are considered simultaneously. The range of applicability of the results obtained is restricted by a low-frequency range, as inertial effects are ignored in our model. The inclusion of the inertial effects cause the theory to be much more complicated as one then needs to solve the Euler-Langevin equation (2) (even for the linear rotator the differential-recurrence equations will involve four indices in that case).

The approach presented in the paper can also be used for the evaluation of transient responses in the dynamic Kerr effect and dielectric relaxation when effects due to the *hyperpolarizability* of the molecule are taken into account (see, e.g., [7]). Moreover, it can be applied (with small modifications) to the calculation of nonlinear magnetic response of superparamagnetic particles [32], where the magnetic relaxation is governed by an equation very similar to Eq. (31).

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APPENDIX: EXPLICIT REPRESENTATION OF SUBMATRICES AND THEIR ELEMENTS IN EQ. (39)

The submatrices $\mathbf{W}_l$, $\mathbf{X}_l$, and $\mathbf{V}_l$ are defined as

$$\mathbf{W}_l=\begin{pmatrix} w^{+}_{l,-l} & 0 & 0 & \cdots & 0 & 0 \\ w_{l,-l+1} & w^{+}_{l,-l+1} & 0 & \cdots & 0 & 0 \\ w^{-}_{l,-l+2} & w_{l,-l+2} & w^{+}_{l,-l+2} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & w_{l,l-2} & w^{+}_{l,l-2} \\ 0 & 0 & 0 & \cdots & w^{-}_{l,l-1} & w_{l,l-1} \\ 0 & 0 & 0 & \cdots & 0 & w^{-}_{l,l} \end{pmatrix}, \tag{A1}$$

$$\mathbf{X}_l=\begin{pmatrix} x_{l,-l} & x^{+}_{l,-l} & x^{++}_{l,-l} & 0 & \ddots & 0 & 0 \\ x^{-}_{l,-l+1} & x_{l,-l+1} & x^{+}_{l,-l+1} & x^{++}_{l,-l+1} & \ddots & 0 & 0 \\ x^{--}_{l,-l+2} & x^{-}_{l,-l+2} & x_{l,-l+2} & x^{+}_{l,-l+2} & \ddots & \vdots & \vdots \\ 0 & \ddots & \ddots & \ddots & \ddots & 0 & 0 \\ \vdots & \ddots & \ddots & \ddots & \ddots & x^{+}_{l,l-2} & x^{++}_{l,l-2} \\ 0 & \ddots & 0 & x^{--}_{l,l-1} & x^{-}_{l,l-1} & x_{l,l-1} & x^{+}_{l,l-1} \\ 0 & \cdots & 0 & 0 & x^{--}_{l,l} & x^{-}_{l,l} & x_{l,l} \end{pmatrix}, \tag{A2}$$

$$\mathbf{V}_l=\begin{pmatrix} \nu^{++}_{l,-l} & 0 & \cdots & 0 & 0 \\ \nu^{+}_{l,-l+1} & \nu^{++}_{l,-l+1} & \ddots & 0 & 0 \\ \nu_{l,-l+2} & \nu^{+}_{l,-l+2} & \ddots & \ddots & \vdots \\ \nu^{-}_{l,-l+3} & \nu_{l,-l+1} & \ddots & \nu^{++}_{l,l-5} & 0 \\ \nu^{--}_{l,-l+4} & \nu^{-}_{l,-l+4} & \ddots & \nu^{+}_{l,l-4} & \nu^{++}_{l,l-4} \\ 0 & \nu^{--}_{l,-l+5} & \ddots & \nu_{l,l-3} & \nu^{+}_{l,l-3} \\ \vdots & \ddots & \ddots & \nu^{-}_{l,l-2} & \nu_{l,l-2} \\ 0 & 0 & \ddots & \nu^{-}_{l,l-1} & \nu^{-}_{l,l-1} \\ 0 & 0 & \cdots & 0 & \nu^{--}_{l,l} \end{pmatrix}, \tag{A3}$$

and have dimensions $(2l+1)\times(2l-1)$, $(2l+1)\times(2l+1)$, and $(2l+1)\times(2l-3)$, respectively. The elements of the submatrices $\mathbf{W}_l$, $\mathbf{X}_l$, and $\mathbf{V}_l$ are given by

$$w_{n,m}=\frac{\gamma_Z^N\xi_N(n+1)}{2}\sqrt{(n^2-m^2)/(2n-1)(2n+1)},$$

$$w^{+}_{n,m}=-(w^{-}_{n,-m})^{*}=\frac{(\gamma_X^N-i\gamma_Y^N)\xi_N(n+1)}{4}\sqrt{(n-m-1)(n-m)/(2n-1)(2n+1)},$$

$$x_{n,m}=\frac{\sigma_N[3(\gamma_Z^N)^2-1][n(n+1)-3m^2]}{2(2n-1)(2n+3)}-\frac{n(n+1)}{2},$$

$$x^{-}_{n,m}=-(x^{+}_{n,-m})^{*}=-\frac{3\sigma_N(2m-1)\gamma_Z^N(\gamma_X^N+i\gamma_Y^N)}{2(2n-1)(2n+3)}\sqrt{(n+1-m)(n+m)},$$

$$x^{--}_{n,m}=(x^{++}_{n,-m})^{*}=-\frac{3\sigma_N(\gamma_X^N+i\gamma_Y^N)^2}{4(2n-1)(2n+3)}\sqrt{(n-m+1)(n-m+2)(n+m-1)(n+m)},$$

$$\nu_{n,m}=\frac{\sigma_N(n+1)}{2(2n-1)}[3(\gamma_Z^N)^2-1]\sqrt{\frac{[n^2-m^2][(n-1)^2-m^2]}{(2n+1)(2n-3)}},$$

$$\nu^{-}_{n,m}=-(\nu^{+}_{n,-m})^{*}=-\frac{(n+1)\sigma_N\gamma_Z^N(\gamma_X^N+i\gamma_Y^N)}{(2n-1)}\sqrt{\frac{(n^2-m^2)(n+m-2)(n+m-1)}{(2n-3)(2n+1)}},$$

$$\nu^{--}_{n,m}=(\nu^{++}_{n,-m})^{*}=\frac{(n+1)\sigma_N(\gamma_X^N+i\gamma_Y^N)^2}{4(2n-1)}\sqrt{\frac{(n+m-3)(n+m-2)(n+m-1)(n+m)}{(2n-3)(2n+1)}}.$$

The vectors of the initial conditions $\mathbf{C}_n(0)$ can be also calculated with the help of matrix-continued fractions by means of Risken's method [18]. Namely, the components $c_{n,m}(0)$ of $\mathbf{C}_n(0)$ are given by

$$c_{n,m}(0)=\langle Y_{n,m}\rangle_{\mathrm{I}}-\langle Y_{n,m}\rangle_{\mathrm{II}}. \tag{A4}$$

We shall further transform Eq. (33) to matrix-recurrence relation:

$$\mathbf{Q}_n^{-}\mathbf{R}_{n-1}^N+\mathbf{Q}_n\mathbf{R}_n^N+\mathbf{Q}_n^{+}\mathbf{R}_{n+1}^N=\mathbf{0},\quad n=1,2,3,\ldots \tag{A5}$$

where

$$\mathbf{R}_n^N=\begin{pmatrix} \langle Y_{2n,-2n}\rangle_N \\ \langle Y_{2n,-2n+1}\rangle_N \\ \vdots \\ \langle Y_{2n,2n}\rangle_N \\ \langle Y_{2n-1,-2n+1}\rangle_N \\ \langle Y_{2n-1,-2n+2}\rangle_N \\ \vdots \\ \langle Y_{2n-1,2n-1}\rangle_N \end{pmatrix}, \tag{A6}$$

The solution of Eq. (A5) is given by

$$\mathbf{R}_n^N = \mathbf{S}_n^N(0)\mathbf{R}_{n-1}^N = \mathbf{S}_n^N(0)\mathbf{S}_{n-1}^N(0)\ldots\mathbf{S}_2^N(0)\mathbf{S}_1^N(0)\frac{1}{\sqrt{4\pi}}, \tag{A7}$$

where

$$\mathbf{S}_n^N(0) = [-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1}^N(0)]^{-1}\mathbf{Q}_n^- . \tag{A8}$$

Thus, the initial conditions $\mathbf{C}_n(0)$ are given by

$$\mathbf{C}_n(0) = [\mathbf{S}_n^{\mathrm{I}}(0)\mathbf{S}_{n-1}^{\mathrm{I}}(0)\ldots\mathbf{S}_1^{\mathrm{I}}(0) - \mathbf{S}_n^{\mathrm{II}}(0)\mathbf{S}_{n-1}^{\mathrm{II}}(0)\ldots\mathbf{S}_1^{\mathrm{II}}(0)]\frac{1}{\sqrt{4\pi}}, \quad n = 1,2,3\ldots \tag{A9}$$

In particular, for $n=1$ we have

$$\mathbf{C}_1(0) = [\mathbf{S}_1^{\mathrm{I}}(0) - \mathbf{S}_1^{\mathrm{II}}(0)]\frac{1}{\sqrt{4\pi}}. \tag{A10}$$

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