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Anisotropic rotational diffusion and transient nonlinear responses of rigid macromolecules in a strong external electric field

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Nonlinear transient responses of polar polarizable particles (macromolecules) diluted in a nonpolar solvent to a sudden change in magnitude of a strong external dc field are evaluated using the anisotropic noninertial rotational diffusion model. The relaxation functions and relaxation times appropriate to the transient dynamic Kerr effect and nonlinear dielectric relaxation are calculated by solving the infinite hierarchy of differential-recurrence equations for statistical moments (ensemble averages of the Wigner *D* functions). The calculations involve matrix continued fractions, which ultimately yield the exact solution of the infinite hierarchy of differential-recurrence relations for the first- and second-order transient responses. © *2007 American Institute of Physics*.
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I. INTRODUCTION

Nonlinear dielectric and Kerr effect relaxation of fluids springs from the rotational motion of molecules in the presence of external electric fields and thermal agitation (see, e.g., Refs. 1 and 2). 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 equations. The Fokker-Planck equation describes the time evolution of the orientational distribution function of molecules in configuration space. The Langevin equation is a stochastic vector differential equation for angular variables describing the orientational dynamics of a molecule. Both approaches are completely equivalent and all observables of interest can be calculated both from the Fokker-Planck and the Langevin equations. The solution of either the Fokker-Planck equation or the Langevin equation for the rotational diffusion can be reduced to that of solving differential-recurrence equations for statistical averages describing the dynamic behavior of appropriate physical quantities. In order to solve these equations, one can use various mathematical methods, which allow one to obtain solutions in a tractable form. In the most general formulation, namely, anisotropic rotational diffusion of asymmetric tops in an electric field (in the *low field strength* limit), a concise theory has been developed by Perrin[3] and others (see, e.g., Refs. 4–15) for the analysis of orientation relaxation of molecules in liquids by various spectroscopic methods (such as dielectric and Kerr effect relaxation, NMR relaxation, fluorescent depolarization, dynamic light scattering, etc.). The majority of these attempts to calculate linear and/or nonlinear responses of a system of molecules to an external field use perturbation theory. Thus it is assumed that the potential energy of a molecule in electric fields is less than the thermal energy so that a small parameter exists. However, perturbation theory may *only* be used for the calculation of the response of a system where there is a small parameter. The response to a field of *arbitrary strength* is an intrinsically nonlinear problem as small parameters no longer exist so that perturbation theory may not be applied.

A deep insight into nonlinear response theory has been gained in the last few decades (see Refs. 16 and 17 and references cited therein for a review), because the *nonlinear response* of the rise, decay, and rapidly rotating field transient dielectric relaxation and Kerr effect arising from arbitrary sudden changes of the external electric field has been calculated. However, the treatment is confined for the most part to isotropic rotational diffusion of spherical top molecules. Recently further progress in the theoretical treatment of nonlinear responses of a system of asymmetric top molecules in strong electric fields has been achieved for the anisotropic noninertial rotational diffusion model[18,19] (see also Ref. 20, Chap. 7). The approach developed in Refs. 18 and 19 involves transformation of the angular variables in the underlying Langevin equation for the anisotropic rotational diffusion of Brownian particles and subsequent direct averaging of the stochastic differential equation so obtained. This method allows one to derive an infinite hierarchy of differential-recurrence equations for the statistical moments (averaged Wigner's *D* functions or appropriate relaxation functions[21]) describing the orientational relaxation of molecules in electric fields. The resulting system of moment equations can be solved by direct matrix diagonalization which involves calculating the eigenvalues and eigenvectors of the system matrix or by a computationally efficient matrix continued fraction method.[20] The solution so obtained may be used for the evaluation of both transient and ac nonlinear responses in strong electric fields. We remark that methods of solution of nonlinear response problems in strong electric

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fields are very similar to those used in the theory of orientational relaxation of molecules in liquid crystals. The orientational relaxation of molecules in liquid crystals is usually interpreted in the context of the rotational diffusion model of a molecule in a mean field potential V (see, for example, Refs. 22–25 and references cited therein). Here the ratio of the mean field potential strength V and thermal energy may also take an arbitrary value. For rotational diffusion in a mean field potential, the corresponding Fokker-Planck equation has the same mathematical form as that for rotational diffusion in an external electric field.[20] The solution of this Fokker-Planck equation can also be reduced to that of an infinite hierarchy of differential-recurrence equations for averaged Wigner's D functions.[22,23,25] Thus theoretical methods developed in the theory of orientational relaxation in liquid crystals (such as straightforward matrix diagonalization,[22] matrix continued fractions,[20,26] etc.) can be applied with some modifications in nonlinear response theory of macromolecules in solutions.[20]

In the present paper, the problem of evaluation of the transient dynamic birefringence and nonlinear dielectric relaxation responses of polar and polarizable macromolecules when the magnitude of a dc electric field is suddenly changed is treated. This problem is truly nonlinear, because the changes in the magnitude of the field may be considerable. Nevertheless, the hierarchy of differential-recurrence equations for the statistical moments can be obtained by averaging the corresponding Langevin equation over its realizations without recourse to the Fokker-Planck equation. By solving this system of moment equations via matrix continued fractions, we calculate the relaxation functions and relaxation times, which describe nonlinear transient responses. Furthermore, we show that the nonlinear decay transient responses can be evaluated in an analytic form.

II. TRANSIENT RESPONSES

Dielectric and Kerr effect relaxation of macromolecules in liquid solutions is usually interpreted using as model the noninertial rotational Brownian motion of a rigid body in an external electric field.[4,12,14,20] Here the relevant quantities are statistical averages involving Wigner's D functions defined as[21]

$$D^J_{M,M'}(\Omega) = e^{-iM\alpha} d^J_{MM'}(\beta) e^{-iM'\gamma},$$

where $d^J_{MM'}(\beta)$ is a real function with various explicit forms given, for example, in Ref. 21 and $\Omega=\{\alpha,\beta,\gamma\}$ are the Euler angles, which determine the orientation of the molecular (body-fixed) coordinate system xyz with respect to the laboratory coordinate system XYZ.

We suppose that the magnitude of an externally uniform dc electric field is suddenly altered at time $t=0$ from $\mathbf{E}_\mathrm{I}$ to $\mathbf{E}_\mathrm{II}$ (the electric fields $\mathbf{E}_\mathrm{I}$ and $\mathbf{E}_\mathrm{II}$ are assumed to be applied parallel to the Z axis of the laboratory coordinate systems). The potential energy $V_N(\Omega)$ $(N=\mathrm{I},\mathrm{II})$ of a dipolar polarizable molecule is given by[13]

$$\begin{aligned} V_N(\Omega) &= -\boldsymbol{\mu}\cdot\mathbf{E}_N - \tfrac{1}{2}\mathbf{E}_N\cdot\hat{\varepsilon}\cdot\mathbf{E}_N + \cdots \\ &= -\mu_Z(\Omega)E_N - \tfrac{1}{2}\varepsilon_{ZZ}(\Omega)E_N^2 + \cdots \\ &= -E_N\sum_{m=-1}^{1}(-1)^m\mu^{(-m)}D^1_{0,m}(\Omega) \\ &\quad - \frac{E_N^2}{3}\sum_{m=-2}^{2}(-1)^m\varepsilon^{(-m)}D^2_{0,m}(\Omega) + \frac{E_N^2}{6}\mathrm{Tr}\,\hat{\varepsilon} + \cdots, \end{aligned} \tag{1}$$

where $\boldsymbol{\mu}$ and $\hat{\varepsilon}$ are the dipole moment vector and electrical polarizability tensor of the molecule, respectively, $\mu_Z(\Omega)$ and $\varepsilon_{ZZ}(\Omega)$ are the projections of $\boldsymbol{\mu}$ and $\hat{\varepsilon}$ on the Z axis of the laboratory coordinate systems XYZ,

$$\mu^{(0)} = \mu_z, \quad \mu^{(\pm 1)} = \mp\frac{1}{\sqrt{2}}(\mu_x \pm i\mu_y)$$

are the spherical components of $\boldsymbol{\mu}$ in terms of the Cartesian components μ_x, μ_y, and μ_z in the molecular coordinate system xyz,

$$\varepsilon^{(\pm 2)} = \sqrt{\frac{3}{8}}(\varepsilon_{xx} - \varepsilon_{yy} \pm 2i\varepsilon_{xy}),$$

$$\varepsilon^{(\pm 1)} = \mp\sqrt{\frac{3}{2}}(\varepsilon_{xz} \pm i\varepsilon_{yz}), \quad \varepsilon^{(0)} = \frac{1}{2}(3\varepsilon_{zz} - \mathrm{Tr}\,\hat{\varepsilon})$$

are the spherical components of $\hat{\varepsilon}$,[13] and $\mathrm{Tr}\,\hat{\varepsilon} = \varepsilon_{xx} + \varepsilon_{xx} + \varepsilon_{zz}$. Here the effects due to the hyperpolarizability of molecules are ignored; however, they may also be included in the theory by adding the corresponding terms in Eq. (1).[17] We are interested in the relaxation of a system of molecules 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 initial distribution function in equilibrium state I is given by the Boltzmann distribution

$$W_\mathrm{I} = Z_\mathrm{I}^{-1}e^{-V_\mathrm{I}/kT}; \tag{2}$$

having altered the field, the distribution function approaches at $t\to\infty$ to a new equilibrium state II with a Boltzmann distribution

$$W_\mathrm{II} = Z_\mathrm{II}^{-1}e^{-V_\mathrm{II}/kT}. \tag{3}$$

Here k is Boltzmann's constant, T is the temperature, and Z_I and Z_II are the partition functions defined as $Z_N = \int e^{-V_N(\Omega)/kT}d\Omega$.

The main objective is to calculate the time-dependent Z components of the electric polarization $P_Z(t)$ and birefringence (optical anisotropy) $\Delta\alpha(t)$. The $P_Z(t)$ and $\Delta\alpha(t)$ are defined in terms of Wigner's D functions as[12,13,20]

$$P_Z(t) = N_0\langle\mu_Z\rangle(t) = N_0\sum_{p=-1}^{1}(-1)^p\mu^{(-p)}\langle D^1_{0,p}\rangle(t), \tag{4}$$

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$$\begin{aligned}\Delta\alpha(t) &= \langle\alpha_{ZZ}-\alpha_{XX}\rangle(t)\\ &= \sum_{m=-2}^{2}\left\{\langle D^{2*}_{0m}\rangle(t)-\frac{1}{\sqrt{6}}[\langle D^{2*}_{2m}\rangle(t)+\langle D^{2*}_{-2m}\rangle(t)]\right\}\alpha^{(m)},\end{aligned} \tag{5}$$

where N_0 is the concentration of macromolecules, μ_Z and α_{ZZ}, α_{XX} are the components of the permanent dipole moment $\boldsymbol{\mu}$ of molecule and optical polarizability tensor $\hat{\alpha}$ in the laboratory coordinate systems XYZ, $\alpha^{(m)}$ are the spherical components of the optical polarizability tensor $\hat{\alpha}$ given by[13]

$$\alpha^{(\pm 2)}=\sqrt{\frac{3}{8}}(\alpha_{xx}-\alpha_{yy}\pm 2i\alpha_{xy}),$$

$$\alpha^{(\pm 1)}=\mp\sqrt{\frac{3}{2}}(\alpha_{xz}\pm i\alpha_{yz}),\quad \alpha^{(0)}=\frac{1}{2}(3\alpha_{zz}-\mathrm{Tr}\,\hat{\alpha}),$$

Tr $\hat{\alpha}=\alpha_{xx}+\alpha_{xx}+\alpha_{zz}$, and the asterisk means the complex conjugate. Hitherto $P_Z(t)$ and $\Delta\alpha(t)$ have been frequently evaluated assuming low field strengths by perturbation theory (see, e.g., Refs. 12 and 14 and references cited therein). For arbitrary field strengths, the calculations have been usually made for isotropic rotational diffusion of spherical top molecules. [16,17]

III. RECURRENCE RELATIONS FOR STATISTICAL AVERAGES

According to Eqs. (4) and (5), the dielectric relaxation and dynamic Kerr effect of (macro)molecules of an arbitrary shape in strong electric fields is completely described by the first and second rank relaxation functions $\langle D^1_{n,m}\rangle(t)$ and $\langle D^2_{n,m}\rangle(t)$, respectively. Thus a theoretical treatment of these responses should proceed by calculating $\langle D^1_{n,m}\rangle(t)$ and $\langle D^2_{n,m}\rangle(t)$. This can be accomplished by averaging the Langevin equation.[18–20]

The Langevin equation for noninertial rotational Brownian motion of a rigid body in a potential $V(\Omega)$ for Wigner's function $D^j_{n,m}[\Omega(t)]$ is[18–20]

$$\begin{aligned}\frac{d}{dt}D^j_{n,m}[\Omega(t)] &= \left(\dot{\alpha}\frac{\partial}{\partial\alpha}+\dot{\beta}\frac{\partial}{\partial\beta}+\dot{\gamma}\frac{\partial}{\partial\gamma}\right)D^j_{n,m}[\Omega(t)]\\ &= (\boldsymbol{\omega}\cdot\nabla)D^j_{n,m}[\Omega(t)],\end{aligned} \tag{6}$$

where $\nabla\equiv\boldsymbol{\delta}/\boldsymbol{\delta\varphi}$ is the orientation space gradient operator, $\boldsymbol{\delta\varphi}$ is an infinitesimal rotation vector, and $\boldsymbol{\omega}(t)=\boldsymbol{\delta\varphi}/\boldsymbol{\delta}t$ is the angular velocity. The latter is given by

$$\boldsymbol{\omega}(t)=\hat{D}\{\boldsymbol{\lambda}(t)-\nabla V[\Omega(t),t]\}/kT. \tag{7}$$

Here $\boldsymbol{\lambda}(t)$ is a random white torque noise imposed by the heat bath, T is the temperature, k is Boltzmann's constant, and $\hat{D}$ is the rotational diffusion tensor. It is convenient to use the molecular coordinate system xyz in which the diffusion tensor $\hat{D}$ is diagonal.

$$\hat{D}=\begin{pmatrix}D_{xx} & 0 & 0\\ 0 & D_{yy} & 0\\ 0 & 0 & D_{zz}\end{pmatrix}. \tag{8}$$

The diagonal components D_{xx}, D_{yy}, and D_{zz} of $\hat{D}$ may be estimated using either the so-called hydrodynamic approach[8,9] or in terms of microscopic molecular parameters[8]

$$D_{ii}=kT/\varsigma_{ii}=\tau^j_J kT/I_{ii}.$$

Here I_{ii} is the principal moment of inertia about the i axis, ς_{ii} is component of friction tensor, and τ^j_J is the angular velocity correlation time about that axis (which can be measured experimentally using NMR techniques[8]). The principal axis system of the diffusion tensor $\hat{D}$ for an asymmetric top molecule may not coincide, in general, with the principal axis system diagonalizing the inertia tensor $\hat{I}$.[8] Thus if the orientation of the diffusion tensor principal axis system is unknown, the nondiagonalized diffusion tensor form must be used. In writing Eqs. (6) and (7), it was assumed that the suspension of Brownian particles (molecules) is monodisperse, nonconducting, and sufficiently dilute to avoid interparticle correlation effects. Rototranslational effects which are important for charged particles with complex shape (like long bent rods) were also ignored. These effects can also be incorporated in the theory as in the low field strength limit.[14]

Equation (6) is a stochastic differential equation for which one should use the Stratonovich interpretation[27] (see also Ref. 20, Sec. 2.3) as that interpretation always constitutes the mathematical idealization of the physical stochastic process of orientational relaxation in the noninertial limit.[20] By averaging Eq. (6) (as described in detail in Refs. 18–20), we have an equation of motion for the expectation value of $D^j_{n,m}[\Omega(t)]$, viz.,

$$\begin{aligned}\frac{d}{dt}\langle D^j_{n,m}\rangle &= \langle\nabla^2_\Omega D^j_{n,m}\rangle-\frac{1}{2kT}[\langle\nabla^2_\Omega(VD^j_{n,m})\rangle\\ &\quad-\langle V\nabla^2_\Omega D^j_{n,m}\rangle-\langle D^j_{n,m}\nabla^2_\Omega V\rangle],\end{aligned} \tag{9}$$

where the angular brackets denote an ensemble averaging and the operator ∇^2_Ω is given by

$$\begin{aligned}\nabla^2_\Omega &= -\hat{\mathbf{J}}\hat{D}\hat{\mathbf{J}}=-(D_{xx}\hat{J}^2_x+D_{yy}\hat{J}^2_y+D_{zz}\hat{J}^2_z)\\ &= -\frac{1}{2\tau_D}\{\hat{\mathbf{J}}^2+2\Delta\hat{J}^2_z+\Xi[(\hat{J}^{+1})^2+(\hat{J}^{-1})^2]\},\end{aligned}$$

where $\hat{\mathbf{J}}^2=\hat{J}^2_x+\hat{J}^2_y+\hat{J}^2_z$, and $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the components of $\hat{\mathbf{J}}$ in the molecular coordinate system defined as[21]

$$\hat{J}_x=\frac{1}{\sqrt{2}}(\hat{J}^{-1}-\hat{J}^{+1}),\quad \hat{J}_y=-\frac{i}{\sqrt{2}}(\hat{J}^{-1}+\hat{J}^{+1}),\quad \hat{J}_z=\hat{J}^0$$

and

$$\hat{J}^{\pm 1}=\frac{i}{\sqrt{2}}e^{\mp i\gamma}\left[\pm\cot\beta\frac{\partial}{\partial\gamma}+i\frac{\partial}{\partial\beta}\mp\frac{1}{\sin\beta}\frac{\partial}{\partial\alpha}\right],$$

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$$\hat{J}^0 = -i\frac{\partial}{\partial\gamma}.$$

Here

$$\tau_D = (D_{xx} + D_{yy})^{-1} \tag{10}$$

is the characteristic relaxation time, and

$$\Delta = \frac{D_{zz}}{D_{xx}+D_{yy}} - \frac{1}{2}, \quad \Xi = \frac{D_{xx}-D_{yy}}{D_{xx}+D_{yy}} \tag{11}$$

are dimensionless parameters characterizing the anisotropy of the diffusion tensor $\hat{D}$. We have also noted that the orientation space gradient operator ∇ can be expressed in terms of the angular momentum operator $\hat{\mathbf{J}}$ as $\nabla = i\hat{\mathbf{J}}$.[4,9,21] For any potential $V(\Omega,t)$, which may be expanded in Wigner's D functions as $V(\Omega,t)=\Sigma_{Q,S,R}v_{R,S,Q}(t)D^{R}_{S,Q}(\Omega)$, one can further simplify Eq. (9) and so one may obtain an infinite hierarchy of *linear* differential-recurrence equations for the expectation values of Wigner's D functions $\langle D^{j}_{nm}\rangle(t)$, viz., (see Refs. 18–20 for details)

$$\frac{d}{dt}\langle D^{j}_{n,m}\rangle(t) = \sum_{j',n',m'} d^{j,n,m}_{j',n',m'}\langle D^{j'}_{n',m'}\rangle(t). \tag{12}$$

Here the matrix elements $d^{j,n,m}_{j',n',m'}$ are expressed in terms of the Clebsch-Gordan coefficients;[21] explicit equations for the $d^{j,n,m}_{j',n',m'}$ are given in Refs. 18–20. We remark that Eq. (12) may also be obtained from the corresponding Fokker-Planck (Smoluchowski) equation for the distribution function $W(\Omega,t)$ of the orientations of macromolecules in configuration space, which is[4,20]

$$\frac{\partial}{\partial t}W = -\hat{\mathbf{J}}\hat{D}\hat{\mathbf{J}}W - \frac{1}{kT}\hat{\mathbf{J}}\hat{D}W\hat{\mathbf{J}}V$$
$$= \nabla^2_{\Omega}W + \frac{1}{2kT}[W\nabla^2_{\Omega} - V\nabla^2_{\Omega}W + \nabla^2_{\Omega}(VW)].$$

We emphasize that the Langevin and Fokker-Planck equation methods are entirely equivalent and yield the same results.[20]

Due to the cylindrical symmetry about the Z axis only the moments $\langle D^{j}_{n,m}\rangle(t)$ with $n=0$ are required in the calculation of the transient responses. For the potential given by Eq. (1), we obtain from Eq. (12) a 31-term recurrence equation for the relaxation functions $c_{j,m}(t)=\langle D^{j}_{0,m}\rangle(t)-\langle D^{j}_{0,m}\rangle_{\mathrm{II}}$ ($j\geqslant 1$, $-j\leqslant m\leqslant j$), viz.,

$$\tau_D\frac{d}{dt}c_{j,m}(t) = \sum_{j'=-2}^{2}\sum_{m'=-3}^{3} e^{j',m'}_{j,m}c_{j+j',m+m'}(t), \quad t>0 \tag{13}$$

(the coefficients $e^{j',m'}_{j,m}$ are listed in the Appendix A). Here we have also noted that the equilibrium averages $\langle D^{j}_{0,m}\rangle_{\mathrm{II}}$ satisfy the recurrence equation $\Sigma_{j'=-2}^{2}\Sigma_{m'=-3}^{3}e^{j',m'}_{j,m}\langle D^{j+j'}_{0,m+m'}\rangle_{\mathrm{II}}=0$. The recurrence Eq. (13) can be solved in terms of matrix continued fractions.[20,26]

IV. MATRIX CONTINUED FRACTION SOLUTION OF EQUATION (13)

We introduce column vectors $\mathbf{C}_j(t)$ defined as

$$\mathbf{C}_n(t) = \begin{pmatrix}\mathbf{c}_{2n-1}(t), \\ \mathbf{c}_{2n}(t)\end{pmatrix}, \quad \mathbf{c}_j(t) = \begin{pmatrix}c_{j,-j}(t)\\ c_{j,-j+1}(t)\\ \vdots \\ c_{j,j}(t)\end{pmatrix} \quad (n\geqslant 1), \tag{14}$$

with $\mathbf{C}_0(t)=\mathbf{0}$. Now, the recurrence Eq. (13) can be transformed into the matrix three-term recurrence equation

$$\tau_D\frac{d}{dt}\mathbf{C}_j(t) = \mathbf{Q}^-_j\mathbf{C}_{j-1}(t) + \mathbf{Q}_j\mathbf{C}_j(t) + \mathbf{Q}^+_j\mathbf{C}_{j+1}(t) \quad (j\geqslant 1), \tag{15}$$

where the matrices $\mathbf{Q}^{\pm}_j$ and $\mathbf{Q}_j$ are given in Appendix A. Invoking the general method for solving the matrix recursion Eq. (15), we obtain an exact solution for $\tilde{\mathbf{C}}_1(\omega)$ and $\tilde{\mathbf{C}}_2(\omega)$ as[20]

$$\tilde{\mathbf{C}}_1(\omega) = \tau_D\mathbf{\Delta}^{\mathrm{II}}_1(\omega)\left\{\mathbf{C}_1(0) + \sum_{j=2}^{\infty}\left(\prod_{k=2}^{j}\mathbf{Q}^+_{k-1}\mathbf{\Delta}^{\mathrm{II}}_k(\omega)\right)\mathbf{C}_j(0)\right\}, \tag{16}$$

$$\tilde{\mathbf{C}}_2(\omega) = \mathbf{\Delta}^{\mathrm{II}}_2(\omega)\mathbf{Q}^-_2\tilde{\mathbf{C}}_1(\omega) + \tau_D\mathbf{\Delta}^{\mathrm{II}}_2(\omega) \times\left\{\mathbf{C}_2(0) + \sum_{j=3}^{\infty}\left(\prod_{k=3}^{j}\mathbf{Q}^+_{k-1}\mathbf{\Delta}^{\mathrm{II}}_k(\omega)\right)\mathbf{C}_j(0)\right\}, \tag{17}$$

where the matrix continued fractions $\mathbf{\Delta}^{\mathrm{II}}_k(\omega)$ are defined by the following recurrence equation

$$\mathbf{\Delta}^{\mathrm{II}}_k(\omega) = [i\omega\tau_D\mathbf{I}_k - \mathbf{Q}_k - \mathbf{Q}^+_k\mathbf{\Delta}^{\mathrm{II}}_{k+1}(\omega)\mathbf{Q}^-_{k+1}]^{-1}, \tag{18}$$

where $\mathbf{I}_k$ is the unity matrix, and the tilde denotes the one-sided Fourier transform, viz., $\tilde{F}(\omega)=\int_0^{\infty}F(t)e^{-i\omega t}dt$. The initial condition vectors $\mathbf{C}_j(0)$ can also be calculated using the matrix continued fractions $\mathbf{\Delta}^{\mathrm{I}}_k(0)$ and $\mathbf{\Delta}^{\mathrm{II}}_k(0)$ (see Appendix A). The matrix continued fraction solution [Eqs. (16) and (17)] so obtained is very convenient for the purpose of computation. All the matrix continued fractions and series involved converge very rapidly; thus, 8–12 downward iterations in calculating these continued fractions and 8–12 terms in the series are enough to estimate the spectra $\tilde{\mathbf{C}}_1(\omega)$ and $\tilde{\mathbf{C}}_2(\omega)$ at an accuracy not <6 significant digits in the majority of cases.

Having determined $\tilde{\mathbf{C}}_1(\omega)$ and $\tilde{\mathbf{C}}_2(\omega)$, one can calculate the spectra $\tilde{c}_{j,m}(\omega)$ of the first and second rank relaxation functions $c_{1,m}(t)=\langle D^{1}_{0,m}\rangle(t)-\langle D^{1}_{0,m}\rangle_{\mathrm{II}}$ ($m=0,\pm 1$) and $c_{2,m}(t)=\langle D^{2}_{0,m}\rangle(t)-\langle D^{2}_{0,m}\rangle_{\mathrm{II}}$ ($m=0,\pm 1,\pm 2$), and the corresponding integral relaxation times $\tau^{\mathrm{int}}_{j,m}$ defined as the area under the corresponding normalized relaxation functions, viz.,[20]

$$\tau^{\mathrm{int}}_{j,m} = \frac{1}{c_{j,m}(0)}\int_0^{\infty}c_{j,m}(t)dt = \frac{\tilde{c}_{j,m}(0)}{c_{j,m}(0)}.$$

Thus one can estimate from Eqs. (4) and (5) the overall behavior of the dynamic Kerr effect and nonlinear dielectric relaxation of macromolecules in terms of the components of the diffusion tensor and the external field parameters for various transient responses.

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V. DECAY TRANSIENT RESPONSE WITH $\mathbf{E}_{\mathrm{II}}=0$

Let us first calculate the decay transient response when a dc field $\mathbf{E}_{\mathrm{I}}$ is suddenly switched off at instant $t=0$. We are interested in the relaxation of a system of molecules starting from an equilibrium state I with the distribution function $W_{\mathrm{I}}=Z_{\mathrm{I}}^{-1}e^{-V_{\mathrm{I}}/kT}$ $(t\leqslant 0)$ to another equilibrium state II with the isotropic distribution function $W_{\mathrm{II}}=1/(8\pi^2)$ $(t\to\infty)$. The step-off transient response with $\mathbf{E}_{\mathrm{II}}=\mathbf{0}$, i.e., the force-free diffusion, is of greatest interest because this solution serves as the basis of perturbation theory. Here the recurrence equations for the relaxation functions $c_{j,m}(t)$ with different j are decoupled so that the analysis of the relaxation behavior is simplified. For $j=1$ and 2, Eq. (13) becomes

$$\tau_D\dot{\mathbf{c}}_1(t)=\mathbf{q}_1^0\mathbf{c}_1(t), \tag{19}$$

$$\tau_D\dot{\mathbf{c}}_2(t)=\mathbf{q}_2^0\mathbf{c}_2(t), \tag{20}$$

where the matrices $\mathbf{q}_1^0=\mathbf{q}_1|_{E_{\mathrm{II}}=0}$ and $\mathbf{q}_2^0=\mathbf{q}_2|_{E_{\mathrm{II}}=0}$ are given by

$$\mathbf{q}_1^0=-\begin{pmatrix}1+\Delta & 0 & \Xi/2\\ 0 & 1 & 0\\ \Xi/2 & 0 & 1+\Delta\end{pmatrix}, \tag{21}$$

$$\mathbf{q}_2^0=-\begin{pmatrix}3+4\Delta & 0 & \sqrt{3/2}\,\Xi & 0 & 0\\ 0 & 3+\Delta & 0 & 3\Xi/2 & 0\\ \sqrt{3/2}\,\Xi & 0 & 3 & 0 & \sqrt{3/2}\,\Xi\\ 0 & 3\Xi/2 & 0 & 3+\Delta & 0\\ 0 & 0 & \sqrt{3/2}\,\Xi & 0 & 3+4\Delta\end{pmatrix}. \tag{22}$$

One can easily solve the systems of linear first-order differential Eqs. (19) and (20) for $\langle D^1_{0,m}\rangle(t)$ and $\langle D^2_{0,m}\rangle(t)$ [see Appendix B, where the explicit solutions for $\langle D^1_{0,m}\rangle(t)$ and $\langle D^2_{0,m}\rangle(t)$ are given by Eqs. (B1)–(B5)]. However, the simplest form of the solution can be given in terms of two sets of the normalized relaxation functions $\psi^j_m(t)$ $(j=1,2)$ defined as

$$\psi^1_0(t)=\frac{\langle D^1_{0,0}\rangle(t)}{\langle D^1_{0,1}\rangle(0)},\qquad \psi^1_{\pm1}(t)=\frac{\langle D^1_{0,1}\rangle(t)\pm\langle D^1_{0,-1}\rangle(t)}{\langle D^1_{0,1}\rangle(0)\pm\langle D^1_{0,-1}\rangle(0)}, \tag{23}$$

for $j=1$ and

$$\psi^2_0(t)=\frac{\langle D^2_{0,2}\rangle(t)-\langle D^2_{0,-2}\rangle(t)}{\langle D^2_{0,2}\rangle(0)-\langle D^2_{0,-2}\rangle(0)},$$

$$\psi^2_{\pm1}(t)=\frac{\langle D^2_{0,1}\rangle(t)\pm\langle D^2_{0,-1}\rangle(t)}{\langle D^2_{0,1}\rangle(0)\pm\langle D^2_{0,-1}\rangle(0)},$$

$$\psi^2_{-2}(t)=\frac{(\Delta+\sqrt{\Delta^2+3\Xi^2/4})\langle D^2_{0,0}\rangle(t)-\sqrt{3/8}\,\Xi[\langle D^2_{0,2}\rangle(t)+\langle D^2_{0,-2}\rangle(t)]}{(\Delta+\sqrt{\Delta^2+3\Xi^2/4})\langle D^2_{0,0}\rangle(0)-\sqrt{3/8}\,\Xi[\langle D^2_{0,2}\rangle(0)+\langle D^2_{0,-2}\rangle(0)]},$$

$$\psi^2_{2}(t)=\frac{\sqrt{3/2}\,\Xi\langle D^2_{0,0}\rangle(t)+(\Delta+\sqrt{\Delta^2+3\Xi^2/4})[\langle D^2_{0,2}\rangle(t)+\langle D^2_{0,-2}\rangle(t)]}{\sqrt{3/2}\,\Xi\langle D^2_{0,0}\rangle(0)+(\Delta+\sqrt{\Delta^2+3\Xi^2/4})[\langle D^2_{0,2}\rangle(0)+\langle D^2_{0,-2}\rangle(0)]}, \tag{24}$$

for $j=2$. The obvious advantage of using the normalized relaxation functions $\psi^j_m(t)$ instead of $\langle D^j_{0,m}\rangle(t)$ is that the decay transient solution is given by the single formula

$$\psi^j_m(t)=e^{-t/\tau^j_m}, \tag{25}$$

where the relaxation times τ^j_m are given in Appendix B, Eqs. (B6) and (B7).

Having determined $\langle D^1_{0,m}\rangle(t)$ and $\langle D^2_{0,m}\rangle(t)$, one can evaluate the time-dependent electric polarization $P_Z(t)$ and the optical anisotropy $\Delta\alpha(t)$ from Eqs. (4) and (5) as

$$P_Z(t)=\sum_{m=-1}^{1}a^1_m e^{-t/\tau^1_m}, \tag{26}$$

$$\Delta\alpha(t)=\sum_{m=-2}^{2}a^2_m e^{-t/\tau^2_m}, \tag{27}$$

where the amplitudes a^j_m are listed in Appendix B. Here only the amplitudes a^j_m depend on the field strength E; the relaxation times τ^j_m depend on the diagonal components of the diffusion tensor $\hat{D}$. In the low field limit, $E\to 0$, the above equation for $P_Z(t)$ and $\Delta\alpha(t)$ can be reduced to known results.[3,14,20] Thus just as for low field strengths,[12,14,20] the decay transients of $P_Z(t)$ and $\Delta\alpha(t)$ are characterized, in general, by three and five exponentials, respectively, with distinct relaxation times. It should be mentioned, however, that for typical values of the diagonal components of $\hat{D}$ the relaxation times τ^j_m and τ^j_{-m} (for particular j and m) are of the same order of magnitude; thus it is difficult to separate the

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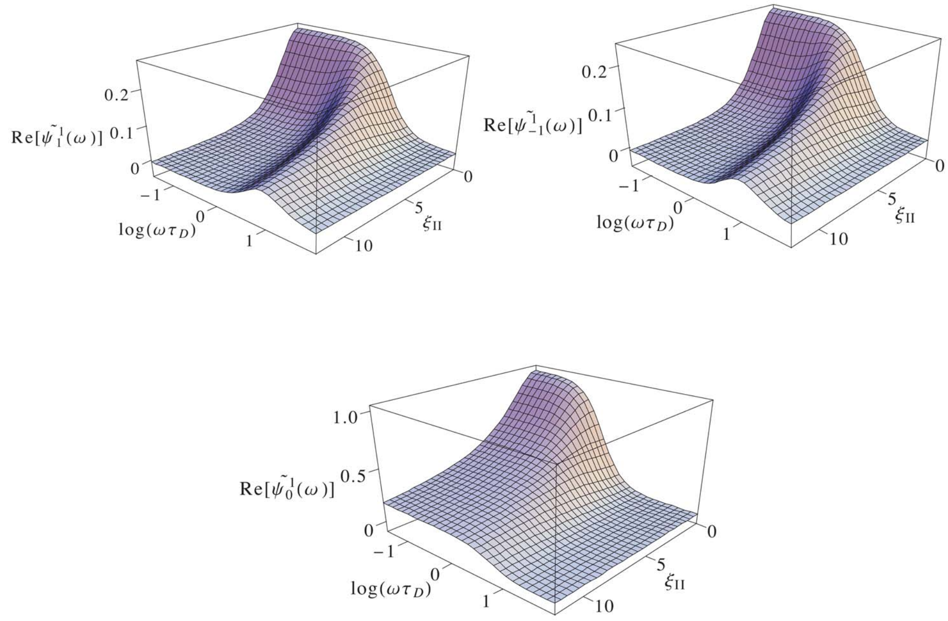

FIG. 1. 3D plots of Re[$\tilde{\psi}_m^1(\omega)$], $m=0,\pm 1$, as functions of the normalized frequency $\omega\tau_D$ and field parameter $\xi_{\rm II}$ for the step-on transient response with $\xi_{\rm I}=0$, $u_x=u_y=1/2$, $u_z=1/\sqrt{2}$, $\Delta=3$, $\Xi=-1/3$, and $\alpha_{sr}=0$, $s,r=x,y,z$ (pure permanent dipole response).

contributions of the corresponding relaxation modes to the decay transients $P_Z(t)$ and $\Delta\alpha(t)$. The overall behavior of $P_Z(t)$ and $\Delta\alpha(t)$ can be characterized by the integral relaxation times $\tau_{\rm int}^1$ and $\tau_{\rm int}^2$ defined as the area under the normalized decay functions $P_Z(t)/P_Z(0)$ and $\Delta\alpha(t)/\Delta\alpha(0)$, viz.,

$$\tau_{\rm int}^1=\int_0^\infty \frac{P_Z(t)}{P_Z(0)}dt=\sum_{m=-1}^{1}\tau_m^1 a_m^1 \Big/ \sum_{m=-1}^{1} a_m^1,$$

$$\tau_{\rm int}^2=\int_0^\infty \frac{\Delta\alpha(t)}{\Delta\alpha(0)}dt=\sum_{m=-2}^{2}\tau_m^2 a_m^2 \Big/ \sum_{m=-2}^{2} a_m^2,$$

where $P_Z(0)=\Sigma_{m=-1}^{1}a_m^1$ and $\Delta\alpha(0)=\Sigma_{m=-2}^{2}a_m^2$. For isotropic rotational diffusion [when $\Delta=\Xi=0$, Eq. (11)], the decay transients $P_Z(t)$ and $\Delta\alpha(t)$ are described by a single exponential, viz.,

$$P_Z(t)=P_Z(0)e^{-t/\tau_D}, \quad \Delta\alpha(t)=\Delta\alpha(0)e^{-3t/\tau_D},$$

where τ_D is given by Eq. (10).

VI. RISE TRANSIENT RESPONSE WITH $\mathbf{E}_{\rm I}=0$

Let us now suppose that a strong constant electric field $\mathbf{E}_{\rm II}$ is suddenly switched on at time $t=0$, so that $\mathbf{E}_{\rm I}=\mathbf{0}$. Here we are interested in the relaxation of a system of molecules starting from an equilibrium state I with the isotropic distribution function $W_{\rm I}=1/(8\pi^2)$ $(t\leqslant 0)$ to another equilibrium state II with the distribution function $W_{\rm II}=Z_{\rm II}^{-1}e^{-V_{\rm II}/kT}$ $(t\to\infty)$. Noting that $\mathbf{C}_j(0)=-\Pi_{k=1}^{j}\mathbf{\Delta}_k^{\rm II}(0)\mathbf{Q}_k^-$ (see Appendix A), Eqs. (16) and (17) can be considerably simplified and are given by

$$\tilde{\mathbf{C}}_1(\omega)=\frac{i}{\omega}[\mathbf{S}_1^{\rm II}(0)-\mathbf{S}_1^{\rm II}(\omega)], \tag{28}$$

$$\tilde{\mathbf{C}}_2(\omega)=\frac{i}{\omega}[\mathbf{S}_2^{\rm II}(0)\mathbf{S}_1^{\rm II}(0)-\mathbf{S}_2^{\rm II}(\omega)\mathbf{S}_1^{\rm II}(\omega)], \tag{29}$$

where $\mathbf{S}_k^{\rm II}(\omega)=\mathbf{\Delta}_k^{\rm II}(\omega)\mathbf{Q}_k^-$. Equations (28) and (29) allow one to calculate the step-on transient responses $\langle D_{0,m}^1\rangle(t)$ and $\langle D_{0,m}^2\rangle(t)$. Having determined $\langle D_{0,m}^1\rangle(t)$ and $\langle D_{0,m}^2\rangle(t)$, one can also calculate the spectra of the normalized relaxation functions $\psi_m^j(t)$ defined by Eqs. (23) and (24). The results of the calculation of Re[$\tilde{\psi}_m^j(\omega)$] versus the normalized frequency $\omega\tau_D$ and nonlinear parameter $E_{\rm II}$ are shown in the three-dimensional (3D) plot Figs. 1 and 2. As the electric field strength $E_{\rm II}$ increases, the dispersion curves are shifted to higher frequencies and the amplitude decreases due to saturation. For the rise transients, the relaxation functions $\psi_m^j(t)$ contain an infinite number of decaying exponentials.

In the low field strength limit, $E_{\rm II}\to 0$, the analysis of the relaxation behavior is considerably simplified. Noting that in this limit $c_{j,m}(t)\sim E_{\rm II}^j$,[17] so that for the calculation of the first- and second-order responses, Eq. (15) reduces to two matrix equations only

$$\tau_D\dot{\mathbf{c}}_1(t)=\mathbf{q}_1^0\mathbf{c}_1(t), \tag{30}$$

$$\tau_D\dot{\mathbf{c}}_2(t)=\mathbf{q}_2^-\mathbf{c}_1(t)+\mathbf{q}_2^0\mathbf{c}_2(t), \tag{31}$$

where the matrices $\mathbf{q}_1^0$ and $\mathbf{q}_2^0$ are defined by Eqs. (21) and (22) and the matrix $\mathbf{q}_2^-$ is

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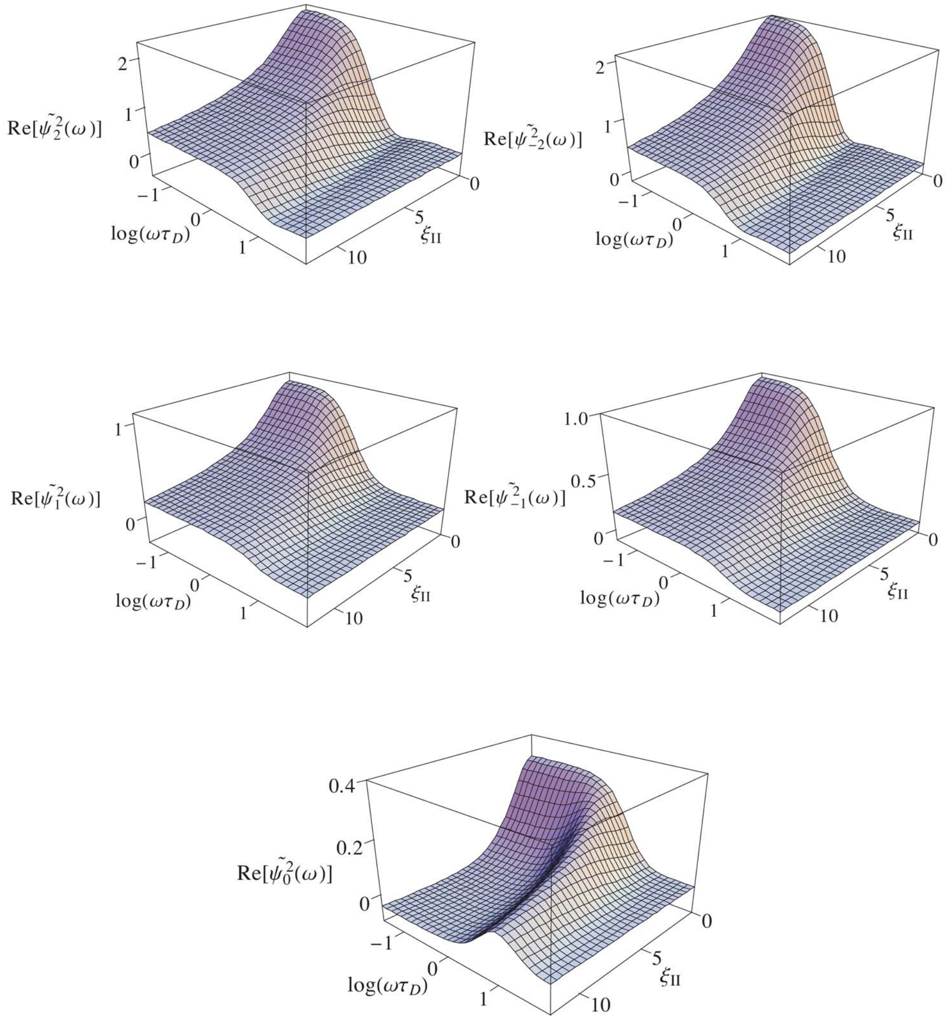

FIG. 2. The same as in Fig. 1 for Re[$\tilde{\psi}_m^2(\omega)$], $m=0,\pm 1,\pm 2$.

$$\mathbf{q}_2^- = \frac{\sqrt{3}}{10}\left(\frac{\mu E_{\mathrm{II}}}{kT}\right)\begin{pmatrix} u^-\Xi - u^+(3+4\Delta) & \sqrt{2}u_z\Xi & 0 \\ 3u_z & \sqrt{1/2}[2u^-\Xi - u^+(3+2\Delta)] & u_z\Xi \\ \sqrt{3/2}(u^- - u^+\Xi) & 2\sqrt{3}u_z & \sqrt{3/2}(u^-\Xi - u^+) \\ u_z\Xi & \sqrt{1/2}[u^-(3+2\Delta) - 2u^+\Xi] & 3u_z \\ 0 & \sqrt{2}u_z\Xi & u^-(3+4\Delta) - u^+\Xi \end{pmatrix},$$

$u^\pm = u_x \pm iu_y$, and u_x, u_y, and u_z are the components of the unit vector $\mathbf{u}=\boldsymbol{\mu}/|\boldsymbol{\mu}|$ directed along the dipole moment of molecule. One can readily solve Eqs. (30) and (31) for $\langle D_{0,m}^1\rangle(t)$ and $\langle D_{0,m}^2\rangle(t)$ just as for decay transients. The solutions for the first-order response functions $\langle D_{0,m}^1\rangle(t)$, which determine the rise transient of electric polarization $P_Z(t)$, coincide with those given in Appendix B for the decay transients with the only difference appearing in the initial conditions $\langle D_{0,m}^1\rangle(0)$. These initial conditions are evaluated analytically just as for the decay transients. The solution for the birefringence rise transient response $\Delta\alpha(t)$ differs from the decay transient solution obtained in Sec. IV. The main difference is that the rise transient of $\Delta\alpha(t)$ depends on the first-order response functions $\langle D_{0,m}^1\rangle(t)$. Here we do not present the solutions for $\Delta\alpha(t)$ explicitly because this solution can be readily obtained from those previously given by Wegener,[14] who showed that at low field strengths, the rise transient of $\Delta\alpha(t)$ is characterized, in general, by eight exponentials with distinct relaxation times τ_m^1 and τ_m^2 defined by Eqs. (B6) and (B7).

VII. CONCLUSIONS

In the present paper, we have given the exact solution (in terms of matrix continued fractions) for nonlinear transient response problems encountered in dielectric relaxation and dynamic Kerr effect when the magnitude of a dc electric field is suddenly changed at time $t=0$ from $\mathbf{E}_{\mathrm{I}}$ to $\mathbf{E}_{\mathrm{II}}$. Various

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particular transient relaxation problems such as transient responses in step-on, step-off, or suddenly reversing fields can be evaluated in the context of the approach developed. The advantage of our approach is that it does not assume low field strengths. In the limit of small field strengths, the results are in complete agreement with those obtained by perturbation procedures.

The theory may be applied to the interpretation of experimental data on nonlinear transient responses of dilute solutions of polar macromolecules in dielectric and Kerr effect relaxation at arbitrary field strengths. Thus it allows one to carry out a quantitative comparison of theoretical predictions with experiments on nonlinear response, where the perturbation approach can no longer be applied. Moreover, it will be possible to achieve a comparison of the theory with available Brownian dynamics computer simulation data for transient responses in strong fields (see, e.g., Refs. 28–30). The use of computer simulation data is preferable for testing the theory, as in computer simulation it is much easier (than in real experiments) to achieve large values of the electric field. The theory developed can be applied (with small modifications) to the calculation of the *nonlinear magnetic* response of magnetic systems such as magnetotactic bacteria in aqueous solutions and ferrofluids (colloidal suspensions of fine magnetic particles), where the dynamics are governed by equations very similar to Eq. (1).[31–33]

ACKNOWLEDGMENT

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APPENDIX A: MATRICES $\mathbf{Q}_n^-$, $\mathbf{Q}_n$, and $\mathbf{Q}_n^+$ AND INITIAL CONDITION VECTORS $\mathbf{C}_j(0)$

The elements of the matrices $\mathbf{Q}_n^-$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n$ are defined by

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_{2n-1} & \mathbf{q}_{2n-1}^+ \\ \mathbf{q}_{2n}^- & \mathbf{q}_{2n} \end{pmatrix}, \quad \mathbf{Q}_n^+ = \begin{pmatrix} \mathbf{s}_{2n-1} & \mathbf{0} \\ \mathbf{q}_{2n}^+ & \mathbf{s}_{2n} \end{pmatrix},$$

$$\mathbf{Q}_n^- = \begin{pmatrix} \mathbf{r}_{2n-1} & \mathbf{q}_{2n}^- \\ \mathbf{0} & \mathbf{r}_{2n} \end{pmatrix}$$

and the matrix elements of the submatrices $\mathbf{q}_j$, $\mathbf{q}_j^\pm$, $\mathbf{s}_j$, and $\mathbf{r}_j$ are defined as

$$\begin{aligned}(\mathbf{q}_j)_{n,m} = {} & \delta_{n,m+3}e_{j,-j+2+m}^{0,-3} + \delta_{n,m+2}e_{j,-j+1+m}^{0,-2} + \delta_{n,m+1}e_{j,-j+m}^{0,-1} \\ & + \delta_{n,m}e_{j,-j-1+m}^{0,0} + \delta_{n,m-1}e_{j,-j-2+m}^{0,1} + \delta_{n,m-2}e_{j,-j-3+m}^{0,2} \\ & + \delta_{n,m-3}e_{j,-j-4+m}^{0,3},\end{aligned}$$

$$\begin{aligned}(\mathbf{q}_j^+)_{n,m} = {} & \delta_{n,m+1}e_{j,-j+m}^{1,-2} + \delta_{n,m}e_{j,-j-1+m}^{1,-1} + \delta_{n,m-1}e_{j,-j-2+m}^{1,0} \\ & + \delta_{n,m-2}e_{j,-j-3+m}^{1,1} + \delta_{n,m-3}e_{j,-j-4+m}^{1,2},\end{aligned}$$

$$\begin{aligned}(\mathbf{q}_j^-)_{n,m} = {} & \delta_{n,m+3}e_{j,-j+2+m}^{-1,-2} + \delta_{n,m+2}e_{j,-j+1+m}^{-1,-1} + \delta_{n,m+1}e_{j,-j+m}^{-1,0} \\ & + \delta_{n,m}e_{j,-j-1+m}^{-1,1} + \delta_{n,m-1}e_{j,-j-2+m}^{-1,2},\end{aligned}$$

$$\begin{aligned}(\mathbf{s}_j)_{n,m} = {} & \delta_{n,m+1}e_{j,-j+m}^{2,-3} + \delta_{n,m}e_{j,-j-1+m}^{2,-2} + \delta_{n,m-1}e_{j,-j-2+m}^{2,-1} \\ & + \delta_{n,m-2}e_{j,-j-3+m}^{2,0} + \delta_{n,m-3}e_{j,-j-4+m}^{2,1} \\ & + \delta_{n,m-4}e_{j,-j-5+m}^{2,2} + \delta_{n,m-5}e_{j,-j-6+m}^{2,3},\end{aligned}$$

$$\begin{aligned}(\mathbf{r}_j)_{n,m} = {} & \delta_{n,m+5}e_{j,-j+4+m}^{-2,-3} + \delta_{n,m+4}e_{j,-j+3+m}^{-2,-2} + \delta_{n,m+3}e_{j,-j+2+m}^{-2,-1} \\ & + \delta_{n,m+2}e_{j,-j+1+m}^{-2,0} + \delta_{n,m+1}e_{j,-j+m}^{-2,1} + \delta_{n,m}e_{j,-j-1+m}^{-2,2} \\ & + \delta_{n,m-1}e_{j,-j-2+m}^{-2,3},\end{aligned}$$

where $\delta_{n,m}$ is Kronecker's delta. The coefficients $e_{j,m}^{j',m'}$ are given by

$$\begin{aligned}e_{j,m}^{0,0} = {} & -\frac{j(j+1)}{2} - \Delta m^2 + \frac{\sigma_{\mathrm{II}}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})[j(j+1) - 3m^2]}{4(2j-1)(2j+3)} \\ & + \Xi\sigma_{\mathrm{II}}\frac{(\varepsilon_{xx} - \varepsilon_{yy})[j(j+1) - 3m^2] + 2i\varepsilon_{xy}m[2j(j+1) - 2m^2 - 1]}{4(2j-1)(2j+3)},\end{aligned}$$

$$e_{j,m}^{0,\pm1} = \pm\sigma_{\mathrm{II}}\frac{\sqrt{(j \mp m)(j \pm m + 1)}}{4(2j-1)(2j+3)}\{(\varepsilon_{xz} \mp i\varepsilon_{yz})(2m \pm 1)(2m\Delta \mp 3) - \Xi(\varepsilon_{xz} \pm i\varepsilon_{yz})[j(j+1) - 3(m \pm 1)^2]\},$$

$$e_{j,m}^{0,\pm2} = \sqrt{[j^2 - (m \pm 1)^2][(j+1)^2 - (m \pm 1)^2]}\left[-\frac{\Xi}{4} \pm \sigma_{\mathrm{II}}\frac{(\varepsilon_{xx} \mp 2i\varepsilon_{xy} - \varepsilon_{yy})(4m\Delta \mp 3) - \Xi(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})(2m \pm 3)}{8(2j-1)(2j+3)}\right],$$

$$e_{j,m}^{0,\pm3} = \mp\frac{\Xi_{\mathrm{II}}(\varepsilon_{xz} \mp i\varepsilon_{yz})}{4(2j-1)(2j+3)}\sqrt{[j^2 - (m \pm 1)^2][j^2 - (m \pm 2)^2](j \mp m)(j \pm m + 3)},$$

$$e_{j,m}^{\pm1,0} = \mp\frac{\xi_{\mathrm{II}}u_z(2j + 1 \mp 1)}{8(2j+1)}\sqrt{(2j + 1 \pm 1)^2 - 4m^2},$$

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$$e_{j,m}^{-1,\pm 1} = \xi_{\mathrm{II}} \frac{\sqrt{(j \mp m)(j \mp m - 1)}}{4(2j+1)} [(\pm u_x - i u_y)(j + 1 \mp 2\Delta m) + (\mp u_x - i u_y)\Xi(j + 1 \pm m)],$$

$$e_{j,m}^{1,\pm 1} = \xi_{\mathrm{II}} \frac{\sqrt{(j \pm m + 1)(j \pm m + 2)}}{4(2j+1)} [(\pm u_x - i u_y)(j \pm 2\Delta m) + (\mp u_x - i u_y)\Xi(j \mp m)],$$

$$e_{j,m}^{-1,\pm 2} = \frac{\xi_{\mathrm{II}} u_z \Xi}{4(2j+1)} \sqrt{[j^2 - (m \pm 1)^2](j \mp m - 2)(j \mp m)},$$

$$e_{j,m}^{1,\pm 2} = -\frac{\xi_{\mathrm{II}} u_z \Xi}{4(2j+1)} \sqrt{[(j+1)^2 - (m \pm 1)^2](j \pm m + 3)(j \pm m + 1)},$$

$$e_{j,m}^{\pm 2,0} = \mp \sigma_{\mathrm{II}} \frac{\sqrt{[(j + 1 \pm 1)^2 - m^2][(j \pm 1)^2 - m^2]}}{8(2j \pm 1)(2j + 2 \pm 1)} [(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy} + \Xi(\varepsilon_{xx} - \varepsilon_{yy}))(2j + 1 \mp 1) \mp 4\Xi i \varepsilon_{xy} m],$$

$$e_{j,m}^{-2,\pm 1} = \pm \sigma_{\mathrm{II}} \frac{\sqrt{(j^2 - m^2)(j \mp m - 1)(j \mp m - 2)}}{2(4j^2 - 1)} \left[(\varepsilon_{xz} \mp i\varepsilon_{yz})(j + 1 \mp m\Delta) - \frac{3}{4}\Xi(\varepsilon_{xz} \pm i\varepsilon_{yz})(j \pm m + 1) \right],$$

$$e_{j,m}^{2,\pm 1} = \pm \frac{\sigma_{\mathrm{II}} \sqrt{[(j+1)^2 - m^2](j \pm m + 2)(j \pm m + 3)}}{2(2j+1)(2j+3)} \left[(\varepsilon_{xz} \mp i\varepsilon_{yz})(j \pm m\Delta) - \frac{3}{4}\Xi(\varepsilon_{xz} \pm i\varepsilon_{yz})(j \mp m) \right],$$

$$e_{j,m}^{-2,\pm 2} = \sigma_{\mathrm{II}} \frac{\sqrt{(j \mp m)(j \mp m - 1)(j \mp m - 2)(j \mp m - 3)}}{8(4j^2 - 1)} \times [(\varepsilon_{xx} \mp 2i\varepsilon_{xy} - \varepsilon_{yy})(j + 1 \mp 2m\Delta) + \Xi(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})(j + 1 \pm m)],$$

$$e_{j,m}^{2,\pm 2} = -\sigma_{\mathrm{II}} \frac{\sqrt{(j \pm m + 1)(j \pm m + 2)(j \pm m + 3)(j \pm m + 4)}}{8(2j+1)(2j+3)} [(\varepsilon_{xx} \mp 2i\varepsilon_{xy} - \varepsilon_{yy})(j \pm 2m\Delta) + \Xi(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})(j \mp m)],$$

$$e_{j,m}^{-2,\pm 3} = \pm \frac{\Xi \sigma_{\mathrm{II}}(\varepsilon_{xz} \mp i\varepsilon_{yz})}{8(4j^2 - 1)} \sqrt{[j^2 - (m \pm 1)^2](j \mp m)(j \mp m - 2)(j \mp m - 3)(j \mp m - 4)},$$

$$e_{j,m}^{2,\pm 3} = \pm \frac{\Xi \sigma_{\mathrm{II}}(\varepsilon_{xz} \mp i\varepsilon_{yz})}{8(2j+1)(2j+3)} \sqrt{[(j+1)^2 - (m \pm 1)^2](j \pm m + 1)(j \pm m + 3)(j \pm m + 4)(j \pm m + 5)},$$

where u_x, u_y, and u_z are the components of the unit vector $\mathbf{u} = \boldsymbol{\mu}/|\boldsymbol{\mu}|$ directed along the dipole moment of molecule, $\xi_{\mathrm{II}} = \mu E_{\mathrm{II}}/(kT)$, and $\sigma_{\mathrm{II}} = E_{\mathrm{II}}^2/(kT)$.

The initial condition vectors $\mathbf{C}_n(0)$ can also be calculated via matrix continued fractions as well. In the equilibrium states I and II, one can write

$$\mathbf{Q}_n^- \mathbf{R}_{n-1}^N + \mathbf{Q}_n \mathbf{R}_n^N + \mathbf{Q}_n^+ \mathbf{R}_{n+1}^N = \mathbf{0},$$

where

$$\mathbf{R}_0^N = (1), \quad \mathbf{R}_n^N = \begin{pmatrix} \mathbf{r}_{2n-1}^N \\ \mathbf{r}_{2n}^N \end{pmatrix}, \quad \mathbf{r}_j^N = \begin{pmatrix} \langle D_{0,-j}^j \rangle_N \\ \langle D_{0,-j+1}^j \rangle_N \\ \vdots \\ \langle D_{0,j}^j \rangle_N \end{pmatrix}.$$

The solution of the above equation is given by

$$\mathbf{R}_n^N = \mathbf{S}_n^N(0) \mathbf{R}_{n-1}^N = \prod_{k=1}^{n} \mathbf{S}_k^N(0),$$

where $\mathbf{S}_k^N(0) = \boldsymbol{\Delta}_k^N(0) \mathbf{Q}_k^-$. Noting that the components $c_{j,m}(0)$ of the initial condition column vectors $\mathbf{C}_n(0)$ are

$$c_{j,m}(0) = \langle D_{0,m}^j \rangle_{\mathrm{I}} - \langle D_{0,m}^j \rangle_{\mathrm{II}},$$

the $\mathbf{C}_n(0)$ are given by

$$\mathbf{C}_n(0) = \mathbf{R}_n^{\mathrm{I}} - \mathbf{R}_n^{\mathrm{II}}.$$

In particular, for $n=1$ we have $\mathbf{C}_1(0) = \mathbf{S}_1^{\mathrm{I}}(0) - \mathbf{S}_1^{\mathrm{II}}(0)$.

APPENDIX B: EXPLICIT SOLUTIONS FOR THE DECAY TRANSIENTS $\langle D_{0,m}^1 \rangle(t)$ AND $\langle D_{0,m}^2 \rangle(t)$

Noting that $\langle D_{0,m}^j \rangle_{\mathrm{II}} = 0$ and $c_{j,m}(t) = \langle D_{0,m}^j \rangle(t)$, the solution of the first-order differential equations (19) and (20) are given by

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$$\langle D^1_{0,0}\rangle(t)=\langle D^1_{0,0}\rangle(0)e^{-t/\tau^1_0}, \tag{B1}$$

$$\langle D^1_{0,\pm1}\rangle(t)=\tfrac{1}{2}[\langle D^1_{0,1}\rangle(0)+\langle D^1_{0,-1}\rangle(0)]e^{-t/\tau^1_1}\pm\tfrac{1}{2}[\langle D^1_{0,1}\rangle(0) \\ -\langle D^1_{0,-1}\rangle(0)]e^{-t/\tau^1_{-1}}, \tag{B2}$$

$$\langle D^2_{0,0}\rangle(t)=\frac{\langle D^2_{0,0}\rangle(0)}{2}(e^{-t/\tau^2_2}+e^{-t/\tau^2_{-2}})-\frac{\Delta}{\sqrt{4\Delta^2+3\Xi^2}} \\ \times\left\{\langle D^2_{0,0}\rangle(0)-\frac{\Xi\sqrt{6}}{4\Delta}[\langle D^2_{0,2}\rangle(0)+\langle D^2_{0,-2}\rangle(0)]\right\} \\ \times(e^{-t/\tau^2_2}-e^{-t/\tau^2_{-2}}), \tag{B3}$$

$$\langle D^2_{0,\pm1}\rangle(t)=\tfrac{1}{2}[\langle D^2_{0,1}\rangle(0)+\langle D^2_{0,-1}\rangle(0)]e^{-t/\tau^2_1}\pm\tfrac{1}{2}[\langle D^2_{0,1}\rangle(0) \\ -\langle D^2_{0,-1}\rangle(0)]e^{-t/\tau^2_{-1}}, \tag{B4}$$

$$\langle D^2_{0,\pm2}\rangle(t)=\pm\tfrac{1}{2}[\langle D^2_{0,2}\rangle(0)-\langle D^2_{0,-2}\rangle(0)]e^{-t/\tau^2_0} \\ +\tfrac{1}{4}[\langle D^2_{0,2}\rangle(0)+\langle D^2_{0,-2}\rangle(0)](e^{-t/\tau^2_2}+e^{-t/\tau^2_{-2}}) \\ +\frac{\Delta}{2\sqrt{4\Delta^2+3\Xi^2}}\left[\langle D^2_{0,-2}\rangle(0)+\langle D^2_{0,2}\rangle(0)\right. \\ \left.+\frac{\Xi\sqrt{6}}{2\Delta}\langle D^2_{0,0}\rangle(0)\right](e^{-t/\tau^2_2}-e^{-t/\tau^2_{-2}}), \tag{B5}$$

where the characteristic relaxation times τ^j_m are defined as

$$\tau^1_0=\tau_D,\quad \tau^1_{\pm1}=\frac{\tau_D}{1+\Delta\pm\Xi/2}, \tag{B6}$$

$$\tau^2_0=\frac{\tau_D}{3+4\Delta},\quad \tau^2_{\pm1}=\frac{\tau_D}{3+\Delta\pm3\Xi/2}, \\ \tau^2_{\pm2}=\frac{\tau_D}{3+2\Delta\pm\sqrt{4\Delta^2+3\Xi^2}}. \tag{B7}$$

Equations (B6) and (B7) for the relaxation times τ^j_m coincide with the known results for free asymmetric tops.[3,7,8,14]

The amplitudes a^j_m in Eqs. (26) and (27) are given by

$$a^1_0=\mu_z\langle D^1_{0,0}\rangle(0),$$

$$a^1_{\pm1}=\frac{1}{\sqrt{2}}\begin{pmatrix} i\mu_y \\ \mu_x \end{pmatrix}[\langle D^1_{0,-1}\rangle(0)\pm\langle D^1_{0,1}\rangle(0)],$$

$$a^2_0=i\frac{\sqrt{6}}{2}\alpha_{xy}[\langle D^2_{0,-2}\rangle(0)-\langle D^2_{0,2}\rangle(0)],$$

$$a^2_{\pm1}=\frac{\sqrt{6}}{2}\begin{pmatrix} i\alpha_{yz} \\ \alpha_{xz} \end{pmatrix}[\langle D^2_{0,-1}\rangle(0)\pm\langle D^2_{0,1}\rangle(0)],$$

$$a^2_{\pm2}=\frac{\sqrt{6}}{8}(\alpha_{xx}-\alpha_{yy})\{(1\pm f)[\langle D^2_{0,-2}\rangle(0)+\langle D^2_{0,2}\rangle(0)] \\ \pm g\langle D^2_{0,0}\rangle(0)\}\pm\tfrac{1}{8}(3\alpha_{zz}-\mathrm{Tr}\,\hat{\alpha}) \\ \times\{g[\langle D^2_{0,-2}\rangle(0)+\langle D^2_{0,2}\rangle(0)]\pm2(1\mp f)\langle D^2_{0,0}\rangle(0)\},$$

with $f=2\Delta/\sqrt{4\Delta^2+3\Xi^2}$ and $g=\sqrt{6}\Xi/\sqrt{4\Delta^2+3\Xi^2}$. The initial condition values $\langle D^j_{0,m}\rangle(0)$ can be evaluated as

$$\langle D^j_{0,m}\rangle(0)=\langle D^j_{0,m}\rangle_{\mathrm{I}}=Z_{\mathrm{I}}^{-1}\int D^j_{0,m}(\Omega)e^{-\beta V_{\mathrm{I}}(\Omega)}d\Omega.$$

In the low field limit, $E_{\mathrm{I}}\to0$, the initial condition values $\langle D^j_{0,m}\rangle(0)$ can be calculated analytically, viz.,

$$\langle D^1_{0,0}\rangle(0)=\frac{E_{\mathrm{I}}}{3kT}\mu_z,\quad \langle D^1_{0,\pm1}\rangle(0)=\mp\frac{E_{\mathrm{I}}(\mu_x\pm i\mu_y)}{3\sqrt{2}kT},$$

$$\langle D^2_{0,0}\rangle(0)=\frac{E^2_{\mathrm{I}}}{30kT}\left(3\varepsilon_{zz}-\mathrm{Tr}\,\hat{\varepsilon}+\frac{2\mu_z^2-\mu_x^2-\mu_y^2}{kT}\right),$$

$$\langle D^2_{0,\pm1}\rangle(0)=\mp\frac{E^2_{\mathrm{I}}}{5\sqrt{6}kT}\left[\varepsilon_{xz}\pm i\varepsilon_{yz}+\frac{\mu_z(\mu_x\pm i\mu_y)}{kT}\right],$$

$$\langle D^2_{0,\pm2}\rangle(0)=\frac{E^2_{\mathrm{I}}}{10\sqrt{6}kT}\left[\varepsilon_{xx}-\varepsilon_{yy}\pm i\varepsilon_{xy}+\frac{(\mu_x\pm i\mu_y)^2}{kT}\right].$$

Thus our decay transient solutions for $P_Z(t)$ and $\Delta\alpha(t)$, Eqs. (26) and (27), reduce to the known results,[3,14,20] viz.,

$$P_Z(t)=\frac{N_0E_{\mathrm{I}}}{3kT}(\mu_x^2e^{-t/\tau^1_1}+\mu_y^2e^{-t/\tau^1_{-1}}+\mu_z^2e^{-t/\tau^1_0})$$

and

$$\Delta\alpha(t)=\frac{E^2_{\mathrm{I}}}{5kT}\left\{\alpha_{xz}\left(\varepsilon_{xz}+\frac{\mu_x\mu_z}{kT}\right)e^{-t/\tau^2_{-1}}+\alpha_{yz}\left(\varepsilon_{yz}+\frac{\mu_y\mu_z}{kT}\right)e^{-t/\tau^2_1}+\alpha_{xy}\left(\varepsilon_{xy}+\frac{\mu_x\mu_y}{kT}\right)e^{-t/\tau^2_0}+\frac{1}{8}[(\alpha_{xx}-\alpha_{yy})\delta^-+(3\alpha_{zz}-\mathrm{Tr}\,\hat{\alpha})\delta^+]\right. \\ \left.\times(e^{-t/\tau^2_2}+e^{-t/\tau^2_{-2}})+\frac{(\alpha_{xx}-\alpha_{yy})(2\Delta\delta^-+3\Xi\delta^+)+(3\alpha_{zz}-\mathrm{Tr}\,\hat{\alpha})(\Xi\delta^--2\Delta\delta^+)}{8\sqrt{4\Delta^2+3\Xi^2}}(e^{-t/\tau^2_2}-e^{-t/\tau^2_{-2}})\right\},$$

where $\delta^-=\varepsilon_{xx}-\varepsilon_{yy}+(\mu_x^2-\mu_y^2)/(kT)$ and $\delta^+=\varepsilon_{zz}-\mathrm{Tr}(\hat{\varepsilon}/3)+(2\mu_z^2-\mu_x^2-\mu_y^2)/(3kT)$.

For isotropic rotational diffusion [when $\Delta=\Xi=0$, Eq. (11)] of symmetric tops with $\varepsilon_{xx}=\varepsilon_{yy}\neq\varepsilon_{zz}$, $\varepsilon_{ij}=0$, $i\neq j$, and $\alpha_{xx}=\alpha_{yy}\neq\alpha_{zz}$, $\alpha_{ij}=0$, $i\neq j$, the above equations for $P_Z(t)$ and $\Delta\alpha(t)$ are simplified to

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$$P_Z(t) = \frac{N_0 E_{\mathrm{I}}}{3kT}(\mu_x^2 + \mu_y^2 + \mu_z^2)e^{-t/\tau_D},$$

$$\Delta\alpha(t) = \frac{(\alpha_{zz} - \alpha_{xx})E_{\mathrm{I}}^2}{15kT}\left[\varepsilon_{zz} - \varepsilon_{xx} + \frac{\mu_z^2 - (\mu_x^2 + \mu_y^2)/2}{kT}\right]e^{-3t/\tau_D}.$$

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