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Rotational Brownian motion and nonlinear dielectric relaxation of asymmetric top molecules in strong electric fields

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A general theoretical treatment of the nonlinear dielectric response of an assembly of asymmetric top molecules in strong electric fields is presented in the context of the noninertial rotational diffusion model. The calculation proceeds by obtaining an infinite hierarchy of recurrence equations for the expectation values of Wigner's *D* functions describing nonlinear relaxation of the system. This hierarchy may be used for the evaluation of both transient and ac nonlinear responses in strong electric fields. The solution of this hierarchy is obtained for the particular case of rigid rodlike molecules in superimposed ac and strong dc bias electric fields, allowing one to evaluate the corresponding nonlinear response. The results are in agreement with available experimental data on nonlinear dielectric relaxation of dilute solutions of polar rodlike molecules in nonpolar solvents.

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I. INTRODUCTION

Dielectric relaxation spectroscopy is a valuable tool in probing dynamical processes in condensed matter. Recently, this method has been extended to the nonlinear regime and applied to the investigation of liquid crystals, polymers, solids, and liquids (see, e.g., [1–10] and references cited therein). These investigations have shown that nonlinear dielectric spectra provide more information on the relaxation processes than can be obtained from linear spectra only. On the other hand, nonlinear experimental data offer an additional important test of theoretical models leading to a better understanding of the properties of the materials. However, the study of nonlinear dielectric spectra requires an adequate theoretical description of dielectric relaxation in strong electric fields.

Here, a theory of nonlinear dielectric relaxation of dielectric fluids in high electric fields is proposed in order to describe the nonlinear dielectric responses in dilute solutions of polar molecules in nonpolar solvents. The theory of electric polarization of dielectric fluids was formulated originally by Debye [11], who calculated the linear dielectric response in the context of the noninertial rotational diffusion model of spherical molecules. That response has a well-known representation in terms of the Debye equation for the complex dielectric permittivity and of the Cole-Cole diagram, which is a perfect semicircle. Linear-response theory was further extended by Perrin [12] and others [13,14] to asymmetric top molecules when the dielectric response becomes more complicated, as rotation about each molecular axis may contribute to the dielectric spectra. The permittivity in linear response is independent of the applied electric-field strength. Many attempts have been made to generalize the Debye theory in order to take into account the nonlinear aspects of dielectric relaxation of polar fluids in high electric fields, however only symmetric top molecules have been usually treated (see [15] and [16] and references cited therein for a review). The traditional theoretical approach to the problem habitually commences with the noninertial Langevin equation for the rotational Brownian motion of a molecule or with the corresponding Smoluchowski equation for the probability distribution function W of orientations of the molecules in configuration space. The Smoluchowski equation can be solved by expanding W in terms of an appropriate complete set of orthogonal functions, usually as a series of spherical harmonics $Y_{l,m}$. This yields an infinite hierarchy of recurrence relations for the moments, namely the expectation values of the spherical harmonics $\langle Y_{l,m}\rangle(t)$ (see, e.g., [16–21]). The underlying Langevin equation can also be reduced to the same moment system (*without recourse* to the Smoluchowski equation) by appropriate transformation of the variables and by direct averaging of the stochastic equation so obtained [16,17,20]. In many practical applications (e.g., for the problem in question), approximate solutions of this hierarchy can be obtained by using perturbation methods as the energy of molecules in external fields is usually (much) less than the thermal energy kT. Moreover, when the perturbation approach is not applicable, one may use the matrix continued fraction method [16,17]. As shown in Refs. [16] and [20], this method is very convenient for the computation of the nonlinear response. In general, the same approach may be used for asymmetric tops by noting that the quantities of interest are averages involving Wigner's D functions [22,23].

The theory of rotational Brownian motion of asymmetric tops in an electric field (in the *low field strength* limit) has been developed by Wegener *et al.* [24–26] in a particular application to the Kerr effect relaxation (the results of Wegener *et al.* [26] were reproduced recently by Hosokawa *et al.* [27]). Here, a theory of nonlinear dielectric relaxation of asymmetric top molecules *in strong electric fields* is developed. As a particular example, the theory is used to evaluate the nonlinear dielectric relaxation in superimposed ac and strong dc bias electric fields for a system of rodlike molecules, where the dipole moment vector may be directed at an arbitrary angle to the long molecular axis. In an experimental context, this technique has been recently proposed by Hellemans *et al.* [7–10] to study the dynamics of molecular liquids. It has been also demonstrated in [7–9] that the experimental data for symmetric top molecules with the dipole

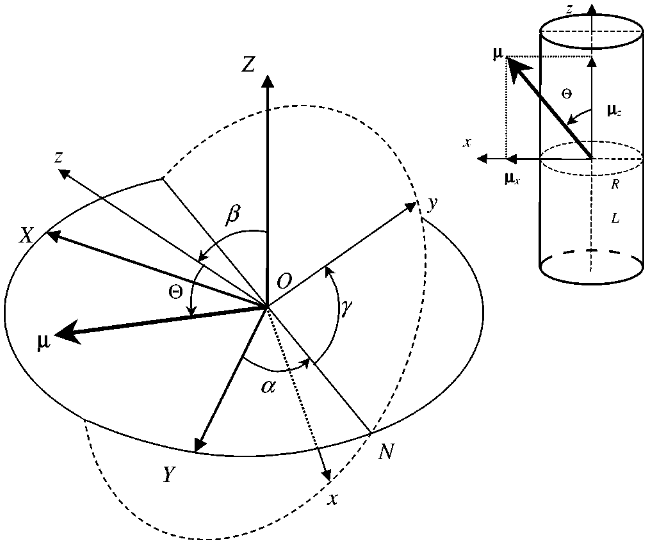

FIG. 1. Geometry of the problem. In the inset, a rodlike molecule is shown.

moment $\boldsymbol{\mu}$ directed along the axis of symmetry are in complete agreement with the theory of Coffey and Paranjape [28]. However, for asymmetric top molecules where several dispersion bands were observed [10] in the nonlinear spectra, no appropriate theory for the interpretation of the experiment data exists. The main objective of the present paper is to develop such a theory.

The paper is arranged as follows. In Sec. II, an infinite hierarchy of recurrence equations for the expectation values of Wigner's D functions describing nonlinear relaxation of an assembly of noninteracting rigid asymmetric top molecules is derived in the context of the Langevin equation approach to the noninertial rotational Brownian motion without recourse to the Fokker-Planck equation. The perturbation solution of this hierarchy is obtained in Sec. III for the particular case of nonpolarizable rodlike molecules in superimposed external ac and strong dc bias electric fields. The results are presented and discussed in Sec. IV. In Appendix A, for the purpose of illustration, the linear-response theory for asymmetric top molecules is given in the context of the developed approach. The system of moment equations of Wigner's D functions describing nonlinear relaxation of nonpolar polarizable asymmetric top molecules is presented in Appendix B.

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

Let us consider the three-dimensional rotational Brownian motion of an asymmetric top molecule in an external field $\mathbf{E}(t)$. The orientation of the molecule is described by the Euler angles $\Omega=\{\alpha,\beta,\gamma\}$ (here the notations from Refs. [22] and [23] are adopted). The Euler angles completely determine the orientation of the molecular (body-fixed) coordinate system *xyz* with respect to the laboratory coordinate system *XYZ* (α, β, and γ are the azimuthal and polar angles and the angle, describing rotation of a molecule around the z axis, respectively, see Fig. 1). The dynamics of the molecule are described by the Euler-Langevin equation for the angular velocity $\boldsymbol{\omega}(t)$ written in the body-fixed coordinate system *xyz* [14,17], viz.,

$$\frac{d}{dt}\hat{I}\boldsymbol{\omega}(t)+\boldsymbol{\omega}(t)\times\hat{I}\boldsymbol{\omega}(t)+\hat{\varsigma}\boldsymbol{\omega}(t)=-\boldsymbol{\nabla}V[\Omega(t),t]+\boldsymbol{\lambda}(t), \tag{1}$$

where $\hat{I}$ is the tensor of inertia of the molecule, $\hat{\varsigma}\boldsymbol{\omega}(t)$ is the damping torque due to Brownian movement, $\hat{\varsigma}$ is the rotational friction tensor, $\boldsymbol{\lambda}(t)$ is the white noise driving torque, again due to Brownian movement [17], so that $\boldsymbol{\lambda}(t)$ has the following properties:

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

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

Here, the overbar means a statistical average over an ensemble of Brownian particles which *all* start at time t with the *same* angular velocity and orientation [17]; δ_{ij} is Kronecker's delta, indices $i,j=1$, 2, 3 correspond to the Cartesian axes *x,y,z* of the molecular coordinate system, and $\delta(t)$ is the Dirac delta function. The term $-\boldsymbol{\nabla}V$ in Eq. (1) represents the torque acting on the molecule in the electric field,

$$V(\Omega,t)=-(\boldsymbol{\mu}\cdot\mathbf{E})-(\mathbf{E}\cdot\hat{\alpha}\cdot\mathbf{E})/2 \tag{2}$$

is the potential energy of the molecule in the field $\mathbf{E}(t)$, $\boldsymbol{\mu}$ is the electric dipole moment vector, $\hat{\alpha}$ is the electric polarizability tensor [here the effects due to hyperpolarizability are neglected, however they may also be included in the theory by adding the corresponding terms in Eq. (2) [16]], and $\boldsymbol{\nabla}\equiv\delta/\delta\boldsymbol{\varphi}$ is the orientation space gradient operator ($\delta\boldsymbol{\varphi}$ is an infinitesimal rotation vector; the properties of $\boldsymbol{\nabla}$ are described in detail in [29]). The torque $-\boldsymbol{\nabla}V$ in Eq. (1) can be expressed in terms of the angular momentum operator $\hat{\mathbf{J}}$ [13]:

$$-\boldsymbol{\nabla}V=-i\hat{\mathbf{J}}V, \tag{3}$$

where the components of $\hat{\mathbf{J}}$ in the molecular coordinate system are [23]

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

$$\hat{J}_z=-i\frac{\partial}{\partial\gamma}, \tag{4}$$

and

$$\hat{J}^{\pm1}=\frac{i}{\sqrt{2}}e^{\mp i\gamma}\left[\pm\cot\beta\frac{\partial}{\partial\gamma}+i\frac{\partial}{\partial\beta}\mp\frac{1}{\sin\beta}\frac{\partial}{\partial\alpha}\right]. \tag{5}$$

The Euler-Langevin Eq. (1) is a vector stochastic differential equation. Here, we shall use the Stratonovich definition [30] of a stochastic differential equation, as that definition always constitutes the mathematical idealization of the dielectric relaxation processes [17]. The Stratonovich definition allows us to apply the methods of ordinary analysis [17,30] at the transformation and solution of Eq. (1).

In the noninertial limit (or in the Debye approximation) when the inertia terms in Eq. (1) may be neglected, the angular velocity $\boldsymbol{\omega}(t)$ may be immediately obtained from Eqs. (1) and (3) as

$$\boldsymbol{\omega}(t)=\hat{\varsigma}^{-1}\{\boldsymbol{\lambda}(t)-i\hat{\mathbf{J}}V(\Omega(t),t)\} \tag{6}$$

(the validity of this approximation is discussed in Sec. IV). On using Eqs. (3) and (6), one can obtain the equation of motion of an arbitrary function $f(\alpha,\beta,\gamma)$:

$$\begin{aligned}\frac{d}{dt}f&=\dot{\alpha}\frac{\partial}{\partial\alpha}f+\dot{\beta}\frac{\partial}{\partial\beta}f+\dot{\gamma}\frac{\partial}{\partial\gamma}f\\&=(\boldsymbol{\omega}\cdot\boldsymbol{\nabla})f\\&=i[(\hat{\varsigma}^{-1}\boldsymbol{\lambda})\cdot\hat{\mathbf{J}}f]+[(\hat{\varsigma}^{-1}\hat{\mathbf{J}}V)\cdot\hat{\mathbf{J}}f].\end{aligned} \tag{7}$$

Equation (7) is a Stratonovich stochastic differential equation with a multiplicative noise term $i[(\hat{\varsigma}^{-1}\boldsymbol{\lambda})\cdot\hat{\mathbf{J}}f]$. First, one can note that for a symmetric tensor $\hat{\varsigma}^{-1}$ and for any V and f the following mathematical identity holds:

$$[(\hat{D}\hat{\mathbf{J}}V)\cdot\hat{\mathbf{J}}f]=\tfrac{1}{2}[V\boldsymbol{\nabla}_{\Omega}^{2}f+f\boldsymbol{\nabla}_{\Omega}^{2}V-\boldsymbol{\nabla}_{\Omega}^{2}(Vf)], \tag{8}$$

where the operator $\boldsymbol{\nabla}_{\Omega}^{2}$ is defined as [13]

$$\boldsymbol{\nabla}_{\Omega}^{2}=-\hat{\mathbf{J}}\cdot\hat{D}\cdot\hat{\mathbf{J}}=-\sum_{k,m=x,y,z}D_{km}\hat{J}_k\hat{J}_m$$

and $\hat{D}=kT\hat{\varsigma}^{-1}$ is the diffusion tensor. Noting Eq. (8), averaging of Eq. (7) over an ensemble of particles yields

$$\frac{d}{dt}\langle f\rangle=\langle\boldsymbol{\nabla}_{\Omega}^{2}f\rangle-\frac{1}{2kT}\langle\boldsymbol{\nabla}_{\Omega}^{2}(Vf)-V\boldsymbol{\nabla}_{\Omega}^{2}f-f\boldsymbol{\nabla}_{\Omega}^{2}V\rangle, \tag{9}$$

where the angular brackets denote ensemble averages. The first term on the right-hand side of Eq. (9) is the noise-induced drift, which is due to the averaging of $i[(\hat{\varsigma}^{1}\boldsymbol{\lambda})\cdot\hat{\mathbf{J}}f]$. The procedures of the transformation for variables and averaging of the Langevin equations have been described in detail in [16,17,31].

In dielectric relaxation, the quantities of interest are averages involving Wigner's D functions defined as [22,23]

$$D_{M,M'}^{J}(\Omega)=e^{-iM\alpha}d_{MM'}^{J}(\beta)e^{-iM'\gamma},$$

where $d_{MM'}^{J}(\beta)$ is a real function whose various explicit forms are given, for example, in Ref. [23]. For Wigner's D functions, Eq. (9) yields

$$\begin{aligned}\frac{d}{dt}\langle D_{n,m}^{j}\rangle=\langle\boldsymbol{\nabla}_{\Omega}^{2}D_{n,m}^{j}\rangle-\frac{1}{2kT}\langle\boldsymbol{\nabla}_{\Omega}^{2}(VD_{n,m}^{j})\\-V\boldsymbol{\nabla}_{\Omega}^{2}D_{n,m}^{j}-D_{n,m}^{j}\boldsymbol{\nabla}_{\Omega}^{2}V\rangle.\end{aligned} \tag{10}$$

In calculations, it is convenient to use the molecular coordinate system in which the diffusion tensor $\hat{D}$ is diagonal so that the operator $\boldsymbol{\nabla}_{\Omega}^{2}$ is simplified to [13]

$$\boldsymbol{\nabla}_{\Omega}^{2}=-(D_{xx}\hat{J}_x^2+D_{yy}\hat{J}_y^2+D_{zz}\hat{J}_z^2). \tag{11}$$

Now, one can note that the operator $\boldsymbol{\nabla}_{\Omega}^{2}$ defined by Eq. (11) can be represented as [13]

$$\begin{aligned}\boldsymbol{\nabla}_{\Omega}^{2}=-\tfrac{1}{2}\{(D_{xx}+D_{yy})\hat{\mathbf{J}}^2+[2D_{zz}-(D_{xx}+D_{yy})]\hat{J}_z^2\\+(D_{xx}-D_{yy})(\hat{J}_x^2-\hat{J}_y^2)\}.\end{aligned} \tag{12}$$

Further, on using the known properties of the angular momentum operators and D functions, viz. [23],

$$\hat{J}_x^2-\hat{J}_y^2=(\hat{J}^{+1})^2+(\hat{J}^{-1})^2,$$

$$\hat{\mathbf{J}}^2D_{n,m}^{j}(\Omega)=j(j+1)D_{n,m}^{j}(\Omega),$$

$$\hat{J}_z^2D_{n,m}^{j}(\Omega)=m^2D_{n,m}^{j}(\Omega),$$

$$\hat{J}^{\nu}D_{n,m}^{j}(\Omega)=-\sqrt{j(j+1)}C_{j,m,1,\nu}^{j,m+\nu}D_{n,m+\nu}^{j}(\Omega)\quad(\nu=\pm1)$$

($C_{j_1,l_1,j_2,l_2}^{j,l}$ are the Clebsch-Gordan coefficients [23]), one may show that

$$\begin{aligned}\boldsymbol{\nabla}_{\Omega}^{2}D_{n,m}^{j}(\Omega)=-\tfrac{1}{2}(D_{xx}+D_{yy})\{[2\Delta m^2+j(j+1)]D_{n,m}^{j}(\Omega)\\+j(j+1)\Xi[C_{j,m,1,1}^{j,m+1}C_{j,m+1,1,1}^{j,m+2}D_{n,m+2}^{j}(\Omega)\\+C_{j,m,1,-1}^{j,m-1}C_{j,m-1,1,-1}^{j,m-2}D_{n,m-2}^{j}(\Omega)]\},\end{aligned} \tag{13}$$

where

$$\begin{aligned}&C_{j,m,1,\pm1}^{j,m\pm1}C_{j,m\pm1,1,\pm1}^{j,m\pm2}\\&\quad=\frac{1}{2j(j+1)}\sqrt{[j^2-(m\pm1)^2][(j+1)^2-(m\pm1)^2]}\end{aligned}$$

and two dimensionless parameters Δ and Ξ have been introduced, viz.,

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

(for the isotropic rotational diffusion, both Δ and Ξ are equal to zero). Thus for any potential V, which may be expanded in D functions as

$$V(\Omega,t)/(kT)=\sum_{Q,S,R}\nu_{R,S,Q}(t)D_{S,Q}^{R}(\Omega), \tag{14}$$

Eq. (10) can be rearranged to yield the system of moment equations, viz.,

$$\begin{aligned}\tau_D\frac{d}{dt}\langle D^j_{n,m}\rangle(t)=&-\left\{\frac{j(j+1)}{2}+\Delta m^2\right\}\langle D^j_{n,m}\rangle(t)-\frac{j(j+1)}{2}\Xi[C^{j,m+1}_{j,m,1,1}C^{j,m+2}_{j,m+1,1,1}\langle D^j_{n,m+2}\rangle(t)\\&+C^{j,m-1}_{j,m,1,-1}C^{j,m-2}_{j,m-1,1,-1}\langle D^j_{n,m-2}\rangle(t)]+\frac{1}{4}\sum_{R,S,Q}\sum_{J=|j-R|}^{j+R}\nu_{R,S,Q}C^{J,n+S}_{j,n,R,S}\{[J(J+1)+4\Delta mQ-j(j+1)\\&-R(R+1)]C^{J,m+Q}_{j,m,R,Q}\langle D^j_{n+S,m+Q}\rangle(t)+\Xi[J(J+1)C^{J,m+Q+1}_{J,m+Q,1,1}C^{J,m+Q+2}_{J,m+Q+1,1,1}C^{J,m+Q}_{J,m,R,Q}\\&-j(j+1)C^{j,m+1}_{j,m,1,1}C^{j,m+2}_{j,m+1,1,1}C^{J,m+2+Q}_{j,m+2,R,Q}-R(R+1)C^{R,Q+1}_{R,Q,1,1}C^{R,Q+2}_{R,Q+1,1,1}C^{J,m+Q+2}_{j,m,R,Q+2}]\langle D^J_{n+S,m+Q+2}\rangle(t)\\&+\Xi[J(J+1)C^{J,m+Q-1}_{J,m+Q,1,-1}C^{J,m+Q-2}_{J,m+Q-1,1,-1}C^{J,m+Q}_{j,m,R,Q}-j(j+1)C^{j,m-1}_{j,m,1,-1}C^{j,m-2}_{j,m-1,1,-1}C^{J,m-2+Q}_{j,m-2,R,Q}\\&-R(R+1)C^{R,Q-1}_{R,Q,1,-1}C^{R,Q-2}_{R,Q-1,1,-1}C^{J,m+Q-2}_{j,m,R,Q-2}]\langle D^J_{n+S,m+Q-2}\rangle(t)\},\end{aligned}\tag{15}$$

where

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

and the known relation [23]

$$D^{j_1}_{l_1,m_1}D^{j_2}_{l_2,m_2}=\sum_{j=|j_1-j_2|}^{j_1+j_2}C^{j,l_1+l_2}_{j_1,l_1,j_2,l_2}C^{j,m_1+m_2}_{j_1,m_1,j_2,m_2}D^{j}_{l_1+l_2,m_1+m_2}$$

has been used. Equation (15) is a general result, which may be applied to evaluate all types of the nonlinear responses (transient, ac stationary, and nonstationary) of polar and polarizable asymmetric top molecules as it does not use the assumption of the low field strengths. Another advantage of the present approach is that it is not based on the quantum theory of a free asymmetric rotor (as that of Favro [13] and others [24–26,32,33]) so that many results obtained in [13,24–26,32,33] in the context of the anisotropic rotational diffusion model may be rederived from Eq. (15) in a much simpler way than before (see Appendix A, where the linear dielectric response for asymmetric top molecules is evaluated).

Equation (15) contains three phenomenological constants—the three diagonal components of the diffusion tensor, viz., D_{xx}, D_{yy}, and D_{zz}. The values of D_{ii} may be estimated either in the context of the so-called hydrodynamic approach [12,32], when the components of the diffusion tensor depend only on the shape of the particle (see Sec. IV), or in terms of microscopic molecular parameters [33]:

$$D_{ii}=kT/\varsigma_{ii}=(\tau_J)_i kT/I_i,\tag{16}$$

where I_i is the principal moment of inertia about the i axis and $(\tau_J)_i$ is the angular velocity correlation time about that axis. The components of the rotational friction tensor ς_{ii} may be related to the intermolecular potential function of the asymmetric rotor [33]

$$\varsigma_{ii}=\frac{2I_i}{\pi}\left\langle\frac{\partial^2}{\partial\theta_i^2}V(\mathbf{R}^N)\right\rangle,\tag{17}$$

where $V(\mathbf{R}^N)$ is the potential energy of N molecules whose positions and orientations are specified by the $6N$-dimensional vector $\mathbf{R}^N$ and θ_i is the angle of rotation about the i axis. Unfortunately, it is very difficult here to evaluate $(\tau_J)_i=\varsigma_{ii}/I_i$ for a model system, however they can be measured experimentally using nuclear-magnetic-resonance techniques [33,34].

On supposing that the electric field $\mathbf{E}$ is directed along the Z axis of the laboratory coordinate system, the polarization $P_Z(t)$ is defined as

$$P_Z(t)=N_0\langle\mu_Z\rangle(t),\tag{18}$$

where N_0 is the concentration of dipolar molecules and the μ_Z is given by [24]

$$\mu_Z(\Omega)=\mu\sum_{p=-1}^{1}(-1)^p u^{(-p)}D^1_{0,p}(\Omega).\tag{19}$$

Here

$$u^{(\pm 1)}=\mp\frac{1}{\sqrt{2}}(u_x\pm iu_y),\quad u^{(0)}=u_z$$

are the irreducible spherical tensor components of the first rank [23], and u_x, u_y, and u_z are the components of a unit vector $\mathbf{u}$ in the direction of $\boldsymbol{\mu}$. Due to the cylindrical symmetry about the Z axis, the moments $\langle D^j_{n,m}\rangle(t)$ with $n=0$ only are required in the calculation of $P_Z(t)$ (as well as the electro-optical birefringence) [25,26]. Hence, one can always insert in Eqs. (14) and (15) the indices $n,S\equiv 0$ so that from a mathematical viewpoint, Eq. (15) becomes a recurrence equation, where only two indices vary. Moreover, the form of Eq. (15) for the longitudinal nonlinear response for *asymmetric tops* becomes very similar to that which appears in evaluating the nonlinear response of *symmetric tops* when the external field has an arbitrary direction [16,20]. A general method of solution of such recurrence equations in terms of matrix continued fractions has been recently developed in Refs. [35–37] and applied to the evaluation of the nonlinear dielectric response in [16,20]. Thus, the problem of the evaluation of the nonlinear response of asymmetric top molecules may be solved just as in [16,20] using matrix continued fractions. Indeed, on using the results of [35–37], one can show that Eq. (15) may be transformed into a matrix three-term differential-recurrence equation

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

$$(n = 1,2,3, \dots), \tag{20}$$

where the elements of the column vector $\mathbf{C}_n(t)$ and of the matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n^-$ are determined by Eq. (15). Equation (20) can be solved in terms of matrix continued fractions for all kinds of nonlinear response (transient, ac stationary, nonstationary) [16,17,20].

The recurrence Eq. (15) for the expectation values of Wigner's D functions can also be obtained from the corresponding Smoluchowski equation for the distribution function $W(\Omega,t)$ of the orientations of asymmetric top molecules, which is [13]

$$\frac{\partial}{\partial t} W = -\hat{\mathbf{J}} \cdot \hat{D} \cdot \left(\hat{\mathbf{J}} W + \frac{1}{kT} W \hat{\mathbf{J}} V \right). \tag{21}$$

As shown in Ref. [31], both approaches are equivalent and yield the same results. However, the Langevin equation approach has, in our opinion, the advantage that it allows one to derive Eq. (15) in a much simpler manner.

For the purpose of illustration, we calculate here the nonlinear response for rigid rodlike molecules in superimposed external ac and strong dc bias electric fields. As far as spherical and symmetric top molecules with the dipole moment $\boldsymbol{\mu}$ directed along the axis of symmetry are concerned, this problem has already been treated in many papers, see, e.g., [15,16,19,28]. However, as mentioned in the Introduction, these results are not applicable to asymmetric top molecules [10].

III. NONLINEAR RESPONSE IN SUPERIMPOSED ac AND STRONG dc BIAS FIELDS: PERTURBATION SOLUTION

In what follows, let us suppose, for simplicity, that the diffusion tensor $\hat{D}$ has only two distinct components $D_{xx} = D_{yy} = D_\perp$ and $D_{zz} = D_\parallel$. This approximation is reasonable for rodlike molecules, where $D_{xx} \approx D_{yy}$ and $D_\parallel$ and $D_\perp$ are the rotational diffusion coefficients about the long and short axes of the molecule, accordingly. Furthermore, let us suppose that the molecules are subjected to superimposed external electric ac $\mathbf{E}_1(t)$ and strong dc bias $\mathbf{E}_0$ fields (both directed along the Z axis) and consider an ensemble of rigid *nonpolarizable* polar molecules, where the dipole vector $\boldsymbol{\mu}$ is oriented at an angle Θ to the direction of the long axis of the molecule (see Fig. 1). Here, the polarizability effects are ignored (equations, which take into account these effects, are given in Appendix B). Without loss of generality, for a rodlike molecule, the molecular coordinate system can always be chosenso that $u_y = 0$, from which $u_x = \sin\Theta, u_z = \cos\Theta$ in Eq. (19). The potential energy of the molecule is then given by

$$\frac{V}{kT} = \sum_{Q=-1}^{1} \nu_{1,0,Q} D_{0,Q}^1, \tag{22}$$

where

$$\nu_{1,0,0} = -\cos\Theta[\xi(t) + \xi_0], \quad \nu_{1,0,\pm 1} = \pm \sin\Theta[\xi(t) + \xi_0]/\sqrt{2}$$

and

$$\xi(t) = \mu E(t)/(kT) \quad \text{and} \quad \xi_0 = \mu E_0/(kT).$$

Now, $\tau_D = (2D_\perp)^{-1}$, $\Delta = [(D_\parallel / D_\perp) - 1]/2$, and $\Xi = 0$ so that Eq. (15) is considerably simplified to yield

$$\begin{aligned}\tau_D \frac{d}{dt}\langle D_{n,m}^j \rangle(t) = {} & -[\Delta m^2 + j(j+1)/2]\langle D_{n,m}^j \rangle(t) \\ & -\frac{1}{4}\sum_{Q=-1}^{1} \sum_{J=|j-1|}^{j+1} \nu_{1,0,Q} C_{j,n,1,0}^{J,n} C_{j,m,1,Q}^{J,m+Q} \\ & \times [j(j+1) + 2 - J(J+1) - 4\Delta m Q] \\ & \times \langle D_{n,m+Q}^J \rangle(t),\end{aligned}$$

which for $n = 0$ may be written as

$$\begin{aligned}\tau_D \frac{d}{dt}\langle D_{0,m}^j \rangle(t) + \left[\frac{j(j+1)}{2} + m^2\Delta\right]\langle D_{0,m}^j \rangle(t) \\ = \frac{[\xi(t) + \xi_0]\cos\Theta}{2(2j+1)} [(j+1)\sqrt{j^2 - m^2}\langle D_{0,m}^{j-1}\rangle(t) \\ - j\sqrt{(j+1)^2 - m^2}\langle D_{0,m}^{j+1}\rangle(t)] + \frac{[\xi(t) + \xi_0]\sin\Theta}{4(2j+1)} \\ \times [(j + 2\Delta m)\sqrt{(j+m+1)(j+m+2)}\langle D_{0,m+1}^{j+1}\rangle(t) \\ - (j - 2\Delta m)\sqrt{(j-m+1)(j-m+2)}\langle D_{0,m-1}^{j+1}\rangle(t) \\ + (j+1-2\Delta m)\sqrt{(j-m-1)(j-m)}\langle D_{0,m+1}^{j-1}\rangle(t) \\ - (j+1+2\Delta m)\sqrt{(j+m-1)(j+m)}\langle D_{0,m-1}^{j-1}\rangle(t)].\end{aligned} \tag{23}$$

Insofar as values of the field parameters ξ_0 and ξ are very small ($\ll 1$) for the majority of polar molecules even at the field strengths $\sim 10^7$ V/m, one may apply perturbation theory in order to calculate the nonlinear response. Here, we shall restrict ourselves to the ac response nonlinear in the dc bias field ξ_0 (up to third order) and linear in the ac field $\xi_1 e^{i\omega t}$ (higher-order terms may be calculated in a similar manner [15]). Now, one can obtain from Eq. (23) equations for

$\langle D^1_{0,0}\rangle$ and $\langle D^1_{0,-1}\rangle - \langle D^1_{0,1}\rangle$, which are necessary to evaluate the nonlinear response from Eq. (18), viz.,

$$\tau_D \frac{d}{dt}\langle D^1_{0,0}\rangle(t) + \langle D^t_{0,0}\rangle(t)$$

$$= [\xi(t)+\xi_0]\left\{ \frac{\cos\Theta}{3}[1-\langle D^2_{0,0}\rangle(t)] - \frac{\sin\Theta}{2\sqrt{6}}[\langle D^2_{0,-1}\rangle(t) - \langle D^2_{0,1}\rangle(t)] \right\}, \qquad (24)$$

$$\tau_D \frac{d}{dt}[\langle D^1_{0,-1}\rangle(t) - \langle D^1_{0,1}\rangle(t)] + (1+\Delta)[\langle D^1_{0,-1}\rangle(t) - \langle D^1_{0,1}\rangle(t)]$$

$$= [\xi(t)+\xi_0]\left\{ \frac{\sqrt{2}(1+\Delta)\sin\Theta}{3} + \frac{(1-2\Delta)\sin\Theta}{3\sqrt{2}} \times \langle D^2_{0,0}\rangle(t) - \frac{\cos\Theta}{2\sqrt{3}}[\langle D^2_{0,-1}\rangle(t) - \langle D^2_{0,1}\rangle(t)] - \frac{(1+2\Delta)\sin\Theta}{2\sqrt{3}}[\langle D^2_{0,-2}\rangle(t) + \langle D^2_{0,2}\rangle(t)] \right\} \qquad (25)$$

and one can seek a solution in the form

$$\langle D^1_{0,0}\rangle(t) \approx \frac{\cos\Theta}{3}[s_0(\xi_0) + \xi_1 e^{i\omega t} x_0(\xi_0,\omega')], \qquad (26)$$

$$\langle D^1_{0,-1}\rangle(t) - \langle D^1_{0,1}\rangle(t) \approx \frac{\sin\Theta}{3\sqrt{2}}[2s_0(\xi_0) + \xi_1 e^{i\omega t} x_1(\xi_0,\omega')], \qquad (27)$$

where $s_0(\xi_0) = \xi_0(1-\xi_0^2/15)$ and $\omega' = \omega\tau_D$. Further, one can evaluate $\langle D^2_{0,0}\rangle(t)$, $\langle D^2_{0,-1}\rangle(t) - \langle D^2_{0,1}\rangle(t)$, and $\langle D^2_{0,-2}\rangle(t) + \langle D^2_{0,2}\rangle(t)$ from Eq. (23) in the linear (in ξ_1) approximation, viz.,

$$\langle D^2_{0,-2}(t)\rangle(t) + \langle D^2_{0,2}(t)\rangle(t) \approx \frac{\xi_0\sin^2\Theta}{5\sqrt{6}}\left\{ \xi_0 + \frac{\xi_1 e^{i\omega t}(3+4\Delta)}{(3+4\Delta+i\omega')}[1+\tfrac{1}{2}x_1(\xi_0,\omega')] \right\}, \qquad (28)$$

$$\langle D^2_{0,-1}(t)\rangle(t) - \langle D^2_{0,1}(t)\rangle(t) \approx \frac{\xi_0\sin 2\Theta}{5\sqrt{6}}\left\{ \xi_0 + \frac{\xi_1 e^{i\omega t}(3+\Delta)}{(3+\Delta+i\omega')} \times \left[1 + \frac{(6+4\Delta)x_0(\xi_0,\omega') + 3x_1(\xi_0,\omega')}{4(3+\Delta)} \right] \right\}, \qquad (29)$$

$$\langle D^2_{0,0}(t)\rangle(t) \approx \frac{\xi_0(1+3\cos 2\Theta)}{60}\left\{ \xi_0 + \frac{3\xi_1 e^{i\omega t}}{(3+i\omega')} \times \left[1 + \frac{4x_0(\xi_0,\omega')\cos^2\Theta - x_1(\xi_0,\omega')\sin^2\Theta}{(1+3\cos 2\Theta)} \right] \right\}. \qquad (30)$$

Having determined x_0 and x_1 from Eqs. (24)–(30), one can calculate the electric polarization from Eq. (18) and, hence, the complex nonlinear dielectric permittivity $\varepsilon_{\mathrm{nonlin}}(\omega,\xi_0)$, viz.,

$$\varepsilon_{\mathrm{nonlin}}(\omega,\xi_0) - \varepsilon_\infty \propto \cos^2\Theta\, x_0(\xi_0,\omega') + \sin^2\Theta\, x_1(\xi_0,\omega')/2$$

and the nonlinear dielectric increment $\delta\varepsilon = \delta\varepsilon' + i\delta\varepsilon''$, i.e., the difference $\varepsilon_{\mathrm{nonlin}}(\omega,\xi_0) - \varepsilon_{\mathrm{lin}}(\omega)$ between the nonlinear, $\varepsilon_{\mathrm{nonlin}}(\omega,\xi_0)$, and linear, $\varepsilon_{\mathrm{lin}}(\omega) = \varepsilon_{\mathrm{nonlin}}(\omega,0)$, dielectric permittivities. The increment $\delta\varepsilon$ can be written as

$$\delta\varepsilon = A(\varepsilon_s,\varepsilon_\infty)F(\omega',\xi_0), \qquad (31)$$

where

$$F(\omega',\xi_0) = -\frac{\xi_0^2}{30}\left\{ \frac{\cos^2\Theta}{1+i\omega'}\left[\frac{2}{3} - \frac{2(1+\Delta)+i\omega'}{(3+i\omega')(1+\Delta+i\omega')} + \frac{\sin^2\Theta}{3+\Delta+i\omega'}\left(3+\Delta + \frac{2(1+\Delta)(3+\Delta)+(6+5\Delta)i\omega'}{2(1+i\omega')(1+\Delta+i\omega')} \right) + \frac{\cos^2\Theta}{3+i\omega'}\left(3 + \frac{3(1+\Delta)+(3+\Delta)i\omega'}{(1+i\omega')(1+\Delta+i\omega')} \right) \right] + \frac{\sin^2\Theta}{2(1+\Delta+i\omega')}\left[\frac{(1-2\Delta)(6+i\omega')}{3(3+i\omega')} + \cos^2\Theta\left(\frac{3(1+\Delta)}{(3+\Delta+i\omega')(1+\Delta+i\omega')} + \frac{2(2\Delta-1)}{(1+i\omega')(3+i\omega')} - \frac{(1-2\Delta)(6+i\omega')}{(3+i\omega')} + \frac{3+2\Delta}{(1+i\omega')(3+\Delta+i\omega')} + \frac{2(6+2\Delta+i\omega')}{(3+\Delta+i\omega')} \right) + \sin^2\Theta\left(\frac{(1+\Delta)(1-2\Delta)}{(1+\Delta+i\omega')(3+i\omega')} + \frac{(1+\Delta)(1+2\Delta)(3+4\Delta)}{(1+\Delta+i\omega')(3+4\Delta+i\omega')} + \frac{(1+2\Delta)(6+8\Delta+i\omega')}{(3+4\Delta+i\omega')} \right) \right] \right\} \qquad (32)$$

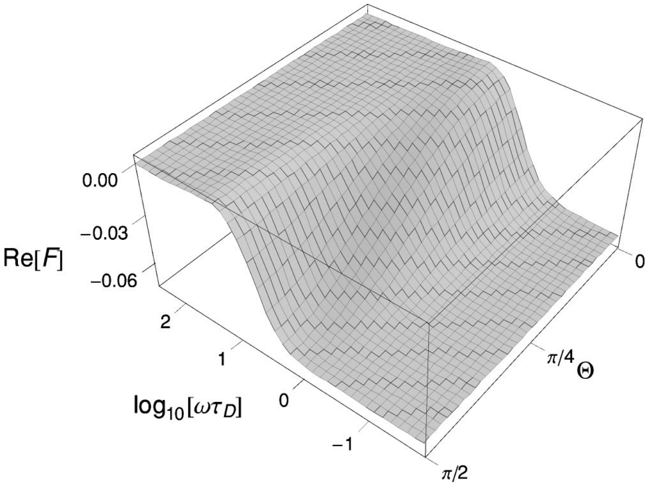

FIG. 2. Re[F] as a function of $\log_{10}(\omega\tau_D)$ and Θ for $\Delta=5$ and $\xi_0=1$.

and the function $A(\varepsilon_s,\varepsilon_\infty)$ takes into account the internal field effects; this function depends on the model of the local field used (appropriate equations for $A(\varepsilon_s,\varepsilon_\infty)$ are given, e.g., in Ref. [10]; the internal field problem for nonlinear dielectrics is discussed, e.g., in Refs. [38] and [39]). For $\Theta=0$ (symmetric top) or $\Delta=0$ (isotropic diffusion), Eq. (32) reduces to the corresponding result of Coffey and Paranjape [28]:

$$F(\omega',\xi_0)\to-\xi_0^2\frac{1+(1+i\omega')(2+i\omega'/3)}{45(1+i\omega')^2(1+i\omega'/3)}. \tag{33}$$

The principal difference between Eqs. (32) and (33) is that Eq. (32) takes into account the contribution of the rotation about the long molecular axis to $\delta\varepsilon$.

IV. RESULTS AND DISCUSSION

The real and imaginary parts of $F(\omega\tau_D,\xi_0)$ [Eq. (32)] as functions of $\log_{10}(\omega\tau_D)$ and of the angle Θ are illustrated by surface plots in Figs. 2 and 3. In Figs. 4 and 5, the real and imaginary parts of $F(\omega\tau_D,\xi_0)$ as functions of $\log_{10}(\omega\tau_D)$ and of Δ are shown. Apparently, the spectra of $F(\omega\tau_D,\xi_0)$ strongly depend on both Θ and Δ because in the anisotropic diffusion ($\Delta\neq0$) the rotation about the long molecular axis contributes to the spectra at $\Theta\neq0°$. Here, five modes with characteristic times τ_D, $\tau_D/3$, $\tau_D/(1+\Delta)$, $\tau_D/(3+\Delta)$, and $\tau_D/(3+4\Delta)$ take part in the nonlinear dielectric relaxation process [the modes characterized by the relaxation times τ_D, $\tau_D/3$, and $\tau_D/(1+\Delta)$, $\tau_D/(3+\Delta)$, and $\tau_D/(3+4\Delta)$ are due to molecular rotation about the short and long molecular axes, respectively].

In order to test the theory, experimental and theoretical dielectric increments $\delta\varepsilon$ of dilute solutions of mesogenic 10-TPEB molecules ($C_{10}H_{21}$—$\varnothing$—$\varnothing$—CH_2—CH_2—$\varnothing$—N═C═S, where $\varnothing=C_6H_4$) in benzene were compared. The spectra of $\delta\varepsilon$ were measured in superimposed strong dc (1.1×10^7 V/m) and small (≈100 V/m) ac electric fields in Ref. [10]. For the 10-TPEB molecule, the angle Θ is markedly different from zero, viz., $\Theta=42°\pm2°$ [10]. In the fitting, the experimental value of the relaxation time $\tau_D=8.57\times10^{-10}$ s [10] has been used so that the only adjustable parameter was Δ. The least mean-squares fitting procedure yields $\Delta\approx3.85$. The comparison of the real and imaginary parts of the experimental and theoretical $\delta\varepsilon$ and of the nonlinear Cole-Cole plot for a dilute solution of 10-TPEB molecules in benzene at 15 °C is shown in Figs. 6 and 7, respectively. It appears that the theory correctly describes the shape of the observed spectra; here, five modes with different characteristic frequencies (due to molecular rotation about the long and short molecular axes) contribute to the spectra. Moreover, the calculation demonstrates that the theory also explains the temperature dependence of the nonlinear dielectric decrement $\delta\varepsilon$: it describes the nonlinear spectra measured at 6 and 25 °C in Ref. [10] for the same value of Δ.

It is of interest to compare the value of Δ so obtained with that estimated in the hydrodynamic limit [12,32]. For long rods ($L\gg R$, where L and R are the half-length and radius of a rod), the hydrodynamic theory yields

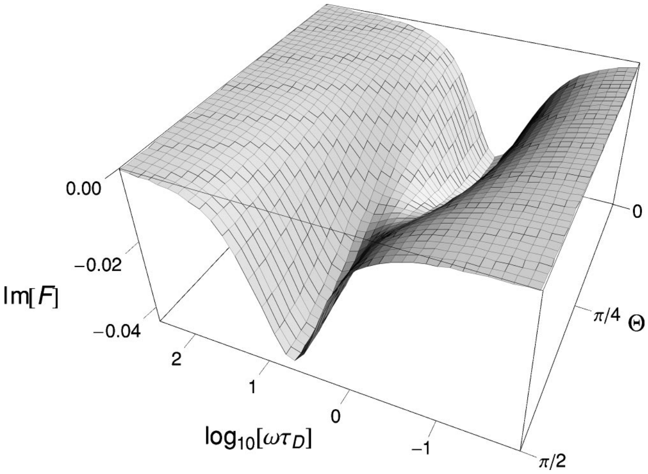

FIG. 3. Im[F] as a function of $\log_{10}(\omega\tau_D)$ and Θ for $\Delta=5$ and $\xi_0=1$.

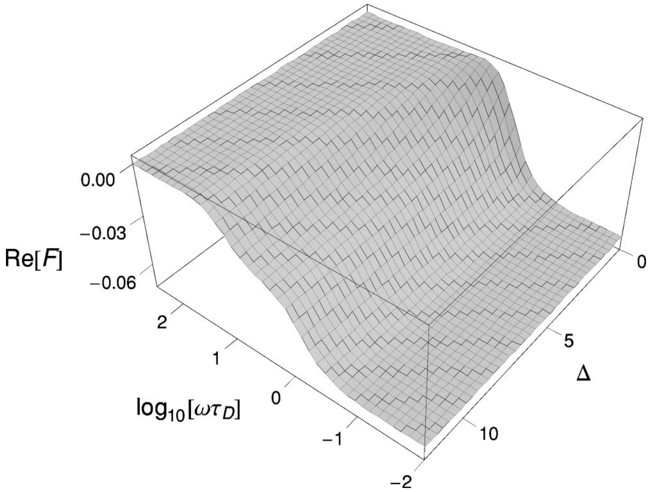

FIG. 4. Re[F] as a function of $\log_{10}(\omega\tau_D)$ and Δ for $\Theta=\pi/4$ and $\xi_0=1$.

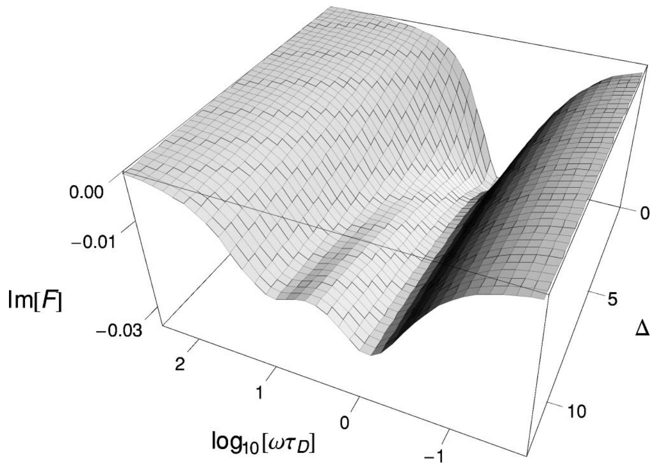

FIG. 5. Im[F] as a function of $\log_{10}(\omega\tau_D)$ and Δ for $\Theta=\pi/4$ and $\xi_0=1$.

$$\Delta=\frac{x^2}{4\ln(2x)}-\frac{1}{2}. \tag{34}$$

Here $x=L/R$ and equations for $D_\parallel$ and $D_\perp$ from Ref. [40] have been used in order to obtain Eq. (34). The value $\Delta\approx3.85$ corresponds to a shape parameter $x\approx6.7$ in Eq. (34) and reasonably characterizes the geometrical structure of the 10-TPEB molecule [10].

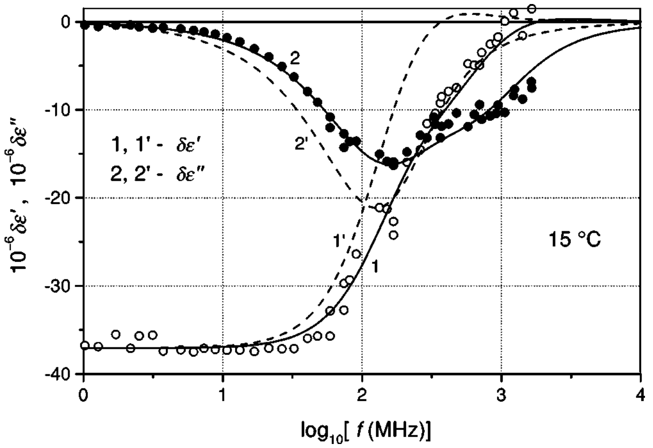

FIG. 6. Nonlinear dielectric spectra $\delta\varepsilon(f)$ $(f=\omega/2\pi)$ of a dilute solution of 10-TPEB molecules ($C_{10}H_{21}$—∅—∅—CH_2—CH_2—∅—N═C═S, where ∅ $=C_6H_6$) in benzene at 15 °C. Solid and open circles are the experimental data from Ref. [10]; solid lines are the best fit from Eq. (32) at $\Delta=3.85$ ($\Theta=42°$ [10]); dashed lines are Coffey-Paranjape, Eq. (33).

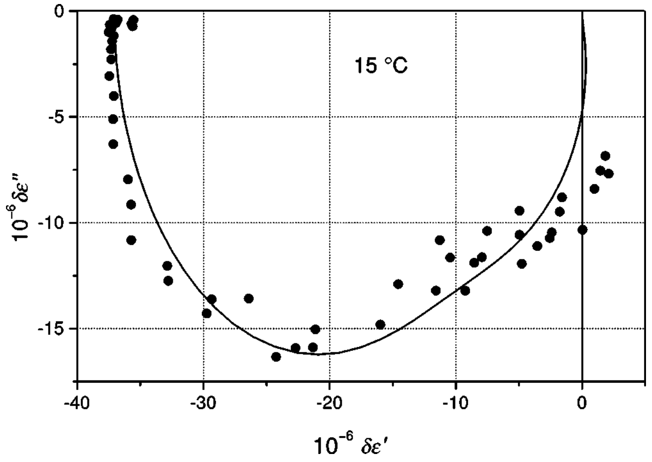

FIG. 7. Nonlinear Cole-Cole plot for a dilute solution of 10-TPEB molecules in benzene at 15 °C. Solid circles are the experimental data from Ref. [10]; solid line is Eq. (32).

In evaluating the nonlinear response in the context of the noninertial rotational diffusion model, we have ignored (i) quantum effects, (ii) dipole-dipole interactions, and (iii) the inertia of the molecules. The condition (i) means that the results of our calculations for weak fields are applicable to the system, where $\eta_i\hbar/I_i\ll1$ [$\hbar$ is the Planck constant and $\eta_i=(I_i/2kT)^{1/2}$ is a characteristic time of the thermal molecular rotation]. In a strong field $\mathbf{E}$, where the characteristic frequency of the system is $\omega_L=(\mu E/I_i)^{1/2}$, the quasiclassical condition can be written in the form $\hbar/(I_i\omega_L)\ll1$. The above inequalities break down in liquids and solutions only for the lightest polar molecules such as HF and HCl, where quantum effects were indeed observed [41]. The assumption (ii) reflects the fact that interparticle (dipole-dipole) correlations are neglected in the Langevin Eq. (1), which is only valid in the zero order of the small parameter $\mu^2N_0/kT\ll1$. The last inequality is satisfied at room temperatures and for dipole moments ~1 D up to a concentration of 10^{21} cm^{-3}. One may expect, however, that the qualitative behavior of the nonlinear response will be similar at higher concentrations of dipoles. The noninertial approximation [assumption (iii)], i.e., $I_i\omega/\varsigma_{ii}\ll1$, is fulfilled in the low-frequency region under consideration (<10 GHz) for the majority of molecules in liquid solutions. The inclusion of the inertial effects causes the theory to be much more complicated as one then needs to solve the inertial Euler-Langevin equation (1) (the differential-recurrence equations will involve six indices in that case). However, in the low field strength limit, the appropriate linear dielectric relaxation theory for asymmetric top molecules has already been developed (see, e.g., [14,42–47]) so that the task of developing the corresponding nonlinear-response theory remains.

To conclude, in the present paper, the moment system [Eq. (15)] governing the kinetics of the polarization of an assembly of asymmetric top molecules in high electric fields has been derived. Equation (15) is a general result which may be used to evaluate various types of nonlinear responses (such as transient, ac stationary responses, etc.) for arbitrary polar and polarizable asymmetric top molecules in strong external fields. The advantage of the approach we have developed is that it does not use the assumption of low field strengths. On solving this system for rodlike polar nonpolarizable molecules, when the dipole vector of the molecule $\boldsymbol{\mu}$ is directed at an arbitrary angle Θ to the long molecular axis, an analytical equation for the nonlinear response in superimposed ac and strong dc bias fields has been derived (which is of importance from an experimental point of view [7–10]). For symmetric top molecules, when $\boldsymbol{\mu}$ is directed along the axis of symmetry of the molecule, the result for the nonlinear dielectric increment [Eq. (32)] reduces to that of Coffey and Paranjape [28]. It was shown that the results obtained are in agreement with experimental data. Our approach can also be used for the evaluation of the dynamic Kerr effect, where the quantities of interest are $\langle D^2_{0,m}\rangle(t)$ [15,24–26]. Moreover, it can be applied (with small modifications) to the calculation of the *nonlinear magnetic* response of liquid 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) [17,48–50]. Thus the approach we have developed provides a useful basis for future studies of the nonlinear response of various physical systems of Brownian asymmetric top particles. Further applications of it will be given elsewhere.

ACKNOWLEDGMENTS

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APPENDIX A: EVALUATION OF THE LINEAR RESPONSE FROM EQ. (15)

Here, we demonstrate how the linear-response theory results for noninteracting asymmetric top molecules can readily be obtained from Eq. (15). Let us suppose that an external spatially uniform small dc electric field **E** ($\xi = \mu E/kT \ll 1$) was applied to the system of asymmetric top molecules at $t=-\infty$ in the direction of the Z axis of the laboratory coordinate system and at time $t=0$ the field has been switched off. We are interested in the decay of the polarization $P_Z(t)$ of the system of the molecules starting at $t=0$ from the equilibrium state I with the Bolzmann distribution function $W_{\mathrm{I}}(\Omega)=C^{-1}\exp[\mu_Z(\Omega)E/(kT)]$ [where C is a normalizing constant and μ_Z is given by Eq. (19)] to the equilibrium state II with the uniform distribution function $W_{\mathrm{II}}(\Omega)=1/8\pi^2$, which is reached at $t\to\infty$.

The relaxation of $P_Z(t)$ given by Eqs. (18) and (19) is completely determined by $\langle D^1_{0,0}\rangle(t)$, $\langle D^1_{0,-1}\rangle(t)$, and $\langle D^1_{0,1}\rangle(t)$. Equations of motion for these functions at $t\geqslant 0$ can be obtained from Eq. (15) at $j=1$, $n=0$, and $m=0,\pm 1$. One has

$$\tau_D \frac{d}{dt}\langle D^1_{0,0}\rangle(t)+\langle D^1_{0,0}\rangle(t)=0, \tag{A1}$$

$$\tau_D \frac{d}{dt}\langle D^1_{0,\pm 1}\rangle(t)+(1+\Delta)\langle D^1_{0,\pm 1}\rangle(t)=-(\Xi/2)\langle D^1_{0,\mp 1}\rangle(t). \tag{A2}$$

The solutions of Eqs. (A1) and (A2) are

$$\langle D^1_{0,0}\rangle(t)=\langle D^1_{0,0}\rangle(0)e^{-(D_{xx}+D_{yy})t}, \tag{A3}$$

$$\langle D^1_{0,-1}\rangle(t)-\langle D^1_{0,1}\rangle(t)=[\langle D^1_{0,-1}\rangle(0)-\langle D^1_{0,1}\rangle(0)] \times e^{-(D_{zz}+D_{yy})t}, \tag{A4}$$

$$\langle D^1_{0,-1}\rangle(t)+\langle D^1_{0,1}\rangle(t)=[\langle D^1_{0,-1}\rangle(0)+\langle D^1_{0,1}\rangle(0)] \times e^{-(D_{zz}+D_{xx})t}, \tag{A5}$$

where the relations

$$\tau_D^{-1}=D_{xx}+D_{yy}, \quad \tau_D^{-1}(1+\Delta-\Xi/2)=D_{zz}+D_{yy}, \quad \tau_D^{-1}(1+\Delta+\Xi/2)=D_{zz}+D_{xx} \tag{A6}$$

have been taken into account. The initial values $\langle D^1_{0,p}\rangle(0)$ in Eqs. (A3)–(A5) are determined from the following equation:

$$\langle D^1_{0,p}\rangle(0)=\int D^1_{0,p}(\Omega)W_1(\Omega)d\Omega$$

in the low field strength limit $[\mu E/(kT)\ll 1]$ so that

$$\langle D^1_{0,0}\rangle(0)=\xi u_z/3+o(\xi),$$
$$\langle D^1_{0,\pm 1}\rangle(0)=\mp\xi(u_x\pm i u_y)/(3\sqrt{2})+o(\xi). \tag{A7}$$

Here, the known properties of D functions [23], viz.,

$$\int D^{j*}_{n,m}(\Omega)D^{j'}_{n',m'}(\Omega)d\Omega=\frac{8\pi^2}{2j+1}\delta_{j,j'}\delta_{n,n'}\delta_{m,m'},$$

$$D^{j*}_{n,m}(\Omega)=(-1)^{n-m}D^{j}_{-n,-m}(\Omega)$$

($d\Omega=\sin\beta\, d\beta\, d\alpha\, d\gamma$ and the asterisk denotes the complex conjugate), have been used. Now one has from Eqs. (16) and (A3)–(A7)

$$P_Z(t)=E\frac{\mu^2 N_0}{3kT}\{u_z^2 e^{-(D_{xx}+D_{yy})t}+u_y^2 e^{-(D_{xx}+D_{zz})t} + u_x^2 e^{-(D_{zz}+D_{yy})t}\}, \tag{A8}$$

which is the result of Perrin [12]. Having determined the $P_Z(t)$, one can also evaluate other dielectric parameters such as the complex dielectric susceptibility and permittivity. We remark that the quantum theory of a rigid asymmetric rotor (which was the basis of the previous theoretical approach [13,24–26]) has not been used to derive Eq. (A8).

APPENDIX B: MOMENT SYSTEM FOR RODLIKE POLARIZABLE MOLECULES

In order to take into account polarizability effects, it is sufficient to derive moment equations for *nonpolar polarizable* molecules only as the contribution of the polarizability term in Eq. (2) is additive. The potential energy V of a nonpolar polarizable molecule in the external electric field **E** applied in the direction of the Z axis of the laboratory coordinate system is given by [24]

$$\frac{V}{kT}=\sum_{Q=-2}^{2}\nu_{2,0,Q}D^2_{0,Q}, \tag{B1}$$

where

$$\nu_{2,0,Q} = -\frac{E^2}{3kT}(-1)^Q \alpha^{(-Q)} \tag{B2}$$

and

$$\alpha^{\pm(2)} = (3/8)^{1/2}(\alpha_{xx} - \alpha_{yy} \pm 2i\alpha_{xy}),$$

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

are the irreducible spherical tensor components of the second rank, which consist of the components α_{mn} of the electrical polarizability tensor $\hat{\alpha}$. Thus Eqs. (15), (B1), and (B2) yield the 25-term recurrence equation, viz.,

$$\begin{aligned}
\tau_D \frac{d}{dt}\langle D^j_{n,m}\rangle(t) &= -\left(\frac{j(j+1)}{2} + \Delta m^2\right)\langle D^j_{n,m}\rangle(t) \\
&\quad - \frac{1}{4}\sum_{Q=-2}^{2}\ \sum_{J=|j-2|}^{j+2} \nu_{2,0,Q}[j(j+1) + 6 - J(J+1) \\
&\quad - 4mQ\Delta] C^{J,n}_{j,n,2,0} C^{J,m+Q}_{j,m,2,Q}\langle D^J_{n,m+Q}\rangle(t).
\end{aligned} \tag{B3}$$

For $n = 0$, Eq. (B3) can be presented as the 15-term recurrence equation:

$$\tau_D \frac{d}{dt}\langle D^j_{0,m}\rangle(t) = \sum_{q,L=-2}^{2} e^{L,q}_{j,m}\langle D^{j+L}_{0,m+q}\rangle(t), \tag{B4}$$

where

$$e^{0,0}_{j,m} = -\frac{j(j+1)}{2} - m^2\Delta + \frac{E^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})}{4kT}\frac{[j(j+1) - 3m^2]}{(2j-1)(2j+3)},$$

$$e^{0,\pm1}_{j,m} = \mp\frac{E^2(\alpha_{xz} \mp i\alpha_{yz})(1 \pm 2m)(3 \mp 2\Delta m)}{4kT(2j-1)(2j+3)} \times \sqrt{(j+1\pm m)(j \mp m)},$$

$$e^{0,\pm2}_{j,m} = -\frac{E^2(\alpha_{xx} - \alpha_{yy} \mp 2i\alpha_{xy})(3 \mp 4m\Delta)}{8kT(2j-1)(2j+3)} \times \sqrt{[j^2 - (m\pm1)^2][(j+1)^2 - (m\pm1)^2]},$$

$$e^{\pm2,0}_{j,m} = \mp\frac{E^2(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})}{8kT} \times \frac{(2j+1\mp1)\sqrt{[(j\pm1)^2 - m^2][(j+1\pm1)^2 - m^2]}}{(2j\pm1)(2j+2\pm1)},$$

$$e^{2,\pm1}_{j,m} = \pm\frac{E^2(\alpha_{xz} \mp i\alpha_{yz})(j \pm m\Delta)}{2kT(2j+1)(2j+3)} \times \sqrt{[(j+1)^2 - m^2](j+2\pm m)(j+3\pm m)},$$

$$e^{-2,\pm1}_{j,m} = \pm\frac{E^2(\alpha_{xz} \mp i\alpha_{yz})(j+1 \mp m\Delta)}{2kT(2j+1)(2j-1)} \times \sqrt{(j^2 - m^2)(j-2\mp m)(j-1\mp m)},$$

$$e^{-2,\pm2}_{j,m} = \frac{E^2(\alpha_{xx} - \alpha_{yy} \mp 2i\alpha_{xy})(j+1 \mp 2m\Delta)}{8kT(2j-1)(2j+1)} \times \sqrt{[(j-1\mp m)^2 - 1][(j-2\mp m)^2 - 1]},$$

$$e^{2,\pm2}_{j,m} = -\frac{E^2(\alpha_{xx} - \alpha_{yy} \mp 2i\alpha_{xy})(j \pm 2m\Delta)}{8kT(2j+3)(2j+1)} \times \sqrt{[(j+2\pm m)^2 - 1][(j+3\pm m)^2 - 1]},$$

$$e^{1,\pm1}_{j,n,m} = e^{-1,\pm1}_{j,n,m} = e^{1,\pm2}_{j,m} = e^{-1,\pm2}_{j,m} = e^{\pm1,0}_{j,m} = 0.$$

Equation (B4) is similar to that solved exactly in Ref. [20] in terms of matrix continued fractions, therefore the approach developed in [20] may also be applied with small modifications to the solution of Eq. (B4).

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