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SOLUTION OF THE SMOLUCHOWSKI EQUATION FOR ROTATIONAL DIFFUSION OF RIGID DIPOLAR AND SYMMETRIC-TOP MOLECULES IN DILUTE SOLVENTS*

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The approximate method of solving the Smoluchowski equation for rotational diffusion of noninteracting rigid, dipolar and symmetric-top molecules under the action of the high intensity electric fields, within Kielich's theory, is proposed. Employing the properties of the spherical harmonic functions and quantum-mechanical angular momentum operators, this paper extends the Kielich classical theory of nonlinear processes of the relaxation of the spherical top molecules for the case of the symmetric-top and for arbitrary shapes of the reorienting external fields.

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1. Introduction

The Smoluchowski equation for rotational diffusion of polar, spherical molecules in dilute solution was used in the theory of linear dielectric relaxation many years ago by Debye [1] and was extended for the case of polar but the asymmetric-top molecules by Perrin [2] and Budo, Fischer and Miyamoto [3].

The theory of rotational diffusion in liquids essentialy hinges on the calculation of ensemble averages describing the time-dependence of the reorientation of molecules in a liquid medium acted on by an external, electric or magnetic potential [4]. These ensemble averages play an important role in the dielectric relaxation, in the Kerr effect consisting in the induction of optical birefringence in naturally isotropic media under the action of an

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external electric fields [5,6] as well as in the classical treatment of nonlinear processes of molecular relaxation in intense electric fields of high and low frequency, proposed by Kielich and co-workers [7–9], or in many others phenomena of molecular electro- and magneto-optics [10,11].

We propose an approximate method of solving the Smoluchowski equation of rotational diffusion of noninteracting rigid, dipolar and symmetric-top molecules under the action of the high-intensity electric or optical fields, sufficient to induce nonlinear polarization in the medium. Our calculus is an extension of the classical Kielich's method [7–9] based on the properties of angular momentum operators and spherical harmonic functions. As the main result a simple set of linear differential equations describing nonlinear rotational diffusion, for an arbitrary time-shapes of the external reorienting fields, is obtained.

This method will be used as the fundamental in the kinetic theory of nonlinear dielectric and electro-optics processes [12,13], especially in the description of the Langevin saturation recently observed in dilute solutions of different dipolar molecules in spherical solvent by the method of nonlinear dielectric effect (NDE) in Leuven and Poznań by Hellemans and Jadżyn groups [15–18].

2. Rotational diffusion of the symmetric-top molecules

Let us consider an isotropic dielectric of volume V consisting of a great number N of noninteracting rigid, dipolar, non-polarizable molecules with the permanent dipole moment component equal to μ_x, μ_y, μ_z, diluted in a solution of non-dipolar and spherical molecules.

The change in the potential energy of the molecules in an external electric field E_Z, applied to the dielectric along the laboratory Z axis, can be expressed in the form

$$V(\vartheta,\varphi;E_Z) = kT[ip_x(Y_{11}+Y_{1-1}) + p_y(Y_{11}-Y_{1-1}) - p_zY_{10}]\,, \qquad (1)$$

where we have introduced the dimensionless parameters of the reorientation of the dipole moment components

$$\begin{aligned} p_\alpha &= \sqrt{\frac{2\pi}{3}}\frac{\mu_\alpha E_Z}{kT}, \\ p_z &= 2\sqrt{\frac{\pi}{3}}\frac{\mu_z E_Z}{kT}\,, \end{aligned} \qquad (2)$$

where $\alpha = x, y$; k is the Boltzmann constant, T — absolute temperature, $i^2 = -1$ and $Y_{lm} \equiv Y_{lm}(\vartheta,\varphi)$ are the well-known spherical harmonic functions [19–21].

In our particular case of an external electric field E_Z the change in the potential energy (1) depends on the polar ϑ and azimuthal φ angles between the z-axis of the molecule and the Z-axis of the laboratory system of coordinates.

To gain insight into the influence of molecular rotational diffusion on physical quantity $Q[\vartheta,\varphi;E_Z(t)]$ at a moment of time t subsequent to the application of the time-dependent electric field $E_Z(t)$ we have recourse to a classical statistical averaging procedure

$$\langle Q[\vartheta,\varphi;E_Z(t)]\rangle \;=\; \frac{1}{4\pi V}\int\limits_0^{2\pi}\int\limits_0^{\pi} Q[\vartheta,\varphi;E_Z(t)]f[\vartheta,\varphi;E_Z(t)]\sin\vartheta d\vartheta d\varphi\,. \tag{3}$$

Now we assume that the time evolution of the dielectric depends on the molecular rotational diffusion, which is governed by the Smoluchowski equation for the time-dependent distribution function $f=f[\vartheta,\varphi;E_Z(t)]$, [4]

$$\frac{\partial f}{\partial t} \;=\; -\sum_{\alpha=x,y,z} D_{\alpha\alpha}\left[\hat{L}_\alpha^2 f - \frac{1}{kT}(i\hat{L}_\alpha)(if\hat{L}_\alpha V)\right] \tag{4}$$

in which $\hat{L}_\alpha$ are the components of the quantum-mechanical angular momentum operator [19,20] and $D_{\alpha\alpha}$ denotes the diagonal components of the rotational diffusion tensor of the molecule, equal to

$$D_{\alpha\alpha} \;=\; \frac{kT}{\beta_\alpha I_{\alpha\alpha}}\,, \tag{5}$$

where $I_{\alpha\alpha}$ denotes the diagonal components of the moment of inertia of the molecule, β_α is the friction constant around the molecular α axis of the molecule.

In the following we will consider the symmetric-top molecules only, for which $D_{xx}=D_{yy}\neq D_{zz}$.

According to the identities

$$\hat{L}^2 \;=\; \hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2\,, \tag{6}$$

and

$$(\hat{L}_\alpha V)(\hat{L}_\alpha f) \;=\; \tfrac{1}{2}\hat{L}_\alpha(\hat{L}_\alpha Vf) - \tfrac{1}{2}V\hat{L}_\alpha^2 f - \tfrac{1}{2}f\hat{L}_\alpha^2 V\,, \tag{7}$$

the Smoluchowski equation for the rotational diffusion of the symmetric-top molecules may be written in the form well adopted for calculations in the basis of spherical harmonic functions

$$\frac{1}{D_{zz}}\frac{\partial f}{\partial t} + \xi\hat{L}^2 f + (1-\xi)\hat{L}_z^2 f = -\frac{1}{2kT}\Big[\xi\hat{L}^2(Vf) + (1-\xi)\hat{L}_z^2(Vf)$$
$$+\xi f\hat{L}^2 V + (1-\xi)f\hat{L}_z^2 V - \xi V\hat{L}^2 f - (1-\xi)V\hat{L}_z^2 f\Big]\,. \tag{8}$$

Here, we have introduced the dimensionless parameter ξ of the anisotropy of rotational diffusion of the symmetric-top molecules

$$\xi = \frac{D_{xx}}{D_{zz}} . \tag{9}$$

The Smoluchowski equation for rotational diffusion of the symmetric-top molecules, in the form given by Eq. (8) is the chief result of this Section. It may be solved by the approximate method of "statistical perturbation calculus" — well suitable in the case of "low molecular reorientation", *i.e.* when all the reorientation parameters in Eq. (2), $p_x, p_y, p_z \ll 1$ — firstly used in theory of nonlinear, third-order processes of rotational relaxation of the spherical-top molecules in intense electric fields of high and low frequency by Kielich [7, 8].

With the electric fields intensities commonly used in the dielectric experiments [12, 15-18] we have just this "low molecular reorientation" case. As an example, the value of the reorientation parameter $\frac{\mu E_0}{kT}$ in nonlinear dielectric relaxation observations of Jadżyn and co-workers for the diluted solutions of 6-CB and 6-CHBT molecules in benzene at $25^0 C$ is equal to 0,04 [16].

The components of the angular momentum operator $\hat{L}$ depend on all three Eulers angles ϑ, φ, ψ, but in the case when the external field is applied along Z-axis, the change in the potential energy $V(\vartheta, \varphi; t)$ and, consequently, the rotational diffusion distribution function $f[\vartheta, \varphi, E_Z(t)]$ depends on two angles ϑ and φ only. This is a significant simplification in our theory.

In the particular case of spherical-top molecules, if $\mu_x = \mu_y = 0$, $\mu_z \neq 0$ and $D_{xx} = D_{yy} = D_{zz} = D$, Eq. (8) reduce to

$$V(\vartheta, t) = -\mu_z E_Z \cos\vartheta , \tag{10}$$

and we obtain from Eq. (8) the familiar Smoluchowski–Debye equation

$$\begin{aligned} 2\tau_1 \frac{\partial f}{\partial t} &= \triangle f + \frac{1}{2kT} \left[\triangle(Vf) + f \triangle V - V \triangle f \right] \\ &= \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial f}{\partial\vartheta} \right) + \frac{1}{kT \sin\vartheta} \frac{\partial}{\partial\vartheta} \left(f \sin\vartheta \frac{\partial V}{\partial\vartheta} \right) \end{aligned} \tag{11}$$

depending on the polar angle ϑ only. Here $\tau_1 = (2D)^{-1}$ is simply the Debye relaxation time of the spherical molecule and $\triangle$ denotes the Laplace operator. The Smoluchowski–Debye equation (11) is fundamental for the extended modern theories of the dielectric relaxation in liquids or nematic liquids crystals and of the dynamic Kerr effect [4-6, 10, 11].

3. Expansion of the rotational distribution function for the symmetric-top molecules

If, when acted on by the time-independent electric-field E_Z, the dielectric is in a thermodynamical equilibrium, its statistical distribution function is given by the Gibbs formula

$$f(\vartheta,\varphi) = \frac{4\pi\exp(\frac{-V}{kT})}{\int\limits_0^{2\pi}\int\limits_0^{\pi}\exp(\frac{-V}{kT})\sin\vartheta d\vartheta d\phi} \tag{12}$$

with the energy $V(\vartheta,\varphi)$ given by Eq. (1). In the case of "low molecular reorientation" the parameters $p_x, p_y, p_z \ll 1$ and it is useful to express the distribution function (12) by the series of powers of these parameters in the spherical harmonics basis

$$f(\vartheta,\varphi) = \sum_{l,m}\sum_{\alpha=x,y,z}\sum_{n=0,1,\ldots} A_{lm}^{\alpha\ldots} p_\alpha^n Y_{lm}(\vartheta,\varphi) \tag{13}$$

with $A_{lm}^{\alpha\ldots}$ being some coefficients of the expansion. We have $A_{lm}^{\alpha\ldots} = 0$ for $\mid m \mid > l$ and for $l < 0$.

When the dielectric is acted on by the time-dependent electric field $E_Z(t)$

$$E_Z(t) = E_Z g(t) \tag{14}$$

with the function $g(t)$ describing this dependency, the equilibrium distribution function (13) may be simply adopted to the time-dependent case by writting

$$f[\vartheta,\varphi;E_Z(t)] = \sum_{l,m}\sum_{\alpha=x,y,z}\sum_{n=0,1,\ldots} A_{lm}^{\alpha\ldots}(t) p_\alpha^n Y_{lm}(\vartheta,\varphi) \tag{15}$$

but now with the time-dependent rotational diffusion functions $A_{lm}^{\alpha\ldots}(t)$ to be determined from Eq. (8). According to Eqs (12), (15) we obtain, with an accuracy to E_Z^3, the expansion

$$f[\vartheta,\varphi;\, E_z(t)] = \frac{1}{4\pi}[f_0 + f_1(\vartheta,\varphi;t) + f_2(\vartheta,\varphi;t) + f_3(\vartheta,\varphi;t) + \ldots], \tag{16}$$

where the succesive components $f_n(\vartheta,\varphi;t)$ of the distribution function f are given by

$$f_0 = 1\,, \tag{17}$$

$$\begin{aligned} f_1(\vartheta,\varphi;t) &= -ip_x A^x_{11}(t)(Y_{11}+Y_{1-1}) - p_y A^y_{11}(t)(Y_{11}-Y_{1-1}) \\ &\quad + p_z A_{10}(t) Y_{10}\,, \end{aligned} \tag{18}$$

$$\begin{aligned} f_2(\vartheta,\varphi;t) &= \frac{1}{2\sqrt{5\pi}}\Bigg\{ -p_x^2\left[\sqrt{\frac{3}{2}}A^{xx}_{22}(t)(Y_{22}+Y_{2-2}) + A^{xx}_{20}(t)Y_{20}\right] \\ &\quad + p_y^2\left[\sqrt{\frac{3}{2}}A^{yy}_{22}(t)(Y_{22}+Y_{2-2}) + A^{yy}_{20}(t)Y_{20}\right] \\ &\quad + p_z^2 A^{zz}_{20}(t)Y_{20} + ip_xp_y\sqrt{6}A^{xy}_{22}(t)(Y_{22}-Y_{2-2}) \\ &\quad - ip_xp_z\sqrt{3}A^{xz}_{21}(t)(Y_{21}-Y_{2-1}) - p_yp_z\sqrt{3}A^{yz}_{21}(t)(Y_{21}-Y_{2-1})\Bigg\}\,, \end{aligned} \tag{19}$$

and

$$\begin{aligned} 4\pi f_3(\vartheta,\varphi;t) &= p_x^3\left[\sqrt{\frac{3}{70}}iA^{xxx}_{33}(t)(Y_{33}+Y_{3-3}) + \frac{3}{5\sqrt{14}}iA^{xxx}_{31}(t)(Y_{31}+Y_{3-1})\right. \\ &\left.+\frac{2}{5}iA^{xxx}_{11}(t)(Y_{11}+Y_{1-1})\right] \\ &+p_y^3\left[-\sqrt{\frac{3}{70}}A^{yyy}_{33}(t)(Y_{33}-Y_{3-3}) + \frac{3}{5\sqrt{14}}A^{yyy}_{31}(t)(Y_{31}-Y_{3-1})\right. \\ &\left.+\frac{2}{5}A^{yyy}_{11}(t)(Y_{11}-Y_{1-1})\right] \\ &+p_z^3\left[\frac{1}{5}\sqrt{\frac{3}{7}}A^{zzz}_{30}(t)Y_{30} - \frac{1}{5}A^{zzz}_{10}(t)Y_{10}\right] \\ &+p_x^2p_y\left[3\sqrt{\frac{3}{70}}A^{xxy}_{33}(t)(Y_{33}-Y_{3-3}) - \frac{3}{5\sqrt{14}}A^{xxy}_{31}(t)(Y_{31}-Y_{3-1})\right. \\ &\left.+\frac{2}{5}A^{xxy}_{11}(t)(Y_{11}-Y_{1-1})\right] \\ &-p_x^2p_z\left[\frac{3}{\sqrt{70}}A^{xxz}_{32}(t)(Y_{32}+Y_{3-2}) + \frac{3}{10}\sqrt{\frac{3}{7}}A^{xxz}_{30}(t)Y_{30} + \frac{2}{5}A^{xxz}_{10}(t)Y_{10}\right] \\ &+p_y^2p_x\left[-3\sqrt{\frac{3}{70}}iA^{xyy}_{33}(t)(Y_{33}+Y_{3-3}) + \frac{3}{5\sqrt{14}}iA^{xyy}_{31}(t)(Y_{31}+Y_{3-1})\right. \end{aligned}$$

$$
\begin{aligned}
&+\frac{2}{5}iA_{11}^{xyy}(t)(Y_{11}+Y_{1-1})\Bigg] \\
&+p_y^2p_z\left[3\sqrt{\frac{2}{35}}A_{32}^{yyz}(t)(Y_{32}+Y_{3-2})-\frac{3}{5}\sqrt{\frac{3}{7}}A_{30}^{yyz}(t)Y_{30}-\frac{2}{5}A_{10}^{yyz}(t)Y_{10}\right] \\
&+p_z^2p_x\left[-\frac{6}{5\sqrt{14}}iA_{31}^{xzz}(t)(Y_{31}+Y_{3-1})+\frac{1}{5}iA_{11}^{xzz}(t)(Y_{11}+Y_{1-1})\right] \\
&+p_z^2p_y\left[\frac{6}{5\sqrt{14}}A_{31}^{yzz}(t)(Y_{31}-Y_{3-1})+\frac{1}{5}A_{11}^{yzz}(t)(Y_{11}-Y_{1-1})\right] \\
&+ip_xp_yp_z\sqrt{\frac{2}{35}}A_{32}^{xyz}(t)(Y_{32}-Y_{3-2})\,. \qquad (20)
\end{aligned}
$$

4. Approximate solution of the Smoluchowski equation for rotational diffusion of rigid, dipolar and symmetric-top molecules in dilute solvent

We insert Eqs (1), (16)–(20) into the Smoluchowski equation (8) and apply the properties of spherical harmonic functions [19-21]

$$
\begin{aligned}
\hat{L}_zY_{lm} &= l(l+1)Y_{lm}, \\
\hat{L}_z^2Y_{lm} &= m^2Y_{lm}, \qquad (21)
\end{aligned}
$$

and

$$
Y_{lm}Y_{\alpha\beta} = \sum_{L,M}\sqrt{\frac{(2l+1)(2\alpha+1)}{4\pi(2L+1)}}C(l\alpha L;m\beta)C(l\alpha L;00)Y_{LM}, \qquad (22)
$$

where $C(l\alpha L;m\beta)$ are Clebsch–Gordan coefficients and summation over the indices L and M in Eq. (22) is governed by the triangle rule $\mid l-\alpha\mid\leq L\leq l+\alpha$. Clebsch–Gordan coefficients are non-zero only for $M=m+\beta$. Now, after multiplying both sides of the Smoluchowski equation by $Y_{\alpha\beta}(\vartheta,\varphi)$, we use the orthogonality relation of the spherical harmonics

$$
\int_0^{2\pi}\int_0^{\pi}Y_{lm}Y_{\alpha\beta}\sin\vartheta d\vartheta = (-1)^{\beta}\delta_{l\alpha}\delta_{m\beta}, \qquad (23)
$$

where $\delta_{\alpha\beta}$ denotes the Kronecker delta.

Finally, by putting equal in Eq. (8) all terms with the same powers p_α^n of the parameters of molecular reorientation p_x, p_y, p_z, we obtain the following sets of linear differential equations for the unknown relaxational functions $A^{\alpha\dots}_{lm}(t)$

$$\begin{aligned}
\tau_{11}\dot{A}^{x}_{11}(t)+A^{x}_{11}(t) &= g(t),\\
\tau_{10}\dot{A}^{z}_{10}(t)+A^{z}_{10}(t) &= g(t),\\
A^{x}_{11}(t) &= A^{y}_{11}(t),
\end{aligned} \tag{24}$$

where the dots denote time-derivatives and the rotational relaxation times of symmetric-top molecules are

$$\tau_{lm} = \left[l(l+1)D_{zz}-m^2(D_{zz}-D_{xx})\right]^{-1}. \tag{25}$$

We see that the linear dielectric relaxation depends on two times

$$\begin{aligned}
\tau_{10} &= (2D_{zz})^{-1},\\
\tau_{11} &= (D_{xx}+D_{zz})^{-1}
\end{aligned} \tag{26}$$

and on the shape of the electric field $g(t)$.

For the relaxational functions $A^{\alpha\alpha}_{lm}(t)$, which are connected with the square of electric field intensity and play an important role in the Kerr effect [4–7], our method gives the following equations

$$\begin{aligned}
\tau_{20}\dot{A}^{xx}_{20}(t)+A^{xx}_{20}(t) &= A^{x}_{11}(t)g(t)\,,\\
\tau_{20}\dot{A}^{zz}_{20}(t)+A^{zz}_{20}(t) &= A^{z}_{10}(t)g(t)\,,\\
\tau_{22}\dot{A}^{xx}_{22}(t)+A^{xx}_{22}(t) &= A^{x}_{11}(t)g(t)\,,\\
\tau_{21}\dot{A}^{xz}_{21}(t)+A^{xz}_{21}(t) &= \left[\frac{1+2\xi}{1+5\xi}A^{z}_{10}(t)+\frac{3\xi}{1+5\xi}A^{x}_{11}(t)\right]g(t)\,.
\end{aligned} \tag{27}$$

Moreover, we have the relations

$$\begin{aligned}
A^{yy}_{20}(t) &= A^{xx}_{20}(t)\,,\\
A^{yz}_{21}(t) &= A^{xz}_{21}(t)\,,\\
A^{yy}_{22}(t) &= A^{xy}_{22}(t)=A^{xx}_{22}(t)\,,
\end{aligned} \tag{28}$$

resulting from the symmetry between the D_{xx} and D_{yy} components of the rotational diffusion tensor of the molecule.

The rotational relaxation times in Eqs (27) are

$$\begin{aligned}
\tau_{20} &= \frac{1}{3}\tau_{10}=(6D_{zz})^{-1},\\
\tau_{21} &= (5D_{zz}+D_{xx})^{-1}\,,\\
\tau_{22} &= (2D_{zz}+4D_{xx})^{-1}\,,
\end{aligned} \tag{29}$$

and it is clear that the accurate analysis of the dielectric relaxation and optical birefringence should be made with the symmetric-top molecule properties. We note that the functions $A_{lm}^{\alpha\alpha}(t)$ depend on $A_{lm}^{\alpha}(t)$ and $g(t)$.

And finally, for the reorientational functions describing the third-order electric polarization $A_{lm}^{\alpha\alpha\alpha}(t)$ we obtain the equations

$$\begin{aligned}
\tau_{10}\dot{A}_{10}^{zzz}(t) + A_{10}^{zzz}(t) &= A_{20}^{zz}(t)g(t)\,,\\
\tau_{10}\dot{A}_{10}^{xxz}(t) + A_{10}^{xxz}(t) &= \frac{1}{2}g(t)\left[3A_{21}^{xz}(t) - A_{20}^{xx}(t)\right]\,,\\
\tau_{11}\dot{A}_{11}^{xxx}(t) + A_{11}^{xxx}(t) &= \frac{g(t)}{2(1+\xi)}\left[3A_{22}^{xx}(t) + (2\xi-1)A_{20}^{xx}(t)\right]\,,\\
\tau_{11}\dot{A}_{11}^{xzz}(t) + A_{11}^{xzz}(t) &= \frac{g(t)}{1+\xi}\left[A_{20}^{xx}(t) + 3\xi A_{21}^{xz}(t) - 2\xi A_{20}^{zz}(t)\right]\,. \quad (30)
\end{aligned}$$

Moreover, the following identities hold

$$\begin{aligned}
A_{10}^{yyz}(t) &= A_{10}^{xxz}(t),\\
A_{11}^{yyy}(t) = A_{11}^{xxx}(t) &= A_{11}^{xxy}(t) = A_{11}^{xyy}(t),\\
A_{11}^{yzz}(t) &= A_{11}^{xzz}(t). \quad (31)
\end{aligned}$$

Equations (25)–(31) with the initial values depending on the experimental conditions, permit the calculation of the respective nonlinear relaxation functions $A_{lm}^{\alpha\alpha\alpha}(t)$ for the arbitrary shapes of reorienting electric field $g(t)$ and are the chief result of this Section.

In the absence of any external fields in $t=0$ we have all $A_{lm}^{\alpha\cdots}(t=0)=0$. For the time-independent field $g(t)=1$, switching on in a sufficiently past time $t=t_0$, the values of all $A_{lm}^{\alpha\cdots}(t_0)=1$. For spherical top molecules $D_{xx}=D_{zz}=D$ and Eqs (25)–(31) reduce to a simpler form considered in [9].

5. Conclusions

This approach to the Smoluchowski equation for the rotational diffusion of the rigid, dipolar and symmetric-top molecules permits an extention of the classical Kielich theory of nonlinear electro-optical processes in a dielectric consisting of spherical molecules and will provide more detailed picture of the dispersion and absorption properties as well as time-evolution of various nonlinear processes [22].

Consider an expansion of an arbitrary physical quantity Q into a series of the spherical harmonics

$$Q[\vartheta,\varphi;E_Z(t)] = \sum_{L,M}\sum_{n=0,1,\ldots} q_{LM}^{n} g^{n}(t) Y_{LM}(\vartheta,\varphi), \quad (32)$$

with q_{LM} being the coefficients of expansion, where the indices L, M depend on the nature of the measured quantity Q, ($L > 0$ and $\mid M \mid < L$) and $n = 0, 1, ...$ denotes the powers of the intensity of the electric field $E_Z(t)$. We can now insert the expansions (3) and (13) into Eq. (32) and use the orthogonality relation (23) for the spherical harmonics. As a result we have a general equality

$$\begin{aligned} \Phi_{LM}[\vartheta, \varphi; E_Z(t)] &= \langle Y_{LM}(\vartheta(t), \varphi(t)) \rangle \\ &= \frac{1}{V} \sum_{l,m} \sum_{n,n'} \sum_{\alpha} (-1)^M p_\alpha^{n'} q_{LM}^n g^n(t) A_{lm}^\alpha(t) \delta_{Ll} \delta_{Mm} \end{aligned} \tag{33}$$

for the ensemble averages $\Phi_{LM}[\vartheta, \varphi; E_Z(t)]$ describing the time-dependence of the rotational diffusion of the symmetric-top molecules in a liquid medium acted on by an external potential and playing an important role in the theory of linear and nonlinear dielectric relaxation.

As an important example we consider the total dipole moment $M_Z[E_Z(t)]$ induced by the time dependent field $E_Z(t)$. On neglecting molecular interactions and the induced polarizability, we have [12–14]

$$\begin{aligned} \frac{1}{N} M_Z[E_Z(t)] &= [-\sqrt{\frac{2\pi}{3}} i\mu_x (Y_{11} + Y_{1-1}) - \sqrt{\frac{2\pi}{3}} \mu_y (Y_{11} - Y_{1-1}) \\ &\quad + 2\sqrt{\frac{\pi}{3}} \mu_z Y_{10}] g(t) \,. \end{aligned} \tag{34}$$

From Eqs (3), (15)–(20), (34) we obtain for the electric polarization of the system the following expansion

$$\langle P_Z(t) \rangle = \langle P_Z^{(1)}(t) \rangle + \langle P_Z^{(3)}(t) \rangle + \dots \,, \tag{35}$$

where the first two components, of the first- and third-order are equal

$$\langle P_Z^1(t) \rangle = [(\mu_x + \mu_y)^2 A_{11}^x(t) + \mu_z^2 A_{10}^z(t)] \frac{\rho E_Z}{3kT} \,, \tag{36}$$

and

$$\begin{aligned} \langle P_Z^{(3)}(t) \rangle &= -\Big\{ (\mu_x^2 + \mu_y^2)^2 A_{11}^{xxx}(t) + \mu_z^4 A_{10}^{zzz}(t) \\ &\quad + (\mu_x^2 + \mu_y^2)^2 [A_{10}^{yyz}(t) + A_{11}^{xzz}(t)] \Big\} \frac{\rho E_Z^3}{45k^3T^3} \,, \end{aligned} \tag{37}$$

and depend on the reorientational functions $A_{lm}^{\alpha\alpha\alpha}(t)$ given by Eqs (30) and the symmetric-top molecular rotational relaxation times τ_{11}, τ_{10}, τ_{20}, τ_{21} and τ_{22}.

Our results permit a qualitative description of nonlinear dispersion and absorption processes as well as detailed detemination of the response of liquid dielectrics to an arbitrary electric reorienting field $E_Z(t)$.

Generally, the dispersion and absorption of the third-order electric polarization component [37] induced in the dielectric medium by by the harmonic electric field, depends on the relaxation times τ_{lm} and on the nonlinear Debye–Kielich factors

$$R_{lm}(n\omega) \;=\; \left(1 - in\omega\tau_{lm}\right)^{-1}, \tag{38}$$

where ω is a frequency of harmonic electric field and $n = 1, 2, 3$. The kinetic theory [22] gives the values of dispersion and absorption bands which are strongly dependent on the anisotropy of the diffusion tensor components ξ. The same rotational relaxation times appear in the description of the rise in time and decay of the third-order electric polarization induced in dielectric media by the rectangular electric field. The resulting time-dependency may be of non-exponential type and significantly depends on the shape of the molecules [23].

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