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RISE AND DECAY IN TIME OF THIRD-ORDER ELECTRIC POLARIZATION IN LIQUIDS COMPOSED OF DIPOLAR SYMMETRIC-TOP MOLECULES*

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Formulae are derived for the rise and decay relaxation functions of third-order electric polarization induced in liquids composed of dipolar, symmetric-top molecules by rectangular pulse with intermolecular interactions neglected. Smoluchowski equation for rotational diffusion of the symmetric-top molecules is applied.

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1. Introduction

The approximate "Smoluchowski–Debye method" for solution of the rotational diffusion equation for non-interacting spherical molecules was used in classical papers of Kielich and co-workers [1] for a description of nonlinear processes of molecular relaxation in intense electric fields. It is our aim to apply the extension of Kielich's method into a medium consisting of non-interacting dipolar but symmetric-top molecules in the presence of two-angles dependent external potential $V(\vartheta,\varphi)$, for a description of the rise and decay in time of third-order electric polarization. This method was described recently in details by one of us [2].

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2. Theory

The Smoluchowski equation of rotational Brownian motion for asymmetric-top molecules may be written in the form [3]:

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

Here $f(\vartheta,\varphi,\psi;t)$ is the distribution function of rotational motion, $D_{\alpha\alpha}$ are the diagonal components of the rotational diffusion tensor of the molecule, $\hat{L}_\alpha$ are the components of a well-known quantum-mechanical angular momentum operator $\hat{L}$, k denotes the Boltzmann constant and T - the absolute temperature, $(i^2 = -1)$. Here the change in potential energy of the molecule in an external electric field $E_Z(t)$ is denoted by $V(\vartheta,\varphi,\psi;t)$, where ϑ,φ,ψ are the Euler angles.

In the case of symmetric-top molecules, this equation reduces to

$$\begin{aligned}\frac{\partial f}{\partial t} &= -D_\perp(\hat{L}^2 - \hat{L}_z^2)f - D_\parallel \hat{L}_z^2 f \\ &\quad -\frac{D_\perp}{2kT}\left[\hat{L}^2 - \hat{L}_z^2)Vf + (f(\hat{L}^2 - \hat{L}_z^2)V - V\hat{L}^2 - \hat{L}_z^2)f\right] \\ &\quad -\frac{D_\parallel}{2kT}\left[(\hat{L}_z^2 Vf + f\hat{L}_z^2 V - V(\hat{L}_z^2 f\right], \end{aligned} \tag{2}$$

where $D_\perp = D_{xx} = D_{yy}$, $D_\parallel = D_{zz}$. If an external electric field is applied along the laboratory Z-axis, both the orientational distribution function f and the change in potential energy of molecules V depend on two angles: polar ϑ and azimuthal angle φ, only. By using the operator identities

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{3}$$

and

$$2(\hat{L}_\alpha f)(\hat{L}_\alpha V) = \hat{L}_\alpha^2(Vf) - V\hat{L}_\alpha^2 f - f\hat{L}_\alpha^2 V, \tag{4}$$

we can write the Smoluchowski equation in the form:

$$\begin{aligned}&2\tau_1\frac{\partial f}{\partial t} + \xi\hat{L}^2 f + (1-\xi)\hat{L}_z^2 f \\ &= -\frac{1}{2kT}\left[\xi\hat{L}^2(Vf) + (1-\xi)\hat{L}_z^2(Vf) + \xi f\hat{L}^2 V + (1-\xi)f\hat{L}_z^2 V\right. \\ &\left.- \xi V\hat{L}^2 f - (1-\xi)V\hat{L}_z^2 f\right], \end{aligned} \tag{5}$$

where $\xi = \frac{D_\perp}{D_\parallel}$ is dimensionless parameter describing the anisotropy of rotational diffusion and $\tau_1 = \frac{1}{2D_\parallel}$ is the Debye relaxation time. Equation (5) can be solved by means of the Smoluchowski–Debye method taking into account the series expansions of orientational distribution function $f(\vartheta,\varphi;t)$ and the potential energy $V(\vartheta,\varphi;t)$ into the powers of the parameters of dipole reorientation p_x, p_y, p_z in the basis of the spherical harmonics functions $Y_{lm}(\vartheta,\varphi)$. We assume, that $p_x, p_y, p_z \ll 1$. With these expansions we can apply some standard properties of the angular momentum operators

$$\hat{L}^2 Y_{lm} = l(l+1) Y_{lm}\,, \tag{6}$$

and

$$\hat{L}_z^2 Y_{lm} = m^2 Y_{lm} \tag{7}$$

together with the orthogonality relation and product and integral rules of the spherical harmonic functions [4] in order to obtain the $f(\vartheta,\varphi;t)$. This method of approximate solution of equation (5), described recently in details in [2] , is valid in the “low molecular reorientation” case only, but is very well fulfilled in modern experimental investigations of nonlinear dielectric effect (NDE), such as recent measurements of the Langevin saturation in dilute solutions of mesogenic 10-TPEB molecules [5].

In special case of the spherical-top molecules, when $\xi = 1$, equation (5) goes into the well-known Smoluchowski equation depending on the scalar diffusion coefficient $D_\perp = D_\| = D$ only [1,3,6] which is fundamental in the Kielich classical theory of non-linear electro-optical processes of molecular rotational relaxation in intense electric fields of high and low frequency [1].

3. The rise in time of linear and nonlinear electric polarization for rectangular reorienting pulse

We consider a medium consisting of dipolar, symmetric-top molecules with the dipole momentum components μ_x, μ_y, μ_z. The change of its potential energy in an external electric field $E_z(t)$, applied along the laboratory Z-axis, is equal

$$\frac{1}{kT} V(\vartheta;\varphi;t) = i p_x (Y_{11} + Y_{1-1}) + p_y (Y_{11} - Y_{1-1}) - p_z Y_{10}\,, \tag{8}$$

where we introduced the dimensionless parameters of dipole moment components reorientation

$$\begin{aligned} p_\alpha &= \frac{\mu_\alpha E}{kT}\sqrt{\frac{2\pi}{3}}, \quad \alpha = x, y\,, \\ p_z &= \frac{2\mu_z E}{kT}\sqrt{\frac{\pi}{3}}. \end{aligned} \tag{9}$$

In the classical statistical mechanics approach the electric polarization $\langle P(t)\rangle$ induced in our medium by an electric field $E_z(t)$ is given by the ensemble averages

$$\begin{aligned}\langle P(t)\rangle &= \rho\int_0^{2\pi}\int_0^{\pi}(\mu_x\sin\vartheta\sin\varphi+\mu_y\sin\vartheta\cos\varphi\\ &\quad+\mu_z\cos\vartheta)f(\vartheta;\varphi;t)\sin\vartheta d\vartheta d\varphi\\ &= \rho\int_0^{2\pi}\int_0^{\pi}[-\mu_x\sqrt{\frac{2\pi}{3}}i(Y_{11}+Y_{1-1})-\mu_y\sqrt{\frac{2\pi}{3}}(Y_{11}-Y_{1-1})\\ &\quad+\mu_z 2\sqrt{\frac{\pi}{3}}Y_{10}]f(\vartheta,\varphi;t)\sin\vartheta d\vartheta d\varphi\,,\end{aligned}\tag{10}$$

of the spherical harmonics Y_{lm}. In equation (10) $\rho=\frac{N}{V}$ is the density of the medium and the reorientational distribution function $f(\vartheta,\varphi;t)$ can be found from equation (5). We assume that the intensity of an external electric field $(t>0)$

$$E_z(t)=E_0g(t)=E_0+\tfrac{1}{2}E_\omega(\mathrm{e}^{-i\omega t}+\mathrm{e}^{i\omega t})\ \ ;\ E_0\gg E_\omega,\tag{11}$$

is sufficiently high to induce the linear $\langle P^{(1)}(t)\rangle$ and the nonlinear $\langle P^{3}(t)\rangle$ polarization in the medium. The total polarization splits into two components

$$\langle P(t)\rangle\ =\ \langle P^{(1)}(t)\rangle+\langle P^{(3)}(t)\rangle+\dots\ ,\tag{12}$$

The time-dependence of the linear component of the polarization is given as

$$\langle P^{(1)}(t)\rangle\ =\ \left[(\mu_x^2+\mu_y^2)A_{11}^x(t)+\mu_z^2A_{10}^z(t)\right]\frac{\rho E_0}{3kT},\tag{13}$$

where the relaxational diffusion functions $A_{lm}^{\alpha}(t)$, which must be found from the differential equations [2]:

$$\begin{aligned}\tau_{10}\dot{A}_{10}^z\ &+\ A_{10}^z=g(t)\,,\\ \tau_{11}\dot{A}_{11}^x\ &+\ A_{11}^x=g(t)\end{aligned}\tag{14}$$

depend on the shape of the electric field $g(t)$ and the relaxation times τ_{lm}. In equations (14) dots denote time derivatives. In the case of the field (11) switched on at the time $t=0$ ($g(t)=0$ for $t<0$) we obtain for the reorientational rise functions $A_{lm}^{\alpha}(t)$ the formulae

$$\begin{aligned}A_{11}^x(t)\ &=\ 1-\mathrm{e}^{-\frac{t}{\tau_{11}}}\,,\\ A_{10}^z(t)\ &=\ 1-\mathrm{e}^{-\frac{t}{\tau_{10}}}\,,\end{aligned}\tag{15}$$

and the reorientational relaxation times for symmetric-top molecules are equal to

$$\tau_{lm} = \left[l(l+1)D_{\|} - m^2(D_{\|} - D_{\perp})\right]^{-1} , \tag{16}$$

and depend on both components of the rotational diffusion tensor. The time-dependency of the nonlinear component of the electric polarization (10) is given by the formula [2]

$$\begin{aligned}\frac{1}{\rho}\langle P^{(3)}(t)\rangle = \; & -\left\{(\mu_x^2+\mu_y^2)^2 A_{11}^{xxx}(t) + \mu_z^4 A_{10}^{zzz}(t)\right. \\ & \left. + (\mu_x^2+\mu_y^2)\mu_z^2\left[A_{10}^{xxz}(t) + A_{11}^{xzz}(t)\right]\right\}\frac{E^3}{45k^3T^3} , \end{aligned}\tag{17}$$

and the nonlinear relaxation functions $A_{lm}^{\alpha\alpha\alpha}(t)$, obey the equations [2]:

$$\begin{aligned}\tau_{10}\dot{A}_{10}^{zzz} + A_{10}^{zzz} &= A_{20}^{zz}g(t) , \\ \tau_{10}\dot{A}_{10}^{xxz} + A_{10}^{xxz} &= \frac{1}{2}g(t)\left[3A_{21}^{xz} - A_{20}^{xx}\right] , \\ \tau_{11}\dot{A}_{11}^{xxx} + A_{11}^{xxx} &= \frac{g(t)}{2(1+\xi)}\left[3A_{22}^{xx} + (2\xi-1)A_{20}^{xx}\right] , \\ \tau_{11}\dot{A}_{11}^{xzz} + A_{11}^{xzz} &= \frac{g(t)}{1+\xi}\left[A_{20}^{xx} + 3\xi A_{21}^{xz} - 2\xi A_{20}^{zz}\right] . \end{aligned}\tag{18}$$

We see from equation (18) that the cubic relaxation functions $A_{lm}^{\alpha\alpha\alpha}(t)$ depend on the quadratic relaxation functions $A_{lm}^{\alpha\alpha}(t)$, which obey the equations [2]:

$$\begin{aligned}\tau_{20}\dot{A}_{20}^{xx} + A_{20}^{xx} &= A_{11}^{x}(t)g(t) , \\ \tau_{20}\dot{A}_{20}^{zz} + A_{20}^{zz} &= A_{10}^{z}(t)g(t) , \\ \tau_{22}\dot{A}_{22}^{xx} + A_{22}^{xx} &= A_{11}^{x}(t)g(t) , \\ \tau_{21}\dot{A}_{21}^{xz} + A_{21}^{xz} &= \left[\frac{1+2\xi}{1+5\xi}A_{10}^{z}(t) + \frac{3\xi}{1+5\xi}A_{11}^{x}(t)\right]g(t) . \end{aligned}\tag{19}$$

The nonlinear reorientational relaxation functions $A_{lm}^{\alpha\alpha\alpha}(t)$, for the electric field (11), are equal to

$$A_{10}^{zzz}(t) = 1 - \frac{3}{4}e^{-\frac{t}{\tau_{10}}} - \frac{1}{4}e^{-\frac{t}{\tau_{20}}} - \frac{3}{2}\frac{t}{\tau_{10}}e^{-\frac{t}{\tau_{10}}} , \tag{20}$$

$$\begin{aligned}A_{11}^{xxx}(t) &= 1 - a_{11}e^{-\frac{t}{\tau_{11}}} + a_{20}e^{-\frac{t}{\tau_{20}}} + a_{22}e^{-\frac{t}{\tau_{22}}} \\ &\quad -b_{11}\frac{t}{\tau_{11}}e^{-\frac{t}{\tau_{11}}} , \end{aligned}\tag{21}$$

$$\begin{aligned} A_{10}^{xxz}(t)+A_{11}^{xzz}(t) &= 2+c_{10}\mathrm{e}^{-\frac{t}{\tau_{10}}}+c_{11}\mathrm{e}^{-\frac{t}{\tau_{11}}}+c_{20}\mathrm{e}^{-\frac{t}{\tau_{20}}} \\ &\quad +c_{21}\mathrm{e}^{-\frac{t}{\tau_{21}}}+d_{10}\frac{t}{\tau_{10}}\mathrm{e}^{-\frac{t}{\tau_{10}}}+d_{11}\frac{t}{\tau_{11}}\mathrm{e}^{-\frac{t}{\tau_{11}}}\,, \end{aligned} \tag{22}$$

where only terms with E_0^3 are included. The coefficients a_{lm}, b_{lm}, c_{lm} and d_{lm} in equations (21) and (22) depend on the anisotropy ξ of the diffusion tensor components $D_\perp$, $D_{||}$, and are equal to

$$\begin{aligned} a_{11} &= 1+\frac{(2\xi-1)(11-\xi)}{2(5-\xi)}+\frac{3(3+7\xi)}{2(1+3\xi)^2}, \\ a_{20} &= 1+\frac{(2\xi-1)(11-\xi)}{2(5-\xi)}, \\ a_{22} &= a_{11}-a_{20}-1\,, \\ b_{11} &= \frac{12(1+\xi)}{(1+3\xi)(5-\xi)}, \qquad \text{for} \quad \xi\neq 5\,, \\ c_{10} &= \frac{2}{1-\xi}\left[\frac{3}{5-\xi}-\frac{9\xi(5+\xi)}{8(1+5\xi)}\right]-\frac{11-\xi}{4(5-\xi)}+\frac{3}{\xi-1}\left(\xi\frac{1+2\xi}{1+5\xi}-\frac{1-2\xi}{2}\right) \\ &\quad +\frac{3}{3+\xi}\left[\frac{3\xi(5+\xi)}{4(1+5\xi)}-\frac{(1+2\xi)(5+\xi)}{(1+5\xi)(3+\xi)}-1\right]-1\,, \\ c_{11} &= \frac{2}{1-\xi}\left[\frac{3}{5-\xi}-\frac{9\xi(5+\xi)}{8(1+5\xi)}\right]+\frac{3}{\xi-1}\left(\frac{\xi+2\xi^2}{1+5\xi}-\frac{1-2\xi}{2}\right) \\ &\quad -\frac{3\xi}{4}\left[1+\frac{5+\xi}{1+5\xi}\left(\frac{3}{4}\xi+\frac{1+2\xi}{3+\xi}\right)-\frac{1-2\xi}{2(\xi-5)}\right], \\ c_{20} &= \frac{9+3\xi}{20-4\xi}, \\ c_{21} &= \frac{3}{4}\xi\left[1+\frac{5+\xi}{1+5\xi}\left(\frac{3}{4}\xi+\frac{1+2\xi}{3+\xi}\right)\right] \\ &\quad -\frac{3}{3+\xi}\left[\frac{3\xi(5+\xi)}{4(1+5\xi)}-\frac{(1+2\xi)(5+\xi)}{(1+5\xi)(3+\xi)}-1\right], \\ d_{10} &= \frac{3(1+2\xi)(5+\xi)}{2(1+5\xi)(3+\xi)}, \\ d_{11} &= -\frac{9\xi^2(5+\xi)}{4(1+5\xi)}\,. \end{aligned} \tag{23}$$

In particular case $\xi=5$ we have

$$\begin{aligned} A_{11}^{xxx}(t) &= 1-\left(\frac{57}{128}+\frac{39}{48}\;\frac{t}{\tau_{11}}+\frac{3t^2}{4\tau_{11}\tau_{20}}\right)\mathrm{e}^{-\frac{t}{\tau_{11}}}+\frac{57}{128}\mathrm{e}^{-\frac{t}{\tau_{22}}}\,, \\ A_{10}^{xxz}(t)+A_{11}^{xzz}(t) &= 2+\frac{741}{832}\mathrm{e}^{-\frac{t}{\tau_{10}}}+\frac{21\cdot 309}{8\cdot 104}\mathrm{e}^{-\frac{t}{\tau_{21}}} \end{aligned}$$

$$-\frac{1855}{208}\mathrm{e}^{-\frac{t}{\tau_{11}}}-\frac{5}{8}\mathrm{e}^{-\frac{t}{\tau_{20}}}-\frac{165}{13\cdot 16}\frac{t}{\tau_{10}}\mathrm{e}^{-\frac{t}{\tau_{10}}}$$
$$-\frac{251}{104}\frac{t}{\tau_{11}}\mathrm{e}^{-\frac{t}{\tau_{11}}}-\frac{1}{4}\frac{t}{\tau_{20}}\mathrm{e}^{-\frac{t}{\tau_{20}}}\,. \tag{24}$$

Equations (12)–(24) describe the influence of the anisotropy of rotational diffusion tensor ξ on the dynamic of electric polarization induced by the rectangular field. The rise components, equations (20)–(24), depend on the exponential terms of the type $\exp(-\frac{t}{\tau_{lm}})$ with the symmetric-top molecule relaxation times $\tau_{10}, \tau_{11}, \tau_{20}, \tau_{21}$ and on the non-exponential terms — $-\frac{t}{\tau_{lm}}\mathrm{e}^{-\frac{t}{\tau_{lm}}}$ — with τ_{10}, τ_{11}. So the rise of the polarizations (13) and (17) may significantly differ from the pure exponential curves.

At a sufficiently long time $t \gg \tau_{lm}$ after switching on of the rectangular electric field $g(t) = E_0$ dielectric attains his steady state (s.s.),

$$A^{\alpha}_{lm}(\text{s.s.}) = A^{\alpha\alpha}_{lm}(\text{s.s.}) = A^{\alpha\alpha\alpha}_{lm}(\text{s.s.}) \;=\; 1, \tag{25}$$

characterized by a stationary value of the electric polarization equal to

$$\langle P(\text{s.s.})\rangle \;=\; \rho\frac{\mu^2 E_0}{3kT}\left(1-\frac{\mu^2 E_0^2}{15k^2T^2}\right), \tag{26}$$

where $\mu^2 = \vec{\mu}\cdot\vec{\mu} = \mu_x^2 + \mu_y^2 + \mu_z^2$. The particular case $\xi = 1$ describes the rotational diffusion of the dipolar but spherical-top molecules [1, 3], [6–8] when the Smoluchowski equation (5) takes the simpler form

$$2\tau_1\frac{\partial f}{\partial t} + \hat{L}^2 f \;=\; = -\frac{1}{2kT}\left[\hat{L}^2(Vf) + f\hat{L}^2 V - V\hat{L}^2 f\right] \tag{27}$$

and the change of the potential energy of the dielectric depends on two angles ϑ and φ. Equation (5) was a basis of the extended Debye theory of dielectric relaxation of nematic liquid crystals by Coffey [8]. For the spherical-top molecules with the permanent dipole components $\mu_x \neq \mu_y \neq \mu_z \neq 0$ we simply have $\xi = 1$ and $\tau_{11} = \tau_{10}, \tau_{22} = \tau_{21} = \tau_{20}$, so equations (14), (18), (19) reduce to the set

$$\begin{aligned}
\tau_{10}\dot{A}^{\alpha}_{1l} + A^{\alpha}_{1l} &= g(t)\,, & l &= 0, 1\,,\\
\tau_{20}\dot{A}^{\alpha\alpha}_{2l} + A^{\alpha\alpha}_{2l} &= g(t)A^{\alpha}_{1l}\,, & l &= 0, 1, 2\,,\\
\tau_{10}\dot{A}^{\alpha\alpha\alpha}_{1l} + A^{\alpha\alpha\alpha}_{1l} &= g(t)A^{\alpha\alpha}_{2l}\,, & l &= 0, 1\,,
\end{aligned} \tag{28}$$

where $\alpha = x, y$.

We see that the rise processes of rotational diffusion depend now on the relaxation times τ_{10} and τ_{20} only and equations (13) and (17) reduce to:

$$\begin{aligned} \langle P^{(1)}(t)\rangle &= \mu^2 A_{10}^{z}(t)\frac{\rho E_0}{3kT}, \\ \langle P^{(3)}(t)\rangle &= -\mu^4 A_{10}^{zzz}(t)\frac{\rho E_0^3}{45k^3T^3}. \end{aligned} \tag{29}$$

In the case of spherical-top molecules for which $\mu_x = \mu_y = 0$ and only $\mu_z \neq 0$ the rise of the nonlinear polarization is simply [9]

$$\langle P^{(3)}(t)\rangle = -\rho\frac{\mu_z^4 E_0^3}{45k^3T^3}A_{10}^{zzz}(t). \tag{30}$$

4. Decay of linear and nonlinear electric polarization

We consider the decay of polarization, after switching the electric field off, at the time $t = t_0$. This case is simpler then that described previously, because we have $V(\vartheta,\varphi;t) = 0$ for $t > t_0$ and the equation (5) takes the simple form

$$\frac{1}{D_\perp}\frac{\partial f}{\partial t} + \xi\hat{L}^2 f + (1-\xi)\hat{L}_z^2 f = 0. \tag{31}$$

The decay of polarization is described by equations (13) and (17) but with the reorientational decay functions $D_{lm}^{(\alpha)}(t)$ instead of rise functions $A_{lm}(t)$. Our extension of the Kielich theory on the symmetric-top molecules gives the linear differential equations for the decay-functions $D_{lm}^{(\alpha)}(t)$

$$\tau_{lm}\dot{D}_{lm}(t) + D_{lm}(t) = 0, \tag{32}$$

where the dot denotes the time-derivative. With a simple assumption that the dielectric has attained the stationary state, given by equations (25, 26), $D_{lm}(t \geq t_0) = 1$, we have just

$$D_{lm}(t) = D_{lm}(t_0)\mathrm{e}^{-\frac{t}{\tau_{lm}}} = \mathrm{e}^{-\frac{t}{\tau_{lm}}} \tag{33}$$

as an exponential decay for all components of the polarization, so the decay of the polarization is equal to

$$\langle P^{(1)}(t)\rangle = \left[(\mu_x^2+\mu_y^2)\mathrm{e}^{-\frac{t}{\tau_{11}}} + \mu_z^2\mathrm{e}^{-\frac{t}{\tau_{10}}}\right]\frac{\rho E_0}{3kT}, \tag{34}$$

$$\langle P^{(3)}(t)\rangle = -(\mu_x^2+\mu_y^2+\mu_z^2)\left[(\mu_x^2+\mu_y^2)\mathrm{e}^{-\frac{t}{\tau_{11}}} + \mu_z^2\mathrm{e}^{-\frac{t}{\tau_{10}}}\right]\frac{\rho E_0^3}{45k^3T^3}. \tag{35}$$

From the above equations we see that the decays of polarization components are simply the superposition of two exponentials with the relaxation times τ_{11} and τ_{10}.

5. Conclusions

Equations (12)–(24) and (35) describe the rise in time and decay of the third-order electric polarization in dielectric media composed of non-interacting symmetric-top molecules. The rotational relaxation times τ_{11}, τ_{22} and τ_{21}, given by formula (16), for the symmetric-top molecules may significantly differ from those of the spherical molecules — $\tau_1 = \tau_{10}$, $\tau_2 = \tau_{20}$. The difference mainly depends on the anisotropy parameter $\xi = D_\perp / D_\|$. In Fig. 1 the ratios

$$\begin{aligned} \tau_{11}/\tau_{10} &= \frac{2}{1+\xi}, \\ \tau_{22}/\tau_{20} &= \frac{3}{1+2\xi}, \\ \tau_{21}/\tau_{20} &= \frac{6}{5+\xi}, \end{aligned} \tag{36}$$

versus the parameter ξ are presented. We can see that all ratios go to zero when $\xi \to \inf$. For $\xi < 1$ these ratios are higher than 1, so the respective exponentials in equations (20)–(22) and (24) grow faster than in the case of spherical molecules.

In Fig. 2 we present the nonlinear relaxation (rise and decay) functions $A_{10}(t)$ and $D_{10}(t)$ *versus* $\frac{t}{\tau_1}$. The corresponding graphs for $A_{11}^{(xxx)}(t)$ and $D_{11}(t)$ are shown in Fig. 5 and for the sums $A_{10}^{(xxz)}(t) + A_{11}^{(xzz)}(t)$ and $D_{10}(t) + D_{11}(t)$ in Fig. 3 and Fig. 4. These curves describe the influence of the anisotropy of the diagonal components of rotational diffusion tensor on the dynamic of the nonlinear dielectric effect (NDE) [10, 11].

Since NDE is an important method for measurements of the Langevin electric saturation in dilute solutions of dipolar molecules [5, 12, 13] it seems that our theory will stimulate the time-dependent investigations of nonlinear dielectric effect.

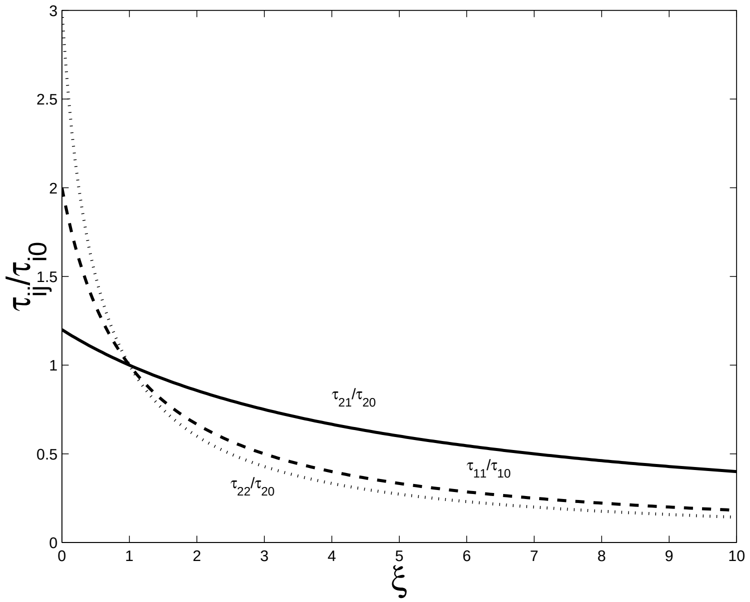

Fig. 1. The ratios τ_{11}/τ_{10}, τ_{22}/τ_{20} and τ_{21}/τ_{20} *versus* the anisotropy parameter ξ.

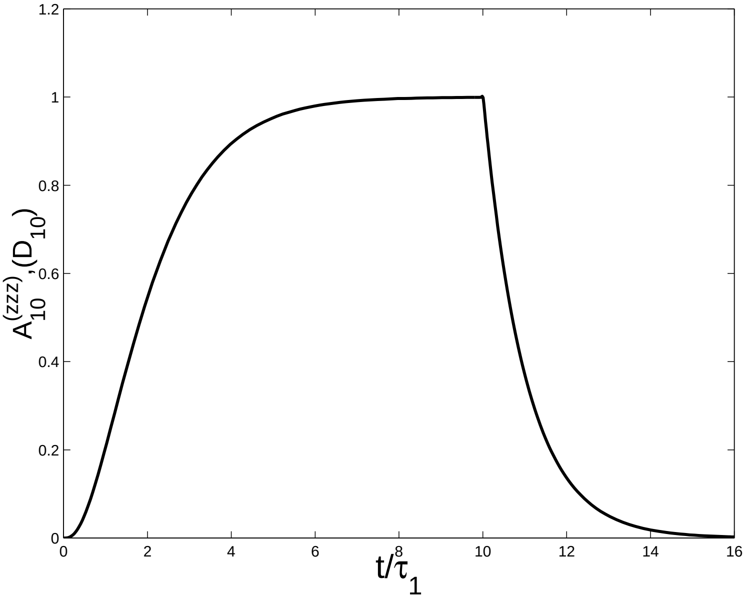

Fig. 2. The nonlinear relaxation functions $A_{10}^{(zzz)}(t)$ (rise) and $D_{10}(t)$ (decay) *versus* t/τ_1 independent of ξ, see the explanation in the text.

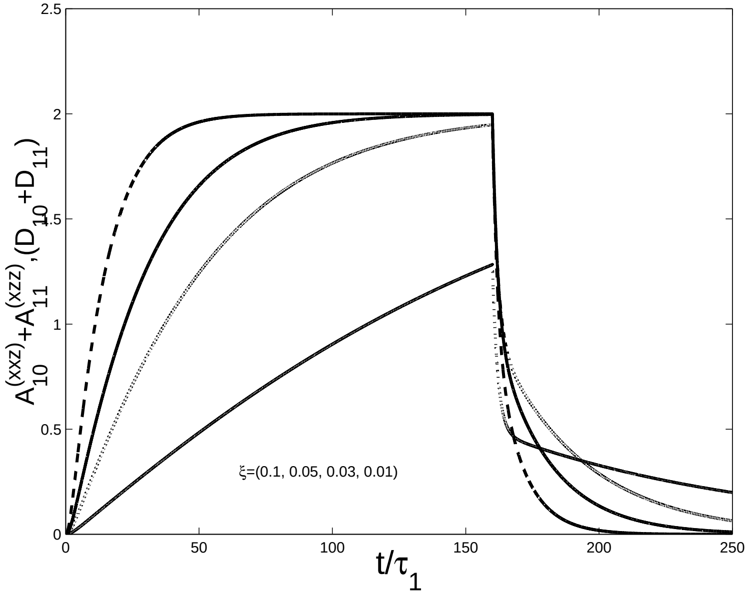

Fig. 3. The nonlinear relaxation functions $A_{10}^{(xxz)}(t) + A_{11}^{(xzz)}(t)$ (rise) and $D_{10}(t) + D_{11}(t)$ (decay) *versus* t/τ_1 for selected values of $\xi \leq 0.5$.

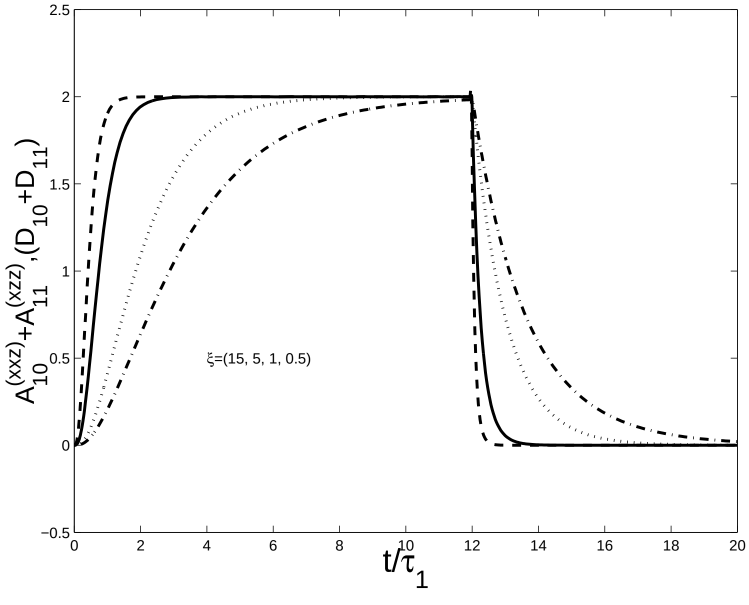

Fig. 4. The nonlinear relaxation functions $A_{10}^{(xxz)}(t) + A_{11}^{(xzz)}(t)$ (rise) and $D_{10}(t) + D_{11}(t)$ (decay) *versus* t/τ_1 for selected values of $\xi \geq 0.5$.

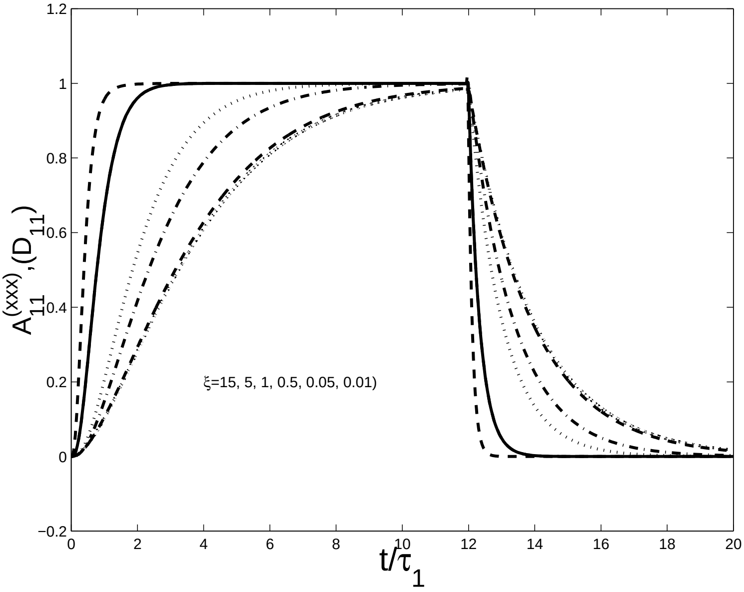

Fig. 5. The nonlinear relaxation functions $A_{11}^{(xxx)}(t)$ (rise) and $D_{11}(t)$ (decay) *versus* t/τ_1 for selected values of ξ.

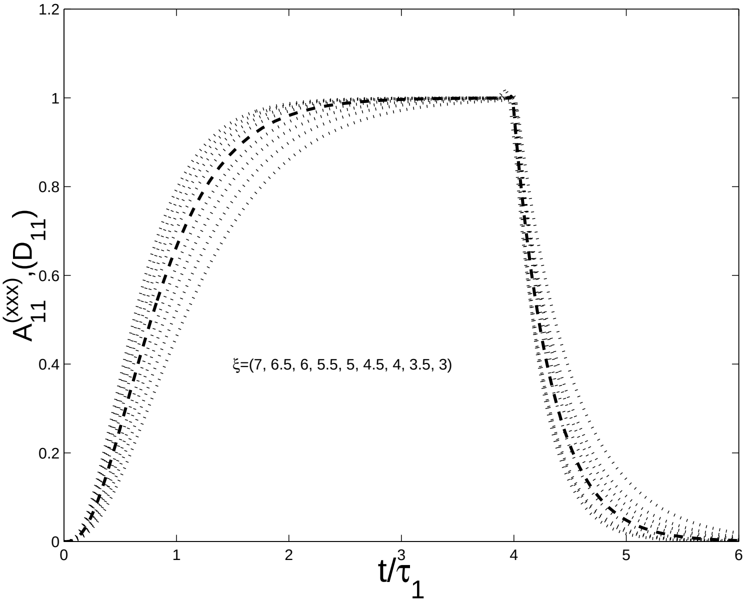

Fig. 6. The nonlinear relaxation functions $A_{11}^{(xxx)}(t)$ (rise) and $D_{11}(t)$ (decay) *versus* t/τ_1 for selected values of ξ around $\xi = 5$.

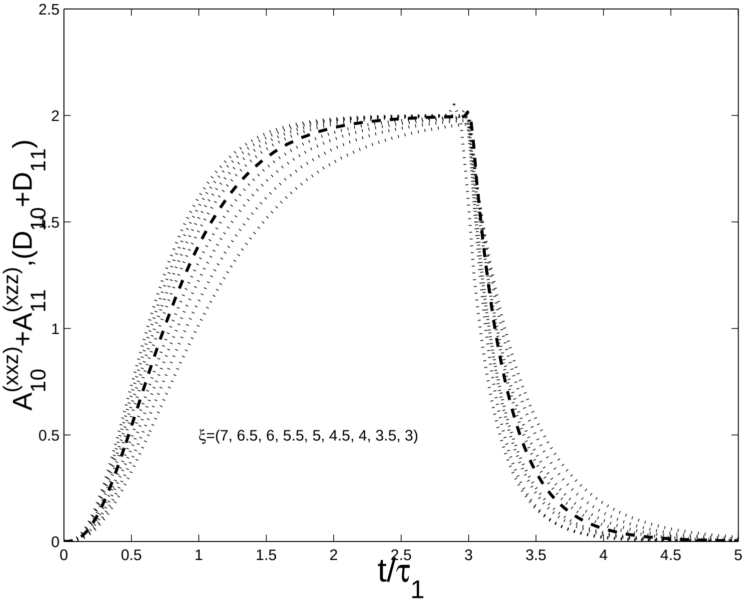

Fig. 7. The nonlinear relaxation functions $A_{10}^{(xxz)}(t) + A_{11}^{(xzz)}(t)$ (rise) and $D_{10}(t) + D_{11}(t)$ (decay) *versus* t/τ_1 for selected values of ξ around $\xi = 5$.

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