

Calculation of the rise transient and relaxation time of the induced dipole Kerr effect

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The exact calculation of the rise transient of the birefringence and the corresponding relaxation times by different theoretical methods is described, in particular the Kerr-effect response of an assembly of nonpolar but anisotropically polarizable molecules following the imposition of a constant electric field is studied by solving the Smoluchowski equation. This equation is transformed into a set of differential recurrence relations containing Legendre polynomials of even order only. By taking the Laplace transform of the birefringence function, it is shown that the singularity at $s=0$ (zero-frequency limit) may be removed so that the relaxation time for the rise process may be exactly expressed as a sum of products of Kummer functions and its first derivatives. The second approach is based on a matrix method where the spectrum of eigenvalues λ_{2j} and their associated amplitudes A_{2j} (extracted from the first components of eigenvectors) are calculated allowing one to express the relaxation time as $\sum A_{2j}(\lambda_{2j}^{-1})$. Numerical values of this time are tabulated for a large range of g values ($0 < g < 40$), g being the parameter measuring the ratio of the orientational energy arising from the electrical polarizabilities to the thermal energy. It is thus demonstrated that the lowest eigenvalue (λ_2) dominates almost completely the rise process. The effective relaxation time is also calculated exactly and expressed very simply as the ratio of two Kummer functions. Its evolution as a function of g leads to behavior similar to that of the relaxation time obtained either from the Kummer functions or from the eigenvalue method. It is characterized by a maximum situated around $g=2$, which is interesting in view of experimental applications. [S1063-651X(96)01307-4]

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I. INTRODUCTION

The exact solution for the dielectric after-effect response following the sudden removal of a dc field for a system of noninteracting polar molecules with uniaxial anisotropy (nematic liquid crystals) has been given by Coffey *et al.* [1]. This has been accomplished by adapting methods used for the solution of the analogous problem of superparamagnetic relaxation [2]. The calculation proceeds by expanding the solution of the Fokker-Planck equation as a series of Legendre polynomials which in turn leads to differential recurrence relations which govern the decay of the electric polarization or magnetization. This set of differential recurrence relations may be solved exactly in terms of a continued fraction whence the frequency dependence of the susceptibility may be calculated by means of linear response theory. The area under the curve of the decay of the polarization is, since the response is linear, the correlation time T of the first Legendre polynomial. This time T provides a global measure of the relaxation behavior of the system [3]. It has also been demonstrated that T may be expressed in closed form as a sum of products of confluent hypergeometric functions (Kummer functions). In turn T may be expressed exactly in integral form since the product of two Kummer functions may be expressed as an integral [2].

The analysis that we have just given pertains to linear response only since it is confined to the behavior of the first Legendre polynomial in the absence of an applied field. It is the purpose of this paper to show how the method we have developed may also be applied to a nonlinear problem of

electro-optics, i.e., the exact calculation of the transient birefringence due to the induced dipole Kerr effect. Thus we shall consider an assembly of nonelectrically interacting nonpolar molecules and we shall suppose that a strong step electric field is applied at the instant $t=0$, and subsequently the molecules only interact through the induced dipole moment. We shall demonstrate how the rise transient of the birefringence may be calculated exactly by expressing the Laplace transform of the birefringence, i.e., the rise transient in terms of continued fractions and we shall demonstrate how the relaxation time defined as the area under the curve of the rise transient may again be exactly expressed in terms of Kummer functions. We remark that this problem, unlike the one considered in Refs. [1, 2], is truly nonlinear and so the concept of relaxation time should be used rather than the correlation time. Furthermore, there is no longer any connection between the transient response and the ac response. We also remark due to the symmetry of the potential arising from the induced moments that the differential recurrence relations decouple into two sets, one for the even Legendre polynomials and the other for the odd Legendre polynomials. The analysis described in Refs. [1, 2] is for the odd set as the even one is in thermodynamic equilibrium. The opposite situation obtains here where the time behavior of the even set is the quantity of interest. The present problem has also been considered by Watanabe and Morita [4]. However, they did not give exact expressions for the relaxation time, merely calculating that quantity under certain limiting approximations; neither did they solve the three-term recurrence relations for the rise transient in continued fraction form.

Since the calculation of the relaxation time is not as straightforward as in the dielectric response, we shall first illustrate our method by considering the simple problem of the calculation of the relaxation time of a series inductance (L)–resistance (R) circuit when a step field is suddenly applied. Then, we shall transpose this definition to our problem of Kerr-effect relaxation and we shall show how the transient response may be obtained by two methods, one by expressing the Laplace transform of the rise transient as a sum of products of continued fractions and calculating the relaxation time in terms of the zero-frequency limit of this quantity, and the other by expressing the set of differential recurrence relations in the form of a set $\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t)$, and calculating the eigenvalues and corresponding eigenvectors of this set as detailed in Refs. [1, 2]. This will verify the exact solutions which we have obtained.

II. GENERAL EXPRESSIONS FOR THE RISE TIME

The Fokker-Planck (or Smoluchowski) equation for an assembly of noninteracting and anisotropically polarizable molecules at time t after the imposition of a step electric field $E(t) = E_0 U(t)$ ($t > 0$) is

$$2\tau_D \frac{\partial W}{\partial t} = \frac{1}{\sin\vartheta} \frac{\partial}{\partial \vartheta} \left[\sin\vartheta \left(\frac{\partial W}{\partial \vartheta} + \frac{1}{kT} \frac{\partial V}{\partial \vartheta} W \right) \right], \quad (1)$$

where the orientational potential energy $V(\vartheta)$ is

$$V(\vartheta) = -kTgU(t)\cos^2\vartheta, \quad (2)$$

τ_D is the Debye dielectric relaxation time, $U(t)$ is the unit step (Heaviside) function, and the nondimensional factor g comparing the potential energy to the thermal energy is defined as

$$g = \frac{\alpha_{\parallel} - \alpha_{\perp}}{2kT} E_0^2 = \frac{\Delta\alpha}{2kT} E_0^2, \quad (3)$$

α_{\parallel} and α_{\perp} representing the principal electric polarizabilities parallel and perpendicular to the symmetry axis of the molecule, respectively.

The distribution function $W(\vartheta, t)$ of orientations is axially symmetric and may therefore be expanded as a series of Legendre polynomials to give just as in Refs. [1, 2] the differential recurrence relation

$$\begin{aligned} \frac{2\tau_D}{l(l+1)} \dot{f}_l + \left[1 - \frac{2gU(t)}{(2l-1)(2l+3)} \right] f_l \\ = \frac{2g(l-1)U(t)}{(2l-1)(2l+1)} f_{l-2} - \frac{2g(l+2)U(t)}{(2l+1)(2l+3)} f_{l+2}, \end{aligned} \quad (4)$$

where

$$f_l(t) = \frac{1}{2l+1} \frac{a_l(t)}{a_0} = \langle P_l(\cos\vartheta) \rangle, \quad (5)$$

the angular brackets denoting the expectation value of P_l with respect to the distribution W , and the a_l 's are the Fourier-Laplace coefficients arising from the expansion in zonal harmonics

$$W(\vartheta, t) = \sum_{l=0}^{\infty} a_l(t) P_l(\cos\vartheta).$$

This recurrence relation decouples into odd and even sets, and the even set appropriate to Kerr-effect relaxation is

$$\begin{aligned} \frac{\tau_D}{k(2k+1)} \dot{f}_{2k} + \left[1 - \frac{2gU(t)}{(4k-1)(4k+3)} \right] f_{2k} \\ = \frac{2g(2k-1)U(t)}{(4k-1)(4k+1)} f_{2k-2} - \frac{2g(2k+2)U(t)}{(4k+1)(4k+3)} f_{2k+2}. \end{aligned} \quad (6)$$

The Laplace transform of the homogeneous solution of this is

$$\begin{aligned} S_{2k}(s) \\ = \frac{2g(2k-1)}{16k^2-1} \\ \frac{s\tau_D}{k(2k+1)} + 1 - \frac{2g}{4k+3} \left(\frac{1}{4k-1} - \frac{2k+2}{4k+1} S_{2k+2}(s) \right), \end{aligned} \quad (7)$$

where

$$S_{2k}(s) = \frac{F_{2k}(s)}{F_{2k-2}(s)}, \quad (8)$$

and $F_{2k}(s)$ is the Laplace transform of $f_{2k}(t)$ such that

$$F_{2k}(s) = \int_0^{\infty} f_{2k}(t) e^{-st} dt. \quad (9)$$

The inhomogeneous solution is determined by noting that all initial conditions vanish save $k=0$ when $f_0(t) = f_0(0) = 1$, whence we easily find that the Laplace transform of the inhomogeneous solution appropriate for Kerr-effect relaxation ($k=1$) is

$$F_2(s) = \frac{1}{s} \frac{\frac{2g}{15}}{\frac{s\tau_D}{3} + 1 - \frac{2g}{21} + \frac{8g}{35} S_4(s)}. \quad (10)$$

This is the Laplace transform of the growth of the birefringence. We also note by the final value theorem of Laplace transformation that

$$\lim_{s \rightarrow 0} s F_2(s) = \frac{\frac{2g}{15}}{1 - \frac{2g}{21} + \frac{8g}{35} S_4(0)} = \lim_{t \rightarrow \infty} f_2(t) = f_2(\infty). \quad (11)$$

It now remains to extract a formula for the relaxation time from this solution. First, we remark that the Laplace transform (denoted by \mathcal{L}) of the rise transient is

$$\mathcal{L}[f_2(\infty) - f_2(t)] = \frac{f_2(\infty)}{s} - F_2(s). \tag{12}$$

The area under this curve is

$$\begin{aligned} \int_0^\infty [f_2(\infty) - f_2(t)] dt &= \lim_{s \rightarrow 0} \int_0^\infty [f_2(\infty) - f_2(t)] e^{-st} dt \\ &= \lim_{s \rightarrow 0} \left[\frac{f_2(\infty)}{s} - F_2(s) \right]. \end{aligned} \tag{13}$$

On inspection, this equation would appear to have a singularity at $s=0$. This is not so, however, as we illustrate first of all by considering a series of R, L circuits with an emf $e(t) = EU(t)$ suddenly applied at $t=0$. The instantaneous current $i(t)$ flowing through these passive elements is

$$i(t) = \frac{e(t)}{R} (1 - e^{-t/\tau}), \tag{14}$$

whence

$$\int_0^\infty [i(\infty) - i(t)] dt = \frac{\tau E}{R} = \tau i(\infty), \tag{15}$$

and so the time constant τ characterizing this electrical circuit is

$$\tau = \frac{1}{i(\infty)} \int_0^\infty [i(\infty) - i(t)] dt = \frac{1}{i(\infty)} \lim_{s \rightarrow 0} \left[\frac{i(\infty)}{s} - I(s) \right], \tag{16}$$

where $I(s)$ is the Laplace transform of $i(t)$.

Now,

$$I(s) = \frac{E}{L} \frac{1}{s(s + 1/\tau)}, \tag{17}$$

so that on decomposition of $I(s)$ into partial fractions we have

$$\tau = \frac{1}{i(\infty)} \lim_{s \rightarrow 0} \left[\frac{i(\infty)}{s} - i(\infty) \left(\frac{1}{s} - \frac{1}{s + 1/\tau} \right) \right] = \frac{L}{R}, \tag{18}$$

as is well known.

We may use an analogous result for the definition of the relaxation time in our Kerr-effect relaxation problem. We have

$$\begin{aligned} T &= \frac{1}{f_2(\infty)} \lim_{s \rightarrow 0} \int_0^\infty [f_2(\infty) - f_2(t)] e^{-st} dt \\ &= \frac{1}{f_2(\infty)} \lim_{s \rightarrow 0} \left[\frac{f_2(\infty)}{s} - F_2(s) \right] = \lim_{s \rightarrow 0} \left[\frac{1}{s} - \frac{F_2(s)}{f_2(\infty)} \right]. \end{aligned} \tag{19}$$

Now,

$$\frac{F_2(s)}{f_2(\infty)} = \frac{\frac{2g}{15} \frac{1}{s}}{s \frac{\tau_D}{3} + 1 - \frac{2g}{21} + \frac{8g}{35} S_4(s)} \frac{1 - \frac{2g}{21} - \frac{8g}{35} S_4(0)}{\frac{2g}{15}}. \tag{20}$$

Equation (19), which yields T , is not defined for $s=0$. In order to overcome this difficulty, we remark that $S_4(s)$ is a continued fraction of the form

$$\frac{A}{Bs + C + DS_6(s)},$$

where A, B, C , and D are constants independent of s . The function $S_6(s)$ is again a continued fraction which depends on $S_8(s)$ and so on, so that after reduction to the same denominator, the numerator of $sF_2(s)$ will always be one degree less than that of the denominator because of the presence of the first degree term Bs . This can therefore be written in the polynomial form as

$$\begin{aligned} \frac{f_2(\infty)}{s} &= \frac{1}{s} \frac{2g/15}{1 - 2g/21 + (8g/35)S_4(0)} = \frac{1}{s} \frac{b_0}{c_0}, \\ F_2(s) &= \frac{1}{s} \frac{2g/15}{s \tau_D/3 + 1 - 2g/21 + (8g/35)S_4(s)} \\ &= \frac{1}{s} \frac{b_0 + b_1s + \dots + b_ns^n}{c_0 + c_1s + \dots + c_{n+1}s^{n+1}}, \end{aligned} \tag{21}$$

where the b_n 's and the c_{n+1} 's are the polynomial coefficients of the numerator and the denominator, respectively, so that

$$\begin{aligned} T &= \frac{c_0}{b_0} \lim_{s \rightarrow 0} \left[\frac{1}{s} \left(\frac{b_0}{c_0} - \frac{b_0 + b_1s + \dots + b_ns^n}{c_0 + c_1s + \dots + c_{n+1}s^{n+1}} \right) \right] \\ &= \frac{c_0}{b_0} \lim_{s \rightarrow 0} \left[\frac{(b_0c_1 - b_1c_0) + s(b_0c_2 - b_2c_0) + \dots + s^{n-1}(b_0c_n - b_nc_0) + b_0c_{n+1}s^n}{c_0(c_0 + c_1s + \dots + c_{n+1}s^{n+1})} \right] = \frac{b_0c_1 - b_1c_0}{b_0c_0}. \end{aligned} \tag{22}$$

This demonstrates how the apparent singularity at $s=0$ disappears, in such a manner that T may be rendered by the formula

$$T = \frac{1}{f_2(\infty)} \lim_{s \rightarrow 0} \left[\frac{f_2(\infty)}{s} - F_2(s) \right]. \tag{23}$$

Equation (22) is very simple and gives the exact relaxation time for the birefringence rise transient. In order to express explicitly the coefficients b_0, b_1, c_0, c_1 , we can expand $S_4(s)$ as a Laurent series about the point $s=0$, namely,

$$S_4(s) = S_4(0) + \sum_{n=1}^{\infty} \frac{s^n}{n!} S_4^{(n)}(0), \tag{24}$$

where

$$S_4^{(n)}(0) = \frac{d^n S_4(s)}{ds^n} \Big|_{s=0}.$$

With the aid of Eqs. (10), (11), and (24) and after some calculation, we obtain

$$\begin{aligned} \frac{f_2(\infty)}{s} - F_2(s) &= \frac{2g}{15} \frac{1}{s} \left[\frac{1}{1 - 2g/21 + (8g/35)S_4(0)} - \frac{1}{s\tau_D/3 + 1 - 2g/21 + (8g/35)S_4(s)} \right] \\ &= \frac{2g}{15} \frac{1}{s} \left\{ \frac{s\tau_D}{3} + 1 - \frac{2g}{21} + \frac{8g}{35} \left[S_4(0) + \sum_{j=1}^{\infty} \frac{s^j}{j!} S_4^{(j)}(0) \right] \right\} - \left(1 - \frac{2g}{21} + \frac{8g}{35} S_4(0) \right) \\ &= \frac{2g}{15} \frac{1}{s} \left(1 - \frac{2g}{21} + \frac{8g}{35} S_4(0) \right) \left\{ \frac{s\tau_D}{3} + 1 - \frac{2g}{21} + \frac{8g}{35} \left[S_4(0) + \sum_{j=1}^{\infty} \frac{s^j}{j!} S_4^{(j)}(0) \right] \right\} \\ &= \frac{2g}{15} \frac{1}{s} \frac{\frac{s\tau_D}{3} + \frac{8g}{35} s S_4'(0) + \frac{8g}{35} \sum_{j=2}^{\infty} \frac{s^j}{j!} S_4^{(j)}(0)}{\left(1 - \frac{2g}{21} + \frac{8g}{35} S_4(0) \right) \left\{ \frac{s\tau_D}{3} + 1 - \frac{2g}{21} + \frac{8g}{35} \left[S_4(0) + \sum_{j=1}^{\infty} \frac{s^j}{j!} S_4^{(j)}(0) \right] \right\}}, \end{aligned} \tag{25}$$

which on taking the zero-frequency limit ($s \rightarrow 0$) yields the exact formula

$$T = \frac{\frac{\tau_D}{3} + \frac{8g}{35} S_4'(0)}{1 - \frac{2g}{21} + \frac{8g}{35} S_4(0)}, \tag{26}$$

where $S_4'(0)$ is the limit as $s \rightarrow 0$ of the first derivative of $S_4(s)$ with respect to s . Equation (26) may also be expressed in closed form [see Eq. (C3) of Ref. [2]], namely,

$$S_n(0) = 1 - \frac{M((n-1)/2, n + \frac{1}{2}, g)}{M((n-1)/2, n - \frac{1}{2}, g)}, \tag{27}$$

where the Kummer (or confluent hypergeometric) function $M(a, b, z)$ is given by

$$\begin{aligned} M(a, b, z) &= 1 + \frac{a}{b} z + \frac{a(a+1)}{b(b+1)} \frac{z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)} \frac{z^3}{3!} \\ &+ \dots, \end{aligned} \tag{28}$$

whence

$$S_4(0) = 1 - \frac{M(\frac{3}{2}, \frac{9}{2}, g)}{M(\frac{3}{2}, \frac{7}{2}, g)}. \tag{29}$$

In order to obtain an expression which is convenient for the numerical calculation of T , we can write

$$S_n(s) = \frac{A_n}{sB_n + C_n + D_n S_{n+2}(s)}, \tag{30}$$

where

$$\begin{aligned} A_n &= 2g \frac{n-1}{4n^2-1}, & B_n &= \frac{2\tau_D}{n(n+1)}, \\ C_n &= 1 - \frac{2g}{(2n-1)(2n+3)}, & D_n &= 2g \frac{n+2}{(2n+1)(2n+3)}, \end{aligned} \tag{31}$$

so that the derivative of $S_n(s)$ with respect to s can be expressed in the form of a recurrence relation, namely,

$$\begin{aligned} S_n'(0) &= -A_n \frac{B_n + D_n S_{n+2}'(0)}{[C_n + D_n S_{n+2}(0)]^2} \\ &= -\frac{1}{A_n} [S_n(0)]^2 [B_n + D_n S_{n+2}'(0)], \end{aligned} \tag{32}$$

which for $n=4$ becomes equal to (see Appendix A)

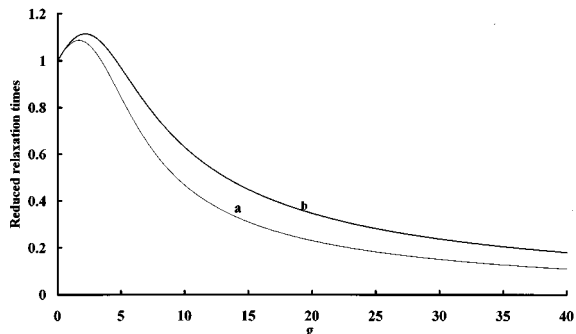


FIG. 1. Comparison of the evolution of the different reduced relaxation times T' (curve a) and T'_{eff} (curve b) as a function of the electrical anisotropy parameter g . Curve a: from Eq. (35), $g_{max}=1.69$; curve b: from Eq. (49), $g_{max}=2.18$.

$$\begin{aligned}
 S'_4(0) = & -\frac{\tau_D}{g} [S_4(0)]^2 \left\{ \frac{21}{20} - \frac{7\sqrt{\pi}}{32} \sum_{k=1}^{N-1} (-1)^{k+1} (4k+9) \frac{\Gamma(k+2)}{\Gamma(k+\frac{7}{2})} \prod_{j=1}^k [S_{2j+4}(0)]^2 \right\} \\
 & + (-1)^N \frac{7\sqrt{\pi}}{4} \frac{1}{4N+7} \frac{\Gamma(N+3)}{\Gamma(N+\frac{3}{2})} \prod_{j=1}^N [S_{2j+2}(0)]^2 S'_{2N+4}(0),
 \end{aligned} \tag{33}$$

where we have used the gamma function Γ defined by

$$\Gamma(z+1) = z\Gamma(z).$$

The remainder of Eq. (33) may be set equal to zero for the order $k=N$, so that from a numerical point of view it is sufficient to calculate the alternating series, that is,

$$S'_4(0) = -\frac{\tau_D}{g} [S_4(0)]^2 \left\{ \frac{21}{20} - \frac{7\sqrt{\pi}}{32} \sum_{k=1}^{N-1} (-1)^{k+1} (4k+9) \frac{\Gamma(k+2)}{\Gamma(k+\frac{7}{2})} \prod_{j=1}^k [S_{2j+4}(0)]^2 \right\}. \tag{34}$$

We have verified that this equation is rapidly convergent and that a very good precision is obtained for $N=5$. Substituting Eq. (34) into Eq. (26) we can write down the final expression for the reduced relaxation time T' normalized to unity,

$$T' = \frac{T}{\tau_D/3} = \frac{1 - 3[S_4(0)]^2 \left[\frac{6}{25} - \frac{\sqrt{\pi}}{20} \sum_{k=1}^N (-1)^{k+1} (4k+9) \frac{\Gamma(k+2)}{\Gamma(k+\frac{7}{2})} \prod_{j=1}^k [S_{2j+4}(0)]^2 \right]}{1 - \frac{2g}{21} + \frac{8g}{35} S_4(0)}, \tag{35}$$

which if so desired may be expressed in terms of Kummer functions as the derivative $S'_{2N+4}(0)$ is no longer involved. The calculation of T (or T') is thus much more involved than in the dielectric case. The reverse is true of the Laplace transform of the Kerr function $F_2(s)$. The evolution of T' is presented in Fig. 1 for different g values varying in the range 0–40.

III. CALCULATION OF THE RISE TIME AND RISE TRANSIENT USING MATRIX METHODS

Having illustrated how one may evaluate the rise transient and the relaxation time by continued fraction methods, we consider how these quantities may be calculated by matrix methods. In order to accomplish this, we arrange our set of recurrence relations in the form

$$\dot{\mathbf{f}}_{2k} = -\frac{1}{2\tau_D} \mathbf{M}\mathbf{f}_{2k} + \mathbf{B}U(t), \quad k=1,2,\dots \tag{36}$$

where $\dot{\mathbf{f}}_{2k}$, \mathbf{f}_{2k} , and \mathbf{B} are column matrices such as

$$\dot{\mathbf{f}}_{2k}(t) = \begin{pmatrix} \dot{f}_2(t) \\ \dot{f}_4(t) \\ \vdots \\ \dot{f}_{2k}(t) \\ \dots \end{pmatrix}, \quad \mathbf{f}_{2k}(t) = \begin{pmatrix} f_2(t) \\ f_4(t) \\ \vdots \\ f_{2k}(t) \\ \dots \end{pmatrix}, \quad \mathbf{B} = \frac{1}{2\tau_D} \begin{pmatrix} \frac{4g}{5} \\ 0 \\ 0 \\ 0 \\ \dots \end{pmatrix}, \tag{37a}$$

and \mathbf{M} is an $n \times n$ matrix characteristic of the rise transient birefringence,

$$\mathbf{M} = \begin{pmatrix} 6\left(1 - \frac{2g}{21}\right) & \frac{48g}{35} & 0 & 0 & 0 & \dots \\ -\frac{40g}{21} & 20\left(1 - \frac{2g}{77}\right) & \frac{80g}{33} & 0 & 0 & \dots \\ 0 & -\frac{420g}{143} & 42\left(1 - \frac{2g}{165}\right) & \frac{224g}{65} & 0 & \dots \\ 0 & 0 & -\frac{336g}{85} & 72\left(1 - \frac{2g}{285}\right) & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (37b)$$

The general solution of this matrix equation is

$$\mathbf{f}_{2k}(t) = \exp(\mathbf{M}'t)\mathbf{f}_{2k}(0) + \int_0^t \exp[\mathbf{M}'(t-t')\mathbf{B}U(t')]dt', \quad (38)$$

where

$$\mathbf{M}' = -\frac{1}{2\tau_D}\mathbf{M}.$$

For the purpose of the calculation of the relaxation time, we are interested in the transient part of this solution which is given by the integral in Eq. (38). For $k=1$, the matrix elements may be expressed in the form

$$\sum_j A_{2j} \exp(-\lambda_{2j}t), \quad j=1,2,3,\dots$$

Since we are concerned here with the rise transient, the relaxation modes of the Kerr function may be written as

$$f_2(t) = f_2(\infty) \left[1 - \sum_j A_{2j} \exp(-\lambda_{2j}t) \right], \quad (39)$$

where the A_{2j} denote the amplitudes of the first components of the successive eigenvectors associated to the eigenvalues λ_{2j} . The longitudinal relaxation time is then the area under this curve, viz.,

$$\begin{aligned} T_{\parallel} &= \lim_{s \rightarrow 0} \left[\frac{1}{s} - \frac{F_2(s)}{f_2(\infty)} \right] = \lim_{s \rightarrow 0} \left[\frac{1}{s} - \left(\frac{1}{s} - \sum_k \frac{A_{2j}}{s + \lambda_{2j}} \right) \right] \\ &= \sum_j A_{2j} \lambda_{2j}^{-1}. \end{aligned} \quad (40a)$$

In Table I, we present the amplitudes and the eigenvalues of the first four modes for different values of the parameter g up to $g=40$. The eigenvalues arise from the solution of the secular equation

$$\det\{s\mathbf{I} - \mathbf{M}'\} = 0,$$

where \mathbf{I} represents the usual identity matrix.

Since the eigenvalues are presented in the form $\lambda_{2j}/6\tau_B$ (τ_B is the birefringence relaxation time equal to $\tau_D/3$), the reduced relaxation time T'_{\parallel} is given by

$$T'_{\parallel} = \frac{T_{\parallel}}{\tau_B} = 6 \sum_j A_{2j} \lambda_{2j}^{-1}. \quad (40b)$$

We also remark that the amplitudes of rank $j=2l$ ($l=1,2,\dots$) are negative, which was not observed for the dielectric response. Satisfactory convergence was obtained using a 30×30 matrix in all cases. It is apparent from Table I that the lowest eigenvalue λ_2 provides an accurate enough representation of the relaxation time since the amplitudes of the other modes (A_4, A_6 , and A_8) become smaller and smaller in comparison with that of the first one (A_2). This behavior is rather similar to that of the dielectric response governed by $\lambda_1, \lambda_3, \lambda_5$, etc. where the mode characterized by λ_1 dominates the response.

IV. COMPARISON OF MATRIX SOLUTIONS WITH THE CONTINUED FRACTION SOLUTIONS

The solution for the relaxation time rendered by a matrix method which may be implemented with a minimum of analysis agrees exactly (within rounding errors) with the continued fraction solution rendered by Eq. (26) for all g values (see the last column of Table I and the second and fourth columns of Table II). The most interesting result of our theoretical approach is that the solution is again dominated by the first mode (λ_2). The Kerr-effect relaxation time, unlike the dielectric one, passes through a maximum at a certain value of g (which may be a useful factor in experiments) before decreasing monotonically to zero for increasing g values. This behavior has also been observed by Morita and Watanabe (see their Fig. 4 in Ref. [4]).

We also compare our solution for the rise transient for the relaxation time with that rendered by the effective eigenvalue. This method may be used here since the rise transient of the electric birefringence for the pure induced dipole mechanism may be approximated by a single exponential term [4] characterized by an effective relaxation time T_{eff} . It is well known, indeed, that when the orientation of the molecules is only due to the anisotropy of the electrical polarizabilities, the Kerr-effect response may be considered as linear—at least for weak fields—according to Kerr's law which relates the birefringence Δn to the square electric field E^2 . On the contrary, this is not true for the process arising from pure permanent (field-off) moments which is, in essence, a nonlinear response and needs two effective relaxation times.

Thus the time behavior of the orientational factor may be written as

TABLE I. Eigenvalues λ_{2j} in the form $\lambda_{2j}/6\tau_B$ of the first four modes of the rise of the birefringence as a value of the parameter g and corresponding amplitudes A_{2j} , $j=1,2,3,\dots$ [T'_{\parallel} is the reduced relaxation time given by Eq. (40b)]. E denotes values of 10^{-n} .

g	λ_2	λ_4	λ_6	λ_8	A_2	A_4	A_6	A_8	T'_{\parallel}
1	5.6143	19.6181	41.6215	71.6229	1.003 777 8	-3.781 8E-03	3.961 1E-06	-1.855 3E-09	1.071 577 5
2	5.5955	19.5135	41.5049	71.5026	1.014 927 2	-1.498 9E-02	6.207 5E-05	-1.157 7E-07	1.083 701 4
3	5.9333	19.6898	41.6521	71.6400	1.034 660 3	-3.498 1Ee-02	3.225 5E-04	-1.346 9E-06	1.035 678 3
4	6.6126	20.1517	42.0657	72.0368	1.065 760 5	-6.683 9E-02	1.086 6E-03	-8.026 4E-06	0.947 277 9
5	7.6121	20.9061	42.7493	72.6952	1.111 749 9	-0.114 614 8	2.898 0E-03	-3.328 5E-05	0.843 808 5
6	8.9031	21.9636	43.7075	73.6180	1.175 822 1	-0.182 358 9	6.645 1E-03	-1.094 3E-04	0.743 499 3
7	10.4483	23.3388	44.9461	74.8085	1.259 597 0	-0.272 955 0	0.013 659 3	-0.000 305 1	0.654 957 0
8	12.2020	25.0504	46.4721	76.2709	1.361 733 8	-0.386 791 5	0.025 796 6	-0.000 751 0	0.580 222 2
9	14.1122	27.1189	48.2945	78.0098	1.476 850 1	-0.520 698 2	0.045 489 6	-0.001 675 9	0.518 225 2
10	16.1255	29.5606	50.4239	80.0308	1.595 816 9	-0.668 191 5	0.075 741 3	-0.003 453 7	0.466 908 4
11	18.1945	32.3799	52.8738	82.3401	1.708 249 1	-0.821 791 7	0.120 003 5	-0.006 663 2	0.424 193 5
12	20.2839	35.5630	55.6606	84.9450	1.806 147 6	-0.976 288 2	0.181 861 7	-0.012 158 9	0.388 311 9
13	22.3724	39.0748	58.8040	87.8538	1.886 130 1	-1.130 298 5	0.264 425 1	-0.021 148 2	0.357 857 1
14	24.4500	42.8623	62.3267	91.0759	1.948 976 3	-1.284 829 0	0.369 400 0	-0.035 269 6	0.331 740 3
15	26.5144	46.8604	66.2515	94.6225	1.997 658 6	-1.440 246 3	0.496 063 9	-0.056 654 5	0.309 124 5
16	28.5666	51.0004	70.5967	98.5066	2.035 568 1	-1.594 023 4	0.640 768 9	-0.087 945 6	0.289 365 1
17	30.6088	55.2187	75.3691	102.7434	2.065 603 0	-1.740 738 2	0.797 740 9	-0.132 229 3	0.271 960 9
18	32.6432	59.4649	80.5565	107.3511	2.089 935 2	-1.874 213 2	0.961 177 7	-0.192 812 2	0.256 519 4
19	34.6717	63.7051	86.1241	112.3509	2.110 095 0	-1.990 150 2	1.127 292 6	-0.272 767 0	0.242 728 8
20	36.6956	67.9216	92.0156	117.7664	2.127 136 0	-2.087 412 5	1.294 653 1	-0.374 205 1	0.230 339 6
21	38.7161	72.1086	98.1590	123.6214	2.141 785 3	-2.167 523 8	1.462 613 9	-0.497 393 6	0.219 149 6
22	40.7338	76.2668	104.4757	129.9351	2.154 553 2	-2.233 336 8	1.629 242 8	-0.640 115 6	0.208 993 5
23	42.7493	80.4001	110.8907	136.7161	2.165 807 0	-2.287 885 7	1.790 394 4	-0.797 882 8	0.199 734 7
24	44.7630	84.5130	117.3409	143.9543	2.175 818 0	-2.333 784 7	1.940 622 2	-0.965 282 2	0.191 259 8
25	46.7752	88.6095	123.7815	151.6162	2.184 792 3	-2.373 062 3	2.075 207 1	-1.137 794 4	0.183 473 4
26	48.7862	92.6929	130.1864	159.6444	2.192 890 2	-2.407 213 4	2.191 785 9	-1.312 750 3	0.176 295 2
27	50.7961	96.7659	136.5449	167.9631	2.200 238 6	-2.437 319 0	2.290 620 4	-1.488 692 6	0.169 656 7
28	52.8052	100.8305	142.8565	176.4865	2.206 940 2	-2.464 162 5	2.373 764 6	-1.663 768 0	0.163 499 4
29	54.8134	104.8881	149.1256	185.1296	2.213 078 9	-2.488 320 1	2.443 972 9	-1.834 524 7	0.157 772 8
30	56.8210	108.9398	155.3586	193.8182	2.218 724 4	-2.510 225 4	2.503 921 9	-1.996 103 5	0.152 433 3
31	58.8279	112.9867	161.5618	202.4964	2.223 934 9	-2.530 212 4	2.555 851 5	-2.143 699 6	0.147 443 1
32	60.8343	117.0294	167.7405	211.1292	2.228 759 6	-2.548 544 8	2.601 495 2	-2.274 194 7	0.142 768 9
33	62.8403	121.0685	173.8992	219.6999	2.233 240 5	-2.565 434 7	2.642 144 3	-2.386 879 3	0.138 381 7
34	64.8458	125.1044	180.0413	228.2050	2.237 413 6	-2.581 056 4	2.678 748 4	-2.483 060 7	0.134 255 9
35	66.8510	129.1376	186.1696	236.6489	2.241 309 9	-2.595 554 9	2.712 009 4	-2.565 131 8	0.130 368 9
36	68.8558	133.1683	192.2862	245.0391	2.244 956 3	-2.609 052 6	2.742 454 6	-2.635 722 5	0.126 700 4
37	70.8603	137.1968	198.3927	253.3839	2.248 376 5	-2.621 653 5	2.770 488 5	-2.697 199 6	0.123 232 6
38	72.8646	141.2234	204.4907	261.6906	2.251 590 9	-2.633 447 2	2.796 429 1	-2.751 479 3	0.119 949 5
39	74.8686	145.2483	210.5811	269.9658	2.254 617 4	-2.644 510 7	2.820 530 5	-2.800 036 3	0.116 836 6
40	76.8723	149.2716	216.6648	278.2145	2.257 473 3	-2.654 912 9	2.843 004 6	-2.843 960 3	0.113 881 2

$$f_2(t) = \langle P_2(\cos\vartheta) \rangle(t) = f_2(\infty) \left[1 - \sum_j A_{2j} \exp(-\lambda_{2j}t) \right], \quad (41)$$

which in terms of the effective eigenvalue λ_{eff} becomes

$$f_2(t) = f_2(\infty) [1 - \exp(-\lambda_{\text{eff}}t)], \quad (42)$$

so that the effective relaxation time T_{eff} is then

$$T_{\text{eff}} = \lambda_{\text{eff}}^{-1} = \frac{\langle P_2(\cos\vartheta) \rangle(0)}{\langle P_2(\cos\vartheta) \rangle(\infty)} = \frac{\dot{f}_2(0)}{f_2(\infty)} = \left(\sum_j A_{2j} \lambda_{2j} \right)^{-1}, \quad (43a)$$

and the reduced effective relaxation time is

$$T'_{\text{eff}} = \frac{T_{\text{eff}}}{\tau_B} = 6 \left(\sum_j A_{2j} \lambda_{2j} \right)^{-1}. \quad (43b)$$

From Table II, it is apparent that T'_{eff} given by Eq. (43b) based on the effective eigenvalue technique is a little different from the numerical values of the relaxation times obtained using continued fraction or matrix methods, and so does not provide a rigorous representation of the rise transient birefringence phenomenon. In particular, this method leads to higher values of the relaxation time as g becomes greater than 1. As already mentioned by Coffey, Kalmykov,

TABLE II. Table of values of the reduced relaxation times from the solutions given by Eqs. (35) and (43b).

g	T'	T'_{eff}	g	T'	T'_{eff}
0.2	1.018 240	1.018 509	13.0	0.357 781	0.507 055
0.4	1.034 718	1.035 819	14.0	0.331 624	0.475 740
0.6	1.049 221	1.051 753	15.0	0.308 955	0.447 948
0.8	1.061 562	1.066 146	16.0	0.289 129	0.423 142
1.0	1.071 578	1.078 845	17.0	0.271 646	0.400 883
1.2	1.079 141	1.089 724	18.0	0.256 111	0.380 807
1.4	1.084 161	1.098 675	19.0	0.242 216	0.362 616
1.6	1.086 591	1.105 625	20.0	0.229 710	0.346 062
1.8	1.086 425	1.110 525	21.0	0.218 392	0.330 936
2.0	1.083 701	1.113 363	22.0	0.208 099	0.317 064
2.2	1.078 499	1.114 155	23.0	0.198 696	0.304 297
2.4	1.070 933	1.112 948	24.0	0.190 070	0.292 511
2.6	1.061 154	1.109 817	25.0	0.182 128	0.281 597
2.8	1.049 337	1.104 860	26.0	0.174 790	0.271 463
3.0	1.035 678	1.098 195	27.0	0.167 988	0.262 029
3.2	1.020 389	1.089 958	28.0	0.161 667	0.253 225
3.4	1.003 688	1.080 292	29.0	0.155 775	0.244 990
3.6	0.985 793	1.069 351	30.0	0.150 271	0.237 272
3.8	0.966 921	1.057 290	31.0	0.145 117	0.230 023
4.0	0.947 278	1.044 262	32.0	0.140 281	0.223 202
5.0	0.843 808	0.969 599	33.0	0.135 734	0.216 772
6.0	0.743 499	0.889 454	34.0	0.131 452	0.210 701
7.0	0.654 956	0.812 812	35.0	0.127 411	0.204 960
8.0	0.580 220	0.743 534	36.0	0.123 592	0.199 523
9.0	0.518 219	0.682 521	37.0	0.119 978	0.194 366
10.0	0.466 895	0.629 319	38.0	0.116 553	0.189 468
11.0	0.424 168	0.582 994	39.0	0.113 302	0.184 810
12.0	0.388 266	0.542 545	40.0	0.110 213	0.180 375

and Massawe [5], this is due to the loss of information on the different time regions of relaxation that are involved. In fact, the second expression in Eq. (43a) represents the initial slope of the rise of the birefringence, which is always interesting experimentally. It is also possible to find another expression for T'_{eff} starting from the set of differential recurrence equations. This has the advantage just as in the transverse dielectric response [1] of providing a simple analytic formula for the relaxation time. Setting $k=1$ in Eq. (6), one obtains

$$\dot{f}_2(t) = -\frac{1}{2\tau_D} \left[6 \left(1 - \frac{2g}{21} \right) f_2(t) + \frac{48g}{35} f_4(t) \right] + \frac{2g}{5\tau_D}, \quad (44)$$

which for $t=0$ reduces to

$$\dot{f}_2(0) = \frac{2g}{5\tau_D} \quad (45)$$

since $f_2(0)=f_4(0)=0$ (initial conditions).

It remains to evaluate the asymptotic value attained by $f_2(t)$ as $t \rightarrow \infty$, i.e., $f_2(\infty)$. The details of that calculation are given in Appendix B. It is found that [6]

$$f_{2k}(\infty) = \frac{g^k}{2} \frac{\Gamma(k + \frac{1}{2})}{\Gamma(2k + \frac{3}{2})} \frac{M(k + \frac{1}{2}, 2k + \frac{3}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)}, \quad (46)$$

so that for $k=1$, one has

$$f_2(\infty) = \frac{2g}{15} \frac{M(\frac{3}{2}, \frac{7}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)} = 1 - \frac{M(\frac{1}{2}, \frac{5}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)}. \quad (47)$$

This equation coincides rigorously with that obtained in another form by Watanabe and Morita in their study of Kerr-effect relaxation in high electric fields [4], but the essential lines of the calculation are not given. Their expression is

$$\lim_{t \rightarrow \infty} \langle P_2(\cos\vartheta) \rangle(t) = \frac{1}{2} \left[\frac{M(\frac{3}{2}, \frac{5}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)} - 1 \right]. \quad (48)$$

Substituting Eqs. (45) and (47) into the second expression of Eq. (43a), one finally finds that the effective relaxation time may be expressed exactly as the ratio of two Kummer functions, namely,

$$T'_{\text{eff}} = \frac{T'_{\text{eff}}}{\tau_D/3} = \frac{M(\frac{3}{2}, \frac{7}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)}, \quad (49)$$

where T'_{eff} represents a reduced relaxation time equal to 1 as $g=0$. The variations of this time against g are plotted in Fig. 1. One remarks that the general behavior of this curve resembles that of $T'(g)$, again possessing a maximum but slightly shifted on the right. Both these plots start from $T'=1$ when $g=0$, and have a maximum situated about $g=2$, and then pass again through a particular value of g ($3 < g < 5$) where $T'=1$. This may be explained as follows: it is well known that the stationary state birefringence for low fields is simply given by $2g/15$, which corresponds to Kerr's law. Equation (47) calculated for any value of the electrical parameter g shows that this stationary state is modulated by the ratio of two Kummer functions, involving deviation from Kerr's law. In particular, this ratio is greater than 1 in the range $0 < g < 5$. Such information may be exploited experimentally.

APPENDIX A: CALCULATION OF THE LAPLACE TRANSFORM $S'_4(0)$

From Eq. (32) we have

$$S'_n(0) = -[S_n(0)]^2 \left[\frac{\tau_D}{g} \frac{4n^2 - 1}{(n-1)n(n+1)} + \frac{(n+2)(2n-1)}{(n-1)(2n+3)} S'_{n+2}(0) \right]. \quad (A1)$$

Now, the next function will be

$$S'_{n+2}(0) = -[S_{n+2}(0)]^2 \left[\frac{\tau_D}{g} \frac{(2n+3)(2n+5)}{(n+1)(n+2)(n+3)} + \frac{(n+4)(2n+3)}{(n+1)(2n+7)} S'_{n+4}(0) \right], \quad (A2)$$

which by substitution into Eq. (A1) yields

$$S'_n(0) = -\frac{\tau_D}{g} [S_n(0)]^2 \left\{ \frac{(2n-1)(2n+1)}{(n-1)n(n+1)} - \frac{(n+2)(2n-1)(2n+3)(2n+5)}{(n-1)(n+1)(n+2)(n+3)(2n+3)} [S_{n+2}(0)]^2 \right\} \\ + \frac{(n+2)(n+4)(2n-1)(2n+3)}{(n-1)(n+1)(2n+3)(2n+7)} [S_n(0)]^2 [S_{n+2}(0)]^2 S'_{n+4}(0). \quad (\text{A3})$$

Since we are only interested here with even values of n , we can set $n=2m$ ($m=1,2,\dots$) so that Eq. (A3) may be written as

$$S'_{2m}(0) = -\frac{\tau_D}{g} \frac{(4m-1)(4m+1)}{(2m-1)2m(2m+1)} [S_{2m}(0)]^2 + [S_{2m}(0)]^2 \sum_{k=1}^{N-1} (-1)^{k+1} \\ \times \frac{(4m+4k+1)!!}{(4m-3)!!} \frac{(4m-1)!!}{(4m+4k-1)!!} \frac{(2m-3)!!}{(2m+2k+1)!!} \frac{(2m+2k-2)!!}{(2m)!!} \prod_{j=1}^k [S_{2j+2m}(0)]^2 \\ + (-1)^N \frac{4m-1}{4m+4N-1} \frac{(2m-3)!!}{(2m+2N-3)!!} \frac{(2m+2N)!!}{(2m)!!} \prod_{j=1}^N [S_{2j+2}(0)]^2 S'_{2N+2m}(0). \quad (\text{A4})$$

On noting that [7]

$$\Gamma(n+\frac{1}{2}) = \frac{(2n-1)!!}{2^n} \sqrt{\pi}, \quad (\text{A5}) \\ (2m+2n)!! = 2^{m+n}(m+n)!,$$

and setting $m=2$ in Eq. (A4), we find the desired result for $S'_4(0)$ given by Eq. (33).

APPENDIX B: EVALUATION OF THE ASYMPTOTIC LIMIT $f_{2n}(\infty)$ AS A RATIO OF TWO KUMMER FUNCTIONS

For the rise transient process, we can adopt the following definition ($x = \cos \vartheta$):

$$f_{2n}(\infty) = \frac{\int_{-1}^{+1} P_{2n}(x) \exp(gx^2) dx}{\int_{-1}^{+1} \exp(gx^2) dx} \\ = \frac{1}{2M(\frac{1}{2}, \frac{3}{2}, g)} \int_{-1}^{+1} P_{2n}(x) \exp(gx^2) dx, \quad (\text{B1})$$

which coincides with the initial condition of the decay process. Then, we can use the same method as that employed by Coffey *et al.* [2] for the magnetic susceptibility and adapt it to even Legendre polynomials. We have

$$\exp(gx^2) = \sum_{n=0}^{\infty} \frac{g^n}{n!} x^{2n}, \quad (\text{B2})$$

and

$$x^{2n} = \sum_{k=0}^n (4k+1) \frac{(2n)!}{(2n+2k+1)!} 2^{2k} \frac{(n+k)!}{(n-k)!} P_{2k}(x). \quad (\text{B3})$$

By using the orthogonality property of the Legendre polynomials and the definition of the Kummer function [Eq. (28)], we obtain ($k=n+N$)

$$f_{2n}(\infty) = \frac{2^{2n}}{M(\frac{1}{2}, \frac{3}{2}, g)} \sum_{k=n}^{\infty} \frac{g^k}{k!} \frac{(2k)!(n+k)!}{(2n+2k+1)!(k-n)!} \\ = \frac{g^n}{2M(\frac{1}{2}, \frac{3}{2}, g)} \sum_{N=0}^{\infty} \frac{g^N}{N!} \frac{\Gamma(n+N+\frac{1}{2})}{\Gamma(2n+N+\frac{3}{2})} \\ = \frac{g^n}{2M(\frac{1}{2}, \frac{3}{2}, g)} \frac{\Gamma(n+\frac{1}{2})}{\Gamma(2n+\frac{3}{2})} M(n+\frac{1}{2}, 2n+\frac{3}{2}, g), \quad (\text{B4})$$

so that for $n=1$

$$f_2(\infty) = \frac{g}{2M(\frac{1}{2}, \frac{3}{2}, g)} \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{7}{2})} M(\frac{3}{2}, \frac{7}{2}, g) = \frac{2g}{15} \frac{M(\frac{3}{2}, \frac{7}{2}, g)}{M(\frac{1}{2}, \frac{3}{2}, g)}, \quad (\text{B5})$$

that is, Eq. (47).

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