

Analytic calculation of the aftereffect solution and correlation time of the induced dipole Kerr effect

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The exact analytic aftereffect functions for the Kerr-effect relaxation of an assembly of symmetric top molecules having induced dipole moments only are calculated from the rotational diffusion equation (Smoluchowski equation). The solution is obtained in the case where the molecules are acted on by a strong dc field E_c , superimposed on which is a weak probe field $E_1(t)$ suddenly switched off at time $t=0$. By calculating the Laplace transforms of these aftereffect functions, two normalized autocorrelation functions are established, thus allowing one to express the corresponding birefringence ac responses by using linear response theory in the manner derived by Coffey *et al.* [Phys. Rev. E **49**, 1869 (1994)] for the longitudinal susceptibility of single-domain ferromagnetic particles. The connection between aftereffect and ac responses holds insofar as only one matrix relaxation function is needed for describing the induced dipole Kerr effect. Then, exact expressions for the correlation time and the effective relaxation time are derived in terms of Kummer functions and compared. It is shown that as soon as the dc field parameter g_c exceeds 3, the birefringence decay process is no longer dominated by the first nonvanishing eigenvalue of the differential matrix set (solution of the Smoluchowski equation) unlike dielectric relaxation, but by the second one. Moreover, dispersion plots and Cole-Cole diagrams as well as phase angles for the second harmonic component are presented for various values of g_c in order to see how they deviate from the Debye-like spectra. [S1063-651X(96)12709-4]

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I. INTRODUCTION

The exact solution for the rise transient of the birefringence and the corresponding relaxation times for an assembly of nonpolar but anisotropically polarizable molecules was recently given by Déjardin, Blaise, and Coffey [1]. This was accomplished starting from the Smoluchowski equation, in which inertia is completely ignored, which governs the time behavior of the orientational probability density function $W(\vartheta, \varphi, t)$. By expanding this function as a series of Legendre polynomials, a set of differential-recurrence relations is obtained, restricted only to the even polynomials, which are of interest for the induced dipole Kerr effect. This set of differential-recurrence relations may be solved exactly in terms of continued fractions, from which the rise transient of the birefringence may be calculated by taking the Laplace transform of the birefringence function, i.e., the ensemble average of the second Legendre polynomial $\langle P_2(\cos \vartheta) \rangle(t)$. Having removed the singularity at $s=0$ (zero-frequency limit), we also expressed the relaxation time defined as the area delimited by the curve of the rise transient and the time axis as a sum of products of Kummer functions and its first derivatives [1].

In this paper, we shall show how it is possible to obtain

exactly the analytic aftereffect solution for an assembly of noninteracting symmetric top molecules comprised of pure induced dipole moments only, thus allowing us to calculate the exact correlation time of the induced dipole Kerr effect. This amounts to studying the decay process of the birefringence following the sudden removal of a small electric field $E_1(t)$ applied in a direction parallel to a strong dc bias electric field E_c , by which the molecules have been influenced for a long time. We shall also demonstrate how the complex alternating birefringence response $\Delta n(\omega) = \Delta n'(\omega) - i\Delta n''(\omega)$ may be calculated from the Laplace transform of the aftereffect function using linear response theory, thus allowing us to show the frequency dependence of the birefringence from the dispersion and absorption spectra $\Delta n'(\omega)$ and $\Delta n''(\omega)$. In this way, linear response theory has been successfully employed in the exact calculation of the complex dielectric or magnetic susceptibilities [2,3] for ac fields applied parallel and perpendicular to a dc bias field. These physical quantities require a knowledge of the first autocorrelation function $C_1(t)$ appealing to the first Legendre polynomial. In our approach to the decay process of Kerr effect relaxation, a similar method may be applied by using the second autocorrelation function $C_2(t)$, namely,

$$C_2(t) = \frac{\langle [P_2(\cos \vartheta)](0)[P_2(\cos \vartheta)](t) \rangle_{|E_1=0} - \langle [P_2(\cos \vartheta)](0) \rangle_{|E_1=0}^2}{\langle [P_2(\cos \vartheta)]^2(0) \rangle_{|E_1=0} - \langle [P_2(\cos \vartheta)](0) \rangle_{|E_1=0}^2}, \quad (1)$$

where the angular brackets represent ensemble averages of the second Legendre polynomial $P_2(\cos\vartheta)$ evaluated in the absence of $E_1(t)$.

It should be noted that the connection existing between the transient response and the ac response holds for pure induced dipole moments only, unlike pure field-off moments, since these latter correspond, strictly speaking, to a nonlinear Kerr effect response. This aspect will be developed in Sec. II. Then we shall verify that the exact solutions which we obtained are in excellent agreement with those obtained by expressing the set of differential recurrence relations in matrix form $\dot{\mathbf{X}}(t) = \mathbf{M}\mathbf{X}(t)$, and calculating the eigenvalues and corresponding amplitudes of the first modes of the birefringence decay. Next we present results yielded by the effective eigenvalue method and compare the effective relaxation time with the correlation time for various values of the dc electric field expressed in terms of the dimensionless parameter g_c defined as

$$g_c = \frac{\alpha_{\parallel} - \alpha_{\perp}}{2kT} E_c^2 = \frac{\Delta\alpha}{2kT} E_c^2, \quad (2)$$

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

II. PERTURBATION SOLUTION OF THE SMOLUCHOWSKI EQUATION IN THE PRESENCE OF INDUCED DIPOLE MOMENTS

We assume that molecules are nonelectrically interacting, which means that, in particular, the dipole-dipole coupling effect is not taken into account, so that we may consider the motion of only one molecule, the others following on the average the same behavior. The orientational potential energy arising from the anisotropy of the polarizability of the molecule acted on by the electric field \mathbf{E} is

$$V = -\frac{1}{2} \mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}, \quad (3)$$

where $\boldsymbol{\alpha}$ is the second-rank electric polarizability tensor.

If the geometric axes of the molecule coincide with those of the polarizability tensor, we have

$$V(\vartheta, t) = -\frac{1}{2} \Delta\alpha E^2 \cos^2\vartheta - \frac{1}{2} \alpha_{\perp} E^2, \quad (4)$$

where ϑ is the angle the symmetry axis of the molecule makes with the field direction. Since the potential energy depends on the polar angle ϑ only, we can ignore the azimuthal dependence on the angle φ in the orientational probability density function so that its time evolution written in terms of operators is (Smoluchowski equation) [4]

$$\frac{\partial f(u, t)}{\partial t} = [\hat{A}_0(u) + 2g(t)\hat{A}_g(u)]f(u, t), \quad (5)$$

where

$$f(u, t) = \int_0^{2\pi} W(\vartheta, \varphi, t) d\varphi, \quad u = \cos\vartheta, \quad (5a)$$

$$\hat{A}_0(u) = D \frac{\partial}{\partial u} \left[(1-u^2) \frac{\partial}{\partial u} \right] = D\Delta_u \quad (5b)$$

is an operator not perturbed by the electric field, D is the rotary diffusion constant, Δ_u is the Laplacian operator with respect to the variable u ,

$$\hat{A}_g(u) = D \left[(3u^2 - 1) - u(1-u^2) \frac{\partial}{\partial u} \right], \quad (5c)$$

is an operator perturbed by the electric field, and $g(t)$ is the parameter measuring the ratio of the orientational energy arising from the electrical polarizabilities to the thermal energy, namely,

$$g(t) = \frac{\Delta\alpha}{2kT} E^2(t). \quad (5d)$$

We shall solve Eq. (5) by using a perturbation method as previously detailed in Refs. [4, 5]. To accomplish this, we rewrite this equation as

$$\frac{\partial f(u, t)}{\partial t} = [\hat{A}_0(u) + e^2 E^2(t) \hat{A}_g(u)]f(u, t), \quad (6)$$

where $e^2 = \Delta\alpha/kT$ may be regarded as a small perturbation parameter.

In the absence of electric field (unperturbed state), the corresponding solution of Eq. (6), called the conditional probability-density function by Morita [5], satisfies the following partial differential equation:

$$\frac{\partial h(u, u', t)}{\partial t} = \hat{A}_0(u)h(u, u', t). \quad (6a)$$

Since $\hat{A}_0(u)$ is a Laplacian operator, $h(u, u', t)$ may be expanded in a series of Legendre polynomials

$$h(u, u', t) = \sum_n \exp[-n(n+1)Dt] P_n(u) P_n(u'), \quad (6b)$$

with the following initial condition (closure relation):

$$h(u, u', 0) = \sum_n P_n(u) P_n(u') = \delta(u - u'), \quad (6c)$$

where $\delta(u - u')$ is the Dirac delta function.

The general solution for $f(u, t)$ is then

$$\begin{aligned} f(u, t) = & \int h(u, u', t) f(u, 0) du' \\ & + e^2 \int \int_0^t h(u, u', t-t') \\ & \times \hat{A}_g(u') E^2(t') f(u', t') du' dt'. \end{aligned} \quad (7)$$

Now, by expanding $f(u, t)$ in a series of even powers of e , we find that

$$f(u,t) = f(u,0) + \sum_{j=1}^{\infty} e^{2j} f_{g,2j}(u,t).$$

If we restrict ourselves to the linear response up to the second order in the electric field strength, we have ($j=1$)

$$f(u,t) = f(u,0) + e^2 f_{g,2}(u,t), \quad (8)$$

where the subscripts g and 2 stand for the dependence on the induced dipole moment and the order of the electric field, respectively, and

$$f_{g,2}(u,t) = \int_0^t \mathbf{h} \mathbf{f}_g(t-t') E^2(t') dt'. \quad (8a)$$

In Eq. (8a), \mathbf{h} represents a row matrix, the elements of which are the Legendre polynomials of even degree,

$$\mathbf{h} = [P_0, P_2, P_4, \dots, P_{2j}, \dots], \quad (8b)$$

while \mathbf{f}_g is a column matrix with the j th term given by

$$f_g^{(2j)} = \exp[-2j(2j+1)Dt] \int P_{2j}(u) \hat{A}_g(u) f(u,0) du. \quad (8c)$$

Let us consider an electric stimulus of the form $E(t) = E_c + E_0 \cos(\omega t)$, that is a strong dc field, superimposed on which is a weak ac field applied in the same direction. We have

$$\begin{aligned} f_{g,2}(u,t) &= \mathbf{h}(E_c^2 + \frac{1}{2}E_0^2) \int_0^t \mathbf{f}_g(t-t') dt' \\ &+ \frac{1}{2} \mathbf{h} E_0^2 \int_0^t \mathbf{f}_g(t-t') \cos(2\omega t') dt' \\ &+ 2\mathbf{h} E_0 E_c \int_0^t \mathbf{f}_g(t-t') \cos(\omega t') dt', \quad (9) \end{aligned}$$

from which we see that the induced dipole Kerr effect resulting from such an electric field consists of three components characterized by the same matrix relaxation function $\mathbf{f}_g(t)$. In the stationary regime corresponding to the physical situation where all the transients disappear, Eq. (9) becomes

$$\begin{aligned} \lim_{t \rightarrow \infty} f_{g,2}(u,t) &= \mathbf{h}(E_c^2 + \frac{1}{2}E_0^2) \int_0^{\infty} \mathbf{f}_g(t) dt \\ &+ \frac{1}{2} \mathbf{h} E_0^2 \left\{ \left[\int_0^{\infty} \mathbf{f}_g(t') \cos(2\omega t') dt' \right] \cos(2\omega t) \right. \\ &+ \left. \left[\int_0^{\infty} \mathbf{f}_g(t') \sin(2\omega t') dt' \right] \sin(2\omega t) \right\} \\ &+ 2\mathbf{h} E_0 E_c \left\{ \left[\int_0^{\infty} \mathbf{f}_g(t') \cos(\omega t') dt' \right] \cos(\omega t) \right. \\ &+ \left. \left[\int_0^{\infty} \mathbf{f}_g(t') \sin(\omega t') dt' \right] \sin(\omega t) \right\}. \quad (10) \end{aligned}$$

In Eq. (10), we find a time- and frequency-independent part and two distinct time-dependent contributions varying at the circular frequency of the alternating field and its second harmonic. We also note that the leading term of this equation proportional to E_c^2 and E_0^2 corresponds to a steady component. Regarding the harmonic components, the terms in 2ω arise from the ac field only, while the terms in ω result from the conjugate action of both ac and dc biasing fields (nonlinear effect). On using the definition of the Fourier-Laplace transforms in the time domain, the Kerr effect response may therefore be expressed as follows:

$$\begin{aligned} f_2(t) &= \lim_{t \rightarrow \infty} e^2 f_{g,2}(u,t) = \Delta n(0) \\ &+ \sum_{j=1}^2 [\Delta n_j'(\omega) \cos(j\omega t) + \Delta n_j''(\omega) \sin(j\omega t)], \quad (11) \end{aligned}$$

where $\Delta n(0)$ is the steady component, and $\Delta n_j'(\omega)$ and $\Delta n_j''(\omega)$ are the real and imaginary parts of the complex electric birefringence functions such that

$$\Delta n(0) = e^2 \mathbf{h}(E_c^2 + \frac{1}{2}E_0^2) \mathbf{F}_g(0), \quad (12a)$$

$$\Delta n_2(\omega) = \Delta n_2'(\omega) - i\Delta n_2''(\omega) = \frac{1}{2} e^2 \mathbf{h} E_0^2 \mathbf{F}_g(2i\omega), \quad (12b)$$

$$\Delta n_1(\omega) = \Delta n_1'(\omega) - i\Delta n_1''(\omega) = 2e^2 \mathbf{h} E_0 E_c \mathbf{F}_g(i\omega), \quad (12c)$$

and $\mathbf{F}_g(s)$ is the one-sided Fourier transform matrix of $\mathbf{f}_g(t)$,

$$\mathbf{F}_g(s) = \int_0^{\infty} \mathbf{f}_g(t) \exp(-st) dt, \quad (12d)$$

the symbolic variable s being equal to $2i\omega$ or $i\omega$.

III. CALCULATION OF THE BIREFRINGENCE ac RESPONSE USING THE LAPLACE TRANSFORM OF THE CORRESPONDING AFTEREFFECT FUNCTIONS

In order to proceed, we consider the rotational Brownian motion of a symmetric top molecule subjected to the total external electric field $E_c + E_1(t)$, where $E_1(t)$ is a small constant field. For the calculation of the birefringence decay, we assume that $E_1(t)$ is suddenly switched off at time $t=0$. So, returning to Eq. (5), and seeking its solution as a series of Legendre polynomials in the form

$$f(u,t) = \sum_{n=0}^{\infty} a_n(t) P_n(u), \quad (13)$$

we obtain the following set of differential-recurrence relations:

$$\begin{aligned} & \frac{\tau_D}{k(2k+1)} \dot{f}_{2k}(t) + \left[1 - \frac{2g_c}{(4k-1)(4k+3)} \right] f_{2k}(t) \\ &= \frac{2g_c(2k-1)}{(4k-1)(4k+1)} f_{2k-2}(t) \\ & \quad - \frac{2g_c(2k+2)}{(4k+1)(4k+3)} f_{2k+2}(t), \quad k=1,2,\dots, \end{aligned} \tag{14a}$$

which is identical to Eq. (4) of Ref. [1] or Eq. (7) of Ref. [6], but where

$$\begin{aligned} f_{2k}(t) &= \langle P_{2k}(u) \rangle(t) - \langle P_{2k}(u) \rangle(t)|_{E_1=0}, \\ f_0(t) &= 0, \end{aligned} \tag{14b}$$

instead of $f_{2k}(t) = \langle P_{2k}(u) \rangle(t)$, and τ_D is the usual Debye relaxation time related to the birefringence relaxation time τ by the relation

$$\tau_D = 3\tau = \frac{1}{2D}. \tag{14c}$$

This set constitutes a three-term recurrence relation, so that we can find its solution in the form of scalar continued fractions as previously derived [1,6].

Since we are interested in the decay process of the birefringence, only a knowledge of $f_2(t)$ is needed; that is,

$$f_2(t) = \int_{-1}^{+1} [P_2(u) - \langle P_2(u) \rangle|_{E_1=0}] f(u,t) du.$$

Taking the Laplace transform of Eq. (14a), we have [see Eq. (28) of Ref. [6]]

$$\begin{aligned} R_{2k}(s) \left[\frac{s\tau_D}{k(2k+1)} + 1 - \frac{2g_c}{(4k-1)(4k+3)} \right. \\ \left. + \frac{2g_c(2k+2)}{(4k+1)(4k+3)} R_{2k+2}(s) \right] &= \frac{\tau_D}{k(2k+1)} \frac{f_{2k}(0)}{F_{2k-2}(s)} \\ & \quad + \frac{2g_c(2k-1)}{16k^2-1}, \end{aligned} \tag{15}$$

where

$$R_{2k}(s) = \frac{F_{2k}(s)}{F_{2k-2}(s)}, \tag{15a}$$

$$F_{2k}(s) = \int_0^\infty f_{2k}(t) \exp(-st) dt. \tag{15b}$$

The initial conditions are given by the functions $f_{2k}(0)$, which may be determined as follows:

$$\begin{aligned} f_{2k}(0) &= \frac{\int_{-1}^{+1} \exp[(g_c + g_1 + g_{c1})u^2] P_{2k}(u) du}{\int_{-1}^{+1} \exp[(g_c + g_1 + g_{c1})u^2] du} \\ & \quad - \langle P_{2k}(u) \rangle|_{E_1=0}, \end{aligned} \tag{16}$$

where

$$g_c = \frac{\Delta\alpha}{2kT} E_c^2, \quad g_1 = \frac{\Delta\alpha}{2kT} E_1^2, \quad g_{c1} = \frac{\Delta\alpha}{kT} E_c E_1,$$

$$g_1, g_{c1} \ll g_c.$$

Insofar as g_1 and g_{c1} are considered small perturbations, we can use the linear approximation for $f_{2k}(0)$, which yields

$$\begin{aligned} f_{2k}(0) &= (g_1 + g_{c1}) [\langle u^2 P_{2k} \rangle|_{E_1=0} - \langle u^2 \rangle|_{E_1=0} \langle P_{2k} \rangle|_{E_1=0}] \\ &= f_{2k}^{(2)}(0) + f_{2k}^{(1)}(0), \end{aligned} \tag{17}$$

where the superscripts (2) and (1) stand for the terms proportional to g_1 and g_{c1} , respectively. We have retained these notations because, as we shall presently see, $f_{2k}^{(2)}(0)$ will allow us to calculate the second harmonic component of the birefringence, and $f_{2k}^{(1)}(0)$ the first one. On using the recursion relation of the Legendre polynomials

$$(4k+1)uP_{2k} = (2k+1)P_{2k+1} + 2kP_{2k-1},$$

and evaluating $\langle P_{2k} \rangle|_{E_1=0}$ and $\langle u^2 \rangle|_{E_1=0}$ as detailed in Ref. [1], Eq. (17) is

$$\begin{aligned} f_{2k}(0) &= (g_1 + g_{c1}) \left[\frac{(2k+1)(2k+2)}{(4k+1)(4k+3)} \frac{g_c^{k+1}}{2M(\frac{1}{2}, \frac{3}{2}, g_c)} \frac{\Gamma(k + \frac{3}{2})}{\Gamma(2k + \frac{7}{2})} M(k + \frac{3}{2}, 2k + \frac{7}{2}, g_c) \right. \\ & \quad \left. + \frac{2k(2k-1)}{(4k-1)(4k+1)} \frac{g_c^{k-1}}{2M(\frac{1}{2}, \frac{3}{2}, g_c)} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(2k - \frac{1}{2})} M(k - \frac{1}{2}, 2k - \frac{1}{2}, g_c) \right] + (g_1 + g_{c1}) \frac{g_c^k}{2M(\frac{1}{2}, \frac{3}{2}, g_c)} \frac{\Gamma(k + \frac{1}{2})}{\Gamma(2k + \frac{3}{2})} \\ & \quad \times M(k + \frac{1}{2}, 2k + \frac{3}{2}, g_c) \left[\frac{(2k+1)^2}{(4k+1)(4k+3)} + \frac{4k^2}{(4k-1)(4k+1)} - \frac{M(\frac{3}{2}, \frac{5}{2}, g_c)}{3M(\frac{1}{2}, \frac{3}{2}, g_c)} \right]. \end{aligned} \tag{18}$$

where we have used the Γ and Kummer (or confluent hypergeometric) functions defined as [7]

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

$$M(a, b, z) = 1 + \sum_{j=1}^{\infty} \frac{(a)_j}{(b)_j} \frac{z^j}{j!},$$

$$(a)_j = \frac{\Gamma(a+j)}{\Gamma(a)},$$

$$(b)_j = \frac{\Gamma(b+j)}{\Gamma(b)} \quad (\text{Pochhammer symbols}).$$

The next step consists in calculating the Laplace transform of the birefringence aftereffect function, that is $F_2(s)$. In order to accomplish this, we adopt the method proposed by Cresser *et al.* [8] and Coffey [9], in which $R_{2k}(s)$ is split into two parts such that

$$R_{2k}(s) = S_{2k}(s) + q_{2k}(s)/F_{2k-2}(s), \quad (19)$$

where $S_{2k}(s)$ is the solution of the homogeneous equation (14a) [$f_{2k}(0)=0$] [see Eq. (7) of Ref. [1] or Eq. (30) of Ref. [6]].

Hence Eq. (15) may be reexpressed in terms of $q_{2k}(s)$ and $S_{2k}(s)$ functions

$$\left[\frac{s\tau_D}{k(2k+1)} + 1 - \frac{2g_c}{(4k-1)(4k+3)} \right] q_{2k}(s) + \frac{2g_c(2k+2)}{(4k+1)(4k+3)} [q_{2k+2}(s) + q_{2k}(s)S_{2k+2}(s)] = \frac{\tau_D f_{2k}(0)}{k(2k+1)}, \quad (20)$$

from which

$$q_{2k}(s) = a_{2k} \left[\frac{\tau_D}{g_c} f_{2k}(0) - b_{2k} q_{2k+2}(s) \right] S_{2k}(s), \quad (21)$$

where

$$a_{2k} = \frac{16k^2 - 1}{2k(4k^2 - 1)}, \quad b_{2k} = \frac{2k(2k+1)(2k+2)}{(4k+1)(4k+3)}. \quad (22)$$

From Eqs. (15b) and (19), we have

$$F_{2k}(s) - F_{2k-2}(s)S_{2k}(s) = q_{2k}(s), \quad (23)$$

so that

$$F_{2k}(s) = \left\{ F_{2k-2}(s) + a_{2k} \left[\frac{\tau_D}{g_c} f_{2k}(0) - b_{2k} q_{2k+2}(s) \right] \right\} S_{2k}(s). \quad (24)$$

For $k=1$, one obtains [$F_0(s)=0$]

$$F_2(s) = a_2 \left[\frac{\tau_D}{g_c} f_2(0) - b_2 q_4(s) \right] S_2(s). \quad (25)$$

The continued fraction $S_2(s)$ depends on $S_4(s)$, which in turn depends on $S_6(s)$, and so on. After some algebra (see details in Appendix A), we finally arrive at the following result:

$$\frac{F_2(s)}{f_2(0)} = \frac{\tau}{s\tau + 1 - \frac{2g_c}{21} + \frac{8g_c}{35} S_4(s)} \times \left[1 + \frac{3}{5} \sum_{n=1}^{\infty} (-1)^n \frac{f_{2n+2}(0)}{f_2(0)} \frac{n+5/4}{(n+3/2)(n+1/2)} \times \frac{\Gamma(n+1)\Gamma(1/2)}{\Gamma(n+1/2)} \prod_{k=1}^n S_{2k+2}(s) \right]. \quad (26)$$

This equation is the exact formulation of the Laplace transform of the decay function $f_2(t)$. It has the same form as the dielectric result of Coffey *et al.* [6] (with odd functions) applied to single-domain ferromagnetic particles. At this stage, one can note the equivalence of the present problem (even functions) with that solved in our previous paper [1] or that in Ref. [6]. However, the initial conditions are completely different here [see Eqs. (16), (17), and (18)], since they can be split into two parts. On the other hand, and correlatively, the aftereffect response resulting from the application of two fields brings into play two F_2 functions. Indeed, on setting $s=2i\omega$ or $s=i\omega$, Eq. (26) allows one to define the one-sided Fourier transforms of the normalized birefringence autocorrelation functions as

$$C_2^{(2)}(2i\omega) = \frac{F_2^{(2)}(2i\omega)}{f_2^{(2)}(0)}, \quad (27a)$$

$$C_2^{(1)}(i\omega) = \frac{F_2^{(1)}(i\omega)}{f_2^{(1)}(0)}. \quad (27b)$$

We may therefore calculate the complex birefringence functions which, using linear response theory are as follows.

For the second harmonic component (2ω),

$$\frac{\Delta n_2(\omega)}{\Delta n_2'(0)} = 1 - 2i\omega \int_0^{\infty} \frac{f_2^{(2)}(t)}{f_2^{(2)}(0)} \exp(-2i\omega t) dt = 1 - 2i\omega \frac{F_2^{(2)}(2i\omega)}{f_2^{(2)}(0)} = 1 - 2i\omega C_2^{(2)}(2i\omega). \quad (28)$$

On recalling that

$$\mathcal{L}[f_2(t)] = -f_2(0) + sF_2(s), \quad (29)$$

where \mathcal{L} denotes ‘‘the Laplace transform of,’’ Eq. (28) becomes

$$\frac{\Delta n_2(\omega)}{\Delta n_2'(0)} = -\mathcal{L}_{2i\omega}[f_2^{(2)}(t)]/f_2^{(2)}(0) = X_2(\omega) - iY_2(\omega), \quad (30)$$

which shows that in the linear approximation the rate of decay of the induced dipole Kerr effect is the negative of its rate of growth (birefringence arising from a continuously applied ac field).

For the first harmonic component (ω),

$$\begin{aligned} \frac{\Delta n_1(\omega)}{\Delta n_1'(0)} &= 1 - i\omega \int_0^\infty \frac{f_2^{(1)}(t)}{f_2^{(1)}(0)} \exp(-i\omega t) dt \\ &= 1 - i\omega \mathcal{C}_2^{(1)}(i\omega) \\ &= -\mathcal{L}_{i\omega}[f_2^{(1)}(t)]/f_2^{(1)}(0) \\ &= X_1(\omega) - iY_1(\omega). \end{aligned} \quad (31)$$

In Eqs. (30) and (31), $X_j(\omega)$ and $Y_j(\omega)$ ($j=1,2$) represent the real and imaginary parts of the normalized birefringence functions. Their evolution as a function of the circular frequency lead to the well-known dispersion spectra. It is also interesting to plot the variations of Y_j as a function of X_j , which yield Cole-Cole-like diagrams. The dispersive nature of the medium is again manifested by the phase angle θ_j existing between the applied field and the Kerr effect response, namely,

$$\theta_j(\omega) = \tan^{-1} \frac{Y_j(\omega)}{X_j(\omega)}. \quad (32)$$

By inspection of Eq. (26), we note that all these quantities are strongly dependent on the parameter g_c . We shall examine this aspect in Sec. IV.

IV. NUMERICAL ANALYSIS OF THE NORMALIZED AMPLITUDES FOR THE BIREFRINGENCE FUNCTIONS

We have just established exact formulas for the induced dipole Kerr effect arising from the coupling between a small ac field, and a strong dc biasing field. Because the alternating field is very small, we have been able to define a linear relaxation behavior with respect to this field. With a view toward obtaining expressions for the harmonic components of the birefringence which may be easy to apply to experiments, we shall now seek to reduce Eqs. (28) and (31) to the first order approximation. This means that we shall take into account only the first term of the sum in Eq. (26), and subsequently we shall neglect $S_{2k+2}(s)$ for k greater than 1: that is, $S_6(s)$, $S_8(s)$, etc.

Hence, for the second harmonic components we have

$$\begin{aligned} X_2(\omega) - iY_2(\omega) &= 1 - \frac{2i\omega\tau}{2i\omega\tau + 1 - \frac{2g_c}{21} + \frac{8g_c}{35} \frac{2g_c/21}{\frac{3}{5}i\omega\tau + 1 - 2g_c/77}} \\ &\times \left[1 - \frac{18f_4^{(2)}(0)}{25f_2^{(2)}(0)} \frac{2g_c/21}{\frac{3}{5}i\omega\tau + 1 - 2g_c/77} \right], \end{aligned} \quad (33)$$

where [from Eq. (18)]

$$\begin{aligned} f_4^{(2)}(0) &= \frac{g_1}{M(\frac{1}{2}, \frac{3}{2}, g_c)} \left[\frac{80g_c^3}{297 \cdot 297} M(\frac{7}{2}, \frac{15}{2}, g_c) \right. \\ &\quad \left. + \frac{4g_c^2}{315} \left(\frac{39}{77} - \frac{M(\frac{3}{2}, \frac{5}{2}, g_c)}{3M(\frac{1}{2}, \frac{3}{2}, g_c)} \right) \right. \\ &\quad \left. \times M(\frac{5}{2}, \frac{11}{2}, g_c) + \frac{8g_c}{315} M(\frac{3}{2}, \frac{7}{2}, g_c) \right], \end{aligned} \quad (34a)$$

$$\begin{aligned} f_2^{(2)}(0) &= \frac{g_1}{M(\frac{1}{2}, \frac{3}{2}, g_c)} \left[\frac{16g_c^2}{3675} M(\frac{5}{2}, \frac{11}{2}, g_c) \right. \\ &\quad \left. + \frac{2g_c}{15} \left(\frac{11}{21} - \frac{M(\frac{3}{2}, \frac{5}{2}, g_c)}{3M(\frac{1}{2}, \frac{3}{2}, g_c)} \right) M(\frac{3}{2}, \frac{7}{2}, g_c) \right. \\ &\quad \left. + \frac{2}{15} M(\frac{1}{2}, \frac{3}{2}, g_c) \right]. \end{aligned} \quad (34b)$$

On setting

$$a = 1 - 2g_c/77, \quad b = 3\omega\tau/5, \quad c = 1 - 2g_c/21, \quad d = 2\omega\tau, \quad (34c)$$

$$A = \frac{16}{735} g_c^2, \quad H = \frac{12}{175} \frac{f_4^{(2)}(0)}{f_2^{(2)}(0)} g_c,$$

Eq. (33) becomes

$$X_2(\omega) - iY_2(\omega) = 1 - \frac{id[(a-H) + ib]}{(a+ib)(c+id) + A}, \quad (35)$$

which, separating the real and imaginary parts, yields

$$X_2(\omega) = \frac{(ac+A)(ac-bd+A) + (bc+dH)(ad+bc)}{(ac-bd+A)^2 + (ad+bc)^2}, \quad (36a)$$

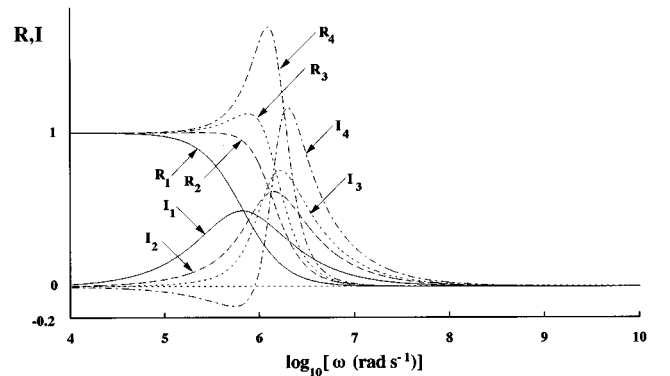


FIG. 1. Dispersion and absorption plots of the second harmonic component of the birefringence. R and I stand for the real and imaginary parts of the normalized complex birefringence. The subscripts 1–4 denote various g_c values. 1, $g_c=3$; 2, $g_c=6$; 3, $g_c=7$; and 4, $g_c=9$.

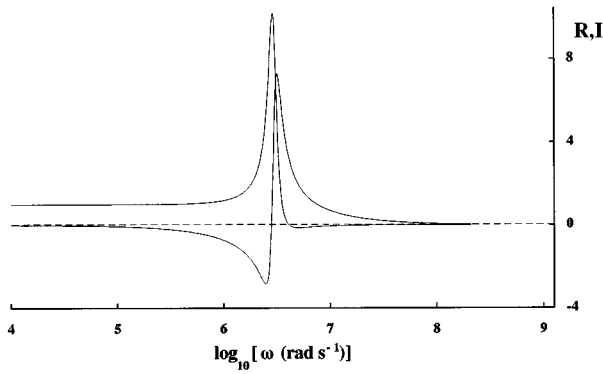


FIG. 2. Same as Fig. 1, for $g_c=18$.

$$Y_2(\omega) = \frac{(ac+A)(ad+bc) - (bc+dH)(ac-bd+A)}{(ac-bd+A)^2 + (ad+bc)^2} \quad (36b)$$

In the particular case when $g_c=0$, we have

$$X_2(\omega) = \frac{1}{1+4\omega^2\tau^2} = \frac{1}{1+(\omega/3D)^2}, \quad (37a)$$

$$Y_2(\omega) = \frac{2\omega\tau}{1+4\omega^2\tau^2} = \frac{(\omega/3D)}{1+(\omega/3D)^2}, \quad (37b)$$

in agreement with previous results [10].

The dispersion spectra represented by $X_2(\omega)$ and $Y_2(\omega)$ are illustrated in Fig. 1 for $g_c=3, 6, 7$, and 9, and in Fig. 2 for $g_c=18$. We note a Debye-like behavior as far as g_c is less than 6. Beyond this value, the real parts $X_2(\omega)$ are characterized by an overshoot [$X_2(\omega) > 1$], while the maxima of the imaginary parts $Y_2(\omega)$ are shifted to the right of the frequency scale for increasing g_c values. Moreover, for $g_c > 7$, $Y_2(\omega)$ takes negative values at low frequencies. A similar trend is observed for $g_c=18$, accompanied by negative values of $X_2(\omega)$ in the high-frequency region which is characteristic of resonant behavior.

Cole-Cole plots are shown in Figs. 3 and 4. Up to $g_c=3$, one may consider that quasisemicircles are obtained, the perfect semicircle corresponding to $g_c=0$. As g_c becomes

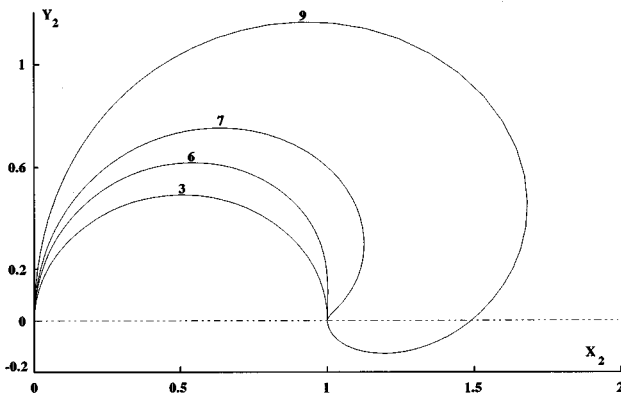


FIG. 3. Cole-Cole plots of the second harmonic component of the birefringence. The numbers above the plots are for various g_c values.

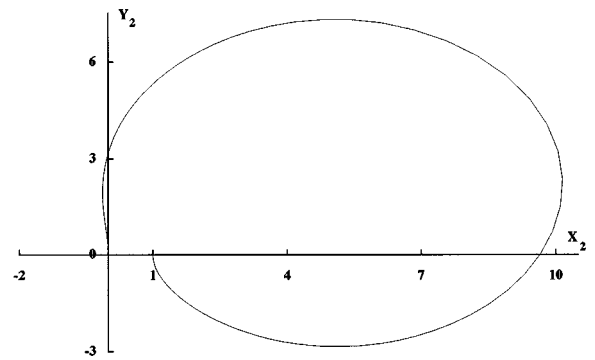


FIG. 4. Same as Fig. 3, for $g_c=18$.

greater than 3, these diagrams are larger and larger, deformed on the right by taking the shape of conchoids of circles. All these curves start from $X_2=1$ and $Y_2=0$ when $\omega=0$, and tend tangentially to the OY_2 axis as $\omega \rightarrow \infty$. g_c values greater than 7 are interesting from an experimental point of view. In this case, indeed, one can solve $Y_2(\omega)=0$, and find a solution which differs from zero. One has

$$\omega\tau = \left(\frac{25}{3} \frac{(ac+A)(H-a)}{10H+3c} \right)^{1/2}, \quad (38)$$

which allows one to extract the birefringence relaxation time τ having determined by experiment the circular frequency for which $Y_2=0$. We have also plotted variations of the phase angle θ_2 as a function of ω , as shown in Figs. 5 and 6, for various g_c values. The general tendency of all these curves is that the asymptotic limit is always $\pi/2$. As long as g_c does not exceed about 7, one remarks that the slope of these S-shaped curves becomes steeper and steeper for increasing g_c values. Then, for $g_c=9$, for example, $\theta_2(\omega)$ starts from zero, and takes negative values before passing again through zero and attaining $\pi/2$. The high value of $g_c=18$ leads to similar conclusions, with, however, a small difference in the midfrequency domain where $\theta_2(\omega)$ slightly exceeds $\pi/2$ before reaching this limiting value.

The same considerations may be used to find the first harmonic components from the corresponding aftereffect function appearing in Eq. (31). By restricting this equation to the first order approximation, one obtains

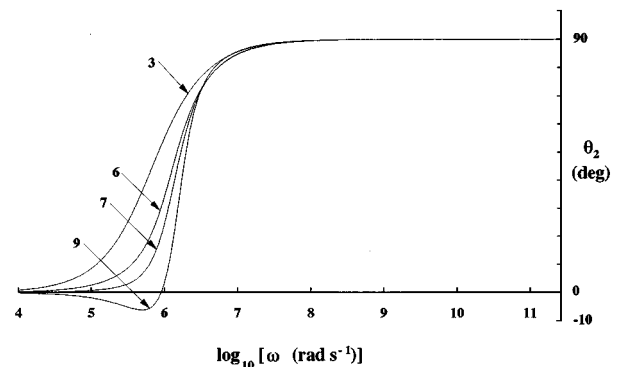


FIG. 5. Plots of the phase angles vs $\log_{10}(\omega/2\pi)$ for the second harmonic component of the birefringence. The numbers indicated by arrows are for various g_c values.

$$\begin{aligned}
& X_1(\omega) - iY_1(\omega) \\
&= 1 - \frac{i\omega\tau}{i\omega\tau + 1 - \frac{2g_c}{21} + \frac{8g_c}{35} \frac{2g_c/21}{\frac{3}{10} i\omega\tau + 1 - 2g_c/77}} \\
&\quad \times \left[1 - \frac{18 f_4^{(1)}(0)}{25 f_2^{(1)}(0)} \frac{2g_c/21}{\frac{3}{10} i\omega\tau + 1 - 2g_c/77} \right], \quad (39)
\end{aligned}$$

where $f_4^{(1)}(0)$ and $f_2^{(1)}(0)$ are given by Eqs. (34a) and (34b), in which g_1 is replaced by g_{c1} .

We have verified that the dispersion plots $X_1(\omega)$ and $Y_1(\omega)$ behave in the same manner as those described by the second harmonic. We simply observe a frequency shift to the right.

V. EXACT EXPRESSIONS FOR THE CORRELATION AND EFFECTIVE RELAXATION TIMES

By definition, the correlation time is the area under the curve of the normalized autocorrelation function $C_2(t)$: that is,

$$T = \lim_{s \rightarrow 0} \int_0^{\infty} C_2(t) \exp(-st) dt = \lim_{s \rightarrow 0} C_2(s) = C_2(0) = \frac{F_2(0)}{f_2(0)}. \quad (40)$$

Since this time corresponds to the limit of zero frequency in the Laplace transform of $C_2(t)$, we obviously have

$$C_2^{(2)}(0) = C_2^{(1)}(0) = C_2(0), \quad (41a)$$

as appears in Eq. (26), where

$$\frac{f_{2n+2}^{(2)}(0)}{f_2^{(2)}(0)} = \frac{f_{2n+2}^{(1)}(0)}{f_2^{(1)}(0)}, \quad (41b)$$

so that there is only one expression for T .

From Eq. (26), in which we set $s=0$, one obtains (reduced relaxation time)

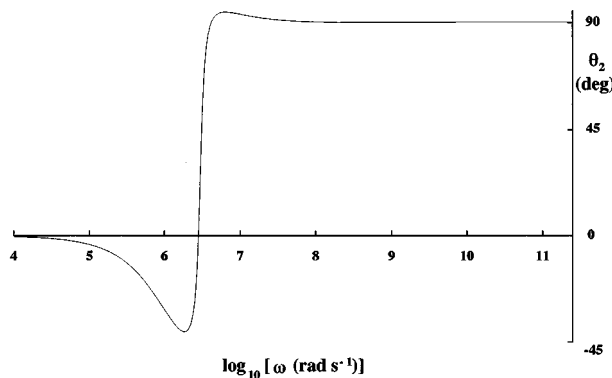


FIG. 6. Same as Fig. 5, for $g_c = 18$.

$$\begin{aligned}
\frac{T}{\tau} = T' &= \frac{1}{1 - \frac{2g_c}{21} + \frac{8g_c}{35} S_4(0)} \\
&\quad \times \left[1 + \frac{3}{5} \sum_{n=1}^{\infty} (-1)^n \frac{f_{2n+2}(0)}{f_2(0)} \frac{n+5/4}{(n+3/2)(n+1/2)} \right. \\
&\quad \left. \times \frac{\Gamma(n+1)\Gamma(1/2)}{\Gamma(n+1/2)} \prod_{k=1}^n S_{2k+2}(0) \right], \quad (42)
\end{aligned}$$

where

$$S_4(0) = \frac{2g_c}{21} \frac{M(\frac{5}{2}, \frac{11}{2}, g_c)}{M(\frac{3}{2}, \frac{7}{2}, g_c)}.$$

On evaluating the product in Eq. (42) (see Appendix B), T' becomes equal to

$$\begin{aligned}
T' &= \frac{M(\frac{3}{2}, \frac{7}{2}, g_c)}{\left(1 + \frac{2g_c}{15}\right) M(\frac{3}{2}, \frac{7}{2}, g_c) - \frac{8g_c}{35} M(\frac{3}{2}, \frac{9}{2}, g_c)} \\
&\quad \times \left[1 + 9 \sum_{n=1}^{\infty} (-1)^n \frac{f_{2n+2}(0)}{f_2(0)} \right. \\
&\quad \times \frac{\Gamma(1/4)\Gamma(3/4)\Gamma(n+1)}{(n+3/2)\Gamma(n+5/4)\Gamma(n+7/4)} \\
&\quad \left. \times \frac{g_c^n}{2^{2n+5}} \frac{M[(2n+3)/2, 2n+7/2, g_c]}{M(\frac{3}{2}, \frac{7}{2}, g_c)} \right]. \quad (43)
\end{aligned}$$

This is an exact expression for the correlation time equal to 1 for $g_c=0$. Its evolution as a function of g_c is illustrated in Fig. 7. In order to ensure correct convergence of the sum in Eq. (43), we have verified that 24 iterations ($n=24$) were sufficient in the range $0 < g_c < 50$. The Kerr effect correlation time passes through a maximum situated about $g_c=1.4$ (which is interesting experimentally) before decaying monotonically to zero for increasing g_c values. This behavior resembles that observed in the rise transient process [1] with,

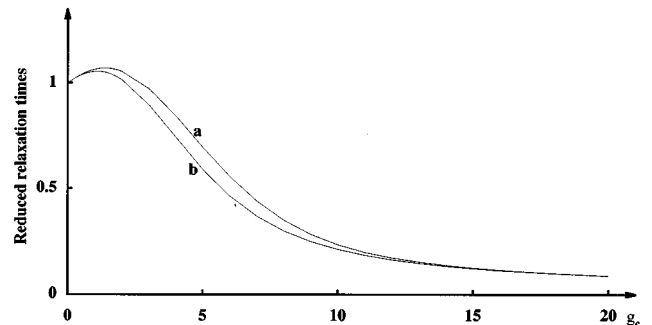


FIG. 7. Comparison of the exact correlation time T' (curve a) with the effective relaxation time T'_{eff} (curve b) as a function of the electrical anisotropy parameter g_c . (T' and T'_{eff} are reduced times).

however, smaller numerical values falling off more and more in proportion to g_c as g_c increases.

We shall now see how equivalent results may be obtained by using matrix methods. This is accomplished by arranging the set of differential recurrence relations [Eq. (14a)] in the form

$$\dot{\mathbf{f}}_{2k}(t) = -\frac{1}{6\tau} \mathbf{M} \mathbf{f}_{2k}(t), \quad k=1,2,\dots, \quad (44)$$

where \mathbf{f}_{2k} and \mathbf{f}_{2k} are column matrices with j th terms given by $f_{2j}(t)$ and $df_{2j}(t)/dt$, respectively, and \mathbf{M} is an $n \times n$ matrix defined by

$$\mathbf{M} = \begin{pmatrix} 6\left(1 - \frac{3g_c}{21}\right) & \frac{48g_c}{35} & 0 & 0 & 0 & \dots \\ -\frac{40g_c}{21} & 20\left(1 - \frac{2g_c}{77}\right) & \frac{80g_c}{33} & 0 & 0 & \dots \\ 0 & -\frac{420g_c}{143} & 42\left(1 - \frac{2g_c}{165}\right) & \frac{224g_c}{65} & 0 & \dots \\ 0 & 0 & -\frac{336g_c}{85} & 72\left(1 - \frac{2g_c}{285}\right) & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (45)$$

The formal solution of Eq. (44) is

$$\mathbf{f}_{2k}(t) = \mathbf{f}_{2k}(0) \exp(\mathbf{M}'t), \quad (46)$$

where

$$\mathbf{M}' = -\frac{1}{6\tau} \mathbf{M},$$

and $\mathbf{f}_{2k}(0)$ is the column vector of initial conditions [Eq. (18)].

Hence the relaxation modes of the decay Kerr function may be written as follows:

$$f_2^{(2)}(t) = g_1 \sum_j A_{2j} \exp(-\lambda_{2j}t), \quad (47a)$$

$$f_2^{(1)}(t) = g_{c1} \sum_j A_{2j} \exp(-\lambda_{2j}t), \quad (47b)$$

where A_{2j} denotes the amplitudes of the first components of the successive eigenvectors associated with the eigenvalues λ_{2j} .

From Eqs. (40) and (47), we have

$$F_2^{(2)}(s) = g_1 \sum_j A_{2j} (s + \lambda_{2j})^{-1}, \quad (48a)$$

$$F_2^{(1)}(s) = g_{c1} \sum_j A_{2j} (s + \lambda_{2j})^{-1}, \quad (48b)$$

so that

$$T = \frac{\sum_j A_{2j} \lambda_{2j}^{-1}}{\sum_j A_{2j}}. \quad (49)$$

The amplitudes and eigenvalues of the first four modes are presented in Table I for various values of the parameter g_c up to $g_c = 20$. Since the eigenvalues are evaluated in the form $\lambda_{2j}/6\tau$, the reduced relaxation time T' is effectively given by

$$T' = \frac{T}{\tau} = 6 \sum_j \frac{A_{2j} \lambda_{2j}^{-1}}{A_{2j}}. \quad (50)$$

It should be noted that all the amplitudes are positive, unlike what was observed for the rise transient response. Moreover, as far as g_c remains small enough (about 4, say), one can consider that the reciprocal of the lowest eigenvalue λ_2 provides a rough description of the correlation time. As soon as g_c becomes greater than 4, it is no longer the first mode which dominates the response, but the second one. This explains the differences observed between our dispersion plots and Cole-Cole diagrams when compared to the Debye spectra [Eqs. (37)]. This means that the decay of the induced dipole Kerr effect characterized by the function $f_2(t)$ cannot, in general, be represented by a single exponential, save for small or very high values of the parameter g_c . By using a 30×30 matrix, excellent agreement was obtained in comparison with the continued fraction methods for all g_c values.

It is now interesting to consider the solution rendered by the effective eigenvalue method. In this approach, it is assumed that the pure induced dipole mechanism may be approximated by a single exponential term characterized by an effective relaxation time T_{eff} , such that

$$f_2^{(2)}(t) = g_1 \exp(-\lambda_{\text{eff}}t), \quad (51a)$$

$$f_2^{(1)}(t) = g_{c1} \exp(-\lambda_{\text{eff}}t), \quad (51b)$$

where $\lambda_{\text{eff}} = T_{\text{eff}}^{-1}$ is the effective eigenvalue. From Eqs. (47),

TABLE I. Eigenvalues in the form $\lambda_{2j}/6\tau$ of the first four modes of the decay of the birefringence as a value of the parameter g_c and corresponding amplitudes A_{2j} , $j=1,2,3,\dots$. T' is the reduced correlation time given by Eq. (5).

g_c	λ_2	λ_4	λ_6	λ_8	A_2	A_4	A_6	A_8	T'
0.2	5.89	19.90	41.90	71.90	0.138	2.93E-09	1.49E-09	3.21E-14	1.017 98
0.4	5.80	19.81	41.82	71.82	0.142	0.000 121	2.45E-08	2.11E-12	1.033 64
0.6	5.72	19.74	41.74	71.74	0.146	0.000 278	1.27E-07	2.46E-11	1.046 78
0.8	5.66	19.67	41.68	71.68	0.149	0.000 505	4.11E-07	1.41E-10	1.057 17
1	5.61	19.62	41.62	71.62	0.151	0.000 803	1.02E-06	5.47E-10	1.064 65
1.2	5.58	19.57	41.58	71.58	0.152	0.001 17	2.14E-06	1.65E-09	1.069 10
1.4	5.56	19.54	41.54	71.54	0.152	0.001 61	4.00E-06	4.21E-09	1.070 42
1.6	5.60	19.52	41.52	71.52	0.152	0.002 11	6.85E-06	9.42E-09	1.068 57
1.8	5.57	19.51	41.51	71.51	0.150	0.002 68	1.10E-05	1.91E-08	1.063 56
2	5.60	19.51	41.50	71.50	0.148	0.003 30	1.67E-05	3.58E-08	1.055 46
3	5.93	19.69	41.65	71.64	0.124	0.006 95	7.86E-05	3.78E-07	0.973 36
4	6.61	20.15	42.07	72.04	0.0925	0.0107	0.000 212	1.81E-06	0.842 85
5	7.61	20.91	42.75	72.70	0.0624	0.0135	0.000 415	5.50E-06	0.695 85
6	8.90	21.96	43.71	73.62	0.0393	0.0151	0.000 654	1.24E-05	0.557 36
7	10.45	23.34	44.95	74.81	0.0235	0.0155	0.000 890	2.29E-05	0.440 79
8	12.20	25.05	46.47	76.27	0.0135	0.0151	0.001 08	3.64E-05	0.349 89
9	14.11	27.12	48.29	78.01	0.007 40	0.0140	0.001 21	5.17E-05	0.282 39
10	16.13	29.56	50.42	80.03	0.003 89	0.0126	0.001 27	6.70E-05	0.233 46
11	18.20	32.38	52.87	82.34	0.001 95	0.0111	0.001 25	8.09E-05	0.198 04
12	20.28	35.56	55.66	84.94	0.000 935	0.009 63	0.001 16	9.20E-05	0.172 00
13	22.37	39.07	58.80	87.85	0.000 431	0.008 36	0.001 02	9.95E-05	0.152 34
14	24.45	42.86	62.33	91.08	0.000 193	0.007 30	0.000 848	0.000 103	0.137 02
15	26.51	46.86	66.25	94.62	8.38E-05	0.006 43	0.000 667	0.000 103	0.124 75
16	28.57	51.00	70.60	98.51	3.58E-05	0.005 72	0.000 494	9.99E-05	0.114 65
17	30.61	55.22	75.37	102.74	1.52E-05	0.005 13	0.000 345	9.41E-05	0.106 16
18	32.64	59.46	80.56	107.35	6.24E-06	0.004 64	0.000 227	8.65E-05	0.098 91
19	34.67	63.71	86.12	112.35	2.57E-06	0.004 20	0.000 142	7.79E-05	0.092 63
20	36.70	67.92	92.02	117.77	1.05E-06	0.003 82	8.49E-05	6.88E-05	0.087 12

$$\lambda_{\text{eff}} = -\frac{\dot{f}_2(0)}{f_2(0)} = \frac{\sum_j A_{2j} \lambda_{2j}}{\sum_j A_{2j}}, \quad (52)$$

and the reduced effective relaxation time is

$$T'_{\text{eff}} = \frac{T_{\text{eff}}}{\tau} = 6 \frac{\sum_j A_{2j}}{\sum_j A_{2j} \lambda_{2j}}. \quad (53)$$

Another expression for T_{eff} may be found starting from the set of differential recurrence relations. This provides a very simple analytic formula for T_{eff} . Setting $k=1$ in Eq. (14a), and noting that $f_0(t)=0$, one has

$$\dot{f}_2(t) = -\frac{1}{6\tau} \left[6 \left(1 - \frac{2g_c}{21} \right) f_2(t) + \frac{48g_c}{35} f_4(t) \right], \quad (54)$$

so that

$$\dot{f}_2(t) = -\frac{1}{6\tau} \left[6 \left(1 - \frac{2g_c}{21} \right) f_2(t) + \frac{48g_c}{35} f_4(t) \right] \quad (55)$$

and

$$T'_{\text{eff}} = \frac{1}{1 - \frac{2g_c}{21} + \frac{8g_c}{35} \frac{f_4(0)}{f_2(0)}}. \quad (56)$$

The variations of T'_{eff} as a function of g_c are plotted in Fig. 7. We find again a maximum at about $g_c=1$. The curve is slightly situated under that of the correlation time up to $g_c=15$, and beyond this value both curves have practically the same behavior (similar asymptotic limit).

ACKNOWLEDGMENT

We would like to thank Professor P. Blaise for the numerical calculations presented in this paper.

APPENDIX A

We seek the exact expression for the Laplace transform of the aftereffect birefringence function, $F_2(s)$. In order to proceed, we recall Eq. (25),

$$F_2(s) = a_2 \left[\frac{\tau_D}{g_c} f_2(0) - b_2 q_4(s) \right] S_2(s),$$

which, using Eq. (22) for $k=2$,

$$q_4(s) = a_4 \left[\frac{\tau_D}{g_c} f_4(0) - b_4 q_6(s) \right] S_4(s), \quad (A1)$$

yields

$$\begin{aligned}
 F_2(s) &= a_2 \frac{\tau_D}{g_c} f_2(0) S_2(s) - a_2 b_2 \left[a_4 \frac{\tau_D}{g_c} f_4(0) \right. \\
 &\quad \left. - a_4 b_4 q_6(s) \right] S_2(s) S_4(s) \\
 &= \frac{\tau_D}{g_c} [a_2 f_2(0) S_2(s) - a_2 b_2 a_4 f_4(0) S_2(s) S_4(s)] \\
 &\quad + a_2 b_2 a_4 b_4 q_6(s) S_2(s) S_4(s). \tag{A2}
 \end{aligned}$$

The complementary function $q_6(s)$ may in turn be expressed as

$$q_6(s) = a_6 \left[\frac{\tau_D}{g_c} f_6(0) - b_6 q_8(s) \right] S_6(s), \tag{A3}$$

so that

$$\begin{aligned}
 F_2(s) &= \frac{\tau_D}{g_c} [a_2 f_2(0) S_2(s) - a_2 b_2 a_4 f_4(0) S_2(s) S_4(s) \\
 &\quad + a_2 b_2 a_4 b_4 f_6(0) S_2(s) S_4(s) S_6(s) - \dots]. \tag{A4}
 \end{aligned}$$

In this form, one can see that Eq. (A4) is an alternating series which can be written as a sum of products of continued fractions,

$$\begin{aligned}
 F_2(s) &= a_2 \frac{\tau_D}{g_c} S_2(s) \left[f_2(0) + \sum_{n=0}^{\infty} (-1)^{n+1} f_{2n+4}(0) \right. \\
 &\quad \left. \times \prod_{k=0}^n a_{2k+4} b_{2k+2} S_{2k+4}(s) \right]. \tag{A5}
 \end{aligned}$$

The product of the coefficients $a_{2k+4} b_{2k+2}$ can be easily calculated. One has

$$\begin{aligned}
 \prod_{k=0}^n a_{2k+4} b_{2k+2} &= \prod_{k=0}^n \frac{(2k+2)(4k+9)}{(2k+5)(4k+5)} \\
 &= \frac{3}{5} \frac{n+9/4}{(n+1/2)(n+3/2)(n+5/2)} \\
 &\quad \times \frac{\Gamma(n+2)\Gamma(1/2)}{\Gamma(n+1/2)}. \tag{A6}
 \end{aligned}$$

Hence Eq. (A5) becomes

$$\begin{aligned}
 \frac{F_2(s)}{f_2(0)} &= a_2 \frac{\tau_D}{g_c} S_2(s) \left[1 + \sum_{n=0}^{\infty} (-1)^{n+1} \frac{f_{2n+4}(0)}{f_2(0)} \right. \\
 &\quad \left. \times \prod_{k=0}^n \frac{(2k+2)(4k+9)}{(2k+5)(4k+5)} S_{2k+4}(s) \right] \\
 &= a_2 \frac{\tau_D}{g_c} S_2(s) \left[1 + \frac{3}{5} \sum_{n=1}^{\infty} (-1)^n \frac{f_{2n+2}(0)}{f_2(0)} \right. \\
 &\quad \left. \times \frac{n+5/4}{(n+1/2)(n+3/2)} \frac{\Gamma(n+1)\Gamma(1/2)}{\Gamma(n+1/2)} \prod_{k=1}^n S_{2k+2}(s) \right], \tag{A7}
 \end{aligned}$$

which is Eq. (26), after having noted from Eqs. (20) and (22a) that

$$\begin{aligned}
 a_2 \frac{\tau_D}{g_c} &= \frac{15\tau}{2g_c}, \\
 S_2(s) &= \frac{2g_c}{15} \frac{1}{s\tau+1 - \frac{2g_c}{21} + \frac{8g_c}{35} S_4(s)}.
 \end{aligned}$$

APPENDIX B

The exact expression for the correlation time given by Eq. (42) may be reduced to Eq. (43) if one explicitly expresses the product of continued fractions $S_{2k+2}(0)$. One has

$$\begin{aligned}
 \prod_{k=1}^n S_{2k+2}(0) &= S_4(0) S_6(0) S_8(0) \dots S_{2n+2}(0) \\
 &= \left(2g_c \frac{3}{7 \times 9} \right) \left(2g_c \frac{5}{11 \times 13} \right) \left(2g_c \frac{7}{15 \times 17} \right) \\
 &\quad \times \dots \times \left(2g_c \frac{2n+1}{(4n+3)(4n+5)} \right) \\
 &\quad \times \frac{M[(2n+3)/2, 2n+7/2, g_c]}{M(\frac{3}{2}, \frac{7}{2}, g_c)}. \tag{B1}
 \end{aligned}$$

By using the definition and the properties of Γ functions, the following products may therefore be calculated:

$$3 \times 5 \times 7 \times \dots \times (2n-1)(2n+1) = 2^{n+1} \frac{\Gamma(n+3/2)}{\Gamma(1/2)}, \tag{B2}$$

$$\begin{aligned}
 &7 \times 11 \times 15 \times \dots \times (4n-1)(4n+3) \\
 &= \frac{1}{3} (4n+3) 4^n \frac{\Gamma(n+3/4)}{\Gamma(3/4)}, \tag{B3}
 \end{aligned}$$

$$\begin{aligned}
 &9 \times 13 \times 17 \times \dots \times (4n+1)(4n+5) \\
 &= \frac{1}{5} (4n+1)(4n+5) 4^n \frac{\Gamma(n+1/4)}{\Gamma(1/4)}, \tag{B4}
 \end{aligned}$$

so that

$$\begin{aligned}
 \prod_{k=1}^n S_{2k+2}(0) &= 15 \frac{g_c^n}{2^{2n+5}} \frac{\Gamma(1/4)\Gamma(3/4)\Gamma(n+3/2)}{\Gamma(1/2)\Gamma(n+7/4)\Gamma(n+9/4)} \\
 &\quad \times \frac{M[(2n+3)/2, 2n+7/2, g_c]}{M(\frac{3}{2}, \frac{7}{2}, g_c)}. \tag{B5}
 \end{aligned}$$

Now, on using the recurrence relation of Kummer's functions [7],

$$azM(a+1, b+1, z) = b(b+1)[M(a, b-1, z) - M(a, b, z)], \quad (\text{B6})$$

one has ($a = \frac{3}{2}$ and $b = \frac{9}{2}$)

$$M(\frac{5}{2}, \frac{11}{2}, g_c) = \frac{21}{2g_c} [M(\frac{3}{2}, \frac{7}{2}, g_c) - M(\frac{3}{2}, \frac{9}{2}, g_c)]. \quad (\text{B7})$$

The leading term of Eq. (42) is then equal to

$$\frac{1}{1 - \frac{2g_c}{21} + \frac{16g_c^2}{735} \frac{M(\frac{5}{2}, \frac{11}{2}, g_c)}{M(\frac{3}{2}, \frac{7}{2}, g_c)}} = \frac{1}{1 + \frac{2g_c}{15} - \frac{8g_c}{35} \frac{M(\frac{3}{2}, \frac{9}{2}, g_c)}{M(\frac{3}{2}, \frac{7}{2}, g_c)}}. \quad (\text{B8})$$

By substituting Eqs. (B5) and (B8) into Eq. (42), the desired result given by Eq. (43) is obtained.

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