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Dielectric properties of a linear rigid rotor in 3D: the case of large collisions

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Abstract. Exact analytical expressions for the dielectric and, for the first time, for the Kerr functions are explicitly calculated in both relaxation and steady-state regimes, by solving the generalized Liouville equation (in the presence of large collisions) for the rotational motion of a linear rigid rotor in 3D. The response functions thus obtained generalize and extend all the results recently published on the topic. The Debye–Smoluchowski or Rocard diffusion models are recovered. In particular, the dielectric response is in full agreement with the analysis of Sack (1957 *Proc. Phys. Soc.* B **70** 402, 414). Nevertheless, we draw the reader's attention to the misprint in the susceptibility formula given by Sack in his equation (2.35).

1. Introduction

The dynamical dielectric relaxation and Kerr electric birefringence, considered here as dynamical properties of an intrinsically isotropic fluid, are of great interest in order to understand the microscopic behaviour of the polar molecules constituting this fluid. These properties are related to the rotational motion of the polar molecules under the action of an electric stress.

The experimental dielectric properties of a fluid at time t can be determined by means of the after-effect function $\chi(t)$ for the dielectric relaxation. This function measures the electric polarization of the fluid and depends directly on the orientation of the polar molecules with respect to the axes of polarization [1–6].

The Kerr electric birefringence results from the anisotropy of the fluid induced by the electric field. The birefringence properties can be determined by means of the Kerr function $\phi(t)$, which is related to the difference between the refractive indexes parallel and perpendicular to the axis of polarization. This function also depends directly on the preferential orientation of the polar molecules [1–6].

In this paper, we present calculations of the functions $\chi(t)$ and $\phi(t)$ in the case of a system of rigid linear polar molecules rotating about fixed centres and interacting with the surrounding via a mechanism of large collisions. The mechanism of large collisions means that in the process of interaction the orientations of the molecules remain unaffected, but the velocity distribution after impact is Maxwellian regardless of the initial velocity [1].

It is also assumed that:

(a) The collisions can be treated as instantaneous compared with the time scale characterizing the evolution of the rotating molecules.

(b) There is no correlation between successive collisions.

Finally, the rotating molecules possess a permanent and induced dipole moment along their axes, interacting with the electric field. Hyperpolarizabilities are ignored in the present case.

The paper is organized as follows. Section 2 deals with general theoretical considerations. In section 3, we determine the relaxation of the functions $\chi(t)$ and $\phi(t)$ generated by a sudden removal of a DC electric field, while in section 4 these functions are studied in the steady-state regime when a cosine alternating electric field is applied. We restrict our calculations up to second order in the electric field.

2. General theoretical considerations

The generalized Liouville equation (in the presence of large collisions) for the probability density function $W(\alpha, \beta, \omega_\alpha, \omega_\beta, t)$ in the configuration angular velocity space associated with the rotational motion of a linear rigid rotor can be written as [1–5]

$$\left[\frac{\partial}{\partial t}+\frac{\omega_\alpha}{\sin\beta}\frac{\partial}{\partial\alpha}+\omega_\beta\frac{\partial}{\partial\beta}+\cot\beta\left(\omega_\alpha^2\frac{\partial}{\partial\omega_\beta}-\omega_\alpha\omega_\beta\frac{\partial}{\partial\omega_\alpha}\right)-\frac{1}{I}\frac{\partial V(t)}{\partial\beta}\frac{\partial}{\partial\omega_\beta}\right]W(\alpha,\beta,\omega_\alpha,\omega_\beta,t)$$
$$= -B\left[W(\alpha,\beta,\omega_\alpha,\omega_\beta,t)-\frac{I}{2\pi kT}\exp\left(-\frac{I(\omega_\alpha^2+\omega_\beta^2)}{2kT}\right)\right.$$
$$\left.\times\int_{-\infty}^{\infty}\mathrm{d}\omega_\alpha'\int_{-\infty}^{\infty}\mathrm{d}\omega_\beta'\,W(\alpha,\beta,\omega_\alpha',\omega_\beta',t)\right]. \tag{1}$$

Here α and β are, respectively, the azimuthal and polar angles of the molecule with respect to the fixed direction of an applied electric field along the polar axis. ω_α and ω_β are the corresponding angular velocities about any axis through the origin perpendicular to the line of symmetry of the molecule. I is the moment of inertia of the rotor about the line of the principal axis through the origin perpendicular to the axis of symmetry. The moment of inertia about this principal axis of symmetry is assumed to be zero. $B = \zeta/I$ is the mean collision rate, interpreted as the ratio of the friction coefficient ζ to the moment of inertia I, similar to the case of the Brownian motion [3–6]. k is the Boltzmann constant, T the absolute temperature, and V the potential energy.

Except for the time derivative term, the left-hand side describes the free motion of the rotor and its interaction with the potential energy, while the right-hand side represents the influence of large collisions with the surroundings.

Our aim is essentially to calculate the after-effect function, which amounts to calculating the autocorrelation function of the second-order Legendre polynomial $P_2(\cos\beta) = \frac{1}{2}(3\cos^2\beta - 1)$. The Kerr function may be calculated from the equation [3–6]

$$\phi(t) = \frac{\int_0^\pi \sin\beta\,\mathrm{d}\beta\int_0^{2\pi}\mathrm{d}\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\beta\,P_2(\cos\beta)\,W}{\int_0^\pi \sin\beta\,\mathrm{d}\beta\int_0^{2\pi}\mathrm{d}\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\beta\,W}. \tag{2}$$

The after-effect function for the dielectric relaxation is defined as [1–6]

$$\chi(t) = \frac{\int_0^\pi \sin\beta\,\mathrm{d}\beta\int_0^{2\pi}\mathrm{d}\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\beta\,\mu\cos\beta\,W}{\int_0^\pi \sin\beta\,\mathrm{d}\beta\int_0^{2\pi}\mathrm{d}\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\alpha\int_{-\infty}^{\infty}\mathrm{d}\omega_\beta\,W}. \tag{3}$$

In our analysis, we consider the potential energy [3–6]

$$V = -\mu E(t)\cos\beta - (\alpha_\parallel - \alpha_\perp)\frac{E^2(t)\cos^2\beta}{2} - \alpha_\perp\frac{E^2(t)}{2} \tag{4}$$

where $E(t)$ is the applied electric field, μ is the permanent dipole moment along the rotor axis of symmetry, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities causing the induced moment of the molecule, respectively parallel and perpendicular to the axis of symmetry of the rotor.

The solution of the generalized Liouville equation (1) can be written [1–6] as

$$W = \frac{I}{8\pi^2 kT}\exp(-x)\left[1 + Z(x,t) + X_1(x,t)\cos\beta + X_2(x,t)\left(\frac{I}{2kT}\right)^{1/2}\omega_\beta \sin\beta \right.$$
$$+Y_1(x,t)P_2(\cos\beta) + Y_2(x,t)\frac{1}{\sqrt{3}}\left(\frac{I}{2kT}\right)^{1/2}\omega_\beta P_2^1(\cos\beta)$$
$$\left. +Y_3(x,t)\frac{1}{\sqrt{3}}\left(\frac{I\omega_\beta^2}{2kT} - \frac{x}{2}\right)P_2^2(\cos\beta)\right] \tag{5}$$

where

$$x = \frac{I(\omega_\alpha^2 + \omega_\beta^2)}{2kT} \tag{6}$$

and

$$P_2^1(\cos\beta) = 3\sin\beta\cos\beta \qquad P_2^2(\cos\beta) = 3\sin^2\beta \tag{7}$$

are the associated second-order Legendre polynomials. To compute $\chi(t)$ and $\phi(t)$ up to second order in the electric field, we assume that $X_1(x,t)$ and $X_2(x,t)$ depend only linearly on $E(t)$ and that $Y_1(x,t)$, $Y_2(x,t)$, $Y_3(x,t)$ and $Z(x,t)$ depend only quadratically on $E(t)$. On substituting (5) in equation (1) together with (4), and equating the coefficients of the various Legendre functions to first and second order in the electric field, we note that, up to second order, we obtain the following matrix systems:

$$\underline{\underline{\mathbf{D}}}_X \underline{\mathbf{X}} = \underline{\mathbf{T}} \tag{8}$$

$$\underline{\underline{\mathbf{D}}}_Y \underline{\mathbf{Y}} = \underline{\mathbf{U}}_X \tag{9}$$

$$\mathbf{D}_Z Z = \mathbf{V}_X \tag{10}$$

where

$$\underline{\underline{\mathbf{D}}}_X = \begin{pmatrix} \frac{1}{B}\frac{\partial}{\partial t} + 1 - \int_0^{+\infty} \mathrm{d}x'\,\mathrm{e}^{-x'} & \sqrt{2\gamma}x \\ -\sqrt{2\gamma} & \frac{1}{B}\frac{\partial}{\partial t} + 1 \end{pmatrix} \tag{11}$$

$$\underline{\mathbf{X}} = \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \tag{12}$$

$$\underline{\mathbf{T}} = \begin{pmatrix} 0 \\ -\sqrt{2\gamma}\dfrac{\mu E(t)}{kT} \end{pmatrix} \tag{13}$$

$$\underline{\underline{\mathbf{D}}}_Y = \begin{pmatrix} \frac{1}{B}\frac{\partial}{\partial t} + 1 - \int_0^{+\infty} \mathrm{d}x'\,\mathrm{e}^{-x'} & \sqrt{6\gamma}x & 0 \\ -\sqrt{6\gamma} & \frac{1}{B}\frac{\partial}{\partial t} + 1 & \sqrt{2\gamma}x \\ 0 & -\sqrt{2\gamma} & \frac{1}{B}\frac{\partial}{\partial t} + 1 \end{pmatrix} \tag{14}$$

$$\underline{\mathbf{Y}} = \begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \end{pmatrix} \tag{15}$$

$$\underline{\mathrm{U}}_X = \begin{pmatrix} -\frac{\sqrt{2\gamma}}{3}\frac{\mu E(t)}{kT}\left(x\frac{\partial}{\partial x}+(1-x)\right)X_2 \\ -\sqrt{\frac{2\gamma}{3}}(\alpha_\parallel-\alpha_\perp)\frac{E^2(t)}{kT}+\sqrt{\frac{2\gamma}{3}}\frac{\mu E(t)}{kT}\left(\frac{\partial}{\partial x}-1\right)X_1 \\ \sqrt{\frac{2\gamma}{3}}\frac{\mu E(t)}{kT}\left(\frac{\partial}{\partial x}-1\right)X_2 \end{pmatrix} \tag{16}$$

$$\mathbf{D}_Z = \left(\frac{1}{B}\frac{\partial}{\partial t}+1-\int_0^{+\infty}\mathrm{d}x'\,\mathrm{e}^{-x'}\right) \tag{17}$$

$$\mathbf{V}_X = \left(\frac{\sqrt{2\gamma}}{3}\frac{\mu E(t)}{kT}\left[x\frac{\partial}{\partial x}+(1-x)\right]X_2\right). \tag{18}$$

The dimensionless parameter γ is

$$\gamma = \frac{kT}{IB^2}. \tag{19}$$

Using (5), we can perform the integrals in (3) and (2) to give

$$\chi(t) = \frac{\mu}{3}\int_0^{+\infty}\mathrm{d}x\,\mathrm{e}^{-x}X_1(x,t) \tag{20}$$

$$\phi(t) = \frac{1}{5}\int_0^{+\infty}\mathrm{d}x\,\mathrm{e}^{-x}Y_1(x,t). \tag{21}$$

Thus, the evolution of $\chi(t)$ and $\phi(t)$ will be completely determined provided that the initial condition for W and the explicit expression of $E(t)$ are given.

3. Dielectric and Kerr relaxation functions

We consider an electric field defined as

$$E(t) = \begin{cases} E_0 & t<0 \\ 0 & t \geqslant 0 \end{cases} \tag{22}$$

where E_0 is a constant field. For $t < 0$, we consider that the system is in equilibrium. The distribution function, when we take into account second-order terms in the electric field, is then

$$W = \frac{I}{8\pi^2 kT}\exp\left(-\frac{I(\omega_\alpha^2+\omega_\beta^2)}{2kT}\right)\left[1+\frac{\mu E_0}{kT}\cos\beta+\left(\alpha_\parallel-\alpha_\perp+\frac{\mu^2}{kT}\right)\frac{E_0^2}{3kT}P_2(\cos\beta)\right]. \tag{23}$$

The corresponding values for the coefficients at $t < 0$ are

$$X_1(x, t<0) = \frac{\mu E_0}{kT} \tag{24}$$

and

$$Y_1(x, t<0) = \left(\alpha_\parallel-\alpha_\perp+\frac{\mu^2}{kT}\right)\frac{E_0^2}{3kT}. \tag{25}$$

For $t \geqslant 0$, we apply to the above matrix equations Laplace transforms defined by

$$\tilde{f}(s) = \mathcal{L}(f(t)) = \int_0^{+\infty}\mathrm{d}t\,\mathrm{e}^{-st}f(t). \tag{26}$$

Taking account of the initial conditions and of (22), and defining the new dimensionless Laplace variable

$$s' = \frac{s}{B} \tag{27}$$

we obtain the two independent systems

$$\begin{pmatrix} (s'+1) & \sqrt{2\gamma}x \\ -\sqrt{2\gamma} & (s'+1) \end{pmatrix} \begin{pmatrix} \tilde{X}_1 \\ \tilde{X}_2 \end{pmatrix} = \begin{pmatrix} \int_0^{+\infty} e^{-x'} \tilde{X}_1' \, dx' + \frac{1}{B}\frac{\mu E_0}{kT} \\ 0 \end{pmatrix} \tag{28}$$

and

$$\begin{pmatrix} (s'+1) & \sqrt{6\gamma}x & 0 \\ -\sqrt{6\gamma} & (s'+1) & \sqrt{2\gamma}x \\ 0 & -\sqrt{2\gamma} & (s'+1) \end{pmatrix} \begin{pmatrix} \tilde{Y}_1 \\ \tilde{Y}_2 \\ \tilde{Y}_3 \end{pmatrix}$$

$$= \begin{pmatrix} \int_0^{+\infty} e^{-x'} \tilde{Y}_1' \, dx' + \frac{1}{B}\left(\alpha_\parallel - \alpha_\perp + \frac{\mu^2}{kT}\right)\frac{E_0^2}{3kT} \\ 0 \\ 0 \end{pmatrix}. \tag{29}$$

In what follows, all quantities having the superscript $'$ are functions dependent on x'.

3.1. Dielectric relaxation function

We can eliminate $\tilde{X}_2$ in the system (28) to have an equation in $\tilde{X}_1$ only

$$\left(s' + 1 + \frac{2\gamma x}{s'+1}\right)\tilde{X}_1 = \int_0^{+\infty} e^{-x'} \tilde{X}_1' \, dx' + \frac{1}{B}\frac{\mu E_0}{kT}. \tag{30}$$

Solving the last expression in $\tilde{X}_1$ and multiplying both sides by $e^{-x'}$, we integrate over x to give

$$\int_0^{+\infty} e^{-x} \tilde{X}_1 \, dx = \frac{s'+1}{2\gamma} \int_0^{+\infty} e^{-x} \frac{\int_0^{+\infty} e^{-x'} \tilde{X}_1' \, dx' + \frac{1}{B}\frac{\mu E_0}{kT}}{x + \frac{(s'+1)^2}{2\gamma}} \, dx. \tag{31}$$

Carrying out the integral over x on the right-hand side of (31) and using (20), we get

$$\tilde{\chi}(s') = \frac{s'+1}{2\gamma} \exp\frac{(s'+1)^2}{2\gamma} E_1\left(\frac{(s'+1)^2}{2\gamma}\right)\left[\tilde{\chi}(s') + \frac{1}{B}\frac{\mu^2 E_0}{3kT}\right] \tag{32}$$

where we used the exponential integral defined [7] as

$$E_1(z) \equiv \int_z^{+\infty} \frac{e^{-u}}{u} \, du \qquad |\arg(z)| < \pi. \tag{33}$$

Thus, we obtain

$$\tilde{\chi}(s') = \frac{(1+s') \exp\frac{(s'+1)^2}{2\gamma} E_1\left(\frac{(s'+1)^2}{2\gamma}\right)}{2\gamma - (s'+1) \exp\frac{(s'+1)^2}{2\gamma} E_1\left(\frac{(s'+1)^2}{2\gamma}\right)} \frac{1}{B}\frac{\mu^2 E_0}{3kT}. \tag{34}$$

By using the identity [7]

$$e^{z}E_1(z)=\cfrac{1}{z+\cfrac{1}{1+\cfrac{1}{z+\cfrac{2}{1+\cfrac{2}{z+\cfrac{3}{1+\cfrac{3}{z+\cdots}}}}}}}\qquad (35)$$

we can also express the result (34) in an appropriate continued fraction form

$$\tilde{\chi}(s')=\cfrac{\frac{1}{B}\frac{\mu^2E_0}{3kT}}{s'+\cfrac{2\gamma}{s'+1+\cfrac{2\gamma}{s'+1+\cfrac{4\gamma}{s'+1+\cfrac{4\gamma}{s'+1+\cfrac{6\gamma}{s'+1+\cfrac{6\gamma}{s'+1+\cdots}}}}}}}.\qquad (36)$$

The inverse Laplace transform of (36) is, up to fourth order in the γ expansion,

$$\begin{aligned}\chi(t)=\frac{\mu^2E_0}{3kT}\Bigg\{&1+\left[-2\,e^{-(Bt)}+2-2\,(Bt)\right]\gamma\\&+\left[4(Bt)\,e^{-(Bt)}+2(Bt)^2-4(Bt)+2(Bt)^2e^{-(Bt)}\right]\gamma^2\\&+\Bigg[4\,(Bt)^2-40\,e^{-(Bt)}-8\,(Bt)-\frac{4\,(Bt)^3}{3}-32\,(Bt)e^{-(Bt)}\\&-16\,(Bt)^2e^{-(Bt)}-(Bt)^4e^{-(Bt)}+40-\frac{16\,(Bt)^3e^{-(Bt)}}{3}\Bigg]\gamma^3\\&+\Bigg[-64\,(Bt)+288\,(Bt)e^{-(Bt)}+16\,(Bt)^2+224\,e^{-(Bt)}+56\,(Bt)^3e^{-(Bt)}\\&+\frac{2\,(Bt)^4}{3}+160\,(Bt)^2e^{-(Bt)}-\frac{8\,(Bt)^3}{3}-224\\&+\frac{38\,(Bt)^5e^{-(Bt)}}{15}+\frac{13\,(Bt)^6e^{-(Bt)}}{45}+14\,(Bt)^4e^{-(Bt)}\Bigg]\gamma^4\\&+O(\gamma^5)\Bigg\}.\end{aligned}\qquad (37)$$

Figure 1 shows the after-effect function for the dielectric relaxation $\chi(\tau)/\chi(0)$ versus the reduced time $\tau = Bt$ for various terms of the expansion in power of γ. It indicates that a suitable estimation of $\chi(\tau)$, correct for short time, has to contain at least the term γ^3.

We note that the first convergent of the continued fraction (36) leads to the same result as the dielectric response deduced from the Fokker–Planck–Kramers (FPK) equation describing

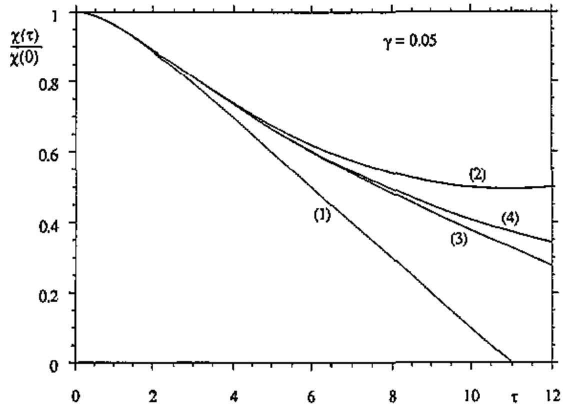

Figure 1. Time evolution of the normalized after-effect function for the dielectric relaxation $\chi(\tau)/\chi(0)$ for $\gamma = 0.05$ versus the reduced time $\tau = Bt$. The numbers (1), (2), (3) and (4) represent the degree of the polynomial expansion in γ taken into account for the expression of $\chi(\tau)$.

the Brownian rotational motion of a rigid linear rod, when a DC field is removed [5, 6]. Indeed, defining the reduced susceptibility

$$\chi_r(s') = \frac{\tilde{\chi}(s')}{\tilde{\chi}(0)} \tag{38}$$

we recover for the first convergent of (36) the result recently deduced in [5, 6], namely

$$\chi_r^{(1)}(s') = \frac{(2s'+2)\gamma}{s'^2 + s' + 2\gamma}. \tag{39}$$

The superscript (1) stands for the order of convergece. The larger convergents of (36) give different responses compared with the FPK solution [5, 6]. Replacing s' by $i\omega'$, we can split (34) into its real and imaginary parts

$$\chi_r(\omega') = \chi_r'(\omega') - i\chi_r''(\omega') \tag{40}$$

corresponding to the usual susceptibility and the loss factor, respectively. This gives for the first convergent

$$\chi_r'^{(1)}(\omega') = \frac{4\gamma^2}{\omega'^4 - 4\omega'^2\gamma + \omega'^2 + 4\gamma^2} \tag{41}$$

$$\chi_r''^{(1)}(\omega') = \frac{2\gamma(1+\omega'^2 - 2\gamma)\omega'}{\omega'^4 - 4\omega'^2\gamma + \omega'^2 + 4\gamma^2}. \tag{42}$$

For $I \to 0$ (corresponding to $B \to \infty$), since the Debye relaxation time

$$\tau_D = \frac{1}{2\gamma B} = \frac{\zeta}{2kT} \tag{43}$$

is finite, the first convergent (39) gives

$$\chi_r^{(0)}(s) = \lim_{B\to\infty} \chi_r^{(1)}(s) = \frac{1}{1+s\tau_D} \tag{44}$$

when we retake the usual Laplace variable s. The relation (44) corresponds to the Debye–Smoluchowski approximation; that is, the limit of the inertial response for very high friction

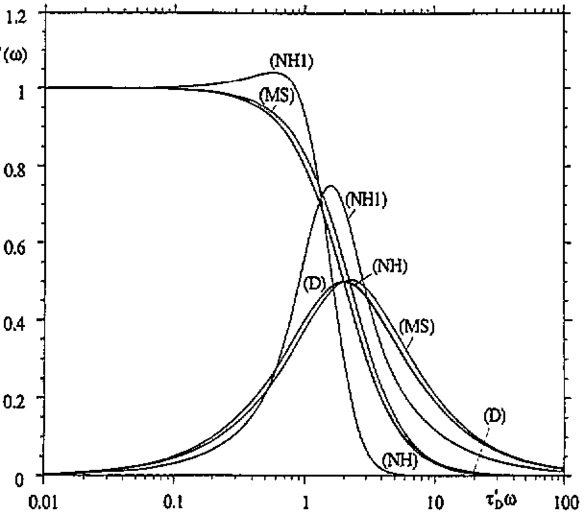

Figure 2. Normalized dispersion plots of the real and imaginary components of the complex susceptibility, $\chi_r'(\omega)$ and $\chi_r''(\omega)$, versus the reduced time $\tau'_D\omega$ for $\gamma = 0.05$ obtained from equation (1), (NH), and the modified Smoluchowski equation, (MS), and for $\gamma = 1$ obtained from equation (1), (NH1). (D) refers to the case of the Debye–Smoluchowski dispersion.

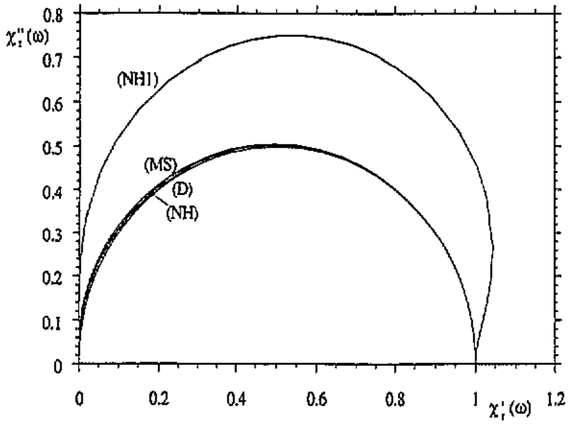

Figure 3. Plots of the imaginary part $\chi_r''(\omega)$ versus the real part $\chi_r'(\omega)$ of the complex susceptibility for $\gamma = 0.05$ obtained from equation (1) (NH) and the modified Smoluchowski equation (MS), and for $\gamma = 1$ obtained from equation (1) (NH1). (D) refers to the Debye–Smoluchowski spectrum.

and vanishingly small inertia. The Debye–Smoluchowski approximation is better known in the harmonic form [8], i.e. putting $s = i\omega$

$$\chi_r^{(0)}(\omega) = \frac{1}{1 + i\omega\tau_D}. \tag{45}$$

This result can be compared with the case of spherical molecules with their polar axis rotating in one plane [8]

$$\chi_{\mathrm{r}}^{(0)}(\omega) = \frac{1}{1 + 2\mathrm{i}\omega\tau_{\mathrm{D}}}. \tag{46}$$

Note that the first convergent susceptibility components (equations (41) and (42)) are nothing but the responses given by the modified Smoluchowski equation [4, 9, 10].

Figure 2 shows how the modified Smoluchowski equation, represented by (MS), versus the reduced time $\tau'_{\mathrm{D}}\omega$ ($\tau'_{\mathrm{D}} = 2\tau_{\mathrm{D}} = \zeta/kT$) overestimates the inertial effects, compared with the more appropriate generalized Liouville equation (1). Indeed, for vanishing inertial moment ($\gamma \sim 0.05$), the spectrum given by the exact solution (equation (34)), represented by (NH) in figure 2 coincides with the ideal Debye–Smoluchowski spectrum (D). For higher values of the inertial moment ($\gamma \sim 1$), the exact solution represented by (NH1) shows a very significant discrepancy with the Debye–Smoluchowski spectrum.

Figure 3 illustrates the Cole–Cole diagram $\chi_{\mathrm{r}}''(\omega) = f(\chi_{\mathrm{r}}'(\omega))$ compared with the equivalent Debye one. For small γ values, all the plots (MS), (D) and (NH) have the same trend, while for $\gamma = 1$ the plot (NH1) has a quite different form.

3.2. Kerr relaxation function

To calculate $\tilde{\phi}(s')$, similarly to the previous subsection, we take the inverse of the square matrix defined in (29). This allows $\tilde{Y}_1$ appearing in the left-hand side of (29) to be expressed as

$$\tilde{Y}_1 = \frac{\left[(s'+1)^2 + 2\gamma x\right]\left[\int_0^{+\infty} \mathrm{e}^{-x'}\tilde{Y}_1'\,\mathrm{d}x' + \frac{1}{B}\left(\alpha_\parallel - \alpha_\perp + \frac{\mu^2}{kT}\right)\frac{E_0^2}{3kT}\right]}{8\gamma[s'+1]\left[\frac{(s'+1)^2}{8\gamma} + x\right]}. \tag{47}$$

Multiplying (47) by e^{-x} and taking the integral of the result over x with (21), we obtain

$$\tilde{\phi}(s') = \frac{1}{4(s'+1)}\left[1 + 3\frac{(s'+1)^2}{8\gamma}\exp\frac{(s'+1)^2}{8\gamma}E_1\left(\frac{(s'+1)^2}{8\gamma}\right)\right] \times\left(\tilde{\phi}(s') + \frac{1}{B}\left(\alpha_\parallel - \alpha_\perp + \frac{\mu^2}{kT}\right)\frac{E_0^2}{15kT}\right) \tag{48}$$

or in a more appropriate form

$$\tilde{\phi}(s') = \frac{\left[1 + 3\frac{(s'+1)^2}{8\gamma}\exp\frac{(s'+1)^2}{8\gamma}E_1\left(\frac{(s'+1)^2}{8\gamma}\right)\right]\frac{1}{B}\left(\alpha_\parallel - \alpha_\perp + \frac{\mu^2}{kT}\right)\frac{E_0^2}{15kT}}{4(s'+1) - \left[1 + 3\frac{(s'+1)^2}{8\gamma}\exp\frac{(s'+1)^2}{8\gamma}E_1\left(\frac{(s'+1)^2}{8\gamma}\right)\right]}. \tag{49}$$

By using (35), this result can also be expressed as a continued fraction

$$\tilde{\phi}(s') = \cfrac{\frac{1}{B}(\alpha_\parallel - \alpha_\perp + \frac{\mu^2}{kT})\frac{E_0^2}{15kT}}{s' + \cfrac{6\gamma}{s'+1+\frac{2\gamma}{s'+1} + \cfrac{8\gamma}{s'+1+\cfrac{16\gamma}{s'+1+\cfrac{16\gamma}{s'+1+\cfrac{24\gamma}{s'+1+\cfrac{24\gamma}{s'+1+\cdots}}}}}}}. \tag{50}$$

The inverse Laplace transform of (50), valid for short time, is, up to fourth order of the γ expansion,

$$\phi(t) = \left(\alpha_{\|} - \alpha_{\perp} + \frac{\mu^2}{kT}\right)\frac{E_0^2}{15kT}\Big\{1 + \left[-6\,\mathrm{e}^{-(Bt)} - 6\,(Bt) + 6\right]\gamma$$
$$+\left[30\,(Bt)^2\mathrm{e}^{-(Bt)} - 72 - 12\,(Bt) + 18\,(Bt)^2 + 84\,(Bt)\mathrm{e}^{-(Bt)} + 72\,\mathrm{e}^{-(Bt)}\right]\gamma^2$$
$$+\Big[-36\,(Bt)^2 - 1080\,(Bt)^2\mathrm{e}^{-(Bt)} - 36\,(Bt)^3 + 1800 - 2016\,(Bt)\mathrm{e}^{-(Bt)}$$
$$-336\,(Bt)^3\mathrm{e}^{-(Bt)} - 57\,(Bt)^4\mathrm{e}^{-(Bt)} + 216\,(Bt) - 1800\,\mathrm{e}^{-(Bt)}\Big]\gamma^3$$
$$+\Big[85536\,(Bt)\mathrm{e}^{-(Bt)} + 43920\,(Bt)^2\mathrm{e}^{-(Bt)} + 54\,(Bt)^4 - 2880\,(Bt)$$
$$+216\,(Bt)^3 + 82656\,\mathrm{e}^{-(Bt)} + 14712\,(Bt)^3\mathrm{e}^{-(Bt)} + 3510\,(Bt)^4\mathrm{e}^{-(Bt)}$$
$$+\frac{2994\,(Bt)^5\mathrm{e}^{-(Bt)}}{5} + \frac{319\,(Bt)^6\mathrm{e}^{-(Bt)}}{5} - 82656 + 288\,(Bt)^2\Big]\gamma^4$$
$$+\mathcal{O}(\gamma^5)\Big\}. \tag{51}$$

The first convergent of the continued fraction (50) now gives

$$\tilde{\phi}^{(1)}(s') = \frac{\frac{1}{B}\left(\alpha_{\|} - \alpha_{\perp} + \frac{\mu^2}{kT}\right)\frac{E_0^2}{15kT}}{s' + \cfrac{6\gamma}{s' + 1 + \cfrac{2\gamma}{s'+1}}}. \tag{52}$$

Defining

$$\Delta n_{\mathrm{r}}(s') = B\frac{\tilde{\phi}(s')}{\phi_0} \tag{53}$$

where

$$\phi_0 = \left(\alpha_{\|} - \alpha_{\perp} + \frac{\mu^2}{kT}\right)\frac{E_0^2}{15kT} \tag{54}$$

we have

$$\Delta n_{\mathrm{r}}^{(1)}(s') = \frac{1}{s' + \cfrac{6\gamma}{s' + 1 + \cfrac{2\gamma}{s'+1}}}. \tag{55}$$

Replacing s' by $\mathrm{i}\omega'$, we can split (53) into its real and imaginary parts as

$$\Delta n_{\mathrm{r}}(\omega') = \Delta n'_{\mathrm{r}}(\omega') - \mathrm{i}\Delta n''_{\mathrm{r}}(\omega'). \tag{56}$$

Figure 4 shows $\Delta n'_{\mathrm{r}}(\omega')$ versus the reduced frequency ω' for the exact solution (NH), the Debye–Smoluchowski case (D) and the approximate response deduced by Kalmykov and Quinn (KQ) (and denoted by $\tilde{C}_0^{(3)}(\omega')$ in their work) [6].

Putting the term $2\gamma/(s'+2) = 0$ and $s' = \mathrm{i}\omega'$ in (55), we recover the result of Kalmykov and Quinn (equation (76) in [6]) and the characteristic time $\tau_{\mathrm{D}2} = \tilde{C}_0^{(2)}(0)/B = \tau_{\mathrm{D}}/3$, ($\tilde{C}_0^{(2)}(\omega')$ being the notation adopted in [6]).

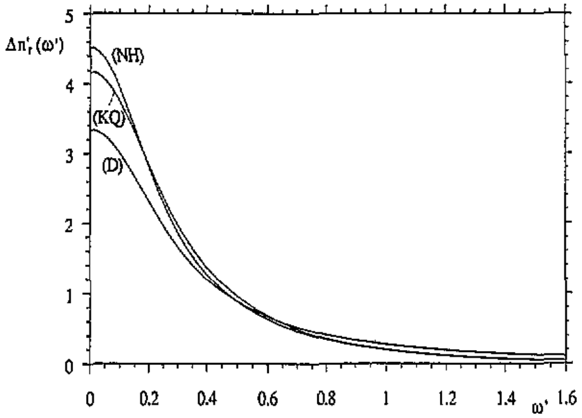

Figure 4. Plots of the real parts $\Delta n_r(\omega')$ of the complex Kerr-effect relaxation function for $\gamma = 0.05$ obtained from equation (1) (NH) and from the work of Kalmykov and Quinn (KQ) . Note that as ω' increases, all approximations converge rapidly, except for the Debye–Smoluchowski diffusion model referred to as (D) on the graph.

4. Steady state of the dielectric and Kerr function for $E(t) = E_0 \cos(\omega t)$

The formal solutions for the coefficients can be written as

$$\begin{pmatrix} X_1(t) \\ X_2(t) \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\mathrm{e}^{\mathrm{i}\omega t} X_1^1(\omega) \\ \frac{1}{2}\mathrm{e}^{\mathrm{i}\omega t} X_2^1(\omega) \end{pmatrix} + \mathrm{CC} \tag{57}$$

$$\begin{pmatrix} Y_1(t) \\ Y_2(t) \\ Y_3(t) \end{pmatrix} = \begin{pmatrix} \frac{1}{4}(Y_1^0(\omega) + Y_1^2(\omega)\mathrm{e}^{2\mathrm{i}\omega t}) \\ \frac{1}{4}(Y_2^0(\omega) + Y_2^2(\omega)\mathrm{e}^{2\mathrm{i}\omega t}) \\ \frac{1}{4}(Y_3^0(\omega) + Y_3^2(\omega)\mathrm{e}^{2\mathrm{i}\omega t}) \end{pmatrix} + \mathrm{CC}\,. \tag{58}$$

Under these conditions, the response functions take the form

$$\chi_{\mathrm{st}}(t) = \tfrac{1}{2}\chi_{\mathrm{st}}(\omega)\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{CC} \tag{59}$$

$$\phi_{\mathrm{st}}(t) = \tfrac{1}{4}(\phi_0(\omega) + \phi_2(\omega)\mathrm{e}^{2\mathrm{i}\omega t}) + \mathrm{CC}\,. \tag{60}$$

The subscript 'st' stands for the steady state. Replacing the expressions (57) and (58) into the two systems (8) and (9) and using the new dimensionless variable

$$\omega' = \omega/B \tag{61}$$

we get the algebraic system of equations

$$\begin{pmatrix} (\mathrm{i}\omega' + 1) & \sqrt{2\gamma}x \\ -\sqrt{2\gamma} & (\mathrm{i}\omega' + 1) \end{pmatrix} \begin{pmatrix} X_1^1 \\ X_2^1 \end{pmatrix} = \begin{pmatrix} \int_0^{+\infty} \mathrm{e}^{-x'} X'^1_1 \,\mathrm{d}x' \\ -\sqrt{2\gamma}\dfrac{\mu E_0}{kT} \end{pmatrix} \tag{62}$$

and

$$\begin{pmatrix} 1 & \sqrt{6\gamma}x & 0 \\ -\sqrt{6\gamma} & 1 & \sqrt{2\gamma}x \\ 0 & -\sqrt{2\gamma} & 1 \end{pmatrix} \begin{pmatrix} Y_1^0 \\ Y_2^0 \\ Y_3^0 \end{pmatrix}$$

$$= \begin{pmatrix} \int_0^{+\infty} \mathrm{e}^{-x'} Y'^0_1 \,\mathrm{d}x' - \frac{\sqrt{2\gamma}}{3}\frac{\mu E_0}{kT}\left[x\frac{\partial}{\partial x} + (1-x)\right] X_2^1 \\ -\sqrt{\frac{2\gamma}{3}}(\alpha_\parallel - \alpha_\perp)\frac{E_0^2}{kT} + \sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x} - 1\right) X_1^1 \\ \sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x} - 1\right) X_2^1 \end{pmatrix} \tag{63}$$

$$\begin{pmatrix} (2i\omega'+1) & \sqrt{6\gamma}x & 0 \\ -\sqrt{6\gamma} & (2i\omega'+1) & \sqrt{2\gamma}x \\ 0 & -\sqrt{2\gamma} & (2i\omega'+1) \end{pmatrix} \begin{pmatrix} Y_1^2 \\ Y_2^2 \\ Y_3^2 \end{pmatrix} \tag{64}$$

$$= \begin{pmatrix} \int_0^{+\infty} e^{-x'} Y_1'^2 \, dx' - \frac{\sqrt{2\gamma}}{3} \frac{\mu E_0}{kT} \left[x \frac{\partial}{\partial x} + 1 - x \right] X_2^1 \\ -\sqrt{\frac{2\gamma}{3}} (\alpha_\parallel - \alpha_\perp) \frac{E_0^2}{kT} + \sqrt{\frac{2\gamma}{3}} \frac{\mu E_0}{kT} \left(\frac{\partial}{\partial x} - 1 \right) X_1^1 \\ \sqrt{\frac{2\gamma}{3}} \frac{\mu E_0}{kT} \left(\frac{\partial}{\partial x} - 1 \right) X_2^1 \end{pmatrix}. \tag{65}$$

Following the procedure developed for the dielectric relaxation, we solve the system (62) to recover the formula of the linear reduced susceptibility, namely

$$\chi_{r,st}(\omega') \equiv \frac{\chi_{st}(\omega')}{\chi_{st}(0)} = \frac{(1+i\omega')(1 - z_1 e^{z_1} E_1(z_1))}{(1+i\omega') - z_1 e^{z_1} E_1(z_1)} \tag{66}$$

where

$$\chi_{st}(0) = \frac{\mu^2 E_0}{3kT} \tag{67}$$

and

$$z_1 = \frac{(1+i\omega')^2}{2\gamma}. \tag{68}$$

We draw the reader's attention to the misprint in the analogous formula given by Sack in [1] (his equation (2.35)). The exact formula was also pointed out in an earlier work by Gaiduk and Kalmykov [2].

Using (35), we can rewrite the reduced steady-state susceptibility in a continued fraction as

$$\chi_{r,st}(\omega') = 1 - \cfrac{i\omega'}{i\omega' + \cfrac{2\gamma}{i\omega' + 1 + \cfrac{2\gamma}{i\omega' + 1 + \cfrac{4\gamma}{i\omega' + 1 + \cfrac{4\gamma}{i\omega' + 1 + \cfrac{6\gamma}{i\omega' + 1 + \cfrac{6\gamma}{i\omega' + 1 + \cdots}}}}}}} \tag{69}$$

which is the same as the result obtained by Sack [1]. The first convergent of (69) gives

$$\chi_{r,st}^{(1)}(\omega') = \frac{2\gamma}{-\omega'^2 + i\omega' + 2\gamma}. \tag{70}$$

Rewriting the reduced susceptibility (66) in the complex form

$$\chi_{r,st}(\omega') = \chi'_{r,st}(\omega') - i\chi''_{r,st}(\omega') \tag{71}$$

the corresponding real and imaginary parts for the first convergent (70) are

$$\chi_{r,st}'^{(1)}(\omega') = \frac{2\gamma\left(-\omega'^2 + 2\gamma\right)}{\omega'^4 - 4\omega'^2\gamma + \omega'^2 + 4\gamma^2} \tag{72}$$

$$\chi_{r,st}''^{(1)}(\omega') = \frac{2\gamma\omega'}{\omega'^4 - 4\omega'^2\gamma + \omega'^2 + 4\gamma^2}. \tag{73}$$

Some particular cases of relevance can be deduced from these results in a straightforward fashion. Using $\omega' = \omega/B$ and (43), equation (70) becomes

$$\chi^{(1)}_{\mathrm{r,\,st}}(\omega) = \frac{1}{1 + \mathrm{i}\omega\tau_{\mathrm{D}} - \omega^2\tau_{\mathrm{D}}/B}. \tag{74}$$

Using (59) and (74), we recover the result of Coffey and McGoldrick (equation (90) in [11a])

$$\langle P_1(\cos\beta(t))\rangle = \frac{\mu E_0}{3kT}\frac{(1-\omega^2\tau_{\mathrm{D}}/B)\cos(\omega t) + \omega\tau_{\mathrm{D}}\sin(\omega t)}{(1-\omega^2\tau_{\mathrm{D}}/B)^2 + (\omega\tau_{\mathrm{D}})^2} \tag{75}$$

which is derived from the modified Smoluchowski equation. For $\gamma \ll 1$, equation (74) gives the Rocard formula [5, 8, 11, 12]

$$\chi^{(1)}_{\mathrm{r,\,st}}(\omega) \cong \frac{1}{(1 + \mathrm{i}\omega\tau_{\mathrm{D}})(1 + \mathrm{i}\omega I/\zeta)}. \tag{76}$$

In the particular case when $B \to \infty$, we recover the Debye result [5, 8, 11, 12]

$$\chi^{(0)}_{\mathrm{r,\,st}}(\omega) = \lim_{B\to\infty} \chi^{(1)}_{\mathrm{r,\,st}}(\omega) = \frac{1}{(1 + \mathrm{i}\omega\tau_{\mathrm{D}})}. \tag{77}$$

Figure 5 shows the steady-state responses $\chi'_{\mathrm{r,\,st}}(\omega')$ and $\chi''_{\mathrm{r,\,st}}(\omega')$ versus the reduced time $\tau'_{\mathrm{D}}\omega$. The curves (NH), (D) and (MS) correspond respectively to (66), (70) and (77) for $\gamma = 0.05$ and the curve (NH1) to (66) for $\gamma = 1$. All the curves converge to zero as ω increases. Moreover, the inertial effects are pronounced for $\omega > \tau'^{-1}_{\mathrm{D}}$. Figure 6 illustrates well how the inertial effects deviate the curves from the ideal case (D).

As the integral on the right-hand side of the system (62) is related to the susceptibility, we can explicitly compute

$$\begin{pmatrix} X^1_1 \\ X^1_2 \end{pmatrix} = \begin{pmatrix} \frac{1}{z_1+x}\left(x + \frac{\mathrm{i}\omega'+1}{2\gamma}\chi_{\mathrm{r,\,st}}(\omega')\right)\frac{\mu E_0}{kT} \\ -\frac{\sqrt{2\gamma}}{\mathrm{i}\omega'+1}\frac{1}{z_1+x}\left(z_1 - \frac{\mathrm{i}\omega'+1}{2\gamma}\chi_{\mathrm{r,\,st}}(\omega')\right)\frac{\mu E_0}{kT} \end{pmatrix}. \tag{78}$$

With these solutions, we are able to solve the systems (63) and (65). By inverting the corresponding matrices, we isolate the terms Y^0_1 and Y^2_1 appearing on the left-hand side of

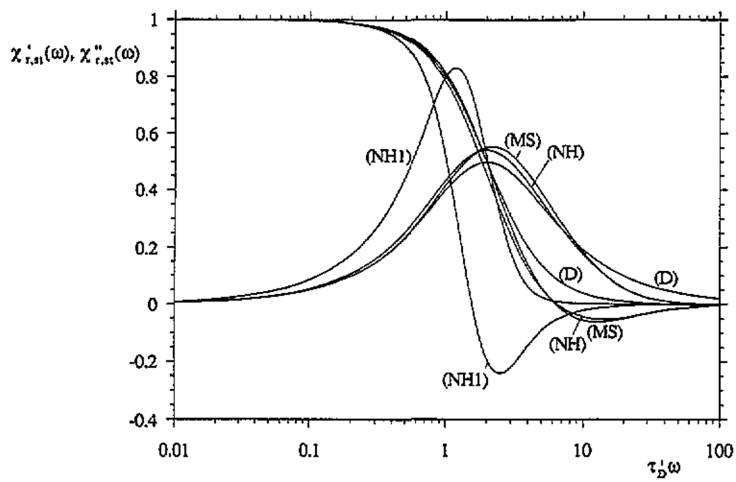

Figure 5. Normalized dispersion plots of the real and imaginary components, $\chi'_{\mathrm{r,\,st}}(\omega)$ and $\chi''_{\mathrm{r,\,st}}(\omega)$, of the steady-state complex susceptibility versus the reduced time $\tau'_{\mathrm{D}}\omega$. Key as in figure 2.

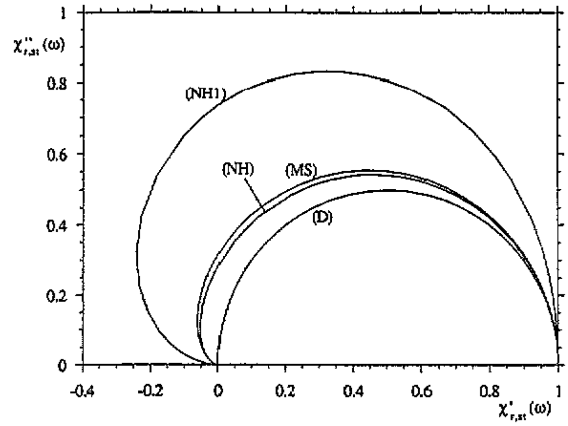

Figure 6. Plots of the imaginary part $\chi''_{r,st}(\omega)$ versus the real part $\chi'_{r,st}(\omega)$ of the steady-state complex susceptibility. Key as in figure 3.

each system. Multiplying both sides by e^{-x} and integrating over x, using (21), we obtain linear equations for $\phi_0(\omega')$ and for $\phi_2(\omega')$:

$$\phi_0(\omega') = \frac{1}{5}\int_0^{+\infty} \frac{e^{-x}}{(1+8\gamma x)}\left\{(1+2\gamma x)\left[5\phi_0(\omega') - \frac{\sqrt{2\gamma}}{3}\frac{\mu E_0}{kT}\left(x\frac{\partial}{\partial x}+1-x\right)X_2^1\right]\right.$$
$$+\sqrt{6\gamma}x\left[\sqrt{\frac{2\gamma}{3}}(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT} - \sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x}-1\right)X_1^1\right]$$
$$\left.+\sqrt{12}\gamma x^2\sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x}-1\right)X_2^1\right\}dx \tag{79}$$

$$\phi_2(\omega') = \frac{1}{5}\int_0^{+\infty} \frac{e^{-x}}{(2i\omega'+1)\left[(2i\omega'+1)^2+8\gamma x\right]}\left\{\left[(2i\omega'+1)^2+2\gamma x\right]\right.$$
$$\times\left[5\phi_2(\omega') - \frac{\sqrt{2\gamma}}{3}\frac{\mu E_0}{kT}\left(x\frac{\partial}{\partial x}+1-x\right)X_2^1\right]$$
$$+\sqrt{6\gamma}x(2i\omega'+1)\left[\sqrt{\frac{2\gamma}{3}}(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT} - \sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x}-1\right)X_1^1\right]$$
$$\left.+\sqrt{12}\gamma x^2\sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}\left(\frac{\partial}{\partial x}-1\right)X_2^1\right\}dx. \tag{80}$$

Computing $\phi_0(\omega')$ and $\phi_2(\omega')$ and using (60), we obtain the result

$$\phi_{st}(t) = \frac{1}{15}\frac{1}{\left[1-\frac{1}{8\gamma}e^{1/8\gamma}E_1\left(\frac{1}{8\gamma}\right)\right]}\left\{\frac{1}{8\sqrt{2\gamma}\left(1-2\sqrt{2\gamma z_1}\right)^2}\right.$$
$$\times\left[(-1+2\sqrt{2\gamma z_1}+4\gamma)e^{1/8\gamma}E_1(\tfrac{1}{8\gamma}) + (-16\sqrt{2z_1}\gamma^{3/2}+32z_1\gamma^2)e^{z_1}E_1(z_1)\right.$$
$$\left.+(8\gamma-16\sqrt{2z_1}\gamma^{3/2})\right]\left(\sqrt{z_1}-\frac{1}{\sqrt{2\gamma}}\chi_{r,st}(\omega')\right)\left(\frac{\mu E_0}{kT}\right)^2$$

$$+\frac{1}{4}\left(1-\frac{1}{8\gamma}e^{1/8\gamma}E_1\left(\tfrac{1}{8\gamma}\right)\right)\left[\left(\frac{\mu E_0}{kT}\right)^2+(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}\right]\Bigg\}$$

$$+\frac{1}{20}\frac{1}{1-\frac{1}{8\sqrt{2\gamma z_2}}(1+3z_2e^{z_2}E_1(z_2))}\left\{\frac{1}{8\sqrt{z_2}(-\sqrt{z_2}+\sqrt{z_1})^2}\right.$$

$$\times\left[(2\,{z_2}^{3/2}\sqrt{z_1}+z_2-2\,{z_2}^2)e^{z_2}E_1(z_2)+(-2\sqrt{z_1z_2}+z_1)e^{z_1}E_1(z_1)\right.$$

$$\left.+(-2\sqrt{z_1z_2}+2\,z_2)\right]\left(\sqrt{z_1}-\frac{1}{\sqrt{2\gamma}}\chi_{r,st}(\omega')\right)\left(\frac{\mu E_0}{kT}\right)^2$$

$$\left.+\frac{1}{4}\left(1-z_2e^{z_2}E_1(z_2)\right)\left[\left(\frac{\mu E_0}{kT}\right)^2+(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}\right]\right\}e^{2i\omega'(Bt)}+\mathrm{cc} \tag{81}$$

where

$$z_2=\frac{(2i\omega'+1)^2}{8\gamma}. \tag{82}$$

In the limit $I\to 0$, that is when $\gamma\to 0$ and $B\to\infty$ with the product $\gamma B=kT/\zeta\equiv D$ constant, the formula (81) gives the result obtained by Débiais from the Smoluchowski equation [13], namely

$$\phi_{st}(t)=\frac{1}{30}\left[\frac{(\frac{\mu E_0}{kT})^2(1-(\omega^2/6D^2))}{\left(1+(\omega/2D)^2\right)\left(1+(\omega/3D)^2\right)}+\frac{(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}}{1+(\omega/3D)^2}\right]\cos(2\,\omega\,t)$$

$$+\frac{1}{30}\left[\frac{(\frac{\mu E_0}{kT})^2((\omega/2D)+(\omega/3D))}{\left(1+(\omega/2D)^2\right)\left(1+(\omega/3D)^2\right)}+\frac{(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}(\omega/3D)}{1+(\omega/3D)^2}\right]\sin(2\,\omega\,t)$$

$$+\frac{(\frac{\mu E_0}{kT})^2}{30\,(1+(\omega/2D)^2)}+\frac{(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}}{30}. \tag{83}$$

The ratios for the time-independent component and for the 2ω frequency time-dependent component, designated respectively by the superscripts 0 and 2, can formally be written in the complex form

$$\Delta n^0_{r,st}(\omega')=\frac{\phi_0(\omega')}{\phi_0(0)}=\Delta n'^0_{r,st}(\omega')-i\Delta n''^0_{r,st}(\omega') \tag{84}$$

$$\Delta n^2_{r,st}(\omega')=\frac{\phi_2(\omega')}{\phi_2(0)}=\Delta n'^2_{r,st}(\omega')-i\Delta n''^2_{r,st}(\omega'). \tag{85}$$

However, the more relevant quantities from the physical point of view are $\Delta n'^0_{r,st}(\omega')$, $\Delta n'^2_{r,st}(\omega')$ and $\Delta n''^2_{r,st}(\omega')$; the imaginary part of $\Delta n^0_{r,st}(\omega')$ being of virtual contribution to the time-independent component (see equation (81)). Defining the parameter

$$R=\frac{(\alpha_\parallel-\alpha_\perp)kT}{\mu^2} \tag{86}$$

we obtain

$$\Delta n^0_{r,st}(\omega')=\frac{1}{\left[1-\frac{1}{8\gamma}e^{1/8\gamma}E_1(\frac{1}{8\gamma})\right]}\frac{1}{2\sqrt{2\gamma}(1-2\sqrt{2}\sqrt{\gamma z_1})^2}$$

$$\times\Big[(-1+2\sqrt{2\gamma z_1}+4\gamma)e^{1/8\gamma}E_1\left(\tfrac{1}{8\gamma}\right)+(-16\sqrt{2z_1}\gamma^{3/2}+32z_1\gamma^2)e^{z_1}E_1(z_1)$$

$$+(8\gamma-16\sqrt{2z_1}\gamma^{3/2})\Big]\frac{\sqrt{z_1}-\frac{1}{\sqrt{2\gamma}}\chi_{r,st}(\omega)}{1+R}+1 \qquad (87)$$

$$\Delta n^2_{r,st}(\omega')=\frac{3}{1-\frac{1}{8\sqrt{2\gamma z_2}}(1+3z_2e^{z_2}E_1(z_2))}$$

$$\times\Bigg\{\Bigg(\frac{(2z_2{}^{3/2}\sqrt{z_1}+z_2-2z_2{}^2)e^{z_2}E_1(z_2)+(-2\sqrt{z_1z_2}+z_1)e^{z_1}E_1(z_1)}{8\sqrt{z_2}(-\sqrt{z_2}+\sqrt{z_1})^2}$$

$$+\frac{(-2\sqrt{z_1z_2}+2z_2)}{8\sqrt{z_2}(-\sqrt{z_2}+\sqrt{z_1})^2}\Bigg)\frac{\sqrt{z_1}-\frac{1}{\sqrt{2\gamma}}\chi_{r,st}(\omega')}{1+R}+\frac{1}{4}\left(1-z_2e^{z_2}E_1(z_2)\right)\Bigg\}. \qquad (88)$$

In the appendix, we show that approximate formulae for (81), (87) and (88), which are valid when $\gamma \ll 1$, give results analogous to those obtained by Coffey and McGoldrick [5, 11] in solving the modified Smoluchowski equation. We point out the misprint in the definition of γ in [11]. The correct expression of γ should not contain the factor $\frac{1}{2}$.

Figures 7 and 8 show the influence of the inertial effects on the steady-state Kerr functions (85).

5. Conclusion

The generalized Liouville equation in the presence of large collisions provides exact analytical expressions of the dielectric and Kerr functions up to second order in the electric field, for all values of the physical parameters involved. Moreover, the results of the Debye–Smoluchowski and modified Smoluchowski models are recovered in the limit regime of very high friction and very small inertia.

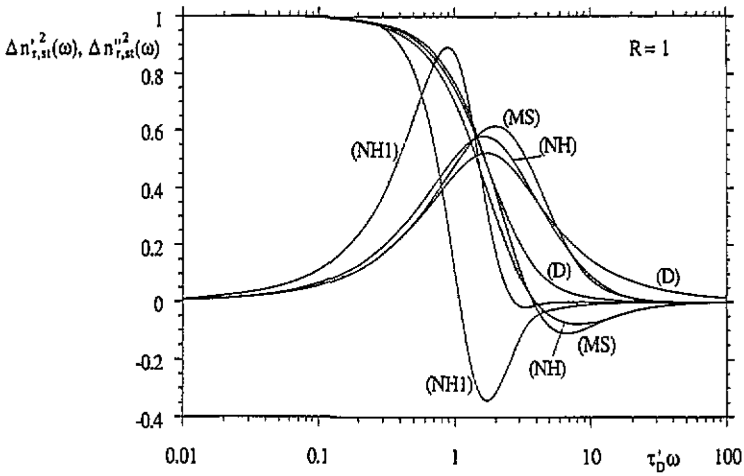

Figure 7. Normalized dispersion plots of the real and imaginary components, $\Delta n'_{r,st}(\omega)$ and $\Delta n''_{rst}(\omega)$, of the time-dependent 2ω frequency term of the steady-state complex Kerr-effect function versus the reduced time $\tau'_D\omega$. Key as in figure 2. We take the value of the parameter $R = 1$.

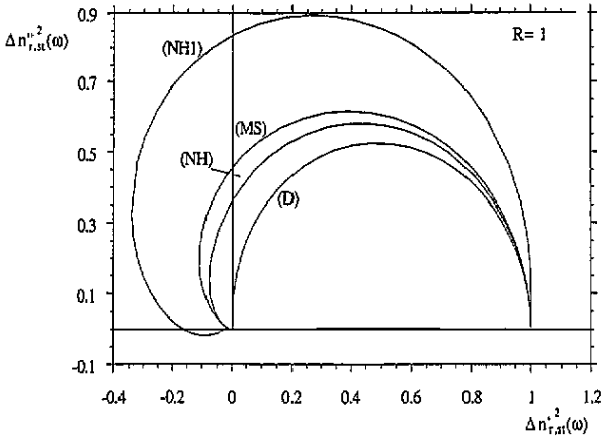

Figure 8. Plots of the imaginary part $\Delta n''_{\mathrm{r,\,st}}(\omega)$ versus the real part $\Delta n'_{\mathrm{r,\,st}}(\omega)$ of the time-dependent 2ω frequency term of the steady-state complex Kerr-effect function. Key as in figure 3. We again take the value of the parameter $R = 1$.

Finally, graphs for small and high values of inertial moment show that the inertial behaviour of the molecule is very apparent at high frequencies.

Appendix

We can evaluate the results (81), (87) and (88) approximately by postulating the following formal solutions for the systems (62), (63) and (65) [5]:

$$\begin{pmatrix} X_1^1 \\ X_2^1 \end{pmatrix} = \begin{pmatrix} \sum_{j=0}^{+\infty} a_j(\omega') L_j^0(x) \\ \sum_{j=0}^{+\infty} b_j(\omega') \frac{1}{\sqrt{j+1}} L_j^1(x) \end{pmatrix} \tag{A1}$$

$$\begin{pmatrix} Y_1^0 \\ Y_2^0 \\ Y_3^0 \end{pmatrix} = \begin{pmatrix} \sum_{j=0}^{+\infty} c_j^0(\omega') L_j^0(x) \\ \sum_{j=0}^{+\infty} d_j^0(\omega') \frac{1}{\sqrt{j+1}} L_j^1(x) \\ \sum_{j=0}^{+\infty} f_j^0(\omega') \frac{1}{\sqrt{(j+1)(j+2)}} L_j^2(x) \end{pmatrix} \tag{A2}$$

$$\begin{pmatrix} Y_1^2 \\ Y_2^2 \\ Y_3^2 \end{pmatrix} = \begin{pmatrix} \sum_{j=0}^{+\infty} c_j^2(\omega') L_j^0(x) \\ \sum_{j=0}^{+\infty} d_j^2(\omega') \frac{1}{\sqrt{j+1}} L_j^1(x) \\ \sum_{j=0}^{+\infty} f_j^2(\omega') \frac{1}{\sqrt{(j+1)(j+2)}} L_j^2(x) \end{pmatrix} \tag{A3}$$

where the generalized Laguerre polynomials

$$L_j^m(x) = \frac{1}{j!} \frac{\mathrm{e}^x}{x^m} \frac{\mathrm{d}^j}{\mathrm{d}x^j} (x^{j+m} \mathrm{e}^{-x}) \tag{A4}$$

are introduced in series form where a_j^1, b_j^1, c_j^0, d_j^0, f_j^0, c_j^2, d_j^2 and f_j^2 are the coefficients depending on the frequency. These polynomials verify the relations

$$\left[x \frac{\partial^2}{\partial x^2} + (m+1-x) \frac{\partial}{\partial x} + j \right] L_j^m(x) = 0 \tag{A5}$$

$$L_j^m(x) = L_j^{m+1}(x) - L_{j-1}^{m+1}(x) \tag{A6}$$

$$xL_j^{m+1}(x) = (j+m+1)L_j^m(x) - (j+1)L_{j+1}^m(x) \tag{A7}$$

$$\left(x\frac{\partial}{\partial x} - x + m\right)L_j^m(x) = (j+1)L_{j+1}^{m-1}(x) \tag{A8}$$

$$\left(\frac{\partial}{\partial x} - 1\right)L_j^m(x) = -L_j^{m+1}(x). \tag{A9}$$

If we substitute the expressions (A1)–(A3) and use the relations (A6)–(A9) above, the first and second equations of each system (62), (63) and (65) are expressed respectively in terms of the $L_j^0(x)$'s and the $L_j^1(x)$'s. The third equations of the systems (63) and (65) are expressed in terms of $L_j^2(x)$'s. Equating the coefficients of the various Laguerre polynomials, we get the following recurrence formulae for these coefficients:

$$\begin{pmatrix} i\omega' a_0^1 + \sqrt{2\gamma} b_0^1 \\ -\sqrt{2\gamma} a_0^1 + (i\omega' + 1) b_0^1 + \sqrt{2\gamma} a_1^1 \\ \cdots \\ -\sqrt{2j\gamma} b_{j-1}^1 + (i\omega' + 1) a_j^1 + \sqrt{(2j+2)\gamma} b_j^1 \\ -\sqrt{(2j+2)\gamma} a_j^1 + (i\omega' + 1) b_j^1 + \sqrt{(2j+2)\gamma} a_{j+1}^1 \\ \cdots \end{pmatrix} = \begin{pmatrix} 0 \\ -\sqrt{2\gamma}\frac{\mu E_0}{kT} \\ \cdots \\ 0 \\ 0 \\ \cdots \end{pmatrix} \tag{A10}$$

$$\begin{pmatrix} [\sqrt{6\gamma} d_0^0] \\ [-\sqrt{6\gamma} c_0^0 + d_0^0 + 2\sqrt{\gamma} f_0^0 + \sqrt{6\gamma} c_1^0] \\ \cdots \\ [-\sqrt{2(j+1)\gamma} d_{j-1}^0 + f_{j-1}^0 + \sqrt{2j\gamma} d_j^0] \\ [-\sqrt{6j\gamma} d_{j-1}^0 + c_j^0 + \sqrt{6(j+1)\gamma} d_j^0] \\ [-\sqrt{2j\gamma} f_{j-1}^0 - \sqrt{6(j+1)\gamma} c_j^0 + d_j^0 \\ \quad + \sqrt{2(j+2)\gamma} f_j^0 + \sqrt{6(j+1)\gamma} c_{j+1}^0] \\ \cdots \end{pmatrix} = \begin{pmatrix} 0 \\ -\sqrt{\frac{2\gamma}{3}}\frac{(\alpha_\parallel - \alpha_\perp)E_0^2}{kT} - \sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT} a_0^1 \\ \cdots \\ -\sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT} b_{j-1}^1 \\ -\frac{\sqrt{2j\gamma}}{3}\frac{\mu E_0}{kT} b_{j-1}^1 \\ \\ -\sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT} a_j^1 \\ \cdots \end{pmatrix} \tag{A11}$$

$$\begin{pmatrix} \left[2\mathrm{i}\omega' c_0^2+\sqrt{6\gamma}d_0^2\right] \\ \left[-\sqrt{6\gamma}c_0^2+(2\mathrm{i}\omega'+1)d_0^2+2\sqrt{\gamma}f_0^2+\sqrt{6\gamma}c_1^2\right] \\ \cdots \\ \left[-\sqrt{2(j+1)\gamma}d_{j-1}^2+(2\mathrm{i}\omega'+1)f_{j-1}^2+\sqrt{2j\gamma}d_j^2\right] \\ \left[-\sqrt{6j\gamma}d_{j-1}^2+(2\mathrm{i}\omega'+1)c_j^2+\sqrt{6(j+1)\gamma}d_j^2\right] \\ \left[-\sqrt{2j\gamma}f_{j-1}^2-\sqrt{6(j+1)\gamma}c_j^2+(2\mathrm{i}\omega'+1)d_j^2 \right. \\ \left. +\sqrt{2(j+2)\gamma}f_j^2+\sqrt{6(j+1)\gamma}c_{j+1}^2\right] \\ \cdots \end{pmatrix} = \begin{pmatrix} 0 \\ -\sqrt{\frac{2\gamma}{3}}\frac{(\alpha_\parallel-\alpha_\perp)E_0^2}{kT}-\sqrt{\frac{2\gamma}{3}}\frac{\mu E_0}{kT}a_0^1, \\ \cdots \\ -\sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT}b_{j-1}^1 \\ -\frac{\sqrt{2j\gamma}}{3}\frac{\mu E_0}{kT}b_{j-1}^1 \\ \\ -\sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT}a_j^1 \\ \cdots \end{pmatrix}. \quad \text{(A12)}$$

Using (A2), (A3) combined with (58), we integrate (21) over x to give

$$\phi_{\mathrm{st}}(t) = \tfrac{1}{20}(c_0^0(\omega) + c_0^2(\omega)\mathrm{e}^{2\mathrm{i}\omega t}) + \mathrm{CC}\ . \quad \text{(A13)}$$

When we neglect the coefficients other than a_0^1, b_0^1, c_0^0, d_0^0, c_0^2 and d_0^2, we only have to solve the first two equations of each system (A10), (A11) and (A12) to get approximate expressions for c_0^0 and c_0^2. The relation (A13) then becomes

$$\phi_{\mathrm{st}}^{(1)}(t) = \frac{1}{5}\left[\frac{\gamma^2\left(\frac{\mu E_0}{kT}\right)^2}{\left(4\,\omega'^2-2\,\mathrm{i}\omega'-6\,\gamma\right)\left(\omega'^2-\mathrm{i}\omega'-2\,\gamma\right)} - \frac{(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}\,\gamma}{8\,\omega'^2-4\,i\omega'-12\,\gamma}\right]\mathrm{e}^{2\,\mathrm{i}\omega'(Bt)}$$

$$-\frac{\gamma\left(\frac{\mu E_0}{kT}\right)^2}{30\,\omega'^2-30\,\mathrm{i}\omega'-60\,\gamma} + \frac{(\alpha_\parallel-\alpha_\perp)\frac{E_0^2}{kT}}{60} + \mathrm{CC}\ . \quad \text{(A14)}$$

This result is analogous to that obtained by Coffey and McGoldrick (equation (91) of [11]) from the modified Smoluchowski equation and to that obtained in a first approximation by Hounkonnou and Navez [5]. The ratios for the component of frequency zero and $2\omega'$ taken separately in this approximation are

$$\Delta n_{\mathrm{r,\,st}}^{0(1)}(\omega') = \frac{\phi^{0(1)}(\omega')}{\phi^{0(1)}(0)} = \Delta n'^{0(1)}_{\mathrm{r,\,st}}(\omega') - \mathrm{i}\Delta n''^{0(1)}_{\mathrm{r,\,st}}(\omega') \quad \text{(A15)}$$

$$\Delta n_{\mathrm{r,\,st}}^{2(1)}(\omega') = \frac{\phi^{2(1)}(\omega')}{\phi^{2(1)}(0)} = \Delta n'^{2(1)}_{\mathrm{r,\,st}}(\omega') - \mathrm{i}\Delta n''^{2(1)}_{\mathrm{r,\,st}}(\omega'). \quad \text{(A16)}$$

We then get

$$\Delta n_{\mathrm{r,\,st}}^{0(1)}(\omega') = \left(-\frac{2\,\gamma}{\omega'^2-\mathrm{i}\omega'-2\,\gamma} + R\right)(1+R)^{-1} \quad \text{(A17)}$$

and

$$\Delta n_{\mathrm{r,\,st}}^{2(1)}(\omega') = \left(\frac{6\,\gamma^2}{\left(2\,\omega'^2-\mathrm{i}\omega'-3\,\gamma\right)\left(\omega'^2-\mathrm{i}\omega'-2\,\gamma\right)} - \frac{3\,R\,\gamma}{2\,\omega'^2-\mathrm{i}\omega'-3\,\gamma}\right)(1+R)^{-1}. \quad \text{(A18)}$$

The corresponding real and imaginary parts are

$$\Delta n'^{0(1)}_{\mathrm{r,\,st}} = \left(-\frac{2\,\gamma\,\left(\omega'^2-2\,\gamma\right)}{\omega'^4-4\,\omega'^2\gamma+\omega'^2+4\,\gamma^2} + R\right)(1+R)^{-1} \quad \text{(A19)}$$

$$\Delta n''^{0(1)}_{\mathrm{r,st}} = \frac{2\gamma\omega'}{\left(\omega'^4 - 4\omega'^2\gamma + \omega'^2 + 4\gamma^2\right)(1+R)} \tag{A20}$$

$$\Delta n'^{2(1)}_{\mathrm{r,st}}$$

$$= \left[\frac{6\gamma^2\left(2\omega'^4 - 7\omega'^2\gamma - \omega'^2 + 6\gamma^2\right)}{36\gamma^4 + \omega'^4 + 5\omega'^6 + 13\omega'^2\gamma^2 - 28\omega'^6\gamma - 16\omega'^4\gamma + 73\omega'^4\gamma^2 - 84\omega'^2\gamma^3 + 4\omega'^8} - \frac{3R\gamma\left(2\omega'^2 - 3\gamma\right)}{4\omega'^4 - 12\omega'^2\gamma + \omega'^2 + 9\gamma^2}\right](1+R)^{-1} \tag{A21}$$

$$\Delta n''^{2(1)}_{\mathrm{r,st}}$$

$$= \left[\frac{-6\gamma^2\omega'\left(-5\gamma + 3\omega'^2\right)}{36\gamma^4 + \omega'^4 + 5\omega'^6 + 13\omega'^2\gamma^2 - 28\omega'^6\gamma - 16\omega'^4\gamma + 73\omega'^4\gamma^2 - 84\omega'^2\gamma^3 + 4\omega'^8} + \frac{3R\gamma\omega'}{4\omega'^4 - 12\omega'^2\gamma + \omega'^2 + 9\gamma^2}\right](1+R)^{-1}. \tag{A22}$$

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