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# Theory of the rotational Brownian motion of a linear molecule in 3D: I. Relaxation and steady-state regimes

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**Abstract.** Exact analytical expressions for the dielectric and Kerr functions in both relaxation and steady-state regimes are explicitly calculated by solving the Fokker–Planck–Kramers (FPK) equation for the rotational Brownian 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 particular cases of the Debye–Smoluchowski and Rocard diffusion models are straightforwardly recovered.

## 1. Introduction

The understanding of dynamical and electric-field-induced optical properties of intrinsically isotropic fluids using the investigations of dielectric relaxation and Kerr electric birefringence is now a field of some activity ([1–4] and references therein). These phenomena, i.e. dielectric relaxation and electric birefringence, are related to the rotational Brownian motion of molecules under the action of an electric stress. This motion has been studied extensively in recent years, giving rise to interesting theoretical developments.

The experimental dielectric behaviour of a fluid is generally expressed in terms of the complex dielectric constant, or more often in terms of the complex relative permittivity  $\epsilon = \epsilon' - i\epsilon''$ , where  $\epsilon'$ , the permittivity, and  $\epsilon''$ , the loss factor, are dependent upon the frequency  $\omega/2\pi$  of the applied complex electric field. When  $\omega$  is zero,  $\epsilon''$  vanishes and  $\epsilon'$  is the static permittivity  $\epsilon_s$ , related to the static relative susceptibility  $\chi_s$  defined in CGS units as  $\chi_s = (\epsilon_s - 1)/4\pi$ .

The complex susceptibility  $\chi(\omega)$  is defined by

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (1)$$

where

$$\chi'(\omega) = \frac{\epsilon'(\omega) - 1}{4\pi} \quad \chi''(\omega) = \frac{\epsilon''(\omega)}{4\pi}. \quad (2)$$

The electric polarization  $P = P(\omega)$  is related to the susceptibility  $\chi = \chi(\omega)$  by

$$P = \chi E \quad (3)$$

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where  $E = E(\omega)$  is the electric field producing  $P$ .

The dielectric relaxation in a dipolar fluid often shows dramatically different behaviour at the low- and high-frequency limits. While the former is often dominated by diffusive motion of the dipolar molecules, the latter is monitored by ultra-fast motions that can be inertial in nature. In many liquids, there is a peak in the dielectric absorption spectrum at a relatively high frequency. This absorption, known as Poley absorption, is often attributed to collective excitations, like librations or dipolarons.

Several different approaches have been invoked to study the dielectric relaxation. The most successful work of anomalous dispersion and dielectric loss in liquids containing polar molecules is that of Debye [5], which proceeds directly from the Smoluchowski equation [1], as appears in Einstein's theory [6] of translational Brownian motion. Under the influence of an alternating electric field, a system of polar molecules is supposed to diffuse by rotational Brownian motion towards an equilibrium distribution in molecular orientation, corresponding to a resultant dielectric polarization. When, at sufficiently high frequency, the rotational diffusion becomes too slow for the establishment of equilibrium with the applied field, the polarization acquires a component out of phase with the field. As a consequence, the displacement current acquires a conductance component in phase with the field, resulting in thermal dissipation of energy from the field. The dependence of the loss factor on frequency is determined by the relaxation time, which is the interval required for the polarization in a static field to decrease to a factor  $1/e$  of its equilibrium value when the field is suddenly removed. The Debye theory, originally developed for spherical molecules with rigid dipoles and a single relaxation time, has been extended to ellipsoidal molecules with three relaxation times.

Even recently, much work [1, 3–5, 7–12, 14–18, 23–25] has been devoted to the Debye or Smoluchowski equations to describe dielectric and Kerr-effect phenomena in liquids. Unfortunately, the rotational diffusion model as originally formulated by Debye is only valid at low frequencies  $\omega\tau_D \leq 1$  ( $\tau_D$  is the Debye relaxation time) because it does not include the effects of molecular inertia. The conditions for which inertial effects have to be taken into consideration in relaxation phenomena have been discussed by Gross [13]. Sack [14] proposed the modified Smoluchowski equation of rotational Brownian motion of molecules in liquids, and determined the conditions of its validity. This equation, which holds for small inertial effects, has been applied by Coffey [15] to calculate the orientational autocorrelation functions of spherically symmetric bodies with a moment inertia and a permanent dipole moment, and [16] to study the influence of dipole–dipole coupling on dielectric and Kerr relaxation. The same equation has also successfully been used recently by Alexiewicz [17, 18] to treat molecular Kerr relaxation theory for liquids in reorienting pulse fields and to take into account the small inertial effects in the time transients of nonlinear electric polarization in liquids. For practical purposes [16] the inertial effects will only start to come into prominence when Brownian motion is used to model high-frequency relaxation processes such as dielectric relaxation and Kerr-effect relaxation.

In the general case, taking into account inertial effects involves the use of an angular velocity-dependent statistical molecular orientation distribution function; this, in turn, requires the solving of the generalized Liouville equation or Kramers (Fokker–Planck–Kramers (FPK)) equation for the rotational Brownian motions of the molecules in the liquid [19]. An account of the modern techniques of solving Kramers equations is to be found in [20]. Some of these techniques have recently been used by a number of authors [21] to describe dielectric relaxation of assemblies of symmetric and asymmetric molecules. Except for the recent works [2–4], this is not the case for the Kerr-effect relaxation, where inertial effects for rotation in only two dimensions are all that have been

studied in depth.

In our recent work [3, 4], we studied the FPK equation for the rotational Brownian motion of a linear polar thin rod-like molecule, subjected to an external electric field, using a series expansion method. Our main aim was to generalize the Debye diffusion model and at large times, to recover the characteristic times elsewhere observed by a microscopic model [3] developed for the analysis of the dynamics of rigid rods (modelling rigid linear polymers) in solution where the solvent is described in terms of explicit particles [3].

In the present paper we present a thorough theoretical analysis of the dielectric and Kerr electric functions in both the relaxation and steady-state regimes, taking into account higher orders of applied electric field. The physical quantities are derived exactly, using the continued fraction methods and some analytical expressions for the susceptibilities and the electric birefringence are given. A global approach to the eigenvalue problem, presented in the appendix, provides a direct method for obtaining the characteristic times.

The paper is organized as follows. Section 2 deals with the general theoretical considerations. In section 3, we derive the after-effect functions for the dielectric and Kerr relaxation. Relevant analytical expressions are provided for the susceptibilities and Kerr phenomena. We show how the physical quantities recently obtained by Kalmykov *et al* could be recovered using the more general theoretical approach derived here. In section 4, we analyse in detail the steady-state dielectric and Kerr functions and provide a straightforward method for recovering particular results published in recent literature.

## 2. General theoretical considerations

We consider the rotational Brownian motion of a polar molecule whose shape is approximated by a thin rod resembling a needle, and which is subjected to an external electric field.

We assume that the angular velocity of the rotor around its line of symmetry is zero. This is achieved if the moment of inertia about the principal axis of symmetry is also zero. We denote by  $I$  the moment of inertia of the rotor about the principal axis through the origin perpendicular to the line of symmetry. The orientational relaxation of the rod is governed by the following torques:

- (i) the electric torque due to the applied electric field;
- (ii) a frictional couple,  $\zeta$  (where  $\zeta$  is the friction coefficient) multiplied by the angular velocity;
- (iii) a random driving couple with no preferential direction which can be determined by the Wiener process, responsible for rotational diffusion at equilibrium.

Under these conditions, the rotational motion following the removal of a DC electric field can be described by the following equations [1–4]:

$$\dot{\omega}_\alpha(t) = -\omega_\alpha(t)\omega_\beta(t) \cot \beta(t) - \frac{\zeta}{I}\omega_\alpha(t) + \frac{\lambda_\alpha(t)}{I} \quad (4)$$

$$\dot{\omega}_\beta(t) = \omega_\alpha^2(t) \cot \beta(t) - \frac{\zeta}{I}\omega_\beta(t) + \frac{\lambda_\beta(t)}{I} \quad (5)$$

where  $\omega_\alpha = \dot{\alpha}(t) \sin \beta(t)$ ;  $\omega_\beta = \dot{\beta}(t)$ .  $\beta$  and  $\alpha$  are the polar and azimuthal angles, respectively,  $\lambda_i$  are the components of a white noise driving torque having no preferential direction and arising from the Brownian motion of the surroundings.

As a result of the presence for a long time of a constant electric field, the dipole moment has attained a steady value. At time  $t = 0$  the field is removed, and the system under the influence of the thermal motion of the environment tends to revert to a random arrangement.

This process is called dielectric relaxation and the term 'after-effect' is often employed to qualify physical quantities related to the relaxation process.

The Kerr-effect relaxation function is defined as the angular average [1-4]

$$\frac{\Delta n(t)}{\Delta n_0} = \frac{\phi(t)}{\phi_0} \equiv \frac{\langle P_2[\cos \beta(t)] \rangle}{\langle P_2[\cos \beta(0)] \rangle} \quad (6)$$

where  $\Delta n_0 = K_n \phi_0$ .  $K_n$  is the Kerr constant,  $P_2(x) = \frac{1}{2}(3x^2 - 1)$  is the Legendre polynomial of order 2 and

$$\phi_0 = \frac{E^2}{15k_B T} \left( \frac{\mu^2}{k_B T} + \alpha_{\parallel} - \alpha_{\perp} \right) \quad (7)$$

where  $\mu$  is the dipole moment,  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the polarizabilities of the molecule parallel and perpendicular to the axis of symmetry of the rotor, respectively,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $E$  is the amplitude of an applied DC field.

The Fokker-Planck-Kramers (FPK) equation for the probability density function  $W(\alpha, \beta, \omega_{\alpha}, \omega_{\beta}, t)$  in configuration angular velocity space associated with the motion is [1-4]

$$\begin{aligned} \frac{\partial W}{\partial t} + \frac{\omega_{\alpha}}{\sin \beta} \frac{\partial W}{\partial \alpha} + \omega_{\beta} \frac{\partial W}{\partial \beta} + \cot \beta \left( \omega_{\alpha}^2 \frac{\partial W}{\partial \omega_{\beta}} - \omega_{\alpha} \omega_{\beta} \frac{\partial W}{\partial \omega_{\alpha}} \right) - \frac{1}{I} \frac{\partial V}{\partial \beta} \frac{\partial W}{\partial \omega_{\beta}} \\ = B \left[ \frac{\partial}{\partial \omega_{\beta}} \left( \omega_{\beta} W + \frac{k_B T}{I} \frac{\partial W}{\partial \omega_{\beta}} \right) + \frac{\partial}{\partial \omega_{\alpha}} \left( \omega_{\alpha} W + \frac{k_B T}{I} \frac{\partial W}{\partial \omega_{\alpha}} \right) \right] \end{aligned} \quad (8)$$

with the normalization condition

$$\int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} \int_0^{\pi} d\beta \sin \beta \int_0^{2\pi} d\alpha W(\alpha, \beta, \omega_{\alpha}, \omega_{\beta}, t) = N \quad (9)$$

where  $B = \zeta/I$ ,  $N$  is a constant, and  $V$  is the potential energy. Hereafter, we will use  $kT$  for  $k_B T$ .

Our aim is to calculate essentially the after-effect function, which amounts to calculating the autocorrelation function of the second-order Legendre polynomial. This autocorrelation function describes the decay of the mean value of  $\Delta n(t)$  following the removal of a constant external field at time  $t = 0$ . The after-effect function may be calculated from the equation [1-3]

$$\phi(t) = \frac{\int_0^{\pi} \sin \beta d\beta \int_0^{2\pi} d\alpha \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} P_2(\cos \beta) W}{\int_0^{\pi} \sin \beta d\beta \int_0^{2\pi} d\alpha \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} W} \quad (10)$$

The after-effect function for the dielectric relaxation is defined as

$$\chi(t) = \frac{\int_0^{\pi} \sin \beta d\beta \int_0^{2\pi} d\alpha \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} \mu \cos \beta W}{\int_0^{\pi} \sin \beta d\beta \int_0^{2\pi} d\alpha \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} W} \quad (11)$$

When the potential energy  $V$  does not depend on the time, any solution of (8) will evolve asymptotically towards the equilibrium function  $W = W_0$

$$W_0 = N \frac{\exp\{-[\frac{1}{2}I(\omega_{\alpha}^2 + \omega_{\beta}^2) + V]/kT\}}{\int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} \int_0^{\pi} d\beta \sin \beta \int_0^{2\pi} d\alpha \exp\{-[\frac{1}{2}I(\omega_{\alpha}^2 + \omega_{\beta}^2) + V]/kT\}} \quad (12)$$

Rewriting (8) in terms of a function  $w = w(\alpha, \beta, \omega_{\alpha}, \omega_{\beta}, t)$  such that

$$W = W_0 w \quad (13)$$

and multiplying the resulting expression by  $w$ , all the left-hand side of (8), except for the term containing the time derivative, disappears after integration over phase space. Thus, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \left( \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} \int_0^{\pi} d\beta \sin \beta \int_0^{2\pi} d\alpha W_0 \frac{w^2}{2} \right) \\ = -B \frac{kT}{I} \left\{ \int_{-\infty}^{\infty} d\omega_{\alpha} \int_{-\infty}^{\infty} d\omega_{\beta} \right. \\ \left. \times \int_0^{\pi} d\beta \sin \beta \int_0^{2\pi} d\alpha W_0 \left[ \left( \frac{\partial w}{\partial \omega_{\alpha}} \right)^2 + \left( \frac{\partial w}{\partial \omega_{\beta}} \right)^2 \right] \right\}. \end{aligned} \quad (14)$$

The relation (14) shows that the time derivative of a positive quantity is negative and equal to zero only when  $w$  is a function of  $\alpha$ ,  $\beta$  and  $t$  only. Subject to this condition, equation (8) is valid only for  $w$  constant. The normalization condition (9) applied to (13) requires this constant to be unity. This means that the positive quantity in (14) will decrease with time until the equilibrium distribution function is attained.

We consider the potential energy [2-4]

$$V = -\mu E(t) \cos \beta - (\alpha_{\parallel} - \alpha_{\perp}) \frac{E^2(t) \cos^2 \beta}{2} - \frac{\alpha_{\perp} E^2(t)}{2}. \quad (15)$$

When one neglects all terms of higher order than the second in  $E(t)$ , a special type of solution can be found in the form [2-4]

$$\begin{aligned} W = \frac{I}{8\pi^2 kT} \exp(-x) \left[ 1 + Z(x, t) + X_1(x, t) \cos \beta + X_2(x, t) \left( \frac{I}{2kT} \right)^{1/2} \omega_{\beta} \sin \beta \right. \\ \left. + Y_1(x, t) P_2(\cos \beta) + Y_2(x, t) \frac{1}{\sqrt{3}} \left( \frac{I}{2kT} \right)^{1/2} \omega_{\beta} P_2^1(\cos \beta) \right. \\ \left. + Y_3(x, t) \frac{1}{\sqrt{3}} \left( \frac{I \omega_{\beta}^2}{2kT} - \frac{x}{2} \right) P_2^2(\cos \beta) \right] \end{aligned} \quad (16)$$

$$x = \frac{I(\omega_{\alpha}^2 + \omega_{\beta}^2)}{2kT} \quad (17)$$

$$\Omega^2 = \omega_{\alpha}^2 + \omega_{\beta}^2. \quad (18)$$

Here  $P_2^1(\cos \beta) = 3 \sin \beta \cos \beta$ ,  $P_2^2(\cos \beta) = 3 \sin^2 \beta$  are the associated Legendre functions of order 2.

In equation (16) the functions  $X_1(x, t)$  and  $X_2(x, t)$  depend linearly on  $E(t)$  while  $Y_1(x, t)$ ,  $Y_2(x, t)$ ,  $Y_3(x, t)$  and  $Z(x, t)$  depend quadratically on  $E(t)$ . On substituting (16) in (8), using (15) and equating the coefficients of the various Legendre functions for the first and second order in the electric field, we establish, after some algebra, the following formal systems:

$$\underline{\underline{D}}_x \underline{\underline{X}} = \underline{\underline{T}} \quad (19)$$

$$\underline{\underline{D}}_y \underline{\underline{Y}} = \underline{\underline{U}}_x \quad (20)$$

$$\underline{\underline{D}}_z \underline{\underline{Z}} = \underline{\underline{V}}_x \quad (21)$$

where

$$\underline{\underline{\mathbf{D}}}_X = \begin{pmatrix} \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (1-x) \frac{\partial}{\partial x} \right) & \sqrt{2\gamma} x \\ -\sqrt{2\gamma} & \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (2-x) \frac{\partial}{\partial x} - \frac{1}{2} \right) \end{pmatrix} \quad (22)$$

$$\underline{\mathbf{X}} = \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \quad (23)$$

$$\underline{\mathbf{T}} = \begin{pmatrix} 0 \\ -\sqrt{2\gamma} \frac{\mu E(t)}{kT} \end{pmatrix} \quad (24)$$

$$\underline{\underline{\mathbf{D}}}_Y = \begin{pmatrix} \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (1-x) \frac{\partial}{\partial x} \right) & \sqrt{6\gamma} x & 0 \\ -\sqrt{6\gamma} & \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (2-x) \frac{\partial}{\partial x} - \frac{1}{2} \right) & \sqrt{2\gamma} x \\ 0 & -\sqrt{2\gamma} & \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (3-x) \frac{\partial}{\partial x} - 1 \right) \end{pmatrix} \quad (25)$$

$$\underline{\mathbf{Y}} = \begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \end{pmatrix} \quad (26)$$

$$\underline{\underline{\mathbf{U}}}_X = \begin{pmatrix} -\frac{\sqrt{2\gamma}}{3} \frac{\mu E(t)}{kT} \left( x \frac{\partial}{\partial x} + (1-x) \right) X_2 \\ -\sqrt{\frac{2\gamma}{3}} (\alpha_{\parallel} - \alpha_{\perp}) \frac{E^2(t)}{kT} + \sqrt{\frac{2\gamma}{3}} \frac{\mu E(t)}{kT} \left( \frac{\partial}{\partial x} - 1 \right) X_1 \\ \sqrt{\frac{2\gamma}{3}} \frac{\mu E(t)}{kT} \left( \frac{\partial}{\partial x} - 1 \right) X_2 \end{pmatrix} \quad (27)$$

$$\underline{\mathbf{D}}_Z = \left[ \frac{1}{B} \frac{\partial}{\partial t} - 2 \left( x \frac{\partial^2}{\partial x^2} + (1-x) \frac{\partial}{\partial x} \right) \right] \quad (28)$$

$$\underline{\mathbf{V}}_X = \left[ \frac{\sqrt{2\gamma}}{3} \frac{\mu E(t)}{kT} \left( x \frac{\partial}{\partial x} + (1-x) \right) X_2 \right]. \quad (29)$$

Here  $\gamma$  is a dimensionless parameter defined as

$$\gamma = \frac{kT}{IB^2}. \quad (30)$$

We note that the generalized Laguerre polynomials defined as

$$L_j^m(x) = \frac{1}{j!} \frac{e^x}{x^m} \frac{d^j}{dx^j} (x^{j+m} e^{-x}) \quad (31)$$

are simply the eigenfunctions of the spatial components of the diagonal terms of the matrices  $\underline{\underline{D}}_x$ ,  $\underline{\underline{D}}_y$  and  $\underline{\underline{D}}_z$ . They obey the relations

$$\left(x \frac{\partial^2}{\partial x^2} + (m+1-x) \frac{\partial}{\partial x} + j\right) L_j^m(x) = 0 \quad (32)$$

$$L_j^m(x) = L_j^{m+1}(x) - L_{j-1}^{m+1}(x) \quad (33)$$

$$x L_j^{m+1}(x) = (j+m+1) L_j^m(x) - (j+1) L_{j+1}^m(x) \quad (34)$$

$$\left(x \frac{\partial}{\partial x} - x + m\right) L_j^m(x) = (j+1) L_{j+1}^{m-1}(x) \quad (35)$$

$$\left(\frac{\partial}{\partial x} - 1\right) L_j^m(x) = -L_j^{m+1}(x). \quad (36)$$

The use of these functions is more relevant, for the differential equation systems giving  $X_i$ ,  $i = 1, 2$  (equation (23)) and  $Y_j$ ,  $j = 1, 3$  (equation (26)), than the Laguerre polynomials ( $m = 0$  for all diagonal components) used in Kalmykov *et al* [2] and in our previous work [4].

Then the systems (23), (26) can be expanded as

$$\underline{\underline{X}} = \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \begin{pmatrix} \sum_{j=0}^{+\infty} a_j(t) L_j^0(x) \\ \sum_{j=0}^{+\infty} b_j(t) \frac{L_j^1(x)}{\sqrt{j+1}} \end{pmatrix} \quad (37)$$

$$\underline{\underline{Y}} = \begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \end{pmatrix} = \begin{pmatrix} \sum_{j=0}^{+\infty} c_j(t) L_j^0(x) \\ \sum_{j=0}^{+\infty} d_j(t) \frac{L_j^1(x)}{\sqrt{j+1}} \\ \sum_{j=0}^{+\infty} f_j(t) \frac{L_j^2(x)}{\sqrt{(j+1)(j+2)}} \end{pmatrix} \quad (38)$$

$$\underline{\underline{Z}} = \sum_{j=0}^{+\infty} g_j(t) L_j^0(x). \quad (39)$$

Using the expressions (37), (38) and (39), and the relations (32)–(36) and equating the coefficients of the various Laguerre polynomials, we get the following differential difference equations:

$$-\sqrt{2j\gamma} b_{j-1} + \frac{1}{B} \frac{d}{dt} a_j + 2j a_j + \sqrt{(2j+2)\gamma} b_j = 0 \quad (40)$$

$$-\sqrt{(2j+2)\gamma} a_j + \frac{1}{B} \frac{d}{dt} b_j + (2j+1) b_j + \sqrt{(2j+2)\gamma} a_{j+1} = -\sqrt{2\gamma} \frac{\mu E(t)}{kT} \delta_{j,0}$$

$$-\sqrt{6j\gamma} d_{j-1} + \frac{1}{B} \frac{d}{dt} c_j + 2j c_j + \sqrt{6(j+1)\gamma} d_j = -\frac{\sqrt{2j\gamma}}{3} \frac{\mu E(t)}{kT} b_{j-1}$$

$$-\sqrt{2j\gamma} f_{j-1} - \sqrt{6(j+1)\gamma} c_j + \frac{1}{B} \frac{d}{dt} d_j + (2j+1) d_j + \sqrt{2(j+2)\gamma} f_j + \sqrt{6(j+1)\gamma} c_{j+1} \quad (41)$$

$$= -\sqrt{\frac{2\gamma}{3}} \frac{(\alpha_{\parallel} - \alpha_{\perp}) E^2(t)}{kT} \delta_{j,0} - \sqrt{\frac{2(j+1)\gamma}{3}} \frac{\mu E(t)}{kT} a_j$$

$$-\sqrt{2(j+2)\gamma} d_j + \frac{1}{B} \frac{d}{dt} f_j + (2j+2) f_j + \sqrt{2(j+1)\gamma} d_{j+1} = -\sqrt{\frac{2(j+2)\gamma}{3}} \frac{\mu E(t)}{kT} b_j$$



$$\frac{1}{B} \frac{d}{dt} g_j + 2j g_j = \frac{\sqrt{2j\gamma}}{3} \frac{\mu E(t)}{kT} b_{j-1} \quad (42)$$

where  $j$  is any natural integer and  $b_{-1} = d_{-1} = f_{-1} = 0$ .

Exploiting the solution form (16) and the expressions (37) and (38), we can perform the integrations in (11) and (10) to obtain

$$\chi(t) = \frac{1}{3} \mu a_0(t) \quad (43)$$

$$\phi(t) = \frac{1}{5} c_0(t). \quad (44)$$

Given the initial condition for  $W$ , we can deduce the corresponding initial conditions for the coefficients  $a_j$ ,  $b_j$ ,  $c_j$ ,  $d_j$ ,  $f_j$  and  $g_j$ . Then, knowing the expression for the applied electric field  $E(t)$ , we are able to derive the evolution of the relevant physical quantities  $\chi(t)$  and  $\phi(t)$  by solving only the systems (40) and (41) without (42). These aspects will be examined in the following sections.

### 3. Dielectric and Kerr relaxation functions

We consider the regime in which the electric field  $E(t)$  is suddenly switched off at  $t = 0$ :

$$E(t) = \begin{cases} E_0 & t < 0 \\ 0 & t \geq 0 \end{cases} \quad (45)$$

where  $E_0$  is a constant electric field. For  $t < 0$ , the system is in equilibrium. Taking into account the second order in  $E_0$ , the distribution function is

$$W = \frac{I}{8\pi^2 kT} \exp\left(-\frac{I(\omega_\alpha^2 + \omega_\beta^2)}{2kT}\right) \left[ 1 + \frac{\mu E_0}{kT} \cos \beta + \left(\alpha_{\parallel} - \alpha_{\perp} + \frac{\mu^2}{kT}\right) \frac{E_0^2}{3kT} P_2(\cos \beta) \right] \quad (46)$$

and the corresponding initial values for the coefficients are

$$a_0 = \frac{\mu E_0}{kT} \quad a_j = 0 \quad j \geq 1 \quad b_j = 0 \quad j \geq 0 \quad (47)$$

$$c_0 = \left(\alpha_{\parallel} - \alpha_{\perp} + \frac{\mu^2}{kT}\right) \frac{E_0^2}{3kT} \quad c_j = 0 \quad j \geq 1 \quad d_j = f_j = 0 \quad j \geq 0. \quad (48)$$

For  $t \geq 0$ , we apply the Laplace transform to the differential difference equations as

$$\tilde{f}(s) = \mathcal{L}(f(t)) = \int_0^{+\infty} dt e^{-st} f(t). \quad (49)$$

Defining the reduced Laplace variable  $s'$  as

$$s' = \frac{s}{B} \quad (50)$$

we obtain the following two independent systems, taking into account the initial conditions previously expressed and (45):

$$\begin{aligned} -\sqrt{2j\gamma} \tilde{b}_{j-1} + (s' + 2j) \tilde{a}_j + \sqrt{(2j+2)\gamma} \tilde{b}_j &= \frac{1}{B} \frac{\mu E_0}{kT} \delta_{j,0} \\ -\sqrt{(2j+2)\gamma} \tilde{a}_j + (s' + 2j + 1) \tilde{b}_j + \sqrt{(2j+2)\gamma} \tilde{a}_{j+1} &= 0 \end{aligned} \quad (51)$$

and

$$\begin{aligned}
 -\sqrt{6j\gamma}\bar{d}_{j-1} + (s' + 2j)\bar{c}_j + \sqrt{6(j+1)\gamma}\bar{d}_j &= \frac{1}{B} \left( \alpha_{\parallel} - \alpha_{\perp} + \frac{\mu^2}{kT} \right) \frac{E_0^2}{3kT} \delta_{j,0} \\
 -\sqrt{2j\gamma}\bar{f}_{j-1} - \sqrt{6(j+1)\gamma}\bar{c}_j + (s' + 2j + 1)\bar{d}_j + \sqrt{2(j+2)\gamma}\bar{f}_j + \sqrt{6(j+1)\gamma}\bar{c}_{j+1} &= 0 \\
 -\sqrt{2(j+2)\gamma}\bar{d}_j + (s' + 2j + 2)\bar{f}_j + \sqrt{2(j+1)\gamma}\bar{d}_{j+1} &= 0
 \end{aligned} \tag{52}$$

which describe the relevant physical phenomena.

### 3.1. Dielectric relaxation function

The system (51) can be transformed by rewriting each coupled equation in the form

$$\bar{a}_0 = \frac{1}{s' + \sqrt{2\gamma} \frac{\bar{b}_0}{\bar{a}_0}} \frac{1}{B} \frac{\mu E_0}{kT} \tag{53}$$

$$\frac{\bar{b}_0}{\bar{a}_0} = \frac{\sqrt{2\gamma}}{1 + s' + \sqrt{2\gamma} \frac{\bar{a}_1}{\bar{b}_0}} \tag{54}$$

⋮

$$\frac{\bar{a}_j}{\bar{b}_{j-1}} = \frac{\sqrt{2j\gamma}}{2j + s' + \sqrt{(2j+2)\gamma} \frac{\bar{b}_j}{\bar{a}_j}} \tag{55}$$

$$\frac{\bar{b}_j}{\bar{a}_j} = \frac{\sqrt{(2j+2)\gamma}}{2j + 1 + s' + \sqrt{(2j+2)\gamma} \frac{\bar{a}_{j+1}}{\bar{b}_j}} \tag{56}$$

⋮

By eliminating the various ratio of coefficients in this new system, we calculate  $\bar{a}_0(s')$  in a continued fraction form. Thus, using (43), we get

$$\bar{\chi}(s') = \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{s' + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{2\gamma}} \cdot \tag{57}$$

$$\frac{1}{s' + 1 + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{2\gamma}}$$

$$\frac{1}{s' + 2 + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{4\gamma}}$$

$$\frac{1}{s' + 3 + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{4\gamma}}$$

$$\frac{1}{s' + 4 + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{6\gamma}}$$

$$\frac{1}{s' + 5 + \frac{\frac{1}{B} \frac{\mu^2 E_0}{3kT}}{6\gamma}}$$

$$\frac{1}{s' + 6 + \dots}$$

The dielectric relaxation function  $\bar{\chi}(s')$ , exact to any order in  $\gamma$ , can be now evaluated by taking the successive convergents of the continued fraction (57). The  $i$ th convergent, denoted by  $\bar{\chi}^{(i)}(s')$ , will be defined considering only the  $(i+1)$  first terms in the series  $\{\bar{a}_j, \bar{b}_j\}$ , assuming all the others are equal to zero.

Defining the reduced susceptibility

$$\chi_r^{(i)}(s') = \frac{\bar{\chi}^{(i)}(s')}{\bar{\chi}^{(i)}(0)} \tag{58}$$

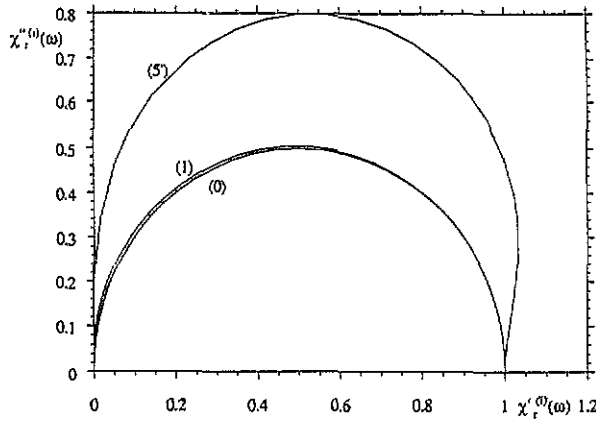


Figure 1. Normalized dispersion plots of the real and imaginary components,  $\chi_r^{(i)}(\omega)$  and  $\chi_r''^{(i)}(\omega)$ , of the complex susceptibility versus the reduced time  $\tau_D' \omega$  ( $\tau_D' = 2\tau_D$ ) for  $\gamma = 0.05$  in the case of the first (1) and second (2) convergent approximations and for  $\gamma = 1$  in the case of the fifth convergent approximation (5'). The order of convergent is indicated by the corresponding number. (0) refers to the Debye dispersion.

the first leads to the expressions

$$\chi_r^{(1)}(s') = \frac{(2s' + 2)\gamma}{s'^2 + s' + 2\gamma}. \quad (59)$$

Replacing  $s'$  by  $i\omega'$ , we can split (58) into its real and imaginary parts, corresponding to the usual susceptibility and the loss factor, respectively

$$\chi_r^{(i)}(\omega') = \chi_r'^{(i)}(\omega') - i\chi_r''^{(i)}(\omega'). \quad (60)$$

For  $I \rightarrow 0$  (corresponding to  $B \rightarrow \infty$ ), since the Debye relaxation time  $\tau_D = (2\gamma B)^{-1} = \zeta/(2kT)$  is finite, the first convergent (equation (59)) gives

$$\chi_r^{(0)}(s) = \lim_{B \rightarrow \infty} \chi_r^{(1)}(s) = \frac{1}{1 + s\tau_D} \quad (61)$$

when we retake the usual Laplace variable  $s$ . The relation (61) corresponds to the Debye approximation; that is, the limit of the inertial response for very high friction and vanishingly small inertia; i.e. the limit of the inertial response as  $\gamma$  tends to zero or  $B$  to infinite.

This result can be compared with the case of the spherical molecules with their polar axes rotating in one plane [1]

$$\chi_r^{(0)}(s) = \frac{1}{1 + 2s\tau_D}. \quad (62)$$

For larger convergents (higher-order convergents of (57)), the effects of the higher-order terms in  $\gamma$  for small  $\gamma$  values are already noticeable with respect to the Debye spectrum, and the third convergent coincides with the second convergent response. For  $\gamma = 1$ , the computation of at least the fifth convergent is necessary in order to get a good approximation. See figure 1.

Figure 2 illustrates Cole-Cole diagram,  $\chi_r''^{(1)}(\omega) = f(\chi_r'^{(1)}(\omega))$ , compared with the equivalent Debye diagram. Let us note that, for small  $\gamma$  values, the second- and third-order convergent responses converge to the first convergent response.

In general, the analytical form of the response function depends, in higher approximations (as is pointed out in [22b]), on the precise nature of the molecular model

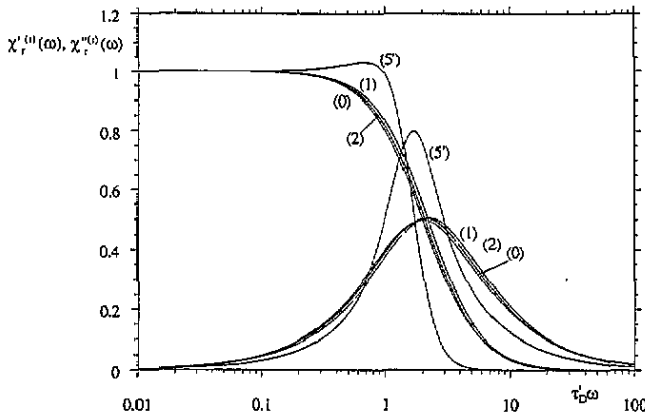


Figure 2. Plots of the imaginary part  $\chi_r^{(i)}(\omega)$  versus the real part  $\chi_r^{(r)}(\omega)$  of the complex susceptibility for  $\gamma = 0.05$  in the case of the first convergent approximation (1) and for  $\gamma = 1$  in the case of the fifth convergent (5'). The second and third convergents coincide with the first convergent. (0) refers to the Debye spectrum.

and on the collision mechanism used to describe the system. Thus, using, for example, the collision mechanism corresponding to case (B) studied by Sack in [22b], we obtain the susceptibility formula

$$\chi(\omega'') = \frac{(1 + i\omega'')[1 + ze^z \text{Ei}(-z)]}{[1 + ze^z \text{Ei}(-z)] + i\omega''} \quad (63)$$

where  $z = (1 + i\omega'')^2 / 2\gamma_1$ ;  $-\text{Ei}(-z) = \int_z^\infty e^{-s} ds/s$  [15], with all physical quantities ( $\omega''$ ,  $\gamma_1$ ) defined as in [22b]. We draw the reader's attention to the misprint in the analogous formula given by Sack in [22b] (his equation (2.35)). The exact formula was also pointed out in an earlier work by Gaiduk and Kalmykov [23].

### 3.2. Kerr-effect relaxation function

To evaluate the Kerr-effect relaxation function (44), we handle the third and fourth set of recurrence equations of (52) to express  $\tilde{f}_j$  only in terms of  $\tilde{d}_j$  and  $\tilde{c}_{j+1}$ , and  $\tilde{f}_{j-1}$  only in terms of  $\tilde{d}_j$  and  $\tilde{c}_j$ . This amounts to writing

$$\tilde{f}_j = \sqrt{\frac{2(j+1)}{6(j+2)}} \tilde{c}_{j+1} + \frac{\sqrt{2\gamma}}{s' + 2(j+1)} \tilde{d}_j \quad (64)$$

$$\tilde{f}_{j-1} = \sqrt{\frac{2(j+1)}{6j}} \tilde{c}_j + \frac{\sqrt{2\gamma}}{s' + 2j} \tilde{d}_j. \quad (65)$$

Eliminating the  $\tilde{f}_j$ 's in the second and fifth equations of (52), the system (52) is reduced to

$$s' \tilde{c}_0 + \sqrt{6\gamma} \tilde{d}_0 = \left( \alpha_{\parallel} - \alpha_{\perp} + \frac{\mu^2}{kT} \right) \frac{E_0^2}{3kT} \quad (66)$$

$$-\sqrt{6\gamma} \tilde{c}_0 + \left( s' + 1 + \frac{2\gamma}{s' + 2} \right) \tilde{d}_0 + 8\sqrt{\frac{\gamma}{6}} \tilde{c}_1 = 0 \quad (67)$$

$$-\sqrt{6j\gamma} \tilde{d}_{j-1} + (s' + 2j) \tilde{c}_j + \sqrt{6(j+1)\gamma} \tilde{d}_j = 0 \quad j \geq 1 \quad (68)$$

$$\begin{aligned}
 & -8\sqrt{\frac{\gamma(j+1)}{6}}\tilde{c}_j + \left(s' + 2j + 1 - \frac{2\gamma}{s' + 2j} + \frac{2\gamma}{s' + 2j + 2}\right)\tilde{d}_j \\
 & + 8\sqrt{\frac{\gamma(j+1)}{6}}\tilde{c}_{j+1} = 0 \quad j \geq 1.
 \end{aligned} \tag{69}$$

By analogy with the computation of the quantity  $\tilde{a}_0(s')$ , we solve the system above established to find  $\tilde{c}_0(s')$ . Using (44),  $\tilde{\phi}(s')$  is expressed as a continued fraction:

$$\tilde{\phi}(s') = \frac{\frac{1}{B} \left( \alpha_{\parallel} - \alpha_{\perp} + \frac{\mu^2}{kT} \right) \frac{E_0^2}{15kT}}{s' + \frac{6\gamma}{s' + 1 + \frac{2\gamma}{s' + 2} + \frac{8\gamma}{s' + 2 + \frac{2\gamma}{s' + 3} + \frac{16\gamma}{s' + 4 + \frac{2\gamma}{s' + 5} + \frac{24\gamma}{s' + 6 + \frac{2\gamma}{s' + 6 + \dots}}}}}. \tag{70}$$

The continued fraction (70), as the exact expression of the Kerr-effect relaxation function (equation (10)), generalizes all approximation solutions recently published in the literature. All the higher-order solutions of the Kerr-effect relaxations obtained by Kalmykov *et al* [2] are simply some approximations of successive convergents up to third order of (70). Indeed, taking the first convergent of (70), i.e. ignoring the term  $8\gamma$ , one finds

$$\Delta n_r^{(1)}(s') = B \frac{\tilde{\phi}^{(1)}(s')}{\phi_0} = \frac{1}{s' + \frac{6\gamma}{s' + 1 + \frac{2\gamma}{s' + 2}}} \tag{71}$$

which gives the characteristic time  $\tau^{(1)} = (1 + \gamma)\tau_{D2}$ .

Putting the term  $2\gamma/(s' + 2) = 0$  and  $s' = i\omega'$ , we recover the result of Kalmykov *et al* (equation (76) in [2]) and the characteristic time  $\tau_{D2} = \tilde{C}_0^{(2)}(0)/B = \tau_D/3$  ( $\tilde{C}_0^{(2)}(\omega')$  being the notation adopted in [2]).

On computing the second convergent of (70), i.e. when we ignore the term  $16\gamma$ , we also recover equation (79) of [2], namely

$$\Delta n_r^{(2)}(s') = B \frac{\tilde{\phi}^{(2)}(s')}{\phi_0} = \frac{1}{s' + \frac{6\gamma}{s' + 1 + \frac{2\gamma}{s' + 2} + \frac{8\gamma}{s' + 2}}} \tag{72}$$

with the characteristic time  $\tau^{(2)} = (1 + 5\gamma)\tau_{D2}$ . This result also coincides precisely with the results obtained by Burshtein and Temkin for the orientational relaxation time of the second-order Legendre polynomial autocorrelation function [24].

The next convergent gives

$$\begin{aligned}
 \Delta n_r^{(3)}(s') &= B \frac{\tilde{\phi}^{(3)}(s')}{\phi_0} \\
 &= \frac{1}{s' + \frac{6\gamma}{s' + 1 + \frac{2\gamma}{s' + 2} + \frac{8\gamma}{s' + 2 + \frac{16\gamma}{s' + 3 - \frac{2\gamma}{s' + 2} + \frac{2\gamma}{s' + 4}}}}}.
 \end{aligned} \tag{73}$$

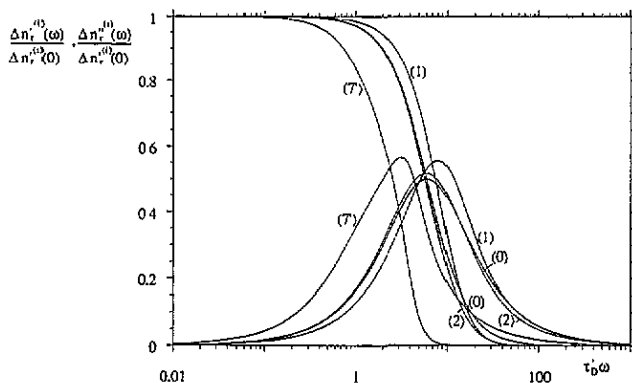


Figure 3. Normalized plots of the real and imaginary parts of the complex Kerr-effect relaxation function  $\Delta n_r^{(i)}(\omega')$  versus the reduced time for  $\gamma = 0.05$  in the case of different convergent approximations and for  $\gamma = 1$  in the case of the seventh convergent (7'). Note that as  $\omega'$  increases, all approximations converge rapidly, except for the Debye diffusion model, (0).

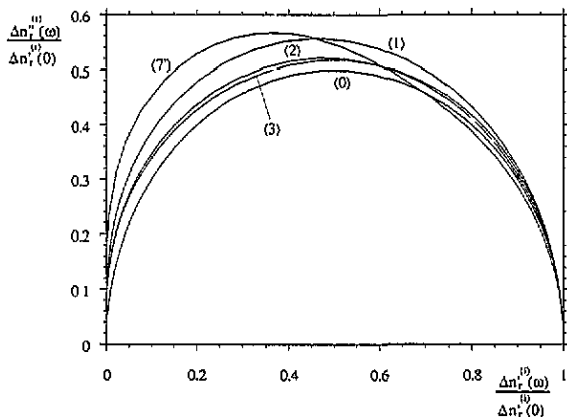


Figure 4. Plots of the imaginary part versus the real part of the complex Kerr-effect relaxation function  $\Delta n_r^{(i)}(\omega')$  for  $\gamma = 0.05$  in the case of different convergent approximations and for  $\gamma = 1$  in the case of (7'). Details otherwise as in figure 2. Note that as  $\omega'$  increases, all approximations converge rapidly, except for the Debye diffusion model, (0).

and

$$\tau^{(3)} = \left( 1 + \gamma + \frac{8\gamma}{2 + \frac{16\gamma}{3 - \frac{\gamma}{2}}} \right) \tau_{D2} \tag{74}$$

or (if  $\gamma \ll 1$ ) ignoring the term  $O(\gamma^3)$  in the development,

$$\tau^{(3)} = (1 + 5\gamma - (32/3)\gamma^2) \tau_{D2}. \tag{75}$$

This result is exactly the same as in equation (84) of [2] and, comparing it with the second convergent result, we can see that  $\tau^{(3)} \simeq \tau^{(2)}$  for small  $\gamma$ . The various convergents are presented in figure 4.

Figures 3 and 4 show that the effects of higher-order convergents are more pronounced for the Kerr-effect relaxation functions than for the dielectric relaxation function previously

shown in figures 1 and 2. This could be easily understood as we deal here with the second-order effect in the electric field. The seventh convergent is necessary to compute the Kerr relaxation function for  $\gamma = 1$ .

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

The formal solutions of the coefficients can be written

$$\begin{aligned} a_j(t) &= \frac{1}{2}a_j^1(\omega)e^{i\omega t} + \text{CC} \\ b_j(t) &= \frac{1}{2}b_j^1(\omega)e^{i\omega t} + \text{CC} \\ c_j(t) &= \frac{1}{4}(c_j^0(\omega) + c_j^2(\omega)e^{2i\omega t}) + \text{CC} \\ d_j(t) &= \frac{1}{4}(d_j^0(\omega) + d_j^2(\omega)e^{2i\omega t}) + \text{CC} \\ f_j(t) &= \frac{1}{4}(f_j^0(\omega) + f_j^2(\omega)e^{2i\omega t}) + \text{CC}. \end{aligned} \quad (76)$$

Under these conditions, the response functions take the form

$$\chi_{\text{st}}(t) = \frac{1}{2}\chi_{\text{st}}(\omega)e^{i\omega t} + \text{CC} \quad (77)$$

$$\phi_{\text{st}}(t) = \frac{1}{4}(\phi_0(\omega) + \phi_2(\omega)e^{2i\omega t}) + \text{CC} \quad (78)$$

where the subscript 'st' stands for the steady state.

Replacing these expressions into the two systems (40) and (41) and defining the new variable  $\omega' = \omega/B$ , we get the algebraic system of equations

$$\begin{aligned} -\sqrt{2j\gamma}b_{j-1}^1 + (i\omega' + 2j)a_j^1 + \sqrt{(2j+2)\gamma}b_j^1 &= 0 \\ -\sqrt{(2j+2)\gamma}a_j^1 + (i\omega' + 2j+1)b_j^1 + \sqrt{(2j+2)\gamma}a_{j+1}^1 &= -\sqrt{2\gamma}\frac{\mu E_0}{kT}\delta_{j,0} \end{aligned} \quad (79)$$

$$\begin{aligned} -\sqrt{6j\gamma}d_{j-1}^0 + 2jc_j^0 + \sqrt{6(j+1)\gamma}d_j^0 &= -\frac{\sqrt{2j\gamma}}{3}\frac{\mu E_0}{kT}b_{j-1}^1 \\ -\sqrt{2j\gamma}f_{j-1}^0 - \sqrt{6(j+1)\gamma}c_j^0 + (2j+1)d_j^0 + \sqrt{2(j+2)\gamma}f_j^0 + \sqrt{6(j+1)\gamma}c_{j+1}^0 \\ &= -\sqrt{\frac{2\gamma}{3}}\frac{(\alpha_{\parallel} - \alpha_{\perp})E_0^2}{kT}\delta_{j,0} - \sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT}a_j^1 \end{aligned} \quad (80)$$

$$-\sqrt{2(j+2)\gamma}d_j^0 + (2j+2)f_j^0 + \sqrt{2(j+1)\gamma}d_{j+1}^0 = -\sqrt{\frac{2(j+2)\gamma}{3}}\frac{\mu E_0}{kT}b_j^1$$

$$-\sqrt{6j\gamma}d_{j-1}^2 + (2i\omega' + 2j)c_j^2 + \sqrt{6(j+1)\gamma}d_j^2 = -\frac{\sqrt{2j\gamma}}{3}\frac{\mu E_0}{kT}b_{j-1}^1$$

$$\begin{aligned} -\sqrt{2j\gamma}f_{j-1}^2 - \sqrt{6(j+1)\gamma}c_j^2 + (2i\omega' + 2j+1)d_j^2 + \sqrt{2(j+2)\gamma}f_j^2 + \sqrt{6(j+1)\gamma}c_{j+1}^2 \\ = -\sqrt{\frac{2\gamma}{3}}\frac{(\alpha_{\parallel} - \alpha_{\perp})E_0^2}{kT}\delta_{j,0} - \sqrt{\frac{2(j+1)\gamma}{3}}\frac{\mu E_0}{kT}a_j^1 \end{aligned} \quad (81)$$

$$-\sqrt{2(j+2)\gamma}d_j^2 + (2i\omega' + 2j+2)f_j^2 + \sqrt{2(j+1)\gamma}d_{j+1}^2 = -\sqrt{\frac{2(j+2)\gamma}{3}}\frac{\mu E_0}{kT}b_j^1.$$

The system (79) gives

$$\frac{\chi_{st}(\omega')}{\chi_{st}(0)} = 1 - \frac{i\omega'}{i\omega' + \frac{2\gamma}{i\omega' + 1 + \frac{2\gamma}{i\omega' + 2 + \frac{4\gamma}{i\omega' + 3 + \frac{4\gamma}{i\omega' + 4 + \frac{6\gamma}{i\omega' + 5 + \frac{6\gamma}{i\omega' + 6 + \dots}}}}}} \quad (82)$$

where

$$\chi_{st}(0) = \frac{\mu^2 E_0}{3kT}. \quad (83)$$

The expression (82) coincides with the result obtained by Sack [22].

By analogy with the previous section's calculations, and defining the reduced steady-state susceptibility for the 'ith' convergent as

$$\chi_{r,st}^{(i)}(\omega') = \frac{\chi_{st}^{(i)}(\omega')}{\chi_{st}^{(i)}(0)} = \chi'_{r,st}{}^{(i)}(\omega') - i\chi''_{r,st}{}^{(i)}(\omega') \quad (84)$$

we get for the first convergent the quantity

$$\chi_{r,st}^{(1)}(\omega') = \frac{2\gamma}{-\omega'^2 + i\omega' + 2\gamma}. \quad (85)$$

Some relevant particular cases can be straightforwardly deduced from these results. Thus, it is interesting to note that, using  $\omega' = \omega/B$ , equation (85) becomes

$$\chi_{r,st}^{(1)}(\omega) = \frac{1}{1 + i\omega\tau_D - \omega^2\tau_D/B} \quad (86)$$

where

$$\tau_D = \frac{1}{2\gamma B} = \frac{\zeta}{2kT} \quad (87)$$

is the Debye relaxation time. Using (77) and (86), we recover the result of Coffey (equation (90) of [21])

$$\langle P_1(\cos[\beta(t)]) \rangle = \frac{\mu E_0}{3kT} \frac{(1 - \omega^2\tau_D/B) \cos(\omega t) + \omega\tau_D \sin(\omega t)}{(1 - \omega^2\tau_D/B)^2 + (\omega\tau_D)^2} \quad (88)$$

derived from the modified Smoluchowski equation. For  $\gamma \ll 1$ , equation (86) becomes the Rocard equation [1, 4, 21]

$$\chi_{r,st}^{(1)}(\omega) \cong \frac{1}{(1 + i\omega\tau_D)(1 + i\omega I/\zeta)}. \quad (89)$$

The characteristic times  $\tau_D$  and  $1/B = I/\zeta$  in this equation can easily be obtained by a simple perturbation method (see the appendix). In the particular case when  $B \rightarrow \infty$ , we recover the Debye result [1, 4, 21], namely

$$\chi_{r,st}^{(0)}(\omega) = \lim_{B \rightarrow \infty} \chi_{r,st}^{(1)}(\omega) = \frac{1}{(1 + i\omega\tau_D)}. \quad (90)$$



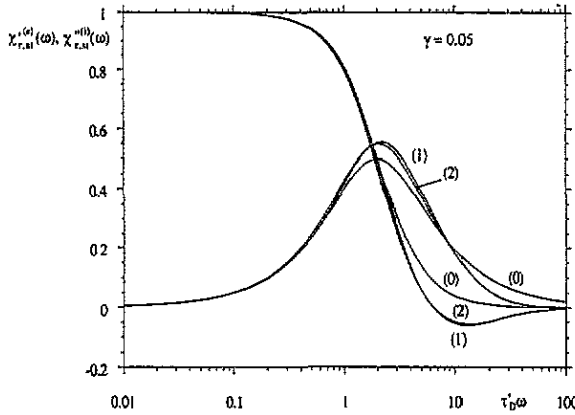


Figure 5. As figure 1, but for the real and imaginary components of the steady-state complex susceptibility,  $\chi_{r,st}^{(i)}(\omega)$  and  $\chi_{r,st}^{n(i)}(\omega)$ , with  $\gamma = 0.05$  for all convergent approximations.

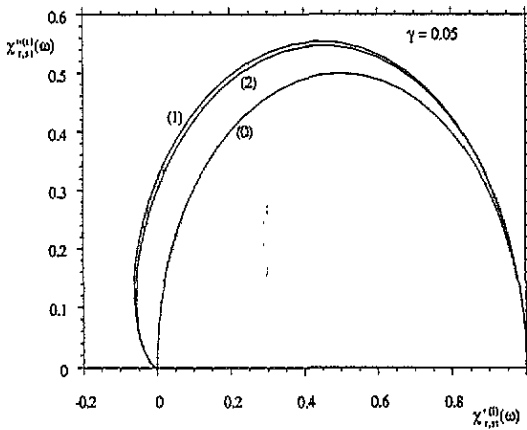


Figure 6. As figure 2, but for the real and imaginary parts of the steady-state complex susceptibility,  $\chi_{r,st}^{(i)}(\omega)$  and  $\chi_{r,st}^{n(i)}(\omega)$ , with  $\gamma = 0.05$  for all convergent approximations. The third convergent coincides with the second convergent identified by (2) in the graph.

Figure 5 shows the steady-state responses  $\chi_{r,st}^{(i)}$  and  $\chi_{r,st}^{n(i)}$  versus the reduced time  $\tau_D \omega$ . The curve  $i = 0$  corresponds to the ideal Debye–Smoluchowski equation diffusion model case. All the curves converge well to zero as  $\tau_D \omega$  increases. Moreover, the inertial effects are more pronounced for  $\omega > \tau_D^{-1}$ . Figure 6 illustrates how the inertial effects deviate the diagrams from the ideal case represented by the Debye spectrum.

Knowing the solution for the  $a_j$  and  $b_j$ , the systems (80) and (81) can be solved using successive approximations. Thus, considering the first convergent approximation for  $a_0$  and assuming that only  $c_0^0$ ,  $d_0^0$ ,  $c_0^2$  and  $d_0^2$  are different from zero, we get

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

$$- \frac{\gamma \left( \frac{\mu E_0}{kT} \right)^2}{30\omega^2 - 30i\omega' - 60\gamma} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT}}{60} + \text{cc.} \tag{91}$$

One can check that this result coincides with the expression obtained by Coffey (equation (91) in [21]) from the modified Smoluchowski equation. However, let us point out the misprint in the definition of  $\gamma$  in [21]. The correct expression should not contain the factor  $\frac{1}{2}$ . In the limit  $I \rightarrow 0$ , which amounts to taking the limit  $\gamma \rightarrow 0$  and  $B \rightarrow \infty$  in the expression (91), and keeping the product  $\gamma B = kT/\zeta = D$  constant, we recover the result obtained by Débiais [25] from the Smoluchowski equation, namely

$$\begin{aligned} \phi_{st}^{(0)}(t) = & \frac{1}{30} \left( \frac{\left(\frac{\mu E_0}{kT}\right)^2 [1 - (\omega^2/6D^2)]}{[1 + (\omega/2D)^2][1 + (\omega/3D)^2]} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT}}{1 + (\omega/3D)^2} \right) \cos(2\omega t) \\ & + \frac{1}{30} \left( \frac{\left(\frac{\mu E_0}{kT}\right)^2 [(\omega/2D) + (\omega/3D)]}{[1 + (\omega/2D)^2][1 + (\omega/3D)^2]} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT} (\omega/3D)}{1 + (\omega/3D)^2} \right) \sin(2\omega t) \\ & + \frac{\left(\frac{\mu E_0}{kT}\right)^2}{30[1 + (\omega/2D)^2]} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT}}{30}. \end{aligned} \quad (92)$$

We now take the first convergent approximation for  $a_0^1$  and let us use the first equation of (79) to deduce  $b_0^1$ . Then, assuming that only the coefficients  $c_0^0, d_0^0, f_0^0, c_1^0, c_0^2, d_0^2, f_0^2$  and  $c_1^2$  in (80), (81) are different from zero, we obtain

$$\begin{aligned} \phi_{st}^{(2)}(t) = & \frac{1}{20} \left( \frac{\gamma^2 \left(\frac{\mu E_0}{kT}\right)^2 (5i\omega' + 2)}{(-8i\omega' \gamma - 3\gamma + 2i\omega'^3 + 3\omega'^2 - i\omega') (\omega'^2 - i\omega' - 2\gamma)} \right. \\ & \left. + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT} \gamma (i\omega' + 1)}{8i\omega' \gamma + 3\gamma - 2i\omega'^3 - 3\omega'^2 + i\omega'} \right) e^{2i\omega' (Bt)} \\ & - \frac{\gamma \left(\frac{\mu E_0}{kT}\right)^2 (3i\omega' + 2)}{60(\omega'^2 - i\omega' - 2\gamma)} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT}}{60} + \text{cc}. \end{aligned} \quad (93)$$

Finally, let us consider the second convergent approximation for  $a_0^1$  and let us use the first expression in (79) to deduce  $b_0^1$ . Thus, assuming that only  $c_0^0, d_0^0, f_0^0, c_1^0, c_0^2, d_0^2, f_0^2$  and  $c_1^2$  in (80), (81) are different from zero, we get

$$\begin{aligned} \phi_{st}^{(3)}(t) = & \frac{1}{20} \left( \frac{\gamma^2 \left(\frac{\mu E_0}{kT}\right)^2 (5\omega'^2 - 12i\omega' - 4)}{(-8i\gamma \omega' - 3\gamma + 2i\omega'^3 + 3\omega'^2 - i\omega') (4i\gamma \omega' + 4\gamma - i\omega'^3 - 3\omega'^2 + 2i\omega')} \right. \\ & \left. + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT} \gamma (i\omega' + 1)}{8i\gamma \omega' + 3\gamma - 2i\omega'^3 - 3\omega'^2 + i\omega'} \right) e^{2i\omega' (Bt)} \\ & + \frac{\gamma \left(\frac{\mu E_0}{kT}\right)^2 (-3\omega'^2 + 8i\omega' + 4)}{60(4i\gamma \omega' + 4\gamma - i\omega'^3 - 3\omega'^2 + 2i\omega')} + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \frac{E_0^2}{kT}}{60} + \text{cc}. \end{aligned} \quad (94)$$

The ratios for the time-independent component and for the  $2\omega$  frequency time-dependent component, taken separately for each  $i$ th approximation (the first superscript 0 (or 2) in the expressions standing for the time-independent (or  $2\omega$  frequency time-dependent)

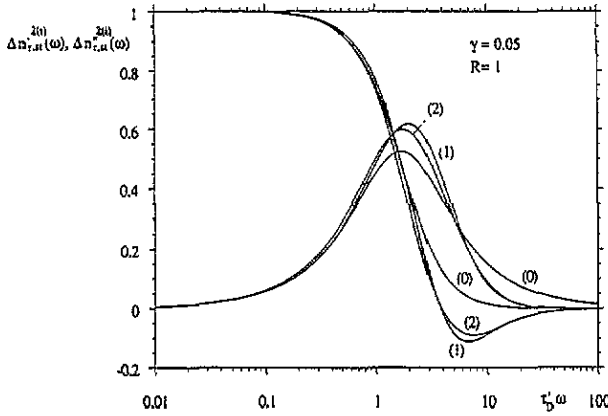


Figure 7. As figure 3, but for the real and imaginary components of the time-dependent  $2\omega$  frequency term of the steady-state complex Kerr-effect function,  $\Delta n_{r,st}^{2(i)}(\omega)$  and  $\Delta n_{r,st}^{2(r)}(\omega)$ , with  $\gamma = 0.05$  for all convergent approximations.

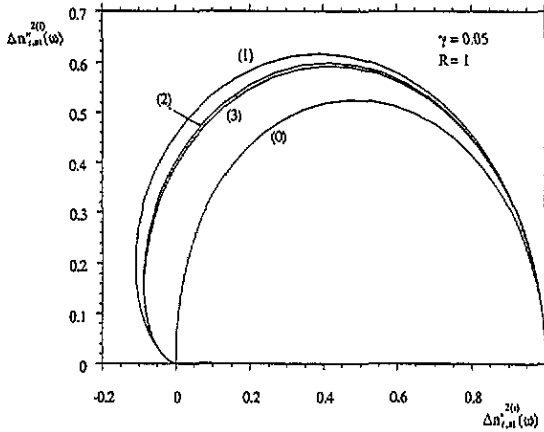


Figure 8. As figure 4, but for the real and imaginary parts of the time-dependent  $2\omega$  frequency term of the steady-state complex Kerr-effect function,  $\Delta n_{r,st}^{2(i)}(\omega)$  and  $\Delta n_{r,st}^{2(r)}(\omega)$ , with  $\gamma = 0.05$  for all convergent approximations.

component), are

$$\Delta n_{r,st}^{0(i)}(\omega) = \frac{\phi_0^{(i)}(\omega)}{\phi_0^{(i)}(0)} = \Delta n_{r,st}^{0(i)}(\omega) - i \Delta n_{r,st}^{0(i)}(\omega) \tag{95}$$

$$\Delta n_{r,st}^{2(i)}(\omega) = \frac{\phi_2^{(i)}(\omega)}{\phi_2^{(i)}(0)} = \Delta n_{r,st}^{2(i)}(\omega) - i \Delta n_{r,st}^{2(i)}(\omega) . \tag{96}$$

Defining the parameter

$$R = \frac{(\alpha_{\parallel} - \alpha_{\perp})kT}{\mu^2} \tag{97}$$

we get, for the above-mentioned first approximation

$$\Delta n_{r,st}^{0(1)}(\omega) = \left( -\frac{2\gamma}{\omega^2 - i\omega' - 2\gamma} + R \right) (1 + R)^{-1} \tag{98}$$

$$\Delta n_{r, st}^{2(1)}(\omega) = \left( \frac{6\gamma^2}{(2\omega^2 - i\omega' - 3\gamma)(\omega^2 - i\omega' - 2\gamma)} - \frac{3R\gamma}{2\omega^2 - i\omega' - 3\gamma} \right) (1 + R)^{-1} \quad (99)$$

Figures 7 and 8 show the influence of the inertial effects on the steady-state Kerr functions. All the responses converge well, except for the first convergent. Moreover, one can see that the modified Smoluchowski equation (curve (1)) overestimates the effects of inertia.

In conclusion, we note that all the continued fraction solutions obtained in this work converge well. Indeed, transforming them by the division of each  $\nu$ th numerator,  $a_\nu$ , by the product of two consecutive  $(\nu - 1)$ th and  $\nu$ th denominators,  $b_{\nu-1}b_\nu$ , the convergence criterion [26, 27]

$$\left| \frac{a_\nu}{b_{\nu-1}b_\nu} \right| \leq \frac{1}{4} \quad (100)$$

can be checked.

The new choice of the generalized Laguerre basis used in this work is imposed by the nature of the uncoupled systems of the differential difference equations deduced from the master equation (equation (8)) in which the formal solution (16) is replaced. Instead of using only the Laguerre polynomials with  $m = 0$ , as in recent works [2, 4], this allows us to give, straightforwardly and more easily, exact analytical expressions for the dielectric and Kerr-effect functions in the case of the rotational Brownian motion of a rigid linear molecule in 3D.

Finally, we would like to point out that any interested reader can obtain on request a more extended version of this paper, including all explicit formulae.

### Appendix

Let us consider the system (51) as an eigenvalue problem where  $s'$  is replaced by  $\lambda_n$ . We then have the matrix equation

$$(H_0 + \sqrt{\gamma}V)\mathcal{X}_n = \lambda_n\mathcal{X}_n \quad (A1)$$

where  $H_0$  is the diagonal matrix and  $V$  is the perturbation term written as

$$H_0 + \sqrt{\gamma}V = \begin{pmatrix} 0 & -\sqrt{2\gamma} & 0 & \dots & 0 & 0 & \dots \\ \sqrt{2\gamma} & -1 & -\sqrt{2\gamma} & \dots & 0 & 0 & \dots \\ 0 & \sqrt{2\gamma} & -2 & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & -\sqrt{2j\gamma} & 0 & \dots \\ 0 & 0 & \dots & \sqrt{2j\gamma} & -2j & -\sqrt{2(j+1)\gamma} & \dots \\ 0 & 0 & \dots & 0 & \sqrt{2(j+1)\gamma} & -(2j+1) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

and where

$$\mathcal{X}_n = \begin{pmatrix} a_0 \\ b_0 \\ a_1 \\ b_1 \\ \dots \\ a_j \\ b_j \\ \dots \end{pmatrix} .$$

The perturbative approach consists in developing

$$\mathcal{X}_n = \mathcal{X}_n^{(0)} + \sqrt{\gamma} \mathcal{X}_n^{(1)} + \gamma \mathcal{X}_n^{(2)} + \dots \tag{A2}$$

$$\lambda_n = \lambda_n^{(0)} + \sqrt{\gamma} \lambda_n^{(1)} + \gamma \lambda_n^{(2)} + \dots . \tag{A3}$$

Substituting the expressions (A2) and (A3) into (A1), and identifying each order in the parameter  $\sqrt{\gamma}$ , we get

$$H_0 \mathcal{X}_n^{(0)} = \lambda_n^{(0)} \mathcal{X}_n^{(0)} \tag{A4}$$

$$H_0 \mathcal{X}_n^{(1)} + V \mathcal{X}_n^{(0)} = \lambda_n^{(0)} \mathcal{X}_n^{(1)} + \lambda_n^{(1)} \mathcal{X}_n^{(0)} \tag{A5}$$

$$H_0 \mathcal{X}_n^{(2)} + V \mathcal{X}_n^{(1)} = \lambda_n^{(0)} \mathcal{X}_n^{(2)} + \lambda_n^{(1)} \mathcal{X}_n^{(1)} + \lambda_n^{(2)} \mathcal{X}_n^{(0)} \tag{A6}$$

$\vdots$

The solution of (A4) for  $n$  even is

$$\mathcal{X}_n^{(0)} = \begin{pmatrix} 0 \\ \dots \\ 0 \\ a_{n/2} = 1 \\ 0 \\ \dots \end{pmatrix}$$

and for  $n$  odd:

$$\mathcal{X}_n^{(0)} = \begin{pmatrix} 0 \\ \dots \\ 0 \\ b_{(n-1)/2} = 1 \\ 0 \\ \dots \end{pmatrix}$$

both with the corresponding eigenvalue

$$\lambda_n^{(0)} = -n . \tag{A7}$$

To solve (A5), we first project at left with the transposed orthonormal solution of order 0,  ${}^t\mathcal{X}_n^{(0)}$  to obtain

$${}^t\mathcal{X}_n^{(0)}(H_0 - \lambda_n^{(0)})\mathcal{X}_n^{(1)} = {}^t\mathcal{X}_n^{(0)}(\lambda_n^{(1)} - V)\mathcal{X}_n^{(0)}. \quad (\text{A8})$$

Because of (A4), equation (A8) becomes

$$\lambda_n^{(1)} = {}^t\mathcal{X}_n^{(0)}V\mathcal{X}_n^{(0)} \quad (\text{A9})$$

and, using (A1), we compute

$$\lambda_n^{(1)} = 0. \quad (\text{A10})$$

Next, projecting (A5) at left with  ${}^t\mathcal{X}_{n'}^{(0)}$  for  $n' \neq n$ , we get, using the orthonormality relations,

$${}^t\mathcal{X}_{n'}^{(0)}H_0\mathcal{X}_n^{(1)} + {}^t\mathcal{X}_{n'}^{(0)}V\mathcal{X}_n^{(0)} = {}^t\mathcal{X}_{n'}^{(0)}\lambda_n^{(0)}\mathcal{X}_n^{(1)}. \quad (\text{A11})$$

Using (A4) and (A7), we deduce

$$(n' - n){}^t\mathcal{X}_{n'}^{(0)}\mathcal{X}_n^{(1)} = {}^t\mathcal{X}_{n'}^{(0)}V\mathcal{X}_n^{(0)} \quad (\text{A12})$$

which allows us to compute

$$\mathcal{X}_n^{(1)} = \sum_{n' \neq n} ({}^t\mathcal{X}_{n'}^{(0)}\mathcal{X}_n^{(1)})\mathcal{X}_n^{(0)} \quad (\text{A13})$$

$$= \sum_{n' \neq n} \frac{{}^t\mathcal{X}_{n'}^{(0)}V\mathcal{X}_n^{(0)}}{(n' - n)}\mathcal{X}_n^{(0)}. \quad (\text{A14})$$

Using (A1), for  $n = 0$  we get

$$\mathcal{X}_0^{(1)} = \sqrt{2}\mathcal{X}_1^{(0)} \quad (\text{A15})$$

for  $n \neq 0$  even

$$\mathcal{X}_n^{(1)} = \sqrt{n+2}\mathcal{X}_{n+1}^{(0)} + \sqrt{n}\mathcal{X}_{n-1}^{(0)} \quad (\text{A16})$$

and for  $n$  odd

$$\mathcal{X}_n^{(1)} = \sqrt{n+1}\mathcal{X}_{n+1}^{(0)} + \sqrt{n+1}\mathcal{X}_{n-1}^{(0)}. \quad (\text{A17})$$

To solve (A6), similarly to (A5) we project at left with  ${}^t\mathcal{X}_n^{(0)}$  to determine  $\lambda_n^{(2)}$ . We get

$$\lambda_n^{(2)} = {}^t\mathcal{X}_n^{(0)}V\mathcal{X}_n^{(1)} \quad (\text{A18})$$

and using expressions (A15)–(A17), for  $n$  even we compute

$$\lambda_n^{(2)} = -2 \quad (\text{A19})$$

and for  $n$  odd

$$\lambda_n^{(2)} = 0. \quad (\text{A20})$$

So, accounting for second order in  $\sqrt{\gamma}$ , for  $n$  even we obtain

$$\lambda_n = -n - 2\gamma + O(\gamma^{3/2}) \quad (\text{A21})$$

and for  $n$  odd

$$\lambda_n = -n + O(\gamma^{3/2}) \quad (\text{A22})$$

with  $B\lambda_n = -(\tau_n)^{-1}$ ,  $\tau_n$  being the characteristic times.

In the particular cases of  $n = 0$  and  $n = 1$  and for  $\gamma \ll 1$ , we recover respectively the Debye and the Rocard characteristic times (equation (89)).

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