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A quantum statistical model of a three-dimensional linear rigid rotator in a bath of oscillators: II. The electrical birefringence in relaxation regime

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Abstract. The Kerr effect relaxation resulting from the sudden removal of a DC field previously applied to a system of dilute rigid linear polar rotators in a sea of non-interacting bath harmonic oscillators is presented. In the quantum mechanical model proposed, we take account of permanent and induced dipole effects while the inertial effect of the bath is described by a collision operator. Hyperpolarizabilities are neglected. We use a generalized master equation governing the evolution of the rotator probability density operator to calculate the Kerr relaxation function $\Phi(t)$. In the search for this function, we define matrix elements $\varphi_{l,l}(t)$ and $\varphi_{l,l+2}(t)$ whose knowledge at all times t , completely gives $\Phi(t)$. We recover the classical limits of the quantum expressions. A quantum result valid for the rotating wave approximation limit is given. This paper is a logical continuation of our recent work.

1. Introduction

The dielectric properties of polar fluids is a field of most research activities in physics, chemistry and technology. In particular, polymer engineers find this domain very fruitful. Through the qualitative and quantitative development of spectral analysis of atmospheric gas composition, the problem of atmospheric pollution and global warming can be tackled. More importantly, the absorption and dispersion of radio waves can be checked, which thus gives the applications in communication.

Two very important dielectric properties, the electrical susceptibility $\chi(t)$ and the Kerr function $\Phi(t)$ [1–5], are the cornerstones of all the above developments.

The response of a dielectric system to the application of an electric field E is the growth of a polarization P . On considering only linear response theory, E and P are in a linear relationship:

$$P(t) = \int_{-\infty}^t \chi(t-t')E(t') dt. \quad (1)$$

The frequency or the spectral function $\chi(\omega)$ called the complex susceptibility is given by [5]:

$$P(\omega) = \chi(\omega)E(\omega) = \left(P(o) - i\omega \int_0^{\infty} e^{-i\omega t} P_{\alpha}(t) dt \right) \quad (2)$$

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where

$$P_\alpha(t) = \langle \mu \cos \beta(t) \rangle. \quad (3)$$

$\beta(t)$ is the angle at time t between the direction of the applied field and the dipole moment vector. $\chi(\omega)$ is a complex function

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (4)$$

with $\chi'(\omega)$ responsible for the dispersive properties of most media while $\chi''(\omega)$, an always positive quantity, is the absorption or the loss factor.

The refractive index tensor \underline{n} undergoes a modification when subjected to a polarizing electric field. This modification depends on the direction of the polarizing field relative to the electric field of the analysing signal. For parallel analysis, the refractive index tensor is $\underline{n}_{\parallel}$ while for perpendicular analysis it is \underline{n}_{\perp} . The Kerr effect is a measure of the difference between these two tensors

$$\Delta \underline{n} = \underline{n}_{\parallel} - \underline{n}_{\perp}. \quad (5)$$

Molecular dynamic studies reveal that \underline{n} is related to the ensemble average of the second-order associated Legendre polynomials in the dipole moment orientation unit vector \underline{u} , $\frac{1}{2}(3u_z^2 - 1)$. We define the Kerr function as [1–3]

$$\Phi(t) = \frac{1}{2} \langle (3u_z^2 - 1) \rangle \quad (6)$$

where the angle brackets $\langle \dots \rangle$ denote ensemble averaging, u_z is the z component of \underline{u} and we assume that the polarizing electric field is parallel to the z -axis of the laboratory frame. The reduced spectral function $\Delta n_r(\omega)$ is obtained from $\Phi(t)$ by using

$$\Delta n_r(\omega) = \frac{1}{\Phi(0)} \left(\Phi(0) - i\omega \int_0^\infty \Phi(t) e^{-i\omega t} dt \right). \quad (7)$$

We consider the rotational motion of a system of rotators embedded in a sea of non-interacting bath oscillators. This problem has been tackled in recent years by many authors [1–3], with all approaches based on classical methods using either the Smoluchowski equation or the generalized Liouville equation also called the Fokker–Planck–Kramer (FPK) equation. In the latter, the molecular orientation distribution function is expanded as a linear combination of the associated Legendre polynomials in $\cos \beta$ [1–3] (where β is the angle between the principal axis of the rotator and the direction of the applied electric field). The coefficients of the respective polynomials are related to the most relevant dielectric properties such as the electrical susceptibility and birefringence or the Kerr effect.

In this paper, we consider the simple case of a quasi-free rotator undergoing intermittent instantaneous collisions with a bath of bosonic oscillators. These collisions lead to heat transfer from the host bath to the rotators. In our model the following assumptions are made.

- (1) The bath oscillator–rotator system is homogeneous.
- (2) The rotator has a needle shape [6], so that the moment of inertia about its longitudinal axis is zero while that measured about a transverse axis passing through the centre is non-zero. The bath effect on the rotator is conceived as a quantum noise described by a collision operator in the considered dynamical equation.
- (3) The rotator–rotator interaction is neglected, as we consider an infinitely dilute solution of rotators in the bath. Thus one rotator can be studied independently of the others.

This paper is organized as follows. In section 2, the master equation governing the evolution of the rotator probability density operator is given; we analyse the stability of the

master equation and energy-balance equations are given. In section 3, master equations are derived for well defined matrix elements; these are solved for different physical conditions leading to the classical Brownian limit and the rotating wave approximation (RWA) limit, respectively. In section 4, we analyse the entropy function evolution from one equilibrium state (in the presence of the electric field) to another (with total field effect vanished or absolute thermal equilibrium). Highlights of the derivation of more relevant equations are presented in the appendices.

2. The theoretical model

Let us consider a symmetric rigid linear rotator, fixed at its centre but free to rotate about the latter [5]. The rotator is in a bath of non-polar mutually non-interacting harmonic oscillators that interact harmonically with one or the other end of the rotator. The centres of mass of the bath oscillators are spatially fixed. So, only the rotational degrees of freedom of the rotator are considered. The rotator possesses a permanent dipole moment susceptible of interacting with an applied electric field. In the quantum treatment, the Hilbert space associated with this model is the tensorial product of the Hilbert space associated with the rotator system H_S and of the bath system H_B [5]:

$$H = H_S \otimes H_B. \quad (8)$$

The system Hamiltonian is the one used in [5].

The electric-field term resulting from the interaction between the permanent dipole (μ) and induced dipole moments and the applied electric field, is found to be:

$$\hat{H}_E(t) = \begin{cases} -\mu E \cos \hat{\beta} - \frac{\alpha_{\parallel} - \alpha_{\perp}}{2} E^2 \cos^2 \hat{\beta} - \frac{\alpha_{\perp}}{2} E^2 \hat{I} & \text{if } t < 0 \\ 0 & \text{if } t \geq 0 \end{cases} \quad (9)$$

where α_{\parallel} and α_{\perp} are, respectively, the rotator polarizability tensor components parallel and perpendicular to the molecular principal axis. We have assumed that the electric field is applied along the z -axis of the laboratory frame. The evolution of the rotator probability density operator is governed by the master equation [5]:

$$\begin{aligned} \frac{\partial \hat{\rho}_S(t)}{\partial t} + \frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(t)] = & -\frac{\zeta}{I} \sum_{l=1}^{\infty} l \{ A_l^* \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}_l^- \hat{\rho}_S(t) - A_l \hat{\mathbf{u}} \cdot \hat{\rho}_S(t) \hat{\mathbf{u}}_l^+ \\ & + B_l \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) - B_l^* \hat{\mathbf{u}} \cdot \hat{\rho}_S(t) \hat{\mathbf{u}}_l^- - A_l^* \hat{\mathbf{u}}_l^- \cdot \hat{\rho}_S(t) \hat{\mathbf{u}} + A_l \hat{\rho}_S(t) \hat{\mathbf{u}}_l^+ \cdot \hat{\mathbf{u}} \\ & + B_l^* \hat{\rho}_S(t) \hat{\mathbf{u}}_l^- \cdot \hat{\mathbf{u}} - B_l \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) \cdot \hat{\mathbf{u}} \} \end{aligned} \quad (10)$$

where

$$A_l = \frac{\omega_D^2}{\omega_D^2 + \omega_L^2} \left(1 + N(\omega_l) + i \left(\kappa(x_l, x_D) - \frac{\omega_l}{2\omega_D} \right) \right) \quad (11)$$

$$B_l = \frac{\omega_D^2}{\omega_D^2 + \omega_l^2} \left(N(\omega_l) + i \left(\kappa(x_l, x_D) + \frac{\omega_l}{2\omega_D} \right) \right) \quad (12)$$

with

$$\kappa(x_l, x_D) = -\left(\frac{1}{x_D} + 2 \sum_{n=1}^{\infty} \frac{x_l^2 - 2\pi x_D n}{(x_l + x_D)(x_l^2 + 4\pi^2 n^2)} \right) \quad (13)$$

and

$$x_j = \beta \hbar \omega_j \quad \beta = \frac{1}{k_B T} \quad n \in \mathbb{Z}^+. \quad (14)$$

We have used the spherical harmonic expansion of the unit vector \hat{u} [5]

$$\hat{u}(t) = \sum_{l=1}^{\infty} (\hat{u}_l^+ + \hat{u}_l^-(t)). \quad (15)$$

A_l^* and B_l^* are the complex conjugates of A_l and B_l , respectively. k_B is the Boltzmann constant, T the absolute temperature, ζ the friction coefficient and $N(\omega_l)$ the occupation number of the rotator quantum level l . The term at the right-hand side of equation (10) is the collision term $\hat{K}\hat{\rho}(t)$. ω_l appearing in the last equation is the angular frequency of the rotator quantum state l . In the absence of the field, this corresponds to the energy:

$$E_l = \frac{\hbar^2}{2I} l(l+1). \quad (16)$$

Equation (10) can now be written as:

$$\frac{\partial \hat{\rho}_S(t)}{\partial t} + \frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(t)] = \hat{K}\hat{\rho}_S(t). \quad (17)$$

The collision operator imposes that the weak coupling limit must be characterized by the inequalities [8] (see also [5]):

$$\frac{\zeta}{I} \ll \frac{k_B T}{\hbar} \quad (18)$$

and

$$\frac{\zeta}{I} \ll \omega_D. \quad (19)$$

It has been shown in [5, 8] that in the case where the first inequality is verified, the coupling effect on the density matrix can be neglected. The classical Brownian and the RWA limits are determined by the value of the mean thermal agitation frequency $\omega_{\text{mean}} = (k_B T/I)^{0.5}$. In the former, ω_{mean} is of the same order of magnitude as the characteristic frequency ζ/I . In this case, the rotator energy is of the same order as the thermal energy, that is, $\hbar^2 l(l+1)/2I \sim k_B T$. Here, we assume that $\omega_D \rightarrow \infty$. The latter limit, corresponding to the RWA limit [7], concerns the weak coupling assumption, $\zeta/I \ll \omega_{\text{mean}}$. In this case we use a theorem by Davies [3, 9, 10] on weak coupling as described in [5].

For equation (17), we consider the field-removal initial condition

$$\hat{\rho}_S(t=0) = \hat{\rho}_S^{\text{eq}}(E \neq 0) = \frac{\text{tr}_B [e^{-\beta(\hat{H}_S + \hat{H}_B + \hat{H}_{SB} + \hat{H}_E)}]}{\text{tr} [e^{-\beta(\hat{H}_S + \hat{H}_B + \hat{H}_{SB} + \hat{H}_E)}]} \quad (20)$$

which corresponds to the canonical equilibrium density operator of the bath-rotator system in the presence of the electric field. On performing a perturbative expansion in $\beta\hat{H}_E$, we obtain (see appendix A)

$$\begin{aligned} \hat{\rho}_S(t=0) &= \frac{e^{-\beta\hat{H}_S}}{\text{tr}_S e^{-\beta\hat{H}_S}} - \frac{\beta}{\text{tr}_S e^{-\beta\hat{H}_S}} \int_0^1 d\alpha e^{-\alpha\beta\hat{H}_S} \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} + \frac{\beta^2}{\text{tr}_S e^{-\beta\hat{H}_S}} \int_0^1 d\alpha \alpha \\ &\quad \times \int_0^1 d\alpha' e^{-(1-\alpha')\alpha\beta\hat{H}_S} \hat{H}_E e^{-\alpha'\alpha\beta\hat{H}_S} \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} + \dots \end{aligned} \quad (21)$$

The symbols tr_S , tr_B and tr denote, respectively, trace norms over the rotator, bath Hilbert spaces and the coupled rotator-bath Hilbert space.

The stability of the master equation (17) can be analysed by assuming its solutions to be of the form

$$\hat{\rho}_S(t) = \hat{\rho}_S^{\text{eq}} \hat{\rho}(t) \quad (22)$$

and defining a Liapounov function as $\text{tr}_S(\hat{\rho}_S^{\text{eq}} \hat{\rho}(t)^2)$. On substituting this solution in the master equation and multiplying both sides of the resulting equation by $\hat{\rho}(t)$ and taking trace we obtain:

$$\begin{aligned} \frac{d}{dt} \sum_{l=0}^{\infty} \sum_{m=-l}^l \rho_{l,l}^{\text{eqm}} \frac{|\rho_{l,l}^m(t)|^2}{2} &= -2B \text{Re} \sum_{l=0}^{\infty} \sum_{m=-l}^l (A_l l^2 + B_{l+1} (l+1)^2) \rho_{l,l}^{\text{eqm}} |\rho_{l,l}^m(t)|^2 \frac{1}{2l+1} \\ &+ 2B \text{Re} \sum_{l=0}^{\infty} \sum_{m=-l}^l A_l \frac{l^2}{2l+1} \rho_{l,l}^{\text{eqm}} |\rho_{l-1,l-1}^m(t)|^2 \\ &+ 2B \text{Re} \sum_{l=0}^{\infty} \sum_{m=-l}^l B_{l+1} \frac{(l+1)^2}{2l+1} \rho_{l,l}^{\text{eqm}} |\rho_{l+1,l+1}^m(t)|^2. \end{aligned} \quad (23)$$

We have assumed that the system is near equilibrium so that all off-diagonal terms in the probability density matrix are neglected. If $\hat{\rho}(t)$ is independent of the rotator variables, $\rho_{l,l}^m(t)$ will be independent of l and m , then the right-hand side of equation (23) equals zero, the expression of the probability density operator is, thus, identically equal to that of the equilibrium distribution with matrix elements $\rho_{l,l}^{\text{eqm}}$. This shows that the positive function to the left of equation (23) decreases exponentially to its equilibrium value when the field is switched off. This ensures the stability of the solutions of equation (17).

In the absence of the field, the energy balance equation is

$$\frac{d}{dt} U = \frac{d}{dt} Q \quad (24)$$

where

$$U(t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \langle l, m | \hat{H}_S \hat{\rho}_S(t) | l, m \rangle. \quad (25)$$

The master equation then gives

$$\frac{d}{dt} Q = 2B[k_B T - U(t)]. \quad (26)$$

In the presence of the field

$$\frac{d}{dt} U = \frac{d}{dt} Q + \frac{d}{dt} W \quad (27)$$

where

$$\frac{d}{dt} W = \frac{d}{dt} \sum_{l=0}^{\infty} \sum_{m=-l}^l \langle l, m | \hat{H}_E \hat{\rho}_S(t) | l, m \rangle. \quad (28)$$

Note that

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l \langle l, m | \hat{H}_E \hat{\rho}_S(t) | l, m \rangle = -E \chi(t) - \frac{\Delta\alpha}{3} E^2 \Phi(t) - \frac{\alpha_{\parallel} + 2\alpha_{\perp}}{6} E^2 \quad (29)$$

where $\chi(t)$ and $\Phi(t)$ are the electric susceptibility and the Kerr effect functions, respectively.

In the case of a DC field, the energy balance becomes

$$\frac{d}{dt} Q = 2B[k_B T - U(t)] - E \frac{d}{dt} \chi(t) - \frac{\Delta\alpha}{3} E^2 \frac{d}{dt} \Phi(t). \quad (30)$$

These results are identical to those previously obtained [8] via the FPK equation. Q is the heat transferred to the rotator from the host bath and the work done by the electric field. In the case where the electric field is applied in the far past and removed at $t = 0$, $\chi(t)$ and

$\Phi(t)$ are exponential decreasing functions of time, decreasing initially rapidly and tending to zero values for large times. Hence, the rate of heat transfer is initially high but reduces to the bath term at the equilibrium state. In the following section we use the established master equation to calculate the Kerr function. Our first paper [5] was devoted to the electrical susceptibility study.

3. The Kerr effect function

3.1. The master equations for the matrix elements

The Kerr effect or the electrical birefringence expresses the modification in the refractive index tensor of a medium as a result of the passage of an electric field through it. For rigid, linear molecules, the refractive index tensor \underline{n} is written as

$$\underline{n} = n\underline{1} + \frac{A}{2} \langle (3\hat{u}\hat{u} - \underline{1}) \rangle \quad (31)$$

where \hat{u} is the molecule orientation unit vector, which here, is the dipole moment orientation unit vector and n is the isotropic refractive index (in the absence of any external stress). A is a constant expressing the intrinsic birefringent properties of the medium. The Kerr function $\Phi(t)$ is related to the component $\langle (3\hat{u}_z\hat{u}_z - \underline{1}) \rangle$ as

$$\Phi(t) = \frac{1}{2} \langle (3\hat{u}_z\hat{u}_z - \underline{1}) \rangle. \quad (32)$$

On using the spherical harmonic representation of the unit vector \hat{u} and the probability density operator $\hat{\rho}_S(t)$ while defining matrix elements

$$\varphi_{l,l}(t) = \sum_{m=-l}^l (l(l+1) - 3m^2) \langle l, m | \hat{\rho}_S(t) | l, m \rangle \quad (33)$$

and

$$\varphi_{l,l+2}(t) = \sum_{m=-l}^l \sqrt{\frac{(l+1-m)(l+1+m)(l+2-m)(l+2+m)}{(2l+1)(2l+3)^2(2l+5)}} \langle l, m | \hat{\rho}_S(t) | l+2, m \rangle \quad (34)$$

we obtain

$$\Phi(t) = \sum_{l=1}^{\infty} \left\{ \frac{1}{(2l-1)(2l+3)} \varphi_{l,l}(t) + \frac{3}{2} (\varphi_{l,l+2}(t) + \varphi_{l,l+2}^*(t)) \right\}. \quad (35)$$

Let us derive the master equations verified by the matrix elements. To get the equation for $\varphi_{l,l}(t)$, we multiply through the master equation (17) from the left by $\sum_{m=-l}^l (l(l+1) - 3m^2) |l, m\rangle \langle l, m|$ and take trace. On using some properties (see appendix C) we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \varphi_{l,l}(t) = & -2B \operatorname{Re} \left[(A_l l^2 + B_{l+1} (l+1)^2) \frac{\varphi_{l,l}(t)}{2l+1} \right. \\ & - A_{l+1} (l+1) \frac{(2l-1)l}{(2l+1)(2l+3)} \varphi_{l+1,l+1}(t) \\ & - B_l l \frac{(l+1)(2l+3)}{(2l+1)(2l-1)} \varphi_{l-1,l-1}(t) (1 - \delta_{l0}) \\ & \left. - 3(B_l l + A_{l+1} (l+1)) \varphi_{l-1,l+1}(t) (1 - \delta_{l0}) \right]. \quad (36) \end{aligned}$$

The initial condition (21), together with some algebra [12], leads to

$$\begin{aligned} \varphi_{l,l}(t=0) = & \frac{e^{-\beta E_l}}{\sum_{l'=0}^{\infty} (2l'+1)e^{-\beta E_{l'}}} \left\{ \frac{l(l+1)(2l+3)}{15} \left[\frac{1}{2} \beta \Delta \alpha E^2 \right. \right. \\ & + \frac{\beta^2 \mu^2 E^2}{\beta(E_l - E_{l-1})} \left. \left. \left\{ \frac{1}{\beta(E_l - E_{l-1})} (e^{\beta(E_l - E_{l-1})} - 1) - 1 \right\} \right] \right\} \\ & + \frac{1}{15} l(l+1)(2l-1) \left[\frac{1}{2} \beta \Delta \alpha E^2 \right. \\ & \left. \left. + \frac{\beta^2 \mu^2 E^2}{\beta(E_{l+1} - E_l)} \left\{ 1 - \frac{1}{\beta(E_{l+1} - E_l)} (1 - e^{-\beta(E_{l+1} - E_l)}) \right\} \right] \right\}. \end{aligned} \quad (37)$$

To get the equation verified by $\varphi_{l,l+2}(t)$, we multiply through equation (17) from the right by $\hat{u}_{l+2z}^+ \hat{u}_{l+1z}^+$ and take trace. The use of similar properties as in equation (36) yields

$$\begin{aligned} \frac{\partial}{\partial t} \varphi_{l,l+2}(t) - \frac{i\hbar}{I} (2l+3) \varphi_{l,l+2}(t) = & -B \left[\left\{ (A_l^* l^2 + B_{l+1}(l+1)^2) \frac{1}{2l+1} \right. \right. \\ & + (A_{l+2}(l+2)^2 + B_{l+3}^*(l+3)^2) \frac{1}{2l+5} \left. \left. \right\} \varphi_{l,l+2}(t) \right. \\ & - \frac{l+2}{2l+3} (B_l^* l + B_{l+2}(l+2)) \varphi_{l-1,l+1}(t) (1 - \delta_{l0}) \\ & - \frac{l+1}{2l+3} (A_{l+1}^*(l+1) + A_{l+3}(l+3)) \varphi_{l+1,l+3}(t) \\ & \left. - 2 \frac{(A_{l+1}(l+1) + B_{l+2}^*(l+2))}{(2l+1)(2l+3)^2(2l+5)} \varphi_{l+1,l+1}(t) \right]. \end{aligned} \quad (38)$$

The initial condition on $\varphi_{l,l+2}(t)$ is

$$\begin{aligned} \varphi_{l,l+2}(t=0) = & \frac{e^{-\beta E_l}}{\sum_{l'=0}^{\infty} (2l'+1)e^{-\beta E_{l'}}} \frac{2(l+1)(l+2)}{15(2l+3)} \\ & \times \left[\frac{1}{2\beta(E_{l+2} - E_l)} (1 - e^{\beta(E_{l+2} - E_l)}) \Delta \alpha \beta E^2 \right. \\ & + \frac{\beta^2 \mu^2 E^2}{\beta(E_{l+1} - E_l)} \left\{ \frac{1}{\beta(E_{l+2} - E_l)} (1 - e^{-\beta(E_{l+2} - E_l)}) \right. \\ & \left. \left. - \frac{1}{\beta(E_{l+2} - E_{l+1})} (e^{-\beta(E_{l+1} - E_l)} - e^{-\beta(E_{l+2} - E_l)}) \right\} \right]. \end{aligned} \quad (39)$$

In equations (36) and (38) $B = \zeta/I$. The exact expression for $\Phi(t)$ can be obtained if equations (36) and (38) are exactly solved using initial conditions (37) and (39). This quantum approach generalizes all results obtained using classical and semiclassical methods [1–3]. Let us now consider the case of the classical Brownian limit.

3.2. The classical Brownian limit

The classical Brownian limit is characterized by the inequalities [5]:

$$a = \frac{\hbar^2}{Ik_B T} \ll 1 \quad \text{and} \quad \frac{\omega_{\text{mean}}}{\omega_D} \ll 1 \quad (40)$$

which express the idea that the rotators perform slow random rotational motions compared with thermal motions and the fact that the thermal agitation frequencies will hardly ever attain the upper limit which corresponds to the Debye limit. Also, the rotator energy

spectrum is regularly continuous. Though the quantum number l can assume large values, the quantity $al = (\hbar^2/Ik_B T)l$ is considered to be always very small compared to 1. We perform changes of functions

$$\varphi_{l,l}(t) = \frac{a}{2}l(l+1)(2l+1) \exp\left[-\frac{\hbar^2}{2Ik_B T}l(l+1)\right] \psi_l(t) \quad (41)$$

$$\varphi_{l,l+2}(t) = \frac{a}{2} \frac{(l+1)(l+2)}{2l+3} \exp\left[-\frac{\hbar^2}{2Ik_B T}l(l+1)\right] (\varphi_l + i(2l+3)\chi_l(t)) \quad (42)$$

while using the continuum hypothesis:

$$\frac{a}{2}l(l+1) \rightarrow x \quad (43)$$

and letting $\psi(x, t)$, $\varphi(x, t)$ and $\chi(x, t)$ be the continuum analogues of the discrete functions $\psi_l(t)$, $\varphi_l(t)$ and $\chi_l(t)$, equations (36) and (38) reduce to second-order coupled partial differential equations.

On using the passage from the discrete to the continuous sum

$$\sum_{l=1}^{\infty} U_l(t) \rightarrow \frac{1}{\sqrt{2a}} \int_0^{\infty} \frac{dx}{\sqrt{x}} U(x, t) \quad (44)$$

we obtain the expression for the Kerr function

$$\Phi(t) = \frac{1}{4} \int_0^{\infty} dx e^{-x} (\psi(x, t) + 3\varphi(x, t)). \quad (45)$$

Let

$$F(x, t) = \psi(x, t) + 3\varphi(x, t) \quad (46)$$

then for dimensionless time $\tau = Bt$, the differential equations become:

$$\frac{\partial}{\partial \tau} F(x, \tau) + 3\alpha x \chi(x, \tau) = 2[xF_{xx}(x, \tau) + (1-x)F_x(x, \tau)] \quad (47)$$

$$\frac{\partial}{\partial \tau} \chi(x, \tau) - \frac{\lambda}{3}(F(x, \tau) - \psi(x, \tau)) = 2[x\chi_{xx}(x, \tau) + (2-x)\chi_x(x, \tau) - \frac{1}{2}\chi(x, \tau)] \quad (48)$$

$$\frac{\partial}{\partial \tau} \psi(x, \tau) = 2 \left[x\psi_{xx}(x, \tau) + (1-x)\psi_x(x, \tau) - \frac{1}{x}\psi(x, \tau) + \frac{1}{4x}F(x, t) \right] \quad (49)$$

$$F(x, 0) = \frac{4E^2}{15} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right) = 4\Phi_{\text{static}} \quad (50)$$

$$\alpha = \frac{8\hbar}{IaB} \quad \text{and} \quad \lambda = \frac{\hbar}{IB}. \quad (51)$$

In matrix form

$$\underline{D}_{\tau,x} \underline{M}(\tau, x) = \underline{0} \quad (52)$$

$$\underline{M}(\tau, x) = \begin{pmatrix} F(\tau, x) \\ \chi(\tau, x) \\ \psi(\tau, x) \end{pmatrix} \quad (53)$$

$$\underline{D}_{\tau,x} = \begin{pmatrix} \frac{\partial}{\partial \tau} - 2[x\frac{\partial^2}{\partial x^2} + (1-x)\frac{\partial}{\partial x}] & 3\alpha x & 0 \\ -\frac{\lambda}{3} & \frac{\partial}{\partial \tau} - 2[x\frac{\partial^2}{\partial x^2} + (2-x)\frac{\partial}{\partial x} - \frac{1}{2}] & 0 \\ 0 & 0 & \frac{\partial}{\partial \tau} - 2[x\frac{\partial^2}{\partial x^2} + (1-x)\frac{\partial}{\partial x}] + \frac{2}{x} \end{pmatrix}. \quad (54)$$

$$\underline{M}(x, 0) = \Phi_{\text{static}} \begin{pmatrix} 4 \\ 0 \\ 1 \end{pmatrix}. \tag{55}$$

The spatial parts of the diagonal terms in the differential operator $\underline{D}_{\tau,x}$ are related to the differential operator whose eigenfunctions are nothing but the generalized Laguerre polynomials $L_j^m(x)$ that verify the following properties [2, 13]:

$$\left(x \frac{d^2}{dx^2} + (m + 1 - x) \frac{d}{dx} + j \right) L_j^m(x) = 0 \tag{56}$$

$$xL_j^{m+1}(x) = (m + j + 1)L_j^m(x) - (j + 1)L_{j+1}^m(x) \tag{57}$$

$$L_j^m(x) = L_j^{m+1}(x) - L_{j-1}^{m+1}(x) \tag{58}$$

$$\left(x \frac{d}{dx} - x + m \right) L_j^m(x) = (j + 1)L_{j+1}^{m-1}(x) \tag{59}$$

$$\left(\frac{d}{dx} - 1 \right) L_j^m(x) = -L_j^{m+1}(x). \tag{60}$$

The orthogonality property of the $L_j^m(x)$ is written as

$$\int_0^\infty dx e^{-x} x^m L_j^m(x) L_{j'}^m(x) = \delta_{jj'}. \tag{61}$$

We, thus, look for solutions to the system (52) in the form

$$\underline{M}(x, \tau) = \sum_{j=0}^\infty \begin{pmatrix} f_j(\tau) L_j^0(x) \\ c_j(\tau) L_j^1(x) \\ d_j(\tau) L_j^0(x) \end{pmatrix}. \tag{62}$$

On using this in the system (47)–(49) while making use of the properties (56)–(60), we obtain the differential difference equations:

$$\left(\frac{d}{d\tau} + 2j \right) f_j(\tau) + 3\alpha((j + 1)c_j(\tau) - jc_{j-1}(\tau)) = 0 \tag{63}$$

$$\left(\frac{d}{d\tau} + 2j + 1 \right) c_j(\tau) - \frac{\lambda}{3}(f_j(\tau) - f_{j+1}(\tau)) + \frac{\lambda}{3}(d_j(\tau) - d_{j+1}(\tau)) = 0 \tag{64}$$

$$2(2j + 1) \left(\frac{d}{d\tau} + 2j \right) d_j(\tau) + 4d_j(\tau) - 2j \left(\frac{d}{d\tau} + 2j - 2 \right) d_{j-1}(\tau) - 2(j + 1) \left(\frac{d}{d\tau} + 2j + 2 \right) d_{j+1}(\tau) - f_j(\tau) = 0. \tag{65}$$

The Kerr function becomes,

$$\Phi(\tau) = \frac{1}{4} f_0(\tau). \tag{66}$$

On taking the Laplace transforms of (63)–(65) and searching for $f_0(s')$ (where $s = s'B$ is the Laplace variable) as a continued fraction [14], we obtain the Kerr function

$$\tilde{\Phi}(s') = \frac{\frac{E^2}{15B} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right)}{s' + \frac{6\gamma}{s' + 1 + \frac{10\gamma}{s' + 2 + \frac{16\gamma}{s' + 3 - \frac{4\gamma}{(s' + 2)(s' + 4)} + \frac{16\gamma}{s' + 4 + \frac{24\gamma}{s' + 5 - \frac{4\gamma}{(s' + 4)(s' + 6)} + \frac{24\gamma}{s' + 6 + \dots}}}}}} \tag{67}$$

where $\gamma = \alpha\lambda/8 = (Ik_B T/\zeta^2)$.

The continued fraction (67), as the exact expression of the Kerr relaxation function in the classical limit obtained from the generalized quantum equations (36), (38), is analogous to the result previously obtained by Hounkonnou *et al* [2], and generalizes all approximate solutions published in the literature. All the higher-order solutions of the Kerr effect relaxation obtained, for example, by Kalmykov *et al* [1] are simply some approximations of the successive convergents, up to the third order, of (67). These are well characterized in [2].

Let us define

$$\Delta n_r(s') = B\tilde{\Phi}(s') / \left[\frac{E^2}{15} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right) \right]. \quad (68)$$

The characteristic times $\tau^{(i)}$, corresponding to the i th convergent of (67), can be calculated using:

$$\tau^{(i)} = \frac{1}{B} \Delta n_r^{(i)}(0). \quad (69)$$

Note that on replacing s' by $i\omega'$ ($\omega' = \omega/B$) in the *zeroth* convergent to get the frequency picture, we obtain

$$\Delta n_r^{(0)}(\omega) = \frac{B\tau_{D2}}{1 + i\omega\tau_{D2}}. \quad (70)$$

This is the rotational diffusion limit [1, 2, 15], with relaxation time

$$\tau^{(0)} = \tau_{D2} \equiv \frac{\zeta}{6k_B T}. \quad (71)$$

The first convergent,

$$\Delta n_r^{(1)}(\omega) = (i\omega + B)\tau_{D2} / \left[1 + i\omega\tau_{D2} - \left(\frac{I\omega^2}{6k_B T} \right) \right] \quad (72)$$

gives the same characteristic time as that obtained for $\Delta n_r^{(0)}(\omega)$. The second convergent gives

$$\tau^{(2)} = (1 + 5\gamma)\tau_{D2}. \quad (73)$$

This result coincides precisely with those obtained by Kalmykov *et al* [1], Hounkonnou *et al* [2] and Burshtein and Temkin [16]. The third convergent gives

$$\tau^{(3)} = (1 + 5\gamma - \frac{40}{3}\gamma^2)\tau_{D2}. \quad (74)$$

For small γ , that is equivalent to small inertia and/or large friction, $\tau^{(3)} \rightarrow \tau^{(2)}$.

A more relevant form for the quantity $\Delta n_r(\omega)$ is its representation in the complex space $\Delta n_r(\omega) = \Delta n_r'(\omega) - i\Delta n_r''(\omega)$. The real part is related to the dispersion factor while the imaginary part accounts for absorption.

Figure 1 shows the frequency dependence of the real parts of the first three convergents of $\Delta n_r(\omega)$. Note that all curves tend asymptotically to zero. Figure 2 shows the evolution of the loss factor $\Delta n_r''(\omega)$.

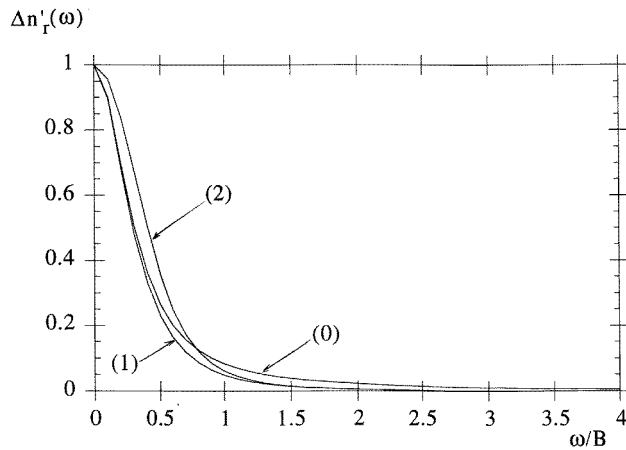


Figure 1. Normalized dispersion coefficient $\Delta n'_r(\omega)$ plots against the reduced frequency ω/B for the Debye diffusion limit (0), the first (1) and the second (2) convergents in the classical Brownian limit for $\gamma = 0.05$.

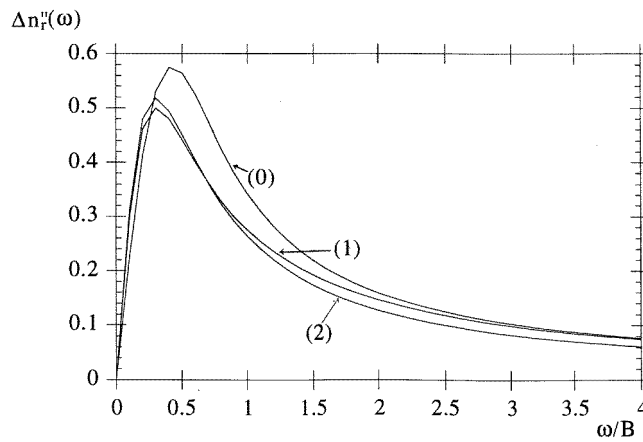


Figure 2. Normalized loss factor $\Delta n''_r(\omega)$ plots against the reduced frequency ω/B for the Debye diffusion limit (0), the first (1) and the second (2) convergents in the classical Brownian limit for $\gamma = 0.05$.

3.3. The rotating wave approximation

With the replacement of \hat{K} by (\hat{K}^\flat) for weak coupling [5], we can neglect all off-diagonal terms in equations (36) and (38). We assume that ω_D is very large compared to both ω_l and ω_{mean} though the latter may attain relatively high values. All terms like $\varphi_{l\pm 1, l\pm 1}$, $\varphi_{l\pm 1, l+2\pm 1}$ and all coupling terms are ignored in the master equations which now read:

$$\left(\frac{\partial}{\partial t} + \Gamma_l\right) \varphi_{l,l}(t) = 0 \tag{75}$$

and

$$\left[\frac{\partial}{\partial t} - i\left(\frac{\hbar}{I}(2l+3) + \Delta\omega_{l+2}\right) + \Gamma_{l+2}\right] \varphi_{l,l+2}(t) = 0 \tag{76}$$

where the positive half widths Γ and the frequency shifts $\Delta\omega$ for $\omega_l/\omega_D \rightarrow 0$ are:

$$\Gamma_l = 2B[l^2(1 + N(\omega_l)) + (l + 1)^2 N(\omega_{l+1})] \frac{1}{2l + 1} \quad (77)$$

$$\Gamma_{l+2} = B \left[l^2(1 + N(\omega_l)) \frac{1}{2l + 1} + (l + 1)^2 N(\omega_{l+1}) \frac{1}{2l + 1} + (l + 2)^2(1 + N(\omega_{l+2})) \frac{1}{2l + 5} + (l + 3)^2 N(\omega_{l+3}) \frac{1}{2l + 5} \right] \quad (78)$$

and

$$\Delta\omega_{l+2} = -2Ba^2(2l + 3) \sum_{n=1}^{\infty} \frac{(2\pi n)^5}{[(2\pi n)^2 + a^2 l^2][(2\pi n)^2 + a^2(l + 1)^2]} \times \frac{1}{[(2\pi n)^2 + a^2(l + 2)^2][(2\pi n)^2 + a^2(l + 3)^2]} \left\{ 1 + \frac{a^2}{(2\pi n)^2} (l^2 + 3l + 3) \right\}. \quad (79)$$

It is important to remark here that equation (75) describes the time relaxation of the diagonal elements of the quantum canonical probability density matrix element. This equation shows that under weak coupling the system remains close to the electric-field imposed equilibrium for a relatively long time since each of its quantum states has a relaxation time which is inversely proportional to the friction coefficient ($\tau_{\text{rel}} \propto 1/\Gamma_l$). From the expression of Γ_l it is obvious that high-energy states relax faster than low-energy ones. Observed relaxation will therefore be accounted for by low-energy states. The non diagonal matrix elements relax in a similar manner but are accompanied by oscillations with frequencies that correspond to the $l \rightarrow l + 2$ rotational transitions.

Equations (75) and (76) have solutions

$$\varphi_{l,l}(t) = \frac{E^2}{15} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right) l(l + 1)(2l + 1) \exp \left[-\frac{\hbar^2}{2Ik_B T} l(l + 1) \right] \times \frac{1}{\sum_{l'=0}^{\infty} (2l' + 1) \exp \left[\frac{-\hbar^2}{2Ik_B T} l'(l' + 1) \right]} \exp(-\Gamma_l t) \quad (80)$$

$$\varphi_{l,l+2}(t) = \frac{E^2}{15} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right) \frac{(l + 1)(l + 2)}{(2l + 3) \sum_{l'=0}^{\infty} (2l' + 1) \exp \left[-\frac{\hbar^2}{2Ik_B T} l'(l' + 1) \right]} \times \exp \left[-\frac{\hbar^2}{2Ik_B T} l(l + 1) \right] \exp \left[-\Gamma_{l+2} t + i \left(\frac{\hbar}{I} (2l + 3) + \Delta\omega_{l+2} \right) t \right]. \quad (81)$$

On substituting these into equation (35) and taking the one-sided Fourier transform,

$$\tilde{\Phi}(\omega) = \int_0^{\infty} dt e^{-i\omega t} \Phi(t) \quad (82)$$

we get the frequency picture of the Kerr function

$$\tilde{\Phi}(\omega) = \tilde{\Phi}'(\omega) - i\tilde{\Phi}''(\omega) \quad (83)$$

where

$$\tilde{\Phi}'(\omega') = \frac{\frac{E^2}{15B} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right)}{\sum_{l'=0}^{\infty} (2l' + 1) \exp \left[-\frac{\hbar^2}{Ik_B T} l'(l' + 1) \right]} \sum_{l=0}^{\infty} \frac{(l + 1) \exp \left[-\frac{\hbar^2}{Ik_B T} l(l + 1) \right]}{2l + 3} \times \left\{ \frac{l(2l + 1)}{2l - 1} \frac{G_l}{\omega'^2 + G_l^2} + \frac{3}{2} (l + 2) M_l \left(\frac{1}{M_l^2 + (\omega' - \frac{\hbar}{IB} (2l + 3) - W_l)^2} \right) \right\}$$

$$\left. + \frac{1}{M_l^2 + (\omega' + \frac{\hbar}{IB}(2l+3) + W_l)^2} \right\} \quad (84)$$

and

$$\begin{aligned} \tilde{\Phi}''(\omega') = & \frac{\frac{E^2}{15B} \left(\frac{\Delta\alpha}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right)}{\sum_{l'=0}^{\infty} (2l'+1) \exp[-\frac{\hbar^2}{Ik_B T} l'(l'+1)]} \sum_{l=0}^{\infty} \frac{(l+1) \exp[-\frac{\hbar^2}{Ik_B T} l(l+1)]}{2l+3} \\ & \times \left\{ \frac{l(2l+1)}{2l-1} \frac{\omega'}{\omega^2 + G_l^2} + \frac{3}{2}(l+2) \left(\frac{\omega' - \frac{\hbar}{IB}(2l+3) - W_l}{M_l^2 + (\omega' - \frac{\hbar}{IB}(2l+3) - W_l)^2} \right. \right. \\ & \left. \left. + \frac{\omega' + \frac{\hbar}{IB}(2l+3) + W_l}{M_l^2 + (\omega' + \frac{\hbar}{IB}(2l+3) + W_l)^2} \right) \right\} \quad (85) \end{aligned}$$

with $\omega' = \omega/B$, $G_l = \Gamma_l/B$, $M_l = \Gamma_{l+2}/B$ and $W_l = \Delta\omega_{l+2}/B$.

The spectral function $\Delta n_r(\omega)$ is deduced from equation (7) as:

$$\Delta n_r(\omega) = \Delta n_r'(\omega') - i\Delta n_r''(\omega') \quad (86)$$

where

$$\begin{aligned} \Delta n_r'(\omega') = & \frac{\hbar^2}{2Ik_B T} \sum_{l=0}^{\infty} \frac{(l+1) \exp[-\frac{\hbar^2}{Ik_B T} l(l+1)]}{2l+3} \left\{ \frac{l(2l+1)}{2l-1} \frac{\omega^2}{\omega^2 + G_l^2} \right. \\ & + \frac{3}{2}(l+2) \left(2 + \frac{\omega'(\omega' - \frac{\hbar}{IB}(2l+3) - W_l)}{M_l^2 + (\omega' - \frac{\hbar}{IB}(2l+3) - W_l)^2} \right. \\ & \left. \left. + \frac{\omega'(\omega' + \frac{\hbar}{IB}(2l+3) + W_l)}{M_l^2 + (\omega' + \frac{\hbar}{IB}(2l+3) + W_l)^2} \right) \right\} \quad (87) \end{aligned}$$

and

$$\begin{aligned} \Delta n_r''(\omega') = & \frac{\hbar^2}{2Ik_B T} \sum_{l=0}^{\infty} \frac{(l+1) \exp[-\frac{\hbar^2}{Ik_B T} l(l+1)]}{2l+3} \left\{ \frac{l(2l+1)}{2l-1} \frac{G_l \omega'}{\omega^2 + G_l^2} \right. \\ & + \frac{3}{2}(l+2) \left(\frac{M_l \omega'}{M_l^2 + (\omega' - \frac{\hbar}{IB}(2l+3) - W_l)^2} \right. \\ & \left. \left. + \frac{M_l \omega'}{M_l^2 + (\omega' + \frac{\hbar}{IB}(2l+3) + W_l)^2} \right) \right\}. \quad (88) \end{aligned}$$

We have described a model Hamiltonian of a system of polar linear rigid rotators in a bath of non polar harmonic oscillators. Quantal equations are given for well defined matrix elements that have been used to calculate the Kerr function. We have recovered the classical Brownian limit developed by many workers [1–3]. A quantal expression for the Kerr function (equation (83)) which is valid for weak coupling (Van Hove limit) [17, 18], has been given. It is the Van Vleck Weisskopf line form for the Kerr function obtained via a mathematical theorem by Davies [9] for the master equation in the interaction picture. In this limit, we ignore all ‘off-diagonal’ terms in the equations governing the evolution of the matrix elements. Neilsen and Gordon [19] concluded from their impact calculations on rotational line broadening of HCl by argon, that off-diagonal elements of the σ -matrix have little influence on the spectral shape for low densities (densities lower than 1500 amagats).

The exact Kerr effect corresponding to the classical Brownian limit is given by the continued fraction in equation (67). The convergence of this fraction is governed by the parameter $\gamma = (Ik_B T/\zeta^2)$. This convergence is assured for small γ , that is, for small

inertia and/or large friction. The different convergents of equation (67) can, therefore, only be applicable to light rotators in dense-bath media. This means that collisions between the rotators and the bath oscillators are frequent and we observe continuous absorption/dispersion spectra as seen in figures 1 and 2. The relaxation time, being the time over which an initial polarization decays in a zero field, must increase with increasing collision frequencies since collisions hinder the drift motion of dipoles which is the agency causing changes in polarization. The characteristic frequency $B = \zeta/I$, is an increasing function of density and pressure [20] of the host bath. It depends also on the rotator. For rotators with characteristics comparable with those of the bath, collisions are likely to involve large exchanges of energies, for example, of the order of $k_B T$.

For large inertia and/or small friction, equation (67) becomes unsuitable for the analysis of the Kerr effect relaxation. For weak coupling (small ζ), we expect that collisions be less frequent and that the system becomes strongly uncorrelated. This should lead to absorption/dispersion spectra characterized by well defined line shapes.

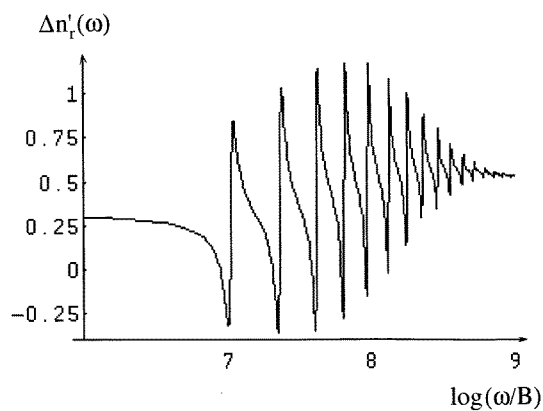


Figure 3. Normalized dispersion lineform $\Delta n'_r(\omega)$ against the Neperian logarithm of the reduced frequency $\ln(\omega/B)$ in the van Hove limit for $B/\omega_{\text{mean}} = 0.001$, and $\hbar^2/(Ik_B T) = 0.05$.

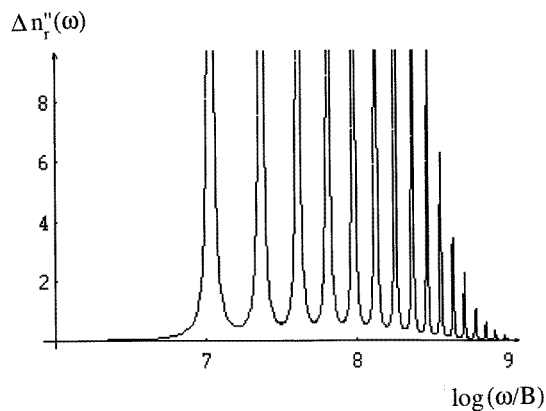


Figure 4. Normalized absorption (loss factor) lineform $\Delta n''_r(\omega)$ against the Neperian logarithm of the reduced frequency $\ln(\omega/B)$ in the van Hove limit for $B/\omega_{\text{mean}} = 0.001$, and $\hbar^2/(Ik_B T) = 0.05$.

Figures 3 and 4 show the frequency dependence of the real and the imaginary parts of the quantity $\Delta n_r(\omega)$, respectively. These curves are obtained for the particular values of the parameters $a = (\hbar^2/Ik_B T) = 0.05$ and $B/(k_B T/I)^{0.5} = 0.001$. All these curves qualitatively well reproduce the absorption and dispersion behaviours of fluids exhibiting quantum effects as depicted by experiments [21]. The latter portray absorption/dispersion resonance lines at well defined frequencies. For large frequencies ($\nu > 10^{14}$ Hz), as seen on the graphs, all resonance phenomena disappear giving rise to zero absorption, whereas dispersion tends asymptotically to a constant non-zero value. For low frequencies ($\nu < 10^{11}$ Hz), resonances are absent but start appearing for frequencies above 10^{11} Hz and become populous in the range 10^{11} Hz $< \nu < 10^{14}$ Hz. We can note that the classical limit gives only one of these absorption lines and that the resonances observed are largely due to low-energy rotators ($l < 10$). It is also important to note that the particular values affixed to the parameters of the model are those of HCl at temperatures between 150 K and 300 K. Frenkel [21] experimented that for HCl (0.06 amagat) at about 180 K in Xe (1.05 amagat), absorption lines appear in the range $10 \text{ cm}^{-1} \leq 1/\lambda \leq 300 \text{ cm}^{-1}$. Our approach gives practically the same range with identical line positions.

These results confirm all deductions made using a similar approach on the electrical susceptibility in [5]. Our results and those of the latter paper are, thus, in good agreement with experimental results [19, 21]. The coherency between the theory and the experiments acts as a stimulant to further investigations of quantum effects on dielectric properties of polar fluids in non-polar thermalized media.

4. Entropy function calculation

We now proceed to analyse the evolution of the entropy from when the system is in equilibrium in the presence of the field until the thermal equilibrium in the absence of the field is attained. In this analysis, we consider that the external electric field is so weak that the system is not far from the thermal equilibrium state. We, therefore, suppose $\hat{\rho}_S(t)$ to be of the form [22]:

$$\hat{\rho}_S(t) = \hat{\rho}_{S\infty}^{\text{eq}}(\hat{I} + \hat{g}(t)) \quad (89)$$

where $\hat{\rho}_{S\infty}^{\text{eq}}$ is the thermal equilibrium probability density operator in zero field conditions. The Boltzmann entropy formula,

$$S(t) = -k_B \langle \hat{\rho}_S(t) \ln \hat{\rho}_S(t) \rangle \quad (90)$$

yields, to first order in $\hat{g}(t)$,

$$S(t) = S_\infty + k_B \sum_l (\beta E_l - 1 + \ln Z_\infty) G_{l,l}(t) \quad (91)$$

where

$$S_\infty = -k_B \sum_l \sum_{m=-l}^l \langle l, m | \hat{\rho}_{S\infty}^{\text{eq}} \ln \hat{\rho}_{S\infty}^{\text{eq}} | l, m \rangle = k_B \left(1 + \ln \left(\frac{2Ik_B T}{\hbar^2} \right) \right) \quad (92)$$

$$G_{l,l}(t) = \sum_{m=-l}^l \langle l, m | \hat{\rho}_{S\infty}^{\text{eq}} \hat{g}(t) | l, m \rangle = \sum_{m=-l}^l \rho_{l,l}^{\text{eq}} g_{l,l}^m(t) \quad (93)$$

and the partition function, Z_∞ is

$$Z_\infty = \sum_l \sum_{m=-l}^l \langle l, m | \exp -\beta \hat{H}_S | l, m \rangle = \frac{2Ik_B T}{\hbar^2}. \quad (94)$$

The density operator $\hat{\rho}_S(t)$ must obey the master equation (17), in particular $\hat{\rho}_{S\infty}^{\text{eq}}$ verifies it since it is an asymptotic solution. $\hat{\rho}_{S\infty}^{\text{eq}}\hat{g}(t)$ is governed by the equation

$$\hat{\rho}_{S\infty}^{\text{eq}}\frac{\partial}{\partial t}\hat{g}(t) = \hat{K}(\hat{\rho}_{S\infty}^{\text{eq}}\hat{g}(t)). \quad (95)$$

On multiplying through this by $\sum_{m=-l}^l |l, m\rangle\langle l, m|$ and taking trace, we obtain

$$\begin{aligned} \frac{\partial}{\partial t}G_{l,l}(t) = -2B \operatorname{Re} \left[(A_l l^2 + B_{l+1}(l+1)^2) \frac{G_{l,l}(t)}{2l+1} - A_{l+1} \frac{(l+1)^2}{2l+3} G_{l+1,l+1}(t) \right. \\ \left. - B_l \frac{l^2}{2l-1} G_{l-1,l-1}(t)(1 - \delta_{l0}) \right]. \end{aligned} \quad (96)$$

It is easily seen from equation (21) that the initial condition on $G_{l,l}(t)$ is

$$G_{l,l}(t=0) = \frac{\hbar^2}{36Ik_B T} \left(\frac{\mu E}{k_B T} \right)^2 \frac{e^{-\beta E_l}}{Z_\infty} (2l+1)(\beta E_l - 1). \quad (97)$$

The entropy, therefore, relaxes from the initial equilibrium value

$$S(0) = k_B \left[1 + \ln \left(\frac{2Ik_B T}{\hbar^2} \right) + \frac{\hbar^2}{36Ik_B T} \left(\frac{\mu E}{k_B T} \right)^2 \right]. \quad (98)$$

We perform the change of function

$$G_{l,l}(t) = \frac{\hbar^2}{36Ik_B T} \left(\frac{\mu E}{k_B T} \right)^2 \frac{e^{-\beta E_l}}{Z_\infty} (2l+1)Y_l(t). \quad (99)$$

where $Y_l(t)$ has the initial condition $Y_l(0) = \beta E_l - 1$. Then, the continuum approximations lead to (where $Y(x, \tau)$ is the continuum analogue of $Y_l(\tau)$),

$$\frac{\partial}{\partial \tau} Y(x, \tau) = 2[xY_{xx}(x, \tau) + (1-x)Y_x(x, \tau) + \frac{1}{2}Y(x, \tau)]. \quad (100)$$

Solutions are sought for as a linear combination of the Laguerre polynomials

$$Y(x, \tau) = \sum_{j=0}^{\infty} y_j(\tau)L_j(x). \quad (101)$$

The initial condition on $G_l(t)$ leads to

$$Y(x, \tau) = y_1(\tau)L_1(x) \quad (102)$$

with $y_1(t) = -e^{-Bt}$. We recover the expression for the entropy

$$S(t) = k_B \left[1 + \ln \left(\frac{2Ik_B T}{\hbar^2} \right) + \frac{\hbar^2}{36Ik_B T} \left(\frac{\mu E}{k_B T} \right)^2 e^{-Bt} \right]. \quad (103)$$

Note that the equilibrium state in the presence of the external field is more stable than that in its absence. This could be predicted, since an external electric field will favour statistical reorientation of dipole moments in its direction, thus increasing the order in the whole system.

Acknowledgments

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Appendix A. The initial condition on $\hat{\rho}_S(t)$

$$\hat{\rho}_S(t=0) = \frac{1}{\text{tr}_S \text{tr}_B e^{-\beta(\hat{H}+\hat{H}_E)}} \text{tr}_B e^{-\beta(\hat{H}+\hat{H}_E)}. \quad (104)$$

Let

$$\hat{Y}(\beta) = e^{-\beta(\hat{H}+\hat{H}_E)} \quad (105)$$

then,

$$\frac{d}{d\beta} \hat{Y}(\beta) = -\hat{Y}(\beta)\hat{H} - \hat{Y}(\beta)\hat{H}_E \quad (106)$$

with solution

$$\hat{Y}(\beta) = \hat{A}(\beta)e^{-\beta\hat{H}} \quad (107)$$

and

$$\hat{A}(\beta) = 1 - \int_0^1 d\alpha \hat{Y}(\alpha\beta)\beta\hat{H}_E e^{-\alpha\beta\hat{H}}. \quad (108)$$

After performing similar expansion for $e^{-\beta\hat{H}} = e^{-\beta(\hat{H}_0+\hat{H}_{SB})}$, for small $\beta\hat{H}_{SB}$ and taking trace over bath variables ($\hat{H}_0 = \hat{H}_S + \hat{H}_B$), we obtain, to second order in $\beta\hat{H}_E$ that:

$$\begin{aligned} \hat{\rho}_S(t=0) &= \frac{e^{-\beta\hat{H}_S}}{\text{tr}_S e^{-\beta\hat{H}_S}} - \frac{\beta}{\text{tr}_S e^{-\beta\hat{H}_S}} \int_0^1 d\alpha e^{-\alpha\beta\hat{H}_S} \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} + \frac{\beta^2}{\text{tr}_S e^{-\beta\hat{H}_S}} \int_0^1 d\alpha \alpha \\ &\quad \times \int_0^1 d\alpha' e^{-(1-\alpha')\alpha\beta\hat{H}_S} \hat{H}_E e^{-\alpha'\alpha\beta\hat{H}_S} \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} + \dots \end{aligned} \quad (109)$$

Appendix B. The initial condition on $\varphi_{l,l}(t)$

$$\varphi_{l,l}(t=0) = \sum_{l=-m}^l (l(l+1) - 3m^2) \langle l, m | \hat{\rho}_S(t=0) | l, m \rangle. \quad (110)$$

On using the properties

$$(a) \langle l, m | e^{-\alpha\beta\hat{H}_S} \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} | l, m \rangle = e^{-\beta E_l} \langle l, m | \beta \hat{H}_E | l, m \rangle \quad (111)$$

and

$$\begin{aligned} (b) \langle l, m | e^{-(1-\alpha')\alpha\beta\hat{H}_S} \beta \hat{H}_E e^{-\alpha\alpha'\beta\hat{H}_S} \beta \hat{H}_E e^{-(1-\alpha)\beta\hat{H}_S} | l, m \rangle \\ = e^{-\beta E_l} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} e^{-\alpha\alpha'\beta(E_{l'}-E_l)} |\langle l, m | \beta \hat{H}_E | l', m' \rangle|^2 \end{aligned} \quad (112)$$

we obtain

$$\begin{aligned} \varphi_{l,l}(t=0) &= \frac{1}{\sum_{l'=0}^{\infty} (2l'+1) e^{-\beta E_{l'}}} \sum_{m=-l}^l (l(l+1) - 3m^2) \\ &\quad \times e^{\beta E_l} \left[1 + \frac{\beta\alpha_{\perp}}{2} E^2 + \langle l, m | \cos^2 \beta | l, m \rangle \frac{\beta\Delta\alpha}{2} E^2 \right. \\ &\quad \left. + \beta^2 \mu^2 E^2 \sum_{l''=0}^{\infty} \sum_{m''=-l''}^{l''} |\langle l, m | \cos \beta | l'', m'' \rangle|^2 \int_0^1 d\alpha \alpha \int_0^1 d\alpha' e^{-\alpha\alpha'\beta(E_{l''}-E_l)} \right]. \end{aligned} \quad (113)$$

This leads to the required expression when the expansion for $\cos \beta$ and the expression for \hat{H}_E (equation (9)) are used.

Appendix C. Proof of the property

$$\sum_{m=-l}^l (l(l+1) - 3m^2) \langle l, m | \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) \hat{\mathbf{u}}_{l+1}^+ | l, m \rangle = -3\varphi_{l-1,l+1}(t)(1 - \delta_{l,0}).$$

On using the spherical harmonic expansion for $\hat{\mathbf{u}}$, we get

$$\begin{aligned} & \sum_{m=-l}^l (l(l+1) - 3m^2) \langle l, m | \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) \hat{\mathbf{u}}_{l+1}^+ | l, m \rangle \\ &= \frac{1}{2} \sum_{m=-l}^l \sum_{m'=-l}^l \sum_{m''=-l+1}^{l+1} (l(l+1) - 3m^2) (-A(l, m') B(l+1, m'')) \\ & \quad \times \hat{\rho}_{l-1,l+1}^{m'+1}(t) \delta_{m,m'} \delta_{m''+1,m} - B(l, m') A(l+1, m'') \hat{\rho}_{l-1,l+1}^{m'-1}(t) \delta_{m,m'} \delta_{m''-1,m} \\ & \quad + 2C(l, m) C(l+1, m) \hat{\rho}_{l-1,l+1}^m(t) \delta_{m,m'} \delta_{m'',m} (1 - \delta_{l,0}) \\ &= -3 \sum_{m=-(l-1)}^{l-1} \left[\frac{(l-1-m)(l-1+m)(l+1-m)(l+1+m)}{(2l-1)(2l+1)^2(2l+3)} \right]^{\frac{1}{2}} \\ & \quad \times \hat{\rho}_{l-1,l+1}^m(t) (1 - \delta_{l,0}) \\ &= -3\varphi_{l-1,l+1}(t)(1 - \delta_{l,0}) \end{aligned} \tag{114}$$

where

$$A(l, m) = \sqrt{\frac{(l-m)(l-m-1)}{(2l-1)(2l+1)}}$$

$$B(l, m) = \sqrt{\frac{(l+m)(l+m-1)}{(2l-1)(2l+1)}}$$

and

$$C(l, m) = \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}.$$

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