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Dielectric relaxation in polar nematic liquid crystals

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The relationship between the complex dielectric permittivity tensor of a polar nematic liquid crystal and the autocorrelation matrix for the permanent dipole moment of a molecule is obtained. The theory is applicable to the whole frequency range which characterizes orientational relaxation in liquid crystals (up to ~5 THz). The models of rotational diffusion and extended rotational diffusion in a mean field nematic potential are used to evaluate the dielectric absorption and dispersion in nematics.

1. Introduction

Dielectric/far infrared (0–THz) spectroscopy is one of the techniques available to probe molecular reorientations in liquid crystals [1, 2]. However, as for isotropic polar dielectrics, the amount of information about molecular reorientation depends, in principle, on the level of development of the molecular dielectric relaxation theory.

In recent years the molecular theory of dielectric relaxation in highly polar isotropic liquid dielectrics has been developing. The important aspect of this is that the theory has taken into account intermolecular correlations explicitly (e.g. [3–7]). On this basis molecular models which account for intermolecular correlations between dipolar molecules (rotational diffusion [3, 7], three-variable theory [1, 3, 4], etc.) have been elaborated. The theory for nematic liquid crystals [1, 2, 5] is not so advanced. In some cases radio/far infrared dielectric spectra of liquid crystals have been analysed in the framework of models of molecular reorientations in isotropic liquids [8, 9]. However, such models are not able to explain the anisotropic properties of liquid crystal dielectric parameters. On the other hand there are a few molecular models of molecular reorientation in anisotropic dielectrics which are based on the rotational diffusion equation [10–14]. Unfortunately, these models are only applicable to the low frequency limit [1]. In addition, in many cases intermolecular interactions between dipolar molecules are not taken into account; this is strictly valid only for dilute solutions of polar molecules in non-polar solvents.

In the present paper we elaborate a molecular theory of dielectric relaxation in polar nematic liquid crystals in the framework of another approach [5, 15]. This approach, based on the memory function formalism [16], allows us to relate the complex dielectric permittivity tensor

$$\varepsilon_{ij}^*(\omega)=\varepsilon_{ij}'(\omega)+i\varepsilon_{ij}''(\omega),$$

to the molecular dipole autocorrelation matrix taking into account intermolecular correlations between dipolar molecules via equilibrium correlation orientation parameters.

To evaluate the components of the molecular dipole autocorrelation matrix two models are used. These are the rotational diffusion and extended rotational diffusion in a mean field potential. (We use the word extended since the model in question may be considered as a generalization of the well-known extended diffusion (J-diffusion) model developed by Gordon [1].) In the mean field approximation it is assumed that every molecule interacts with a static potential U. In spite of its limited sphere of applicability, the mean field approximation has clear physical interpretation and allows us to make quantitative estimates of liquid crystal dielectric parameters. The rotational diffusion model is only applicable to the low frequency range ($\omega\tau_\gamma^N < 1$, where τ_γ^N is the macroscopic orientational relaxation time). The model of extended rotational diffusion in a mean field potential [17, 18] is an example of a model which may be used in the high frequency range (up to ~5 THz) as well. We examine a particular case of this model applying to liquid crystals, viz., the extended rotational diffusion in the Maier–Saupe potential [19]

$$U(\theta) = -U_0 \cos^2\theta,$$

where U_0 is a constant and θ is the polar angle made by the molecule with the director. Note that the rotational diffusion in the Maier–Saupe potential is considered in [10, 13, 19].

In § 2 the general formula for the complex dielectric permittivity tensor $\varepsilon_{ij}^*(\omega)$ is presented. In § 3 the relationship between $\varepsilon_{ij}^*(\omega)$ and the tensor molecular dipole correlation function is obtained. Section 4 contains a discussion of the model of rotational diffusion in a mean field potential. The extended rotational diffusion model in the Maier–Saupe potential is considered in § 5 where an analytical solution is given for the anisotropic case.

2. Dielectric spectra and correlation functions

With respect to a laboratory coordinate system (x, y, z) in which the director $\mathbf{n}$ defines the z direction, the dielectric permittivity tensor $\varepsilon_{ij}^*(\omega)$ is diagonal and has only two independent components, viz., $\varepsilon_\parallel^*(\omega) = \varepsilon_{zz}^*(\omega)$ and $\varepsilon_\perp^*(\omega) = \varepsilon_{xx}^*(\omega) = \varepsilon_{yy}^*(\omega)$. Other components equal zero. In the zero wavevector limit, the components of the complex dielectric permittivity tensor

$$\varepsilon_\gamma^*(\omega) = \varepsilon_\gamma'(\omega) + i\varepsilon_\gamma''(\omega),$$

of a polar nematic liquid crystal are given by [1, 20]

$$\varepsilon_\gamma^*(\omega) - (n_\infty^\gamma)^2 = \frac{4\pi R_\gamma(\omega)}{kT}\left[\phi_\gamma^N(0) + i\omega \int_0^\infty \phi_\gamma^N(t) \exp(i\omega t)\,dt\right], \quad \gamma = \parallel, \perp, \tag{1}$$

where

$$\phi_\gamma^N(t) = \langle M_\gamma(0) M_\gamma(t)\rangle, \quad (\gamma = \parallel, \perp),$$

are the macroscopic autocorrelation functions of the parallel and perpendicular components of the dipole moment per unit volume $\mathbf{M}$, the brackets $\langle\ \rangle$ indicate an equilibrium ensemble average, n_∞^γ is the infrared refractive index and $R_\gamma(\omega)$ is the internal field factor connecting the local and applied electric fields. The dipole moment $\mathbf{M}$ of an ensemble of N interacting dipolar molecules is defined as

$$\mathbf{M}(t) = \sum_{i=1}^{N} \boldsymbol{\mu}_i(t),$$

where $\boldsymbol{\mu}$ is the dipole moment vector of the ith molecule. Hence

$$\phi_\gamma^N(t)=\left\langle \sum_{i,j=1}^{N} \mu_i^\gamma(0)\mu_j^\gamma(t) \right\rangle, \quad (\gamma=\parallel, \perp). \tag{2}$$

For the model of an ellipsoidal cavity surrounded by an infinite dielectric continuum with the same complex permittivity tensor $\varepsilon_\gamma^*(\omega)$ the internal field factor $R_\gamma(\omega)$ is given by [20]

$$R_\gamma(\omega)=\varepsilon_\gamma^*(\omega)/\{\varepsilon_\gamma^*(\omega)-\sigma_\gamma(\omega)[\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2]\}, \tag{3}$$

where $\sigma_\gamma(\omega)$ are the components of the depolarization tensor which are defined as

$$\sigma_\gamma(\omega)=\frac{a_x a_y a_z}{2[\varepsilon_{xx}^*(\omega)\varepsilon_{yy}^*(\omega)\varepsilon_{zz}^*(\omega)]^{1/2}}\int_0^\infty \frac{ds}{[s+a_\gamma^2/\varepsilon_\gamma^*(\omega)]D(s)},$$

with

$$D(s)^2=[s+a_x^2/\varepsilon_{xx}^*(\omega)][s+a_y^2/\varepsilon_{yy}^*(\omega)][s+a_z^2/\varepsilon_{zz}^*(\omega)];$$

a_i are the semi-axes of the ellipsoidal cavity. Another equation for $R_\gamma(\omega)$ may be obtained from equation (28) of [20] but only by making the unrealistic assumption that the permittivity tensor $\varepsilon_\gamma^*(\omega)$ for the material surrounding the cavity is frequency independent and equal to the static tensor $\varepsilon_\gamma^*(0)$ [20]. In this case we have

$$R_\gamma(\omega)=\frac{\varepsilon_\gamma^*(0)-\sigma_\gamma(0)[\varepsilon_\gamma^*(0)-\varepsilon_\gamma^*(\omega)]}{\varepsilon_\gamma^*(0)-\sigma_\gamma(0)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]}. \tag{4}$$

According to these equations even when the macroscopic autocorrelation functions are known it is still not possible to calculate the complex permittivity because the depolarization tensor depends on the sample cavity dimensions which are arbitrary. This dependence on the geometry of the sample is an unsatisfactory feature of the analysis but one which also occurs for isotropic media [20]. However, as pointed out in [20] it does not present a major problem in the case under consideration when the cavity contains many molecules for then its shape is immaterial and it is expedient to choose a spherical sample since the depolarization tensor is independent of its size.

Edwards and Madden [14] have criticized the approach of calculating the permittivity tensor based on equation (1) from the point of view that when the cavity concept is used in a theory it is very difficult to see how dipole–dipole correlations can be used systematically to relate the frequency dependence of the permittivity to reorientations of single molecules. In [14] they have generalized for the anisotropic case the Sullivan and Deutch theory [6] of dielectric relaxation in isotropic polar media. In this theory neither a cavity nor an internal field factor are used explicitly. However, as we shall show the theory of Edwards and Madden predicts actually the same result as given by equation (1) for the internal field factor $R_\gamma(\omega)$ defined by equation (4) with $(n_\infty^\gamma)^2=1$ (in [14] a system of non-polarizable molecules was considered). In the present paper results will be given in the form which is consistent with both approaches.

Note that only low frequency (relaxational) molecular processes are displayed clearly in the frequency dependence of $\varepsilon_\gamma^*(\omega)$, whereas it is very difficult to obtain high frequency behaviour of liquid crystals. In the high frequency region it is more suitable to analyse the absorption coefficient [1]

$$\begin{aligned}\alpha_\gamma(\omega) &= 2\frac{\omega}{c}\,\mathrm{Im}\,\{\sqrt{[\varepsilon^*_\gamma(\omega)]}\},\\ &= \frac{\omega\varepsilon''_\gamma(\omega)}{cn_\gamma(\omega)},\end{aligned} \tag{5}$$

where

$$\begin{aligned}n_\gamma(\omega) &= \mathrm{Re}\,\{\sqrt{[\varepsilon^*_\gamma(\omega)]}\},\\ &= \sqrt{\left(\frac{\sqrt{[\varepsilon'^2_\gamma(\omega)+\varepsilon''^2_\gamma(\omega)]}+\varepsilon'_\gamma(\omega)}{2}\right)},\end{aligned}$$

is the refractive index and c is the speed of light.

3. Relationship between $\varepsilon^*_\gamma(\omega)$ and the molecular dipole correlation function

For any correlation function

$$\phi_A(t) = \langle A(0)A(t)\rangle,$$

of a dynamic variable $A(t)$, the function $\phi^N_\gamma(t)$ obeys the equation [16]

$$\frac{d}{dt}\phi^N_\gamma(t) = -\int_0^t K^N_\gamma(t-t')\phi^N_\gamma(t')dt', \quad (\gamma = \|, \perp), \tag{6}$$

where

$$K^N_\gamma(t) = \frac{\langle \dot{M}_\gamma(0)|\hat{Q}_\gamma \exp(-i\hat{Q}_\gamma\hat{L}\hat{Q}_\gamma t)\hat{Q}_\gamma|\dot{M}_\gamma(0)\rangle}{\langle M_\gamma(0)|M_\gamma(0)\rangle}, \tag{7}$$

is the memory function of the correlation function $\phi^N_\gamma(t)$

$$M_\gamma(0) = \sum_{i=1}^{N} \mu^\gamma_i(0), \quad \dot{M}_\gamma(0) = \frac{d}{dt}M_\gamma(t)|_{t=0},$$

$\hat{L}$ is the Liouville operator

$$|M_\gamma(t)\rangle = \exp(-iLt)|M_\gamma(0)\rangle, \quad \hat{Q}_\gamma = \hat{1} - \hat{P}_\gamma,$$

and

$$\hat{P}_\gamma = |M_\gamma(0)\rangle\langle M_\gamma(0)|M_\gamma(0)\rangle^{-1}\langle M_\gamma(0)|,$$

is the projection operator which effects the variables A and B according to the rule

$$\langle A|\hat{P}_\gamma|B\rangle = \langle A|M_\gamma(0)\rangle\langle M_\gamma(0)|M_\gamma(0)\rangle^{-1}\langle M_\gamma(0)|B\rangle,$$

where $\langle A|B\rangle$ denotes the scalar product of the two vectors $\langle A|$ and $|B\rangle$ in the Hilbert space of dynamic variables and $\langle A|B\rangle \equiv \langle AB\rangle$ by definition [16].

The one sided Fourier transform of equation (6) yields

$$\tilde{\phi}^N_\gamma(\omega) = \phi^N_\gamma(0)/[-i\omega + \tilde{K}^N_\gamma(\omega)], \tag{8}$$

where

$$\begin{Bmatrix}\tilde{K}^N_\gamma(\omega)\\ \tilde{\phi}^N_\gamma(\omega)\end{Bmatrix} = \int_0^\infty \begin{Bmatrix}K^N_\gamma(t)\\ \phi^N_\gamma(t)\end{Bmatrix}\exp(i\omega t)\,dt.$$

Substituting this equation into equation (1) we obtain

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{R_\gamma(\omega)}=\frac{4\pi\phi_\gamma^N(0)}{kT[1-i\omega/\tilde{K}_\gamma^N(\omega)]}. \tag{9}$$

This equation yields the relationship between components of the complex permittivity $\varepsilon_\gamma^*(\omega)$ and memory function spectrum $\hat{K}_\gamma^N(\omega)$ tensor. As shown in Appendix A equation (9) with $R_\gamma(\omega)$ defined by equation (4) can be simplified to

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2}=\frac{1}{1-i\omega s_\gamma(\omega)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]}, \tag{10}$$

where

$$s_\gamma(\omega)=\frac{kT}{4\pi\phi_\gamma^N(0)\tilde{K}_\gamma^N(\omega)}.$$

For non-polarizable molecules (i.e. $n_\infty^\gamma=1$) this equation coincides with that predicted by the theory of Edwards and Madden [14].

The memory function $K_\gamma^N(t)$ has the structure of the correlation function of the variable $\dot{M}_\gamma(t)$, however there are some differences. Namely, only the part of $\dot{M}_\gamma(0)$ orthogonal to $M_\gamma(0)$, viz. $\hat{Q}_\gamma|\dot{M}_\gamma(0)\rangle$, enters into the definition of the memory function $K_\gamma^N(t)$ (see equation (9)). In addition, the dynamic operator $\hat{Q}_\gamma\hat{L}\hat{Q}_\gamma$ is the projection of the Liouville operator $\hat{L}$ corresponding to the fluctuations of $M_\gamma(0)$. Since slow fluctuations of M_γ are excluded from the dynamic operator $\hat{Q}_\gamma\hat{L}\hat{Q}_\gamma$ which determines the relaxation of the memory function $K_\gamma^N(t)$, the latter decays very rapidly compared to $\phi_\gamma^N(t)$ [16].

Since $\langle M_\gamma(0)\dot{M}_\gamma(0)\rangle=0$ [16] and

$$\frac{d}{dt}\boldsymbol{\mu}_i(t)=[\boldsymbol{\Omega}_i(t)\times\boldsymbol{\mu}_i(t)], \tag{11}$$

where $\boldsymbol{\Omega}_i(t)$ is the angular velocity of ith molecule, it can be shown that the memory functions $K_\parallel^N(t)$ and $K_\perp^N(t)$ are represented as the sums of the terms

$$C_{ij}^\parallel(t)=C^\parallel\langle[\boldsymbol{\Omega}_i(0)\times\boldsymbol{\mu}_i(0)]_\parallel[\boldsymbol{\Omega}_j(t_\mathrm{p})\times\boldsymbol{\mu}_j(t_\mathrm{p})]_\parallel\rangle, \tag{12}$$

$$C_{ij}^\perp(t)=C^\perp\langle[\boldsymbol{\Omega}_i(0)\times\boldsymbol{\mu}_i(0)]_\perp[\boldsymbol{\Omega}_j(t_\mathrm{p})\times\boldsymbol{\mu}_j(t_\mathrm{p})]_\perp\rangle, \tag{13}$$

respectively, where $C^\parallel$ and $C^\perp$ are constants, the subscript p on the time variable t indicates the projected time dependence specified by the relation [3]

$$|A(t_\mathrm{p})\rangle=\exp(-i\hat{Q}_\gamma\hat{L}\hat{Q}_\gamma t)|A(0)\rangle.$$

Since the dynamic angular velocity correlations of different molecules are absent at $t=0$ at equilibrium, i.e. $\langle\Omega_{mi}(0)\Omega_{mj}(0)\rangle=0$ if $i\neq j$ $(m=x,y,z)$, the contribution of terms $C_{ij}^\gamma(t)$ with $i\neq j$ to the memory function $\tilde{K}_\gamma^N(t)$ is probably much smaller than that of terms with $i=j$ at an arbitrary time t. It is frequently argued that dynamic angular velocity correlations between different molecules may be ignored in isotropic liquids (e.g. [21, 22]). Experimental evidence that these correlations between different molecules in liquid crystals are small has been given by light scattering experiments [23]. Gierke and Flygare [23] have shown that the dynamic angular velocity correlations are very small for second rank properties. However, since they give the sufficient condition we assume that dynamic correlations are also small for first rank properties. This assumption can also be justified theoretically for isotropic dielectrics [3].

Thus, neglecting the dynamic angular velocity correlations in equation (9) and taking into consideration that slow fluctuations of M_γ are excluded from the dynamic operator $\hat{Q}_\gamma \hat{L} \hat{Q}_\gamma$, we obtain from the exact equations (6) and (7) the following approximate equations for the macroscopic correlation function $\phi_\gamma^N(t)$ and the memory function $K_\gamma^N(t)$

$$\frac{d}{dt}\phi_\gamma^N(t) = -g_\gamma^{-1}\int_0^t K_\gamma^s(t-t')\phi_\gamma^N(t')\,dt', \tag{14}$$

and

$$K_\gamma^N(t) = g_\gamma^{-1} K_\gamma^s(t). \tag{15}$$

Here $K_\gamma^s(t)$ is the memory function of the normalized molecular dipole correlation function

$$C_\gamma(t) = \langle \mu_i^\gamma(0)\mu_i^\gamma(t)\rangle / \langle \mu_i^\gamma(0)^2\rangle,$$

the memory function $K_\gamma^s(t)$ is also defined by equation (7) where the macroscopic moment M_γ is everywhere changed to the molecular dipole moment μ_i^γ

$$g_\gamma = \left\langle \sum_{i,j=1}^{N} \mu_i^\gamma(0)\mu_j^\gamma(0) \right\rangle \Big/ \left\langle \sum_{i=1}^{N} \mu_i^\gamma(0)^2 \right\rangle, \tag{16}$$

is the static equilibrium orientational correlation factor (an analogue of the Kirkwood g factor in isotropic liquids) characterizing the intermolecular interactions and the local structure of a liquid crystal.

The functions $C_\gamma(t)$ and $K_\gamma^s(t)$ and their one sided Fourier transforms $\tilde{C}_\gamma(\omega)$ and $\tilde{K}_\gamma^s(\omega)$ are related by equations which are analogous to equations (6) and (8)

$$\frac{d}{dt}C_\gamma(t) = -\int_0^t K_\gamma^s(t-t')C_\gamma(t')\,dt', \tag{17}$$

and

$$\tilde{C}_\gamma(\omega) = 1/[-i\omega + \tilde{K}_\gamma^s(\omega)]. \tag{18}$$

One sided Fourier transformation of equation (14) and combination of the result obtained with equations (8) and (18) gives

$$\tilde{\phi}_\gamma^N(\omega) = \frac{\phi_\gamma^N(0) g_\gamma \tilde{C}_\gamma(\omega)}{1 + i\omega(1-g_\gamma)\tilde{C}_\gamma(\omega)}. \tag{19}$$

Since

$$\phi_\gamma^N(0) = g_\gamma \langle \mu_i^\gamma(0)^2\rangle N,$$

we can obtain from equations (1) and (19) that

$$\frac{\varepsilon_\gamma^*(\omega) - (n_\infty^\gamma)^2}{R_\gamma(\omega)} = \frac{G_\gamma g_\gamma[1 + i\omega\tilde{C}_\gamma(\omega)]}{1 + i\omega(1-g_\gamma)\tilde{C}_\gamma(\omega)}, \tag{20}$$

where

$$G_\gamma = 4\pi g_\gamma \langle \mu_i^\gamma(0)^2\rangle N/kT.$$

For a rod-like molecule $\langle \mu_i^\gamma(0)^2\rangle$ are equal to [19]

$$\left.\begin{aligned} \langle \mu_i^{\parallel}(0)^2\rangle &= \mu^2[1-(1-3\cos^2\beta)S]/3, \\ \langle \mu_i^{\perp}(0)^2\rangle &= \mu^2[1+(1-3\cos^2\beta)S/2]/3, \end{aligned}\right\} \tag{21}$$

where μ is the dipole moment of the molecule, $S=(3\langle\cos^2\theta\rangle-1)/2$ is the usual order parameter, β and θ are the angles between the molecular axis and vectors $\boldsymbol{\mu}_i$ and $\mathbf{n}$ respectively. The dipole moment μ may be estimated from [19]

$$\mu=\mu_0[(\bar{n}_\infty)^2+2]/3,$$

where μ_0 is the gas phase dipole moment and

$$(\bar{n}_\infty)^2=(n_\infty^{\parallel 2}+2n_\infty^{\perp 2})/3.$$

(The electric field induced moment caused by time dependent collisional motions is assumed to be much smaller than the permanent moment).

In the low ω limit (i.e. $\omega=0$) equation (20) coincides precisely with the Kirkwood–Fröhlich equation for the anisotropic case [19]

$$\frac{[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]\{\varepsilon_\gamma^*(0)-\sigma_\gamma(0)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]\}}{\varepsilon_\gamma^*(0)(\bar{n}_\infty^2+2)^2}=\frac{4\pi\langle\mu_i^\gamma(0)^2\rangle g_\gamma N}{9kT}. \tag{22}$$

In the limit of high frequencies, i.e. $\omega\to\infty$, when $\tilde{C}_\gamma(\omega)$ is expanded as [16]

$$\tilde{C}_\gamma(\omega)=\frac{i}{\omega}-\frac{i\langle\mu_i^\gamma(0)\ddot{\mu}_i^\gamma(0)\rangle}{\langle\mu_i^\gamma(0)^2\rangle\omega^3}+\mathrm{O}(\omega^{-5}),$$

and the internal field factor $R(\omega)$ tends to unity, equation (20) becomes

$$\varepsilon_\gamma^*(\omega)=(n_\infty^\gamma)^2+\frac{4\pi N\langle\mu_i^\gamma(0)\ddot{\mu}_i^\gamma(0)\rangle}{kT\omega^2}+\mathrm{O}(\omega^{-4}). \tag{23}$$

Thus, in this limit the dielectric permittivity $\varepsilon_\gamma^*(\omega)$ does not depend on the correlation parameter g_γ.

From equation (23) and one of the Kramers–Kronig relations

$$\varepsilon_\gamma'(\omega)-(n_\infty^\gamma)^2=\frac{2}{\pi}\int_0^\infty\frac{\omega'\varepsilon_\gamma''(\omega')}{\omega'^2-\omega^2}\,d\omega',$$

which leads to the following high frequency asymptotic expansion

$$\varepsilon_\gamma'(\omega)=(n_\infty^\gamma)^2-\frac{2}{\pi\omega^2}\int_0^\infty\omega'\varepsilon_\gamma''(\omega')\,d\omega'+\mathrm{O}(\omega^{-4}),$$

we obtain the sum rules

$$\int_0^\infty\omega\varepsilon_\gamma''(\omega)\,d\omega=-\frac{2\pi^2N\langle\mu_i^\gamma(0)\ddot{\mu}_i^\gamma(0)\rangle}{kT}, \tag{24}$$

and

$$\int_0^\infty\omega\tfrac{1}{3}[\varepsilon_{xx}''(\omega)+\varepsilon_{yy}''(\omega)+\varepsilon_{zz}''(\omega)]\,d\omega=-\frac{2\pi^2N\langle\boldsymbol{\mu}_i(0)\cdot\ddot{\boldsymbol{\mu}}_i(0)\rangle}{kT}. \tag{25}$$

The average $\langle\boldsymbol{\mu}_i(0)\cdot\ddot{\boldsymbol{\mu}}_i(0)\rangle$ in this equation may now be evaluated by differentiating the motion equation (11) and taking into account the known equation of rigid body rotation

$$\hat{I}\frac{d}{dt}\boldsymbol{\Omega}_i(t)=\mathbf{N}_i(t), \tag{26}$$

where $\hat{I}$ is the inertia tensor and $\mathbf{N}_i(t)$ is the torque acting on the ith molecule. We find

$$\frac{d^2}{dt^2}\boldsymbol{\mu}_i(t)+\Omega_i^2(t)\boldsymbol{\mu}_i(t)-\boldsymbol{\Omega}_i(t)(\boldsymbol{\mu}_i(t)\boldsymbol{\Omega}_i(t))$$

$$=\hat{I}^{-1}[\mu^2\mathbf{N}_i(t)-\boldsymbol{\mu}_i(t)(\boldsymbol{\mu}_i(t)\mathbf{N}_i(t))]. \tag{27}$$

Thus

$$\langle\boldsymbol{\mu}_i(0)\ddot{\boldsymbol{\mu}}_i(0)\rangle=-\mu^2\langle\Omega_i^2(0)\rangle+\langle(\boldsymbol{\mu}_i(0)\boldsymbol{\Omega}_i(0))^2\rangle. \tag{28}$$

Equation (20) can be used to evaluate the dielectric permittivity spectra $\varepsilon_\gamma^*(\omega)$ in the 0–THz frequency range provided the molecular correlation function spectra $\tilde{C}_\gamma(\omega)$ and correlation factors g_γ are known. Unfortunately, exact calculations of the spectra $\tilde{C}_\gamma(\omega)$ and g_γ factors are very difficult tasks and can be carried out only for model systems by computer simulation (since the computer simulation method allows us to calculate the spectra $\tilde{C}_\gamma(\omega)$ and $\tilde{\phi}_\gamma^N(\omega)$ and the factors g_γ independently it would be interesting to make use of computer experiments in order to test the validity of equation (19)). However, in order to evaluate the spectra $\varepsilon_\gamma^*(\omega)$ we can estimate the values of g_γ from the Kirkwood–Fröhlich equation (22) and make use of experimental spectra $\tilde{C}_\gamma(\omega)$ obtained from infrared rotation/vibration absorption spectra. Furthermore, we may hope that models of molecular reorientation which give simple spectra $\tilde{C}_\gamma(\omega)$ will prove to be applicable to semiquantitative evaluations of spectra $\varepsilon_\gamma^*(\omega)$.

As a first example let us consider the well-known rotational diffusion model in a mean field potential.

4. Rotational diffusion in a mean field potential

For known versions of this model (e.g. [10–13]) the molecular dipole correlation functions $C_\gamma(t)$ and their spectra $\tilde{C}_\gamma(\omega)$ may be written as

$$C_\gamma(t)=\sum_{n=1}^{N_\gamma}a_n^\gamma\exp(-t/\tau_n^\gamma), \tag{29}$$

and

$$\tilde{C}_\gamma(\omega)=\sum_{n=1}^{N_\gamma}a_n^\gamma\tau_n^\gamma/(1-i\omega\tau_n^\gamma), \tag{30}$$

where τ_n^γ are the relaxation times

$$\sum_{n=1}^{N_\gamma}a_n^\gamma=1,\quad N_\gamma\geqslant 1,$$

(the values of $N_\parallel$ and $N_\perp$ depend on the shape of the mean field potential). Substitution of this equation into (19) yields

$$\tilde{\phi}_\gamma^N(\omega)=\frac{\phi_\gamma^N(0)g_\gamma\sum_{n=1}^{N_\gamma}a_n^\gamma\tau_n^\gamma\prod_{k(k\neq n)}^{N_\gamma}(1-i\omega\tau_k^\gamma)}{\prod_{n=1}^{N_\gamma}(1-i\omega\tau_n^\gamma)+i\omega(1-g_\gamma)\sum_{n=1}^{N_\gamma}a_n^\gamma\tau_n^\gamma\prod_{k(k\neq n)}^{N_\gamma}(1-i\omega\tau_k^\gamma)}. \tag{31}$$

Decomposing the right hand side of this equation into simple fractions, we find

$$\tilde{\phi}_\gamma^N(\omega)=\phi_\gamma^N(0)\sum_{n=1}^{N_\gamma}b_n^\gamma\tau_n'^\gamma/(1-i\omega\tau_n'^\gamma), \tag{32}$$

or in the time domain

$$\phi_\gamma^N(t)=\phi_\gamma^N(0)\sum_{n=1}^{N_\gamma} b_n^\gamma \exp(-t/\tau_n'^\gamma),$$

where $(\tau_n'^\gamma)^{-1}$ are the roots of the following equation of degree N_γ

$$P_{N_\gamma}(x)=\prod_{n=1}^{N_\gamma}[(\tau_n^\gamma)^{-1}-x]+x(1-g_\gamma)\sum_{n=1}^{N_\gamma} a_n^\gamma \prod_{k(k\neq n)}^{N_\gamma}[(\tau_k^\gamma)^{-1}-x]=0, \tag{33}$$

the coefficients b_n^γ are functions of g_γ, a_m^γ and $\tau_m^\gamma(m=1\ldots N_\gamma)$ and satisfy the condition

$$\sum_{n=1}^{N_\gamma} b_n^\gamma=1.$$

Inserting this equation into equation (20) we obtain

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{R_\gamma(\omega)}=G_\gamma g_\gamma\sum_{n=1}^{N_\gamma} b_n^\gamma/(1-i\omega\tau_n'^\gamma). \tag{34}$$

For example, let us consider the cases when $N_\gamma=1$ and $N_\gamma=2$. If $N_\gamma=1$ we have

$$\tau_1'^\gamma=g_\gamma\tau_1^\gamma \quad \text{and} \quad b_1^\gamma=a_1^\gamma. \tag{35}$$

For R_γ given by equation (4) for the case of $n_\infty^\gamma=1$ equations (34) and (35) lead to the same results as those predicted by the theory of Edwards and Madden [14] if it is applied to the diffusion model with the same assumptions.

If $N_\gamma=2$ the values of $(\tau_n'^\gamma)^{-1}$ are equal to the roots of the square equation $P_2(x)=0$ (33) and are given by

$$(\tau_{1,2}'^\gamma)^{-1}=[A_\gamma\pm B_\gamma]/2g_\gamma\tau_1^\gamma\tau_2^\gamma, \tag{36}$$

where

$$A_\gamma=a_2^\gamma\tau_1^\gamma+a_1^\gamma\tau_2^\gamma+g_\gamma(a_1^\gamma\tau_1^\gamma+a_2^\gamma\tau_2^\gamma),$$

and

$$B_\gamma=(A_\gamma^2-4g_\gamma\tau_1\tau_2)^{1/2}.$$

The coefficients b_γ are determined from the following system of equations

$$\left.\begin{array}{c} b_1^\gamma\tau_1'^\gamma+b_2^\gamma\tau_2'^\gamma=g_\gamma(a_1^\gamma\tau_1^\gamma+a_2^\gamma\tau_2^\gamma), \\ b_1^\gamma+b_2^\gamma=1, \end{array}\right\} \tag{37}$$

subject to equation (36). The result is

$$b_1=-g_\gamma(a_1^\gamma\tau_1^\gamma+a_2^\gamma\tau_2^\gamma)B_\gamma^{-1}-(C_\gamma-1)^{-1}, \tag{38}$$

$$b_2=g_\gamma(a_1^\gamma\tau_1^\gamma+a_2^\gamma\tau_2^\gamma)B_\gamma^{-1}+C_\gamma(C_\gamma-1)^{-1}, \tag{39}$$

where

$$C_\gamma=(A_\gamma-B_\gamma)/4g_\gamma\tau_1^\gamma\tau_2^\gamma.$$

Unfortunately, the rotational diffusion model is only applicable to the low frequency range ($\omega\tau_\gamma^N<1$). As an example of a model which may be used in the high frequency range (up to ~5 THz) as well, we consider the extended rotational diffusion in the Maier–Saupe potential [10, 13, 21]

$$U(\theta)=-U_0\cos^2\theta, \tag{40}$$

where $U_0=3AS/2V^2$, A is a constant, S is the order parameter and V is the molar volume. The model of extended diffusion in the potential $U(\theta)$ given by equation (40) was proposed and simulated numerically for the isotropic case in [24]. We now give the analytical solution for the anisotropic case.

5. Extended rotational diffusion in the Maier–Saupe potential

This model has been discussed in detail elsewhere [17,24]. Here only a brief description of the model is given. It is assumed that a classical rigid rotator, whose permanent dipole moment is μ and moment of inertia is I, rotates in the potential given by equation (40). Rotation of the dipole is interrupted by instantaneous collisions, i.e. the duration of collisions is assumed to be much smaller than the average time between collisions, τ. The collisions take place at random times governed by a Poisson law and randomize both the magnitude and direction of the angular velocity $\boldsymbol{\Omega}$, the random values of $\boldsymbol{\Omega}$ being governed by a Boltzmann law. It is also assumed that collisions do not change the orientation of a rotator in space. In this version of the model we introduce two adjustable parameters τ and U_0 which are in close relation to the molecular dynamics of its physical meaning and hence they may be considered as quantitative characteristics of molecular reorientations in liquid crystals.

In the framework of the memory function approach the model under consideration may be formulated as follows. Let us introduce the memory function

$$K_\gamma^s(t)=K_\gamma^c(t)\exp(-t/\tau), \tag{41}$$

where $K_\gamma^c(t)$ is the memory function corresponding to the correlation function $C_\gamma^c(t)$ for collisionless rotation of a dipole in the potential $U(\theta)$. The functions $K_\gamma^c(t)$ and $C_\gamma^c(t)$ are related to each other by

$$\frac{d}{dt}C_\gamma^c(t)=-\int_0^t K_\gamma^c(t-t')C_\gamma^c(t')\,dt'. \tag{42}$$

By means of one sided Fourier transforms the system of equations (17), (41) and (42) can be easily solved

$$\tilde{C}_\gamma(\omega)=\frac{\tilde{C}_\gamma^c(\omega+i/\tau)}{1-\tilde{C}_\gamma^c(\omega+i/\tau)/\tau}. \tag{43}$$

Exact formulas for the Fourier–Laplace transforms $\tilde{C}_\parallel^c(\omega+i/\tau)$ and $\tilde{C}_\perp^c(\omega+i/\tau)$ for collisionless rotation of a dipole in the Maier–Saupe potential have been derived in [17]. Equations for $\tilde{C}_\parallel^c(\omega+i/\tau)$ and $\tilde{C}_\perp^c(\omega+i/\tau)$ are given in Appendix B.

The real, $\chi'(\omega)$, and imaginary, $\chi''(\omega)$, parts of the normalized complex polarizability

$$\begin{aligned}\chi(\omega)&=1+i\omega\tilde{C}_\gamma(\omega),\\ &=\frac{1+(i\omega-1/\tau)\tilde{C}_\gamma^c(\omega+i/\tau)}{1-\tilde{C}_\gamma^c(\omega+i/\tau)/\tau},\end{aligned}$$

and the function $\eta\omega\chi''(\omega)$, which corresponds approximately to the absorption coefficient $\alpha(\omega)$ given by equation (7), are shown in figures 1 and 2 for different values of the model parameters τ and $\rho^2=U_0/kT$. Substituting $\tilde{C}_\gamma(\omega)$ from equation (43) into equation (19) we can obtain

$$\tilde{\Phi}_\gamma^N(\omega)=\frac{\phi_\gamma^N(0)g_\gamma\tilde{C}_\gamma^c(\omega+i/\tau)}{1+[i\omega(1-g_\gamma)-\tau^{-1}]\tilde{C}_\gamma^c(\omega+i/\tau)}. \tag{44}$$

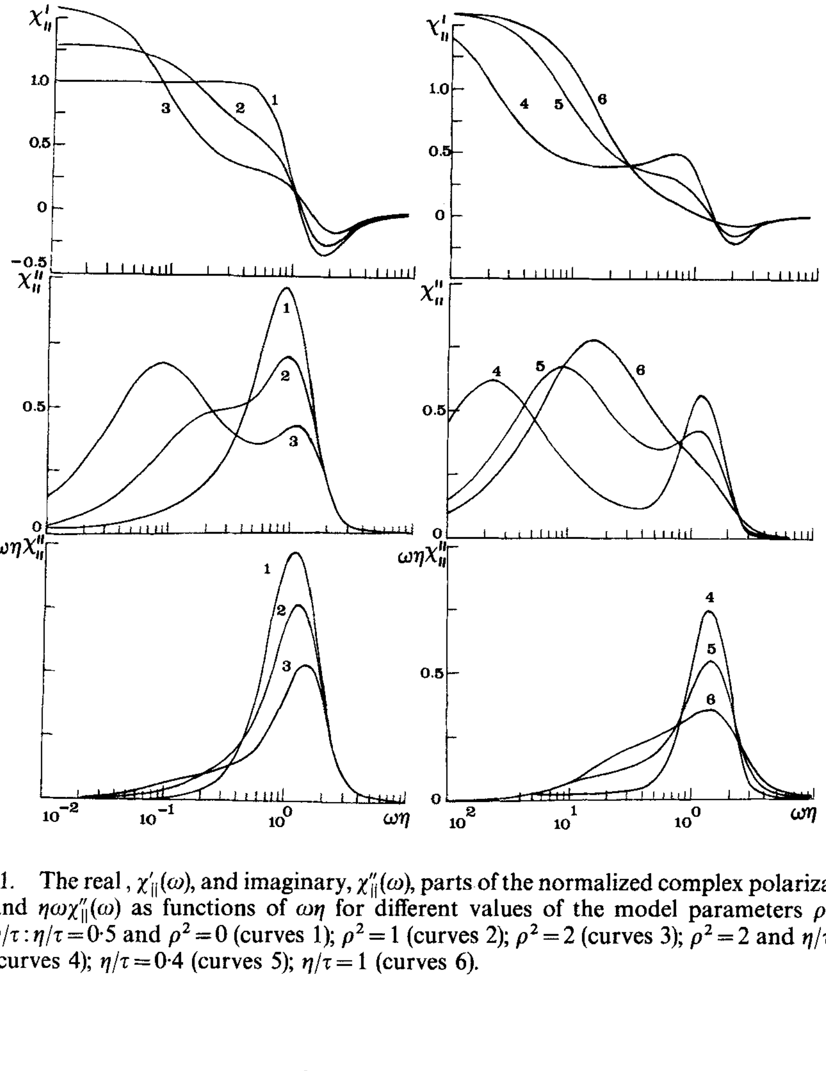

Figure 1. The real, $\chi'_{\|}(\omega)$, and imaginary, $\chi''_{\|}(\omega)$, parts of the normalized complex polarizability and $\eta\omega\chi''_{\|}(\omega)$ as functions of $\omega\eta$ for different values of the model parameters ρ^2 and η/τ: $\eta/\tau = 0{\cdot}5$ and $\rho^2 = 0$ (curves 1); $\rho^2 = 1$ (curves 2); $\rho^2 = 2$ (curves 3); $\rho^2 = 2$ and $\eta/\tau = 0{\cdot}1$ (curves 4); $\eta/\tau = 0{\cdot}4$ (curves 5); $\eta/\tau = 1$ (curves 6).

The frequency dependencies Re $\{\tilde{\phi}_\gamma^N(\omega)\}$ given by equation (44) are usually lorentzian with a half-width $\approx(\tau_\gamma^N)^{-1}$, where

$$\begin{aligned}\tau_\gamma^N &= \tilde{\phi}_\gamma^N(0)/\phi_\gamma^N(0),\\ &= g_\gamma \frac{\tau \tilde{C}_\gamma^c(i/\tau)}{\tau - \tilde{C}_\gamma^c(i/\tau)},\end{aligned} \qquad (45)$$

is the macroscopic dipole moment relaxation time, and with a prominence on the high frequency wing of the spectra. At some values of the model parameters τ and U_0, this prominence may be displayed as a separate maximum which is due to librations of molecules.

Now using equations (1) and (44) we can obtain

$$\frac{\varepsilon_\gamma^*(\omega) - (n_\infty^\gamma)^2}{R_\gamma(\omega)} = \frac{g_\gamma G_\gamma[1 + i\omega\tilde{C}_\gamma^c(\omega + i/\tau)]}{1 + [i\omega(1 - g_\gamma) - \tau^{-1}]\tilde{C}_\gamma^c(\omega + i/\tau)}, \qquad (46)$$

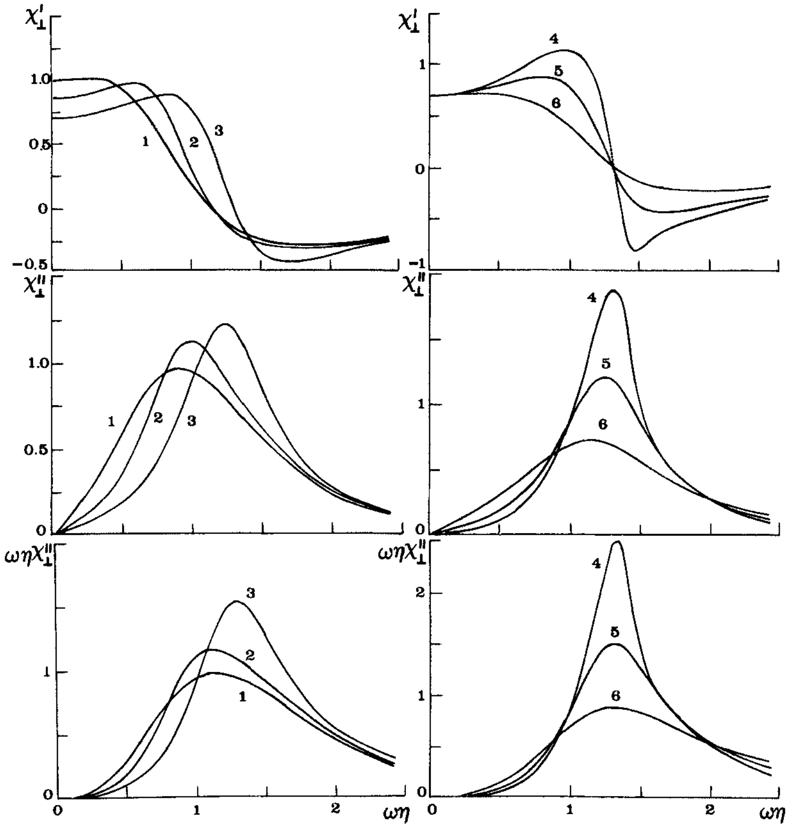

Figure 2. The real, $\chi'_\perp(\omega)$, and imaginary, $\chi''_\perp(\omega)$, parts of the normalized complex polarizability and $\eta\omega\chi''_\perp(\omega)$ as functions of $\omega\eta$ for different values of the model parameters ρ^2 and η/τ: $\eta/\tau = 0{\cdot}5$ and $\rho^2 = 0$ (curves 1); $\rho^2 = 1$ (curves 2); $\rho^2 = 2$ (curves 3); $\rho^2 = 2$ and $\eta/\tau = 0{\cdot}1$ (curves 4); $\eta/\tau = 0{\cdot}4$ (curves 5); $\eta/\tau = 1$ (curves 6).

where

$$G_\parallel = 4\pi\mu^2 N\Lambda(\rho), \quad G_\perp = 2\pi\mu^2 N(1-\Lambda(\rho)),$$

and

$$\Lambda(\rho) = \left[2\rho\exp(-\rho^2)\int_0^\rho \exp(x^2)\,dx\right]^{-1} - 1/(2\rho^2).$$

Notice some important properties of the model in question.

(i) In the low frequency limit ($\omega\tau_\gamma^N < 1$) equation (46) may be reduced to

$$\frac{\varepsilon_\gamma^*(\omega) - (n_\infty^\gamma)^2}{R_\gamma(\omega)} = \frac{G_\gamma g_\gamma}{1 - i\omega\tau_\gamma^N}, \tag{47}$$

where τ_γ^N is given by equation (45). If collisions are frequent enough (i.e. $\eta/\tau \gg 1$, where $\eta^{-1} = (2kT/I)^{1/2}$ is the average thermal angular velocity), then taking into account that $\tilde{C}_l^c(z)$ has the following asymptotic expansion

$$\tilde{C}_\gamma^c(z) = i/z - i\ddot{C}_\gamma^c(0)/z^3 + O(z^{-5}), \quad z \to \infty,$$

where

$$\ddot{C}^c_{\parallel}(0)=\frac{\Lambda(\rho)-1}{2\eta^2\Lambda(\rho)},\quad \ddot{C}^c_{\perp}(0)=\frac{\Lambda(\rho)+1}{2\eta^2(\Lambda(\rho)-1)},\tag{48}$$

from equation (45) we can obtain

$$\tau^N_{\parallel}=g_{\parallel}\frac{2\eta^2\Lambda(\rho)}{\tau(1-\Lambda(\rho))},\quad \tau^N_{\perp}=g_{\perp}\frac{2\eta^2(1-\Lambda(\rho))}{\tau(1+\Lambda(\rho))}.\tag{49}$$

Equations (48) for $\ddot{C}^c_{\gamma}(0)$, which are defined as

$$\ddot{C}^c_{\gamma}(0)=\langle\mu_{\gamma}(0)\ddot{\mu}_{\gamma}(0)\rangle/\langle\mu_{\gamma}(0)^2\rangle,$$

were obtained with the help of equations (B 2) and (B 3) in Appendix B. For the case of $\rho^2 \gg 1$ equations (49) are simplified to

$$\tau^N_{\parallel}=g_{\parallel}2\eta^2\rho^2/\tau,\quad \tau^N_{\perp}=g_{\perp}\eta^2/\rho^2\tau,\tag{50}$$

while in the opposite limit ($\rho^2 \ll 1$)

$$\tau^N_{\parallel}=g_{\parallel}\eta^2(1+2\rho^2/5)/\tau,\quad \tau^N_{\perp}=g_{\perp}\eta^2(1-\rho^2/5)/\tau.\tag{51}$$

As seen from equations (50) and (51) with an increase in the potential barrier ρ^2 the relaxation time $\tau^N_{\parallel}$ is enhanced while the relaxation time $\tau^N_{\perp}$ is decreased. It can be shown that such behaviour of $\tau^N_{\perp}$ is valid for arbitrary values of η/τ as well.

(ii) In the absence of the potential (i.e. in the limit $U_0 \to 0$) the results obtained coincide precisely with those predicted by the J-diffusion model [18].

(iii) The sum rules from equations (24) and (25) become

$$\int_0^{\infty}\omega\varepsilon''_{\parallel}(\omega)\,d\omega=2\frac{\pi^2\mu^2N}{I}[1-\Lambda(\rho)],\tag{52}$$

$$\int_0^{\infty}\omega\varepsilon''_{\perp}(\omega)\,d\omega=\frac{\pi^2\mu^2N}{I}[1+\Lambda(\rho)],\tag{53}$$

and

$$\int_0^{\infty}\omega\tfrac{1}{3}[\varepsilon''_{\parallel}(\omega)+2\varepsilon''_{\perp}(\omega)]\,d\omega=\frac{4\pi^2\mu^2N}{3I}.\tag{54}$$

It is of importance that for the average dielectric loss $(\varepsilon''_{\parallel}(\omega)+2\varepsilon''_{\perp}(\omega))/3$ the integral absorption does not depend on the potential magnitude U_0 and (explicitly) temperature and coincides precisely with the sum rule of Gordon [1]. In the high barrier limit ($\rho^2 \gg 1$) the sum rules from equations (52) and (53) are simplified to

$$\int_0^{\infty}\omega\varepsilon''_{\parallel}(\omega)\,d\omega=\frac{2\pi^2\mu^2N}{I\rho^2},\quad \int_0^{\infty}\omega\varepsilon''_{\perp}(\omega)\,d\omega=\frac{\pi^2\mu^2N}{I}(2-\rho^{-2}).\tag{55}$$

Within the framework of the model under consideration we can account for the specific features of dielectric spectra of nematic liquid crystals at low (radio/microwave) frequencies and in the far infrared range.

At low frequencies the model describes the relaxation (Debye) spectrum. In such a case the results from equations (49)–(51) are in qualitative agreement with the available experimental data (e.g. [19]) and with theoretical estimates [10, 13], from which it follows that the relaxation time $\tau^N_{\parallel}$ increases and $\tau^N_{\perp}$ decreases in nematic liquid crystals as compared to the relaxation time in the isotropic phase. The essential difference between the theories [10, 13] is that for the model in question the relaxation times depend on the microscopic parameters τ and U_0 which are closely associated with molecular dynamics and the predicted equations (49)–(51) contain the effects of the orientational dipole–dipole correlations as well as those dynamical effects discussed in [10, 13]; it is in agreement with the theory of Edwards and Madden [14]. In the far infrared range, on the basis of the model considered, we can also reproduce the librational absorption band (Poley absorption) and account for the excess absorption; i.e. the excess of the intensity of this band over the Debye plateau [1]. Moreover the model allows us to explain the features of the polarized spectra [25, 26]: the increase in absorption for the case $\mathbf{E}\perp\mathbf{n}(\gamma=\perp)$ and the decrease in absorption for the case $\mathbf{E}\|\mathbf{n}(\gamma=\|)$ compared to the isotropic phase (see equations (55)). Physically this is due to the fact that for $\mathbf{E}\|\mathbf{n}$ the charges of a molecular dipole are moving for most of the time perpendicularly to the field $\mathbf{E}(t)$ and hence absorb the electromagnetic wave energy poorly, whereas at $\mathbf{E}\perp\mathbf{n}$ these charges move mostly in the direction of the field $\mathbf{E}$ and hence interact effectively with it. This result is in agreement with available experimental data (e.g. [25, 26]).

The sum rules from equations (52)–(55) can be used to evaluate the magnitude of absorption due to variable dipole moments that are induced by the nearest environment and collisions of molecules [1]. Just as for isotropic liquids, the magnitude of the induced absorption in liquid crystals can be estimated from the difference $\Delta = \Pi_{\text{exp}} - \Pi_{\text{theor}}$, where Π_{theor} is the theoretical value of the corresponding sum rule and Π_{exp} is the experimentally measured magnitude of the integrated absorption intensity. The use of the elaborated theory in more careful comparisons with experimental data and the generalization of the model for the case of an arbitrary direction of the dipole moment with the long axis of a molecule will be investigated in subsequent work.

I wish to thank Professors V. I. Gaiduk and O. V. Betsky for their interest in the present work.

Appendix A

For the internal field factor $R_\gamma(\omega)$ given by equation (4) we can make a further transformation of equation (9). Indeed we have from equation (4) and (9)

$$\frac{[\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2]\{\varepsilon_\gamma^*(0)-\sigma_\gamma(0)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]\}}{[\varepsilon_\gamma^*(\omega)-\varepsilon_\gamma^*(0)]\sigma_\gamma(0)+\varepsilon_\gamma^*(0)}=\frac{4\pi\phi_\gamma^N(0)}{kT[1-i\omega/\tilde{K}_\gamma^N(\omega)]}. \qquad \text{(A 1)}$$

Taking into account that according to equations (1) and (3) or equation (A 1) the dielectric constant tensor $\varepsilon_\gamma^*(0)$ is given by

$$\frac{[\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2]\{\varepsilon_\gamma^*(0)-\sigma_\gamma(0)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]\}}{\varepsilon_\gamma^*(0)}=\frac{4\pi\phi_\gamma^N(0)}{kT}, \qquad \text{(A 2)}$$

we obtain from equation (A 1)

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2}\,\varepsilon_\gamma^*(0)=\frac{[\varepsilon_\gamma^*(\omega)-\varepsilon_\gamma^*(0)]\sigma_\gamma(0)+\varepsilon_\gamma^*(0)}{1-i\omega/\tilde{K}_\gamma^N(\omega)}, \qquad \text{(A 3)}$$

or

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2}\left\{\varepsilon_\gamma^*(0)-\frac{[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]\sigma_\gamma(0)}{1-i\omega/\tilde{K}_\gamma^N(\omega)}\right\}=\frac{[\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2]\sigma_\gamma(0)+\varepsilon_\gamma^*(0)}{1-i\omega/\tilde{K}_\gamma^N(\omega)}. \qquad \text{(A 4)}$$

Algebraic transformations of equation (A 4) lead to

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2}=\left[1-\frac{i\omega\varepsilon_\gamma^*(0)}{\tilde{K}_\gamma^N(\omega)\{[\varepsilon_\gamma^*(\omega)-\varepsilon_\gamma^*(0)]\sigma_\gamma(0)+\varepsilon_\gamma^*(0)\}}\right]^{-1}. \tag{A 5}$$

Taking into consideration equation (A 2) we can rearrange equation (A 5) as

$$\frac{\varepsilon_\gamma^*(\omega)-(n_\infty^\gamma)^2}{\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2}=\frac{1}{1-i\omega s_\gamma(\omega)[\varepsilon_\gamma^*(0)-(n_\infty^\gamma)^2]}, \tag{A 6}$$

where

$$s_\gamma(\omega)=\frac{kT}{4\pi\phi_\gamma^N(0)\tilde{K}_\gamma^N(\omega)}. \tag{A 7}$$

For the case of non-polarizable molecules (i.e. $n_\infty^\gamma=1$) equations (A 6) and (A 7) coincide with those predicted by the theory of Edwards and Madden [14]; the difference is that in [14] another definition for the memory function $K_\gamma^N(t)$ was used.

Appendix B

To describe the orientation of a dipole let us introduce the polar angles θ, ϕ, where θ is measured from the z axis. The Fourier–Laplace transforms of the molecular dipole correlation functions $C_\gamma^c(t)$ for a collisionless rotating dipole in the Maier–Saupe potential from equation (40) are given by

$$\tilde{C}_\gamma^c(\omega+i/\tau)=\int_0^\infty \exp\left[(i\omega t-1/\tau)t\right]\frac{\langle\mu_\gamma(0)\mu_\gamma(t)\rangle}{\langle\mu_\gamma(0)^2\rangle}\,dt, \tag{B 1}$$

where $\mu_\parallel(t)=\mu\cos\theta(t)$ and $\mu_\perp(t)=\mu\sin\theta(t)\cos\phi(t)$ are determined by solving equation (27) which in the case under consideration is reduced to the following non-linear equations of motion

$$\frac{d^2}{dt^2}\mu_\parallel(t)+\frac{2H}{I}\mu_\parallel(t)=\frac{2U_0}{I}\mu_\parallel(t)-\frac{4U_0}{\mu^2 I}\mu_\parallel^3(t), \tag{B 2}$$

$$\frac{d^2}{dt^2}\mu_\perp(t)+\frac{2H}{I}\mu_\perp(t)=-\frac{4U_0}{\mu^2 I}\mu_\parallel^2(t)\mu_\perp(t). \tag{B 3}$$

Here the energy

$$H=\frac{I\mathbf{\Omega}^2(t)}{2}+U(\theta(t))=\frac{p_\theta^2(t)}{2I}+\frac{p_\phi^2(t)}{2I\sin^2\theta(t)}-U_0\cos^2\theta(t),$$

is a constant of the motion, $\mathbf{\Omega}$ is the angular velocity of the dipole

$$p_\theta=I\theta \quad \text{and} \quad p_\phi=I\phi\sin^2\theta,$$

are the angular momenta canonically conjugated to the angles θ and ϕ respectively, the brackets $\langle(\ldots)\rangle$ designate an ensemble average

$$\langle(\ldots)\rangle=C^{-1}\int_0^\pi\int_0^{2\pi}\int_{-\infty}^\infty\int_{-\infty}^\infty(\ldots)\exp(-H/kT)\,d\theta(0)\,d\phi(0)\,dp_\theta(0)\,dp_\phi(0), \tag{B 4}$$

$$C=8\pi^2 IkT\int_0^\rho \exp(-x^2)\,dx/\rho, \quad \rho^2=U_0/kT.$$

For further treatment it is convenient to make use of the normalized variables

$$t'=t/\eta, \quad z=(\omega+i/\tau)\eta, \quad u_\gamma(t)=\mu_\gamma(t)/\mu, \quad h=H/kT,$$

where $\eta=(I/2kT)^{1/2}$. Taking into account that p_ϕ is a constant of the motion, we obtain from equation (B 2) after integration

$$\left(\frac{d}{dt'}u_{\|}(t')\right)^2=[h+\rho^2u_{\|}(t')][1-u_{\|}^2(t')]-r^2, \tag{B 5}$$

where $r^2=p_\phi^2/2IkT$. The Fourier–Laplace transforms $\tilde{C}_\gamma^c(\omega+i/\tau)$ can be calculated by the same general mathematical method that was used in [27, 28] to evaluate the Fourier–Laplace transform of the orientational autocorrelation function for a system of free asymmetric-top molecules.

The solution of equation (B 5) with initial condition $u_{\|}(0)=\cos\theta(0)$ can be expressed in terms of the jacobian doubly periodic functions $\mathrm{dn}(u|m)$ and $\mathrm{cn}(u|m)$ [29]

$$u_{\|}(t')=\begin{cases} e_2^{1/2}\,\mathrm{dn}(s|k^2), & k<1, \qquad \text{(B 6)}\\ e_2^{1/2}\,\mathrm{cn}(ks|k^{-2}), & k>1, \qquad \text{(B 7)}\end{cases}$$

where

$$s=\rho e_2^{1/2}t'+\xi, \quad k^2=(e_2-e_1)/e_2,$$

$$\xi=e_2^{1/2}\int_{e_2^{1/2}}^{\cos\theta(0)}[(x^2-e_1)(e_2-x^2)]^{-1/2}\,dx,$$

e_1 and e_2 are the roots of the square equation $(h+\rho^2x)(1-x)-r^2=0$

$$e_1=\frac{(\rho^2-h)}{2\rho^2}-\frac{1}{2\rho^2}[(\rho^2+h)^2-4\rho^2r^2]^{1/2}, \quad e_2=\frac{(\rho^2-h)}{2\rho^2}+\frac{1}{2\rho^2}[(\rho^2+h)^2-4\rho^2r^2]^{1/2}.$$

The inequalities $k<1$ and $k>1$ are valid in two regions of physically possible variations of the variables h and r. On the $\{h,r\}$ plane these regions are determined by the inequalities

$$(2\rho|r|-\rho^2)<h<r^2 \quad \text{and} \quad h>r^2.$$

The solution from equation (A 6) describes librations of a dipole in the potential wells (in the vicinity of $\theta=0$ and $\theta=\pi$) while the solution from equation (B 7) corresponds to rotation hindered by the potential.

In order to evaluate the integrals in equations (B 1) and (B 4) we introduce the variables $\{\xi,\phi,h,l\}$ instead of $\{\theta,\phi,p_\theta,p_\phi\}$; the jacobian of the transformation of the variables is given by

$$\begin{aligned} J&=\frac{(\partial\theta\partial\phi\partial p_\theta\partial p_\phi)}{(\partial\xi\partial\phi\partial h\partial r)},\\ &=\frac{IkT}{\rho e_2^{1/2}}. \end{aligned} \tag{B 8}$$

Then we use the following Fourier series expansions of the elliptic functions $\mathrm{cn}(u|m)$ and $\mathrm{dn}(u|m)$ (see [30])

$$\mathrm{cn}(u|m)=\frac{2\pi}{m^{1/2}K(m)}\sum_{n=0}^{\infty}\frac{q(m)^{n+1/2}}{1+q(m)^{2n+1}}\cos\frac{\pi(n+1/2)u}{K(m)}, \tag{B 9}$$

$$\mathrm{dn}\,(u|m) = \frac{\pi}{2K(m)} + \frac{2\pi}{K(m)} \sum_{n=1}^{\infty} \frac{q(m)^n}{1+q(m)^{2n}} \cos\frac{\pi n u}{K(m)}, \tag{B 10}$$

where

$$q(m) = \exp\left[-\pi K(1-m)/K(m)\right],$$

$K(m)$ is the complete elliptic integral of the first kind [29]. The analytical integration over ϕ, ξ and t' in equation (B 1) taking into account equations (B 4)–(B 10) and after tedious algebra leads to

$$\tilde{C}^{c}_{\|}(\omega+i/\tau) = \frac{i\eta}{z} - \left\{\left[\int_{-\rho^2}^{0}\int_{0}^{(h+\rho^2)/2\rho} + \int_{0}^{\rho^2}\int_{h^{1/2}}^{(h+\rho^2)/2\rho}\right]\sum_{n=1}^{\infty} C_{2n}(z|k^2)\,dh\,dr\right\}$$

$$- \int_{0}^{\infty}\int_{0}^{h^{1/2}} \sum_{n=1}^{\infty} C_{2n-1}(k^{-1}z|k^{-2})\,dh\,dr, \tag{B 11}$$

where

$$C_n(u|m) = \frac{i2\eta\pi e_2^{1/2}\exp(-h-\rho^2)\rho^2[\rho-F(\rho)]^{-1}}{uK(m)\,\mathrm{ch}^2\left[\dfrac{\pi n K(1-m)}{2K(m)}\right]\left\{1-\left[\dfrac{2uK(m)}{n\pi\rho e_2^{1/2}}\right]^2\right\}},$$

$$F(\rho) = \exp(-\rho^2)\int_0^{\rho}\exp(x^2)\,dx,$$

is the Dawson integral [29]. The integration over h and r is calculated numerically.

There are two ways to find $u_\perp(t')$. The first one is to solve equation (B 3) directly which is reduced to the Lambe equations [31]

$$\frac{d^2}{ds^2}u_\perp(s) = [A + n(n+1)k^2\,\mathrm{sn}^2(s|k^2)]u_\perp(s), \qquad (k<1),$$

$$\frac{d^2}{d(ks)^2}u_\perp(ks) = [Ak^{-2} + n(n+1)k^{-2}\,\mathrm{sn}^2(ks|k^{-2})]u_\perp(ks), \quad (k>1),$$

where $n=1$ and $A=(h+2e_2\rho^2)/e_2\rho^2$. The second way is to express $u_\perp(t')$ via $u_{\|}(t')$ given by equations (A 5) and (A 6) and $\phi(t')$; the latter can be found from the constant of motion $p_\phi(0)=\dot{\phi}(t)\sin^2\theta(t)$. We find easily that

$$\phi(t') = \phi(0) + \frac{r}{\rho e_2^{1/2}}\int_{\xi}^{s}\frac{dx}{1-e_2\,\mathrm{dn}^2(x|k^2)}. \tag{B 12}$$

Let us make use of the second way. For $k<1$ we have

$$u_\perp(t') = [1-e_2\,\mathrm{dn}^2(s|k^2)]^{1/2}\cos\left[\phi(0) + \frac{r}{\rho e_2^{1/2}}\int_{\xi}^{s}\frac{dx}{1-e_2\,\mathrm{dn}^2(x|k^2)}\right],$$

or

$$u_\perp(t') = (1-e_2)[1-k^2\,\mathrm{sn}^2(ia|k^2)\,\mathrm{sn}^2(s|k^2)]^{1/2}$$

$$\times\cos\left[\phi(0) + \frac{r}{\rho e_2^{1/2}(1-e_2)}\int_{\xi}^{s}\frac{dx}{1-k^2\,\mathrm{sn}^2(ia|k^2)\,\mathrm{sn}^2(x|k^2)}\right], \tag{B 13}$$

where $\mathrm{sn}^2(ia|k^2)=e_2/(e_2-1)$, $\mathrm{sn}(u|m)$ is the jacobian elliptic function [29]. Using known formulas [29, 30]

$$1-m\,\mathrm{sn}^2(a|m)\,\mathrm{sn}^2(u|m)=\Theta^2(0)\frac{\Theta(u+a)\Theta(u-a)}{\Theta(u)^2\Theta(a)^2},$$

$$\int_0^u \frac{dx}{1-m\,\mathrm{sn}^2(a|m)\,\mathrm{sn}^2(x|m)}=u+\frac{\mathrm{sn}(a|m)}{\mathrm{cn}(a|m)\,\mathrm{dn}(a|m)}\left[\frac{\Theta'(a)}{\Theta(a)}+\frac{1}{2}\ln\frac{\Theta(u-a)}{\Theta(u+a)}\right],$$

$$\frac{\Theta'(a)}{\Theta(a)}=\frac{H'(a)}{H(a)}+\frac{\mathrm{cn}(a|m)\,\mathrm{dn}(a|m)}{\mathrm{sn}(a|m)},$$

where $\Theta(u)$ and $H(u)$ are the Θ functions [29], the prime $'$ designates differentiation with respect to a, we can express $u_\perp(t')$ as

$$u_\perp(t')=\frac{(1-e_2)^{1/2}\Theta(0)}{2\Theta(ia)}\left\{\exp\{i[\phi(0)+\lambda t']\}\frac{\Theta(s+ia)}{\Theta(s)}\left[\frac{\Theta(\xi-ia)}{\Theta(\xi+ia)}\right]^{1/2}\right.$$
$$\left.+\exp\{-i[\phi(0)+\lambda t']\}\frac{\Theta(s-ia)}{\Theta(s)}\left[\frac{\Theta(\xi+ia)}{\Theta(\xi-ia)}\right]^{1/2}\right\}, \tag{B 14}$$

where $\lambda=i\rho e_2^{1/2}H'(ia)/H(ia)$, the parameter a is given by

$$a=F(\mathrm{arctg}\,(|\mathrm{sn}\,(ia|k^2)|)|1-k^2), \tag{B 15}$$

$F(\alpha|m)$ is the incomplete elliptic integral of the first kind [29].

For the case $k>1$ the expression for $u_\perp(t)$ has the same form as that given by equation (B 14) with the only difference, namely the parameters k^2, λ, s and ξ must be everywhere replaced by k^{-2}, $k\lambda$, ks and $k\xi$ respectively and the parameter a must be determined from the equation $\mathrm{sn}^2(ia|k^{-2})=(e_2-e_1)/(e_2-1)$ which has the solution given by equation (B 15).

Further calculations can be carried out as described. Namely, using the known Fourier series expansion (see [30])

$$\frac{\Theta(u+a)}{\Theta(u)}=\frac{\pi H(a)}{2K(m)H'(0)}\sum_{n=-\infty}^{n=\infty}\frac{\exp[i\pi nu/K(m)]}{\sin\left\{\frac{\pi}{2K(m)}[a+2inK(1-m)]\right\}}, \tag{B 16}$$

and integrating analytically over ξ, ϕ and t', we can obtain

$$\tilde{C}^c_\perp(\omega+i/\tau)=\frac{i\eta}{z}-\left\{\left[\int_{-\rho^2}^{0}\int_0^{(h+\rho^2)/2\rho}+\int_0^{\rho^2}\int_{h^{1/2}}^{(h+\rho^2)/2\rho}\right]\sum_{n=-\infty}^{\infty}S_n(z|k^2)\,dh\,dr\right\}$$
$$-\int_0^\infty\int_0^{h^{1/2}}\sum_{n=-\infty}^{\infty}S_n(k^{-1}z|k^{-2})\,dh\,dr, \tag{B 17}$$

where

$$S_n(u|m)=\frac{i\eta\pi e_2^{1/2}\exp(-h-\rho^2)\rho^2[F(\rho)(2\rho^2+1)-\rho]^{-1}}{uK(m)\,\mathrm{sh}^2\left\{\frac{\pi}{2K(m)}[a+2nK(1-m)]\right\}\left\{1-u^2\left[\lambda+\frac{n\pi\rho e_2^{1/2}}{K(m)}\right]^{-2}\right\}}.$$

The integrations over r and h remain numerical. As for asymmetric top molecules [27, 28] the final results given by equations (B 11) and (B 17) have the form of a very rapidly converging series of double integrals that is the consequence of the very rapidly converging series from equations (B 9), (B 10) and (B 16) in all cases, except when moduluses k and k^{-1} are very near unity. These results are exact and are convenient for numerical calculations.

It is of importance to notice that in the absence of the potential $U(\theta)$ equations (B 11) and (B 17) are reduced to

$$\tilde{C}^{c}_{\parallel}(\omega+i/\tau)=\tilde{C}^{c}_{\perp}(\omega+i/\tau)=-i\eta z e^{-z^2}E_1(-z^2), \tag{B 18}$$

where $E_1(x)$ is the integral exponential function [29], that is in full agreement with the result of the free rotation model [18].

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