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Fluctuating hydrodynamic response in the dielectric relaxation of nematic liquid crystals

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ABSTRACT. The effects of thermal fluctuations and hydrodynamic backflows on the dielectric relaxation of thermotropic nematic liquid crystals are studied by using a stochastic formulation of the nematodynamic equations. We construct a stochastic amplitude equation to describe the initial stages of the reorientational dynamics. We then use this equation to calculate analytically the average electric dipole moment, the dipole correlation function and the dielectric relaxation function in the direction perpendicular to the director axis, where a non-Debye response is expected. The real and imaginary parts of the transverse dielectric constant are then evaluated as functions of the field frequency for both cases, namely, when backflows are taken into account and when they are totally neglected. We find that for low field frequencies, the difference in their values in these cases may be as high as 75% and 40%, respectively. This is also manifested, though less noticeably, in the transverse Cole-Cole plot, which is no longer a semicircle indicating a non-Debye relaxation. The magnitude of the corrections suggest that these effects should be measurable and in this sense, our analysis indicates a tendency in the dielectric response and suggests new experiments to be performed. The difficulties associated with the description of the response for the whole reorientation process are briefly discussed.

RESUMEN. Se utiliza una formulación estocástica de las ecuaciones nematodinámicas para estudiar los efectos producidos por las fluctuaciones térmicas y los contraflujos hidrodinámicos sobre la relajación dieléctrica de cristales líquidos nemáticos termotrópicos. Se construye una ecuación de amplitud estocástica que describe las etapas iniciales de la dinámica reorientacional del nemático. A partir de ella se calculan analíticamente el momento dipolar eléctrico promedio, la función de correlación dipolar y la función de relajación dieléctrica en la dirección transversal al eje óptico incluyendo los efectos de los contraflujos inducidos. Las partes real e imaginaria de la constante dieléctrica se calculan como función de la frecuencia del campo eléctrico aplicado, con y sin efectos hidrodinámicos. Se muestra que para frecuencias bajas del campo, la diferencia entre estos valores puede ser, respectivamente, hasta de un 75% y un 40%. Este efecto se manifiesta también, aunque de manera menos notable, en el diagrama Cole-Cole el cual no es un semicírculo, indicando un proceso de relajación diferente al de Debye. Estos resultados sugieren que estos efectos podrían

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ser medibles y, en este sentido, el modelo propuesto indica una tendencia y sugiere la realización de experimentos nuevos. Se discute brevemente la respuesta esperada para el proceso completo de reorientación.

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1. INTRODUCTION

The classical theory of dielectric relaxation is due to Debye and gives the time rate of change of the macroscopic polarization in terms of the motion of the individual dipoles. Debye introduced a model for the rotational Brownian motion of assemblies of dipoles and assumed that the tendency of the molecular dipole moments to align parallel to the applied field is counteracted by rotational diffusion [1, 2]. He described the dynamics in terms of the Smoluchowski equation assuming a dilute solution of polar molecules in a non-polar (isotropic) solvent. By using the general theory of linear response for a dielectric medium in an external field, Debye obtained the well-known dielectric relaxation function [3]

$$\epsilon^*(\omega) - \epsilon(\infty) = \frac{\epsilon(0) - \epsilon(\infty)}{1 + \omega\tau_{\mathrm{D}}}. \tag{1}$$

Here, $\epsilon^*(\omega) \equiv \epsilon' - i\epsilon''$ is the complex dielectric permittivity at the frequency ω of the applied field, and $\epsilon(0)$, $\epsilon(\infty)$ denote, respectively, the dielectric constants under a static and in an electric field of infinite frequency. The parameter τ_{D} is a relaxation time that depends on the molecular properties of the system. Note that if $\omega\tau_{\mathrm{D}}$ is eliminated from the real and imaginary parts of Eq. (1), the equation of a circle is obtained. Consequently, if the relaxation can be described by Eq. (1), a plot of ε'' *vs.* ε' (Cole-Cole) should give a semicircle.

It should be pointed out that in deriving the above expression, Debye made strong simplifications that amount to neglect the effects of inertia, memory and the interactions between the molecules. But in spite of these simplifications, experiments have shown that many materials are correctly described by Eq. (1). There are, however, substances that deviate from it when high frequency values of the alternating electric field are used, leading to nonexponential decays. Although much theoretical effort has been devoted to explain the non-Debye behavior in polymeric and glassy systems, this has not been the case for dipolar liquids or liquid crystals. For the latter the long-range orientational correlations and the presence of hydrodynamic flow affect significantly the dynamics of the dipole moments leading to experimentally well established non-Debye dielectrical behavior [4, 5].

Recent generalizations of Debye's theory have mainly focoused on taking into account the effects of inertia and memory on dielectric relaxation by using stochastic formulations based on Langevin-like equations [6–9]. The basic purpose in this paper is concerned with a different but related aspect, namely, with how to describe the dielectric relaxation of a nematic liquid crystal taking into account the presence of thermal fluctuations and the effect of the hydrodynamic backflows which are inevitably induced by the orientational

deformation. In the case of a nematic liquid crystal Eq. (1) can be applied to each of the components of the dielectric constant, parallel, $\varepsilon^*_{\parallel}$, and perpendicular, $\varepsilon^*_{\perp}$, to the director axis. The corresponding Cole-Cole plots have been measured and for $\varepsilon^*_{\parallel}$ a semicircle is indeed obtained; however, for $\varepsilon^*_{\perp}$ deviations from a semicircle are observed indicating a distribution of relaxation times [10].

Strictly speaking, backflow effects in liquid crystals are always present. They have been known for long time [11] and their essential effect is to reduce constraints [12, 13]. In addition of taking them into account, here we shall focous on the time evolution of the spatial orientational fluctuations associated with the orientational transition of the nematic when the magnitude of an alternating external field is switched from an initial value $E_{\rm i} < E_{\rm c}$, smaller than a critical one $E_{\rm c}$, to a final value $E_{\rm f} > E_{\rm c}$. During this process the system becomes unstable and the rodlike molecules of the nematic tend to align with the applied electric field. The standard analysis of this transient dynamics is deterministic and based on a mean field approach which neglects spatial inhomogeneities and thermal fluctuations [14]. However, as is well known from the behavior of other multistable nonequilibrium systems [15], a proper description of the decay of an unstable state should include fluctuations, which are anomalously large during the transient reorientation processes as compared to those in equilibrium. Furthermore, at the transition point where the reorientation begins, a correlation length diverges and the spatial fluctuations associated with the orientation of the molecules are expected to be important.

Using a stochastic formulation of the nematodynamic equations we describe the behavior of these fluctuations and calculate the average dipole moments. In terms of them we then derive the corresponding dielectric relaxation function for the transverse direction to the director axis where a non-Debye behavior is expected, and when backflows are explicitly taken into account. In this sense the theory presented here gives the fluctuating hydrodynamics corrections to the dielectric response of the nematic liquid crystals. This response is calculated *only* for the initial stages of the reorientation where the lowest order mode dominates. We show that for these nonequilibrium states the presence of flow produces an increase as high as 75% and 40% for $\varepsilon'_{\perp}(\omega)$ and $\varepsilon''_{\perp}(\omega)$, respectively, in a low frequency range of the external field, between 1–200 Hz. We also show that backflows give rise to a non-Debye Cole-Cole plot, although the effect is less noticeable than for the $\varepsilon'_{\perp}$ and ε'' *vs.* ω plots. Since we are not aware of any measurements of dielectric relaxation of nematics in the presence of flow, a direct comparison with experimental results was not carried out. However, such large effects could be measurable and in this sense, this work suggests new experiments to be performed.

To this goal the article has been organized as follows. In the next section we define the model and write down the basic stochastic dynamic equations for the director and the reorientation angle for the particular geometry under consideration. Then, under the well defined approximations of negligible inertia and minimal coupling, from these equations we derive a stochastic amplitude equation for the Fourier's amplitude, $\theta(t)$, of the reorientation angle and for the dominant mode just above threshold. This linear, scalar stochastic equation simplifies the dynamic description and contains the effect of backflows through an effective viscosity coefficient. In the next section we calculate the first two moments of the reorientation angle probability distribution and in terms

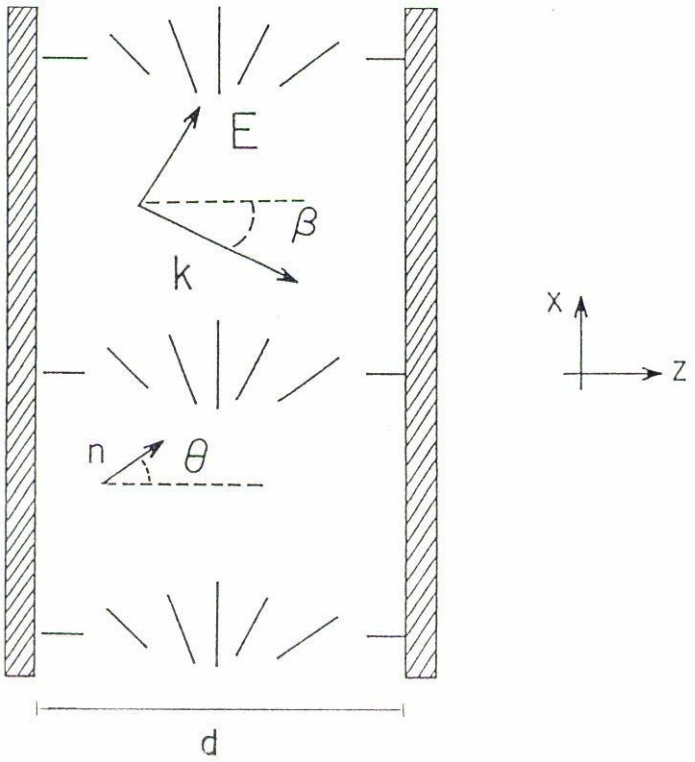

FIGURE 1. Schematics of a linearly polarized electric field acting on a homeotropically aligned nematic crystal film.

of them we calculate the equilibrium electric dipole correlation function. Then we use these quantities to evaluate analytically the complex dielectric function $\varepsilon^*_\perp(\omega)$ in the transverse direction and plot its real, $\varepsilon'_\perp(\omega)$, and imaginary, $\varepsilon''_\perp(\omega)$, parts as functions of ω for PAA (para-azoxyanisole). The corresponding Cole-Cole plots with and without backflow effects are also calculated and their differences in these two cases are shown. Finally, in the last section we summarize our results and conclude by making some further physical remarks.

2. MODEL AND BASIC EQUATIONS

We consider a nematic liquid crystal layer of thickness d along the z axis and contained between two parallel dielectric plates, as shown in Fig. 1. The transverse dimensions, L, along the x and y directions are large compared to d, but the cell has a finite volume $V = L^2 d$. Since it is well known that the hydrodynamic effects are enhanced for bend geometries [12], we consider an initial homeotropic configuration of the director field $\mathbf{n}$ where it is everywhere perpendicular to the plates, $\mathbf{n}^0 = (0, 0, 1)$. We assume strong anchoring boundary conditions for the director at the plates.

In the absence of an external field the nematic will retain its initial orientation $\mathbf{n}^0$. However, if it is excited by an obliquely applied external field with a constant polarization in the x–z plane, the orientation of the director inside the cell will vary with time and position and will be described by the local director field $\mathbf{n}(\mathbf{r}, t)$. Actually, the unit vector $\mathbf{n}$ is a hydrodynamic variable which characterizes the preferred direction of the long axis of the molecules. Apart from the mass density, the specific entropy and the momentum density, the director is the only additional hydrodynamic variable for a nematic; there are no other degrees of freedom in the hydrodynamics of nematics. This behavior results from the spontaneous breaking of the symmetry O(3) and from the fact that for small wave vectors $\mathbf{k}$, the director's susceptibility diverges as k^{-2} [16].

If the electric field always remains in the plane of incidence, it is reasonable to assume that the reorientation of $\mathbf{n}$ also takes place in the x–z plane, assumption that has been confirmed by experimental measurements of optical properties of nematics under reorientation [17]. Therefore, we also assume

$$\mathbf{n}(x, z, t) = [\sin\theta(x, z, t),\ 0,\ \cos\theta(x, z, t)] \tag{2}$$

where θ is the reorientation angle between $\mathbf{n}$ and $\mathbf{n}^0$. Consistently, we consider the backflow to be a shear flow of the form

$$\mathbf{v}(x, z, t) = [v_x(x, z, t),\ 0,\ 0] \tag{3}$$

which satisfies stick boundary conditions on the plates $v_x(z = 0,\ d) = 0$.

Using the stochastic formulation of the nematodynamic equations [18], the general dynamical equations for the director and velocity fields can be written in the form

$$d_t n_\beta = -\frac{1}{\gamma_1}\frac{\delta F}{\delta n_\beta} + \Gamma_{\beta\gamma}(\mathbf{n})\frac{\delta F}{\delta v_\gamma} + \xi_\beta(\mathbf{r}, t), \tag{4}$$

$$d_t v_\beta = L_{\beta\gamma}(\mathbf{n})\frac{\delta F}{\delta v_\gamma} - \Gamma^+_{\beta\gamma}(\mathbf{n})\frac{\delta F}{\delta n_\gamma} + \partial_\alpha \Omega_{\alpha\beta}(\mathbf{r}, t), \tag{5}$$

where $d_t \equiv d/dt \equiv \partial/\partial t + \mathbf{v}\cdot\nabla$ denotes the usual material derivative and F is the Helmholtz free energy functional

$$F = \int_v d\mathbf{r}\,(f_{el} + f_{em} + f_{hyd}) \equiv \frac{1}{2}\int_v d\mathbf{r}\, K_{\alpha\beta\gamma\delta}\left(\frac{\partial n_\alpha}{\partial x_\beta}\right)\left(\frac{\partial n_\gamma}{\partial x_\delta}\right) - \frac{1}{2}\int_v d\mathbf{r}\,\frac{\mathbf{E}\cdot\mathbf{D}}{8\pi} + \frac{1}{2}\int_v d\mathbf{r}\,\rho v^2, \tag{6}$$

where x_i $(i = 1, 3)$ are the components of the position vector in the plane x–z. The first term in Eq. (6) gives the Oseen-Frank distortion free energy in terms of Frank's elastic constants K_1, K_2, K_3, and the tensor $K_{\alpha\beta\gamma\delta}$ is defined as

$$K_{\alpha\beta\gamma\delta} = K_1(\delta_{\alpha\delta} - n_\alpha n_\delta)(\delta_{\beta\gamma} - n_\beta n_\gamma) + K_2\varepsilon_{\alpha\beta\mu}\varepsilon_{\gamma\delta\nu}n_\mu n_\nu + K_3(\delta_{\alpha\gamma} - n_\alpha n_\gamma)n_\beta n_\delta, \tag{7}$$

where $\varepsilon_{\alpha\beta\mu}$ is the totally antisymmetric Levi-Civita tensor and the kinetic operators $L(\mathbf{n})$ and $\Gamma(\mathbf{n})$ are given by

$$L_{\beta\gamma}(\mathbf{n}) = \partial_\alpha M_{\alpha\beta\gamma\delta}(\mathbf{n})\partial_\delta, \tag{8}$$

$$M_{\alpha\beta\gamma\delta}(\mathbf{n}) = \frac{1}{\rho^2}[2(\nu_1+\nu_2-2\nu_3)n_\alpha n_\beta n_\gamma n_\delta + \nu_2(\delta_{\beta\delta}\delta_{\alpha\gamma}+\delta_{\alpha\delta}\delta_{\beta\gamma}) + (\nu_3-\nu_2)(n_\alpha n_\gamma\delta_{\delta\beta}+n_\alpha n_\delta\delta_{\gamma\beta}+n_\beta n_\gamma\delta_{\delta\alpha}+n_\beta n_\delta\delta_{\gamma\alpha})], \tag{9}$$

$$\Gamma_{\beta\gamma}(\mathbf{n}) = \frac{1}{2\rho}[(\lambda+1)n_\alpha\partial_\alpha\delta_{\beta\gamma}+(\lambda-1)n_\alpha\partial_\beta\delta_{\alpha\gamma}]. \tag{10}$$

In Eqs. (8)–(10) we have used the abbreviation $\partial_\alpha \equiv \partial/\partial n_\alpha$ and $\lambda = \gamma_1/\gamma_2$, γ_1, γ_2, ν_1, ν_2, ν_3 denote several viscosity coefficients. $\rho(\mathbf{r},t)$ is the local mass density and Γ^+ denotes the adjoint operator which is here defined in the sense of integration by parts and transposing matrix indexes. The operator L is self-adjoint, $L = L^+$.

The second term in Eq. (6) is the electromagnetic free energy given in terms of the displacement vector $\mathbf{D}$. It should be emphasized that in writing this expression we have assumed, as is usually the case, that the magnetic susceptibility of the nematic is much smaller than its dielectric susceptibility; that is, that the liquid crystal is non-magnetic [19]. The relation between the nematic and the optical field is expressed through the constitutive relation

$$\mathbf{D} = \underline{\underline{\varepsilon}} \cdot \mathbf{E}, \tag{11}$$

where the dielectric tensor $\underline{\underline{\varepsilon}}$ is given by

$$\varepsilon_{ij} = \varepsilon_\perp\delta_{ij} + \varepsilon_a n_i n_j. \tag{12}$$

Here $\varepsilon_a \equiv \varepsilon_{||} - \varepsilon_\perp$ is the dielectric anisotropy, where $\varepsilon_{||}$, $\varepsilon_\perp$ denote, respectively, the nematic's dielectric constants along the parallel and perpendicular directions to $\mathbf{n}$.

The third term in Eq. (6) gives the hydrodynamic contribution to the free energy [20], and the symbols $\delta F/\delta n_\beta$ and $\delta F/\delta v_\gamma$ denote the functional derivatives of F.

The noise sources ξ_β and $\partial_\alpha\Omega_{\alpha\beta}$ in Eqs. (4) and (5) are Gaussian white noises with zero mean and satisfy fluctuation-dissipation theorems such that the equilibrium distribution associated with these equations has the canonical form $P_{eq}[\mathbf{n}(\mathbf{r}),\mathbf{v}(\mathbf{r})] \propto \exp[-F/k_BT]$, that is [18]

$$\langle\xi_\beta(\mathbf{r},t)\xi_\gamma(\mathbf{r}',t)\rangle = \frac{2k_BT}{\gamma_1}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\delta_{\beta\gamma}, \tag{13}$$

$$\langle\Omega_{\alpha\beta}(\mathbf{r},t)\Omega_{\delta\gamma}(\mathbf{r}',t')\rangle = 2k_BTM_{\alpha\beta\delta\gamma}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{14}$$

$$\langle\partial_\alpha\Omega_{\alpha\beta}(\mathbf{r},t)\,[\partial_\delta\Omega_{\delta\gamma}(\mathbf{r}',t)]\rangle = -2k_BTL_{\beta\gamma}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{15}$$

where k_B is Boltzmann's constant and T the temperature. The noise sources ξ_β and $\partial_\alpha\Omega_{\alpha\beta}$ are uncorrelated.

3. INITIAL STAGES

We now specialize Eqs. (4) and (5) to the particular geometry considered in this model and introduce a minimal coupling approximation in which the $\mathbf{n}$ dependence of the operators $\Gamma_{\beta\gamma}(\mathbf{n})$ and $L_{\beta\gamma}(\mathbf{n})$ is approximated by substituting $\mathbf{n}$ by the initial orientation $\mathbf{n}^0$. It should be stressed that this procedure retains only the initial coupling between $\mathbf{n}$ and $\mathbf{v}$, which is essential in the initial stages of the reorientation, but keeps the full nonlinearity in the director's dynamic which is present in the dissipative term $\delta F/\delta n_\beta$ in Eq. (4). Since all elastic constants have typical values of the same order of magnitude for thermotropic nematics, for simplicity we also make the equal elastic constants approximation, $K \equiv K_1 = K_2 = K_3$, and assume that the incident field is of the form

$$\mathbf{E}(t) = \mathbf{E}\cos(\omega t), \tag{16}$$

where $\mathbf{E}$ denotes a constant polarization.

Under these approximations the dynamical equations (4) and (5) become

$$\partial_t\theta(z,t) \equiv \gamma_1^{-1}\left(K\partial_z^2\theta + \frac{\mathrm{i}}{8\pi}\varepsilon_0\varepsilon_\mathrm{a}|\mathbf{E}|^2\sin\beta\cos\beta\right) + \frac{\lambda+1}{2}\partial_z v_x + \xi_x(z,t), \tag{17}$$

$$\rho\partial_t v_x(z,t) = \nu_3\partial_z^2 v_x - K\frac{\lambda+1}{2}\partial_z^3 n_x + \partial_z\Omega_{zx}(z,t). \tag{18}$$

Here $\partial_t \equiv \frac{\partial}{\partial t}$, $\partial_{x_i} \equiv \frac{\partial}{\partial x_i}$ $(i = x, z)$, β is the incidence angle and $|\mathbf{E}|^2$ is proportional to the intensity of the applied field, $I = (c|\mathbf{E}|^2/8\pi)$, where c is the speed of light in vacuum and ε_0 is the permittivity of free space. Note that in writing these equations we have also assumed spatial homogeneity in the x–direction so that the relevant component of the shear backflow is $v_x(z,t)$. If the aspect ratio of the cell is chosen in such a way that the transverse dimension z is small as compared to x, this is a reasonable assumption.

To proceed further, we make the approximation of negligible inertia in which the director field is considered to be a slow variable and the velocity field is assumed to follow instantaneously the director's dynamics [14]. It amounts to eliminate v_x from the deterministic parts of Eqs. (17)–(18) and is accomplished by setting $\partial_t v_x = 0$ in Eq. (18). Integrating the resulting equation once with respect to z, substitution into Eq. (17) and taking the approximation of small angles $(\theta \to 0)$, we arrive at the following reorientation equation with hydrodynamic effects:

$$\partial_t\theta(z,t) \equiv K\left[\gamma_1^{-1} + \frac{(\lambda+1)^2}{4\nu_3}\right]\partial_z^2\theta + \gamma_1^{-1}\frac{\varepsilon_0\varepsilon_\mathrm{a}}{8\pi}E_xE_z + \frac{\lambda+1}{2\nu_3}\Omega_{zx}(z,t) + \xi_x(z,t). \tag{19}$$

This stochastic equation describes the initial stages of the reorientation process; however, even with the simplifications made, it remains rather complicated. To simplify it further, it is convenient to examine the behavior of the Fourier modes of $\theta(z,t)$ by using the

following Fourier transforms compatible with the imposed boundary conditions:

$$\theta(z,t) = \sum_{m=0}^{\infty} \theta_m(t) \cos[(2m+1)\pi z/d], \tag{20}$$

with similar transformations for the noise terms $\xi_x(z,t)$ and $\Omega_{zx}(z,t)$. The index m identifies the discrete modes in the z-direction and this transformation leads to the following stochastic amplitude equation:

$$d_t\theta_m(t) = \frac{W_m}{\overline{\gamma}_1}\theta_m(t) + \gamma_1^{-1}\frac{\varepsilon_0\varepsilon_a}{8\pi}E_xE_z + \eta_m(t). \tag{21}$$

Here $\overline{\gamma}_1$ is an effective viscosity coefficient which contains the effect due to the hydrodynamic coupling in the dynamics, *i.e.*,

$$\overline{\gamma}_1 = \gamma_1 \frac{1}{1+\alpha_2^2/(\nu_3\gamma_1)}, \tag{22}$$

with $\alpha_2 = -\frac{\lambda+1}{2}\gamma_1$, where α_2 is a Leslie coefficient. $W_m/\overline{\gamma}_1$ is the amplification factor of the fluctuations during the transient dynamics associated with the switching on of the electric field. The explicit form of W_m is

$$W_m = -K(2m+1)^2(\Pi/d)^2. \tag{23}$$

It should be pointed out that the amplification factor $W_m/\overline{\gamma}_1$ contains two well differentiated contributions. On the one hand, W_m comes from the form of the free energy; it is therefore independent of the dynamics and of the hydrodynamic couplings. On the other hand, $\overline{\gamma}_1$ contains the dynamic effects originated in the backflows.

The relaxation time of the different modes is given by $\tau_m = -\overline{\gamma}_1/W_m$; therefore the mode $m = 0$ has the larger relaxation time and is the dominant mode. Actually, the values of τ_m define the time scale on which our description of the early stages of the reorientation is valid. For instance, for CBOOA, τ_m can be estimated as 0.986 s and for PAA is approximately 1.45 s, which are times accessible to experiment.

The noise source $\eta_m(t)$ is the following linear combination of the Fourier amplitudes $\xi_{m,x}(t)$ and $\Omega_{m,zx}(t)$ of the original noise sources:

$$\eta(t) \equiv \xi_{m,x}(t) - \rho(\lambda+1)/2\Omega_{m,zx}(t). \tag{24}$$

Thus, it is still Gaussian with zero mean and is completely characterized by its correlation $\langle\eta(t)\eta(t')\rangle$. It can be easily shown that it obeys a fluctuation-dissipation relation similar to Eq. (13) but with the effective viscosity $\overline{\gamma}_1$,

$$\langle\eta_m(t)\eta_{m'}(t')\rangle = 2\frac{2k_BT}{\overline{\gamma}_1 V}\delta_{m,m'}\delta(t-t'). \tag{25}$$

This results show that within the approximations made, the whole effect of the coupling between the director and velocity fields is to replace γ_1 by $\overline{\gamma}_1$.

Now, since the critical field can be estimated as $E_c = (\pi/d)(4\pi K/\varepsilon_a)^{1/2}$ [21], to be consistent with the minimal coupling approximation we assume that the external field intensity is just above threshold and that only the dominant mode $m = 0$ is excited. It should be stressed that the reduction of Eqs. (17)–(18) to a normal-form amplitude equation with the inclusion of noise terms is the key idea of our development. This reduces the problem posed by a stochastic partial differential equation, [Eqs. (17)–(18)], to an ordinary, linear stochastic differential equation for a scalar variable [Eq. (21)]. This method is of general validity and can be applied to a variety of similar problems [22].

4. DIELECTRIC RESPONSE

The total electric dipole moment $\mathbf{p}(t)$ of a rodlike nematic polymeric solution consists of two parts, namely, a permanent dipole $\mathbf{p}_p$ and an induced dipole $\mathbf{p}_i$

$$\mathbf{p} = \mathbf{p}_p + \mathbf{p}_i = \mu\mathbf{u} + \underline{\underline{\alpha}} \cdot \mathbf{E}(t), \tag{26}$$

where $\mathbf{E}(t)$ is the external field, μ is the magnitude of the permanent dipole moment and $\underline{\underline{\alpha}}$ is the polarizability tensor which can be written in terms of the parallel and perpendicular polarizabilities as

$$\alpha_{ij} = \tfrac{1}{3}(\alpha_{||} + 2\alpha_{\perp})\delta_{ij} + \Delta\alpha(u_i u_j - \delta_{ij}/3), \tag{27}$$

where $\Delta\alpha \equiv \alpha_{||} - \alpha_{\perp}$ denotes the polarizability asymmetry. Now, according to the molecular theory of Doi and Edwards for nematic polymeric solutions [23], the vector $\mathbf{u}$ in Eqs. (26) and (27) should be interpreted as a unit vector tangent to the primitive chain. This suggests that for a rodlike nematic, $\mathbf{u}$ describes the director $\mathbf{n}$ vector field itself. Since $\mathbf{n}$ is a hydrodynamic variable, this identification implies that the dipolar moment is also a local variable described in terms of a polarizability local density of the form (27) but replacing $\mathbf{u}$ with $\mathbf{n}$. This has the important consequence that the reorientation of rodlike nematic liquid crystals can now be studied in terms of the stochastic dynamics of $\mathbf{n}$. Actually, the quantity that is measured in dielectric relaxation experiments is the average value of the total dipole moment $\mathbf{p}$ over the distribution of reorientation angles,

$$\langle\mathbf{p}\rangle = \mu\langle\mathbf{n}\rangle + \langle\underline{\underline{\alpha}}\rangle \cdot \mathbf{E}(t). \tag{28}$$

Then, using Eq. (27) $\langle\mathbf{p}\rangle$ can be expressed in terms of the moments $\langle\mathbf{n}\rangle$ and $\langle\mathbf{nn}\rangle$. However, in the limit of small orientation and incidence angles considered in the previous section, this general expression reduces to

$$\langle p_x(z,t)\rangle = (\mu + \Delta\alpha\, E\beta\cos\omega t)\langle\theta(z,t)\rangle + E\beta\cos\omega t(\Delta\alpha\langle\theta^2(z,t)\rangle\alpha_{||}), \tag{29}$$

$$\langle p(z,t)\rangle = \mu + E\cos\omega t(\alpha_{||} + \Delta\alpha\beta\langle\theta(z,t)\rangle). \tag{30}$$

Thus, it is clear that in order to calculate $\langle\mathbf{p}\rangle$ it is necessary to evaluate first the moments $\langle\theta(z,t)\rangle$ and $\langle\theta^2(z,t)\rangle$ from the stochastic amplitude Eq. (21) and Eq. (25). For given θ_0

and for the dominant mode $m = 0$, these equations yield

$$\langle\theta(t)\rangle \equiv \overline{\langle\theta(z,t)\rangle} = \frac{2}{\pi}\theta_0 e^{-t/\tau} \tag{31}$$

and

$$\langle\theta^2(t)\rangle \equiv \overline{\langle\theta^2(z,t)\rangle} = A\tau + (\theta^2 - A\tau)e^{-2t/\tau}, \tag{32}$$

where τ is the relaxation time for the dominant mode $\tau \equiv \overline{\gamma}_1 d^2/K\pi^2$ and $A \equiv 2k_B T/\overline{\gamma}_1$. The overbar in Eqs. (31) and (32) denotes an spatial average over the transverse coordinate z and k_B is Boltzmann's constant. It should be remarked that the hydrodynamic backflows produced by the reorientation do indeed affect the relaxation time τ through the effective viscosity $\overline{\gamma}_1$ given by Eq. (22).

On the other hand, the dielectric function is defined by [24]

$$\left(\frac{\varepsilon^*(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)}\right)_{ij} = \delta_{ij} - i\omega \int_0^\infty dt\, e^{-i\omega t}\psi_{ij}(t), \tag{33}$$

where $\psi_{ij}(t)$ is the normalized relaxation function. It is well known that in the high temperature limit and for the linear response regime [25], $\psi_{ij}(t)$ may be identified with the electric dipole equilibrium correlation function

$$\psi_{ij}(t) = \frac{\langle p_i(t)p_j(0)\rangle}{\langle p_i(0)p_j(0)\rangle}, \tag{34}$$

where $p_i(t)$ is the electric dipole moment of the system averaged over z and the angular brackets denote an equilibrium average. The electric dipole correlation function is defined in terms of the conditional average of the dipole moment as

$$\langle p_i(t)p_j(0)\rangle = \langle p_i(0)\langle p_j(t)\rangle_{p_i(0)}\rangle^{\text{eq}}. \tag{35}$$

Now, as mentioned in Sect. 1, for the nematic cell considered and under the approximations made in the last section, it is to be expected that the dielectric function perpendicular to the director axis, $\varepsilon_\perp^*(\omega)$, should depend only on $\psi_{xx}(t)$. Then, if we first calculate $\langle p_x(t)\rangle_{p_x(0)}$ from Eqs. (29), (31) and (32), and if the resulting expression is then substituted into Eq. (34) we arrive at

$$\psi_{xx}(t) = (A_1 + A_2\cos\omega t)e^{-t/\tau} + (A_3\cos\omega t)e^{-2t/\tau}. \tag{36}$$

Here the coefficients A_i, $i = 1, 2, 3$, are well defined functions of the material parameters and of the amplitude E of the field and their explicit expressions are given by

$$A_1 \equiv \frac{A_1'}{A} = B_0\left[(\alpha_\perp + \Delta\alpha\,\theta_0^2/2)E\beta + (2\Delta\alpha\theta_0/\pi)E + B_0\right], \tag{37}$$

$$A_2 \equiv \frac{A_2'}{A} = B_0^2\Delta\alpha\, E/\mu, \tag{38}$$

$$A_3 = \frac{A_3'}{A} = B_0\Delta\alpha E B_2, \tag{39}$$

$$A = B_0\left\{B_0 + E\left[2\alpha_\perp\beta + (B_1 + \theta_0^2/2)\beta\Delta\alpha + B_2\Delta\alpha + 4\theta_0\Delta\alpha/\pi\right]\right\}, \tag{40}$$

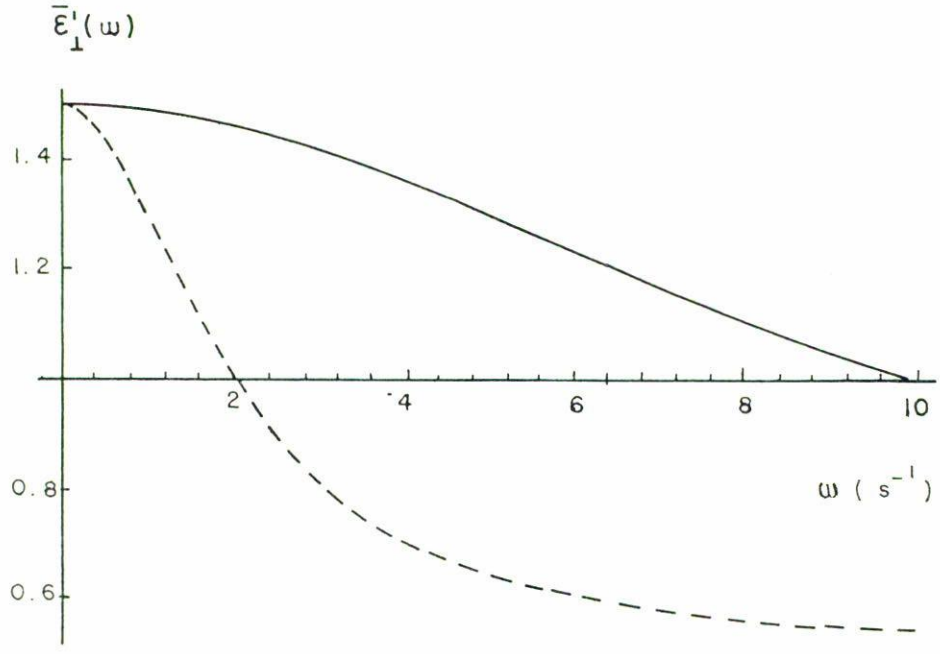

FIGURE 2a. Normalized real part of the dielectric constant, $\bar{\varepsilon}'(\omega) \equiv \varepsilon'(\omega)/[\varepsilon(0) - \varepsilon(\infty)]$, as defined by Eq. (46), plotted *vs.* ω for PAA at 125°C. The material parameters for PAA were taken from [28, 29]. $E = 10^{-3}$ din/esu and $d = 10^{-3}$ cm. (—) corresponds to the presence of backflows and (- - -) when they are totally neglected.

where we have identified

$$B_0 = \frac{2\mu\theta_0}{\pi}, \tag{41}$$

$$B_1 = \frac{k_B T}{\bar{\gamma}_1 V}\tau, \tag{42}$$

$$B_2 = \frac{\theta_0^2}{2} - B_1, \tag{43}$$

$$\theta_0 = \left(\frac{2k_B T}{VK}\right)^{1/2} \frac{d}{\pi}. \tag{44}$$

From the above equations follows that in the strictly linear response regime, where Eq. (34) is independent of the field, Eq. (36) reduces to a single relaxation exponential $\psi_{xx}(t) \cong A_1 \exp(-t/\tau)$, in agreement with Debye's description.

On the other hand, it is important to point out that when the system relaxes towards to a new equilibrium state through the reorientation process, vibration mechanisms inherent to the system may force it to oscillate harmonically with a certain characteristic frequency [26, 27]. However, since it has been suggested that this effect is significant only for high frequencies [27] and since in this work we only consider low frequencies, in deriving Eq. (36) we have entirely neglected this possibility. It should also be emphasized that

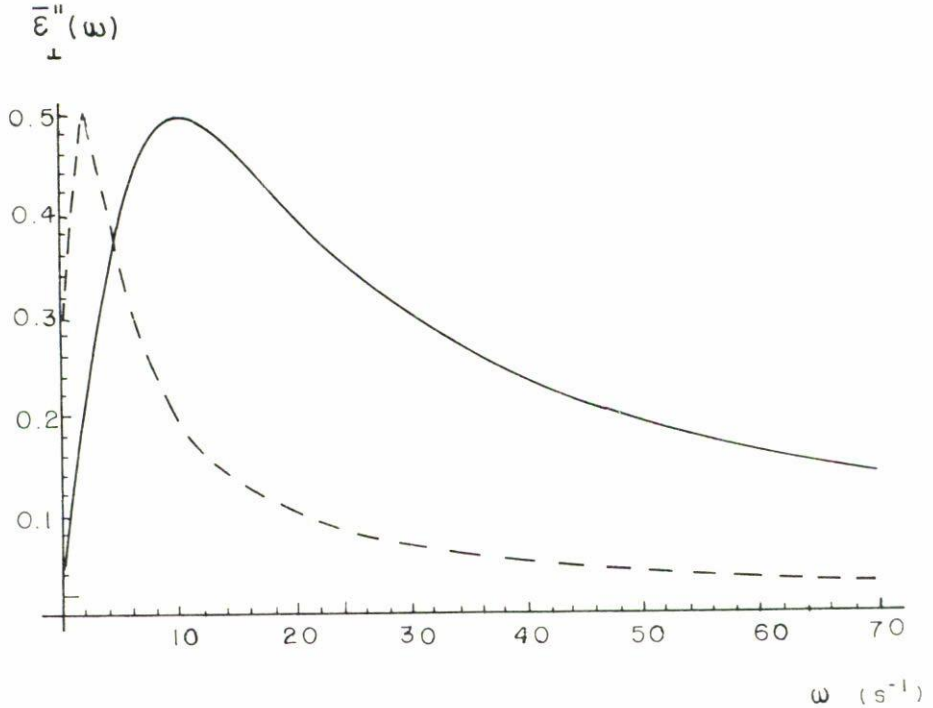

FIGURE 2b. The same as in Fig. 2a for the loss modulus $\bar{\varepsilon}''(\omega) \equiv \varepsilon''(\omega)/[\varepsilon(0) - \varepsilon(\infty)]$.

the correlation function given by Eq. (36) is essentially the product of an exponential function times an harmonic one. This form agrees with the one assumed by Kubo [26] for the description of the dielectric relaxation of solutions of polar molecules, although in our case the presence of two relaxation times, $\tau = \overline{\gamma}_1 d^2/K\pi^2$ and $\tau/2$ indicates a non-Debye effect. Furthermore, our expression (36) contains explicitly the effect of hydrodynamic flows (backflows) in the relaxation through the presence of the effective viscosity $\overline{\gamma}_1$. The real and imaginary parts of the dielectric function $\varepsilon^*_{\perp}(\omega) \equiv \varepsilon'_{\perp}(\omega) - i\varepsilon''(\omega)$, can now be calculated from Eqs. (33) and (36) to the same order of approximation as $\psi_{xx}(t)$. This yields

$$\varepsilon'_{\perp}(\omega) = \varepsilon_{\perp}(0) - [\varepsilon_{\perp}(0) - \varepsilon_{\perp}(\infty)] \left\{ (A_1 + A_3/4) \frac{\omega^2}{\omega^2 + \tau^{-2}} + \frac{A_2}{4} \frac{\omega^2}{\omega^2 + (2\tau)^{-2}} \right\} \tag{45}$$

and

$$\varepsilon''_{\perp}(\omega) = [\varepsilon_{\perp}(0) - \varepsilon_{\perp}(\infty)] \left\{ A_1 \frac{\omega}{\tau} \frac{1}{\omega^2 + \tau^{-2}} + \frac{A_2}{2} \omega\tau \frac{2(2\tau)^{-2} - \omega^2}{\omega^2 + (2\tau)^{-2}} + \frac{A_3}{4} \omega\tau \frac{2\tau^{-2} + \omega^2}{\omega^2 + \tau^{-2}} \right\}. \tag{46}$$

For typical values of the material parameters of PAA [28, 29], the above expressions are evaluated as functions of ω in the low frequency range 0.7–200 Hz both, for the case when

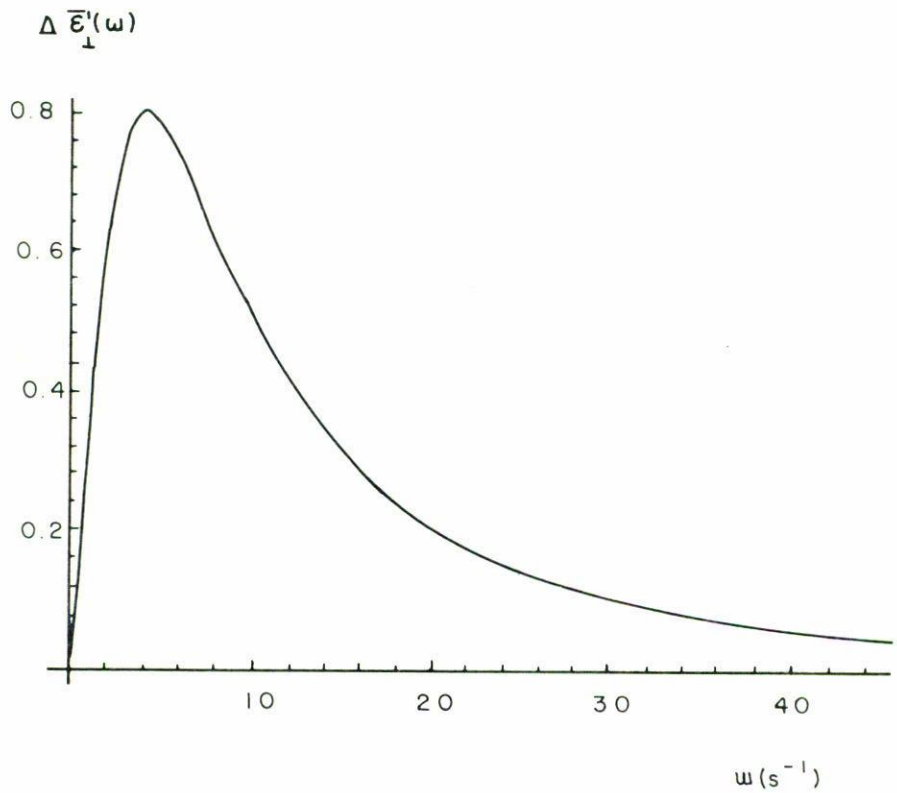

FIGURE 3a. The difference $\Delta\bar{\varepsilon}'_{\perp}(\omega) \equiv \Delta\varepsilon'_{\perp}(\omega)/[\varepsilon_{\perp}(0) - \varepsilon_{\perp}(\infty)]$ as a function of the frequency.

backflows are present and for a quiescent nematic. These plots are shown in Figs. 2. As can be seen from Fig. 2a, backflows induce a slower decay of $\varepsilon'_{\perp}(\omega)$. The same occurs for the loss modulus $\varepsilon''_{\perp}(\omega)$ as shown in Fig. 2b, but the maximum shifts towards higher frequencies. However, it is perhaps more instructive to plot the differences between these values, $\Delta\varepsilon'_{\perp}(\omega) \equiv \varepsilon'^{\,H}_{\perp}(\omega) - \varepsilon'^{\,0}_{\perp}(\omega)$ and $\Delta\varepsilon''_{\perp}(\omega) \equiv \varepsilon''^{\,H}_{\perp}(\omega) - \varepsilon''^{\,0}_{\perp}(\omega)$, which are given in Fig. 3. The superscripts ^{H} and ^{0} denote, respectively, the values with and without backflow effects. From these curves it can be clearly seen that the hydrodynamic flows induced by the reorientation process produce a significant and in principle measurable effect. The maximum difference may be as high as 75% for $\Delta\varepsilon'_{\perp}(\omega)$ and 40% for $\Delta\varepsilon''_{\perp}(\omega)$. This then shows that in the low frequency range 0.7–100 Hz, the presence of backflows may induce an important change in the dielectric functions in the transverse direction of a thermotropic nematic.

This effect induced by backflows in the dielectric constants is less noticeable in the transverse Cole-Cole plot. Indeed, in Fig. 4 we show these plots for PAA when there is no flow and when backflows are present. The curvature of this plot changes due to backflows departing from a semicircle (Debye), although the difference with respect to the case without flow is less noticeable that in Fig. 2.

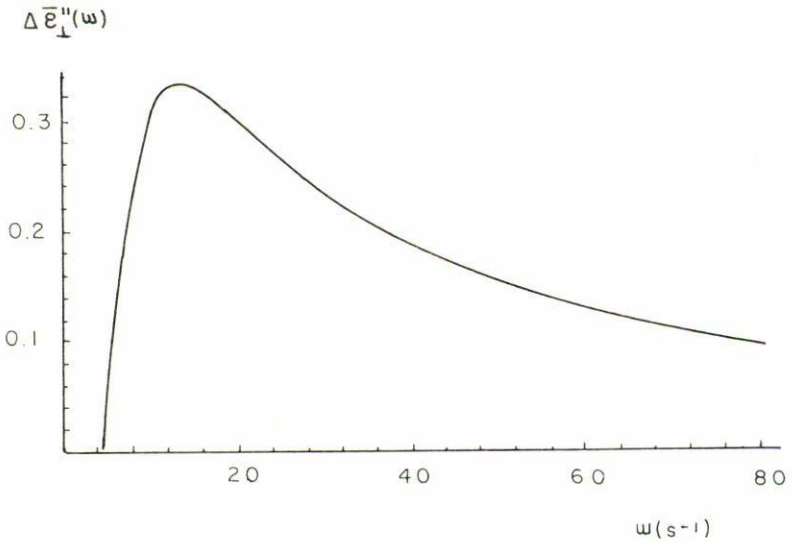

FIGURE 3b. The same as in Fig. 3a for $\Delta\varepsilon''_{\perp}(\omega) \equiv \Delta\varepsilon''_{\perp}(\omega)/[\varepsilon_{\perp}(0) - \varepsilon_{\perp}(\infty)]$.

5. CONCLUDING REMARKS

There are several aspects of the results of the previous sections that deserve further elaboration.

First, it is important to stress once again that the identification of the unit vector **u** tangent to the polymeric chain in the molecular theory of Doi and Edwards, with the nematic's director, allowed us to use a stochastic formulation of the nematodynamic equations to describe the dielectric response in terms of the stochastic dynamics of reorientation. Within this context, we have also shown that these hydrodynamic couplings, which are always present in the initial stages of the reorientational dynamics, induce significant changes on the dielectric moduli $\varepsilon'_{\perp}(\omega)$ and $\varepsilon''_{\perp}(\omega)$ of the nematic. These changes may be as high as 75% and 40%, respectively, even for a low field frequency interval between 0.7 Hz and 100 Hz. In principle, such a large effect should be detectable, but whether or not it can be measured remains to be assessed.

Secondly, it is also important to stress that our dynamical description is restricted to the initial nonstationary stages of the reorientation process. In Sect. 2 we assumed small deviation angles which lead to the linearized equations (17) and (21) which in turn allowed us to carry out an analytical treatment. However, strictly speaking, close to equilibrium, this class of nonequilibrium states do not comply with the Onsager's hypothesis on the regression of the fluctuations. This may be seen already from Eq. (20) which implies that the fluctuation $\langle\theta^2(z,t)\rangle - \langle\theta(z,t)\rangle^2$ do not decay as the average. In spite of this, we have used as a first approximation, several results that, admittedly, are only valid for the linear response regime. An example of this situation is the use we have made of the expression relating the dielectric and relaxation functions including terms linear in the field. This lead us to a non-Debye expressions for the dielectric constant and to the

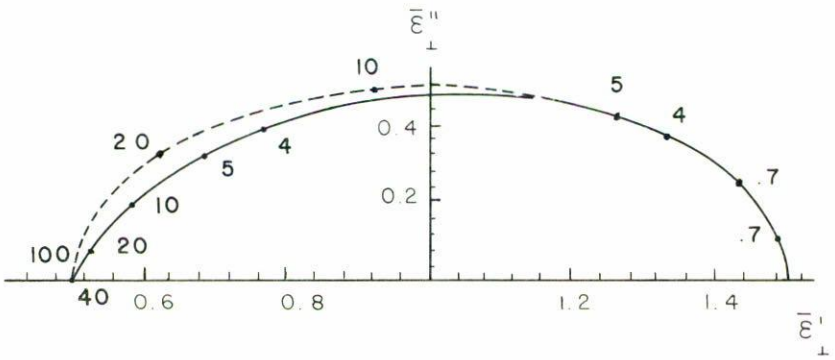

FIGURE 4. Transverse Cole-Cole plot for the real and imaginary parts of $\bar{\varepsilon}_\perp(\omega) \equiv \varepsilon_\perp(\omega)/[\varepsilon_\perp(0) - \varepsilon_\perp(\infty)]$, as given by Eqs. (45) and (46). (—) denotes the results with hydrodynamics effects and (- - -) when backflows are ignored. The dots on the curves denote the frequencies given in Hz.

asymmetric Cole-Cole diagrams of the previous section. To justify the validity of this approximation it is important to mention, on the one hand, that the predictions of our model are in qualitative agreement with experimentally measured Cole-Cole plots [5, 6]. On the other hand, the form (36) for the correlation function, which is essentially the product of an exponential function times an harmonic one, agrees with the one assumed by Kubo on the basis of a linear response theory description of dielectric relaxation of solutions of polar molecules [24, 26]. It is also worth pointing out that predictions such as an electric field dependent dielectric constant for the nonequilibrium states considered, are in agreement with the predictions of molecular theories [23], where the birefringence of nematics is a second order effect in the electric field [30].

Thirdly, it should be mentioned that our stochastic description in terms of a linear Langevin type amplitude equation is fully consistent with descriptions based on equivalent equations such as the Fokker-Planck equation [31]. However, a complete description of the whole reorientation relaxation is described by highly nonlinear equations [30, 32] of the form

$$\gamma_1 \frac{\partial \theta(z,t)}{\partial t} = K \frac{\partial^2 \theta}{\partial z^2} + \frac{\varepsilon_a}{8\pi}[\sin 2\theta(|E_x|^2 - |E_z|^2) - 2E_x E_z^* \cos 2\theta] = 0, \tag{47}$$

where $*$ denotes complex conjugate. It is apparent that the consideration of the whole reorientation process would substantially complicate the analysis. This is due, on the one hand, to the nonlinear character of the equation and, on the other hand, to the fact that the dynamics of the field is coupled with that of the nematic. Although even in this case an analytical treatment is feasible [33], the simplicity of the model is lost. Furthermore, to construct an amplitude equation associated with this highly nonlinear equation is not a trivial matter due to the inconsistencies that may arise between nonlinearities and fluctuations in this case [34]. However, the predictions of the proposed linearized model are indicative as to what to expect for the complete process. Our results show a tendency in the dielectric response due to backflow effects. Since to our knowledge,

descriptions of dielectric relaxation in liquid crystals with hydrodynamic coupling are practically inexistent, our description suggests new experiments to be performed.

Finally, it should be stressed that beyond the linearized regimes considered here, there is no reason to expect that the lowest order mode will dominate the dynamics. In this case *all* the modes should be included in the description of the reorientation dynamics and *all* must contribute to the dielectric response. The analysis of this situation is a much more complicated problem than the one considered here and should take into account the coupling and competition among all the Fourier modes. A way to take into account this features is to use renormalization group methods. This generalization is presently under way [35].

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