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Rotational viscosity, dynamic phenomena, and dielectric properties in a long-chain liquid crystal: NMR study and theoretical treatment

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The rotational diffusion constants $D_\perp$ and $D_\parallel$, rotational viscosity coefficients γ_i $(i=1,2)$, the orientational correlation times τ_{mn}^L, and the dielectric permittivities for nematic liquid crystals (NLCs) are investigated. γ_i are calculated by a combination of existing statistical-mechanical approach (SMA) and NMR relaxation theory, both based on a rotational diffusion model. In the rotational diffusion model, it is assumed that the reorientation of an individual molecule is a stochastic Brownian motion in a certain potential of mean torque. According to the SMA, γ_i are found to be a function of temperature, density, rotational diffusion constant for tumbling motions, and the orientational order parameters. The order parameters and rotational diffusion constant are obtained from an analysis of NMR measurements. Reasonable agreement between the calculated and experimental values of γ_i for 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) is obtained. The orientational correlation times, and the longitudinal and transverse components of the real $\chi_j'(\omega)$ and imaginary $\chi_j''(\omega)$ $(j=\parallel,\perp)$ parts of the complex susceptibility tensor for 8OCB molecules in the nematic phase are also obtained.

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I. INTRODUCTION

Liquid crystals are characterized by a long-range orientational order among mesogenic molecules whose structures usually consist of a rigid central core to which attached one or more flexible hydrocarbon chains. It is known that molecular flexibility is crucial in determining the physical properties of liquid crystals (LCs) [1]. Recent experimental and theoretical studies have shed significant light on the role of internal degrees of freedom on the NMR observables, notably measurements of deuterium quadrupole splittings [1–3] and spin-lattice relaxation times [1–8] in mesogens. The theoretical treatment of dynamical processes of flexible molecules in an anisotropic medium is not an easy task [1–5]. This often requires a certain number of simplifying assumptions which may only be justified by comparison between the model predictions and experiments. But there is an additional avenue which would allow us to further examine the validity of our models; it is to carry out a statistical-mechanical treatment of the coupling between macroscopic LC properties and molecular structure, and is then followed by comparisons of, for example, rotational viscosity and dielectric susceptibility coefficients with the experimental data. This implies that the rotational diffusion constants and the set of orientational order parameters can be obtained from NMR measurements of quadrupolar splittings and deuteron Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times in LCs as a function of temperature. Using these results for calculations, in the framework of the statistical-mechanical approaches (SMAs) [9–13], the autocorrelation times, rotational viscosity and dielectric properties of any realistic mesogenic molecules, such as 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB), can be studied in the nematic phase.

In this work, we use information obtained from an analysis of deuteron spin-lattice relaxation times T_{1Z} and T_{1Q} measurements for a chain-deuterated 8OCB-d_{17} sample which shows a nematic (N) and smectic A (SmA) phase upon decreasing the temperature [8]. From these relaxation times, the extraction of the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ is possible, where $\omega_0/2\pi$ is the Larmor frequency. These spectral parameters at different carbon sites allow us to separate the internal conformational changes in the molecules from the global molecular reorientations. In particular, the measured spectral densities of chain deuterons should contain dynamical information on reorientation of molecules as well as internal rotations of various carbon-carbon bonds in their chains. The reorientation of the molecules in LCs can be described by the rotational diffusion model [14,15], which assumes a stochastic Brownian process for molecular reorientations in which each molecule moves in time as a sequence of small angular steps caused by collisions with its surrounding molecules and under the influence of a potential of mean torque set up by these molecules. Each molecule is characterized by a rotational diffusion tensor whose principal elements $(D_{xx}=D_{yy}=D_\perp, D_{zz}=D_\parallel)$ are determined in a frame fixed on the molecule. When dealing with molecules with internal degrees of freedom, the number of different conformations in the chain of the molecule can be generated using the rotameric state model [16]. It is customary to treat molecular dynamics of flexible molecules using a decoupling model [6,17,18], in which conformational transitions within the chain are assumed not to depend on the reorientation of the entire molecule. The rotational diffusion tensor is assumed to be the one for an "average" conformer. The model allows us to obtain $D_\perp$ and $D_\parallel$ as function of the temperature.

On the other hand, in contrast to isotropic liquids, where a

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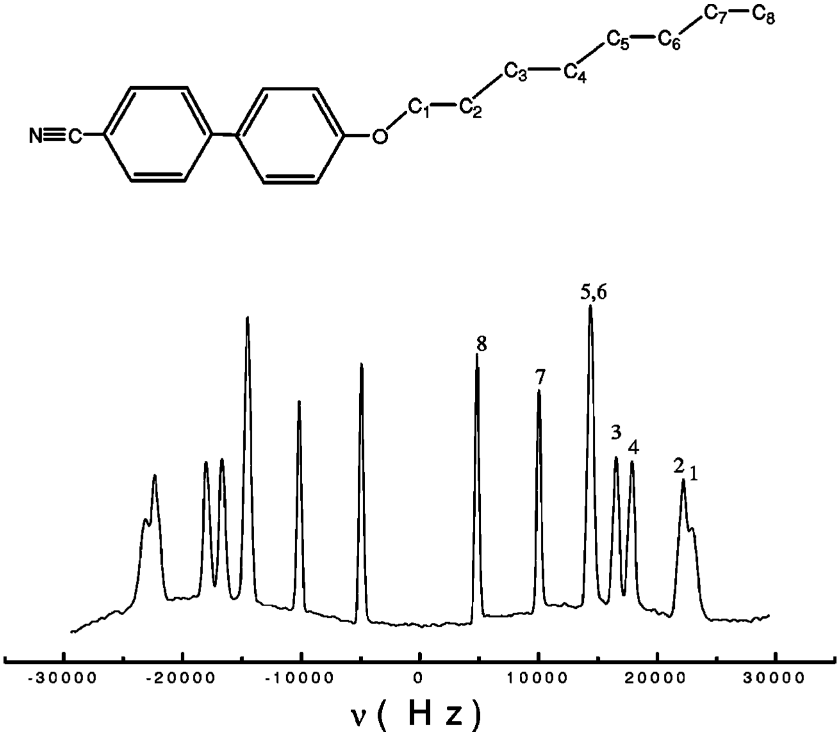

FIG. 1. A typical deuteron NMR spectrum of 8OCB-d_{17} showing the peak assignment, together with the chemical formula of 8OCB.

single rotational viscosity coefficient is sufficient to characterize the flow properties, liquid crystals, and other anisotropic systems require several such coefficients. A common approach for determination of viscosity coefficients uses statistical-mechanical theory [9–13,19–21] and is based on the rotational diffusion model [22]. In such a treatment, the system is determined by the time-dependent single-particle orientational distribution function (ODF) governed by a Fokker-Planck-type kinetic equation. Recently, we investigated [12] the validity of various theories where the rotational viscosity coefficients were expressed as certain polynomials of equilibrium orientational order parameters and inversely proportional to the rotational self-diffusion coefficient in the nematic phase.

Measurements of the dielectric constants of nematic liquid crystals (NLCs) have been a subject of interest from the beginning of investigations of these materials [23–29], and continue to do so. The reason why many reports are still concerned with the dielectric constants of well-known materials such as 8OCB [24,25] is that the measurements are far from being trivial. The outline of this article is as follows. A brief description of the deuteron NMR study of molecular order and dynamics is given in Sec. II. The statistical-mechanical approaches for the rotational viscosity and numerical calculations for γ_i $(i=1,2)$ are given in Sec. III. A description of the theory of dielectric relaxation is given in Sec. IV. Conclusions are summarized in Sec. V

II. DEUTERON NMR STUDY OF MOLECULAR DYNAMICS

Molecular motions have the effect of modulating the anisotropic part of magnetic interactions, producing a random time-dependent perturbation which ultimately induces nuclear spin relaxation. In anisotropic media, the magnetic interactions are not averaged to zero. Hence NMR spectral patterns will reflect ordering of molecules in such media. In this section, a brief description of essential results from a deuteron NMR study of 8OCB [8] is given to aid the discussion of rotational viscosities and dielectric relaxation below. The details in data analysis using the decoupled model for the correlated internal motions can be found in Ref. [8]. The rotational diffusion model [30,31] is employed to describe small step diffusions of molecules in a potential of mean torque. Figure 1 shows a typical deuteron NMR spectrum of 8OCB-d_{17} together with its chemical formula. As seen in this figure, each distinct quadrupolar doublet can be assigned to a particular methylene deuterons and the smallest splitting arises from the end methyl deuterons. As 8OCB contains an alkyloxy chain, it has many distinct chain configurations. Using the additive potential method [1], the observed quadrupolar splittings were modeled to give the potential of mean torque experienced by each molecule. As a consequence, the second-rank order parameters of an ‘‘average’’ conformer were obtained at each temperature. This in turn gives the potential parameters a_{20} and a_{22} [30] in the second rank potential of mean torque

$$\frac{U(\beta,\gamma)}{k_B T}=a_{20}\left(\frac{3}{2}\cos^2\beta-\frac{1}{2}\right)+a_{22}\sqrt{\frac{3}{2}}\sin^2\beta\cos 2\gamma, \tag{1}$$

which is needed to solve the rotational diffusion problem. In addition, order parameters $\overline{P_{2L}}$ $(L=1,2,3,\dots)$ can easily be evaluated. Figure 2 summaries these order parameters in the nematic phase of 8OCB. Because of correlated internal bond rotations in the flexible alkyloxy chain, a decoupled

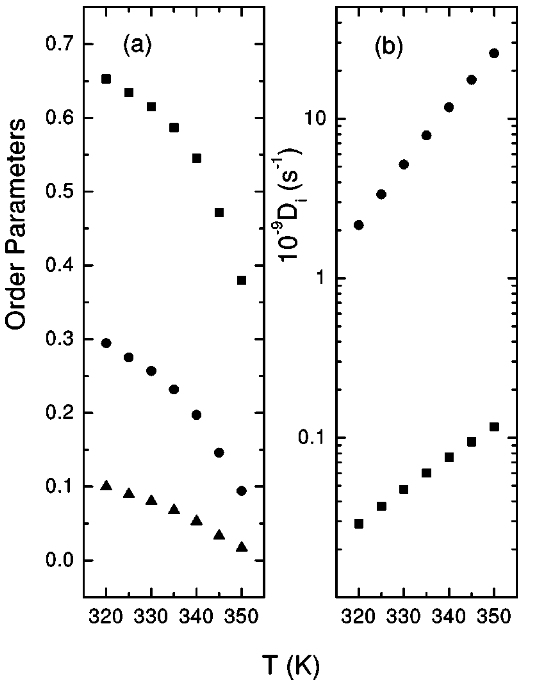

FIG. 2. Plots of order parameters $\overline{P_2}$ (squares), $\overline{P_4}$ (circles) and $\overline{P_6}$ (triangles) (a) and rotational diffusion constants $D_\parallel$ (circles) and $D_\perp$ (squares) (b) as functions of the temperature.

model [1,17,18] was used to give the spectral densities of methylene deuterons on C_i in 8OCB:

$$J_m^{(i)}(m\omega)=\frac{3\pi^2}{2}(q_{CD}^{(i)})^2\sum_n \sum_{n'} \sum_{k=1}^{577} \times\left(\sum_{l=1}^{577} d_{n0}^2(\theta_{M,Q}^{(i)l})\exp[-in\psi_{M,Q}^{(i)l}]x_l^{(1)}x_l^{(k)}\right) \times\left(\sum_{l'=1}^{577} d_{n',0}^2(\theta_{M,Q}^{(i)l'})\exp[-in'\psi_{M,Q}^{(i)l'}]x_{l'}^{(1)}x_{l'}^{(k)}\right) \times\sum_j \frac{(\beta_{mnn'}^2)_j[(\alpha_{mnn'}^2)_j+|\lambda_k|]}{m^2w^2+[(\alpha_{mnn'}^2)_j+|\lambda_k|]^2}, \tag{2}$$

where $q_{CD}^{(i)}=165\,\mathrm{kHz}$ is the quadrupolar coupling constant, $\theta_{M,Q}^{(i)l}$ and $\psi_{M,Q}^{(i)l}$ are the polar angles for the C_i-D bond of the conformer l in the molecular frame fixed on the molecular core, λ_k and $\mathbf{x}^{(k)}$ are the eigenvalues and eigenvectors from diagonalizing the transition rate matrix, and $(\alpha_{mnn'}^2)_j/D_\perp$, the decay constants, and $(\beta_{mnn'}^2)_j$, the relative weights of the exponentials in the correlation functions, are the eigenvalues and eigenvectors from diagonalizing the matrix of the rotational diffusion operator [30]. In the above equation, the number 577 is the number of distinct conformers available to the octyloxy chain in 8OCB. The transition rate matrix contains three phenomenological jump constants k_1, k_2, and k_3 for the so-called one-bond, two-bond, and three-bond motions, respectively. The rotation diffusion tensor is characterized by two principal values $D_\perp$ and $D_\parallel$ in the molecular frame, where $D_\parallel$ and $D_\perp$ are for rotation of the molecule about its long axis, and for rotation about one of its short axes, respectively. The rotational diffusion constants appear in Eq. (2) through the decay constants $(\alpha_{mnn'}^2)_j$. Again by modeling the observed spectral densities for carbons 1 to 7 at two different Larmor frequencies, both the rotational diffusion constants and jump rate constants were obtained. For completeness, we reproduce the $D_\perp$ and $D_\parallel$ values also in Fig. 2.

III. FORMULAS FOR THE ROTATIONAL VISCOSITY

The classical approach to the viscosity of LCs, in the framework of the Ericksen-Leslie theory [32,33], assumes that the flow properties can be described by six Leslie coefficients α_i $(i=1,\ldots,6)$ which satisfy the Parodi relation [34] $\alpha_2+\alpha_3=\alpha_6-\alpha_5$. Hence only five of the six coefficients α_i are independent. In the isotropic phase all α_i, except α_4, equal zero, and α_4 is the shear viscosity of an isotropic liquid. The coefficients $\gamma_1=\alpha_3-\alpha_2$ and $\gamma_2=\alpha_3+\alpha_2=\alpha_6-\alpha_5$ are called the rotational viscosity coefficients and play a crucial role in a number of applications (see, for example, Ref. [23]). They determine, in the absence of hydrodynamics flow, the dissipation of energy due to only the rotation of the director $\mathbf{n}$ under the action of external forces.

Recently, statistical-mechanical approaches (SMAs) for theoretical treatment of rotational viscosity [9–13,19–21] have been proposed. These theories are based on the rotational diffusion model [22]. These approaches rest also on the concept of treating of the phenomenological stress tensor [34] $\overline{\sigma}$ as an average of its microscopic equivalent σ based on an appropriate nonequilibrium orientational distribution function $f(\mathbf{u},t)$ in the form $\overline{\sigma}=\int d\mathbf{u}f(\mathbf{u},t)\sigma$, where $\mathbf{u}$ is the unit vector along the molecular symmetry axis. Under the assumption that microscopic molecular motion in the NLC can be considered as a rotational Brownian motion in an external mean potential U, the following kinetic Fokker-Planck equation determines the ODF f

$$\dot{f}-\nabla_u\cdot\left[fD_\perp\nabla_u\left(\log f+\frac{U}{k_BT}\right)\right] +\nabla_u\cdot[f\mathbf{M}\cdot\mathbf{u}+pf(\mathbf{E}-\mathbf{nn})\cdot\mathbf{W}\cdot\mathbf{u}]=0, \tag{3}$$

where k_B is the Boltzmann constant, T is the temperature, p is a particle geometric factor usually taken as $p=(a^2-1)/(a^2+1)$, a is the length-to-breadth ratio of the molecule, and $\mathbf{E}$ is a unit tensor, and M and W are the symmetric and antisymmetric parts of the flow velocity gradient $v_{i,j}=\partial v_i/\partial x_j$ [19,20]. The external mean potential in Eq. (3) is given by Eq. (1) except for simplicity in solving the above equation, we have set $a_{22}=0$. This is justified by the small values of molecular biaxiality found for 8OCB [8]. Note that the last two terms of Eq. (3) correspond to the molecular reorientations and the interaction between the low velocity gradient and the director, respectively. Four combinations of α_i, namely, α_1, $\alpha_2+\alpha_3$, α_4, and $\alpha_5+\alpha_6$ are connected with the symmetric part of the stress tensor σ_{ij}^{s}, whereas other two $\gamma_1=\alpha_3-\alpha_2$ and $\gamma_2=\alpha_2+\alpha_3$ with the asymmetric part σ_{ij}^{a} [34]. The average of the symmetric part of stress tensor $\overline{\sigma^s}$, in according with the Kuzuu-Doi method, [19] can be calculated exactly without solving the Fokker-Planck equation, and by just replacing the statistical averaging with nonequilibrium distribution function by the expression containing only the known equilibrium one. As a result, a set of microscopic expressions for the symmetric Leslie coefficients can be obtained [19]. Thus, the expression for the γ_2, in according with the Kuzuu-Doi (KD) method can be written as

$$\gamma_2=-\frac{k_B T_{\rho}}{D_{\perp}} p \overline{P}_2, \tag{4}$$

where $\rho=N/V$ is the number density of molecules.

On the other hand, a separate calculation of γ_1 requires the averaging of the antisymmetric part of the microscopic stress tensor, $\overline{\sigma^a}=\int d\mathbf{u} f(\mathbf{u},t)\sigma^a$. This can be done using an appropriate nonequilibrium ODF, determined by solving Eq. (3). In case of small velocity gradient, one can write f in the form $f=f_0(1+h)$, where $f_0=f_0(\mathbf{n}\cdot\mathbf{u})=f_0(\cos\beta)$ is the local equilibrium ODF and depends only on the polar angle β between the director and the molecular symmetry axis, and the stationary correction h

$$h=g_0\mathbf{nn}\colon\mathbf{M}+g_1\mathbf{ne}\colon\mathbf{W}+g_2\mathbf{ne}\colon\mathbf{M}+g_3\mathbf{ee}\colon\mathbf{M}, \tag{5}$$

where $\mathbf{e}$ is the unit vector perpendicular to the director, g_i are scalar functions dependent only on the polar angle β. We use the invariant multiple dot convention in $\mathbf{nn}\colon\mathbf{M}=n_i n_j M_{ji}$, where the convention of summing over repeated Cartesian indices is used.

According to the analysis based on the statistical-mechanical averaging of the microscopic stress tensor, γ_1 can be rewritten in the form [19,20]

$$\gamma_1=\int_0^{\pi} f_0(\cos\beta)\frac{\partial U}{\partial\beta} g_1(\beta)\sin\beta d\beta. \tag{6}$$

A particular form of $g_1(\beta)$ should be provided by the solution of the orientational Fokker-Planck equation [Eq. (3)], which governs the Brownian motion of a particle in the ''flowing'' anisotropic medium. In the stationary case, Eq. (3) can be transformed to linear, nonhomogeneous differential equations of second order for the function $g_1(\beta)$ [13,21]. The general solution $g_1(\beta)$ for Eq. (3) can be obtained by a numerical method, for example, using the second-order Runge-Kutta method [13].

Recently, a general method for calculations of the viscosity coefficients in biaxial NLC, based on the change in the Helmholtz free energy caused by the shear flow was proposed by Fialkowski [11]. The appropriate kinetic equation is also written in the approximation of the low velocity gradient field, which rotates each molecule with a certain average angular velocity. In the limiting case of vanishing biaxial order, the system becomes uniaxial and the expression for γ_1 can be rewritten in the form

$$\gamma_1=\frac{\rho k_B T}{D_{\perp}}\xi_1^F, \tag{7}$$

where

$$\frac{\xi_1^F}{\overline{P}_2^2}=p\frac{35}{5\overline{P}_2+16\overline{P}_4+14},$$

where $\overline{P}_4$ is the fourth-rank order parameter.

An efficient SMA based on the Zubarev nonequilibrium statistical operator [35] for the calculation of γ_1 in the uniaxial NLC was proposed by Nemtsov [10] and Zakharov [9]. The essence of this approach is that not only the autocorrelation of the microscopic stress tensor is considered as in Ref. [20], but also additional correlations of the stress tensors with the director and fluxes with the order parameter tensor are also taken into account. Calculations of these correlations in the NLC show that they give significant contributions to the viscosity coefficients [9,10]. It is so because there are interactions between the hydrodynamical flow of the fluid and the molecular orientations. As results, γ_1 can be found to be dependent on the temperature, density and a certain polynomials of $\overline{P}_2$ as

$$\gamma_1=\frac{k_B T_{\rho}}{D_{\perp}}\xi_1^{NZ}, \tag{8}$$

where

$$\frac{\xi_1^{NZ}}{\overline{P}_2^2}=\frac{9.54+2.77\overline{P}_2}{2.88+\overline{P}_2+12.56\overline{P}_2^2+4.69\overline{P}_2^3-0.74\overline{P}_2^4}.$$

Thus, according to Eqs. (4), (7), and (8), γ_i $(i=1,2)$ are found to be inversely proportional to the rotational diffusion constant $D_{\perp}$ in nematic liquid crystals.

The temperature dependences of the rotational viscosity coefficients for 8OCB are shown in Fig. 3. The experimental values were obtained by using the three Miesowicz and two Leslie coefficients (α_5,α_6) which were determined by direct measurements [36] in the temperature range corresponding to the nematic phase. The density ρ of 8OCB is equal to $1.8\times10^{15}\,\mathrm{m}^{-3}$. The KD, NZ, and Fiałkowski models were employed to estimate the theoretical values. Using Eqs. (4), (7), and (8) together with the parameters $D_{\perp}$ and $\overline{P}_{2L}$ $(L=1,2)$ determined from the NMR measurements, we obtained the viscosity values in close agreement with experiment.

IV. ORIENTATIONAL CORRELATION TIMES AND DIELECTRIC PROPERTIES

Rotational dynamics of molecules in an anisotropic phase can be described by the small step diffusion model [15,30,36]. In general, however, the rotational motion of an uniaxial molecule in a nematic phase is conveniently characterized using the orientational time correlation function (TCF):

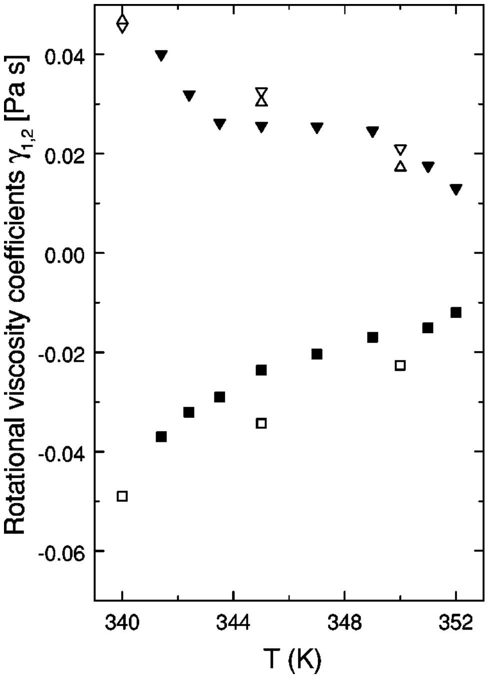

FIG. 3. Temperature dependence of γ_i ($i=1,2$) at fixed density, calculated using Eq. (4) (γ_2, open squares), Eq. (7) (γ_1, open down triangles), Eq. (8) (γ_1, open up triangles), and measured values γ_1 (solid triangles) and γ_2 (solid squares), respectively.

$$\Phi^L_{mn}(t)=\langle D^{L*}_{mn}[\Omega(0)]D^L_{mn}[\Omega(t)]\rangle, \tag{9}$$

where $D^L_{mn}(\Omega)$ is the Wigner rotational matrix element of rank L, and $\Omega=(\alpha,\beta,\gamma)$ is a set of time-dependent Euler angles, which define the orientation of the molecular axis system relative to the director frame. The projection index m is related to the director coordinate system, whereas molecular properties are dictated by the projection index n. Different spectroscopic methods provide correlation functions with different rank values of L. First rank ($L=1$) TCFs are relevant for infrared and dielectric spectroscopies, while TCFs with $L=2$ appear in the expressions for nuclear spin relaxation rates and Raman band shapes. The initial values of the TCFs $\langle D^{L*}_{mn}[\Omega(0)]D^L_{mn}[\Omega(t)]\rangle$ can be expressed in terms of the orientational order parameters [30]. Notice that the first rank TCFs at $t=0$ depend on $\overline{P}_2$ only, while for the second rank correlation function both $\overline{P}_2$ and $\overline{P}_4$ are required.

In general, the correlation functions may be written as infinite sums of decaying exponentials. Here, we employ a single exponential approximation [4,15] to give

$$\Phi^L_{mn}(t)=\Phi^L_{mn}(\infty)+[\Phi^L_{mn}(0)-\Phi^L_{mn}(\infty)]\exp\left(-\frac{t}{\tau^L_{mn}}\right). \tag{10}$$

In order to determine molecular reorientations, we need a model to give the correlation times τ^L_{mn} in terms of rotational diffusion constants [37–41]. Based on the short time expansion of the TCFs, an expression for the correlation times was proposed:

TABLE I. The orientational time correlations τ^L_{mn} for 8OCB molecules in the nematic phase.

T (K)	340	345	350
τ^1_{00}/ns	30.4	19.5	12.1
τ^2_{00}/ns	1.68	1.52	1.36
τ^1_{10}/ns	2.37	2.27	2.22
τ^1_{01}/ps	82.3	56	38.4
τ^1_{00}/τ^2_{00}	18.11	12.83	8.9

$$\frac{1}{\tau^L_{mn}}=c^L_{mn}D_\perp+n^2(D_\parallel-D_\perp), \tag{11}$$

where the coefficients c^L_{mn}, which depend on $\overline{P}_2$ and $\overline{P}_4$, are tabulated in Refs. [37–39]. We note that the τ^1_{00}, τ^1_{10}, and τ^2_{00} are solely determined by the tumbling motion

$$\tau^1_{00}=\left[D_\perp\frac{2-2\overline{P}_2}{1+2\overline{P}_2}\right]^{-1}, \tag{12}$$

$$\tau^1_{10}=\left[D_\perp\frac{2+\overline{P}_2}{1-\overline{P}_2}\right]^{-1}, \tag{13}$$

$$\tau^2_{00}=\left[6D_\perp\frac{7+5\overline{P}_2-12\overline{P}_4}{7+10\overline{P}_2+18\overline{p}_4-35\overline{p}_2^2}\right]^{-1}, \tag{14}$$

whereas τ^1_{01} depend on $D_\perp$ and $D_\parallel$ according to

$$\tau^1_{01}=\left[D_\parallel+D_\perp\frac{1+2\overline{P}_2}{1-\overline{P}_2}\right]^{-1}. \tag{15}$$

Results for the time correlations τ^1_{00}, τ^1_{10}, τ^1_{01}, and τ^2_{00} are given in Table I. We also presented in Table I the values of the well known ratio between the correlation times τ^1_{00}/τ^2_{00}. It should be noted that in the case of an isotropic liquid $\tau^1_{00}/\tau^2_{00}=3$. Having obtained a set of the correlation times τ^1_{mn}, it is now possible to describe the dielectric relaxation processes in the nematic phase of the 8OCB.

The complex dielectric permittivity tensor $\epsilon_{ik}(\omega)=\epsilon'_{ik}(\omega)-i\epsilon''_{ik}(\omega)$ have been measured in a wide frequency range [23], and show Debye type of relaxation at microwave frequencies ($\omega/2\pi\sim10^{10}$ Hz). For the uniaxial NLCs, in the laboratory coordinate system XYZ, where the Z axis coincides with the direction $\mathbf{n}$, there are only two independent components of the tensor $\epsilon_{ik}(\omega)$, one perpendicular $\epsilon_\perp(\omega)=\epsilon_{XX}(\omega)=\epsilon_{YY}(\omega)$, and the other parallel $\epsilon_\parallel(\omega)=\epsilon_{ZZ}(\omega)$ to the director $\mathbf{n}$. In the case that the intermolecular correlations are ignored, one can write the expression for the components of the normalized complex susceptibility tensor $\chi_j(\omega)$ in the form [42]

$$\chi_j(\omega)=\frac{\epsilon_j(\omega)-\epsilon_{j\infty}}{\tilde{R}_j(\omega)}=C_j(0)-i\omega\int_0^\infty C_j(t)\exp(-i\omega t)dt$$
$$=C_j(0)-i\omega\tilde{C}_j(i\omega),$$

where $j=(\perp,\parallel)$, $\tilde{R}_j(\omega)=(4\pi\mu^2\rho/k_BT)R_j(\omega)$, and $R_j(\omega)$ are the frequency dependent factors of the internal field, $\epsilon_{j\infty}$ are the high frequency limits of the components of the tensor $\epsilon_{ik}(\omega)$. Here $C_j(t)$ and $\tilde{C}_j(i\omega)$ are the components of the tensor dipole autocorrelation function and their Fourier transformations, respectively, and may be represented by [42]

$$C_\parallel(t)=\langle\mu_{zz}(0)\mu_{zz}(t)\rangle=\Phi^1_{00}(t), \tag{16}$$

$$C_\perp(t)=\langle\mu_{xx}(0)\mu_{xx}(t)\rangle=\langle\mu_{yy}(0)\mu_{yy}(t)\rangle=\Phi^1_{10}(t), \tag{17}$$

where $\Phi^1_{i0}(t)$ $(i=0,1)$ are the first-rank time correlation functions, $\mu_{\alpha\alpha}$ are the projections of the dipole moment vector μ on the laboratory axis α $(\alpha=x,y,z)$.

Using Eqs. (16),(17) with functions

$$\Phi^1_{00}(t)=\Phi^1_{00}(0)\exp\left(-\frac{t}{\tau^1_{00}}\right)=\frac{1+2\overline{P_2}}{3}\exp\left(-\frac{t}{\tau^1_{00}}\right) \tag{18}$$

and

$$\Phi^1_{10}(t)=\Phi^1_{10}(0)\exp\left(-\frac{t}{\tau^1_{10}}\right)=\frac{1-\overline{P_2}}{3}\exp\left(-\frac{t}{\tau^1_{10}}\right), \tag{19}$$

we may derive the expressions for the components of the tensor $\chi_j(\omega)$ interpreted in the framework of the Brownian motion of a particle in a mean-field potential $U(\beta)$ as

$$\chi_\parallel(\omega)=\chi'_\parallel(\omega)-i\chi''_\parallel(\omega)=\Phi^1_{00}(0)\left[1-\frac{y_1^2}{1+y_1^2}-i\frac{y_1}{1+y_1^2}\right], \tag{20}$$

where $y_1=\omega\tau^1_{00}$, and

$$\chi_\perp(\omega)=\chi'_\perp(\omega)-i\chi''_\perp(\omega)=\Phi^1_{10}(0)\left[1-\frac{y_2^2}{1+y_2^2}-i\frac{y_2}{1+y_2^2}\right], \tag{21}$$

where $y_2=\omega\tau^1_{10}$. The relaxation times τ^1_{i0} and $\Phi^1_{i0}(0)$ $(i=0,1)$ are calculated using Eqs. (12), (13), (18), and (19). The values of $\overline{P_2}$ and $D_\perp$ are again those obtained from our NMR measurements for 8OCB in the temperature range corresponding to the nematic phase.

The results of the calculations of the longitudial dielectric dispersion $\chi'_\parallel(\omega)$ and absorption $\chi''_\parallel(\omega)$ for 8OCB molecules at a number of temperatures ($T=340,345,350$ K) are shown in Fig. 4. The results for the transverse dielectric dispersion $\chi'_\perp(\omega)$ and absorption $\chi''_\perp(\omega)$ for the same thermodynamics conditions are shown in Fig. 5. The longitudinal dielectric loss spectra $\chi''_\parallel(\omega)$ show magnitudes which decrease with

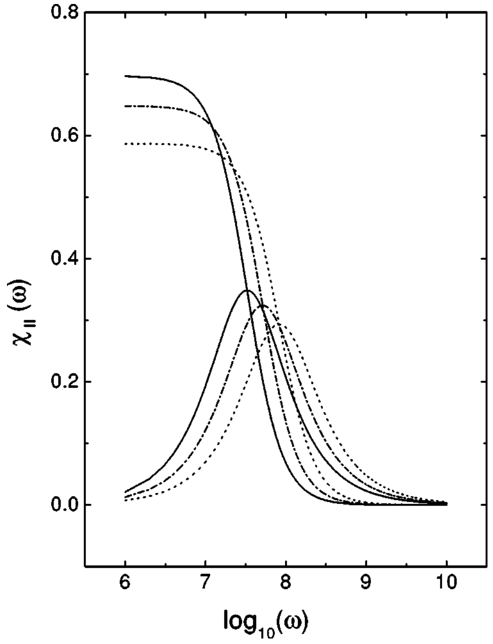

FIG. 4. The real and imaginary parts of the longitudinal susceptibility $\chi_\parallel(\omega)=\chi'_\parallel(\omega)-i\chi''_\parallel(\omega)$ calculated using Eq. (20) at three values of the temperature [$T=340$ (solid lines); 345 (dashed dotted lines); 350 K (dotted lines)], where $\omega/2\pi$ is in Hz. Upper curves correspond to $\chi'_\parallel(\omega)$, whereas lower ones correspond to $\chi''_\parallel(\omega)$, respectively.

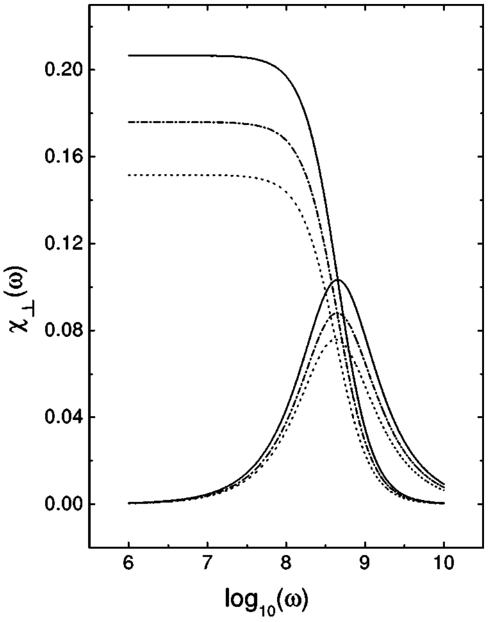

FIG. 5. The real and imaginary parts of the transverse susceptibility $\chi_\perp(\omega)=\chi'_\perp(\omega)-i\chi''_\perp(\omega)$ calculated using Eq. (21) at three values of the temperature [$T=350$ (solid lines); 345 (dashed dotted lines); 340 K (dotted lines)], where $\omega/2\pi$ is in Hz. Upper curves correspond to $\chi'_\perp(\omega)$, whereas lower ones correspond to $\chi''_\perp(\omega)$, respectively.

the growth of the temperature, and have one loss peak which shifts to the higher frequency region upon increasing the temperature. The magnitudes of the transverse dielectric loss spectra $\chi''_{\perp}(\omega)$, on the contrary, increase with increasing the temperature, and its loss peak remains at the same frequency of $\sim 1.99 \times 10^3$ MHz.

V. CONCLUSION

In this paper, we investigate the rotational diffusion constants D_j $(j=\parallel,\perp)$ and rotational viscosity coefficients γ_i $(i=1,2)$ in the nematic phase of 8OCB. γ_i are investigated by a combination of existing statistical-mechanical approaches and the existing NMR relaxation theory, both based on a rotational diffusion model. In the rotational diffusion model, it is assumed that the reorientation of an individual molecule is a stochastic Brownian motion in a certain potential of mean torque. According to Eqs. (4), (7) and (8), γ_i are found to be proportional to a function of $\overline{P_{2L}}$ $(L=1,2)$, density, and inversely proportional to $D_{\perp}$, which corresponds to the molecular tumbling in the nematic phase. It should be pointed out that the Fiałkowski [Eq. (7)] and NZ [Eq. (8)] theories exhibit different dependences on the order parameters as manifested in the factor ξ_1^F and ξ_1^{NZ}. This difference originates in the averaging procedures applied to the balance equations. In the high-temperature limit, i.e., close to the clearing point, both theories predict that $\gamma_1 \sim \overline{P_2^2}$. Such behavior of the rotational viscosity is in agreement with the mean field approximation as was pointed out by the Gennes and Prost [34].

We have also calculated the values of various orientational correlation times τ_{00}^1, τ_{10}^1, τ_{01}^1, and τ_{00}^2 for 8OCB molecules at a number of temperatures. In addition to these correlation times, we have obtained values of the longitudinal and transverse components of the real χ'_j and imaginary χ''_j part of the complex susceptibility tensor for 8OCB molecules. We found that the components of the loss spectra are characterized by the low frequency peaks and shoulders, both shifted to the high frequency region upon increasing the temperature, and effectively described by the Debye type mechanism with corresponding relaxation times. Thus the combination of the NMR relaxation techniques and statistical mechanics theories provides a powerful tool for investigations of both the rotational and dielectric properties of real nematics. We believe that this paper shows not only some useful routes for estimating the rotational viscosities, but also analyzing the dielectric properties. Furthermore, the rotational diffusion constant for molecular tumblings in the decoupled model for the chain dynamics seems to produce reasonable values of γ_1 and γ_2, lending support to the NMR relaxation model.

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[1] R. Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals*, 2nd ed. (Springer-Verlag, New York, 1997).

[2] R. Y. Dong, J. Chem. Phys. **88**, 3962 (1988).

[3] P. A. Beckmann, J. W. Emsley, G. R. Luckhurst, and D. L. Turner, Mol. Phys. **59**, 97 (1986).

[4] *Molecular Dynamics of Liquid Crystals*, edited by G. R. Luckhurst and C. A. Veracini (Kluwer Academic, Dordrecht, 1994).

[5] J. P. Caniparoli, A. Grassi, and C. Chachaty, Mol. Phys. **63**, 419 (1988).

[6] A. Ferrarini, G. J. Moro, and P. L. Nordio, Liq. Cryst. **8**, 593 (1988).

[7] R. Y. Dong and G. M. Richards, J. Chem. Soc., Faraday Trans. **88**, 1885 (1992).

[8] R. Y. Dong, Phys. Rev. E **60**, 5631 (1999).

[9] A. V. Zakharov, Phys. Lett. A **193**, 471 (1994); Fiz. Tverd. Tela (St. Petersburg) **40**, 1945 (1998) [Phys. Solid State **40**, 1765 (1998)].

[10] V. B. Nemtsov, Mol. Cryst. Liq. Cryst. **192**, 229 (1990).

[11] M. Fialkowski, Phys. Rev. E **58**, 1955 (1998).

[12] A. V. Zakharov, A. V. Komolkin, and A. Maliniak, Phys. Rev. E **59**, 6802 (1999).

[13] A. V. Zakharov and A. Maliniak, Eur. Phys. J. E (to be published).

[14] J. H. Freed, J. Chem. Phys. **41**, 2077 (1964); W. Huntress, Jr., Adv. Magn. Reson. **4**, 1 (1970).

[15] P. L. Nordio and P. Busolin, J. Chem. Phys. **55**, 5485 (1971); P. L. Nordio, G. Rigatti, and U. Segre, Mol. Phys. **25**, 129 (1973).

[16] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969).

[17] R. Y. Dong, Phys. Rev. A **43**, 4310 (1991).

[18] R. Y. Dong and G. M. Richards, Chem. Phys. Lett. **171**, 389 (1990).

[19] N. Kuzuu and M. Doi, J. Phys. Soc. Jpn. **52**, 3486 (1983).

[20] M. A. Osipov and E. M. Terentjev, Phys. Lett. A **134**, 301 (1989); Z. Naturforsch. A **44**, 785 (1989).

[21] A. Chrzanowska and K. Sokalski, Phys. Rev. E **52**, 5228 (1995).

[22] E. N. Ivanov, Zh. Eksp. Teor. Fiz. **45**, 1509 (1963) [Sov. Phys. JETP **18**, 1041 (1964)].

[23] W. H. de Jeu, *Physical Properties of Liquid Crystal Materials* (Gordon and Breach, New York, 1980).

[24] J. Jadzyn and G. Czechowski, Liq. Cryst. **4**, 157 (1989).

[25] S. Urban, B. Gestblom, H. Kresse, and R. Dabrowski, Z. Naturforsch. A **51**, 834 (1996).

[26] J. Jadzyn, S. Czerbas, G. Czechowski, A. Burczyk, and R. Dabrowski, Liq. Cryst. **26**, 437 (1999).

[27] S. Urban, A. Würflinger, and B. Gestblom, Phys. Chem. Chem. Phys. **11**, 2787 (1999).

[28] D. Demus and T. Inukai, Liq. Cryst. **26**, 1257 (1999).

[29] J. Jadzyn, G. Czechowski, R. Douali, and C. Legrand, Liq. Cryst. **26**, 1591 (1999).

[30] R. Tarroni and C. Zannoni, J. Chem. Phys. **95**, 4550 (1991).

[31] P. L. Nordio and U. Serge, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Aca-

demic Press, London, 1979), Chap. 18.

[32] J. L. Ericksen, Arch. Ration. Mech. Anal. **4**, 231 (1960).

[33] F. M. Leslie, Arch. Ration. Mech. Anal. **28**, 265 (1968).

[34] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, 1995).

[35] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).

[36] A. G. Chmielewski, Mol. Cryst. Liq. Cryst. **132**, 319 (1986).

[37] J. H. Freed, J. Chem. Phys. **66**, 4183 (1977).

[38] I. Dozov, N. Kirov, and M. P. Fontana, J. Chem. Phys. **81**, 2585 (1984).

[39] N. Kirov, I. Dozov, and M. P. Fontana, J. Chem. Phys. **83**, 5267 (1985).

[40] G. Moro and P. L. Nordio, Chem. Phys. Lett. **96**, 192 (1983).

[41] A. Szabo, J. Chem. Phys. **81**, 150 (1984).

[42] G. Luckhurst and C. Zannoni, Proc. R. Soc. London, Ser. A **343**, 389 (1975).