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Dielectric and elastic properties of liquid crystals

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The structural properties, the static and relaxation dielectric coefficients [ϵ_j and $\epsilon_j(\omega)$ $(j=\|,\perp)$], the rotational diffusion constants $D_\perp$ and $D_\|$, the orientational correlation times τ^1_{i0} $(i=0,1)$, and the bulk elastic constants K_i $(i=1,2,3)$ are investigated for polar liquid crystals, such as 4-*n*-pentyl-4′-cyanobiphenyl (5CB). ϵ_j are calculated by a combination of the existing molecular theory and statistical-mechanical approach (SMA) that takes into account translational and orientational correlations as well as their coupling, whereas $\epsilon_j(\omega)$ are calculated by combining SMA and nuclear magnetic resonance relaxation theory, both based on a rotational diffusion model in which the reorientation of an individual molecule is assumed as stochastic Brownian motion in a potential of mean torque. Reasonable agreement between the calculated and experimental values of ϵ_j and $\epsilon_j(\omega)$ for 5CB is obtained. The bulk Frank elastic constants K_i $(i=1,2,3)$, for splay, twist, and bend distortion modes, as well as their ratios K_3/K_1 and K_2/K_1 are also obtained.

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I. INTRODUCTION

The problem of predicting physical properties of liquid crystalline compounds based upon information on molecular shape and intermolecular interactions remains one of the most fundamental problems in liquid crystals (LCs) physics. In recent years, the Gay-Berne (GB) model [1] has been frequently used for describing interactions between anisotropic molecules. Since the molecules that form the LC system often possess strong polar groups, the dipolar GB potential [2–6] with an axial dipole at the center or near the end of the molecule is more appropriate for the description of such systems. In the case of polar LCs, such as *n*-cyanobiphenyls, the angle between the para axis and the long molecular axis is small, and this leads to a large axial value of dipole moment, for example $\sim 5D$ for 4-*n*-pentyl-4′- cyanobiphenyl (5CB). Among the most important properties of such compounds, the dielectric coefficients and Frank elastic constants play a crucial role in several applications such as twisted-nematic displays [7]. The reason why many reports are still concerned with the dielectric and elastic coefficients of well known materials like 5CB is that their measurements are nontrivial [8–13]. Other reasons for choosing 5CB among the other cyanobiphenyls are its convenient temperature range for the nematic liquid crystalline phase, namely, from 295.6 to 305.2 K, and its nearly uniaxial molecular symmetry [10]. In particular, several nuclear magnetic resonance (NMR) investigations of the orientational order, molecular structure, and dynamical processes have been reported [14,15], and therefore a large data set is available for comparison with results from the theoretical routes. In addition, the explosive development of computer power has made it possible to investigate the 5CB molecule using detailed atom-atom interaction potentials [16–18]. In order to elucidate the role of intermolecular dipole-dipole correlations in the calculations of the static dielectric permittivity in the nematic phase of 5CB, we use the molecular model in which these correlations are treated explicitly. The statistical-mechanical theory based upon the method of conditional distribution functions [5,6,19] has been applied to calculations of the nearest-neighbor (NN) and the next NN correlators as well as order parameters. The method takes into account translational and orientational correlations as well as their coupling. Using a dipolar GB potential, calculations have been carried out in the framework of the molecular model that provides relationship between the static dielectric coefficients and the pair orientational correlators for the neighbors [20].

Dielectric relaxation in the nematic LCs is usually interpreted in the context of the rotational diffusion model [21], i.e., a stochastic Brownian process for molecular reorientations is used 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 $(D_{xx}=D_{yy}=D_\perp, D_{zz}=D_\|)$ are determined in a frame fixed on the molecule. NMR measurements of quadrupolar splittings, and deuteron Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times in LCs allow the determination of these principal elements and order parameters as a function of temperature [22]. Using these results together with data for static dielectric permittivity, the complex dielectric permittivity of realistic mesogenic molecules, such as 5CB, can be studied in the nematic phase.

In addition, we have investigated the Frank elastic constants (ECs) of 5CB. Clearly, the ECs being material properties, reflect the underlying microscopic interactions and correlations. Therefore, these studies should lead to a greater insight about parameters that influence the structure of nematic phases. There are several microscopic theories for bulk

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ECs K_i $(i=1,2,3)$ [5,23–29] in which these coefficients are related to structural quantities such as the single-particle orientational distribution function, and the direct correlation function (DCF) of a nematic system. The central difficulty of these theories is the calculation of the DCF in the nematic phase. Recently, calculations of the ratio $K_i/\overline{K}$ $[\overline{K}=\frac{1}{3}(K_1+K_2+K_3)]$ in the framework of the statistical mechanical approach [5] have been reported. Here we extend our investigations and perform calculations of the absolute values the bulk Frank elastic constants for a dipolar GB fluid.

It should be pointed out that in practice it is difficult to measure the absolute values of these elastic constants [11–13]. Thus, we hope that our theoretical route will be useful for the estimation of the absolute values of the Frank elastic constants. The paper is organized as follows. A brief description of the statistical—mechanical treatment and the numerical solution of the resulting nonlinear integral equations is given in Sec. II. The formulas for the static and relaxation dielectric permittivities are given in Sec. III and Sec. IV, respectively. The statistical-mechanical approach and numerical calculations for the Frank elastic constants are given in Sec. V. Conclusions are made in Sec. VI.

II. STATISTICAL-MECHANICAL TREATMENT

We consider here a classical one-component fluid, consisting of cylindrically symmetric particles; let $\mathbf{q}_i$ denote their center-of-mass coordinates, and $\mathbf{e}_i$ denote unit vectors defining their orientations; in the following the collective symbol $i\equiv(\mathbf{q}_i,\mathbf{e}_i)$ will be used. Particles can be identified, to a certain approximation, as prolate ellipsoids of revolution, each with major semiaxis $\sigma_\parallel$ and minor semiaxis $\sigma_\perp$, respectively [1]. One considers N such particles occupying a volume V at the temperature T, and can ideally subdivide the total volume into N cells, each with volume $v=V/N$, in a simple-cubic lattice. The treatment used here further assumes that each cell is occupied by one and only one particle; this seems reasonable for a condensed system. Particles are assumed to interact via a pairwise additive potential $\Phi(ij)$, so that the total interaction energy for the N particles is $U=\Sigma_{i<j}\Phi(ij)$. The quantity $\exp(-U/k_BT)$ is the canonical probability density. Upon integrating the coordinates of remaining particles, one can define single-particle probability densities $F_i(i)$, two-particle probability densities $F_{ij}(ij)$, and so on [5,6,19,30]. The infinite hierarchy is truncated here at the two-particle level. By partitioning the space mentioned above, $F_i(i)$ is the probability density for a single particle confined inside a cell of volume v, and $F_{ij}(ij)$ is a joint probability density for two particles confined in two different cells. The above-mentioned functions can also be written in terms of mean-force potentials (MFPs) following the approach outlined in [5,6,19,30]. In terms of the MFPs $\psi_{i,j}(i)$, these functions can be written as

$$F_j(j)=\frac{\psi_j(j)}{\int_j d(j)\psi_j(j)}, \qquad (1)$$

$$F_{ij}(ij)=F_i(i)F_j(j)V(ij)\psi_{i,j}(i)^{-1}\psi_{j,i}(j)^{-1}. \qquad (2)$$

Here

$$\psi_j(j)=\prod_{i\neq j}\psi_{j,i}(j),\ \int_j d(j)=\int_w d\mathbf{q}_j d\mathbf{e}_j,$$

$$w=v\otimes\alpha,$$

and

$$V(ij)=\exp\left[-\frac{\Phi(ij)}{k_BT}\right],$$

where α denotes the volume associated with orientations. In Eqs. (1) and (2), $\Pi_{j\neq i}$ runs over all neighbors of cell *i*. The subscripts before the comma correspond to the MFP dependence on the coordinates of particles; the subscripts after the comma correspond to the average states. In the following we take into account only pair correlations between cells. It should be pointed out that the last three factors in Eq. (2) reflect correlations between cells, that distinguish the present approach from mean-field approximations. The singlet function $F_i(i)$ automatically satisfies the normalization condition $\int_i d(i)F_i(i)=1$. Using the relation between singlet and binary functions [5,30] $F_i(i)=\int_j d(j)F_{ij}(ij)$, that follows from their definitions, one obtains a closed system of nonlinear integral equations (IEs) involving MFPs [5,6,30]

$$\psi_{i,j}(i)=\int_j d(j)V(ij)\psi_{j,i}^{-1}(j)F_j(j). \qquad (3)$$

After solving Eq. (3), one can compute a number of correlators of a liquid crystalline system, expressed in terms of one- and two-particle functions

$$\overline{P}_{2L}=\langle P_{2L}(\cos\ \beta)\rangle=\int_i d(i)F_i(i)P_{2L}(\cos\beta), \qquad (4)$$

$$\langle\mathbf{e}_i\cdot\mathbf{e}_j\rangle=\int_i d(i)\int_j d(j)F_{ij}(ij)\mathbf{e}_i\cdot\mathbf{e}_j, \qquad (5)$$

$$\overline{\kappa}=\left\langle P_2(\cos\beta)\cos\frac{2\pi z}{d}\right\rangle=\int_i d(i)F_i(i)P_2(\cos\beta)\cos\frac{2\pi z}{d}, \qquad (6)$$

as well as the Helmholtz free energy

$$f=\frac{F}{N}=-k_BT\ln\int_i\psi_i(i)d(i). \qquad (7)$$

Here $\overline{P}_{2L}$ is the even order parameters, P_{2L} denote the Legendre polynomials, β is the polar angle, i.e., the angle between the long axis of the molecule and the director, the latter taken to coincide with the cell *z* axis, and *d* is the layer spacing of the Smectic-A (Sm*A*) phase. The coupling order parameter $\overline{\kappa}$ is a measure of the amplitude of the density wave describing the layered structure in the Sm-*A* phase. The nematic phase is characterized by $\overline{\kappa}=0$ and $\overline{P}_{2L}\neq 0$ [10].

Except for linear problems, solving a five-dimensional problem, Eq. (3), is very complicated, and there is no good general method for systems of more than one nonlinear equation. The solution $\psi_{i,j}(i)$ is invariably obtained by a numerical iterative procedure, using the formula

$$\psi^{m[k+1]}(P_i)=\{\psi^{m[k]}(P_i)\hat{L}\psi^{m[k]}(P_i)\}^{1/2}, \tag{8}$$

or

$$\psi^{m[k+1]}(P_i)=\{\psi^{m[k]}(P_i)+\hat{L}\psi^{m[k]}(P_i)\}/2, \tag{9}$$

for $m=1,2,\ldots,l$. Here $\hat{L}$, $\|\hat{L}\|\leqslant 1$ is the five-dimensional nonlinear integral operator defined by Eq. (3) in the space w, and P_i is a five-dimensional vector in the same space, k is the iteration number, and l is the number of neighbors. The algorithms, Eqs. (8) and (9), were implemented as follows: the initial approximation was to set $\psi_{i,j}^{m[0]}$ as constant; the integrals in the right-hand side of Eqs. (8) or (9) were calculated by the Sobol's method [31], using the Haar functions for calculating multidimensional integrals

$$\int_0^1 dx_1 \ldots \int_0^1 dx_n f(x_1,x_2,\ldots,x_n)\approx(1/M)\sum_{\alpha=1}^{M} f(P_\alpha). \tag{10}$$

Here the points P_α are uniformly distributed (mod 1) in the n-dimensional unit cube. These points belong to a LP_τ sequence [31], and were obtained by means of an LP_τ generator [32]; M is the number of points, and the precision of the calculation is $R\sim O(M^{-1}\ln^n M)$ versus $\sim O(1/\sqrt{M})$ for Monte Carlo integration. Calculations were carried out using $M=10^3$, corresponding to 10^6 points for a Monte Carlo integration of comparable accuracy. This has been achieved because LP_τ sequences possess a more uniformly distributed set of M points in the five-dimensional unit hypercube than independent random sequences. The iterative procedure was repeated for various neighbors of the ith cell; in order to keep the treatment numerically tractable, we took the truncating of the interaction potential at second-nearest neighbors. The convergence criterion $\delta=|\psi^{[k+1]}(P_i)-\psi^{[k]}(P_i)|/|\psi^{[k]}(P_i)|$ for the iterative procedures, Eqs. (8) and (9), was chosen equal to 10^{-4}. Two points should be noted. First, in the present calculation we considered only a simple-cubic structure, with six-nearest neighbors and 12 next-nearest neighbors; this implies that we deal with a system of 18 nonlinear equations in a five-dimensional space. We are aware of the fact that the correlations are strong beyond the next-nearest neighbors in view of the long-range nature of dipolar term in the dipolar GB fluid; the computations become, however, very heavy and suffer, in addition, from numerical instabilities. The second point concerns the convergence of the iterative procedure; the algorithm Eqs. (8) and (9) exhibit a poor convergence in the vicinity of N-Sm$-A$ phase transition point, because the function $\psi_{i,j}(i)$ is not a smoothly varying one. Taking these points into account, we restrict the present paper to investigations of the nematic phase with interactions from only first- and second-nearest neighbors.

The kernel of $V(i,j)$ integral equations in Eq. (3) is determined by the pair interaction potential; this was chosen to be the sum of a Gay-Berne and dipole-dipole interactions

$$\Phi(ij)=\Phi_{GB}(ij)+\Phi_{dd}(ij).$$

The GB term $\Phi_{GB}(ij)=4\epsilon_0\epsilon(R^{-12}-R^{-6})$, where $R=(q_{ij}-\sigma+\sigma_\perp)/\sigma_\perp$, $q_{ij}=|\mathbf{q}_i-\mathbf{q}_j|$, is defined by a Lennard-Jones (12-6) potential [1], with range σ and strength ϵ that depend on the relative orientation of the particles $\mathbf{e}_i$ and $\mathbf{e}_j$, the orientations of the particles with respect to the intermolecular vector between their center-of-mass positions $\mathbf{e}_{ij}=\mathbf{q}_{ij}/|\mathbf{q}_{ij}|$, the molecular anisotropy parameter $\gamma=\sigma_\parallel/\sigma_\perp$ that controls the length-to-breadth ratio of the repulsive core, and another set of parameters, which can be used to adjust the ratio between end-to-end and side-by-side well depths, denoted by ϵ_e/ϵ_s, and the exponent parameters ν and μ, which are included in $\epsilon=\epsilon_1^\nu(\mathbf{e}_i,\mathbf{e}_j)\epsilon_2^\mu(\mathbf{e}_{ij},\mathbf{e}_i,\mathbf{e}_j)$. The dipolar term is defined by $\Phi_{dd}(ij)=(\Delta^2/q_{ij}^3)\{\mathbf{e}_i\cdot\mathbf{e}_j-3\mathbf{e}_{ij}\cdot\mathbf{e}_i\mathbf{e}_{ij}\cdot\mathbf{e}_j\}$, where Δ is the magnitude of the molecular dipole moment. In the case of polar LCs, such as 5CB, the dipole moment ($\Delta\sim 5D$ [33,34]) is directed from the polar head to the hydrophobic tail of the molecule. Simulation studies have shown that the dipolar GB pair potential provides a useful model for the interactions between real mesogenic molecules. However, the variety of parameterizations that have been used in [1–5] yields very different potential forms. Whereas a value for $\sigma_\parallel/\sigma_\perp$ of 3 is reasonable for 5CB molecules ($\sigma_\parallel\approx 1.8$ nm, $\sigma_\perp\approx 0.59$ nm), it is not known to what extent the values used for the other parameters are appropriate. In an attempt to answer this question, we have adopted the potential for 5CB with parameters $\nu=2$, $\mu=0.98$, and $\epsilon_e/\epsilon_s=0.245$. It should also be pointed out that for the convergence of the iterative procedure, the algorithm Eqs. (8) and (9) is very sensitive to the choice of both parameters ϵ_e/ϵ_s and μ, which vary the value of the well depth.

Our calculations have employed the units of distance $\sigma_\perp=0.59$ nm and energy $\epsilon_0=2.07\times 10^{-21}$ J. Thus, the reduced units for number density $\rho=N\sigma_\perp^3/V\approx 0.512$, temperature $\theta=k_BT/\epsilon_0$, dipole moment $\mu^*=\Delta/(\epsilon_0\sigma_\perp^3)^{1/2}\approx 2.5$, and anisotropy parameter $\gamma=3$ were used. The orientational order of LCs is traditionally quantified in terms of order parameters. Comparing for 5CB at temperature $T=300$ K the $\overline{P}_2$ and $\overline{P}_4$ values obtained from the integral equations approach (i), $\overline{P}_2$ and $\overline{P}_4$ obtained from the molecular dynamics (MD) simulation of 5CB [29] (ii), which were carried out using the conventional potential energy function composed of intra- and intermolecular contributions [17,18,29], and experimental data derived from polarized laser Raman scattering (iii) [35] shows the following results: (i) $\overline{P}_2=0.789$; $\overline{P}_4=0.38$, (ii) $\overline{P}_2=0.504$; $\overline{P}_4=0.188$, (iii) $\overline{P}_2=0.61$; $\overline{P}_4=0.15$, respectively. Both the IEs method and MD simulation use the same value of Δ. It should be pointed out that the values of the order parameters calculated in the framework of MD simulation using various degrees of approximation in the interaction models [17,18,29] and different definitions of molecular coordinate systems lead to widely different $\overline{P}_2$ and $\overline{P}_4$ values

($\overline{P_2}\in[0.505,0.72];\overline{P_4}\in[0.18,0.31]$ [17]). Interpretation of experimental results is also dependent on the selection of molecular frame [35]. Based on these facts, such deviations among the three cases are not surprising. For all temperatures, values of the coupling order parameter $\overline{\kappa}$ were found to be $\overline{\kappa}=9.5\times10^{-2}$, confirming the nematic character of the phase. Because we found a small change in the values of the Helmholtz free energy from -15.55 (nearest neighbors) to -15.67 (nearest and next-nearest neighbors), the restriction in taking only first and second neighbors into account appears quite reasonable. In the previous paper, a comparison of the theory, that takes into account only nearest and next-nearest neighbors, with the Monte Carlo simulations for the same pair potential shows a quantitative agreement [5]. It should be pointed out that in the Monte Carlo simulations [36] of the dipolar GB system the cut-off radius $r_c=1.4\sigma_\perp$ was comparable with the one used in our calculations $r_c=\sqrt{2}\sigma_\perp$. Nevertheless, the problem of accounting the long-range nature of dipolar interactions may require further attention [37,38].

III. THE STATIC DIELECTRIC PROPERTIES OF THE NEMATIC LIQUID CRYSTAL

The static dielectric constant is orientation independent in isotropic liquids, and is thus characterized by a single value ϵ_i. Due to the anisotropic nature of LCs this constant becomes different in the nematic phase with two components: parallel ($\epsilon_\parallel$) and perpendicular ($\epsilon_\perp$) to the director **n** can be distinguished. In the case of nonpolar LCs the values of $\epsilon_\parallel$ and $\epsilon_\perp$ are similar to the isotropic liquid, ϵ_i [10], while for polar LCs such as 5CB $\epsilon_\parallel$ and $\epsilon_\perp$ differ substantially. The average dielectric permittivity $\overline{\epsilon}$ is defined as

$$\overline{\epsilon}=\frac{\epsilon_\parallel+2\epsilon_\perp}{3}. \tag{11}$$

For 5CB, at the nematic-isotropic transition the change of the average permittivity $\delta\epsilon_{NI}=\overline{\epsilon}-\epsilon_i$ is negative and $\overline{\epsilon}$ decreases slowly in the nematic phase with decreasing temperature [10]. According to the molecular theory [20], the components of the dielectric permittivity in an infinite geometry are given by

$$\epsilon_j^2-B_j\epsilon_j-D_j=0, \tag{12}$$

where $B_j=(A_j+1-y_j)/(1+y_j)$, $D_j=y_j/(1+y_j)$, and $j=(\parallel,\perp)$. Unknown coefficients y_j and A_j are functions of ϵ_j and short-range correlations exist between dipole moments inside a sphere centered on particle i, of radius R_0 large compared with the molecular sizes and embedded in a dielectric continuum of infinite extent having the same dielectric constant as the medium inside the sphere. The short-range correlations can be calculated in the framework of the statistical mechanical scheme described above as

$$t_j=\left\langle \mathbf{e}_i^j\cdot\sum_{m\in R_0}\mathbf{e}_m^j\right\rangle, \tag{13}$$

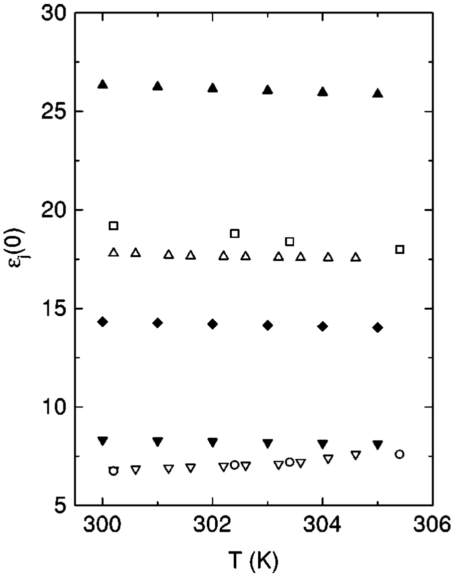

FIG. 1. The temperature dependence of the static dielectric constants $\epsilon_j(0)$ $(j=\parallel,\perp)$ for 5CB. Solid symbols represent points calculated using Eq. (14); $\epsilon_\parallel$ (up triangles), $\epsilon_\perp$ (down triangles), $\overline{\epsilon}$ (diamonds). Open triangles and squares ($\epsilon_\parallel$) and down triangles with circles ($\epsilon_\perp$) are experimental data Refs. [8] and [33], respectively.

where $j=(\parallel,\perp)$, $m\neq i$, and $\langle\cdots\rangle$ is defined as in Eq. (5). The final expressions for A_j and y_j now take the form

$$A_j=\frac{4\pi\rho\mu^{*2}}{\theta}t_j,$$

$$y_\parallel=\frac{\xi}{\Omega}\left(1-\frac{1}{\Omega^{1/2}}\arctan\Omega^{1/2}\right),$$

$$y_\perp=\frac{1}{2\Omega}\left(-1+\frac{\xi}{\Omega^{1/2}}\arctan\Omega^{1/2}\right).$$

Here $\Omega=\xi-1$ and $\xi=\epsilon_\parallel/\epsilon_\perp$. The set of roots that leads to reasonable values of the $\epsilon_\parallel$ and $\epsilon_\perp$ can be evaluated iteratively using the formula

$$\epsilon_j^{[k+1]}=\frac{B_j(\epsilon_j^{[k]})}{2}+\left(\frac{B_j^2(\epsilon_j^{[k]})}{4}+D_j(\epsilon_j^{[k]})\right)^{1/2}, \tag{14}$$

where k is the iteration number. Figure 1 shows the temperature dependence of calculated and experimental data for static dielectric permittivity of 5CB. Reasonable agreement is observed between the calculated values and experimental results reported in Refs. [8,9] and [33].

IV. DIELECTRIC RELAXATION IN THE NEMATIC PHASE AND ORIENTATIONAL CORRELATION TIMES

The complex dielectric permittivity tensor $\epsilon_{ik}(\omega) = \mathrm{Re}\,\epsilon_{ik}(\omega) - i\,\mathrm{Im}\,\epsilon_{ik}(\omega)$ for 5CB has been measured in the a wide frequency range and shown Debye-type relaxation at frequencies (1 kHz $\leqslant \omega/(2\pi) \leqslant$ 13 MHz) [39]. For uniaxial nematic liquid crystal (NLC), in the laboratory coordinate system XYZ, where the Z axis coincides with the director $\mathbf{n}$, 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 $\mathbf{n}$. One can write the components of the normalized complex permittivity tensor in the form [40]

$$\frac{\epsilon_j(\omega)-1}{\epsilon_j-1} = 1 - i\omega\int_0^{\infty} C_j(t)\exp(-i\omega t)\,dt, \tag{15}$$

where $C_j(t)$ are the components of the tensor dipole autocorrelation function, and may be represented by

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

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

where $\Phi^1_{i0}(t)$ $(i=0,1)$ are first-rank time correlation functions, e_α are the projections of the unit vector $\mathbf{e}$ along the dipole moment onto the laboratory axis α $(\alpha = X,Y,Z)$.

Using Eqs. (16) and (17) with functions [41]

$$\Phi^1_{00}(t) = \Phi^1_{00}(0)\exp\left(-\frac{t}{\tau^1_{00}}\right) = \frac{1+2\overline{P}_2}{3}\exp\left(-\frac{t}{\tau^1_{00}}\right), \tag{18}$$

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 permittivity tensor $\epsilon_{ik}(\omega)$ as

$$\frac{\epsilon_{\parallel}(\omega)-1}{\epsilon_{\parallel}-1} = 1 - \Phi^1_{00}(0)\frac{i\omega\tau^1_{00}}{1+i\omega\tau^1_{00}}, \tag{20}$$

and

$$\frac{\epsilon_{\perp}(\omega)-1}{\epsilon_{\perp}-1} = 1 - \Phi^1_{10}(0)\frac{i\omega\tau^1_{10}}{1+i\omega\tau^1_{10}}. \tag{21}$$

Different spectroscopic methods provide time correlation functions (TCFs) $\Phi^L_{mn}(t)$ 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. Based on the short time expansion of the TCFs, an expression for the correlation times was proposed

$$\frac{1}{\tau^L_{mn}} = c^L_{mn}D_{\perp} + n^2(D_{\parallel} - D_{\perp}), \tag{22}$$

where the coefficients c^L_{mn}, that depend on $\overline{P}_2$ and $\overline{P}_4$, are tabulated in Refs. [42,43]. We note that the τ^1_{00} and τ^1_{10} are solely determined by the tumbling motion of the molecule,

$$\tau^1_{00} = \left[D_{\perp}\frac{2-2\overline{P}_2}{1+2\overline{P}_2}\right]^{-1}, \tag{23}$$

$$\tau^1_{10} = \left[D_{\perp}\frac{2+\overline{P}_2}{1-\overline{P}_2}\right]^{-1}. \tag{24}$$

Recently, the time correlation functions τ^1_{i0} $(i=0,1)$ for 5CB at one temperature (300 K) have been calculated [44]. It was done using dynamical parameters obtained from the MD simulation, based on realistic atom-atom interaction potential. Here we extend, in the framework of the NMR relaxation theory, our study of 5CB over a wider temperature range. The details in the data analysis using the decoupling model for the correlated internal motions can be found in Ref. [14]. The rotational diffusion model [21,45,46] is employed to describe small step rotational diffusions of molecules in a potential of mean torque. Using the additive potential method [14], the observed quadrupolar splittings were modeled to give the potential of mean torque experienced by each molecule. Because of correlated internal bond rotations in the flexible pentyl chain, a decoupled model [14,22] was used to give the spectral densities of methylene deuterons on C_i in 5CB:

$$\begin{aligned} J^{(i)}_m(m\omega) = {} & \frac{3\pi^2}{2}(q^{(i)}_{CD})^2\sum_n\sum_{n'}\sum_{k=1}^{81}\left(\sum_{l=1}^{81} d^2_{n0}(\theta^{(i)l}_{M,Q})\right.\\ & \left.\times\exp[-in\psi^{(i)l}_{M,Q}]x^{(1)}_l x^{(k)}_l\right)\\ & \times\left[\sum_{l'=1}^{81} d^2_{n',0}(\theta^{(i)l'}_{M,Q})\exp[-in'\psi^{(i)l'}_{M,Q}]x^{(1)}_{l'}x^{(k)}_{l'}\right]\\ & \times\sum_j\frac{(\beta^2_{mnn'})_j[(\alpha^2_{mnn'})_j+|\lambda_k|]}{m^2w^2+[(\alpha^2_{mnn'}t)_j+|\lambda_k|]^2} \end{aligned} \tag{25}$$

where $q^{(i)}_{CD} = 165$ kHz is the quadrupolar coupling constant, $\theta^{(i)l}_{M,Q}$ and $\psi^{(i)l}_{M,Q}$ are the polar angles for the C_i-D bond of the conformer l in the frame fixed on the molecular core, λ_k and $\mathbf{x}^{(k)}$ are the eigenvalues and eigenvectors from diagonalizing the transition rate matrix, and $(\alpha^2_{mnn'})_j/D_{\perp}$, the decay constants, and $(\beta^2_{mnn'})_j$, the relative weights of the exponentials in the time correlation functions, are the eigenvalues and eigenvectors from diagonalizing the matrix of the rotational diffusion operator [46]. In the above equation, the number 81 is the number of distinct conformers available to the pentyl chain of 5CB. The transition rate matrix contains three phenomenological jump constants k_1, k_2, and k_3 for the so-

TABLE I. The rotational diffusion coefficients D_j $(j=\|,\perp)$ and the orientational time correlations τ^1_{i0} $(i=0,1)$ calculated using Eqs. (23) and (24) with $\overline{P}_2=0.51$ for 5CB molecules in the nematic phase at 300 K. The last two columns are obtained from the MD simulation [44].

$D_\|$ $(\times 10^{-8})$ (s)	$D_\perp$ $(\times 10^{-8})$ (s)	τ^1_{00} (ns)	τ^1_{10} (ns)	τ^1_{00} (ns)	τ^1_{10} (ns)
12.4	5.32	38.6	3.66	28.9	2.83

called one-bond, two-bond, and three-bond motions, respectively. The rotation diffusion tensor is characterized by two principal values $D_\perp$ and $D_\|$ in the molecular frame, and these appear in Eq. (25) through the decay constants $(\alpha^2_{mnn'})_j$. By modeling the observed spectral densities for carbons 1–4 at two different Larmor frequencies and several temperatures, both the rotational diffusion constants D_j $(j=\|,\perp)$ can be expressed in an Arrhenius form as $D_j=D^0_j \exp - E_j/RT$, where $D^0_\|=3.25\times 10^{16}$ s^{-1}, $E_\|=4.26\times 10^4$ J/mol, $D^0_\perp=1.63\times 10^{14}$ s^{-1}, $E_\perp=3.725\times 10^4$ J/mol, and R is the gas constant. For completeness we reproduce $D_\|$ and $D_\perp$, and tabulate the calculated τ^1_{00} and τ^1_{10} values at temperature 300 K ($\overline{P}_2=0.51$ from NMR) in Table I. Note that the last two columns are values that have been obtained from the MD simulation, with $\overline{P}_2=0.504$ and $D_\perp=1.4\times 10^8$ s^{-1} [44].

Having obtained time correlation functions τ^1_{i0} $(i=0,1)$, it is possible to calculate the complex dielectric permittivity coefficients $\epsilon_j(\omega)$ $(j=\|,\perp)$ using Eqs. (20) and (21). The results of the calculations of the longitudinal and transverse dielectric permittivities $\mathrm{Re}\,\epsilon_j(\omega)$ and absorption $\mathrm{Im}\,\epsilon_j(\omega)$ for 5CB molecules at $T=300$ K, both for time correlation functions obtained in the framework NMR relaxation theory and by MD simulation [44] are shown in Fig. 2. It should be pointed out that our values of the static permittivity coefficients were calculated using the statistical-mechanical theory that takes into account translational and orientational correlations between dipoles as well as their coupling, whereas in the case of MD simulation the same coefficients have been calculated in the framework of the mean-field theory. This leads to different values for $\mathrm{Re}\,\epsilon_j(\omega)$, whereas their dielectric loss values for the nematic phase of 5CB correspond to a maximum at the frequency of $\nu=\omega/(2\pi)\sim 6$ MHz, which is very close to the experimental data measured at the atmospheric pressure [39].

V. FORMULAS FOR THE FRANK ELASTIC CONSTANTS

In an ideal NLC, the molecules are oriented on the average along the director $\mathbf{n}$ [10]. However, the presence of thermal fluctuations or confining surfaces impairs this ideal configuration. Distortion of the orientational order occurs and varies from point to point. The distortion of the director field $\mathbf{n}(\mathbf{q})$ can be determined by minimizing the functional of the free energy that takes the form

$$F=\int dV f_F+\int dS(f_{13}+f_{24}+f_s), \tag{26}$$

where

$$f_F=\frac{1}{2}[K_1(\boldsymbol{\nabla}\mathbf{n})^2+K_2(\mathbf{n}\boldsymbol{\nabla}\times\mathbf{n})^2+K_3(\mathbf{n}\times\boldsymbol{\nabla}\times\mathbf{n})^2], \tag{27}$$

and $f_{13}=k_{13}\mathbf{k}\cdot\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})$, $f_{24}=-(K_2+k_{24})\mathbf{k}\cdot[\mathbf{n}\boldsymbol{\nabla}\cdot\mathbf{n}+\mathbf{n}\times(\boldsymbol{\nabla}\times\mathbf{n})]$, and f_s is the anchoring energy at the interface. Here k_{13} and k_{24} are surfacelike bulk elastic terms and k_{13} can vanish on symmetry grounds [47], and $\mathbf{k}$ is a unit vector normal to the surface S confining the NLC. The first term in Eq. (26) describes the energy associated with the three basic types of deformation with the bulk Frank ECs K_1, K_2, K_3, for splay, twist, and bend [26,27] distortions, respectively. Over the years, quite a few microscopic theories for the bulk ECs K_i $(i=1,2,3)$ have been developed [23–28]. Recently, calculations of the ratio $K_i/\overline{K}$, both for the usual GB fluid and for the dipolar GB fluid, have been carried out on a simple-cubic system, and for a range of temperatures and densities corresponding to the nematic phase [5]. On the other hand, it is difficult to measure experimentally the absolute values of these coefficients. However, it has been shown [11,12] that the experimental results for

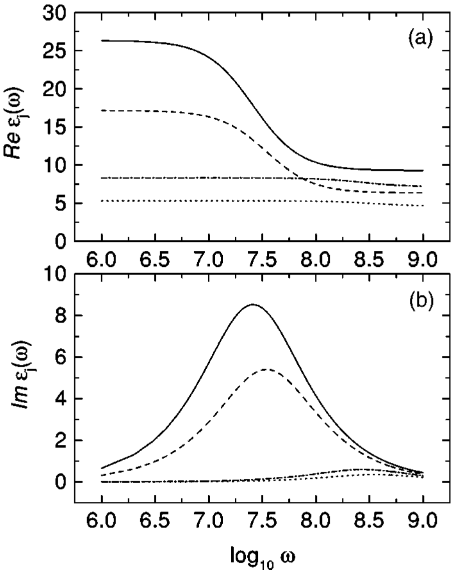

FIG. 2. The real and imaginary parts of the longitudinal and transverse dielectric permittivity $\epsilon_j(\omega)=\mathrm{Re}\,\epsilon_j(\omega)-i\,\mathrm{Im}\,\epsilon_j(\omega)$ $(j=\|,\perp)$ calculated using Eqs. (20) and (21) at $T=300$ K, where $\omega/2\pi$ is in Hz; solid and dotted lines in (a) are longitudinal and transverse components of $\mathrm{Re}\,\epsilon_j(\omega)$, obtained for the τ^1_{i0} $(i=0,1)$ determined in the framework NMR relaxation theory, respectively, whereas dashed and dash-dotted lines obtained for the τ^1_{i0} $(i=0,1)$ determined due to MD simulation [44]. The same lines in (b) are for $\mathrm{Im}\,\epsilon_j(\omega)$.

splay and twist Frank elastic constants have a weak temperature dependence, whereas the bend elastic constant rapidly increases with temperature. In this paper we present an investigation of elasticity phenomena in a nematic LC formed by 5CB molecules, using a combination of existing statistical mechanical approaches proposed in Refs. [5,25,28]. In the framework of these approaches the bulk elastic constants are connecting with structural quantities such as the orientational distribution and direct correlation functions as

$$\frac{K_1}{\overline{K}}=1+\lambda(5-9z), \tag{28}$$

$$\frac{K_2}{\overline{K}}=1-\lambda(1+3z), \tag{29}$$

$$\frac{K_3}{\overline{K}}=1-4\lambda(1-3z), \tag{30}$$

where $z=(\overline{\cos^4\beta}-\overline{\cos^6\beta})/(\overline{\cos^2\beta}-\overline{\cos^4\beta})$, and $\lambda=\eta/[2(3-\eta)]$ is a geometric factor of the molecule with $\eta=(\gamma^2-1)/(\gamma^2+1)$. In the density-functional approach [25,28] the quantity $\overline{K}$ is given as

$$\overline{K}=\frac{1}{3}(K_1+K_2+K_3)=B\overline{P_2^2}\theta\frac{10\overline{P}_2-24\overline{P}_4+14}{105}\frac{3-\eta}{6\eta}, \tag{31}$$

where B is a factor that has the dimension of force and may be written as [5,25,28]

$$B=3\pi\rho^2\eta^3M_4b^2\frac{1+\frac{1}{14}\eta^2}{1-\eta^2}\left[\frac{\epsilon_0}{\sigma_\perp}\right]. \tag{32}$$

Here $b=4\pi\rho\eta^2M_2[1+(3/14)\eta^2]/[3(1-\eta^2)]$ is a dimensionless factor and M_{2L} $(L=1,2)$ can be expressed in terms of the DCF $C(ij)$ as

$$M_{2L}=-\int\int C(\mathbf{q}_i,\mathbf{e}_i,\mathbf{q}_j,\mathbf{e}_j)|\mathbf{q}_i-\mathbf{q}_j|^L d\mathbf{q}_i d\mathbf{e}_i d\mathbf{q}_j d\mathbf{e}_j. \tag{33}$$

Here $\mathbf{q}_i$ denote the coordinate of the ith molecule in the volume v. The averaged functions $\overline{\cos^n\beta}$ are

$$\overline{\cos^2\beta}=\frac{2\overline{P}_2+1}{3},$$

$$\overline{\cos^4\beta}=\frac{20\overline{P}_2+8\overline{P}_4+7}{35},$$

$$\overline{\cos^6\beta}=\frac{110\overline{P}_2+72\overline{P}_4+16\overline{P}_6+33}{231}.$$

Thus, according to Eqs. (28)–(30) we can calculate the absolute values of K_i $(i=1,2,3)$ provided that $\overline{P}_{2L}$ $(L=1,2,3)$ and $C(ij)$ are known. While the order parameters for various LCs are usually found easily, an accurate determination of the DCF for a nematic state is still a formidable task.

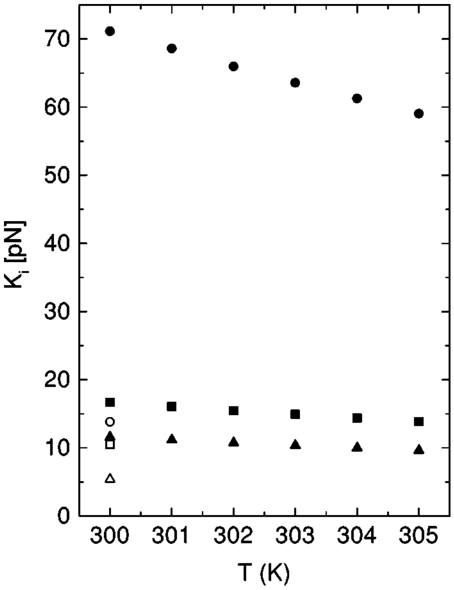

FIG. 3. The temperature dependence of the Frank elastic coefficients K_i $(i=1,2,3)$ for 5CB. Solid symbols represent points calculated using Eqs. (28), (29), and (30); circles (K_3), squares (K_1), and triangles (K_2), respectively. Open circle (K_3), square (K_1), and triangle (K_2) are experimental data (Ref. [11]), respectively.

Using classical Percus-Yevick closure approximation and the binary correlation function $F_{ij}(ij)$ obtained in the framework of the statistical mechanical scheme described in Sec. II, we may determine the DCF in the form [48]

$$C(ij)=F_{ij}(ij)[1-V^{-1}(ij)], \tag{34}$$

where $V(ij)$ has been defined above by the pair intermolecular potential. Having obtained the DCF $C(ij)$ and the set of $\overline{P}_{2L}$ $(L=1,2,3)$ it is possible to calculate ECs K_i. Figure 3 shows the temperature dependence of the K_i using this approach. Three different approximations have been combined for the calculation of the ECs: (i) the nonlinear IEs theory that requires access to the set of order parameters and the binary correlation function, (ii) the classical Percus-Yevick approximation for the DCF, and (iii) Nemtsov and Zakharov density-functional approach that implies that higher order parameters (i.e., $\overline{P}_6$) and higher moments (i.e., M_4) of the DCF are used. Taking into account these approximations as well as the fact that the Percus-Yevick closure works well mostly for short-range intermolecular potentials and the difficulty with measuring the absolute values of these coefficients, the qualitative agreement between our calculations and the experimental values (Fig. 3) obtained using the Fredericksz transition method [11,12] is heartening. It should be noted that the direct measure of the absolute values of the ECs is a difficult task and in practice the ratios K_3/K_1 and K_2/K_1 can be directly measured with greatest accuracy by means of, for

TABLE II. Ratio of the Frank elastic coefficients K_3/K_1, K_2/K_1 for 5CB at 300 K calculated using the nonlinear IEs method and using experimental data (EXP) [11].

	IE ($\mu^*=0$)	IE ($\mu^*\approx 2.5$)	EXP
K_3/K_1	4.258	4.264	1.31
K_2/K_1	0.694	0.695	0.505

example, the light scattering [10]. Calculated and measured ratios at 300 K are tabulated in Table II.

VI. CONCLUSION

In this paper, we present an investigation of the structure, dielectric, and elastic phenomena as well as dynamics of nematic liquid crystals, formed by 4-n-pentyl-4-n'-cyanobiphenyl, using a combination of existing statistical mechanical theory based upon the method of conditional distribution function and NMR relaxation theory. In order to elucidate the role of the intermolecular dipole-dipole correlations in calculating the structural, static and elastic coefficients we used the method of nonlinear integral equations, in which translational, orientational, and mixed correlations were taken into account. Using the dipolar GB potential and molecular model that allowed us to express the static dielectric permittivity constants in terms of dipolar correlators [20], the dielectric constants were calculated and compared with results obtained experimentally [8,9,33]; a good agreement between theory and experiment was found. Calculations of the dielectric relaxation coefficients and orientational correlation times at temperatures and density corresponding to the nematic phase of 5CB also show good agreement with the MD simulation [44] and experimental data [39]. We have also determined the absolute values of splay (K_1), twist (K_2), and bend (K_3) elastic constants, and their ratios K_3/K_1 and K_2/K_1 in the nematic phase of 5CB. Statistical-mechanical approach used for calculations of the elastic coefficients rest on the model in which the K_i ($i=1,2,3$) depend on the direct correlation function and set of order parameters. The method also takes into account both the intermolecular attraction and steric repulsion, but is unable to describe the effect due to flexibility of the molecules. Since the structure of the mesogenic cyanobiphenyl molecules is characterized by a rigid central core to which is attached one (or more) flexible hydrocarbon chain, the ability to account for the chain flexibility in the final expressions for the elastic coefficients is an important step towards their most general expressions. Of course, the present GB model of the intermolecular interactions is unable to account for the flexibility in real mesogenic compounds. On the other hand, this limitation is counterbalanced by the simplicity of the present approach, which can be used to calculate many physical parameters of nematic liquid crystals. It is noted that the long-range nature of the dipolar GB potential requires further investigations, including perhaps better numerical approaches. Thus, the combination of the NMR relaxation techniques and statistical mechanics theories provides a powerful tool for investigating both the dielectric and elastic properties of real nematics. We believe that this paper not only shows some useful routes for estimating the elasticity, but also for analyzing the dielectric properties in nematic liquid crystals. Furthermore, the rotational diffusion constant for molecular tumblings in the decoupled model for the chain dynamics seems to produce reasonable values of dielectric loss in the nematic phase of 5CB, lending support to the NMR relaxation model.

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