Dynamic and Dielectric Properties of Liquid Crystals

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Abstract—The structural properties, static \( \varepsilon_r \) and relaxation \( \varepsilon_r(\omega) \) permittivities \( (j = \parallel, \perp) \), time correlation functions \( \Phi_{ij}(t) \) \((i = 0, 1) \) and \( \Phi_{ij}^2(t) \), and orientational relaxation times \( \tau_{ij}^1(t) \) \((i = 0, 1) \) of 4-n-pentyl-4' -cyanobiphenyl (5CB) molecules in the nematic phase are investigated in the framework of the statistical–mechanical theory and the molecular dynamics method. The permittivities \( \varepsilon_r \) are calculated within a statistical–mechanical approach with the inclusion of translational, orientational, and mixed correlations in the description of the anisotropic systems. The time correlation functions \( \Phi_{00}(t) \) and \( \Phi_{01}^2(t) \) and the orientational relaxation times \( \tau_{01}^1(t) \) of 5CB molecules are calculated using the molecular dynamics method for liquid-crystal systems simulated by realistic intramolecular and intermolecular atom–atom interactions. The results of calculations and the experimental data for 5CB are in good agreement. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The characteristic feature of anisotropic systems such as liquid crystals is that they exhibit a long-range orientational order due to an anisotropic nature of intermolecular interaction. There exist a number of theoretical approaches to analyzing the relation between the measured macroscopic parameters and the microscopic structure of liquid-crystal systems [1]. Among these methods, the statistical–mechanical approach and molecular dynamics calculations seem to hold the greatest promise. This can be explained by the fact that these techniques make it possible, on the one hand, to calculate directly the macroscopic characteristics of liquid crystals in the framework of reasonable approximations using model intermolecular interaction potentials and, on the other hand, to determine the averaged parameters on the basis of realistic interaction potentials both between atoms inside molecules forming an anisotropic system and between atoms of different molecules [1, 2].

In the present work, the above theoretical approaches were used to investigate the dynamic and dielectric properties of the nematic phase of 4-n-pentyl-4' -cyanobiphenyl (5CB). For this purpose, the time correlation functions, orientational relaxation times, and orientation distribution functions were derived by the molecular dynamics method [3, 4]. The choice of the nematic phase of 5CB was made primarily for the following reasons: (i) this compound has a simple phase diagram, and (ii) the nematic phase is observed in the temperature range corresponding to the nematic phase were calculated in the framework of the statistical–mechanical theory. Moreover, the time correlation functions were obtained from molecular...
dynamics calculations, which made it possible to calculate the orientational relaxation times with the use of realistic interatomic interaction potentials [3, 4].

This paper is organized as follows. Section 2 covers the basic principles of the statistical–mechanical description of a system of interacting dipoles. Within this approach, we calculated the orientation distribution functions, the pair correlation functions, and the order parameters. Sections 3 and 4 present the results of calculations of the relaxation times and the static and relaxation permittivities of a nematic liquid crystal formed by 5CB molecules.

2. THE PAIR CORRELATION FUNCTION

The pair correlation functions for the nematic phase of 5CB are calculated in the framework of the equilibrium statistical mechanics [15] based on the method of conditional distributions [12]. We consider a single-component system composed of ellipsoidal molecules of length \( s_\parallel \) and width \( s_\perp \) in a volume \( V \) at a temperature \( T \). The volume of the system is divided into \( N \) cells, each occupying a volume \( v = V/N \). As a first approximation, we take into account only the states of the system for which each cell contains one molecule [16]. The potential energy of this system can be represented in the form

\[
U = \sum_{i<j} \Phi(i, j),
\]

where \( \Phi(i, j) \) is the pair intermolecular interaction potential, \( i \equiv (r_i, e_i) \), and \( r_i \) and \( e_i \) are the vectors specifying the position and the orientation of the \( i \)th molecule, respectively. Now, we perform the integration of the quantity \( \exp[-U/k_BT] \) (where \( k_B \) is the Boltzmann constant), which is the probability density of finding the system at points 1, 2, 3, ..., \( N \) at a temperature \( T \) [12, 15]. As a result, we determine partial distribution functions, namely, the one-particle distribution function \( F(i) \) (the probability density of finding a particle inside the \( i \)th cell), the pair distribution function \( F(i, j) \) (the probability density of finding two particles in the \( i \)th and \( j \)th cells), etc. [12, 16]. In the present work, we will restrict our consideration to the case of two-particle correlations.

The functions \( F(i) \) and \( F(i, j) \) can be expressed in terms of the mean-force potentials [12, 16]

\[
F(i) = \frac{\Psi(i)}{\int \Psi(i) d(i)},
\]

\[
F(i, j) = F(i) F(j) V(i, j) \Psi_{i,j}^{-1}(i) \Psi_{i,j}^{-1}(j),
\]

(2)

where

\[
\Psi_{i,j}(i) = \prod_{i<j} \psi_{i,j}(j),
\]

(3)

\[
\psi_{i,j}(j) = \int_{\Delta} d(j) = \int_{V} d \mathbf{r}_j \int_{\alpha} d e_j,
\]

\[
V(i, j) = \exp[-\Phi(i, j)/k_BT],
\]

and \( \alpha \) is the volume associated with the orientation of the \( i \)th molecule. The functions \( F(i) \) satisfy the normalizing condition

\[
\int F(i) d(i) = 1,
\]

and the constraint

\[
\int F(i) F(j) d(i) d(j) = \int F(i) d(i),
\]

which relates the one-particle and two-particle distribution functions, allows us to derive a closed integral equation with respect to the mean-force potential \( \Psi_{i,j}(i) \) [12, 16]:

\[
\Psi_{i,j}(i) = \int V(i, j) \Psi_{i,j}^{-1}(j) F(j) d(j).
\]

Equation (3) can be solved only by the numerical method described in detail in [16, 17]. With the use of the solution \( \Psi_{i,j}(i) \) and Eq. (2), we can calculate the pair correlation function \( F(i, j) \), the orientation distribution function \( f_0(\cos \beta_i) = \int F(i) d \mathbf{r}_i d \varphi_i \) (where \( \varphi_i \) is the azimuthal angle of the unit vector \( e_i \)), the order parameters of the liquid-crystal system

\[
\bar{P}_{2L} = \int F(i) P_{2L}(\cos \beta_i) d(i),
\]

the correlators

\[
\langle e_i \cdot e_j \rangle = \int d(i) \int d(j) F(i, j)(e_i \cdot e_j),
\]

(5)

\[
\bar{\mathcal{R}} = \int d(i) F(i) \cos(2 \pi \zeta_i / d) P_2(\cos \beta_i),
\]

(6)

and the Helmholtz free energy

\[
f = \frac{F}{N} = k_B T \ln \int d(i) \Psi(i).
\]

Here, \( P_{2L} \) (\( L = 1, 2, \) and 3) are the Legendre polynomials, \( \beta \) is the polar angle formed by the long molecular axis and the director \( \mathbf{n} \) aligned along the \( z \) axis, and \( d \) is the distance between two layers of the smectic-A phase.

The parameter \( \bar{\mathcal{R}} \) is the measure of the density wave amplitude of the layered structure of the phase. The nematic phase is characterized by \( \bar{\mathcal{R}} = 0 \) and \( P_{2L} \neq 0 \).

The kernel \( V(i, j) \) of the integral equation (3) is determined by the pair intermolecular interaction potential chosen as the sum of the Gay–Berne potential and the dipole–dipole interaction potential: \( \Phi(i, j) = \Phi_{GB}(i, j) + \Phi_{DD}(i, j) \). The former potential can be written in the form

\[
\Phi_{GB}(i, j) = 4 \varepsilon \xi \xi_0 (R^{-12} - R^{-6}),
\]

where \( R = (r - \sigma + \sigma_\perp) / \sigma_\perp \) and \( r = |r_i - r_j| \). The parameters \( \sigma \) and \( \xi \) are the width and the depth of the potential well, respectively. These parameters depend on the orientation of the unit vectors \( e_i \) and \( e_j \) (where \( e = r / |r| \)), the geometric parameter of the molecule \( \gamma = \sigma_\parallel / \sigma_\perp \), and the two exponents \( \nu \) and \( \mu \) in the relationship \( \varepsilon = \varepsilon_\nu (e_i, e_j) \varepsilon_\mu (e_i, e_j) \). The formulas for \( \varepsilon_\nu \) and \( \varepsilon_\mu \) are given in [13]. The dipole–dipole interaction potential has the form

\[
\Phi_{DD}(i, j) = \Delta^2 \varepsilon^2 / r^3 [(e_i \cdot e_j) - 3(e_i \cdot e_i)(e_j \cdot e_j)],
\]

where \( \Delta \) is the dipole moment of the 5CB molecule (\( \Delta \sim 5 D \) [14]). The intermolecular interaction parameters used in our calcula-
The order parameters calculated by the molecular dynamics method with different parametrizations of the potential energy of the system [3, 4, 20] and molecular coordinate systems [21] considerably differ from each other [22]: 0.5 ≤ \( P_2 \) ≤ 0.72 and 0.18 ≤ \( P_4 \) ≤ 0.31. The interpretation of the experimental data also depends on the choice of the coordinate system [23]. Compound 5CB over the entire range of the existence of the nematic phase is characterized by the parameter \( \bar{\chi} = 9.5 \times 10^{-2} \), which confirms that there is a nematic ordering in the phase. It was also found that the dimensionless Helmholtz free energy \( f/e_0 \) of the system is equal to −15.55 with due regard only for the nearest neighbors and −15.67 with allowance made for the nearest and next-to-nearest neighbors. Such an insignificant change in this integral characteristic indicates that, in the framework of the statistical theory allowing for the translational, orientational, and mixed correlations, it is quite reasonable to take into account the nearest and next-to-nearest neighbors.

3. STATIC PERMITTIVITY OF A NEMATIC LIQUID CRYSTAL

The static permittivity of an isotropic liquid is determined by the scalar quantity \( \varepsilon_s \) [24]. The dielectric properties of uniaxial liquid-crystal systems are characterized by two permittivity tensor components \( \varepsilon_{ij} \), which are parallel (\( \varepsilon_{xx} = \varepsilon_{yy} \)) and perpendicular (\( \varepsilon_{zz} = \varepsilon_{xy} = \varepsilon_{yz} \)) to the director orientation \( \mathbf{n} \) [5]. The difference between \( \varepsilon_s \) and \( \varepsilon_{xx} \) is insignificant for nonpolar liquid crystals but is substantial for polar liquid crystals such
as 5CB. For these two components, the mean permittivity $\bar{\varepsilon}$ can be defined by the expression

$$\bar{\varepsilon} = \frac{2\varepsilon_\parallel + \varepsilon_\perp}{3}. \quad (9)$$

For 5CB, the value of $\delta\varepsilon_{NI} = \bar{\varepsilon} - \varepsilon$, at the temperature $T_{NI}$ of the nematic–isotropic liquid phase transition is negative and the permittivity $\bar{\varepsilon}$ slowly decreases with a decrease in the temperature [5]. According to the molecular theory proposed by Edwards and Madden [25], the permittivity tensor components can be calculated from the quadratic equation

$$\varepsilon_j^2 - B_j \varepsilon_j - D_j = 0, \quad (10)$$

where $B_j = \frac{A_j + 1}{1 + y_j}$ and $D_j = \frac{y_j}{1 + y_j}$ ($j = \parallel, \perp$). The unknown coefficients $A_j$ and $y_j$ are functions of $t_j$ and $\varepsilon_j$, respectively. The quantity $t_j$ is given by the formula

$$t_j = \left\langle \mathbf{e}_j \cdot \sum_{m \in R_B} \mathbf{e}_m \right\rangle, \quad (11)$$

where $m \neq j$ and $\langle \ldots \rangle$ is defined by relationship (5). Summation in formula (11) is carried out over all the dipoles located inside the sphere of radius $R_B$ with the center at the $j$th molecule. All correlators of the type $\langle \mathbf{e}_j \cdot \mathbf{e}_m \rangle$ can be calculated in terms of the statistical–mechanical theory described in Section 2. The relationships for $A_j$ and $y_j$ have the form [25]

$$A_j = \frac{4\pi \rho \mu^2}{\Theta} t_j, \quad y_j = \frac{\xi}{\Omega} \left(1 - \frac{1}{\Omega^{1/2}} \tan^{-1} \Omega^{1/2}\right), \quad (12)$$

where $\Omega = \xi - 1$ and $\xi = \varepsilon/\varepsilon_i$. Equation (10) can be solved using the iterative procedure

$$\varepsilon_j^{[k+1]} = \frac{B_j (\varepsilon_j^{[k]} + \frac{D_j (\varepsilon_j^{[k]} + 4)}{4} + D_j (\varepsilon_j^{[k]} + 4))^{1/2}}{2}, \quad (13)$$

where $k$ is the iteration number. Figure 2 shows the temperature dependences of the permittivities $\varepsilon_j$ ($j = \parallel, \perp$) calculated according to Eq. (10) with the use of the correlators $t_j$ obtained in the framework of the statistical–mechanical theory. The experimental data on the static permittivity for the nematic phase of 5CB [6, 11] are also presented in Fig. 2. It should be noted that the calculated and experimental data are in good agreement.

### 4. DIELECTRIC RELAXATION AND THE RELAXATION TIMES OF 5CB

For 5CB, the permittivity relaxation tensor $\varepsilon_{\alpha\beta}(\omega) = \text{Re} \varepsilon_{\alpha\beta}(\omega) - i \text{Im} \varepsilon_{\alpha\beta}(\omega)$, which was measured over a wide frequency range (1 kHz $\leq \omega/2\pi \leq 13$ MHz [9]), is characterized by a Debye relaxation. In the laboratory coordinate system with the $z$ axis coinciding with the director orientation $\mathbf{n}$, the tensor components $\varepsilon_{\alpha\beta}(\omega)$ for uniaxial nematics can be written in the following form [26]:

$$\frac{\varepsilon_{\beta}(\omega) - 1}{\varepsilon_{\beta} - 1} = 1 - i\omega \int C_\beta(t) \exp(-i\omega t) dt, \quad (14)$$

where $C_\beta(t)$ are the tensor components of the dipole autocorrelation function. These components can be represented by the relationships

$$C_{\parallel \parallel} = \langle e_z(0) e_z(t) \rangle = \Phi_{00}(t), \quad (15)$$

$$C_{\perp \perp} = \langle e_x(0) e_x(t) \rangle = \langle e_y(0) e_y(t) \rangle = \Phi_{10}(t). \quad (16)$$

Here, $\Phi_{00}(t)$ ($i = 0, 1$) are the first-rank time correlation functions and $e_\alpha$ ($e_\alpha \equiv e_\alpha$) are the projections of the unit vector $\mathbf{e}$ onto the $\alpha$ axes ($\alpha = x, y, z$). The functions $\Phi_{00}(t)$ can be written in the exponential form [2]

$$\Phi_{00}(t) = \Phi_{00}(0) \exp(-t/\tau_{00}^1) \quad (17)$$

$$= \frac{1 + 2P_2^1}{3} \exp(-t/\tau_{00}^1),$$
It should be noted that different spectroscopic techniques make it possible to determine the relaxation times \( \tau_m \) and the time correlation functions \( \Phi_m(t) \) at specific values of \( L \). In particular, the first-rank time correlation functions \( (L = 1) \) can be obtained using IR and dielectric spectroscopy \[27\], whereas the second-rank time correlation functions \( (L = 2) \) can be determined by NMR spectroscopy \[28\]. Three time correlation functions, \( \Phi_{10}(t) \) \( (j = 0, 1) \) and \( \Phi_{00}(t) \), calculated in terms of the molecular dynamics method described in Section 2 are shown in Fig. 3. A technique for calculating these functions and the orientational relaxation times \( \tau_{i0}(i = 0, 1) \) was described in detail in \[3, 4\]. The relaxation times \( \tau_{i0} \) calculated within the molecular dynamics formalism and determined using NMR spectroscopy \[29\] for the nematic phase of 5CB at 300 K are presented in the table.

From relationships (19) and (20) and the relaxation times \( \tau_{i0} \) \( (i = 0, 1) \), we can calculate the coefficients of the complex permittivity tensor \( \varepsilon_j(\omega) \) \( (j = ||, \perp) \). Figure 4 presents the real parts \( \text{Re} \varepsilon_j(\omega) \) and the imaginary parts \( \text{Im} \varepsilon_j(\omega) \) of the permittivity tensor components \( \varepsilon_j(\omega) \) calculated for the nematic phase of 5CB at a temperature of 300 K. The frequency \( \nu = \frac{\omega}{2\pi} \) at which both longitudinal \( \text{Im} \varepsilon_{||}(\omega) \) and transverse \( \text{Im} \varepsilon_{\perp}(\omega) \) components of the permittivity tensor \( \varepsilon(\omega) \) exhibit a maximum of the dielectric loss is in close agreement with the frequency \( \nu_{\exp} = 6 \text{ MHz} \) determined experimentally for the nematic phase of 5CB at atmospheric pressure \[9\].

**Fig. 3.** Time correlation functions for 5CB molecules in the nematic phase according to molecular dynamics calculations.

\[
\Phi_{00}^1(t) = \Phi_{10}^1(0) \exp(-t/\tau_{10}^1) = \frac{1 - \frac{1}{3}p_2}{3} \exp(-t/\tau_{10}^1).
\]

**Fig. 4.** Real and imaginary parts of the permittivity tensor \( \varepsilon_j(\omega) \) \( (j = ||, \perp) \) calculated according to relationships (19) and (20) for (1) longitudinal and (2) transverse components \( \varepsilon_j(\omega) \) \( (\omega/2\pi \text{ in Hz}) \) at a temperature of 300 K.

<table>
<thead>
<tr>
<th>Molecular dynamics method</th>
<th>NMR spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{00} ), ns</td>
<td>( \tau_{10}^1 ), ns</td>
</tr>
<tr>
<td>38.6</td>
<td>3.66</td>
</tr>
<tr>
<td>( \tau_{10} ), ns</td>
<td>( \tau_{10}^1 ), ns</td>
</tr>
<tr>
<td>28.9</td>
<td>2.83</td>
</tr>
</tbody>
</table>
5. CONCLUSIONS

Thus, in the present work, the dynamic and dielectric properties of the nematic liquid crystal formed by 5CB molecules were investigated in the framework of the statistical–mechanical theory (based on the method of conditional distributions) and the molecular dynamics method (with the use of realistic interatomic interaction potentials). Within these approaches, we calculated the orientation distribution functions \( f_0(\cos \beta) \) of 5CB molecules, the order parameters \( P_{2L} \) \((L = 1 \text{ and } 2)\), the orientational correlators \( \langle \varepsilon_i \cdot \varepsilon_j \rangle \), the static \( \langle \varepsilon_i \rangle \) and relaxation \( \langle \varepsilon_i(\omega) \rangle \) permittivities \((j = ||, \perp)\), the orientational relaxation times \( \tau_{i0}^1 \) \((i = 0, 1)\) and \( \tau_{i0}^2 \) \((i = 0, 1)\) and \( \Phi_{i0}^j(t) \) \((i = 0, 1)\). The results obtained were compared with the available experimental data and with the results derived within other independent theoretical approaches. In particular, the relaxation times \( \tau_{10}^1 \) \((i = 0, 1)\) and the order parameter \( P_2 = 0.504 \) \((T = 300 \text{ K})\) determined in our work permitted us to calculate the rotational self-diffusion coefficient \( D_\perp \) for 5CB molecules according to the equation \( \tau_{10}^1 = [D_\perp(2 + \bar{P}_2)/(1 - \bar{P}_2)]^{-1} \) \[27\]. The result obtained \((D_\perp = 1.4 \times 10^8 \text{ s}^{-1})\) was compared with the self-diffusion coefficient \( (D_\perp = 5.32 \times 10^8 \text{ s}^{-1}) \) determined from the experimental NMR data \[29\]. The above results give grounds to make the inference that the molecular dynamics method used in combination with the statistical–mechanical theory is a valuable tool for studying the macroscopic and microscopic properties of real liquid-crystal materials.

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REFERENCES


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