

## Rotational viscosity in a nematic liquid crystal: A theoretical treatment and molecular dynamics simulation

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The rotational viscosity coefficient  $\gamma_1$  of 4-*n*-pentyl-4'-cyanobiphenyl in the nematic phase is investigated by combination of existing statistical-mechanical approaches (SMAs), based on a rotational diffusion model and computer simulation technique. The SMAs rest on a model in which 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 SMAs,  $\gamma_1$  is found to be a function of temperature, density, rotational diffusion coefficient, and a number of order parameters (OPs). The diffusion coefficient and the OPs were obtained from an analysis of a trajectory generated in a molecular dynamics simulation using realistic atom-atom interactions. In addition, a set of experimentally determined diffusion coefficients and OPs was used for evaluation of  $\gamma_1$ . Reasonable agreement between calculated and experimental values of  $\gamma_1$  is obtained. It is shown that near the clearing point  $\gamma_1$  is proportional to  $\bar{P}_2^2$ , where  $\bar{P}_2$  is the second-rank OP. This limiting value of  $\gamma_1$  is in agreement with mean-field theory. [S1063-651X(99)05206-X]

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### I. INTRODUCTION

During the past decade thermotropic liquid crystals have attracted considerable scientific attention. This attention can be partly ascribed to many spectacular technical applications. A particular effort has been made to establish relationship between macroscopic liquid crystalline (LC) properties and molecular structure. A useful approach in these studies is provided by combination of theoretical aspects of statistical mechanics [1] and computer simulation technique [2].

In the present paper we combine these methods in order to investigate rotational viscosity of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) (see Fig. 1) in the nematic phase. Here we use order parameters (OPs) and rotational diffusion coefficients obtained from experiments and from an analysis of a trajectory generated in a molecular dynamics (MD) simulation. This simulation was performed using realistic atom-atom interactions in order to facilitate the analysis of molecular structure and dynamics. The details of the simulation are provided elsewhere [3,4]. 5CB has served as a model system for many theoretical and experimental investigations. The reason is a simple phase diagram, nearly uniaxial symmetry and a convenient temperature range of the LC phase, namely, between 295 and 307 K. In particular, many inves-

tigations using nuclear magnetic resonance (NMR) [5] on deuterium [6–8], carbon-13 [9,10], and proton [11] nuclei have been reported studying the molecular structure and diffusion processes of 5CB. These processes have also been investigated using computer simulation methods for a number of interaction potentials [3,12–14].

The present paper is organized as follows: A description of the statistical-mechanical formulas for the rotational viscosity is given in Sec. II. Simulated liquid crystal and rotational self-diffusion are discussed in Sec. III. Numerical results for rotational viscosity coefficient and conclusion are summarized in Sec. IV.

### II. STATISTICAL-MECHANICAL FORMULAS FOR THE ROTATIONAL VISCOSITY

The rotational viscosity of LCs is an extremely important property whose fundamental physics is far from being completely understood [15–23]. Two different frameworks have been used in the theoretical treatment of this concept: (i) the microscopic (“structural”) approaches based on the detailed description of motion of the individual particles [24–26] and (ii) “phenomenological” approaches for uniaxial nematic LCs (NLCs) in the framework of the Ericksen-Leslie (EL) [27,28] theory, which is based on continuous hydrodynamics of nematic liquid crystals, where the macroscopic viscous stress tensor  $\bar{\sigma}_{ij}$  is given by

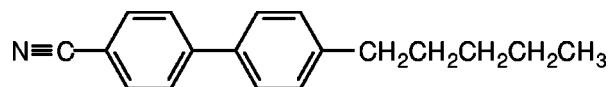


FIG. 1. 5CB molecule.

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$$\begin{aligned} \bar{\sigma}_{ij} = & \alpha_1 n_i n_j n_k n_l A_{kl} + \alpha_2 n_i N_j + \alpha_3 n_j N_i + \alpha_4 A_{ij} + \alpha_5 n_i n_k A_{kj} \\ & + \alpha_6 n_j n_k A_{ki}, \end{aligned} \quad (1)$$

and

$$\begin{aligned} N_i = & \dot{n}_i - w_{ij} n_j, \quad 2w_{ij} = v_{i,j} - v_{j,i}, \\ 2A_{ij} = & v_{i,j} + v_{j,i}, \quad \dot{\mathbf{n}} = \frac{d\mathbf{n}}{dt}, \quad v_{i,j} = \frac{\partial v_i}{\partial x_j}. \end{aligned}$$

Here the unit vector  $\mathbf{n}$  denotes the nematic director,  $\mathbf{N}$  is the angular velocity of the director relative to that of the fluid, and  $A_{ij}$  is symmetric part of the second-rank tensor of the velocity gradient. The coefficients  $\alpha_1$  to  $\alpha_6$  in Eq. (1) are Leslie viscosity coefficients and satisfy the general Onsager-Parodi relation  $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$ . The coefficient  $\gamma_1 = \alpha_3 - \alpha_2$  is called the rotational viscosity coefficient (RVC) and plays a crucial role in a number of applications (see, for example, [16]). The main aim of our investigation is to present theoretical calculations of  $\gamma_1$  in the framework of existing microscopic approaches [18,21–23], using the rotational self-diffusion coefficient (RSC) determined in the MD simulation.

An efficient microscopic approach to the dynamical properties of the LC is based on the rotational diffusion model, which assumes that the reorientation of an individual molecule is a stochastic Brownian motion in a certain potential of mean torque [29]. In such a treatment the system is determined by the time-dependent single-particle orientational distribution function (ODF) governed by an appropriate kinetic equation.

A theory that relates the macroscopic viscous stress tensor  $\bar{\sigma}_{ij}$  to microscopic parameters was presented by Osipov and Terentjev [21]. This theory is formulated using an EL-type equation and rests on thermodynamic assumptions about changes of the free energy. The main feature of the theory is in the form of the nonequilibrium ODF  $\bar{f}(\mathbf{a}, t)$ , where  $\mathbf{a}$  is the orientation of the unit vector of the long axis of the molecule. They have proposed a model where the flow of the fluid breaks the cylindrical symmetry of the NLC and suggest, within the assumption of low velocity gradients, that the nonequilibrium ODF can be written in the form  $\bar{f} = f(1 + h)$ , where  $f$  is the local equilibrium ODF and the small correction  $h$  is determined by the velocity gradients combined with the components of the director  $\mathbf{n}$  and another vector  $\mathbf{e}$ , perpendicular to the director. The general expression for  $h$  has the form [21]

$$h = c_0 n_i n_j A_{ij} + c_1 n_i e_j A_{ij} + c_2 n_i e_j A_{ij}^a + c_3 e_i e_j A_{ij}, \quad (2)$$

where  $A_{ij}^a$  is an asymmetric part of the velocity gradient and  $c_i$  are correction functions dependent only on the angle  $\theta$  between the director and the orientation of the molecule. After averaging of the microscopic equivalent of the macroscopic viscous stress tensor  $\bar{\sigma}_{ij} = \int \bar{f} \sigma_{ij} d\mathbf{a}$  and comparing with the formula (1), the final expressions for all Leslie coefficients  $\alpha_i (i=1, \dots, 6)$  have been obtained.

It should be pointed out that the expressions for the Leslie coefficients in the Osipov-Terentjev (OT) approach can be

transformed to a form that was obtained by Kuzuu and Doi [20] using other method. In particular, the expression for the RVC takes the form [21]

$$\gamma_1 = \frac{\rho k T}{D_{\perp}} g_1(y), \quad (3)$$

where  $g_1(y) = \frac{1}{6} y^{1/2} \exp y$ , and  $y = J_0 \bar{P}_2 / kT$ ,  $T$  is the temperature,  $k$  is the Boltzmann constant,  $J_0 = 4.5 k T_c$  according to mean-field theory, with  $T_c$  the clearing temperature,  $\bar{P}_2$  is the second-rank OP, and  $D_{\perp}$  is a RSC corresponding to the molecular tumbling. The function  $g_1$  in Eq. (3) is a result of an assumption that the relaxation time of the molecular rotation about the  $\mathbf{n}$  axis (the azimuthal angle  $\varphi$ ) is much smaller than the time of reorientation with respect to the polar angle  $\theta$ . In fact, the anisotropic nature of the rotational dynamics of the 5CB molecule was demonstrated in relevant time correlation functions (Fig. 7 in Ref. [3]). So, assuming the stationary reorientation process in the field  $v_{i,j}$ , the distribution function can be considered as being averaged over  $\varphi$ . Although the problem of the  $\varphi$  term in the kinetic equation has been pointed out [30–32], only recently has a systematic analysis of the subject been presented [33].

The OT approximation was corrected by Nemtsov [18] and Zakharov [22] (NZ) in the framework of an approach that is based on the random walk theory together with some ideas of the Zubarev nonequilibrium statistical operator [34]. The essence of this correction is that not only autocorrelation of the microscopic stress tensor as in Ref. [21] is considered, but also additional correlation of the stress tensors with the director and fluxes with the OP tensor are taken into account. Calculations of these correlations in the NLC show that they give significant contributions to the viscosity coefficients [22,35]. It is so because there are interactions between the hydrodynamical flow of the fluid and the molecular orientations. The procedure for constructing the RVC  $\gamma_1$  for the nematic phase has been described in Refs. [22,35]. As a result,  $\gamma_1$  can be written as a function of temperature  $T$ , density  $\rho = N/V$ , and second-rank OP  $\bar{P}_2$ :

$$\gamma_1 = \frac{\rho k T}{D_{\perp}} g_2(\bar{P}_2), \quad (4)$$

where  $g_2(\bar{P}_2)$  is a rational function

$$g_2(\bar{P}_2) = 3 \bar{P}_2^2 \frac{3.181 + 0.757 \bar{P}_2}{2.881 + \bar{P}_2 + 12.56 \bar{P}_2^2 + 4.69 \bar{P}_2^3 - 0.743 \bar{P}_2^4}.$$

Recently, a general method for calculation of the viscosity coefficients in a biaxial NLC was proposed by Fiałkowski [23]. It is also based on change in the Helmholtz free energy caused by the shear flow. Here the kinetic equation is written in the approximation of the low velocity gradient field, which rotates each molecule with a certain average angular velocity. In the limiting case, when appropriate biaxial OPs vanish and the system becomes uniaxial, one can rewrite the expression for the RVC in the form [23]

$$\gamma_1 = \frac{\rho k T}{D_{\perp}} g_3(\bar{P}_2, \bar{P}_4), \quad (5)$$

where

$$g_3(\bar{P}_2, \bar{P}_4) = \frac{70\bar{P}_2^2}{16\bar{P}_4 + 5\bar{P}_2 + 14},$$

where  $\bar{P}_4$  is the fourth-rank order parameter. Thus, according to Eqs. (3)–(5),  $\gamma_1$  is found to be inversely proportional to the rotational self-diffusion constant in the nematic liquid crystal.

It should be pointed out that the three microscopic theories proposed for the description of the rotational viscosity and characterized by the functions  $g_1$ ,  $g_2$ , and  $g_3$  are based on different physical models. The original OT theory was significantly improved by NZ by including the effects of correlations of the stress tensor with the director and fluxes with OPs tensors. The averaging in the framework of Fiałkowski's approach, on the other hand, is based on using an explicit form of the nonequilibrium ODF. We note that in the high temperature limit both NZ's and Fiałkowski's theories predict that  $\gamma_1 \sim \bar{P}_2^2$ . The limiting value of the OT approach is  $\gamma_1 \sim \sqrt{\bar{P}_2}$ .

Equations (3)–(5) allow us to calculate  $\gamma_1$  provided the temperature dependence of  $\bar{P}_2$ ,  $\bar{P}_4$ , and  $D_\perp$  is known. While values of the order parameters for various LCs are usually fairly easily found, the determination of motional constants for rotational diffusion constitutes a formidable task.

### III. SIMULATED LIQUID CRYSTAL AND ROTATIONAL SELF-DIFFUSION

The details of the simulation procedure, force field parameters, and an extended analysis have been provided elsewhere [3,4,14]. Here we only summarize general aspects and give some properties of the simulated liquid crystal. The MD simulation was carried out on a system consisting of 110 5CB molecules in a rectangular cell, assuming a density of  $1 \text{ g cm}^{-3}$ . The total length of the simulation was 1.5 ns and a trajectory of 510 ps was used in the final analysis. The mesogens were modeled using the potential functions presented in Ref. [14], which include intra- and intermolecular interactions. The temperature was kept at 300 K using an algorithm corresponding to the  $NVT$  ensemble. The instantaneous orientation of the director  $\mathbf{n}$  was determined from the Cartesian ordering matrix  $\mathbf{Q}_{zz}$  [36],

$$Q_{zz}^{\alpha\beta} = \frac{1}{N} \sum_{j=1}^N \frac{1}{2} (3 \cos \theta_{z\alpha}^j \cos \theta_{z\beta}^j - \delta_{\alpha\beta}), \quad (6)$$

where  $N$  is the number of 5CB molecules and  $\theta_{z\alpha}^j$  is the angle between the long molecular axis  $z$  and an axis  $\alpha$  fixed in the simulation box. The diagonalization of  $\mathbf{Q}_{zz}$  gives three eigenvalues; the eigenvector associated with the largest eigenvalue corresponds to the nematic director.

Figure 2 shows the single-particle ODF  $f(\cos \theta)$ , obtained from the MD simulation by the method described in Ref. [14]. Here  $\theta$  is the angle between the molecular symmetry axis and the nematic director. The order parameters can be calculated by averaging appropriate functions over all molecules at every time step of the simulation or by using the ODF

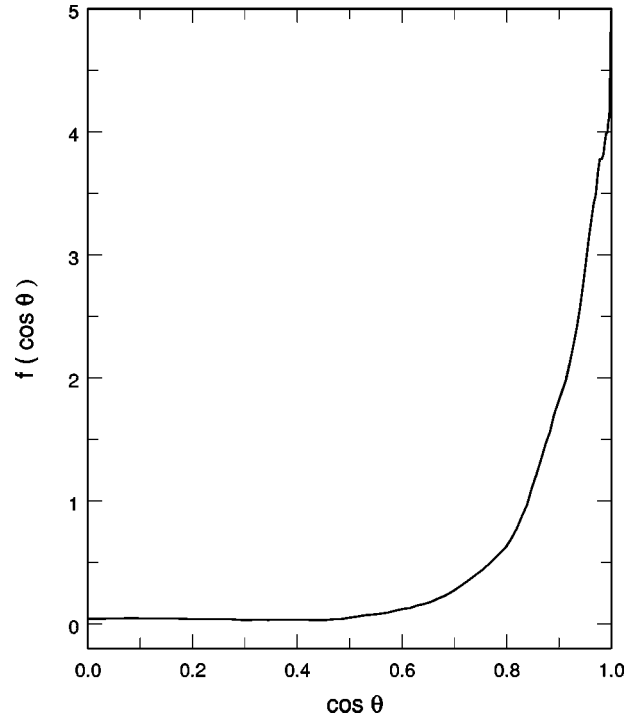


FIG. 2. Singlet orientational distribution function for 5CB, calculated from the MD simulation at  $T=300 \text{ K}$ , and density  $1 \text{ g cm}^{-3}$ .

$$\bar{P}_2 = \int \frac{1}{2} (3 \cos^2 \theta - 1) f(\cos \theta) \sin \theta d\theta, \quad (7)$$

$$\bar{P}_4 = \int \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) f(\cos \theta) \sin \theta d\theta. \quad (8)$$

The following results were obtained for the lowest OPs:  $\bar{P}_2 = 0.658 \pm 0.01$ ,  $\bar{P}_4 = 0.292 \pm 0.01$ , and the biaxiality parameter  $S_{xx} - S_{yy} = 0.05$ . Here  $S_{\alpha\alpha}$ , with  $\alpha = x, y, z$ , are the diagonal elements of the OP tensor. For a rigid uniaxial molecule it is possible to define a molecular fixed frame in which the rotational diffusion tensor is diagonal with principal components  $D_\perp$  and  $D_\parallel$ , where  $D_\parallel$  describes the spinning motion of the molecule about its symmetry axis.

Several theoretical approaches for the description of the rotational diffusion have been proposed. In particular, for uniaxial molecules in the nematic phase two models were considered: (i) extension of random walk theory [37] and (ii) a rotational Brownian motion in a mean-field potential using the above-mentioned OT theory [21] for the appropriate kinetic Fokker-Planck equation. The first model is based on the assumption that molecular reorientation proceeds through a random sequence of large-amplitude jumps. Of course, it is a drastic approximation, but as a result one can write a simple expression for  $D_\perp$  as

$$D_\perp = \pi^3 \left( \frac{kT}{2\pi I_\perp} \right)^{1/2} f\left(\cos \frac{\pi}{2}\right), \quad (9)$$

where  $I_\perp = 7.41 \times 10^{-37} \text{ g cm}^2$  is the molecular moment of inertia corresponding to the short axis of 5CB and  $f[\cos(\pi/2)]$  is the value of the ODF at  $\theta = \pi/2$ , which cor-

responds to the molecular orientation orthogonal to the director. Using the ODF obtained in the MD simulation and plotted in Fig. 2, we estimated the RSC to be  $D_{\perp} = 0.8 \times 10^{11} \text{ s}^{-1}$ . In the framework of the second approach, the expression for the RSC is [21,38]

$$D_{\perp} = \frac{p^2}{100(1-c)\rho^2 s^6} \frac{1}{kT} \left( \frac{G^3}{I_{\perp}} \right)^{1/2} \exp\left( -\frac{G+I_0}{kT} \right), \quad (10)$$

where  $c$  is the volume fraction of ellipsoidal molecules,  $\rho$  is the number density of molecules, ( $c = 0.5-0.6$  for dense molecular liquids),  $p = l/s$  is the molecular length-to-width ratio, assumed to be 3 for 5CB molecule. In Ref. [21] the intermolecular pair potential was chosen to be the sum of two contributions, one isotropic  $G$  and the other anisotropic  $I_0$ , with  $G \gg I_0$ . According to the electro-optical method [38], the value of  $G$  for the 5CB molecule was estimated to be  $1.74 \times 10^{-13} \text{ erg}$ , which leads to the value of  $D_{\perp} = 0.8 \times 10^{12} \text{ s}^{-1}$ . The corresponding values obtained from experiments using deuterium [6] and carbon-13 [9] NMR are  $(0.5-1.5) \times 10^8 \text{ s}^{-1}$  and  $3.5 \times 10^8 \text{ s}^{-1}$ , respectively. Thus the motional constants for 5CB derived from the theoretical models are several orders of magnitude too high.

Rotational dynamics of molecules in anisotropic phase can also be described by the small step diffusion model [39,40]. This model is based on the assumption that molecular reorientations proceed through a random sequence of infinitesimal angular jumps.

In general, however, the molecular rotational motion is conveniently characterized using normalized orientational time correlation function (TCF)

$$\Phi_{mn}^L(t) = \frac{\langle D_{mn}^{L*}(\Omega(0)) D_{mn}^L(\Omega(t)) \rangle}{\langle D_{mn}^{L*}(\Omega(0)) D_{mn}^L(\Omega(0)) \rangle}, \quad (11)$$

where  $D_{mn}^L(\Omega)$  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. We calculate the TCF from the MD trajectory. The molecular coordinate system is defined using the eigenvectors of the moment of the inertia tensor. In the following we focus our attention on the second-rank TCF ( $L=2$ ). In general, the correlation functions may be written as infinite sums of decaying exponentials. Here, we employ a single exponential approximation [2]

$$\Phi_{mn}(t) = \Phi_{mn}(\infty) + [\Phi_{mn}(0) - \Phi_{mn}(\infty)] \exp\left( -\frac{t}{\tau_{mn}} \right). \quad (12)$$

Several physical models have been proposed for the interpretation of the correlation times  $\tau_{mn}$  [41-43] in terms of rotational diffusion constants for a uniaxial molecule. These approaches give, in fact, identical results for the correlation times

$$\tau_{mn}^{-1} = c_{mn} D_{\perp} + n^2 (D_{\parallel} - D_{\perp}), \quad (13)$$

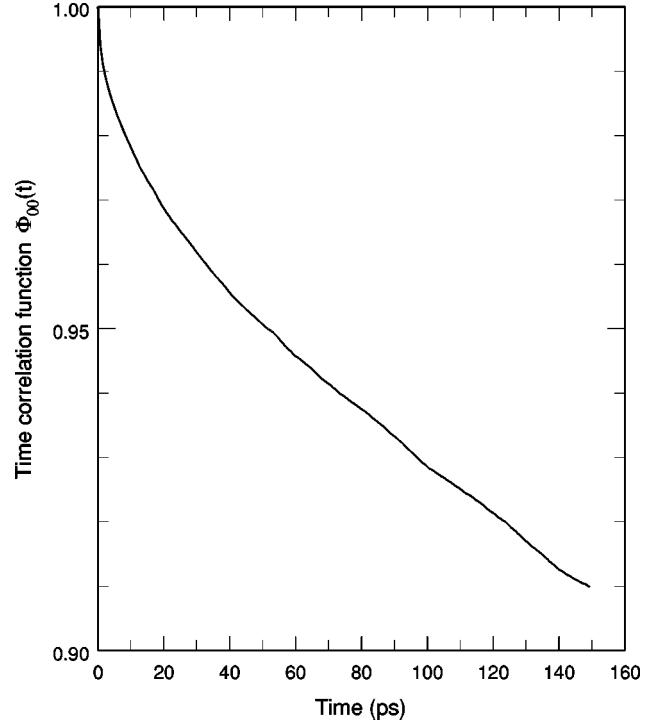


FIG. 3. Normalized orientational time correlation function  $\Phi_{00}(t)$  for 5CB in the nematic phase, calculated from the MD simulation at  $T = 300 \text{ K}$ .

where the coefficients  $c_{mn}$ , which depend on  $\bar{P}_2$  and  $\bar{P}_4$ , are tabulated in Ref. [41]. We note that the TCF with  $m=n=0$  is solely determined by the tumbling motion and  $\tau_{00}$  is related to  $D_{\perp}$  by

$$\tau_{00} = \left[ 6 D_{\perp} \frac{7 + 5\bar{P}_2 - 12\bar{P}_4}{7 + 10\bar{P}_2 + 18\bar{P}_4 - 35\bar{P}_2^2} \right]^{-1}. \quad (14)$$

The time correlation function  $\Phi_{00}$  calculated from the trajectory is shown in Fig. 3. It should be pointed out that in the infinite limit the TCF is  $\Phi_{00}(\infty) = \langle D_{00}^{2*} \rangle \langle D_{00}^2 \rangle$ , which simply corresponds to a product of two second-rank order parameters. Thus the limiting value  $\Phi_{00} = 0.45$ . We fitted  $\Phi_{00}$  to a single exponential [Eq. (12)] in the time interval 50–150 ps, which resulted in an average value of the correlation time  $\tau_{00} = 1080 \text{ ps}$ . The RSC derived from Eq. (14), at  $T = 300 \text{ K}$ , with  $\bar{P}_2 = 0.658$  and  $\bar{P}_4 = 0.292$  from our MD simulation, is  $D_{\perp} = 0.8 \times 10^8 \text{ s}^{-1}$ , which is in good agreement with experimental  $^2\text{H}$  NMR  $(0.5-1.5) \times 10^8 \text{ s}^{-1}$  [6] values. The reason for the range indicated is that the value of the RSC depends on the dynamic model used for the interpretation of nuclear spin relaxation rates. According to one of the models used in [6], the temperature dependence of  $D_{\perp}$  can be expressed in an Arrhenius form as  $D_{\perp} = D^{ex} \exp(-E_1/kT)$ , where  $D^{ex} = 5.76 \times 10^{17} \text{ s}^{-1}$ , and  $E_1 = 0.92 \times 10^{-12} \text{ erg}$ .

#### IV. NUMERICAL RESULTS FOR RVC AND CONCLUSIONS

The temperature dependence of the rotational viscosity coefficient  $\gamma_1$  is shown in Fig. 4. The experimental values

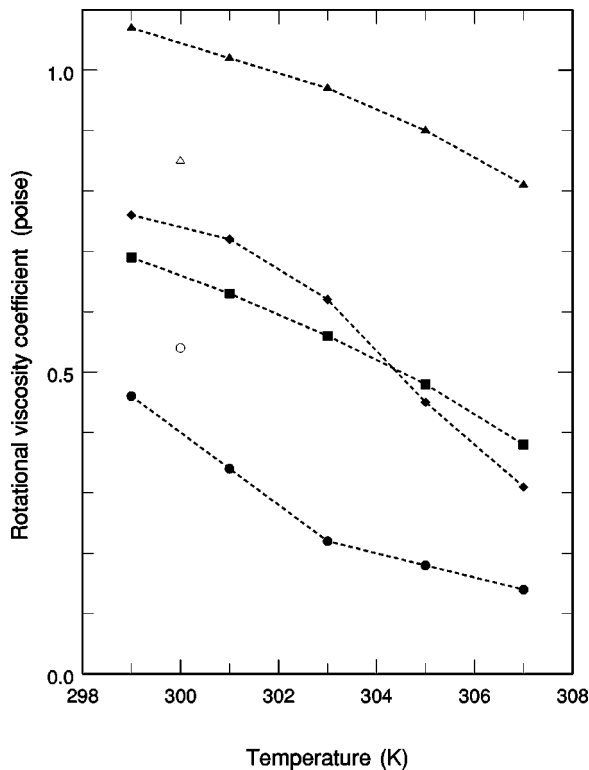


FIG. 4. Temperature dependence of  $\gamma_1$  at fixed density calculated using Eq. (4) (circles), Eq. (5) (triangles), and Eq. (15) (diamonds) and measured by means of electro-optical method (squares). The RVC calculated using Eqs. (4) and (5) with  $D_{\perp}$  and the OPs, obtained from the MD simulation, are indicated by the open circle and open triangle, respectively.

were determined using electro-optical method and were taken from [38], while the OT, NZ and Fiałkowski models were employed to estimate the other curves. The temperature dependence of  $D_{\perp}$  and of the OPs was obtained from deuterium NMR experiments [6]. In addition, these parameters at 300 K were determined from the MD simulation. First we noted that the original OT theory [21] [Eq. (3)], predicts viscosity that is one order of magnitude too high. In fact, a modification of this equation, by taking  $J_0/kT_c$  as the fitting parameter, based on experimental results, was recently proposed [38]:

$$\gamma_1 = g_0 \left( \frac{T}{T_c} \right)^4 \left( \frac{kT_c}{E_2} \right)^3 \left( \frac{J_0 \bar{P}_2}{kT_c} \right)^{1/2} \exp \left( \frac{E_2 + J_0 \bar{P}_2}{kT} \right), \quad (15)$$

where  $g_0 = 1.02 \times 10^{-3}$  [P] is the proportionality constant,  $E_2 \approx 3$  G =  $5.23 \times 10^{-13}$  ergs is the activation energy, and  $J_0/kT_c = 2.59$ .

Note that in Eq. (15) the rotational viscosity is no longer explicitly dependent on the diffusion constant  $D_{\perp}$ . This is so because a macroscopic friction coefficient was introduced in [38], while the OT theory rests on a microscopic, molecular interpretation.

The agreement between the experimental, and calculated [using Eq. (15)], viscosity is very good. The other theories, expressed in Eqs. (4) and (5), show a greater deviation from the experimental data. In fact, the NZ theory [Eq. (4)] underestimates  $\gamma_1$  slightly, while the viscosity derived by applying the Fiałkowski model [Eq. (5)] is somewhat too high. Using Eqs. (4) and (5) together with the parameters  $D_{\perp}$  and OPs, determined from the MD simulation, we obtained the viscosity values in close agreement with experiments. It should be noted that the Fiałkowski [Eq. (5)] and NZ [Eq. (4)] theories exhibit a different dependence on the OPs, which is manifested in the factors  $g_3$  and  $g_2$ . This difference originates in the averaging procedures applied to the balance equations. In the high-temperature limit, i.e., close to the isotropic transition, both theories predict that  $\gamma_1 \sim \bar{P}_2^2$ . Such behavior of the RVC is in agreement with the mean field approximation, which in fact was pointed out by de Gennes and Prost (see Ref. [1]).

We believe that this paper shows some simple and useful routes for the estimation of the rotational viscosity coefficient. Thus the combination of theory, computer simulation, and experiments provides a powerful tool for investigations of rotational viscosity. In particular, the two approaches (Fiałkowski and NZs) enable one relate a macroscopic property (rotational viscosity) of a liquid crystalline phase to molecular parameters, such as diffusion constants.

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