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Nematiclike viscosity coefficients of ferroelectric liquid crystals in their smectic-C^* phase

A. V. Zakharov*
Saint Petersburg Institute for Machine Sciences, Russian Academy of Sciences, Saint Petersburg 199178, Russia

V. Domenici† and C. A. Veracini‡
Dipartimento di Chimica e Chimica Industriale, Universita di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

R. Y. Dong§
Department of Physics and Astronomy, Brandon University, Brandon, Manitoba, Canada R7A 6A9
and University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

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The five nematiclike viscosity coefficients corresponding to the Smectic-C^* (SmC^*) phase are calculated by a combination of the existing statistical-mechanical approach and NMR theory, based on a rotational diffusion model for two ferroelectric smectogens. The order parameter S_2, the smectic tilt angle θ, and the rotational diffusion coefficient $D_\perp$, corresponding to molecular tumbling in the SmC^* phase, for the ferroelectric smectogens 4-[4′-(1-methylheptyloxy)]biphenyl′-(10-undecenyloxy)benzoate and (*S*)-[4-(2-methylbutyl)phenyl]-4′-*n*-octylbiphenylcarboxylate have been obtained by means of ^{2}H NMR spectroscopy and these data have been used to calculate viscosity quantities. For practical purposes a specific form of the functional dependence of S_4 on S_2 is used. As the main result, our calculations also predict a laminar flow regime in a high shear flow for these liquid crystal compounds.

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During the past few years a great deal of attention has been focused on the flow dynamics of smectic-C^* (SmC^*) liquid crystals in a shear flow [1–3]. Despite the fact that certain qualitative advances have been achieved in the construction of a phenomenological theory of the hydrodynamical properties of SmC^* liquid crystals (LCs), it is still too early to talk about the development of a theory which would make it possible to describe the viscous processes from first principles, based only on the form of the Hamiltonian. But, since the rotational viscosity coefficients play a crucial role in the number of applications, the question of a microscopic interpretation of these coefficients inevitably arises. It has been shown that the general theory for description of the macroscopic flow properties of the SmC^* system demands 20 viscosity coefficients. In accordance with the stress tensor expression σ_{ij} [see, for instance, Eqs. (3.14) and (3.15), Ref. [2]] for the SmC^* phase, each of these 20 coefficients can be classified into one of four groups. The first group consists solely of one contribution which is independent of both the director $\hat{\mathbf{n}}$ and its projection $\hat{\mathbf{c}}$ onto the smectic plane [3] and therefore corresponds to the usual isotropic contribution (μ_0) to the viscous stress tensor σ_{ij} [see Eq. (6.219), Ref. [3]]. The second group consists of those viscosities which are connected to the director $\hat{\mathbf{n}}$ and independent of the vector $\hat{\mathbf{c}}$. This group consists of four viscosities [see Eq. (6.220), Ref. [3]] whose terms, being independent of $\hat{\mathbf{c}}$, suggest that the smectic tilt angle $\theta=0$, and for this reason they are called smectic-*A*-like viscosities. The third group of viscosities is connected to the terms that only depend upon the vector $\hat{\mathbf{c}}$, and consists of four contributions [see Eq. (6.221), Ref. [3]]. They have been designated as nematiclike viscosities [μ_3, μ_4, λ_2, and λ_5 in the notation of Eq. (6.221) of Ref. [3]]. The fourth group consists of the remaining 11 viscosities, associated with coupling terms, since they depend upon both $\hat{\mathbf{n}}$ and $\hat{\mathbf{c}}$.

Comparison between the five Leslie viscosity coefficients of the nematic liquid crystal [4,5] and the corresponding nematiclike viscosity coefficients of a SmC^* liquid crystal [3] gives us

$$\mu_0 = \alpha_4, \tag{1}$$

$$\mu_4 = \tfrac{1}{2}\theta^2(\alpha_5 + \alpha_6), \tag{2}$$

$$\lambda_2 = \tfrac{1}{2}\theta^2\gamma_2, \tag{3}$$

$$\lambda_5 = \tfrac{1}{2}\theta^2\gamma_1, \tag{4}$$

and

$$\mu_3 = \theta^4\alpha_1, \tag{5}$$

where μ_i ($i=3,4$), and λ_2 and λ_5 are four viscosities associated with the nematiclike rotational viscosities of SmC^*, γ_1 and γ_2 are the rotational viscosity coefficients (RVCs), α_i ($i=1,4,5,6$) are four of the six Leslie viscosity coefficients [4,5] of nematic liquid crystals, and $\theta=\theta(T)$ is the tilt angle of the SmC^* phase, i.e., the angle that the director $\hat{\mathbf{n}}$ makes with the layer normal. So the coefficient μ_0 is independent of the tilt angle $\theta(T)$, whereas the μ_3 coefficient depends on the

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*Author to whom correspondence should be addressed. Electronic mail: Alexandre.Zakharov@fys.kuleuven.ac.be; www.ipme.ru

†Electronic mail: valentin@dcci.unipi.it

‡Electronic mail: verax@dcci.unipi.it

§Electronic mail: dong@brandonu.ca

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fourth power of θ while the other three depend only on the second power of θ. Thus one expect the μ_3 viscosity coefficient to vanish faster than the other four coefficients when the system approaches T_{C^*A}.

Recently, a statistical-mechanical approach for the theoretical treatment of rotational viscosity has been proposal [6,7]. As a result, expressions for both γ_1 and γ_2 can be written in the form

$$\gamma_i = \frac{k_B T \rho}{D_\perp} f_i(S_2), \tag{6}$$

where

$$f_i(S_2) = \begin{cases} g(S_2), & i = 1, \\ -pS_2, & i = 2. \end{cases}$$

Here

$$g(S_2) = S_2^2 \frac{9.54 + 2.77S_2}{2.88 + S_2 + 12.56S_2^2 + 4.695S_2^3 - 0.74S_2^4},$$

$\rho = N/V$ the particle number density, k_B is the Boltzmann constant, T is the temperature, p is a molecular geometric factor taken as $p = (a^2 - 1)/(a^2 + 1)$, a is the molecular length-to-breadth ratio of the molecule, and $D_\perp$ is the rotational diffusion coefficient. The Leslie coefficients α_i ($i = 1,4,5,6$) are expressed in terms of the micro and macro parameters as follows [6]:

$$\alpha_1 = -\frac{k_B T \rho}{D_\perp} p^2 S_4, \tag{7}$$

$$\alpha_4 = \frac{k_B T \rho}{D_\perp} \frac{p^2}{35} (7 - 5S_2 - 2S_4), \tag{8}$$

$$\alpha_5 + \alpha_6 = \frac{k_B T \rho}{D_\perp} \frac{p^2}{7} (3S_2 + 4S_4), \tag{9}$$

where S_{2L} ($L = 1,2$) are the even-rank order parameters.

Thus, according to Eqs. (1)–(9), λ_i ($i = 2,5$) and μ_i ($i = 0,3,4$) are found to be proportional to the density, temperature, and certain polynomials of order parameters (OPs), and inversely proportional to the rotational self-diffusion coefficient $D_\perp$, which corresponds to molecular tumbling in the SmC^* phase. It should be pointed out here that the expressions for the nematiclike viscosity coefficients (λ_2, λ_5, μ_3, and μ_4) are given for uniaxial molecules. This is justified by the small values of the molecular biaxiality $\xi = S_{xx} - S_{yy}$ found to be equal to $\xi \sim 0.039$, for the phenyl, and $\xi \sim 0$, for the biphenyl rings of the ferroelectric smectogen 4-[4′-(1-methylheptyloxy)]biphenyl′- (10-undecenyloxy) benzoate (11EB1M7), and $\xi \sim 0.0009$ for the ferroelectric smectogen (*S*)-[4-(-2-methylbutyl)phenyl]-4′-*n*-octylbiphenyl carboxylate (8BEF5) [see Figs. 1(a) and 1(b), respectively], within their SmC^* temperature ranges.

The orientational OP S_2, the tilt angle θ [8], and the rotational diffusion coefficient $D_\perp$ for these ferroelectric smectogens 11EB1M7 and 8BEF5 within the SmC^* temperature range have been studied by means of ^{2}H NMR spectroscopy.

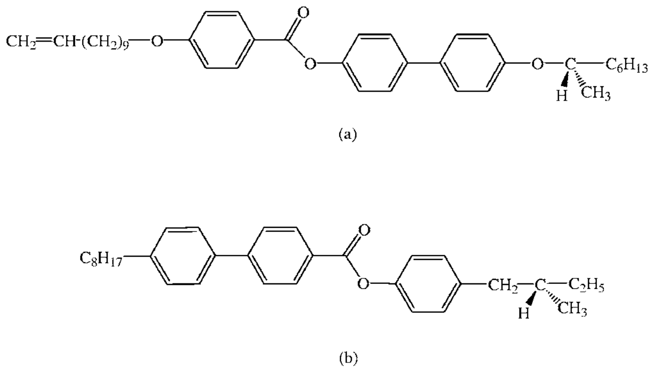

FIG. 1. Molecular structure of the ferroelectric smectogens 11EB1M7 (a) and 8BEF5 (b), respectively.

In particular, for the first mesogen (11EB1M7), by means of the analysis the of ^{2}H NMR spectra, the orientational OP S_2 ($\equiv S_{zz}$) and the tilt angle θ in the temperature range corresponding to the SmC^* phase has been obtained [9], while for the second smectogen (8BEF5), a complete analysis of ^{2}H NMR data has been published in Ref. [10]. From the dynamic point of view, ^{2}H NMR spin-lattice relaxation times have been measured for both compounds in their smectic-*A* and -C^* phases. Dynamic parameters (diffusional coefficients and activation energies) describing the individual overall molecular and internal motions have been obtained in the Sm*A* phase by applying available rotational diffusion theories for uniaxial phases. Comments and results on the dynamic behavior in this phase have been published in Refs. [11,12] for 11EB1M7 and 8BEF5.

Concerning the SmC^* phase, even though relaxation times can also be measured, there are several difficulties in linking them to the dynamic parameters. These difficulties, both theoretical and experimental, are due either to the phase biaxiality or to the dependence of the relaxation times on the polar angles defining the position of the local phase director with respect to the external magnetic field. In fact, on the one side the theoretical models taking into account phase biaxiality are quite complex; on the other side such a model would require an unavailable large set of experimental data. For this reason a quantitative analysis of relaxation times in such phases requires several approximations and only recently has a different approach been applied to the ferroelectric mesogens 11EB1M7 [11] and 8BEF5 [13,14], respectively.

The approach used to extract dynamic parameters from Deuterium NMR alloyed the quantitative analysis of relaxation times in tilted smectic phases by means of the existing theoretical models, based on the assumption of phase uniaxiality, taking into account the effects of the tilt angle on the measured relaxation times, as reported in the literature [11,13,14].

Figures 2(a) and 2(b) shows the trend of the orientational order parameter S_{zz} ($\equiv S_2$) as obtained from ^{2}H NMR analysis. In the case of 8BEF5 the orientational OP was determined by analysis of the phenyl and first CD fragments [14], whereas in the case of 11EBM7 the OP was chosen as the bigger value between the two OPs corresponding to the phenyl and biphenyl fragments [9]. Within the SmC^* phase the OP S_2 ranges from 0.830 to 0.856 for 8BEF5 [see Fig. 2(a)]

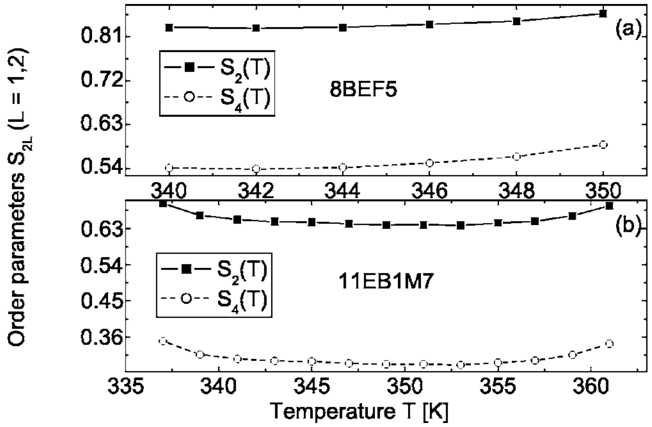

FIG. 2. Temperature dependence of the order parameter $S_2(T)$ (solid symbols) measured by the ^{2}H NMR technique [12,11] and calculated using Eq. (10) $S_4(T)$ (open symbols), at fixed density for 8BEF5 (a) and 11EB1M7 (b).

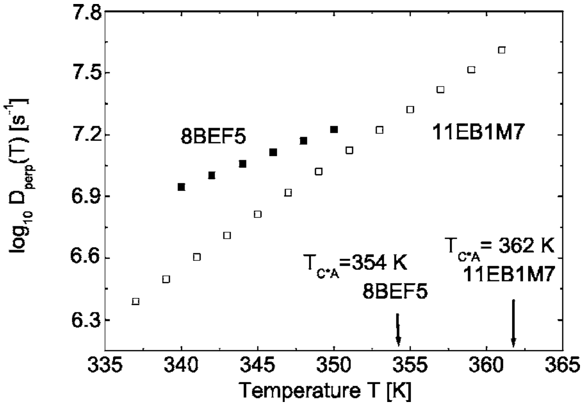

FIG. 4. Temperature dependence of rotational diffusion coefficient $D_\perp$ measured by ^{2}H-NMR technique, at fixed density both for 11EB1M7 (open symbols) (Ref. [11]) and 8BEF5 (solid symbols) (Ref. [12]) molecules in the SmC^* phase.

and from 0.692 to 0.638 for 11EB1M7 [see Fig. 2(b)], respectively, and the tilt angle $\theta(T)$, evaluated from the ^{2}H NMR spectra for the long molecular axis, increases from 13.5° to 18.5° and then again decreases to 12° for 11EB1M7 (see Fig. 3), and decreases from 11° to 4.5° for 8BEF5 (see Fig. 3), on increasing the temperature.

The temperature dependence of the diffusion coefficient $D_\perp$ obtained from ^{2}H NMR relaxation times, for both smectogens, is reported in Fig. 4. The tumbling coefficients for both 11EB1M7 [11] and 8BEF5 [13] ferroelectric mesogens in their SmC^* phase were determined by applying a suitable global target fitting procedure, together with the CAGE software [15]. Taking into account that the tumbling diffusion coefficients are very sensitive to the choice of the experimental spectral densities, obtained from ^{2}H NMR relaxation times, a large set of these experimental spectral densities have been accounted for during these calculations. It was found that the magnitudes of the tumbling diffusion coefficients are smaller than the magnitudes of the spinning diffusion coefficients, in the temperature range corresponding to the SmA and SmC^* phases. Based on the results reported in Refs. [11,13], we concluded that the tumbling motion was characterized by a slightly higher activation energy in the SmC^* phase than in the SmA phase. However, no discontinuities have been observed on passing from the SmA to the SmC^* phase in the high-frequency regime of motions detected by NMR.

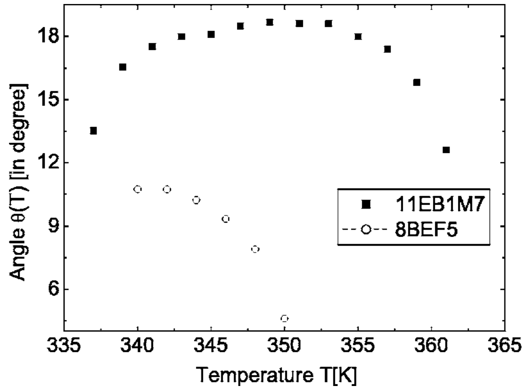

FIG. 3. Temperature dependence of the tilt angle $\theta(T)$ measured by the ^{2}H NMR technique for 8BEF5 (Ref. [12]) and 11EB1M7 (Ref. [11]) compounds.

In order to analyze the dependence of the viscosity coefficients of Eqs. (1)–(5), a specific form of the functional dependence of S_4 on S_2 is needed. For practical purposes the relation between S_4 and S_2 can be closely approximated in the experimentally relevant interval of $S_2 \in [0.4, 0.8]$ by the fit function [16]

$$S_4 = S_2[1-(1-S_2)^\nu], \tag{10}$$

with $\nu=0.6$. Such a functional dependence of S_4 on S_2 is motivated by maximum entropy arguments and supported by the results of computer simulations [17]. Within the SmC^* phase the order parameter S_4 ranges from 0.54 to 0.58 for 8BEF5 [see Fig. 2(a)], and from 0.35 to 0.30 for 11EB1M7 [see Fig. 2(b)]. The number density ρ of 8BEF5 (at $340 \leqslant T \leqslant 350$ K) has been fixed to the value 1.5×10^{27} m^{-3}, whereas the molecular length-to-breadth ratio was fixed to the value 3.5. The value of the number density ρ of 11EB1M7 (at $339 \leqslant T \leqslant 360$ K) has been fixed to the value 2×10^{27} m^{-3}, whereas the molecular length-to-breadth ratio was fixed to the value 4.2. The temperature dependencies of the viscosity coefficients μ_i ($i=0,3,4$) for both 8BEF5 and 11EB1M7 compounds are shown in Figs. 5(a) and 6(a), whereas the values of the RVCs λ_i ($i=2,5$) for the same compounds are shown in Figs. 5(b) and 6(b), respectively. Analysis of the calculated data for μ_3 and μ_4 shows that in the vicinity of the phase transition temperature T_{C^*A} the values of these coefficients vanish, whereas the value of μ_0 does not vanish and corresponds to the isotropic contribution to the bulk viscosity. In the hydrodynamics of LCs a great deal of attention has been focused on the flow dynamics of LCs in a shear flow [1–7]. The flow of a SmC^* phase is characterized by a unit vector along the optical axis (the direction $\hat{\mathbf{n}}$) and governed by the shear flow velocity $\mathbf{v}$. If the director is disturbed in the shear plane [x-y plane, defined by the liquid crystal flow (x direction) and the velocity gradient in the y

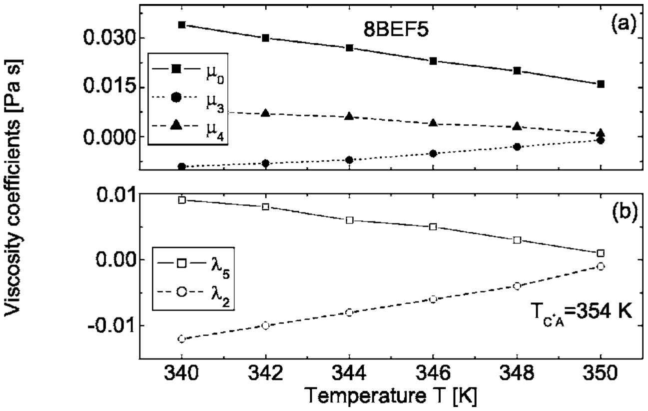

FIG. 5. (a) Temperature dependence of μ_i $(i=0,3,4)$ calculated using Eqs. (1), (5), and (2), and (b) λ_i $(i=2,5)$ calculated using Eqs. (3) and (4), at fixed density for 8BEF5 molecules in the SmC^* phase.

direction; z is the normal to the smectic plane] and then allowed to relax, one deals with a twofold result. First, the hydrodynamic torque $T_{vis}=\frac{1}{2}(\lambda_5+\lambda_2\cos 2\alpha)\dot{\gamma}$ exerted per unit volume of SmC^* phase in a shear flow vanishes when the director aligns at an equilibrium angle

$$\alpha=\frac{1}{2}\cos^{-1}\left(-\frac{\lambda_5}{\lambda_2}\right) \qquad (11)$$

with respect to the direction of flow velocity $\mathbf{v}$. Here $\dot{\gamma}=\partial v_x/\partial y$ is the shear rate. Second, the director continuously rotates in the shear plane. Such a shear flow is realized with a sample in the bookshelf geometry, allowing one of the glass plates to move with respect to the other along the smectic layers. It is clear from this equation that if $|\lambda_5|>|\lambda_2|$, no real solution for α exists. Physically, this means that in this case the director will tumble within the smectic planes under shear flow of the SmC^*. But there is one extra possibility for shearing flow when a transverse pressure gradient will force the molecules to hop between the layers. Analysis of the calculated data for the RVCs λ_2 and λ_5 shows that $|\lambda_2|>|\lambda_5|$, for the temperature range in which the molecules of 11EB1M7 and 8BEF5 exhibit the SmC^* phase. Physically, this means that in this case the director $\hat{\mathbf{n}}$ will align at an angle α to the shear flow direction. The temperature dependence of the flow alignment angle $\alpha(T)$ is shown in Fig. 7. It is found that the values of the angle $\alpha(T)$ in the case of the 8BFE5 compound grow slowly from ~19° till ~19.5°, whereas in the case of the 11EB1M7 compound these values vary between 16° and 18° within the SmC^* phase.

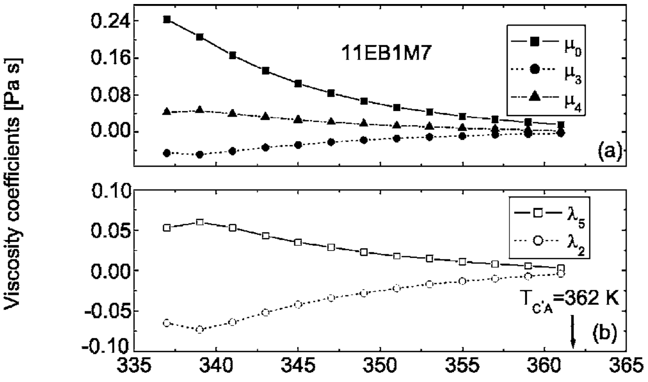

FIG. 6. (a) Temperature dependence of μ_i $(i=0,3,4)$ calculated using Eqs. (1), (5), and (2), and (b) λ_i $(i=2,5)$ calculated using Eqs. (3) and (4), at fixed density for 11EB1M7 molecules in the SmC^* phase. The arrow shows the phase transition temperature T_{C^*A} ~362 K.

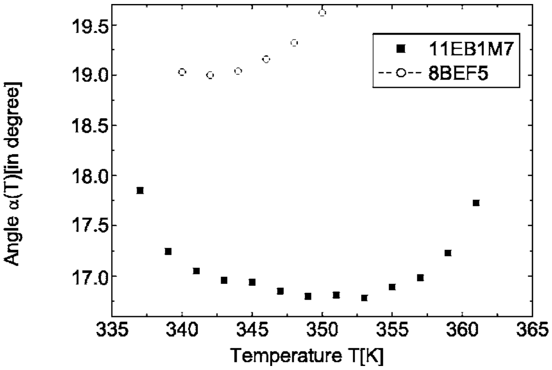

FIG. 7. Temperature dependence of the calculated alignment angle $\alpha(T)=(1/2)\cos^{-1}(-\lambda_5/\lambda_2)$ for both 8BEF5 and 11EB1M7 compounds.

In summary, we have investigated four μ_3, μ_4, λ_2, and λ_5 nematiclike and one μ_0 isotropic viscosity coefficient in the SmC^* phase of the ferroelectric smectogens 11EB1M7 and 8BEF5 by using the rotational diffusion coefficient $D_\perp$, a set of the order parameters S_{2L} $(L=1,2)$, and the tilt angle θ, as determined by NMR.

Although the general theory for description of the macroscopic flow properties of a SmC^* phase demands 20 viscosity coefficients, by means of comparisons between the five Leslie viscosities of nematic liquid crystals and the corresponding nematiclike viscosity coefficients of a SmC^* liquid crystal, the microscopic expressions for these nematiclike terms are presented as an explicit function of temperature, of a set of the OPs, of the tilt angle, and of the rotational diffusion coefficient $D_\perp$. In order to analyze the dependence of μ_i $(i=0,3,4)$ and λ_i $(i=2,5)$, a specific form of the functional dependence of S_4 on S_2 has been used. The theory predicts that the coefficient μ_0 is independent of θ, the μ_3 term depends on the fourth power of θ, while the other three depend only on the second power of θ. We found that the μ_3 viscosity coefficient vanishes faster than the other four coefficients when the system approaches T_{C^*A}. Our analysis also shows that the absolute values of the RVCs λ_i $(i=2,5)$ in the SmC^* phase of 11EB1M7 are approximately five times higher than the values for these viscosities of 8BEF5. We also found that the hydrodynamic torque exerted per unit volume of the SmC^* phase vanishes when the director $\hat{\mathbf{n}}$ aligns at an angle $\alpha(T)$ with respect to the flow direction. We note that the molecular expressions for the RVCs and the Leslie coefficients have been obtained by averaging both the symmetric and antisymmetric parts of the microscopic stress tensor with an appropriate nonequilibrium orientational distribution function. In the case of the small velocity gradient approximation, the general expressions for these viscosity coefficients were given in terms of the micro and macro parameters, and flow alignment or, alternatively, tumbling is seen to be controlled by the molecular aspect ratio, the second OP, and the tilt angle, and not affected by dynamical coefficients. But this is valid only in the framework of that approximation and by no means universal.

Taking into account that at the present time there is almost no experimental information regarding the SmC^* viscosity coefficients, we hope that the theoretical route presented here can provide a basis for the future investigations of viscosity phenomena in the SmC^* phases based upon self-consistent statistical-mechanical theories [18]. We believe that the present study not only shows some useful routes for estimating the viscosity of the ferroelectric LCs, but also clarifies the role of NMR spectroscopy in obtaining the dynamic information.

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