

## Nematic liquid crystal viscosity: Inadequacies of microscopic theories

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Recently Janik *et al.* reported measurements of the Miesowicz viscosity coefficients of the nematic liquid crystal and confronted them with the results of the available theoretical models. They found that none of them can be successfully applied for the purpose of the Miesowicz-type experiment. In this paper I present an explanation why the microscopic theories seem inadequate. In particular, I analyze the applicability and conclusions of the Osipov-Terentjev model, whose final predictions are highlighted to be the same as those of the Kuzuu-Doi theory. It has been shown that the microscopic theories can perfectly explain the behavior of the Miesowicz coefficients difference  $\eta_3 - \eta_2$  but are inadequate to study their ratio  $\eta_3 / \eta_2$ , which is contributed by the Leslie coefficient  $\alpha_4$ . A disagreement between experimental data and the theoretical results for  $\alpha_4$  is attributed to the fact that the isotropic contribution to  $\alpha_4$  in the nematic phase is beyond the scope of the theories that are based on the anisotropic orientational distributions.

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In a recent paper [1] Janik *et al.* presented an extended experimental study of the viscous properties of different mixtures of mesogenic 4-cyano-4'-octyloxybiphenyl (8 OCB) and 4-butylbenzoate 4'-isothiocyanatephenyl (4 TPB). They measured the Miesowicz coefficients  $\eta_1$ ,  $\eta_2$ , and  $\eta_3$  for different mixture compositions, over a wide range of temperature. Because there are many ways to present and analyze the viscosity coefficients, their ratios, and combinations, it seems of great practical importance to choose the most characteristic one in order to systematize the viscosity data. In view of this, Janik *et al.* examined several proportionalities and relations, either of phenomenological and/or theoretical character, vs their experimental results. In particular, they focused on certain ratios of the viscosities associated with the symmetric part of the stress tensor, and on the Knepe *et al.* (KSS) relations [2]. According to the existing microscopic theory of Kuzuu and Doi (KD) [3] [and also to the final results of the Osipov-Terentjev (OT) approach [4]], all the symmetric viscosities are predicted to be polynomials in the order parameters with strictly constant coefficients, and scaled with an appropriate diffusion term. On the basis of this prediction, Janik *et al.* proposed a type of relation that allows one to analyze the roles of ordering and diffusion separately. The second set of relations that they considered are phenomenological formulas of KSS, which assume that each Miesowicz coefficient can be expressed as a linear combination of the other two.

This Brief Report addresses the problem of the applicability of the nematoviscosity theory for the purpose of experimentalists as it has appeared on the grounds of the work of Janik *et al.* In view of the above I distinguish two aspects. The first aspect is related to the nature, suitability, and conclusions of the OT model within the course of its development. Since early formulations of the OT theory gave some incorrect predictions, the whole approach frequently meets with much criticism, as in [1]. It seems important to make it perfectly clear that the OT model with all its elements cor-

rectly worked out predicts the *same* formulas for the viscosities as the KD theory. In what follows I shall be using the abbreviation KDOT to refer to the final common results of these theories. The second aspect concerns the problem of the shear viscosity coefficient  $\alpha_4$  (and consequently the Miesowicz coefficient  $\eta_3$ ). For a long time it has not been fully realized that in a more ordered phase like the nematic, the value of  $\alpha_4$  consists *de facto* of two contributions: isotropic ( $\alpha_4^{\text{iso}}$ ) and nematic ( $\alpha_4^{\text{nem}}$ ) [4]. The expression *nematic contribution* is used here for the results obtained strictly within the framework of the analysis resting upon the orientation-dependent elements (distribution functions and stresses), as in the case of the KDOT theory. At the same time the behavior of the isotropic liquid phase remains entirely beyond the scope of the KDOT theory. Although there have been a few attempts at investigating the transport properties of the isotropic phase of a fluid consisted of anisotropic particles (e.g., hard ellipsoids [5,6]), to my knowledge there exists no attempt to build a theory of their isotropic shear viscosity *in the nematic phase*. A direct consequence of this situation is, for instance, that the Knepe phenomenological formulas, which are significantly influenced by  $\alpha_4^{\text{iso}}$ , cannot be fully understood from a theoretical point of view. This conclusion is also valid for the ratio of the Miesowicz coefficients  $\eta_3 / \eta_2$ , which attracts a special concern of experimentalists. It may come as surprise that the situation is different for the values of  $\eta_3 - \eta_2$ . It has been shown that KDOT theory can perfectly explain the experimental finding of Janik *et al.* that  $\eta_3$  is always larger than  $\eta_2$ .

I begin by presenting a summary of results of the key papers that contain the evolution of the OT approach [4,7,8]. Then I discuss the findings for  $\alpha_4$ ,  $\eta_3 - \eta_2$ , and  $\eta_3 / \eta_2$  that are available both from theoretical models and experiments.

The OT model of the nematic viscosity has been developed in three successive papers [4,7,8]. The differences among these papers result from the used assumptions. A more detailed discussion of their validity might help to understand this approach.

In the first paper (OT1) [7] the fundamental ideas of the OT model have been proposed, namely, how to calculate the

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macroscopic stress tensor  $\boldsymbol{\sigma}$  and the microscopic expressions for the Leslie viscosity coefficients  $\alpha_i$  from the statistical average of the microscopic stress tensor  $\boldsymbol{\sigma}^{\text{mic}}$ :

$$\boldsymbol{\sigma} = \int \boldsymbol{\sigma}^{\text{mic}} f(\mathbf{a}) d\mathbf{a}. \quad (1)$$

In Eq. (1)  $f(\mathbf{a})$  stands for the nonequilibrium distribution function of the molecular orientations  $\mathbf{a}$ . A particular form of  $f(\mathbf{a})$  should be provided by the solution of the orientational Fokker-Planck (FP) equation,

$$\frac{\partial f}{\partial t} = D_r \partial_k \left( \partial_k f + \frac{f}{kT} \partial_k V_{\text{mf}} \right) - \partial_k (f \omega_k), \quad (2)$$

which governs the Brownian motion of a particle in the flowing anisotropic medium. The first term on the right-hand side of Eq. (2) describes the diffusion effect with a drift caused by the mean-field potential  $V_{\text{mf}}$ . The operator of infinitesimal rotations  $\partial_k = \epsilon_{kij} a_i (\partial / \partial a_j)$  relates to the gradient operator in the usual translational diffusion.  $D_r$  stands here for the rotational diffusion coefficient and  $k$  is Boltzmann's constant. Since the macroscopic flow rotates the molecules with a certain angular velocity  $\boldsymbol{\omega}$ , the corresponding changes in the distribution function  $f(\mathbf{a})$  are taken into account by the second term on the right-hand side of Eq. (2).

Assumptions in the OT type of calculations may concern only two aspects of the theory: the expression for  $\boldsymbol{\sigma}^{\text{mic}}$  and the way of solving the kinetic equation (2).

In OT1 the expressions for the viscosities are determined due to the ansatz for the microscopic stress tensor  $\boldsymbol{\sigma}^{\text{mic}}$ . A general structure of  $\boldsymbol{\sigma}^{\text{mic}}$  can be derived by analyzing the change in the free energy caused by the particles' rotation due to the macroscopic flow [3]. Consequently,  $\boldsymbol{\sigma}^{\text{mic}}$  exhibits a similarity to the free energy functional: it is composed of entropic and interaction terms. An analogous feature is exhibited by the FP equation itself. It is possible to see that the entropic term of  $\boldsymbol{\sigma}^{\text{mic}}$  is straightforwardly connected with the standard Brownian term in Eq. (2), whereas the interaction part of  $\boldsymbol{\sigma}^{\text{mic}}$  is related to the drift motion term. In [7] the authors omitted the entropic contribution to  $\boldsymbol{\sigma}^{\text{mic}}$ . At the same time it is not possible to omit the corresponding term in the FP equation without destroying it. As a result, the expressions presented in [7] for the symmetric viscosities are not correct, though their magnitude can be regarded to be reasonable. This latter fact is due to the competition of the entropy and interaction terms in nematic liquid crystals.

The configurational entropy contribution has been included in the second paper (OT2) [8]. In the paper, however, the analysis of the symmetric stress tensor is *not* performed within the framework of the OT approach, but implemented directly from KD [3]. To find a solution for the rotational viscosities the authors used the assumption of fast precession of the molecule around the optical axis of the system. This idea justifies omitting the terms in the FP equation that depend on the azimuthal angle  $\varphi$ . Also, effectively, the originally two-variable differential equations become transformable into one-dimensional integrals.

In the third paper (OT3) [4] the symmetric viscosity coefficients are derived strictly within the OT model and shown to be *exactly* the same as the KD formulas. Since in OT3 the

calculation of the KD formulas from the OT integrals have not been explicitly presented, an illustrative example of such a derivation for  $\alpha_4^{\text{nem}}$  ( $\alpha_4 = 2\eta_3$ ) will be given here. An OT-type integral for  $\alpha_4^{\text{nem}}$  has been found as [4]

$$\alpha_4^{\text{nem}} = \frac{1}{2} C \pi \int \rho_2 f_0 \left\{ 3kT \sin^2 \theta + \frac{1}{2} \frac{\partial V_{\text{mf}}}{\partial \theta} \sin(2\theta) \right\} d(\cos \theta), \quad (3)$$

in which  $\rho_2$ , the nonequilibrium perturbation, is

$$\rho_2 = \frac{1}{2D_r} C \sin^2 \theta. \quad (4)$$

$C = (p^2 - 1)/(p^2 + 1)$  is the shape anisotropy form factor, with  $p$  being the particle's length-to-width ratio. Using Eqs. (3) and (4) and  $df_0/d\theta = -(f_0/kT)dV_{\text{mf}}/d\theta$ , the expression for  $\alpha_4^{\text{nem}}$  becomes

$$\begin{aligned} \alpha_4^{\text{nem}} &= \frac{kT}{4D_r} C^2 \pi \int \sin^2 \theta \left\{ f_0 3 \sin^2 \theta - \frac{1}{2} \frac{\partial f_0}{\partial \theta} \sin 2\theta \right\} d(\cos \theta) \\ &\quad - \frac{kT}{4D_r} C^2 \pi \int f_0 \left\{ 3 \sin^5 \theta + \frac{1}{2} \frac{\partial}{\partial \theta} (\sin^3 \theta \sin 2\theta) \right\} d\theta. \end{aligned} \quad (5)$$

After integrating by parts one obtains

$$\begin{aligned} \alpha_4^{\text{nem}} &= -\frac{kT}{4D_r} C^2 \pi \int d\theta f_0 \{ 3 \sin^5 \theta + (4 \sin^3 \theta \cos^2 \theta - \sin^5 \theta) \} \\ &= \frac{kT}{2D_r} C^2 \frac{2}{35} (7 - 5S_2 - 2S_4), \end{aligned} \quad (6)$$

which is exactly the expression for  $\alpha_4^{\text{nem}}$  in the KD formulation [3].

Transformation of the OT-approach integrals into the KD formulas is possible only if the full form of the FP equation is considered *including* all the  $\varphi$ -dependent terms [this is the necessary condition to obtain the perturbation  $\rho_2$  in the form as presented by Eq. (4)]. This fact also reveals that in OT2 the formulas for the antisymmetric and symmetric viscosities are obtained under contradictory assumptions for the azimuthal precession. The problem of the fast precession has been already pointed out by Stepanov and replied by Osipov and Terentjev [9]. On the basis of Brown's analysis of the Fokker-Planck equation [10], Stepanov claims that the reorientation of the nematic molecule is not related to the process of overcoming an energy barrier, but is simply a turn of the molecule to the nearest direction of the symmetry axis. For completeness one should add that undeniable achievement of OT2 is the statistical model for the rotational diffusion coefficient  $D_r$ , which scales both the symmetric and the antisymmetric viscosities and which has not been investigated by Kuzuu and Doi.

Janik *et al.* paid special attention to the relation between the Miesowicz coefficients  $\eta_2$  and  $\eta_3$  [1]. They found a general feature that values of  $\eta_2$  are always smaller than  $\eta_3$ . Another striking observation is that the ratio  $\eta_3/\eta_2$  has a tendency to be either constant or exhibit values that subtly vary over the range of 0.1. The closest theoretical explanation

to their experimental findings about the constant ratio is the result of OT1, that the Miesowicz coefficients  $\eta_2$  and  $\eta_3$  should be equal. However, the ratio observed in experiment is not close to 1.0 but to 0.9. In order to understand this disagreement the authors discussed possible connections of the various modes of molecular reorientations and viscosity types. They became convinced that a plausible reason of the above disagreement (and equity of  $\eta_2^{\text{OT}}$  and  $\eta_3^{\text{OT}}$ ) is the OT1 assumption about strong elongation of the molecule, for which the inertial moments fulfill the inequity  $I_{\perp} \gg I_{\parallel}$  and which allows them to rule out the reorientation mode associated with rotation about the long molecular axis. Since, in practice, it has been attested that the latter reorientations are meaningful, they can be thought to lower the value  $\eta_2$  as compared to  $\eta_3$ . Theoretical details of the OT analysis, as already mentioned above, indicate a different reason of the equity of  $\eta_2^{\text{OT}}$  and  $\eta_3^{\text{OT}}$ , i.e., the negligence of the configurational entropy effect. This fact has a much different meaning from the assumption  $I_{\perp} \gg I_{\parallel}$ . It is important to emphasize this, since configurational entropy effect is very significant also for infinitely thin particles ( $I_{\parallel}=0$ ) as, for instance, in the Onsager theory of hard rods.

To find a theoretical explanation of the findings of Janik *et al.*, let us consider the available information about  $\eta_3$  and  $\eta_2$ . According to KDOT, the difference between these two coefficients is given by the expression

$$\begin{aligned} \eta_3 - \eta_2 &= -\frac{1}{2}(\alpha_2 + \alpha_6) \\ &= \frac{ckT}{4D_r} C \left[ C \frac{-1}{7} (3S_2 + 4S_4) + S_2 + \left(1 - \frac{1}{\lambda}\right) S_2 \right], \end{aligned} \quad (7)$$

where

$$\lambda = C \frac{S_2}{\left\langle g \frac{dV_{mf}}{d\theta} \right\rangle}. \quad (8)$$

$S_2, S_4$  are the order parameters and  $g$  is an asymmetric component of the solution  $f$  of the FP equation.

According to Eq. (7), the relation between  $\eta_3$  and  $\eta_2$  strongly depends on the order degree of the system and on its rotational properties, especially on  $\gamma_1 = \langle g dV_{mf}/d\theta \rangle$ . The value  $1/\lambda$  refers to the definition of the extinction angle  $\chi$ ,

$$\cos 2\chi = -\frac{\gamma_1}{\gamma_2} = \frac{1}{\lambda}, \quad (9)$$

and is always less than unity as long as the system is beyond the tumbling regime. Taking this fact into account and the

TABLE I. Recommended data for  $\alpha_4, \alpha_5, \alpha_6$  viscosities for 4-methoxybenzylidene-4-n-butylaniline (MBBA) [11].

$T$ (°C)	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\alpha_5 + \alpha_6$
20	0.1095	0.1071	-0.0471	0.06
25	0.0826	0.0779	-0.0336	0.0443
30	0.0644	0.0572	-0.0244	0.0328
35	0.0515	0.0417	-0.01763	0.02407
40	0.0422	0.0285	-0.01244	0.01606
42	0.0394	0.0224	-0.01086	0.01154
44	0.0374	0.0136	-0.00917	0.00443

property that nematic order parameters are always less than unity ( $S_2, S_4 \leq 1$ ) one can immediately see that by virtue of Eq. (7) the inequality  $\eta_2 < \eta_3$  is always fulfilled. This result perfectly corresponds to the experimental data and tests the applicability of the KDOT theory.

However, if one takes into account the ratio  $\eta_3/\eta_2$ ,

$$\frac{\eta_3}{\eta_2} = \frac{\frac{1}{2} \alpha_4}{\frac{1}{2} (\alpha_2 + \alpha_4 + \alpha_6)}, \quad (10)$$

the situation becomes more complicated because of the influence of  $\alpha_4$ . It is so that the microscopic theories can consider *only* the nematic contribution to  $\alpha_4 = 2\eta_3$  and in any experiment the total, isotropic and nematic, effect is detected. To see this one can look, for instance, at the relationship between values of  $\alpha_4$  and  $\alpha_5 + \alpha_6$ . Due to KDOT results, the expression for  $\alpha_5 + \alpha_6$  reads

$$\alpha_5 + \alpha_6 = \frac{kT}{D_r} C^2 (3S_2 + S_4)/7. \quad (11)$$

Comparing Eqs. (6) and (11) it emerges that the general inequality  $\alpha_4 < \alpha_5 + \alpha_6$  holds for any liquid crystalline compound, whereas experimentally,  $\alpha_4 > \alpha_5 + \alpha_6$  (see Table I with the results for MBBA quoted from [11]) has been found.

Despite the large number of works devoted to understanding nematic liquid crystal viscosity, there are still many unknowns. The present paper is motivated, then, by the importance of the viscosity experiments, which can provide information that is not accessible from the theory side, and may therefore help steer the theoretical investigation. Particular attention has been paid to the isotropic contribution to  $\eta_3$ , which is much stronger than the nematic one and for which there is at present no theoretical description.

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