

Microscopic Stress Tensor of Nematic Liquid Crystal Binary Mixtures

Agnieszka Chrzanowska^a and Pawel T. Jochym^b

^a Cracow University of Technology, Institute of Physics, ul. Podchorążych 1, 30-084 Cracow, Poland

^b H. Niewodniczański Institute of Nuclear Physics, ul. Radzikowskiego 152, 31-342 Cracow, Poland

Z. Naturforsch. **51a**, 147–150 (1996); received September 6, 1995

A microscopic stress tensor for the binary nematic mixture of anisotropic molecules is presented. Its simple additive character is beneficial for hydrodynamics studies. We pay attention to mixtures of disc and rodlike molecules which may exhibit interesting hydrodynamic properties.

1. Introduction

The range of commercial display devices which utilise liquid crystals (LC) is widely known and still increasing. Recently mixtures exhibiting mesomorphic properties have gained a considerable attention. Their temperature and viscoelastic characteristics are more suitable for LC-devices and cannot be obtained with pure substances. Since the features of a LC device are strictly related to the viscosity, hydrodynamic models are of special interest. Moreover, the study and understanding of the viscous properties of mixtures can help in designing new, improved materials and is also important for kinetic theories of transport phenomena.

From the molecular theories [1–5] of one-component nematic systems it emerges that the microscopic stress tensor σ^μ plays a fundamental role. It represents an energetic response of the system to the deformations caused by the velocity gradient field and thus lies at the root of viscosity considerations.

The general method of obtaining σ^μ for a one-component system was put forward by Doi in 1981 [1]. But neither in [1] nor in [2] a completely correct form of σ^μ was introduced. Another approach was introduced by Osipov and Terentjev [4]. However, also in this case σ^μ does not exhibit the feature that the symmetric part is related to the molecule formfactor $f(p)$, whereas the antisymmetric part is *not*. As it has been proved in [5], this feature of σ^μ is crucial for the fulfilment of the Parodi equality [6]. Note that Onsager relations [7], whose liquid crystal counterpart is the Parodi rela-

tion, decide about correctly constructed transport theory.

A systematic derivation and a completely correct form of σ^μ for a one-component systems by the use of the Doi idea [1] is given in [8]. It should also be mentioned that this form allows to prove the equivalence of the two hydrodynamic molecular approaches of Osipov-Terentjev (OT) and Kuzuu-Doi (KD), which provide complete and satisfactory description of viscous properties at the molecular level [5].

In the present paper the Doi idea is applied to a binary mixture in order to find a formula for the stress tensor. The starting point of this idea is the expression for the free energy. The considered system is influenced by a small velocity gradient. This field causes a molecule to move along a periodic Jefferey's orbit with a certain angular velocity [9]. As a consequence, the distribution function and the free energy are changed. The change in the free energy is equal to the inner product of the stress and deformation tensors. The emerging stress tensor has the form of averages of certain microscopic expressions, which depend on the orientations of molecules and appropriate mean potentials.

In this paper we introduce σ^μ for a binary mixture and consider consequences emerging of its form.

2. Microscopic Stress Tensor

Let us consider a mixed nematic system of N_A particles of A and N_B particles of B. The molecules are anisotropic and characterized by the lengths L_A and L_B and the diameters d_A and d_B .

Reprint requests to Dr. A. Chrzanowska.

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A starting point is the expression for the orientational free energy coming from the density functional theory in the second virial approximation [10]:

$$\begin{aligned} \beta \mathcal{F} = & \int (\ln \varrho_{1A} - 1) \varrho_{1A} d\mathbf{a}_{1A} \\ & + \int (\ln \varrho_{1B} - 1) \varrho_{1B} d\mathbf{a}_{1B} \\ & - \frac{1}{2} \int f^{AA} \varrho_{1A} \varrho_{2A} d\mathbf{a}_{2A} \\ & - \frac{1}{2} \int f^{BB} \varrho_{1B} \varrho_{2B} d\mathbf{a}_{1B} d\mathbf{a}_{2B} \\ & - \int f^{AB} \varrho_{1A} \varrho_{1B} d\mathbf{a}_{1A} d\mathbf{a}_{1B}, \end{aligned} \quad (1)$$

where ϱ_i denotes the one-particle distribution function describing the probability of finding a given molecule with the orientation \mathbf{a}_i and is normalized to the number of particles N_i . f^{ij} is an interaction kernel related to the direct correlation function.

Under a small deformation ε a nematic liquid crystal reacts like an elastic system and changes its energy by $\delta \mathcal{F}$:

$$\delta \mathcal{F} = \langle \sigma^\mu \rangle : \varepsilon^+ + O(\varepsilon^2), \quad (2)$$

where $\langle \sigma^\mu \rangle$ is the stress tensor and ε is the deformation tensor which moves a point from r_α to $r'_\alpha = r_\alpha + \varepsilon_{\alpha\beta} r_\beta$. We are interested in the effect caused by a small velocity gradient field. Thus, the deformation tensor for an infinitesimal time δt is $\varepsilon = \mathbf{k} \delta t$ with $\mathbf{k} = (\nabla \cdot \mathbf{v})^+$ as the velocity gradient tensor. The velocity field rotates the molecule with a certain velocity Ω , which is dependent on the kind of the molecule and has the form [2, 8, 9]

$$\Omega = \frac{p^2 - 1}{p^2 + 1} \mathbf{a} \times (\mathbf{A} \cdot \mathbf{a}) - \mathbf{a} \times (\mathbf{g} \cdot \mathbf{a}), \quad (3)$$

where $p = L/d$ is the length to width ratio of the molecule and \mathbf{A} and \mathbf{g} are the symmetric and antisymmetric parts of the velocity gradient tensor \mathbf{k} , respectively:

$$A_{\alpha\beta} = \frac{1}{2} (\partial_\alpha v_\beta + \partial_\beta v_\alpha), \quad (4)$$

$$g_{\alpha\beta} = \frac{1}{2} (\partial_\alpha v_\beta - \partial_\beta v_\alpha). \quad (5)$$

In the case of a binary mixture we should bear in mind that molecules of kind A and B have different angular velocities due to their geometrical dimensions. As will be shown below, it influences the statistical variables and the stress tensor itself.

Under the assumed deformation, the direction \mathbf{a} of the individual molecule is changed to $\mathbf{a}' = \mathbf{a} + \delta \mathbf{a}$, where $\delta \mathbf{a} = \mathbf{a} \times \delta \Theta$. The small angle $\delta \Theta$ is

$$\delta \Theta = \Omega \delta t = \mathbf{a} \times \frac{(p^2 \varepsilon - \varepsilon^+) \cdot \mathbf{a}}{p^2 + 1}. \quad (6)$$

Accordingly, the distribution functions ϱ_A and ϱ_B are changed to the new values ϱ'_A and ϱ'_B :

$$\varrho' = \varrho_0 + \delta \varrho, \quad (7)$$

where

$$\delta \varrho = -\nabla_{\mathbf{a}} \cdot (\delta \mathbf{a} \varrho_0), \quad (8)$$

and where ϱ_0 is the equilibrium distribution function. Thus the variation of the free energy (1) can be expressed as

$$\begin{aligned} \beta \delta \mathcal{F} = & \int (\delta \varrho_A + \delta \varrho_A \ln \varrho_A) d\mathbf{a}_A \\ & + \int (\delta \varrho_B + \delta \varrho_B \ln \varrho_B) d\mathbf{a}_B \\ & - \int f^{AA} \varrho_{1A} \delta \varrho_{2A} d\mathbf{a}_{1A} d\mathbf{a}_{2A} \\ & - \int f^{BB} \varrho_{1B} \delta \varrho_{2B} d\mathbf{a}_{1B} d\mathbf{a}_{2B} \\ & - \int f^{AB} \varrho_{1B} \delta \varrho_{2A} d\mathbf{a}_{1A} d\mathbf{a}_{2B} \\ & - \int f^{AB} \varrho_{1A} \delta \varrho_{2B} d\mathbf{a}_{1B} d\mathbf{a}_{2A}. \end{aligned} \quad (9)$$

As has been shown in [8], terms of the type $\int \delta \varrho$ are zero, and of the type $\int \delta \varrho \ln \varrho$ they read

$$\int \delta \varrho \ln \varrho d\mathbf{a} = \langle \partial_j \delta a_j \rangle_{\varrho}. \quad (10)$$

The forms of the interaction terms can be simplified using the state equations for the binary mixture [10]:

$$\ln(\varrho_A) = \int f^{AA} \varrho_A d\mathbf{a}_A + \int f^{AB} \varrho_B d\mathbf{a}_B, \quad (11)$$

$$\ln(\varrho_B) = \int f^{BB} \varrho_B d\mathbf{a}_B + \int f^{AB} \varrho_A d\mathbf{a}_A. \quad (12)$$

Bearing in mind that $\varrho = \exp(-U/k_B T)$, the interaction contribution to $\delta \mathcal{F}$ is

$$\int U_A \delta \varrho_A d\mathbf{a} + \int U_B \delta \varrho_B d\mathbf{a}. \quad (13)$$

Equation (13) can be transformed (see Appendix in [8]) as

$$\begin{aligned} & \int U_A \delta \varrho_A d\mathbf{a} + \int U_B \delta \varrho_B d\mathbf{a} \\ & = -\langle \delta a_{jA} \partial_j U_A \rangle_{\varrho_A} - \langle \delta a_{jB} \partial_j U_B \rangle_{\varrho_B}. \end{aligned} \quad (14)$$

The infinitesimal changes in the orientations \mathbf{a} due to the small deformations $\varepsilon_{\alpha\beta}$ are

$$\begin{aligned} \delta a_j = & \frac{p^2 - 1}{p^2 + 1} [a_\alpha a_j a_\beta \varepsilon_{\alpha\beta}^+ - a_\beta \varepsilon_{j\beta}^+] \\ & - \frac{p^2}{p^2 + 1} a_\beta (\varepsilon_{j\beta} - \varepsilon_{j\beta}^+). \end{aligned} \quad (15)$$

Applying (15) to (10) and (14) we obtain

$$\sigma = \sigma_A + \sigma_B = \langle \sigma_A^\mu \rangle_{\varrho_A} + \langle \sigma_B^\mu \rangle_{\varrho_B}, \quad (16)$$

where σ^μ may be splitted into the symmetric part

$$\sigma_{\alpha\beta}^{\text{sym}} = \frac{p^2 - 1}{p^2 + 1} \left[3k_B T \left(a_\alpha a_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) + \frac{1}{2} \left(a_\alpha \frac{\partial U}{\partial a_\beta} + a_\beta \frac{\partial U}{\partial a_\alpha} \right) \right] \quad (17)$$

and the antisymmetric part

$$\sigma_{\alpha\beta}^{a\text{sym}} = \frac{1}{2} \left(a_\alpha \frac{\partial U}{\partial a_\beta} - a_\beta \frac{\partial U}{\partial a_\alpha} \right). \quad (18)$$

An important feature, which should be mentioned while looking at the form of σ^μ , is its additive character. The binary stress tensor appears to be a sum of terms of the similar structure written for each component of the system. There are no cross-terms combining explicitly features of the components A and B. The mutual interaction of the different kinds of particles has already been taken into account while establishing the distribution functions ϱ_A and ϱ_B . This additive character of σ^μ suggests that, if one disposes of a method, either experimental or theoretical, which allows to establish appropriate distribution functions for each component in a mixture, the expressions (16–18) could serve as a tool for the analysis of its hydrodynamic features.

3. Closing Remarks

From the form of σ^μ we can predict two theoretically possible interesting cases. The first concerns the symmetric part of hydrodynamic properties.

Let us assume the case of a mixture of rodlike (r) and disclike (d) molecules, where the geometric ratios fulfill the equality

$$p_r = \frac{1}{p_d} \quad (19)$$

and all particles have the same distribution functions and mean potentials:

$$f_r = f_d, \quad U_r = U_d. \quad (20)$$

These conditions induce that the symmetric part of the stress tensor (16) vanishes. Bearing in mind the expression for the Leslie viscous stress tensor [11] for

a nematic system

$$\sigma_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\mu A_{\mu\alpha} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha}, \quad (21)$$

(where n denotes the director, $N_\alpha = \dot{n}_\alpha - (\omega \times n)_\alpha$ is the rotation vector of the system, $\omega = \frac{1}{2} \text{rot} v$ is the flow rotation angular velocity and $\alpha_1 \dots \alpha_6$ are the Leslie viscosity coefficients) we see that the following nematic viscosity coefficients must be zero:

$$\alpha_1, \quad \alpha_4, \quad \alpha_2 + \alpha_3, \quad \alpha_5 + \alpha_6. \quad (22)$$

It should be remarked that α_4 is the nematic contribution. The above considerations do not relate to the isotropic values, so if the system assumed above would have an experimental nonzero value of α_4 , this would mean that a purely isotropic effect has been measured.

By virtue of the Parodi relation [6]

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \quad (23)$$

it emerges that the rotational viscous coefficient $\gamma_2 = \alpha_6 - \alpha_5$ is also zero. So, by virtue of (22) $\alpha_5 = 0$ and $\alpha_6 = 0$. The only nonzero coefficient is the rotational coefficient γ_1 :

$$\gamma_1 = 2\alpha_3 = -2\alpha_2. \quad (24)$$

The above situation, albeit theoretically possible, might be unlikely to encounter in the real systems. In known mixtures of rod and disclike molecules the particles are ordered in the mutually perpendicular directions and therefore cannot have similar distribution functions. In this case we might rather expect interesting features concerning antisymmetric viscosity properties. If different particles are ordered perpendicularly, the derivatives in the expressions for σ^μ will have different signs for rods than for discs. Effectively antisymmetric viscosity coefficients should have lower values than for pure compounds. This situation is more real and might be of great importance in view of the large effort put into investigation of new materials with low rotational viscosity, which is desired in, production of fast switchable liquid crystal devices.

Acknowledgement

This work was supported by the Polish Government Project No. 22377 92 03.

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