Viscosity Coefficients of a Nematic Mixture: Statistical Theory Approach

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A statistical theory of the rotational diffusion of a molecule in a two-component anisotropic mixture is developed, based on the Fokker-Planck approximation for the one-particle orientational distribution function. The friction constant of the molecular rotation is determined from the three-particle correlation function, which takes into account interactions A–A, A–B, B–A and B–B between two sorts of molecules. The Leslie coefficients obtained possess a complicated dependence on mixture concentration together with a dependence on temperature and the molecular parameters of the components. In particular, the rotational viscosity coefficient γ_1 is proportional to a polynomial of third-order in concentrations c_A and c_B with coefficients proportional to $\exp\{J_A c_A + J_B c_B\}\sqrt{J_A c_A + J_B c_B}$.

1. Introduction

In our previous papers [1, 2] we have derived a consistent molecular-statistical approach to the viscosity of simple uniaxial nematic liquid crystals. The continuous hydrodynamics of a nematic is determined by the corresponding viscous stress tensor [3]

$$\sigma_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\varrho A_{\mu\varrho} + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\beta n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha , \quad (1)$$

where $A_{\alpha\beta} = \frac{1}{2}(\hat{\partial}_\alpha v_\beta + \hat{\partial}_\beta v_\alpha)$ is the symmetrical part of the flow velocity gradients tensor $g^{\alpha\beta}$; $N_\alpha = \dot{n}_\alpha - [\boldsymbol{\omega} \times \boldsymbol{n}]_\alpha$, where $\boldsymbol{\omega} = 1/2 \operatorname{rot} \boldsymbol{v}$. Here the unit vector $\boldsymbol{n}$ is the nematic director and $\boldsymbol{\omega}$ the flow rotation angular velocity. The purpose of the molecular-statistical theory is to determine the macroscopic viscous constants $\alpha_1 - \alpha_6$ (the so-called Leslie coefficients) in terms of molecular parameters: geometry, mechanical properties and intermolecular interactions.

The viscous coefficients are very important parameters of a nematic liquid crystal. From the practical point of view the most interesting one is the rotational viscosity coefficient $\gamma_1 = \alpha_3 - \alpha_2$ (which corresponds to the pure director rotation $\dot{\boldsymbol{n}}$), because it determines the reorientation times of various applied systems. γ_1 (like the other Leslie coefficients) strongly depends on the temperature and is very sensitive to the molecular structure [4, 5].

Mixtures of different compounds are often used as nematic materials and the problem of choosing the proper substances and mixture concentration is arising. Therefore it is important to extend the microscopic theory to the case of different kinds of molecules interacting in the media, and to make it possible to predict the values of the viscosity coefficients of a mixture if the concentration and the molecular characteristics are known.

A consistent approach to the microscopic viscosity theory means that one has to determine the non-equilibrium distribution of the probability $W(\Omega, \hat{g})$ of finding a molecule in a definite position in the configurational space $\Omega = \{\boldsymbol{r}, \boldsymbol{v}, \boldsymbol{\alpha}, \boldsymbol{\omega}\}$, where $\boldsymbol{\alpha}$ and $\boldsymbol{\omega}$ denote the molecular orientation and angular velocity, and the deviation from the equilibrium distribution W_0 is determined by the gradients of the nonuniform flow velocity $\hat{g}$. As soon as $W(\Omega, \hat{g})$ is known, one should use it for averaging the microscopic (molecular) stress tensor $\hat{\boldsymbol{\sigma}}^M$ (see [6]) in order to derive the continuous hydrodynamics. Working in this way we have obtained the Leslie coefficients for a pure nematic [1] (see also the earlier models [7, 8]) and smectic C [2] liquid crystals. In this paper we are considering two kinds of molecules (A) and (B) with different (A–A), (A–B) and (B–B) interactions, and our purpose is to determine the concentration dependence of the rotational viscosity coefficient γ_1.

The paper is organized as follows: the next section is devoted to the evaluation of the distribution func-

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tions; the main difficulty here is the estimation of the microscopic friction constants for both molecules when one has to take into account interactions between three particles, $(1 \Leftrightarrow 2)$ and $(1 \Leftrightarrow 3)$. Then the microscopic stress tensor $\hat{\sigma}^{M}$ for the mixture will be derived and, finally, its averaging will provide the expression for the rotational viscosity coefficient.

2. Microscopic Friction Constants and Distribution Functions

It has been discussed in [1] that the advantage of the orientational order in liquid crystals is that a mean field is present in the system and that one can use the one-particle distribution function $W^{(1)}$ to describe the molecular rotational diffusion. Correlational corrections can be sufficient close to phase transitions, for example, but in the deep nematic phase the main contribution to the viscosity coefficients still comes from the mean-field approximation. So it is reasonable to consider the microscopic molecular motion in a liquid crystal as a rotational Brownian motion which should be described by the appropriate one-particle Fokker-Planck equation. This approximation corresponds to the concept of the "model of suspension", which has been usd by some authors previously [7, 8].

The main ideas of the Fokker-Planck equation derivation have been presented in our previous works; in the case of a two component mixture the molecules of each sort have probability distribution functions W^{A} and W^{B} which are determined by the equations

$$\frac{\partial}{\partial t} W^{A,B} + \partial_k(\omega_k W^{A,B}) + \frac{1}{I_{\perp}^{A,B}} \cdot \frac{\partial}{\partial \omega_k}(\Gamma_k^{A,B} W^{A,B}) \quad (2)$$

$$= \frac{1}{I_{\perp}^{A,B}} \cdot \lambda^{A,B} \frac{\partial}{\partial \omega_k}\left(\omega_k - \Psi_k^{A,B} + \frac{kT}{I_{\perp}^{A,B}} \cdot \frac{\partial}{\partial \omega_k}\right) W^{A,B},$$

where the differential operator on the unit sphere $\partial_k = \varepsilon_{kij} a_i \partial/\partial a_j$, $\boldsymbol{a}$ is the orientation of the long molecular axis, $\boldsymbol{\omega} = [\boldsymbol{a} \times \dot{\boldsymbol{a}}]$ is the angular velocity of the transversal rotation, $I_{\perp}$ the component of the corresponding molecular inertia tensor $I_{ij} = I_{\perp}\delta_{ij} + (I_{\parallel} - I_{\perp}) a_i a_j$, and $\boldsymbol{\Gamma}$ is the moment of elastic forces acting on the corresponding molecule from the mean field: $\Gamma_k^{A,B} = -\partial_k U_{A,B}^{m.f.}(\boldsymbol{a}, \boldsymbol{n})$. The microscopic friction moment of force (see [1, 6]) $\hat{\lambda}(\boldsymbol{\omega} - \boldsymbol{\Psi})$ acts on the molecule when its instant angular velocity $\boldsymbol{\omega}$ deviates from the mean velocity $\boldsymbol{\Psi}$, which is determined by the local flow rotation:

$$\boldsymbol{\Psi} = \mathrm{Rot}\, \boldsymbol{v} - (\boldsymbol{a} \cdot \mathrm{Rot}\, \boldsymbol{v})\, \boldsymbol{a} + \frac{p^2 - 1}{p^2 + 1} [\boldsymbol{a} \times \hat{A} \cdot \boldsymbol{a}],$$

$p = L/D$ is the molecular length-to-breadth ratio. Note that the fast relaxation of the molecular rotation about its long axis $\boldsymbol{a}$ is already integrated out from (2).

It has been shown in [1] that the anisotropic part of the tensor $\hat{\lambda}$ does not contribute to the stress tensor averaging in the mean field approximation; the direct calculation of the friction constant λ was the main achievement of that work. Our purpose here is to express λ in terms of definite molecular parameters of the mixed compounds and their concentrations, using the general expression which has been obtained from the fluctuation-dissipation theorem [9] or, even earlier, from the Brownian motion Langevin equation derivation [6]. In our case, the molecule of sort A, for example, is influenced, during its rotation, by the surrounding particles, and that process can be effectively accounted for as the microscopic friction in the corresponding Langevin equation with the constant λ, determined by the equilibrium correlator of instant moments of force, acting on this molecule:

$$\lambda^{A} = \frac{1}{3kT} \int_0^{\infty} \langle \boldsymbol{\Gamma}^{A}(t), \boldsymbol{\Gamma}^{A}(0) \rangle_{eq.}\, dt, \quad (3)$$

$$\text{where} \quad \langle \boldsymbol{\Gamma}^{A} \rangle_{eq.} = 0.$$

The above expression is valid in the same approximation, when it is possible to use the Brownian motion model to describe the properties of the liquid itself: at sufficiently low temperatures, for example, when the average intermolecular collisions do not considerably change their momentum values and directions. This approximation seems to be valid in liquid crystals.

The Fokker-Planck equation in the kinetic theory can be used when the stochastic force correlator has the very short relaxation time τ^{A}. This time can be estimated as the ratio of the free angular volume fraction per molecule $\Delta\theta^{A}$ to the mean velocity of a thermal rotation $\propto \sqrt{kT/I_{\perp}^{A}}$. The free volume $\Delta\theta^{A}$ is approximately determined by the molecular dimensions L_A and D_A and the number density $c_A = N_A/V$: $\Delta\theta^{A} \propto (\sqrt{4/\pi c_A L_A - D_A})/L_A \ll D_A/L_A$ (see also [10]). Now the friction constant λ^{A} is qualitatively equal to

$$\lambda^{A} \simeq \tau^{A} \langle (\Gamma^{A}(0))^2 \rangle_{eq.} \approx \Delta\theta^{A} \sqrt{I_{\perp}^{A}/kT}\, \langle (\Gamma^{A}(0))^2 \rangle_{eq.}. \quad (4)$$

In the thermodynamic limit the main contribution to the average in (4) are mixed three-particle correlators (compare with the corresponding expression for

the pure system [1]):

$$\langle (\Gamma^{\mathrm{A}})^2 \rangle \approx N_{\mathrm{A}}^2 \langle \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 2_{\mathrm{A}})\, \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 3_{\mathrm{A}}) \rangle + N_{\mathrm{A}} N_{\mathrm{B}} \langle \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 2_{\mathrm{A}})\, \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 3_{\mathrm{B}}) \rangle + N_{\mathrm{A}} N_{\mathrm{B}} \langle \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 2_{\mathrm{B}})\, \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 3_{\mathrm{A}}) \rangle + N_{\mathrm{B}}^2 \langle \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 2_{\mathrm{B}})\, \hat{\partial}_{1_{\mathrm{A}}} U(1_{\mathrm{A}}, 3_{\mathrm{B}}) \rangle, \tag{5}$$

where subscripts like "1_{A}" mean that the first molecule is of the sort A; $U(1, 2)$ is the pair potential of interaction between molecules "1" and "2" and the angular gradient is, as usual, $\hat{\partial}_k = \varepsilon_{kij}\, a_i\, \partial/\partial a_j$. We shall use the following model for the attraction part of the pair potential (see [11]):

$$U(1_{\mathrm{A}}, 2_{\mathrm{A}}) \simeq -\frac{\tilde{G}^{\mathrm{AA}}}{r_{12}^6} - \frac{1}{r_{12}^6} [\tilde{I}_0^{\mathrm{AA}} (\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2 + \tilde{I}_2^{\mathrm{AA}} (\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)(\boldsymbol{a}_1 \cdot \boldsymbol{u}_{12})(\boldsymbol{a}_2 \cdot \boldsymbol{u}_{12})], \tag{6}$$

where $\boldsymbol{r}_{12} = |\mathrm{r}_{12}|\, \boldsymbol{u}_{12}$ and usually the constants of anisotropic attraction are smaller than the isotropic one: $\tilde{I}_0, \tilde{I}_2 \ll \tilde{G}$ (see [12, 13]). The steric repulsive part of the intermolecular potential can be taken into account using the step function $\Theta(r_{12} - \xi_{12})$, which excludes the interpenetration of the molecular hard cores during the future integration and depends on the closest distance of approach for two molecules; for example, this distance between A and B particles is

$$\xi_{12}^{\mathrm{AB}} \equiv \min(r_{12}^{\mathrm{AB}}) \approx \frac{d_{\mathrm{A}} + d_{\mathrm{B}}}{2} + \frac{L_{\mathrm{A}} + L_{\mathrm{B}} - d_{\mathrm{A}} - d_{\mathrm{B}}}{4} [(\boldsymbol{a}_1 \cdot \boldsymbol{u}_{12})^2 + (\boldsymbol{a}_2 \cdot \boldsymbol{u}_{12})^2]. \tag{7}$$

The averaging in (5) should be provided with the joint three-particle probability distribution function, because variables of three different molecules are involved in each term. The reasonable approximation for this function is (see [1, 6])

$$W_{\mathrm{eq.}}^{(3)}(1, 2, 3) \cong e^{-U(1,2)/kT}\, e^{-U(1,3)/kT}\, e^{-U(2,3)/kT} \cdot W_{\mathrm{eq.}}^{(1)}(1)\, W_{\mathrm{eq.}}^{(1)}(2)\, W_{\mathrm{eq.}}^{(1)}(3), \tag{8}$$

which means neglection of the direct three-particle collisions and indirect pair interaction via the third particle. In [1] we used the saddle-point approximation during integration over spatial coordinates in (5), when the main contribution to it is determined by the molecular form-factor (7). Following the integration procedure suggested in [1], we can obtain the estimation for the microscopic friction constants in the two-component mixture. The explicit expressions for arbitrary L_{A}, L_{B}, D_{A}, and D_{B} are very complicated and will be presented in the other publications. Here we are going to describe a mixture of compounds which are not tremendously different in their geometrical shapes; in the limit $D_{\mathrm{A}} \approx D_{\mathrm{B}}$ the estimations for the λ's are

$$\lambda^{\mathrm{A}} \approx 100(1-\phi)\, D^6 \left(\frac{D}{L_{\mathrm{A}}}\right) (kT)^4 \sqrt{I_{\perp}^{\mathrm{A}}/kT} \cdot \left\{ c_{\mathrm{A}}^2 \left(\frac{1}{G^{\mathrm{AA}}}\right)^2 e^{3G^{\mathrm{AA}}/kT} + c_{\mathrm{A}} c_{\mathrm{B}} \left(\frac{2}{\frac{G^{\mathrm{AB}} + 2G^{\mathrm{AA}}}{3}\, G^{\mathrm{AB}}}\right) \frac{\tilde{J}_0^{\mathrm{AA}}}{\tilde{J}_0^{\mathrm{AB}}}\, e^{(G^{\mathrm{AA}} + 2G^{\mathrm{AB}})/kT} + c_{\mathrm{B}}^2 \left(\frac{3}{2G^{\mathrm{AB}} + G^{\mathrm{BB}}}\right)^2 e^{(2G^{\mathrm{AB}} + G^{\mathrm{BB}})/kT} \right\}$$

and a similar expression for λ^{B}, where the parameter ϕ is the volume fraction of molecules (usually for dense molecular liquids $\phi \propto 0.5$–0.6), all $G \equiv \tilde{G}/D^6$. $J^{\mathrm{A,B}}$ are the mean field potential constants for the both sorts of molecules: $U_{\mathrm{A,B}}^{\mathrm{m.f.}} = 1 - J^{\mathrm{A,B}} \langle P_2 \rangle (\boldsymbol{a} \cdot \boldsymbol{n})^2$, where

$$J^{\mathrm{A}} \approx c_{\mathrm{A}}\, 2\pi (\tilde{I}_2^{\mathrm{AA}} + \tfrac{2}{3}\, \tilde{I}_0^{\mathrm{AA}})/D_{\mathrm{A}}^3 + c_{\mathrm{B}}\, 2\pi (\tilde{I}_2^{\mathrm{AB}} + \tfrac{2}{3}\, \tilde{I}_0^{\mathrm{AB}}) \Big/ \left(\frac{D_{\mathrm{A}} + D_{\mathrm{B}}}{2}\right)^3, \tag{9}$$

and similar expression for J^{B}, where $\langle P_2 \rangle$ denotes the nematic order parameter. Let us note that it is the mean field potential $U^{\mathrm{m.f.}}(\boldsymbol{a}, \boldsymbol{n})$ which determines the corresponding equilibrium one-particle distribution function of the molecule in the nematic liquid crystal. In the opposite limiting case, when one of the interacting molecules has a much greater breadth (suppose we have doped the ordinary nematic "A" with some non-mesogenic molecules "B" with $L_{\mathrm{A}} \approx L_{\mathrm{B}}$, but $D_{\mathrm{B}} \gg D_{\mathrm{A}}$), the expression for the friction constant λ_{A} takes the essentially asymmetric form

$$\lambda^{\mathrm{A}} \approx 100(1-\phi) \left(\frac{D_{\mathrm{A}}}{L_{\mathrm{A}}}\right) (kT)^4 \sqrt{I_{\perp}^{\mathrm{A}}/kT} \left\{ c_{\mathrm{A}}^2\, \frac{D_{\mathrm{A}}^6}{(\tilde{G}^{\mathrm{AA}}/D_{\mathrm{A}}^6)^2} \exp[3\tilde{G}^{\mathrm{AA}}/kT\, D_{\mathrm{A}}^6] + c_{\mathrm{A}} c_{\mathrm{B}}\, \frac{0.01\, D_{\mathrm{A}}^3 D_{\mathrm{B}}^3}{(\tilde{G}^{\mathrm{AA}}/D_{\mathrm{A}}^6 + 256\, \tilde{G}^{\mathrm{AB}} D_{\mathrm{A}}^2/D_{\mathrm{B}}^8)\, \tilde{G}^{\mathrm{AB}}/D_{\mathrm{B}}^6}\, \frac{\tilde{J}_0^{\mathrm{AA}}}{\tilde{J}_0^{\mathrm{AB}}} \exp\{[\tilde{G}^{\mathrm{AA}}/D_{\mathrm{A}}^6 + 2G^{\mathrm{AB}}]/[(D_{\mathrm{A}} + D_{\mathrm{B}})/2]^6]/kT\} + c_{\mathrm{B}}^2\, \frac{0.2\, D_{\mathrm{B}}^2}{[(128\, \tilde{G}^{\mathrm{AB}} + \tilde{G}^{\mathrm{BB}})/D_{\mathrm{B}}^6]^2} \exp\{2\tilde{G}^{\mathrm{AB}}/[(D_{\mathrm{A}} + D_{\mathrm{B}})/2]^6 + \tilde{G}^{\mathrm{BB}}/D_{\mathrm{B}}^6]/kT\} \right\}.$$

Let us emphasize the mainly isotropic form of the nematic friction constants; all anisotropic effects give only small corrections to (8). One could expect this fact because the nematic and the isotropic phase of a liquid crystal are very similar to each other as fas as the local order is concerned. The activation Arrhenius law in the temperature dependence of the λ's is the other important feature of (8). Note that the activational energy is mainly determined by the isotropic intermolecular attraction $\tilde{G}/r_{12}^6$ (see (6)) and possesses a very weak term perature dependence.

Now, when all parameters of (2) are known, one has to obtain the linear nonequilibrium correction to the one-particle distribution functions, which are proportional to the gradients of the flow velocity $\hat{g}$ and, hence, determine the classical hydrodynamics. The procedure of solving (2) does not differ from that in the case of a one-component nematic system (see [1, 2]); let us present here the final expressions for the antisymmetrical part of this correction, which determine the rotational viscosity:

$$W_a^{\mathrm{A,B}} \approx \exp\left[-\frac{I_\perp^{\mathrm{A,B}}(\boldsymbol{\omega}-\boldsymbol{\Psi}^{\mathrm{A,B}})^2}{2kT} - \frac{U_{\mathrm{A,B}}^{\mathrm{m.f.}}(\boldsymbol{a}\cdot\boldsymbol{n})}{kT}\right]\cdot\left(1+h_a^{\mathrm{A,B}}(\theta)\,\frac{\boldsymbol{n}\cdot\hat{g}_a\cdot\boldsymbol{a}}{\sin(\theta)}\right), \tag{10}$$

where

$$h_a^{\mathrm{A,B}} \simeq -\frac{1}{\varepsilon_{\mathrm{A,B}}}\int_0^\theta \frac{\exp\{U_{\mathrm{A,B}}^{\mathrm{m.f.}}(x)/kT\}}{\sin(x)}\int_0^x \exp\{-U_{\mathrm{A,B}}^{\mathrm{m.f.}}(z)/kT\}\left(\frac{\partial U_{\mathrm{A,B}}^{\mathrm{m.f.}}(z)/kT}{\partial z}\right)\sin(z)\,\mathrm{d}z\,\mathrm{d}x\,,$$

$$\varepsilon_{\mathrm{A,B}} = \sqrt{I_\perp^{\mathrm{A,B}}kT}/\lambda^{\mathrm{A,B}}, \qquad g_a^{\mu\varrho} = \tfrac{1}{2}(\partial_\mu v_\varrho - \partial_\varrho v_\mu)\,,$$

and the argument of double integration is the angle between the molecular long axis $\boldsymbol{a}$ and the mean field direction $\boldsymbol{n}$: $(\boldsymbol{a}\cdot\boldsymbol{n}) = \cos(\theta)$.

3. Averaging of the Microscopic Stress Tensor

It can be easily shown that in the case of a mixture of different molecules the microscopic molecular stress tensor $\hat{\boldsymbol{\sigma}}^{\mathrm{M}}$, which is determined by the local conservation law for the microscopic momentum density $\frac{\partial}{\partial t}\boldsymbol{p}(\boldsymbol{r}) = -\mathrm{Grad}\,\hat{\boldsymbol{\sigma}}^{\mathrm{M}}(\boldsymbol{r})$, transforms to the sum of contributions from each component (see [1, 2]):

$$\hat{\boldsymbol{\sigma}}^{\mathrm{M}} = \Bigg\{-\tfrac{1}{2}\Big(\sum_i{}_{\mathrm{A}} + \sum_i{}_{\mathrm{B}}\Big)\left[\Big(\sum_{j\neq i}{}_{\mathrm{A}} + \sum_{j\neq i}{}_{\mathrm{B}}\Big)\boldsymbol{r}_{ij}\frac{\partial U(i,j)}{\partial \boldsymbol{r}_{ij}}\right] + \Big(\sum_i{}_{\mathrm{A}} + \sum_i{}_{\mathrm{B}}\Big)\frac{\boldsymbol{v}_i\boldsymbol{v}_i}{m_i} + \Big(\sum_i{}_{\mathrm{A}} + \sum_i{}_{\mathrm{B}}\Big)[\hat{I}_i\times\hat{I}_i^{-1}\cdot\boldsymbol{\Gamma}_i]$$

$$+\Big(\sum_i{}_{\mathrm{A}} + \sum_i{}_{\mathrm{B}}\Big)(\boldsymbol{\omega}_i\boldsymbol{\omega}_i\cdot\hat{I}_i + [\boldsymbol{\omega}_i\times\hat{I}_i\times\boldsymbol{\omega}_i] - \hat{I}_i\,\omega_i^2)\Bigg\}\,\delta(\boldsymbol{r}-\boldsymbol{r}_i), \tag{11}$$

where $\boldsymbol{v}_i$ and $\boldsymbol{\omega}_i$ are the translational and angular velocities of the i-th molecule, m_i and $\hat{I}_i$ are its mass and inertia tensor, $U(i,j)$ is the pair potential of i-th and j-th molecules interaction and $\boldsymbol{\Gamma}_i$ is the moment of force acting on the i-th molecule from its surrounding: $\boldsymbol{\Gamma}_i = -(\sum_{\mathrm{A}} + \sum_{\mathrm{B}})_{j\neq i}[\boldsymbol{a}_i\times\partial/\partial\boldsymbol{a}_i]\,U(i,j)$ (see (2) and (6)).

It has been shown [8] that in the mean field approximation and in the $I_\parallel \ll I_\perp$ limit the symmetrical part of the microscopic stress tensor can be evaluated exactly using the one-particle Fokker-Planck equation during integration by parts. The rotational viscosity evaluation requires the averaging of the antisymmetrical part of the microscopic stress tensor with the corresponding nonequilibrium distribution function, which is given by (10). Performing the averaging over velocities in (11) we obtain the antisymmetrical part of $\hat{\boldsymbol{\sigma}}^{\mathrm{M}}$ in the mean field approximation:

$$\hat{\boldsymbol{\sigma}}_a^{\mathrm{M}} \simeq \tfrac{1}{2}c_{\mathrm{A}}\left(\boldsymbol{a}\frac{\partial U_{\mathrm{A}}^{\mathrm{m.f.}}}{\partial \boldsymbol{a}} - \frac{\partial U_{\mathrm{A}}^{\mathrm{m.f.}}}{\partial \boldsymbol{a}}\boldsymbol{a}\right)$$

$$+\tfrac{1}{2}c_{\mathrm{B}}\left(\boldsymbol{a}\frac{\partial U_{\mathrm{B}}^{\mathrm{m.f.}}}{\partial \boldsymbol{a}} - \frac{\partial U_{\mathrm{B}}^{\mathrm{m.f.}}}{\partial \boldsymbol{a}}\boldsymbol{a}\right). \tag{12}$$

Averaging of this expression with the distribution functions $W^{\mathrm{A,B}}$ determines the Leslie coefficients α_2

and α_3 (see (1)), $\gamma_1 = \alpha_3 - \alpha_2$:

$$\alpha_2 = -\tfrac{1}{2}(c_A \lambda^A + c_B \lambda^B)\langle P_2\rangle - \tfrac{1}{2}\gamma_1,$$

$$\alpha_3 = -\tfrac{1}{2}(c_A \lambda^A + c_B \lambda^B)\langle P_2\rangle + \tfrac{1}{2}\gamma_1,$$

$$\gamma_1 = \frac{1}{2}\int_0^\pi \left\{ c_A\, w_0^A(\theta)\frac{\partial U_A^{m.f.}}{\partial\theta} h_a^A(\theta) + c_B\, w_0^B(\theta)\frac{\partial U_B^{m.f.}}{\partial\theta} h_a^B(\theta)\right\} \sin(\theta)\, d\theta\,, \quad (13)$$

where $\langle P_2\rangle$ is the nematic order parameter and $w_0^{A,B} \propto \exp(-U_{A,B}^{m.f.}/kT)$.

In the nematic phase the mean field coupling constants $J^{A,B}$ are high enough ($J/kT_c \simeq 4.5$ in the Maier-Saupe theory, for example) to justify the use of the saddle point approximation during the integration in (13). In this approximation the expression for the rotational viscosity coefficient γ_1 of the two component nematic mixture takes the form

$$\gamma_1 \simeq \frac{1}{6}\left\{ c_A \lambda^A \sqrt{\frac{J^A\langle P_2\rangle}{kT}}\exp[J^A\langle P_2\rangle/kT] + c_B \lambda^B \sqrt{\frac{J^B\langle P_2\rangle}{kT}}\exp[J^B\langle P_2\rangle/kT]\right\}, \quad (14)$$

where the microscopic friction constants $\lambda^{A,B}$ and the mean-field coupling constants $J^{A,B}$ have been given by (8) and (9).

4. Discussion

In this paper we have considered the Brownian motion of a molecule in a flowing two-component nematic mixture and derived the parameters of the Fokker-Planck equations for the nonequilibrium one-particle distribution functions describing the stochastic motion and rotation of the two kinds of molecules.

We have used a very simple model for a liquid crystal, i.e. a system of cylindrically symmetric rod-like particles which interact via the mean field potential. This is, however, the first necessary step in the development of a consistent molecular theory of the rheological properties of liquid crystals. The question arises here, which properties of the viscous coefficients, observed in real nematic mixtures, can be described with the help of this simple model. Let us remind that close molecular dimensions of the components ($D_A \approx D_B$) has been used during the estimation of

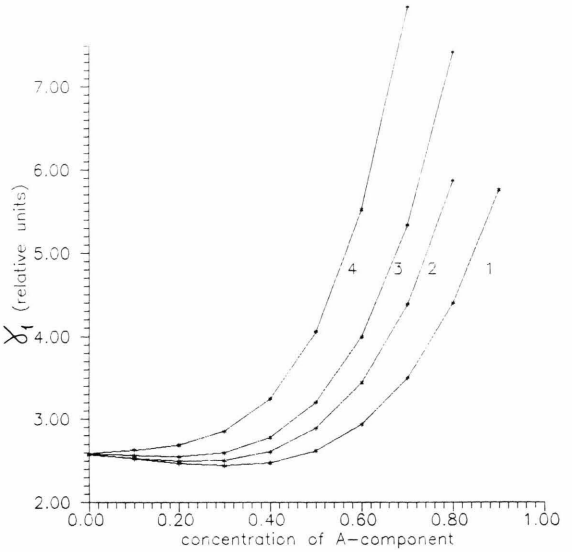

Fig. 1. Normalized rotational viscosity γ_1 versus concentration x of the mixture component A at increasing A $\Leftrightarrow$ A interaction. Curves 1, 2, 3 and 4 correspond to the interaction parameters (see (6)) G^{AA}, G^{AB}, G^{BB}, and I^{AA}, I^{AB}, I^{BB} (in eV units).
(1): 0.2, 0.15, 0.1 and 0.04, 0.03, 0.02.
(2): 0.203, 0.15, 0.1 and 0.041, 0.03, 0.02.
(3): 0.205, 0.15, 0.1 and 0.042, 0.03, 0.02.
(4): 0.208, 0.15, 0.1 and 0.045, 0.03, 0.02.

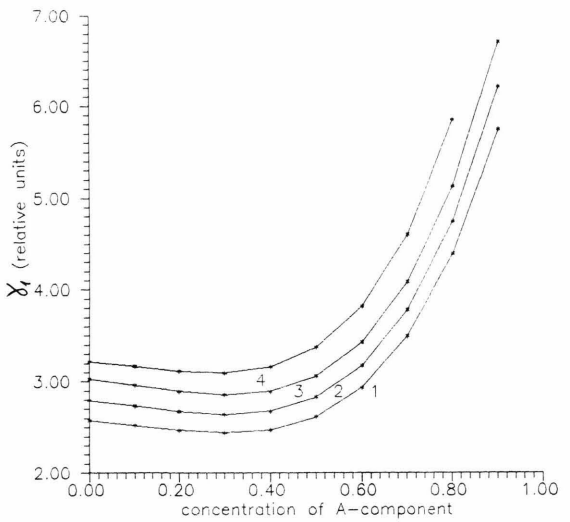

Fig. 2. Normalized rotational visosity γ_1 versus concentration x of the mixture component A at increasing anisotropic part of interaction. Curves 1, 2, 3 and 4 correspond to the interaction parameters (see (6)) G^{AA}, G^{AB}, G^{BB} and I^{AA}, I^{AB}, I^{BB} (in eV units).
(1): 0.2, 0.15, 0.1 and 0.04, 0.03, 0.02.
(2): 0.2, 0.15, 0.1 and 0.041, 0.031, 0.021.
(3): 0.2, 0.15, 0.1 and 0.042, 0.032, 0.022.
(4): 0.2, 0.15, 0.1 and 0.044, 0.033, 0.022.

the λ's (the general expression for arbitrary dimensions is too complicated to carry any information).

The main results of the present paper are the expressions (8) and (13) for the effective microscopic (molecular) rotational friction constant λ^A, λ^B and rotational viscosity coefficient γ_1 for the two component nematic mixture. The theory enabled to determine the concentration dependence of these important parameters. Note that according to (8) the friction constants $\lambda^{A,B}$ possess an exponential temperature dependence, which is mainly responsible for the experimentally observed temperature variation of the viscous coefficients. At the same time the temperature and concentration variation of the rotational viscosity γ_1 is characterized by an additional exponential term with a smaller activation energy, proportional to the corresponding order parameter and determined by the mean field potential barriers $J^{A,B} \propto c_A + c_B$ (see (9)).

Even the approximate expression for the viscosity coefficient γ_1 still contains too many specific parameters, which can be very different for various types of molecules and interactions. Let us try, using some estimations, to determine some possibilities of γ_1 behaviour with varying concentration.

The main difficulty is to find out the coupling constants in the pair potentials (see (6)). They can be estimated using the results of direct quantum chemical calculations of the intermolecular interaction energy for typical nematics [12, 13]. Let us take, for example, $G^{AA} \propto 0.2$ eV, $G^{BB} \propto 0.1$ eV and $G^{AB} \propto 0.15$ eV. Generally, the anisotropic coupling constants are much smaller; let us take $I^{AA} \propto 0.04$ eV, $I^{BB} \propto 0.02$ eV and $I^{AB} \propto 0.03$ eV (we will assume, for simplicity, that both lengths $L_A \approx L_B \propto 30$ Å and also $D_A \approx D_B \propto 5$ Å). Then the plot of the γ_1 dependence on the relative concentration $x = N_A/(N_A + N_B)$ is presented in Figs. 1, 2 as the curves 1. Curves 2, 3, 4 in Fig. 1 correspond to increasing coupling between A $\Leftrightarrow$ A molecules. Curves 2, 3 and 4 in Fig. 2 correspond to an increasing anisotropic-to-isotropic coupling relation for both kinds of molecules. Let us mention that the numerical value of the viscous coefficient γ_1 is very sensitive to the values of the coupling constants and to their relations, and that the dependence on concentration is strongly nonlinear.

As an example of many possible predictions, following from our theoretical expressions (8) and (13), one can suggest to dope a dipolar nematogen with inert, weakly interacting molecules of approximately the same shape (or thicker) in order to obtain a mixture with lower viscosity than that of the pure original compound. Generally speaking, the present theory provides the possibility of optimization in looking for a compromise between different macroscopic properties required in a given application, and to find out optimal molecular parameter relations for the compounds used in such applications.

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