Rheological properties of a liquid-crystal solution of rodlike molecules

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The dynamics of a liquid-crystal solution of long rodlike macromolecules is investigated on the basis of the molecular kinetic equation of Doi and Edvards. The following basic results are obtained: 1) The ratio of the third and second Leslie viscosity coefficients is $\alpha_3/\alpha_2 < 0$, therefore the Leslie angle is meaningless for the system considered. This affects substantially its rheological properties. 2) The viscous stresses have two essentially different relaxation times (τ_r' and τ_r''), with $\tau_r'/\tau_r'' \sim U_0/T \sim 10^{-7}$, where U_0 is the characteristic energy of the rod in the external field that sets the director orientation. The fact that the dissolved particles are macromolecules manifests itself in large absolute relaxation times ($\tau_r'' \sim 10^3$ sec), which lend themselves therefore to mechanical experiments.

PACS numbers: 46.60.Bd, 51.20. + d

1. INTRODUCTION

It is known that liquid-crystal ordering sets in in a sufficiently concentrated athermic solution of extreme-rigid-chain (rodlike).[1,2] One can include among such systems solutions of helical synthetic and biological polypeptides, as well as aromatic polyamides. The experimental investigation of their rheological properties is the subject of many papers.[3-5]

The purpose of the present paper is a theoretical investigation of such liquid-crystal solution on the basis of the molecular approach of Doi and Edvards. In such a system, unlike in low-molecular liquid crystal, there exists a large parameter, viz., the ratio of the macromolecule length L to its diameter d, $L/d \gg 1$. The presence of this large parameter enabled Doi and Edvards to describe the dynamics of the system within the framework of a consistent microscopic theory,[6-8] which was used in Refs. 6–9 to study in detail the dynamics of equilibrium-isotropic solutions. The needed principles of this theory are expounded in Sec. 2.

The investigation of the molecular dynamics of a liquid-crystal solution is desirable, in particular, because its results can be compared with the phenomenal theory of Leslie, Ericsen, and Parodi (see, e.g., Ref. 10). For example, it is possible to connect the Leslie viscosity parameters with the molecular parameters. The papers of Doi[11] and Marrucci,[12] in which the Leslie angle and the Leslie coefficients were calculated for a liquid-crystal solution, are shown in Sec. 3 to be based on an incorrect assumption. In Sec. 3 is developed another method, free of such an assumption, of calculating the Leslie coefficients, and the results obtained in this section differ qualitatively from the results of Refs. 11 and 12.

The system considered, being a solution of macromolecules, is characterized by longer relaxation time than low-molecular liquids. Therefore the frequency dependence of the Miesowicz viscosities, which is investigated in Sec. 4, can be obtained in mechanical experiments.

2. PRINCIPLES OF THE THEORY OF DOI AND EDVARDS

Rotational Brownian motion of rods (length L, diameter d, $L \gg d$) is described, in accord with Refs. 8, 9, 11, and 12, by the following diffusion equation:

$$\frac{\partial f}{\partial t} = \nabla[\hat{D}_r(\nabla f + f \nabla U_{tot}/T)] - \nabla\{[\hat{g}\mathbf{n} - (\mathbf{n}\hat{g}\mathbf{n})\mathbf{n}]f\}, \quad (1)$$

where $f = f(\mathbf{n})$ is the density of the rod distribution in orientation and is specified by the unit vector $\mathbf{n}$, $\nabla = \nabla_\mathbf{n}$ is the gradient in orientation space, T is the temperature, $\hat{D}_r = \hat{D}_r(\mathbf{n}, [f])$ is the rotational-diffusion coefficient, $U_{tot} = U_{self} + U_{ext}$ is the sum of the potentials of the mean-molecular and external fields acting on the given rod, and $\hat{g}$ is the tensor of the velocity gradients of the macroscopic flow.

The analysis of Eq. (1) with an anisotropic diffusion coefficient is quite difficult. Therefore, following Refs. 8, 9, 11, and 12, we replace $\hat{D}_r$ by an effective constant (independent of $\mathbf{n}$) diffusion coefficient D_r of the order of[8]

$$D_r \approx \beta \frac{T \ln L/d}{\eta_s L^3 (cL^3)^2} \left[\frac{4}{\pi}\int f(\mathbf{n})f(\mathbf{n}')\sin\gamma_{\mathbf{nn}'} \, do \, do'\right]^{-2}, \quad (2)$$

where η_s is the solvent viscosity, c is the rod concentration, $\gamma_{\mathbf{nn}'}$ is the angle between $\mathbf{n}$ and $\mathbf{n}'$, and β is a numerical factor.

As shown by Onsager,[1] the mean molecular field takes at $L \gg d$ the form

$$U_{self}(\mathbf{n}, [f]) = 2cTL^2 d \int \sin\gamma_{\mathbf{nn}'} f(\mathbf{n}') do' \quad (3)$$

so that at $c \gtrsim 1/L^2 d$ the rods tend to be oriented in the same direction (nematic order is produced in the system), where the equilibrium distribution density is given by

$$f(\mathbf{n}) = \text{const} \exp(-U_{self}/T). \quad (4)$$

Besides the kinetic equation, it is necessary to know the form of the stress tensor. It is shown in Ref. 11 that the traceless part of this tensor is equal to

$$\sigma_{\alpha\beta} = 3cT\langle n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}\rangle + c\left\langle\frac{\partial U_{tot}}{\partial n_\alpha}n_\beta\right\rangle, \quad (5)$$

and the averaging is carried out here with the aid of the distribution function in orientation, which is obtained from Eq. (1).

The Leslie coefficients of the liquid-crystal phase are calculated in the next section on the basis of Eqs. (1)–(5).

3. LESLIE VISCOSITY COEFFICIENTS

Let the solution be located in an external field

$$U_{\text{ext}}(\mathbf{n}) = -qT(\mathbf{nu})^2,$$

where q is a dimensionless parameter of the field and the unit vector $\mathbf{u}$ specifies its direction. If the magnetic field $\mathbf{H}$ is external, then

$$q = \frac{1}{2}\chi_a H^2/T, \tag{6}$$

where χ_a is the anisotropy of the molecular susceptibility. If the flow-velocity gradients are small enough ($g \ll q$), the director is parallel to the field direction $\mathbf{u}$. The stress tensor takes then the form (see Ref. 10)

$$\sigma_{\alpha\beta} = \alpha_1 u_\alpha u_\beta A_{\gamma\gamma'} u_\gamma u_{\gamma'} - \alpha_2 \Omega_{\alpha\gamma} u_\gamma u_\beta - \alpha_3 u_\alpha \Omega_{\beta\gamma} u_\gamma$$

$$+ \alpha_4 A_{\alpha\beta} + \alpha_5 A_{\alpha\gamma} u_\gamma u_\beta + \alpha_6 u_\alpha A_{\beta\gamma} u_\gamma,$$

where

$$A_{\alpha\beta} = (g_{\alpha\beta} + g_{\beta\alpha})/2, \quad \Omega_{\alpha\beta} = (g_{\alpha\beta} - g_{\beta\alpha})/2,$$

and α_L are the Leslie coefficients.

To determine the Leslie coefficient it suffices thus to find $\sigma_{\alpha\beta}$ in first order in $g_{\alpha\beta}$. We divide $\sigma_{\alpha\beta}$ into symmetric and antisymmetric parts:

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^s + \sigma_{\alpha\beta}^a.$$

We multiply (1) by $\eta_{\alpha\beta}(\mathbf{n}) = (3n_\alpha n_\beta - \delta_{\alpha\beta})/2$ and integrate with respect to do. Comparing the resultant expression with (5) we find

$$\sigma_{\alpha\beta}^s = \frac{cT}{2D_r}\left(\langle g_{\alpha\gamma} n_\gamma n_\beta + n_\alpha g_{\beta\gamma} n_\gamma - 2n_\alpha n_\beta g_{\gamma\gamma'} n_\gamma n_{\gamma'}\rangle - \frac{2}{3}\frac{\partial S_{\alpha\beta}}{\partial t}\right), \tag{7}$$

where $S_{\alpha\beta} = \langle \eta_{\alpha\beta}(\mathbf{n})\rangle$;

$$\sigma_{\alpha\beta}^a = \frac{1}{2}c\left\langle \frac{\partial U_{\text{ext}}}{\partial n_\alpha}n_\beta - \frac{\partial U_{\text{ext}}}{\partial n_\beta}n_\alpha\right\rangle. \tag{8}$$

Let $f(\mathbf{n}) = f_0(\mathbf{n}) + \psi(\mathbf{n})$, where $f_0(\mathbf{n}) = \text{const}\, e^{-u_0}$ is the equilibrium distribution function, $\psi(\mathbf{n})$ the first-order correction, and $u_0 = U_{\text{tot}}(\mathbf{n}, [f_0])$. It is convenient to introduce a spherical coordinate system with the vector $\mathbf{u}$ as the polar axis. The function $f_0(\mathbf{n})$ is axisymmetric, so that in the zeroth approximation we have

$$\langle n_\alpha n_\beta\rangle = \int f_0(\mathbf{n}) n_\alpha n_\beta\, do = \frac{1}{3}\delta_{\alpha\beta}(1-s) + s u_\alpha u_\beta, \tag{9}$$

$$\langle n_\alpha n_\beta n_\gamma n_{\gamma'}\rangle = k_1 u_\alpha u_\beta u_\gamma u_{\gamma'}$$

$$+ k_2 \overbrace{(u_\alpha u_\beta \delta_{\gamma\gamma'} + \ldots)}^{\text{6 terms}} + k_3 \overbrace{(\delta_{\alpha\beta}\delta_{\gamma\gamma'} + \ldots)}^{\text{3 terms}}, \tag{10}$$

where

$$k_1 = r, \quad k_2 = (s-r)/7, \quad k_3 = (1 - \tfrac{10}{7}s + \tfrac{3}{7}r)/15;$$

and s is the equilibrium order parameter:

$$s = \langle P_2(\cos\theta)\rangle, \quad r = \langle P_4(\cos\theta)\rangle. \tag{11}$$

Taking the stationary character of the problem into account, this yields

$$\sigma_{\alpha\beta}^s = \left[\frac{2}{3}(1-s) - 4k_3\right]A_{\alpha\beta} + s(A_{\alpha\gamma} + \Omega_{\alpha\gamma})u_\gamma u_\beta + s u_\alpha (A_{\beta\gamma} + \Omega_{\beta\gamma})u_\gamma$$

$$- 4k_2(u_\alpha A_{\beta\gamma} u_\gamma + A_{\alpha\gamma} u_\gamma u_\beta) - 2(k_1 u_\alpha u_\beta + k_2 \delta_{\alpha\beta})A_{\gamma\gamma'} u_\gamma u_{\gamma'}. \tag{12}$$

We proceed now to the antisymmetric part of the stress tensor. We transform (8) into

$$\sigma_{\alpha\beta}^a = \tfrac{1}{3}qcT\int \psi(\mathbf{n})[\eta_{\alpha\gamma}(\mathbf{n})u_\gamma u_\beta - \eta_{\beta\gamma}(\mathbf{n})u_\gamma u_\alpha]do_\mathbf{n}. \tag{13}$$

Linearizing (1), we arrive at the equation

$$D_r \hat{P}\psi = G, \tag{14}$$

where

$$\hat{P}\psi = \nabla^2\psi + \nabla(\psi\nabla u_0) + \nabla\left[f_0 \frac{1}{T}\nabla\int\frac{\delta U_{\text{self}}(\mathbf{n})}{\delta f(\mathbf{n}')}\psi(\mathbf{n}')do_{\mathbf{n}'}\right], \tag{15}$$

$$G = \nabla\{[\hat{g}\mathbf{n} - (\mathbf{n}\hat{g}\mathbf{n})\mathbf{n}]f_0\}. \tag{16}$$

It is convenient to resolve the source G into terms proportional to $e^{\pm im\chi}$ with $m = 0,1$ (χ is the azimuthal angle):

$$G(\mathbf{n}) = \frac{1}{2}\nabla(f_0\nabla Y_0)g_{\alpha\beta}u_\alpha u_\beta + \frac{1}{2}\nabla[f_0\nabla(Y_1 e_\alpha u_\beta)]$$

$$\times(g_{\alpha\beta} + g_{\beta\alpha}) + \frac{1}{2}\frac{\partial f_0}{\partial\theta}e_\alpha u_\beta(g_{\alpha\beta} - g_{\beta\alpha})$$

$$+ \frac{1}{2}\nabla\left\{f_0\nabla\left[Y_2\left(e_\alpha e_\beta + \frac{1}{2}u_\alpha u_\beta\right)\right]\right\}g_{\alpha\beta}, \tag{17}$$

where

$$Y_0 = P_2(\cos\theta), \quad Y_1 = \sin\theta\cos\theta, \quad Y_2 = \sin^2\theta, \quad \mathbf{n} = \mathbf{u}\cos\theta + \mathbf{e}\sin\theta.$$

The solution of (14) can obviously represented in similar form

$$\psi(\mathbf{n}) = \psi_0(\theta)g_{\alpha\beta}u_\alpha u_\beta + \psi_1(\theta)e_\alpha u_\beta g_{\alpha\beta} + \psi_1^+(\theta)e_\beta u_\alpha g_{\alpha\beta}$$

$$+ \psi_2(\theta)(e_\alpha e_\beta + \tfrac{1}{2}u_\alpha u_\beta)g_{\alpha\beta}. \tag{18}$$

Introducing the notation

$$c_m = qD_r\int\psi_m(\theta)Y_m(\theta)do, \quad m = 0,1,1^+,2, \tag{19}$$

we reduce (13) to the form

$$\sigma_{\alpha\beta}^a = \frac{cT}{2D_r}\{(c_1 - c_1^+)(\Omega_{\alpha\gamma}u_\gamma u_\beta - \Omega_{\beta\gamma}u_\alpha u_\gamma)$$

$$+ (c_1 + c_1^+)(A_{\alpha\gamma}u_\gamma u_\beta - A_{\beta\gamma}u_\alpha u_\gamma)\}. \tag{20}$$

It remains to find c_1 and c_1^+. Assume for the time being that there is no external field. It is then easy to show that the operator $\hat{P}$ has a doubly degenerate zero eigenvalue corresponding to the eigenfunctions

$$\psi_0(\mathbf{n}) = \frac{\partial f_0}{\partial\theta}e^{\pm i\chi}.$$

The conjugate function $\varphi_0(n)$ satisfies the equation

$$\hat{P}^+\varphi_0 = 0, \tag{21}$$

which can be transformed into

$$\nabla^2\varphi_0 - \nabla\varphi_0\nabla u_0 = \frac{\partial u_0}{\partial\theta}e^{\pm i\chi}, \tag{22}$$

with, obviously, $\varphi_0(\mathbf{n}) = \varphi(\theta)e^{\pm i\chi}$. We now turn on the external field again, after which we regard (22) as the definition of φ_0. Multiplying (14) from the left by $\varphi_0(\mathbf{n})$ and integrating with respect to all the coordinates, we obtain

$$\int \frac{\partial U_{\text{ext}}}{\partial \theta} e^{\pm i\chi}\psi(\mathbf{n}) do = \int G(\mathbf{n})\varphi(\theta)e^{\pm i\chi} do. \qquad (23)$$

Substituting (17) and (18) in (23) we obtain c_1 and c_1^+:

$$c_1 = s\frac{N-\Gamma}{N-2\Gamma}, \qquad c_1^+ = \frac{-\Gamma}{N-2\Gamma}s, \qquad (24)$$

where

$$N = -\frac{1}{2}\int \varphi(\theta)\frac{\partial f_0}{\partial \theta} do,$$

$$\Gamma = -\frac{1}{2}\int \varphi(\theta)\left(3f_0\sin\theta\cos\theta + \frac{\partial f_0}{\partial \theta}\sin^2\theta\right)do.$$

Transforming (24) with the aid of (22), we obtain ultimately

$$c_1 = s+\Gamma, \qquad c_1^+ = -\Gamma, \qquad \Gamma = \frac{1}{2}\left\langle\frac{\partial \varphi_0}{\partial \theta}\sin^2\theta\right\rangle. \qquad (25)$$

Equations (12) and (30) determine the Leslie coefficients (we leave out the common factor $cT/2D_r$):

$$\alpha_1 = -2r, \qquad \alpha_4 = \frac{2}{35}(7-5s-2r),$$

$$\alpha_2 = -2(s+\Gamma), \qquad \alpha_5 = \frac{2}{7}(5s+2r), \qquad (26)$$

$$\alpha_3 = 2\Gamma, \qquad \alpha_6 = -\frac{4}{7}(s-r).$$

It follows from (12), (22), and (25) that in the isotropic phase we have $s = r = \Gamma = 0$, therefore the coefficients $\alpha_1, \alpha_2, \alpha_3, \alpha_5, \alpha_6$ vanish there, as they should. In addition, as can be seen from (26), the Parodi relation $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$ is identically satisfied, as should likewise be expected. If the order parameter s is close to unity, i.e., $s = 1 - \varepsilon, \varepsilon \ll 1$ (this condition is in fact satisfied in a liquid-crystal solution of rigid rods, since $s \gtrsim 0.8$, Ref. 1), Eqs. (26) can be simplified. In this case $\nabla u_0 \gg 1$, therefore the first term in the left-hand side of (22) can be neglected, after which the equation can be easily solved:

$$\varphi(\theta) = \theta, \quad \theta < \pi/2, \quad \varphi(\theta) = \theta - \pi, \quad \theta > \pi/2.$$

We have thus $\Gamma \approx 1/2\langle\sin^2\theta\rangle = \varepsilon/3$. In addition, $r = 1 - 10/3\varepsilon$, and in first order in ε we have therefore

$$\alpha_1 = -2\left(1 - \frac{10}{3}\varepsilon\right), \qquad \alpha_4 = \frac{2}{3}\varepsilon,$$

$$\alpha_2 = -2\left(1 - \frac{2}{3}\varepsilon\right), \qquad \alpha_5 = 2\left(1 - \frac{5}{3}\varepsilon\right), \qquad (27)$$

$$\alpha_3 = \frac{2}{3}\varepsilon, \qquad \alpha_6 = -\frac{4}{3}\varepsilon.$$

It can be seen that $\alpha_3/\alpha_2 \approx -1/3\varepsilon < 0$. This differs qualitatively from the results of Refs. 11 and 12, where it was found that $\alpha_3/\alpha_2 > 0$. In addition, it is shown here that $\alpha_6 \approx -4/$
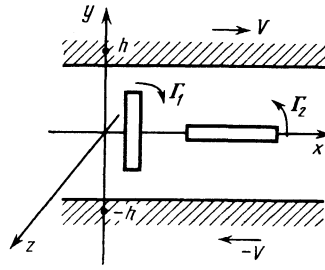

FIG. 1. The upper plate moves along the x axis with velocity V, and the lower with oppositely directed velocity. The distance between the plates is $2h$.

3ε is less than zero, just as in low-molecular liquid crystals, contradicting the results of Ref. 12, where $\alpha_6 = 0$.

As a result of the negative $\vartheta = \alpha_3/\alpha_2$ the Leslie angle θ_0, defined by the relation $\tan^2\theta_0 = \vartheta$, becomes meaningless. In addition, all the indicated features influence substantially the rheological properties of the system. Consider, e.g., flow in the form of a simple shift between two parallel plates (Fig. 1); let the director be oriented at the surfaces of the plates along the flow direction (the x axis). It is known[13] that at $\vartheta > 0$ such a flow is always stable, and at $\vartheta < 0$ the flow becomes unstable already at very low shift velocities, when the Ericsen number (defined in the Appendix) is $Er = Er_{c1} \approx 1.2|\vartheta|^{-1/2}$, and the resultant structure is stationary and homogeneous in the plane of the plates, i.e., along the axes x and z). The situation wherein the plates orient the director perpendicular to the flow plane is investigated in the Appendix. It is shown there that in this case the stabilities are also interchanged at $Er = Er_{c2}$ and modulation sets in along the z axis of the structure, with $Er_{c2}/Er_{c1} \approx 500$ near the liquid-crystal transition point.

The causes of the indicated difference between the results obtained here and in Refs. 11 and 12 are connected with the additional "separation approximation" of the form $\langle n_\alpha n_\beta n_\gamma n_{\gamma'}\rangle \approx \langle n_\alpha n_\beta\rangle\langle n_\gamma n_{\gamma'}\rangle$, used in Refs. 11 and 12. It can be seen from (10) that this approximation can lead to an error on the order of 100%.

The reason why $\vartheta < 0$ in a sufficiently strongly ordered state can be explained in the following manner. Let the Couette-flow velocity be $V_x = gy$. From the definition of the Leslie coefficient it follows that $\vartheta = \Gamma_2/\Gamma_1$, where Γ_1 is the torque that tends to rotate the director from the position along the velocity gradient into the position along the stream, and Γ_2 vice versa (Fig. 1). Clearly, $\Gamma_1 > 0$. We shall show that $\Gamma_2 < 0$. Let the director be oriented initially along the stream. If the ordering is high enough, the distribution function $f(n)$ is localized on small sections of the unit sphere near the x axis; these sections can be regarded as locally plane. On the section with coordinate $x = 1$ the flux $\dot{\mathbf{n}} = \hat{g}\mathbf{n} - (\mathbf{n}\hat{g}\mathbf{n})\mathbf{n}$ is specified by the equations $\dot{y} = -gy^2, \dot{z} = -gyz$. Since y is negative everywhere, the distribution function as a whole (meaning also the director) will move in the negative y direction, i.e., $\Gamma_2 < 0$.

A particularly complete theoretical analysis is possible if the equilibrium distribution function is approximated by an equation in the form
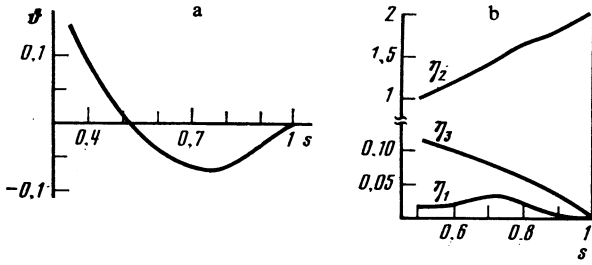
FIG. 2. Dependence of the ratio $\alpha_3/\alpha_2\vartheta$ (a) and of the Miesowicz viscosities η_1, η_2, η_3 (the factor $cT/2D_r$ was left out) (b) on the order parameter s.

$$f_0 = \mathrm{const} \exp (A \cos^2 \theta), \quad \text{i.e.,} \quad u_0 = -A \cos^2 \theta + \mathrm{const}, \qquad (28)$$

where A is a parameter. This approximation corresponds to the Maier-Saupe approximation for U_{self}:

$$U_{\mathrm{self}} = -\mathrm{const}\, \eta_{\alpha\beta}(\mathbf{n}) S_{\alpha\beta}. \qquad (29)$$

Equation (22) can be easily solved in this approximation. The dependence of $\vartheta = -\Gamma/(s+\Gamma)$ on the order parameter s, obtained by solving (22) using (25), is shown in Fig. 2a. At small $s < s_{\mathrm{inv}} = 0.53$ we have $\vartheta > 0$; at $s = s_{\mathrm{inv}}$ ϑ reverses sign and reaches a negative absolute value $\vartheta = -0.066$ at $s = 0.74$. As applied to low-molecular liquid crystals, the obtained value of s_{inv} can be treated, of course, only as a rough estimate and the result means that at sufficiently small $s \sim 0.3$–0.4, when the Maier-Saupe theory holds for these systems, ϑ is positive. As for the rigid-rod solution considered in the present paper, the approximation (28) works here very well. For example, the equilibrium liquid-crystal-transition characteristics calculated with the aid of a trial function of the form (28) differ from the exact ones by less than 1%.

We write

$$r = \langle P_4(\cos \theta) \rangle = \int f_0(\mathbf{n}) P_4(\cos \theta)\, do;$$

averaging with a distribution function of the type (28), we get

$$r = \frac{1}{24}\left[14 + 10 s(A) - 105 \frac{s(A)}{A} \right]$$

(the dependence of s on A is shown in Fig. 3). All the Leslie coefficients can thus be expressed now in terms of s.

The dependence of the Miesowicz viscosities

$$\eta_1 = (\alpha_3 + \alpha_4 + \alpha_6)/2, \quad \eta_2 = (\alpha_4 + \alpha_5 - \alpha_2)/2, \quad \eta_3 = \alpha_4/2 \qquad (30)$$

on s is shown in Fig. 2b. It can be seen that the usual relation $\eta_2 > \eta_3 > \eta_1$ is satisfied.
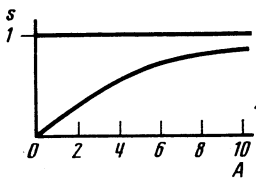

FIG. 3. Order parameter s vs the parameter A.

4. FREQUENCY DEPENDENCE OF THE MIESOWICZ VISCOSITIES

The method developed in the preceding section can be used to investigate the frequency dependence of the Miesowicz viscosities.

In the symmetric part of the stress tensor (7), the first term is independent of the frequency, so that it can be uniquely determined from the frequency dependent terms, since $\sigma_{\alpha\beta} \to 0$ as $\omega \to \infty$. The second term in (7) is proportional to $\partial S_{\alpha\beta}/\partial t = -i\omega S_{\alpha\beta}$ (the time dependence is given by the factor $e^{-i\omega t}$). In the notation of (18) and (19), $S_{\alpha\beta}$ can be written in the form

$$S_{\alpha\beta} = \frac{1}{qD_r}\left\{ \frac{3}{2}\left(c_0 + \frac{1}{8}c_2 - c_1 - c_1^+\right) u_\alpha u_\beta A_{\gamma\gamma'} u_\gamma u_{\gamma'} \right.$$

$$+ \frac{3}{4}(c_1 - c_1^+)(\Omega_{\alpha\gamma} u_\gamma u_\beta + \Omega_{\beta\gamma} u_\alpha u_\gamma) + \frac{3}{8}c_2 A_{\alpha\beta}$$

$$\left. + \frac{3}{4}\left(c_1 + c_1^+ - \frac{1}{2}c_2\right)(A_{\alpha\gamma} u_\gamma u_\beta + A_{\beta\gamma} u_\alpha u_\gamma) \right\}. \qquad (31)$$

Combining (7), (20), and (31), we obtain the Miesowicz viscosities accurate to the frequency-independent terms (the common factor $cT/2D_r$ was omitted):

$$\eta_1 = c_1^+ \left(\frac{i\omega}{2qD_r} - 1\right), \quad \eta_2 = \eta_1 + \frac{i\omega}{qD_r}(c_1 - c_1^+), \quad \eta_3 = \frac{i\omega}{8qD_r}c_2. \qquad (32)$$

To determine the quantities c_i it is necessary to modify the linearized equation (14) to allow for the time dependence:

$$(D_r \hat{P} + i\omega)\psi = G. \qquad (33)$$

We use now the approximation (28), (29). Even at the liquid-crystal transition point we have in a rod solution $A \approx 8$ (Ref. 1), so that we can seek the solution of (33) in the form of an expansion in $1/A$. To find the viscosity in principal order in $1/A$, it suffices to calculate c_1 in the zeroth, c_2 in the first, and c_1^+ in second orders in $1/A$. The ordinary differential equations that follow for $\psi_m(0)$ from (33) can be easily solved with the aid of the substitution $\psi_m(\theta) = \bar{\psi}_m(\theta) f_0(\theta)$. Substituting these solutions in (19) we obtain

$$c_1 = \frac{Q}{Q - i\Omega}, \quad c_2 = \frac{2Q}{A}\frac{1}{2 - i\Omega}$$

$$c_1^+ = -\frac{Q}{2A}\frac{1}{Q - i\Omega}\left[1 + \frac{1}{A}\frac{1 + 2i\Omega + 7\Omega^2}{(3 - i\Omega)(1 - i\Omega)} \right] \qquad (34)$$

$$\times \left[1 + \frac{1}{A}\frac{1 - Q}{Q - i\Omega}\frac{i\Omega}{1 - i\Omega} \right]$$

where $Q = q/A$, $\Omega = \omega/(2AD_r)$. Finally, substituting (34) in (32) and adding the frequency-independent term, we obtain the Miesowicz viscosities

$$\eta_1 = \frac{1}{2A^2}\left[\frac{Q}{Q - i\Omega} - \frac{2}{1 - i\Omega} + \frac{14}{3 - i\Omega} \right]$$

$$\eta_2 = \frac{2Q}{Q - i\Omega}, \quad \eta_3 = \frac{1}{A}\frac{1}{2 - i\Omega}. \qquad (35)$$
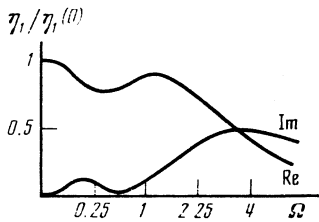
FIG. 4. Dependence of the relative viscosity $\eta_1(\Omega)/\eta_1(0)$ on the frequency.

The dependences of η_2 and η_3 on ω take thus the form of ordinary dispersion functions, and the characteristic frequency (reciprocal relaxation time) for η_3 is equal to $\omega' \equiv 1/\tau_r' = 4AD_r$, and for η_2

$$\omega'' \equiv 1/\tau_r'' = Q\omega'/2 \ll \omega',$$

since usually $Q \ll 1$ (see below). In order of magnitude we have $\tau_r'/\tau_r'' = Q/2 \sim U_0/T$, where $U_0 \sim qT \langle \sin^2 \theta \rangle$ is the characteristic energy of the rod in an external field. Connected with the frequency dependence of η_1 is a relaxation spectrum consisting of three frequencies: $\omega'/2$, $3\omega'/2$, and the much lower frequency ω''. Plots of the real and imaginary parts of η_1 vs the frequency at $Q = 0.1$ (this value of Q was chosen purely by way of illustration) are shown in Fig. 4.

This behavior of the viscosities can be qualitatively understood in the following manner. It can be seen from (5) that the stresses, meaning also the viscosity, are governed by deviations of the distribution function from equilibrium. These deviations can be subdivided into a shift of $f(\mathbf{n})$ as a whole (small rotation of the director) and a deformation of this function without a shift. In the former case the stresses are due solely to the external field, and in the latter exclusively to internal forces. In a geometry corresponding to the third Miesowicz viscosity (director perpendicular to the flow plane) the symmetry is such that only deformation of $f(\mathbf{n})$ takes place. Therefore the characteristic frequency is, in accord with (1), of the order of $\omega' \sim D_r \nabla^2 \sim D_r A$. When the director is along the flow-velocity gradient (second viscosity), we deal mainly with a shift of $f(\mathbf{n})$, so that only the "field" term of (1) need be taken into account:

$$\omega'' \sim D_r \nabla^2 U_{ext}/T \sim qD_r.$$

Finally, when the director is oriented by the field along the flow (first viscosity), both shift and deformation of $f(\mathbf{n})$ appear to equal degree, so that a role in the $\eta_1(\omega)$ dependence is played by two frequency scales, one of the order of ω' and the other of the order of $\omega'' \ll \omega'$.

To conclude this section, we estimate the values of ω' and ω'' near the liquid-crystal transition in a solution of rods of length $L = 100$ Å and diameter $d = 5$ Å in sulfuric acid at room temperature. We determine the value of the diffusion coefficient from Eq. (2), recognizing that at the transition point $c_a L^3 = 5.5L/d$, and $A = 8$ (Ref. 1). The coefficient β in (2) can be regarded very approximately as equal to unity. Assume an external magnetic field $H = 10^4$ Oe and a molecular-susceptibility anisotropy $\chi_a = 10^{-7}Ld^2$ (10^{-7} is the characteristic anisotropy of the susceptibility per unit vol-

ume for aromatic polyamids), then $Q = q/A \sim 10^{-7}$ [see Eq. (6)], and

$$\omega' = 1/\tau_r' \sim 10^4 \ \sec^{-1}, \quad \omega'' = 1/\tau_r'' \sim 10^{-3} \ \sec^{-1}.$$

It can be seen from these estimates that the characteristic frequencies are relatively small and can be achieved in mechanical experiments.

We have thus investigated here the dynamics of a liquid-crystal solution of maximum-chain-rigidity macromolecules. The uniqueness of the object considered is that it combines the properties of a liquid crystal and a polymer. No less interesting a situation arises in a solution of semiflexible macromolecules, which are so long that they cannot preserve a rodlike confirmation and turn into coils. The polymer property should become in this case even more strongly manifest.

The author thanks A. R. Khokhlov, S. A. Pikin, and E. I. Kats for helpful discussions.

APPENDIX

We consider here the simplest flow between two parallel plates (Couette flow, Fig. 1) and obtain the region of its stability in the case when the director is oriented near the plate surface perpendicular to the flow plane (along the z axis).

Besides the Reynolds number $Re = \rho Vh/|\alpha_2|$ (ρ is the average density of the solution), a convenient characteristic of the flow is the Ericsen number

$$Er = |\alpha_2| Vh/K_1 = \lambda Re,$$

where K_1 is the first elastic constant of the liquid crystal. The parameter $\lambda = |\alpha_2|^2/\rho K_1$ is very large. Thus, for a solution of rods 100 Å long and 5 Å in diameter in sulfuric acid we have $\lambda \sim 10^{13}$ (the elastic constants can be estimated from the free energy of the liquid-crystal solution[1]:

$$K_1 \sim T(cL^2 d)^2/dA'^h, \quad K_3/K_1 \sim 2A, \quad \text{(A1)}$$

and the parameter $A \gg 1$ characterize the degree of ordering). Thus, the region $Er \sim 1$ corresponds to $Re \ll 1$.

At sufficiently small Ericsen numbers the system is described by a linear profile of the flow velocity

$$V_x^{(0)}(r) = Vy/d, \quad V_y^{(0)} = V_z^{(0)} = 0$$

and by a homogeneous distribution of the director

$$u(r) = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

Let

$$V(r) = V^{(0)}(r) + v(r), \quad u(r) = \begin{pmatrix} u \\ w \\ 1 \end{pmatrix},$$

where v, u, and w are perturbations. It can be shown that the dependence of the perturbations on x leads to their additional damping (cf. Ref. 13); we assume therefore that $\partial/\partial x = 0$. The linearized Navier-Stokes equations and the equations that describe the director motion take then the form 14

$$0 = \frac{1}{2}\alpha_4 v_{x,yy} + \gamma_5 v_{x,zz} + \alpha_2 \frac{\partial u_{,z}}{\partial t} + \frac{1}{2}(\alpha_5 - \alpha_2)gw_{,z},$$

$$0 = -p_{,y} + \gamma_6 v_{y,yy} + \gamma_5 v_{y,zz} + \alpha_2 \frac{\partial w_{,z}}{\partial t} + \frac{1}{2}(\alpha_5 + \alpha_2)gu_{,z},$$

$$\text{(A2)}$$

$$0 = -p_{,z} + \gamma_4 v_{z,yy} + \gamma_3 v_{z,zz} + \alpha_3 \frac{\partial w_{,y}}{\partial t} + \frac{1}{2}(\alpha_6 + \alpha_3)gu_{,y},$$

$$v_{y,y} + v_{z,z} = 0, \tag{A3}$$

$$K_2 u_{,yy} + K_3 u_{,zz} = \gamma_1 \frac{\partial u}{\partial t} + \alpha_2 gw + \alpha_2 v_{x,z},$$

$$K_1 w_{,yy} + K_3 w_{,zz} = \gamma_1 \frac{\partial w}{\partial t} + \alpha_3 gu + \alpha_2 v_{y,z} + \alpha_3 v_{z,y},$$

where p is the pressure,

$$g = V/d, \quad \gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_4 = (\alpha_3 + \alpha_4 + \alpha_6)/2,$$

$$\gamma_3 = \gamma_4 + \alpha_1 + \alpha_3, \quad \gamma_5 = (\alpha_4 + \alpha_5 - \alpha_2)/2, \quad \gamma_6 = (\alpha_4 - \alpha_5 - \alpha_2)/2.$$

No account is taken in the Navier-Stokes equations (A2) of the inertial terms, since they are of the order of $\lambda^{-1} \ll 1$ in the region $\mathrm{Er} \sim 1$. The boundary conditions call for vanishing of all the perturbations on the plate surface:

$$u = w = v = 0 \quad \text{at} \quad y = \pm h. \tag{A4}$$

The solution of the system (A2)–(A4) can be represented as a product of a function of y by $\exp(iq_z z - i\omega t)$; this solution depends parametrically on the wave number q_z and on the number l of the zeros in the interval $-h \leqslant y < h$. If $l \gg 1$, the boundary conditions (A4) can be neglected and it can be formally assumed that $q_y = \pi l / 2h$. The system (A2), (A3) reduces then to an algebraic one that can be transformed into

$$-q_y^2(K_2 + K_3\zeta)u = -i\omega\lambda_1 u + \alpha_2\varkappa_1 gw,$$
$$-q_y^2(K_1 + K_3\zeta)w = -i\omega\lambda_2 w + \alpha_2\varkappa_2 gu, \tag{A5}$$

where

$$\zeta = \frac{q_z^2}{q_y^2}, \quad \lambda_1 = \gamma_1 - \frac{2\alpha_2^2\zeta}{\alpha_4 + 2\gamma_5\zeta}, \quad \lambda_2 = \gamma_1 - \frac{(\alpha_3 - \zeta\alpha_2)^2}{\gamma_4 + (\gamma_3 + \gamma_6)\zeta + \gamma_5\zeta^2}$$

$$\varkappa_1 = 1 - \frac{(\alpha_5 - \alpha_2)\zeta}{\alpha_4 + 2\gamma_5\zeta}, \quad \varkappa_2 = \vartheta - \frac{1}{2}(\vartheta - \zeta)\frac{(\alpha_6 + \alpha_3) - \zeta(\alpha_5 + \alpha_2)}{\gamma_4 + (\gamma_3 + \gamma_6)\zeta + \gamma_5\zeta^2}.$$

It is easy to show that $\lambda_1 > 0$, $\lambda_2 > 0$, $\varkappa_1 > 0$, whence it follows that at the stability-loss point we have not only $\mathrm{Im}\,\omega = 0$ but also $\mathrm{Re}\,\omega = 0$. Therefore the critical velocity gradient g_c is given by

$$g_c^2 = \left(\frac{\pi l}{2h}\right)^4 \frac{(K_2 + K_3\zeta)(K_1 + K_3\zeta)}{|\alpha_2|^2\varkappa_1\varkappa_2}, \tag{A6}$$

which must be minimized with respect to the parameters ζ and l. Clearly, the minimum of (A6) corresponds to the smallest possible $l = 1$, when (A6), derived for $l \gg 1$, becomes approximate. An analysis of the particular cases (see also Ref. 14) shows, however, that even for $l = 1$ the error in (A6) does not exceed 10–20%.

Depending on the relation between the Leslie coefficients, minimization of (A6) with respect to ζ leads to the

following results. If $\vartheta > \vartheta_c > 0$ ($\vartheta_c \sim 10^{-3}$ for MBBA), the minimum corresponds to $\zeta = 0$, therefore

$$\mathrm{Er}_c \approx \left(\frac{\pi}{2}\right)^2 \left(\frac{2\gamma_4}{\alpha_4\vartheta}\right)^{1/2} \left(\frac{K_2}{K_1}\right)^{1/4}, \quad q_z^{(c)} = 0, \quad \omega_c = 0, \tag{A7}$$

i.e., at $\mathrm{Er} = \mathrm{Er}_c$ we are dealing here with a change in stability and with formation of an unmodulated structure. This regime was considered in Ref. 14 for MBBA at 25 °C. If $(\alpha_6 - \alpha_3)/2\gamma_5 < \vartheta < \vartheta_c$, the most dangerous is $\zeta \neq 0$:

$$\mathrm{Er}_c \sim 1, \quad q_z^{(c)} \sim \pi/2h, \quad \omega_c = 0$$

(we left out the dependence on the ratios of the Leslie coefficients and on the elastic constants. In this case the stability loss at $\mathrm{Er} = \mathrm{Er}_c$ leads thus to a structure modulated along the z axis. This is precisely the regime realized for the considered liquid-crystal solution of rods, and the critical parameters are:

$$\mathrm{Er}_{c2} \approx 2\pi^2 \frac{K_3}{K_1}A \approx 4\pi^2 A^2, \quad q_z^{(c)} \approx \frac{2^{-1/4}\pi}{h} = \frac{1.9}{h}, \quad \omega_c = 0. \tag{A8}$$

Let us compare the instability threshold, when the plate orients the director along the stream (the x axis) $\mathrm{Er}_{c1} = 1.2|\vartheta|^{-1/2}$ (Ref. 15) with the threshold Er_{c2}, near the liquid-crystal transition: $\mathrm{Er}_{c2}/\mathrm{Er}_{c1} \approx 23A^{3/2} \approx 500$, since $A \approx 8$. Thus, if the director is perpendicular to the flow plane the instability threshold is 500 times higher than for orientation along the stream.

Finally, there can exist in principle one more regime, when $\vartheta < (\alpha_6 - \alpha_3)/2\gamma_5$. Leaving out the calculations, we present the final result. Stability is lost in this case much later than in all the preceding ones:

$$\mathrm{Re}_c \sim 1 \quad (\mathrm{Er}_c \sim \lambda \gg 1), \quad q_z^{(c)} \sim \pi/2h, \quad \omega_c \sim g_c \sim |\alpha_2|/\rho h^2.$$

In other words, we have here not a change of stability, but a transition to a flow that is periodic in time and modulated along the z axis.

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Translated by J. G. Adashko