Tumbling of Rodlike Polymers in the Liquid-Crystalline Phase under Shear Flow

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ABSTRACT: The two-dimensional model introduced by Marrucci and Maffettone[1] to describe the nematic phase of rodlike polymers in a shear flow has been explored in the limit of small shear rate. A tumbling motion for the director n of the nematic phase has been found. Explicit expressions for the shear and normal stresses have been derived for both the elastic and viscous contributions. Suitable averages over the multidomain structure give rise to a stationary macroscopic response. Consistently with experiments the normal stresses are found to be positive in the linear limit. The present results, together with those of ref 1, indicate that the model is able to describe the experimentally observed behavior of normal stresses, i.e., the positive to negative to positive transitions with increasing shear rate. The transition from a stationary to a tumbling situation with increasing nematic potential is also analyzed and discussed.

1. Introduction

In the last years the interest in liquid-crystalline polymers (LCP) has increased significantly in view of their possible applications as self-reinforced materials. Nonetheless their rheology is still poorly understood.

Experiments have shown that the rheology of LCP's is much more complex than that of ordinary polymers, showing unusual effects such as, e.g., the occurrence of negative normal stresses in steady shear flow.[2–6] A further complication in the experiments on LCP's arises from the multidomain structure, which makes the equilibrium state ill-defined.[7]

The only available theory is that of Doi,[8] which describes many features of the rheology of rodlike polymers in the nematic phase. Although successful in many respects, it has a few controversial points. The theory does not allow for the occurrence of negative normal stresses. It is carried out by introducing a mathematical approximation (the decoupling approximation), by way of which, a stable shear flow is always predicted.[8,9] On the other hand, calculations made without that approximation, which become possible in the linear limit,[10,11] predict tumbling of the director due to shear.

Recently Marrucci and Maffettone[1] have introduced a two-dimensional analogue of the Doi model, which, in spite of the irrealistic assumption of dimensionality, has revealed many interesting features. The model can be solved at high shear rates without the decoupling approximation of Doi. It predicts a change from negative to positive normal stresses with increasing shear rate, starting from a critical value below which a stationary solution can no longer be found. This sign change is in agreement with experiments.[2–6] According to experiments, a second sign change is expected at lower values of the shear rate, where the lack of stationary solutions speaks in favor of a tumbling situation. Of course, the analysis of the tumbling case is complicated by the time-dependent nature of the phenomenon.

In this paper we perform the analysis of the nonstationary case in the linear limit. We obtain explicit expressions for the motion of the director n of the nematic phase, for the orientational distribution function, and for the shear and normal stresses.

2. Orientational Distribution in Two Dimensions

2.1. General Case. We consider the two-dimensional orientational distribution introduced in ref 1. The orientation of a rod in the plane is specified by the angle θ. Under a shearing flow the distribution $f(\theta,t)$ will obey the equation

$$\frac{\partial f}{\partial t} = D\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial \theta} + \frac{f}{K_B T}\frac{\partial V}{\partial \theta}\right) + \frac{\partial}{\partial \theta}(f\Gamma \sin^2 \theta) \tag{1}$$

where D is the rotational diffusivity of the rods, Γ is the shear rate, and V is the self-consistent potential, which induces the nematic state. We assume a potential of the Maier–Saupe type

$$V = -UK_B T(\langle \cos 2\theta\rangle \cos 2\theta + \langle \sin 2\theta\rangle \sin 2\theta) \tag{2}$$

where U is the nondimensional intensity of the potential.

In order to deal with nondimensional quantities, hereafter we measure time in units of D^{-1} and introduce a nondimensional shear rate

$$G = \Gamma/2D \tag{3}$$

The equilibrium (i.e., $\Gamma = 0$, $\partial f/\partial t = 0$) and stationary (i.e., $\partial f/\partial t = 0$, $\Gamma \neq 0$) solutions of eq 1 have been fully described in ref 1. In the equilibrium case eq 1 reduces to

$$\frac{df}{d\theta} + \frac{f}{K_B T}\frac{dV}{d\theta} = 0 \tag{4}$$

The normalized equilibrium solution can be written as

$$f_0(\theta) = \frac{\exp(a \cos 2\theta)}{\int_0^\pi \exp(a \cos 2\theta')\, d\theta'} \tag{5}$$

where we have denoted

$$a = U\langle \cos 2\theta\rangle_0 \tag{6}$$

The subscript 0 stands for the average over the equilibrium distribution function, $f_0(\phi)$:

$$\langle \ldots\rangle_0 = \int_0^\pi f_0(\phi')\ldots d\phi' \tag{7}$$

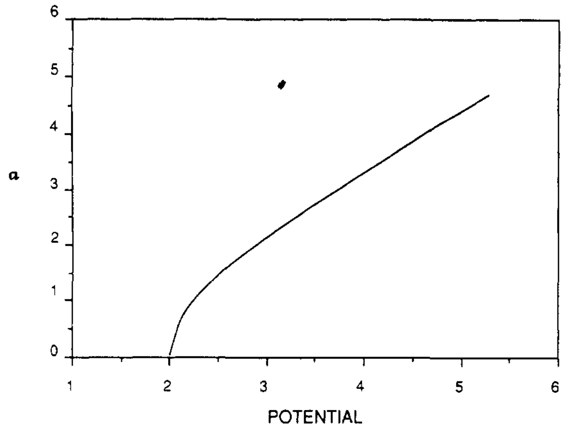

Figure 1. Dependence of the a parameter on the potential, U. Through a, all equilibrium properties of the nematic phase can be calculated.

We have oriented the axes in such a way as to obtain

$$\langle \sin 2\theta \rangle_0 = 0 \tag{8}$$

The value of the parameter a is explicitly computed as a function of the potential U in ref 1, by solving the nonlinear eq 6. The result is reported in Figure 1.

In the equilibrium case the orientation of the director is arbitrary. Therefore we may set the condition (8), by orienting the director along the x axis. In the general case we introduce the angle ϕ defined as

$$\theta = \alpha + \phi \tag{9}$$

where α is defined through the condition

$$\langle \sin 2\phi \rangle = 0 \tag{10}$$

The angular shift α defines the "director" under flow conditions in analogy with the static case. Contrary to ref 1, where only steady-state conditions were considered, here α can be a function of time.

In the variable ϕ and with use of the potential of eq 2, eq 1 becomes

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \phi}\left(\frac{\partial f}{\partial \phi} + 2U\langle \cos 2\phi \rangle (\sin 2\phi) f\right) + \frac{\partial}{\partial \phi}[\dot{\alpha} f + 2G(\sin^2 (\alpha + \phi)) f] \tag{11}$$

In the tumbling case, the function $f(\phi,t)$ describes the "breathing" motion of the distribution of rods around the director α. The evolution of $\alpha(t)$ is implicitly contained in eq 10. To obtain an explicit equation, we take the average of eq 11 weighted with a factor sin 2ϕ. Repeated integration by parts together with eq 10 and the periodicity condition

$$f(0,t) = f(\pi,t) \tag{12}$$

gives

$$\dot{\alpha} = G\left[\cos 2\alpha \frac{\langle \cos^2 2\phi \rangle}{\langle \cos 2\phi \rangle} - (\sin 2\alpha) \frac{\langle \sin 2\phi \cos 2\phi \rangle}{\langle \cos 2\phi \rangle} - 1\right] - 2U\langle \sin 2\phi \cos 2\phi \rangle \tag{13}$$

The solution of eq 13 describes the tumbling of the director $\alpha(t)$.

Equations 11 and 13 are fully equivalent to eq 1. They are coupled, but they outline how the evolution of the orientational distribution function $f(\theta,t)$ can be interpreted in terms of the motion of the director $\alpha(t)$ and a sort of breathing, $f(\phi,t)$, around it.

2.2. Small Shear Rates. In the limit of small shear rates, i.e., $G \to 0$, the distribution function $f(\phi,t)$ will be slightly different from the static solution. Up to first order in G, we write

$$f(\phi,t) = f_0(\phi)[1 - \langle 1 \rangle_1 + h(\phi,t)] \tag{14}$$

where the function h is of the order G, and the term $\langle 1 \rangle_1$ accounts for the normalization of f. The subscript 1 stands for the average over the extra function

$$\langle ... \rangle_1 = \int_0^\pi f_0(\phi')\, h(\phi',t) ... \mathrm{d}\phi' \tag{15}$$

In the limit of small shear rates eq 13 simplifies considerably. Since only terms of order G must be retained, the averages within broken brackets can be computed to zero order. They are

$$\langle \cos 2\phi \rangle_0 = a/U \tag{16a}$$

from the definition of eq 6

$$\langle \cos 2\phi \sin 2\phi \rangle_0 = 0 \tag{16b}$$

in view of the symmetry of $f_0(\phi)$ (eq 5)

$$\langle \cos^2 2\phi \rangle_0 = (U-1)/U \tag{16c}$$

which is obtained by integrating by parts eq 6. Therefore eq 13 becomes

$$\dot{\alpha} = G[(\cos 2\alpha)(U - 1/a) - 1] - U\langle \sin 4\phi \rangle_1 \tag{17}$$

Also eq 11 simplifies considerably for small G. In fact, since $\alpha(t)$ is expected to be invertible (small initial fluctuations, if any, are bound to decay over a time scale of order 1 (i.e., D^{-1}), whereas the characteristic time of the main motion is G^{-1}, i.e., much larger than unity for $G \to 0$), we may regard the distribution to be a function of ϕ and α (still indicated with the symbol f), instead of ϕ and t; i.e.

$$f(\phi,t) = f(\phi,t(\alpha)) = f(\phi,\alpha(t)) \tag{18}$$

from which

$$\partial f/\partial t = (\partial f/\partial \alpha)\dot{\alpha} \tag{19}$$

Thus, since both $\dot{\alpha}$ and $\partial f/\partial \alpha$ are (at most) of order G, $\partial f/\partial t$ is (at most) of order G^2 and can be neglected. Equation 11 then becomes

$$\partial f/\partial \phi + f\{2[a(1 - \langle 1 \rangle_1) + U\langle \cos 2\phi \rangle_1] \sin 2\phi + G[(\cos 2\alpha)(U-1)/a - 1 + 2\sin^2 (\phi + \alpha)] - U\langle \sin 4\phi \rangle_1\} = K_1(\alpha) \tag{20}$$

where eq 17 has been used and K_1 is an (as yet) unknown function of α. It will be determined from the normalization condition.

The expression (20) has the form (the dependencies on α are not indicated explicitly)

$$\partial f/\partial \phi + fP(\phi) - K_1 = 0 \tag{21}$$

which has the general solution

$$f(\phi) = K_1 \exp[-g(\phi)]\{K_2 + \int_0^\phi \exp[g(\phi')]\, \mathrm{d}\phi'\} \tag{22}$$

with

$$g(\phi) = \int_0^\phi P(\phi')\, \mathrm{d}\phi' \tag{23}$$

and K_2 is determined from the periodicity condition, eq 12. By carrying out all the indicated calculations to first order in G, we get the extra function h, defined in eq 14 as

$$h(\phi,\alpha) = (\cos 2\phi)(U\langle\cos 2\phi\rangle_1 - a\langle 1\rangle_1) - G[(\phi - Q(\phi)/M)[(\cos 2\alpha)(U-1)/a - (U/G)\langle\sin 4\phi\rangle_1] - (1/2)\sin(2\phi + 2\alpha)] \quad (24)$$

with

$$Q(\phi) = \int_0^\phi \exp[-a\cos 2\phi']\, d\phi' \quad (25)$$

and

$$M = (1/\pi)Q(\pi) \quad (26)$$

Equation 24 still contains averages weighted with $h(\phi,\alpha)$ itself, namely, $\langle\cos 2\phi\rangle_1$, $\langle 1\rangle_1$, and $\langle\sin 4\phi\rangle_1$. However, by writing these averages in an explicit form through their definition, eq 15, we obtain a linear system of three equations in terms of these three quantities. The coefficients of the linear system are combinations of averages based on the equilibrium distribution and can be computed explicitly. After straightforward calculations, we obtain

$$\langle\sin 4\phi\rangle_1 = \frac{G}{U}(\cos 2\alpha)\left(\frac{U-1}{a} - \frac{a}{U}\frac{M^2}{M^2-1}\right) \quad (27a)$$

$$\langle\cos 2\phi\rangle_1 = \frac{G}{2}(\sin 2\alpha)\left(\frac{U-1}{2U - U^2 + a^2}\right) \quad (27b)$$

$$\langle 1\rangle_1 = \frac{G}{2}(\sin 2\alpha)\left(\frac{a}{2U - U^2 + a^2}\right) \quad (27c)$$

Inserting eqs 27a–c into eq 24, we get

$$h(\phi,\alpha) = \frac{G}{2}\left\{(\sin 2\alpha\cos 2\phi)\left(\frac{U}{2U - U^2 + a^2}\right) - (\cos 2\alpha)\left[\left(\phi - \frac{Q(\phi)}{M}\right)\frac{2a}{U}\frac{M^2}{M^2-1} - \sin 2\phi\right]\right\} \quad (28)$$

Equation 28 completely specifies the orientational distribution function $f(\phi,\alpha)$ up to first order in G. Similarly, by inserting eq 27a into eq 17, we get

$$\dot{\alpha} = G[C\cos 2\alpha - 1] \quad (29)$$

where

$$C = \frac{a}{U}\frac{M^2}{M^2-1} \quad (30)$$

Notice that, by putting $\dot{\alpha} = 0$, we obtain the stationary condition for the director; i.e.,

$$\cos 2\alpha = 1/C \quad (31)$$

(which is equivalent to eq 3.7 of ref 1). The stationary solution disappears for $C < 1$, which corresponds to $U > U_{\text{critical}} \cong 2.41$. In this case the director keeps tumbling indefinitely. Its evolution is given by integrating eq 29 as

$$\alpha(t) = \arctan\left[-[(1-C)/(1+C)]^{1/2}\tan((1-C^2)^{1/2}Gt)\right] \quad (32)$$

The period is

$$T = \frac{\pi}{G(1-C^2)^{1/2}} \quad (33)$$

We note the dependence on the strain Gt, rather than on time and shear rate independently. Inspection of eq 32 shows that for values of C close to 1 the time spent by the director at values of α close to 0 constitutes the largest part of the rotation period. The time evolution for the director, eq 32, is equal to that obtained with the Leslie–Ericksen equation when the Leslie coefficient α_3 is positive.[12]

3. Stress Tensor

3.1. General Case. Following ref 1, the elastic and viscous contribution to the stress tensor can be readily calculated. They are

$$\frac{\sigma^E_{12}}{cK_BT} = \langle\cos 2\phi\rangle\left[(\sin 2\alpha)(1 - U\langle\sin^2 2\phi\rangle) + \frac{U}{2}(\cos 2\alpha)\langle\sin 4\phi\rangle\right] \quad (34)$$

$$\frac{\sigma^E_{11} - \sigma^E_{22}}{cK_BT} = 2\langle\cos 2\phi\rangle\left[(\cos 2\alpha)(1 - U\langle\sin^2 2\phi\rangle) - \frac{U}{2}(\sin 2\alpha)\langle\sin 4\phi\rangle\right] \quad (35)$$

$$\frac{\sigma^V_{12}}{cK_BT} = \beta G[1 - (\cos 4\alpha)\langle\cos 4\phi\rangle + (\sin 4\alpha)\langle\sin 4\phi\rangle] \quad (36)$$

$$\frac{\sigma^V_{11} - \sigma^V_{22}}{cK_BT} = 2\beta G[(\sin 4\alpha)\langle\cos 4\phi\rangle + (\cos 4\alpha)\langle\sin 4\phi\rangle] \quad (37)$$

where

$$\beta \cong D/D_0 < 1 \quad (38)$$

is the ratio between the rotational diffusivity of the rods in a concentrated solution, i.e., the same diffusivity as in eq 1, and that in a dilute solution.

3.2. Low Shear Rate. For small values of the shear rate eqs 34–37 can be computed to first order in G. The calculation involves averages $\langle...\rangle_0$ and $\langle...\rangle_1$, which are computed in the same manner as done in eqs 16 and 27. The results for the elastic and viscous stresses are, respectively

$$\frac{\sigma^E_{12}}{cK_BT} = G\frac{1}{2U}[1 - A\cos^2 2\alpha] \quad (39)$$

$$\frac{\sigma^E_{11} - \sigma^E_{22}}{cK_BT} = G\frac{1}{2U}A\sin 4\alpha \quad (40)$$

$$\frac{\sigma^V_{12}}{cK_BT} = \beta G\left[1 - \frac{U-2}{U}\cos 4\alpha\right] \quad (41)$$

$$\frac{\sigma^V_{11} - \sigma^V_{22}}{cK_BT} = 2\beta G\frac{U-2}{U}\sin 4\alpha \quad (42)$$

where A is given by

$$A = 2 - U + aC \quad (43)$$

4. Averages of Stresses

Equations 39–42 give the stress tensor for a single nematic crystal as a function of the director orientation α. For $U < U_{\text{critical}}$ the director can assume a stationary value $\bar{\alpha}$, given by eq 31. In that case equilibrium values of the components of the stress tensor can be readily obtained by substituting the stationary value $\bar{\alpha}$ in eqs 39–42. For $U > U_{\text{critical}}$ the components of the stress tensor will vary periodically, following the motion of $\alpha(t)$ (eq 32). However, the actual experimental situation is that of a polydomain structure. The material consists of many domains, each domain having its own director motion. Thus a macroscopic stress tensor will be an average over the domain orientational distribution $\mathcal{F}(\alpha)$ of the single-domain expressions.

In the context of an oscillatory shear, Larson and Mead[13] considered the same problem, i.e., how to obtain the macroscopic response of a multidomain LCP sample. They used an isotropic distribution, i.e., $\mathcal{F}(\alpha) = 1/\pi$. This assumption was reasonable in their case since for small-amplitude oscillatory shearing no net orientation is achieved in the material. A different situation is expected in our case because, although no stationary orientation is achieved, the director spends the largest part of the rotational period at angles close to 0. Therefore we can expect that, whatever the original domain orientation may have been, after application of a shear rate G, it will evolve to some function peaked around $\alpha = 0$.

$\mathcal{F}(\alpha)$ must satisfy a continuity equation

$$\frac{\partial}{\partial t}\mathcal{F}(\alpha) = -\frac{\partial}{\partial \alpha}[\dot{\alpha}\mathcal{F}(\alpha)] + E \qquad (44)$$

where the term E accounts for interactions among domains (due to Frank elasticity), which are supposed to be weak. This term is essential to achieve a stationary distribution, but it can perhaps be neglected to compute the stationary distribution itself. If this is the case, i.e., if E is negligible under stationary conditions, we get

$$\mathcal{F}(\alpha) = \frac{K}{\dot{\alpha}} = \frac{K}{G[C\cos(2\alpha) - 1]} \qquad (45)$$

where eq 29 has been used. The normalization factor is

$$K = 1/\int_0^\pi \mathrm{d}\alpha/\dot{\alpha} \qquad (46)$$

Equation 45 does not yet completely specify the domain orientational distribution since, in the general case, G is not the same in all domains. Let us assume, however, that local variations in G are accounted for by specifying the domain orientation only, i.e., that G becomes a $G(\alpha)$. In such a case, to within first order in G, all macroscopic results remain unchanged for whatever choice of $G(\alpha)$. Consider for example the viscosity. It will be

$$\eta_{\mathrm{macro}} = \frac{\sigma_{12\,\mathrm{macro}}}{G_{\mathrm{macro}}} = \frac{\int_0^\pi \mathcal{F}(\alpha)\,\sigma_{12}(\alpha)\,\mathrm{d}\alpha}{\int_0^\pi \mathcal{F}(\alpha)\,G(\alpha)\,\mathrm{d}\alpha} \qquad (47)$$

From eqs 39 and 41, which give the elastic and viscous contributions to the local shear stress, we define an α-dependent domain viscosity, $\eta(\alpha)$, as

$$\sigma_{12}(\alpha) = \eta(\alpha)\,G(\alpha) \qquad (48)$$

where $\sigma_{12} = \sigma^{E}_{12} + \sigma^{V}_{12}$ and $G(\alpha)$ is the local shear rate. Therefore, via eq 45, we get

$$\eta_{\mathrm{macro}} = \frac{\int_0^\pi \frac{\eta(\alpha)}{[C\cos(2\alpha) - 1]}\,\mathrm{d}\alpha}{\int_0^\pi \frac{1}{[C\cos(2\alpha) - 1]}\,\mathrm{d}\alpha} \qquad (49)$$

which does not depend on the function $G(\alpha)$.

A similar result is found for the normal stress difference, which, to first order in G, is given by (compare eqs 40 and 42)

$$\frac{(\sigma_{11} - \sigma_{22})_{\mathrm{macro}}}{G_{\mathrm{macro}}} = \left(\frac{A}{2U} + 2\beta\frac{U-2}{U}\right)\frac{\int_0^\pi \frac{\sin 4\alpha}{[C\cos(2\alpha) - 1]}\,\mathrm{d}\alpha}{\int_0^\pi \frac{1}{[C\cos(2\alpha) - 1]}\,\mathrm{d}\alpha} \qquad (50)$$

However, the integral in the numerator of eq 50 is nil. The conclusion is therefore reached that, in the tumbling region,

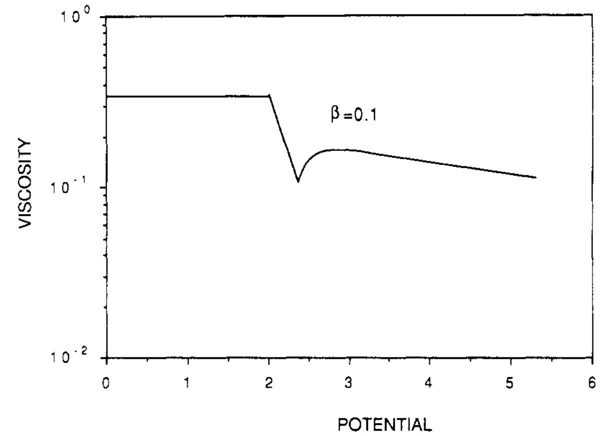

Figure 2. Nondimensional viscosity vs U. The β-parameter describes the relative importance of the viscous and elastic contributions.

the normal stress difference is of an order greater than 1 in the shear rate.

Unfortunately, for quantities of an order greater than 1 in G, the macroscopic average depends on $G(\alpha)$, which, in its turn, is related to the unknown boundary conditions linking neighboring domains. By analogy with the Voigt and Reuss averages used in the mechanics of composite materials, we can envisage two extreme situations in between which the actual situation should fall.[13] In one extreme, we assume that all domains have the same shear stress (as if they were stacked, one on the top of the other, perpendicularly to the shearing surfaces). In the other extreme, all domains are assumed to have the same G (as if they were lined, one after the other, along the shearing surfaces). The latter case gives simply

$$\mathcal{F}(\alpha) = \frac{K_G}{[C\cos(2\alpha) - 1]} \qquad (51)$$

whereas for a constant shear stress, eq 45 becomes

$$\mathcal{F}(\alpha) = \frac{K_\sigma \eta(\alpha)}{[C\cos(2\alpha) - 1]} \qquad (52)$$

5. Results

All averages to be considered in this section involve integrals of the form

$$\int_0^\pi \frac{\cos^n 2\alpha}{C\cos(2\alpha) - 1}\,\mathrm{d}\alpha$$

which can be integrated analytically for each n.[14]

The average of viscosity (eq 49) gives

$$\frac{\eta_{\mathrm{macro}}}{cK_BT} = C_1 - C_2\frac{1 - (1 - C^2)^{1/2}}{C^2} \qquad (53)$$

where

$$C_1 = \frac{1 + 4\beta(U-1)}{2U} \qquad C_2 = \frac{(2-U)(1+4\beta) + ac}{2U} \qquad (54)$$

The viscosity vs the potential U is shown in Figure 2 for $\beta = 0.1$. For $U < U_{\mathrm{critical}}$ the stationary solutions have been reported. These are obtained as

$$\eta/cK_BT = C_1 - C_2/C^2 \qquad (55)$$

We note three distinct regions in Figure 2: (1) isotropic for $U < 2$ in which the nondimensional viscosity does not depend on the potential U; (2) nematic stationary for $2 < U < U_{\mathrm{critical}}$ where the viscosity sharply decreases; (3)

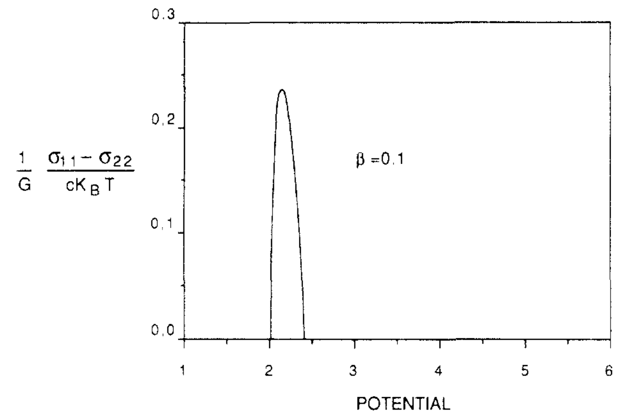

Figure 3. Normal stress difference linear in G in a small range of U values.

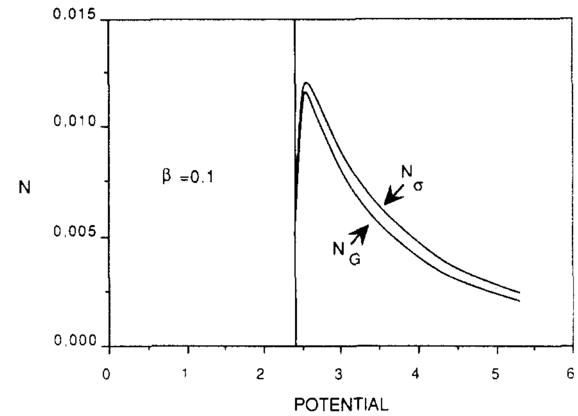

Figure 4. Viscous part of the normal stress difference coefficient in the range of U values where normal stresses are quadratic in G. The two curves are obtained by assuming that either G or σ_{12} is the same in all domains.

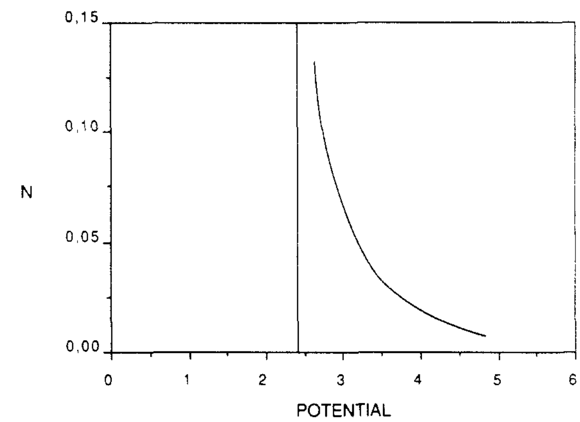

Figure 5. Elastic part of the normal stress difference coefficient in the range of U values where normal stresses are quadratic in G. The curve is obtained by assuming that G is the same in all domains.

nematic tumbling for $U > U_{\text{critical}}$ where the viscosity increases, goes through a maximum, and then decreases.

In order to compare the predictions of Figure 2 with the experimental results on lyotropic LCP's,[2,3,5] we should convert the nondimensional quantities reported in Figure 2 to the corresponding dimensional ones. Regarding the potential, it can perhaps be assumed that U is proportional to the concentration c. Conversion of the viscosity requires, however, the multiplicative factor cK_BT/D; i.e., it involves the diffusion coefficient whose dependence on c is not well established, especially in the region of the isotropic–nematic transition. Qualitatively, it is known that D is a strong decreasing function of the concentration in the isotropic region whereas it increases abruptly after the transition to the nematic phase.

Regarding the normal stress difference, we have already mentioned that in the tumbling region it is zero to first order in G. As is well-known, it is similarly zero (to first order in G) in the isotropic region. Conversely, in the stationary nematic situation ($2 < U < U_{\text{critical}}$), we find a nonzero first-order result, given by

$$\frac{1}{G}\frac{(\sigma_{11}-\sigma_{22})}{cK_BT} = \left(\frac{A}{2U} + 2\beta\frac{U-2}{U}\right)\frac{2}{C}\left[1-\frac{1}{C^2}\right]^{1/2} \quad (56)$$

Equation 56 is reported in Figure 3. Notice that a normal stress difference linear in G was found by Doi[8] throughout the nematic phase. That result was consistent with the fact that only stationary (i.e., nontumbling) solutions were found.

In the tumbling region, it is possible to readily calculate the second-order viscous contribution to normal stresses. In fact, eq 37 has the form of a front factor proportional to G times a term containing averages over the distribution function. Since these averages are known to first order in G, we can calculate $\sigma^V_{11} - \sigma^V_{22}$ up to second order in G. The same does not apply to eq 35 for the elastic contribution where averages up to second order would be required. We obtain

$$\frac{\sigma^V_{11}-\sigma^V_{22}}{cK_BT} = 2\beta G^2\frac{1}{aU}\langle\cos 2\alpha\rangle[1 - A\langle\cos 4\alpha\rangle] \quad \text{2nd order} \quad (57)$$

The averages over domains of eq 57, by using either eq 51 or eq 52, give the macroscopic normal stress difference coefficient as

$$N_G = \left(\frac{\sigma^V_{11}-\sigma^V_{22}}{cK_BT}\right)_{\text{macro}} / G^2 = \mathcal{H}(C) \quad (58)$$

for constant shear rate, and

$$N_\sigma = \left(\frac{\sigma^V_{11}-\sigma^V_{22}}{cK_BT}\right)_{\text{macro}} / G_{\text{macro}}^2 = \eta_{\text{macro}}\frac{1}{C_1}\frac{C}{C^2-(C_2/C_1)}[C\mathcal{H}(C) - (C_2/C_1)^{1/2}\mathcal{H}(C_2/C_1)] \quad (59)$$

for constant stress, where

$$\mathcal{H}(x) = \frac{2\beta}{aU}\left(\frac{1-(1-x^2)^{1/2}}{x} - A\frac{2-x^2-2(1-x^2)^{1/2}}{x^3}\right) \quad (60)$$

The viscous contribution to the normal stress difference coefficient N vs the potential U for $\beta = 0.1$ is reported in Figure 4, in the two limiting cases (eqs 58 and 59) for $U > U_{\text{critical}}$. The difference between the two extreme results is minor. The viscous normal stress difference is positive throughout.

As mentioned before, the elastic contribution to second order in G cannot be readily calculated in closed form. Figure 5 shows the results that are obtained numerically in the limit of small G values. They form a part of the results, reported elsewhere,[15] which completely cover the range of G values up to the stationary solution considered in ref 1. In view of the minor differences that are found, only the constant shear rate situation has been reported in Figure 5. In any event, also the sign of the elastic contribution is positive at small G values.

6. Conclusions

The equations that give the rate of change of the director and of the distribution function of rod orientations (in two dimensions), here written for a general time-dependent shear flow, have been solved in the limit of small values of the shear rate. The results can be summarized as follows.

In the potential range $2 < U < U_{\text{critical}} \cong 2.41$ the first-order expansion in the shear rate G gives (i) a decreasing nondimensional viscosity and (ii) a positive normal stress difference. The director aligns to a stationary angle $\bar{\alpha}$ in this region. The angle $\bar{\alpha}$ progressively decreases as U increases, reaching zero at $U = U_{\text{critical}}$.

For values of the potential above U_{critical}, the expansion predicts tumbling of the director. Thus, problems associated to the multidomain structure of the sample arise. By assuming that interactions due to Frank elasticity are weak, the orientational domain distribution can be derived, which is a prerequisite to calculation of the macroscopic averages.

To within first order in G, we find a nondimensional viscosity that goes through a maximum in this region. The first normal stress difference is zero to the same order. To second order in G, however, a nonzero contribution to the normal stress difference is found. Thus, a shear flow of a nematic phase generates a normal stress difference, which is either first order or second order in G depending on whether the system is nontumbling or tumbling, respectively. The experimental indications on this behavior that can be found in refs 2, 3, and 6 are not conclusive since both logarithmic slopes of about unity and larger than unity have been found. Further work appears necessary to explore this point in greater detail.

All results of normal stress difference obtained in this work, i.e., at small values of G, are positive in sign. This fact, together with the results obtained in ref 1, appears to confirm the positive to negative to positive transitions of the normal stress difference with increasing the shear rate, in full agreement with the experimental observations.

Of course, reservations on these results must be made in view of the two-dimensional nature of this analysis. Quantitatively, the results will certainly change in three dimensions, similar to what is found for the case of suspensions.[16,17] Qualitatively, however, it is expected that the two-dimensional analysis already portrays the correct behavior. A recent numerical extension to the three dimensions carried out by Larson[18] fully confirms this expectation.

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