Tumbling Regime of Liquid-Crystalline Polymers

G. Marrucci

Dipartimento di Ingegneria Chimica, Università di Napoli, Piazzale Tecchio, 80125 Napoli, Italy

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ABSTRACT: The tumbling behavior of LCPs at low shear rates is investigated with the help of the Leslie–Ericksen theory restricted to the planar case and to the one-constant approximation. It is shown that the director distortions induced by the tumbling nature of the nematic may easily reach down to the molecular level, where they get saturated. A rotational motion of the director becomes unavoidable in such a case. The time-dependent structure of the director field is then investigated, thus obtaining definite predictions about the shear dependence of the viscosity in the low shear rate range.

1. Introduction

It is well-known that liquid-crystalline polymers (LCPs) usually exhibit a polydomain texture. The director, or optical axis, of the nematic phase varies in space over distances on the order of a few microns or less, showing no net macroscopic orientation. Also well-known is the fact that a flow may alter this situation. At high shear rates, the director becomes uniformly oriented in the shear direction, thus generating, temporarily at least, a monodomain structure.

At low shear rates, where the polydomain texture prevails, there exist indications that LCPs are nematics of the tumbling type. Direct experimental evidence of tumbling has become available only recently[1,2] and would probably be insufficient for generalizations. Theoretically, however, the prediction that rodlike polymers are nematics of the tumbling type at low shear rates appears well founded. The development of the theory up to now can be summarized as follows.

First, Doi laid down the general equations describing the dynamics of rodlike polymers.[3] In view of the high complexity of these equations, Doi also introduce a mathematical simplification, as a consequence of which the prediction was made that rodlike polymers are of the flow-orienting type at all shear rates.[3,4] Soon after, however, Semenov[5] and Kuzuu and Doi[6] were able to show that, in the limit of vanishing shear rates, the exact theory predicts tumbling nematics.

More recently, by solving for the orientational distribution in two dimensions,[7] it was shown that rodlike polymers switch from the tumbling situation to the flow-orienting one with an increase in the shear rate, the transition occurring in a range of shear rates where the first normal stress difference is negative. The theory offered a satisfactory explanation of the peculiar normal stress effect, as experimentally observed in LCPs, thus giving support to the contention that LCPs are in fact of the tumbling type at low shear rates. The recent extension of Larson[8] to the full three-dimensional situation further removes possible reservations about the validity of the two-dimensional results obtained in ref 7. Larson also shows that the theoretical results are robust, since they are essentially independent of the form chosen for the nematogenic potential (Onsager potential vs the Maier–Saupe one).

On the assumption that LCPs are tumbling nematics at low shear rates, this paper develops some considerations on the polydomain structure, which should correspondingly be expected. Indeed, all theoretical works so far developed for rodlike polymers refer to a fictitious monodomain situation where both the director and the velocity gradient are spatially homogeneous. On the other hand, in the context of the Leslie–Ericksen continuum theory, tumbling nematics have been considered.[9–14] These works refer to low molecular weight (LMW) nematics, and, as such, they cannot be immediately extended to the polymeric case. They provide, however, the starting point to afford a discussion of the tumbling regime in LCPs.

2. Leslie–Ericksen Theory for Tumbling Nematics

Throughout the paper, the simple shear flow between parallel plates will be considered. Cartesian coordinates are chosen, such that the x and y axes are along the shear direction and along the normal to the plates, respectively. As in most cases where analytic solutions are looked for, the analysis is here limited to the "in plane" case, by which it is meant that the director is everywhere parallel to the x–y plane at all times. Thus, the angle θ formed with, say, the x axis suffices to identify the director.

Due to the shear flow, the director is acted upon by a viscous torque, which attempts to rotate it about the z axis. This torque depends on both the director orientation θ and its rate of change $\dot{\theta}$, according to the equation (for the Leslie–Ericksen equations, compare either the original works[15–17] or a textbook, e.g., ref 18)

$$T_z = (\alpha_3 - \alpha_2)\{\dot{\theta} + (1/2)\dot{\gamma}(1 - \lambda \cos 2\theta)\}, \qquad \lambda = (\alpha_2 + \alpha_3)/(\alpha_2 - \alpha_3) \quad (2.1)$$

where $\dot{\gamma}$ is the shear rate, and α_2 and α_3 are two of the Leslie coefficients characterizing the nematic.

A nematic is of the tumbling type if α_2 and α_3 are opposite in sign. In such a case, since $-1 < \lambda < 1$, we cannot have both $T_z = 0$ and $\dot{\theta} = 0$, because the equation $1 - \lambda \cos 2\theta = 0$ is never satisfied. Thus, a stationary director ($\dot{\theta} = 0$) is possible only if there exists some other torque that balances T_z. Conversely, if $T_z = 0$, the director "tumbles" according to the equation

$$\dot{\theta} = -(1/2)\dot{\gamma}(1 - \lambda \cos 2\theta) \quad (2.2)$$

The possibility that $\dot{\theta}$ is nil in tumbling nematics, T_z being balanced by a torque arising from Frank elasticity, was considered in great detail by Carlsson.[13] The stationary solution is such that the director varies spatially along the y direction only. If θ only depends on y, the elastic torque is given by $K\, d^2\theta/dy^2$ (in the single-constant approximation $K_1 = K_3 = K$). Therefore, from eq 2.1, the

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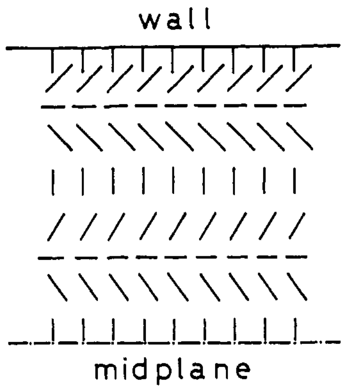

Figure 1. Director field in the shear flow of a tumbling nematic. The director winds up repeatedly from midplane to wall.

stationary solution must obey the equation

$$K\, d^2\theta/dy^2 = (1/2)(\alpha_3 - \alpha_2)\dot{\gamma}(1 - \lambda \cos 2\theta) \qquad (2.3)$$

Equation 2.3 is not sufficient to solve the problem, because the shear rate $\dot{\gamma}$ is itself a local quantity, i.e., it will depend on y. Thus, eq 2.3 contains two unknown functions, $\theta(y)$ and $\dot{\gamma}(y)$. The problem is closed by considering the force balance in the x direction, which dictates that the shear stress, σ, is independent of y. Then, since σ, $\dot{\gamma}$, and θ are further related by the Leslie–Ericksen constitutive relation (for $\dot{\theta} = 0$)

$$\sigma = (1/2)\dot{\gamma}(\alpha_1 \sin^2\theta \cos^2\theta - \alpha_2 \sin^2\theta + \alpha_3 \cos^2\theta + \alpha_4 + \alpha_5 \sin^2\theta + \alpha_6 \cos^2\theta) \qquad (2.4)$$

eliminating $\dot{\gamma}$ from eqs 2.3 and 2.4 gives a differential equation for the $\theta(y)$ function where σ acts as a constant parameter (just like K, and the six Leslie coefficients).

As shown by Carlsson,[13] the solution of the equation takes the form of a "winding up" of the director along y. For the sake of clarity, a qualitative sketch of the solution is represented in Figure 1. The number of turns made by the director across the thickness of the nematic layer increases with an increase in either the shear stress σ or the layer thickness itself.

The solution considered by Carlsson in simple shear,[13] as well as that found by Rey and Denn in converging flows,[14] certainly corresponds to idealizations. Indeed, it is assumed that no defects or disclinations are present in the nematic, i.e., that the director field is continuous at all points. Moreover, the solutions found are not always stable.[14] Yet, they demonstrate a conceptually important point. They show that not necessarily a tumbling nematic actually tumbles. It may be prevented from doing so by Frank elasticity, which, by means of a suitable distortion of the director field, equilibrates the flow-induced torque.

In the next section, it will be shown that such an occurrence, if possible in LMW nematics, is unlikely in LCPs, particularly in rodlike polymers.

3. Distortion Saturation Effect

Half the bracketed quantity in eq 2.4 represents the θ-dependent viscosity of the nematic, i.e., the viscosity that is measured when holding the director uniformly fixed at a given θ by means, e.g., of a strong magnetic field. Thus, for whatever nematic, the Leslie coefficients must be such that a positive sign of that quantity results for all θ values.

Eliminating $\dot{\gamma}$ from eqs 2.3 and 2.4 then gives an equation of the form

$$K\, d^2\theta/dy^2 = \sigma f(\theta) \qquad (3.1)$$

where, for tumbling nematics, $f(\theta)$ has a *fixed sign.* In particular, for rodlike molecule nematics (as opposed to disklike ones), the sign of $f(\theta)$ is positive, because $\alpha_2 < 0$ for them.

Since $f(\theta)$ is periodic (of period π), and is of order 1 for all values of θ, the properties of the solution of eq 3.1 over large distances ($\Delta y \gg (K/\sigma)^{1/2}$) can be studied by approximating eq 3.1 with the simple form

$$K\, d^2\theta/dy^2 = \sigma \qquad (3.2)$$

Measuring y from the midplane of the sheared layer, and in view of the symmetries of the problem, the solution of eq 3.2 is

$$\theta(y) = (\sigma/2K)y^2 + \theta(0) \qquad (3.3)$$

which shows that θ grows indefinitely with y, a result first noted by Cladis and Torza.[10]

If h is the half-thickness of the layer, the number N of turns made by the director is given by

$$N = [\theta(h) - \theta(0)]/\pi = \sigma h^2/2\pi K \qquad (3.4)$$

Equation 3.3 also shows that the distance d over which the director makes one turn (i.e., $\theta(y + d) - \theta(y) = \pi$) is not a constant across the thickness of the layer. For $y = 0$, it is $d = (2\pi K/\sigma)^{1/2}$, whereas, with an increase in $|y|$, it soon becomes

$$d = \pi K/\sigma|y| \qquad (3.5)$$

reaching a minimum at the walls ($d = \pi K/\sigma h$).

These results mark a profound difference between tumbling LMW nematics and tumbling LCPs. Indeed, whereas K is of the same order of magnitude for both classes of substances, LCPs have much larger viscosities than LMW nematics, so that σ is expected to be large even at low shear rates. As a consequence, the values of d in LCPs may easily become as small as the dimension L of the nematogenic unit, especially in rodlike polymer nematics, for which L is the polymer length.

The condition for this event to occur is obtained from eq 3.5:

$$\sigma h L/K > 1 \qquad (3.6)$$

For typical values of the parameters in LCPs ($K \simeq 10^{-6}$ dyn, $\sigma = 10$ dyn/cm^2 or more, $L = 10^{-6}$ cm or more), this inequality is satisfied for h values of the order of 1 mm, or even less.

Let us now consider the distortion $d\theta/dy$, which, according to eq 3.3, increases linearly with y

$$d\theta/dy = (\sigma/K)y \qquad (3.7)$$

If the condition of eq 3.6 is fulfilled, there exists a value of y where the distortion becomes

$$d\theta/dy = 1/L \qquad (3.8)$$

In an order of magnitude sense, $1/L$ should represent a saturation value for the distortion. Distortions larger than $1/L$, by implying that the director makes a full turn over a distance comparable to the length of the rodlike molecule, cannot be elastically sustained. They are quickly eliminated by a local molecular rearrangement. In other words, the range of distortions where Frank elasticity applies has an upper limit. As the distortion approaches $1/L$, the elastic response progressively weakens, and no larger distortions can be achieved.

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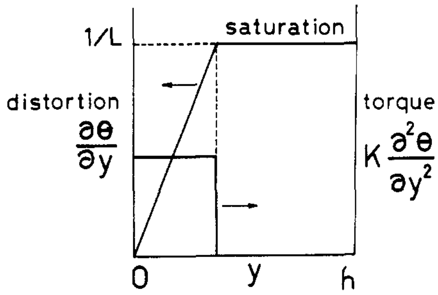

Figure 2. Main features of the distortion diagram across the layer thickness. From center to wall, the distortion first increases and then saturates to the value $1/L$. The torque is virtually constant in the first part and drops to zero in the second.

Figure 2 schematically portrays the distortion diagram over the thickness of the sheared layer, under conditions where the inequality of eq 3.6 is satisfied. Starting at the midplane, the distortion grows linearly up to the saturation value, remaining constant thereafter. In the same figure, the elastic torque $d^2\theta/dy^2$ is also reported, showing a discontinuity where the distortion saturates.

The predictions of this simple analysis should now be apparent. In the region close to the midplane, the situation is not different from that previously considered in LMW nematics, i.e., the elastic torque is capable of preventing actual tumbling of the nematic. In the rest of the layer, conversely, since the distortion cannot grow any further, the elastic torque drops to zero, and the director cannot be prevented from tumbling. As required by dynamical equilibrium, the viscous torque will vanish in that region, together with the elastic one, thus determining suitable nonzero values of $\dot{\theta}$ (compare eqs 2.1 and 2.2).

4. Analysis of Tumbling

The concept of a distortion saturation leads to the conclusion that, insofar as the inequality in eq 3.6 is satisfied, actual tumbling should take place in some parts of the sheared layer. The statement made at the end of the previous section, whereby the elastic and viscous torques are zero in the tumbling region, is too crude, however. As shown in this section, that statement is only true in some average sense, not necessarily locally. The role played by Frank elasticity within the tumbling zone, possibly a nonnegligible one, remains to be elucidated.

The reason why further analysis is needed is that eq 3.1 (and its approximate form, eq 3.2) holds true only as long as no tumbling actually takes place, i.e., for the stationary solution discussed by Carlsson.[13] In the layer where tumbling occurs, a time-dependent function $\theta(y,t)$ is to be considered instead, obeying the equation

$$K\,\partial^2\theta/\partial y^2 = (\alpha_3 - \alpha_2)\{\dot{\theta} + (1/2)\dot{\gamma}(1 - \lambda\cos 2\theta)\} \tag{4.1}$$

where the complete equation for the viscous torque, eq 2.1, has been used, and $\dot{\theta} = \partial\theta/\partial t$ is understood. (Actually, $\dot{\theta}$ is a convected time derivative in general. In the solution looked for, however, the fluid velocity is along x, and $\partial\theta/\partial x = 0$.)

Equation 4.1 is to be coupled with the shear stress equation so as to eliminate $\dot{\gamma}$. Since $\dot{\theta}$ is nonzero, eq 2.4 becomes in this case

$$\sigma = (\alpha_3\cos^2\theta - \alpha_2\sin^2\theta)\dot{\theta} + (1/2)\dot{\gamma}\eta(\theta) \tag{4.2}$$

where $\eta(\theta)$ is the bracketed quantity in eq 2.4.

Equation 4.1 can then be written as

$$K\,\partial^2\theta/\partial y^2 = \sigma f(\theta) + (\alpha_3 - \alpha_2)\{1 - (1/2)(1 - \lambda\cos 2\theta)\,f(\theta)\}\dot{\theta} \tag{4.3}$$

where $f(\theta)$ is the same as in eq 3.1, i.e.

$$f(\theta) = (\alpha_3 - \alpha_2)(1 - \lambda\cos 2\theta)/\eta(\theta) \tag{4.4}$$

Nondimensional space and time variables are now introduced, in the following way

$$y = y/L, \quad t = t\sigma/(\alpha_3 - \alpha_2) \tag{4.5}$$

whereby

$$\dot{\theta} = \dot{\theta}(\alpha_3 - \alpha_2)/\sigma \tag{4.6}$$

Equation 4.3 then becomes

$$\partial^2\theta/\partial y^2 = S[f(\theta) + \{1 - (1/2)(1 - \lambda\cos 2\theta)f(\theta)\}\dot{\theta}] \tag{4.7}$$

where S is the nondimensional stress

$$S = \sigma L^2/K \tag{4.8}$$

The solutions of eq 4.7 must also obey the "saturation" condition

$$\max\,(\partial\theta/\partial y) = 1 \tag{4.9}$$

corresponding to the requirement that, in dimensional variables, the distortion nowhere exceeds $1/L$.

In order to proceed with the solution, the orientational distribution function of the director $F(\theta)$ is first introduced. $F(\theta)$ is defined by the condition that $F(\theta)\,d\theta$ gives the volume (or mass) fraction of material the director of which is between θ and $\theta + d\theta$. Because all θ-functions relevant to our problem are periodic of period π, here and in the following it is understood that the values of θ are restricted to the interval $0 \le \theta < \pi$.

If the layer of tumbling material is macroscopically in a steady state, $F(\theta)$ is independent of time. It then follows that, if $\partial\theta/\partial y$ and $\dot{\theta} = \partial\theta/\partial t$ are viewed as functions of θ, they must be, to within a constant factor, one and the same function; i.e.

$$\dot{\theta} = -c\,\partial\theta/\partial y \tag{4.10}$$

Indeed, if the distribution is observed at any given time, one must find

$$F(\theta)\,d\theta = dy/l \tag{4.11}$$

where l is the "wavelength" of the function $\theta(y,t)$. On the other hand, if the distribution is obtained by observing the change in time of orientation at a given location, one must find

$$F(\theta)\,d\theta = dt/T \tag{4.12}$$

where T is the tumbling period. Thus, for any value of θ, eq 4.10 holds true, with $c = l/T$. (The minus sign in eq 4.10 is due to the fact that $\dot{\theta}$ is always negative during a tumbling motion, whereas $\partial\theta/\partial y$ is everywhere positive.) In other words, if the macroscopic response is steady in time, the solutions of eq 4.7 must be of the form $\theta(y - ct)$, where c is a wave velocity.

By using well-known chain rules of calculus, eq 4.7 then becomes

$$(1/2)d(\dot{\theta}^2)/d\theta = Sc^2[f(\theta) + \{1 - (1/2)(1 - \lambda\cos 2\theta)f(\theta)\}\dot{\theta}] \tag{4.13}$$

Equation 4.13 must be solved for the function $\dot{\theta}(\theta)$ subjected to the periodicity condition

$$\dot{\theta}(\theta + \pi) = \dot{\theta}(\theta) \tag{4.14}$$

as well as to the saturation condition

$$\max|\dot{\theta}(\theta)| = c \tag{4.15}$$

which determines c.

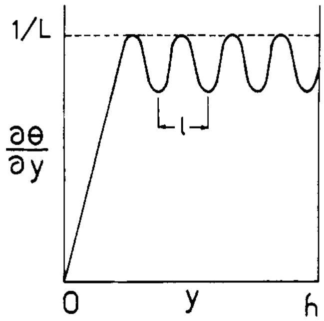

Figure 3. Same diagram of Figure 2 in a refined form. In the tumbling region the distortion shows a wavy pattern, periodically reaching the saturation value $1/L$.

Figure 3 shows the qualitative features of the solution in terms of the distortion $\partial\theta/\partial y$ throughout the thickness of the sheared layer. The ramp at the left corresponds to the linear growth of the distortion in the nontumbling region discussed in the previous section. (The exact solution in eq 3.1 actually predicts a "wavy" ramp instead of a linear one.) Tumbling sets in at the point where the distortion first reaches its saturation value, $1/L$, generating the periodic structure reported on the right of the diagram. In the tumbling region, the distortion periodically reaches the limiting value $1/L$, while keeping somewhat below that value in between. Of course, the diagram in Figure 3 also changes periodically in time, with a horizontal shift of the waves. (The ramp also becomes slightly time-dependent, but this is of no consequence in what follows.)

Although the solution of eq 4.13 is everywhere continuous, the points where the distortion achieves its maximum value $1/L$ (i.e., the wave crests) actually correspond to "walls" where Frank elasticity breaks down. In between these walls, however, the role played by Frank elasticity remains significant. This will become apparent by considering the influence of S upon the solution of eq 4.13.

5. Solution of the Tumbling Equation

Under the two limiting conditions of either very small or very large values of S, eq 4.13 can be solved in closed form. It should be noted that the condition of eq 3.6 ($\sigma hL/K > 1$), which is here assumed to hold true, does not prohibit that $S = \sigma L^2/K$ be small, since $L \ll h$.

In view of the following calculations, it is convenient to rewrite eq 4.4 in the form

$$f(\theta) = (1 - \lambda \cos 2\theta)/(1 - \mu - \epsilon - \lambda \cos 2\theta + \mu \cos^2 2\theta) \tag{5.1}$$

where

$$\mu = (1/4)\alpha_1/(\alpha_2 - \alpha_3) \tag{5.2}$$

$$\epsilon = (\alpha_3 - \alpha_4 - \alpha_6)/(\alpha_3 - \alpha_2) \tag{5.3}$$

With the expressions of the Leslie coefficients for rodlike polymers as predicted by Kuzuu and Doi,[6] λ, μ, and ϵ turn out to be positive numbers; λ and μ are of order unity (in fact, somewhat less than 1), whereas ϵ is much smaller.

Low Shear Rates. As S approaches zero, eq 4.13 is satisfied by a function $\dot{\theta}(\theta)$, which approaches a constant value. Frank elasticity, which is dominant in this limit, imposes that everywhere the director tumbles with a fixed speed at all times. In order to find this constant velocity, eq 4.13 is integrated term by term over a whole cycle, which gives in general

$$0 = \int_0^\pi f(\theta)\, d\theta + \int_0^\pi [1 - (1/2)(1 - \lambda \cos 2\theta) f(\theta)]\dot{\theta}\, d\theta \tag{5.4}$$

Then, since $\dot{\theta}$ is a constant in this limit, eq 5.4 gives

$$|\dot{\theta}| = c = I_1/(\pi - (1/2)I_1 + (1/2)\lambda I_2) \tag{5.5}$$

where I_1 and I_2 are the integrals

$$I_1 = \int_0^\pi f(\theta)\, d\theta = (\pi/\sqrt{2})[(1 + A_1)/(B + D)^{1/2} + (1 - A_1)/(B - D)^{1/2}] \tag{5.6}$$

$$I_2 = \int_0^\pi \cos 2\theta\, f(\theta)\, d\theta$$

$$I_2 = (\pi\lambda/\mu)\{(1 - \mu/\lambda^2)[(1 + A_2)/(B + D)^{1/2} + (1 - A_2)/(B - D)^{1/2}]/\sqrt{2} - 1\} \tag{5.7}$$

In these expressions, D, A_1, A_2, and B are the following groupings of the basic material constants λ, μ, and ϵ

$$D = [1 - 4\mu(1 - \mu - \epsilon)/\lambda^2]^{1/2} \tag{5.8}$$

$$A_1 = (1 - 2\mu/\lambda^2)/D \tag{5.9}$$

$$A_2 = \frac{1 + \mu(2\mu + 2\epsilon - 3)/\lambda^2}{D(1 - \mu/\lambda^2)} \tag{5.10}$$

$$B = 1 - 2\mu(1 - \epsilon)/\lambda^2 \tag{5.11}$$

The tumbling period T is obtained as

$$T = \int_0^\pi \frac{d\theta}{|\dot{\theta}|} = \pi/c \tag{5.12}$$

where c is given by eq 5.5. Then, in view of the general relationship among T, c, and wavelength l, the latter is obtained as

$$l = cT = \pi \tag{5.13}$$

High Shear Rates. As S approaches infinity, the solution of eq 4.13 becomes

$$\dot{\theta} = -f(\theta)/[1 - (1/2)(1 - \lambda \cos 2\theta) f(\theta)] \tag{5.14}$$

which might be called the "free" tumbling solution, i.e., one totally unimpeded by Frank elasticity. (By contrast, the previous limiting case might be called "constrained" tumbling.)

The maximum tumbling speed is here achieved at $\theta = \pi/2$, corresponding to a value of c given by

$$c = 2(1 + \lambda)/(1 - \lambda^2 - 2\epsilon) \tag{5.15}$$

The tumbling period is calculated as

$$T = \int_0^\pi \frac{d\theta}{|\dot{\theta}|} = \pi/2 - \pi\mu[1 - (1 - \lambda^2)^{1/2}]/\lambda^2 - \pi\epsilon/(1 - \lambda^2)^{1/2} \tag{5.16}$$

From eqs 5.15 and 5.16 the wavelength is obtained as

$$l = \pi(1 + \lambda)\{1 - 2\mu[1 - (1 - \lambda^2)^{1/2}]/\lambda^2 - 2\epsilon/(1 - \lambda^2)^{1/2}\}/(1 - \lambda^2 - 2\epsilon) \tag{5.17}$$

A quantitative comparison between constrained and free tumbling can be made by using realistic values of the Leslie coefficients and, therefore, of λ, μ, and ϵ, such as provided, e.g., in ref 6. It is found that the tumbling period is about the same in the two cases, whereas the wavelength

l is larger, possibly much larger, in the free tumbling case than in the constrained one. For example, by assuming a dimensionless rod concentration $C = 1.5$,[6] we find $T = 0.621$ from eq 5.16 and $T = 0.634$ from eq 5.12, whereas $l = 486$ from eq 5.17 as opposed to $l = 3.14$ for constrained tumbling.

With reference to Figure 3, it should finally be noted that the free tumbling case also corresponds to the largest wave amplitude. As S decreases, both the wavelength and the amplitude decrease, toward π and toward 0, respectively.

The solution of eq 4.13 for values of S in between the extreme cases considered above is readily found numerically. A convenient policy is that of assigning a value to the group $Q = Sc^2$. Once the periodic solution of eq 4.13 for that value of Q has been found by some trial and error scheme, eq 4.15 gives the value of c, from which S is backed up.

6. Values of the Viscosity

Within the tumbling zone, the shear rate is itself a periodic function of space and time or, equivalently, a function of θ. From $\dot{\theta}(\theta)$, as determined in the previous section, the function $\dot{\gamma}(\theta)$ is obtained through eq 4.2, which, in nondimensional form, is rewritten as

$$\dot{\gamma}(\theta) = 2f(\theta)/(1 - \lambda \cos 2\theta) - f(\theta)\,\dot{\theta}(\theta) \qquad (6.1)$$

where use has been made of eqs 4.4–4.6. The average over a cycle is given by

$$\bar{\dot{\gamma}} = (1/T)\int_0^T \dot{\gamma}(t)\,\mathrm{d}t = (1/T)\int_0^\pi \frac{\dot{\gamma}(\theta)}{|\dot{\theta}(\theta)|}\,\mathrm{d}\theta = (2/T)\int_0^\pi \frac{f(\theta)}{|\dot{\theta}(\theta)|(1 - \lambda \cos 2\theta)}\,\mathrm{d}\theta + (1/T)\int_0^\pi f(\theta)\,\mathrm{d}\theta \qquad (6.2)$$

The quantity $\bar{\dot{\gamma}}$ represents the effective shear rate (in the nondimensional time units of eq 4.5) within the tumbling layer. If η and $\dot{\gamma}_{\mathrm{dim}}$ are dimensional viscosity and shear rate, respectively, it can be written

$$\eta/(\alpha_3 - \alpha_2) = \sigma/\dot{\gamma}_{\mathrm{dim}}(\alpha_3 - \alpha_2) = 1/\bar{\dot{\gamma}} \qquad (6.3)$$

Thus, the reciprocal of the expression on the right-hand side of eq 6.2 gives the viscosity of the tumbling layer, made nondimensional with respect to $\alpha_3 - \alpha_2$.

Using the results of the previous section, for extreme values of S we find

small S

$$\eta/(\alpha_3 - \alpha_2) = (2I_3/\pi + I_1/T_c)^{-1} \qquad (6.4)$$

large S

$$\eta/(\alpha_3 - \alpha_2) = (1 - \lambda^2)^{1/2} T_f/2\pi \qquad (6.5)$$

where T_c and T_f are the constrained and free tumbling periods as given by eqs 5.12 and 5.16, respectively; I_1 is given by eq 5.6, and I_3 is the integral

$$I_3 = \int_0^\pi \frac{f(\theta)}{1 - \lambda \cos 2\theta}\,\mathrm{d}\theta = \pi(2)^{1/2}\mu[(B - D)^{-1/2} - (B + D)^{-1/2}]/D\lambda^2 \qquad (6.6)$$

with B and D as defined in the previous section.

The viscosity expressions in eqs 6.4 and 6.5 are numerically very close. If the predictions of Kuzuu and Doi[6] for the Leslie coefficients are used again, with $C = 1.5$ (corresponding to a viscosity anisotropy $|\alpha_2|/\alpha_3$ of ca. 40), the values that are obtained from eqs 6.4 and 6.5 are 0.025 and 0.031, respectively, nor is the situation different for other choices of C.

The viscosity of the nontumbling layer also is of a similar magnitude. In order to calculate this value of viscosity, it is sufficient to set $\dot{\theta} = 0$ in eq 6.1. Then, since on the average all values of θ are equally represented in the "windings" of the nontumbling layer, it may be written

$$\bar{\dot{\gamma}} = (1/\pi)\int_0^\pi \dot{\gamma}(\theta)\,\mathrm{d}\theta = (2/\pi)\int_0^\pi \frac{f(\theta)}{1 - \lambda \cos 2\theta}\,\mathrm{d}\theta \qquad (6.7)$$

from which

$$\eta/(\alpha_3 - \alpha_2) = 1/\bar{\dot{\gamma}} = \pi/(2I_3) \qquad (6.8)$$

Although a comparison between eqs 6.4 and 6.8 immediately shows that the viscosity of the nontumbling layer is somewhat larger, it is barely so. Again for $C = 1.5$, the value obtained from eq 6.8 is 0.033.

The somewhat larger viscosity of the nontumbling layer with respect to the tumbling one might perhaps explain the nonlinear, S-shaped, deformation profile along the thickness of the layer, which has been observed in some shear experiments.[19] On the other hand, from the results so far obtained, no hint of the well-known region I behavior has emerged.[20] By this name, the leftmost part of the viscosity vs shear rate curve is indicated, showing a pronounced shear-thinning effect. By further increasing the shear rate, the decreasing viscosity in region I approaches a plateau value (region II). The region I behavior is so typical of LCPs, of whatever "chemistry" they may be constituted, as to suggest that it should be predicted by a universal theory.

7. Ordering Arguments in Favor of Region I Behavior

Up to this point, the Ericksen stress, that is, the contribution to the stress tensor arising from distortions of the director field, was never mentioned. The reason for ignoring this contribution becomes apparent when considering that, for the planar case, the x–y component of the Ericksen stress is given by

$$\sigma^{\mathrm{E}} = -K\partial\theta/\partial x\ \partial\theta/\partial y \qquad (7.1)$$

Thus, in all x-independent solutions previously examined, $\sigma^{\mathrm{E}} = 0$, and the shear stress expression in eq 4.2 is in fact complete.

On the other hand, the solutions so far considered, which assume (among other things) that the director is independent of x and z, certainly correspond to idealizations. In the shear flow of LCPs at low shear rates, no special regularities have been observed; rather, the general impression is one of chaos.

Let us then slightly relax the idealization, by letting θ depend on x, as well as on y and t, all other assumptions about the director and velocity fields remaining unmodified. In fact, in order to simplify matters, the shear rate, $\dot{\gamma}$, instead of the shear stress, σ, is here assumed to be a constant throughout the sheared sample. Notice that, had the latter simplification been used in the mathematical development of the previous sections, the results would not have changed in their essential features; simpler expressions would have been obtained, however.

In view of the x and y dependence of the distortion field, the torque balance, eq 4.1, now becomes

$$K/(\alpha_3 - \alpha_2)(\partial^2\theta/\partial x^2 + \partial^2\theta/\partial y^2) = \dot{\theta} + (1/2)\dot{\gamma}(1 - \lambda \cos 2\theta) \qquad (7.2)$$

where $\dot{\theta}$ is given by

$$\dot{\theta} = \partial\theta/\partial t + \dot{\gamma}y\,\partial\theta/\partial x \quad (7.3)$$

$\dot{\gamma}y$ being the x component of the velocity (the only nonzero component under the assumptions here adopted).

The function $\theta(x,y,t)$ may be decomposed in the following way

$$\theta(x,y,t) = \Theta(y,t) + \varphi(x,y,t) \quad (7.4)$$

where Θ is an x-independent solution of eq 7.2, such as those previously found. Correspondingly, it is

$$\dot{\theta} = \dot{\Theta} + \partial\varphi/\partial t + \dot{\gamma}y\,\partial\varphi/\partial x \quad (7.5)$$

Equations 7.4 and 7.5 are substituted into eq 7.2, generating the following equation for the "perturbation" function, $\varphi(x,y,t)$

$$K/(\alpha_3 - \alpha_2)(\partial^2\varphi/\partial x^2 + \partial^2\varphi/\partial y^2) = \partial\varphi/\partial t + \dot{\gamma}y\,\partial\varphi/\partial x - (1/2)\dot{\gamma}\lambda\{\cos(2\Theta + 2\varphi) - \cos 2\Theta\} \quad (7.6)$$

No attempt will here be made at finding solutions of eq 7.6. An ordering argument seems possible, however.

In order to make time and space variables nondimensional in eq 7.6, a time and a length, characteristic of the physical problem described by eq 7.6, are required. In regards to time, the obvious choice is $1/\dot{\gamma}$ (which is the equivalent of $(\alpha_3 - \alpha_2)/\sigma$ of the previous sections).

In regards to length, conversely, it so appears that the choice must be significantly different from that made in the previous sections. In fact, the molecular length L, which plays a central role in the basic solution $\Theta(y,t)$, should not be important in the perturbation problem, unless the perturbation itself gives rise to distortions as large as $1/L$. The overall size of the system, i.e., the layer thickness h, should also be irrelevant in the perturbation problem of eq 7.6, which, like the basic periodic solution $\Theta(y,t)$, has a local nature. The following choice of a characteristic perturbation length seems, therefore, mandatory

$$l_{\text{pert}} = \{K/(\alpha_3 - \alpha_2)\dot{\gamma}\}^{1/2} \quad (7.7)$$

The nondimensional form of eq 7.6 then becomes

$$\partial^2\varphi/\partial x^2 + \partial^2\varphi/\partial y^2 = \partial\varphi/\partial t + y\,\partial\varphi/\partial x - (1/2)\lambda\{\cos(2\Theta + 2\varphi) - \cos 2\Theta\} \quad (7.8)$$

where the function $\Theta(y,t)$ depends parametrically on the nondimensional group S (see previous sections) here redefined as

$$S = (\alpha_3 - \alpha_2)\dot{\gamma}L^2/K \quad (7.9)$$

However, since Θ is the argument of sine and cosine functions, the last term in eq 7.8 is of order unity (for finite perturbations) for all values of S. It follows that the distortions, which are predicted by eq 7.8, themselves must be of order unity for all values of S. Of particular importance is the distortion along x

$$\partial\varphi/\partial x = 1 \text{ (nondimensional)} \quad (7.10)$$

or, in dimensional variables

$$\partial\varphi/\partial x = 1/l_{\text{pert}} = \{(\alpha_3 - \alpha_2)\dot{\gamma}/K\}^{1/2} \quad (7.10')$$

where the equality is understood in an order of magnitude sense. Equation 7.10 shows that the distortion along x, if it exists, should grow with the square root of the shear rate. Of course, also this component of the distortion can never exceed $1/L$.

It is now possible to reconsider the viscosity problem. If there are distortions along x, the shear stress, σ, is made up of two parts, the Ericksen stress as well as the so-called viscous stress, i.e., that directly linked to the Leslie coefficients

$$\sigma = \sigma^{V} + \sigma^{E} \quad (7.11)$$

The viscous stress, the only one considered in the previous sections, is virtually proportional to the shear rate. It was shown in the preceding section that the tumbling viscosity, η, is essentially independent of the S parameter, i.e., of the shear rate. Conversely, the Ericksen stress is essentially proportional to the square root of the shear rate. Indeed, in eq 7.1, $\partial\theta/\partial y = \partial\Theta/\partial y$ is of order $1/L$ whereas $\partial\theta/\partial x = \partial\varphi/\partial x = 1/l_{\text{pert}}$. The total stress can therefore be written as

$$\sigma = \eta\dot{\gamma} + (1/L)\{K(\alpha_3 - \alpha_2)\dot{\gamma}\}^{1/2} \quad (7.12)$$

The resulting total viscosity is then given by

$$\eta_{\text{total}} = \sigma/\dot{\gamma} = \eta + (1/L)\{K(\alpha_3 - \alpha_2)/\dot{\gamma}\}^{1/2} \quad (7.13)$$

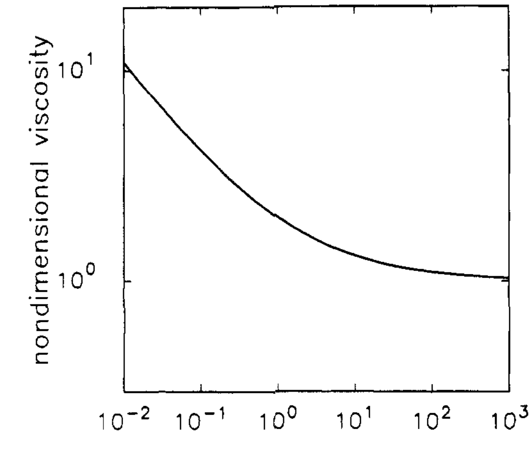

Figure 4. Region I behavior of the viscosity of LCPs predicted by eq 7.13. The viscosity has been normalized to the plateau value of region II.

Equation 7.13 predicts a shear-thinning viscosity at low shear rates, with a $-1/2$ power law, and a constant viscosity η at higher shear rates, when the last term in eq 7.13 becomes negligibly small with respect to η. Figure 4 shows a logarithmic diagram of eq 7.13: η_{total}/η is plotted vs $\dot{\gamma}\tau$, where $\tau = L^2\eta^2/K(\alpha_3 - \alpha_2)$ is a characteristic time.

To be precise, the slope in the shear-thinning region of Figure 4 is not strictly $-1/2$ because, in the Ericksen stress term, the average distortion along y is not strictly $1/L$ but rather $1/l$, where l is the wavelength of the tumbling pattern depicted in Figure 3. Now, although l is L times a numerical factor, this factor does increase (possibly by a large amount; see section 5) with an increase in the shear rate, as the transition from constrained to free tumbling takes place. A somewhat steeper slope would then result from this effect. The above-reported value of the characteristic time τ also changes to $\tau = l^2\eta^2/K(\alpha_3 - \alpha_2)$ if free tumbling has set in. The value of the shear rate marking the transition from region I to region II may decrease significantly in such a case.

8. Concluding Remarks

The main conclusions of this work can be summarized as follows.

(i) Since LCPs (very probably) are tumbling nematics at low shear rates, the Leslie–Ericksen theory should be used with the proviso that the distortion may easily reach a saturation value determined by a characteristic molecular length. Under steady-state conditions (as observed macroscopically), the actual tumbling motion of the director appears to require a distortion saturation. This saturation effect should not be crucially affected by an "out-of-plane" component of the director, here assumed to be nil. Indeed, unless the director is everywhere essentially aligned along the vorticity axis of the shear flow (i.e., it is fully out of the plane), the in-plane component remains of order unity, and all semiquantitative results arising from eq 3.2 remain valid. Rather, the large distortions inevitably induced by a shear flow in tumbling nematics may constitute an effective source of defects and disclinations. Generating defects may be a way of partially relaxing large distortions.

(ii) The viscous shear stress is essentially proportional to the shear rate, through a characteristic viscosity, which can be calculated from the Leslie coefficients. Whether the material is totally prevented from tumbling by Frank elasticity or it actually tumbles (either freely or in a constrained way), the viscosity it displays is virtually the same in all cases.

(iii) A nonzero Ericksen shear stress will also arise in a shear flow, however, if, as appears likely, the director is not constant along the shear direction. In such a case, the Ericksen shear stress is predicted to grow approximately with the square root of the shear rate. The contribution of this stress might perhaps explain the region I behavior of the observed "apparent" viscosity.

(iv) Along the thickness of a sheared sample, differences in the distortion pattern may exist, which would give rise to slightly different values of the local viscosity. It is possible, in particular, that a central layer of material exhibits a somewhat larger viscosity than the material at the walls.

Before concluding, it appears necessary to comment about the compatibility of the physical picture of tumbling LCPs presented in this paper with some scaling laws, which appear to be well obeyed in many experiments. For example, in the step-up experiments of Mewis and Moldenaers[21] the period of the damped oscillations of the transient stress response is found to scale with $1/\dot{\gamma}$, where $\dot{\gamma}$ is the shear rate after the step. Is this result compatible with the concept that the distortion in the layer thickness direction is saturated? The answer is positive because, although the distortion is saturated in the y direction, it is far from saturation in the shear direction. Thus, the length scaling is that of eq 7.7, and the time scaling is in fact $1/\dot{\gamma}$. More generally, one should note that the scaling of eq 7.7 leads to the concept of a limiting value for the Ericksen number, in agreement with the discussion reported, e.g., by Burghardt and Fuller.[22]

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