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RODLIKE MOLECULE DYNAMICS. THE TUMBLING REGIME

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Abstract The dynamical equation for the orientational distribution function of rodlike molecules, derived in the seventies for the case of spatially uniform conditions, has been recently extended by Doi and coworkers to include the case of nonuniform situations. This general equation is here specialized, and suitably simplified, in order to deal with the difficult problem of tumbling nematics in a shear flow.

Keywords: nematics, rodlike molecules, dynamics, tumbling

INTRODUCTION

The equation which describes the dynamics of rodlike molecules in spatially homogeneous systems, applicable to either the isotropic or the nematic phases, has been known for some time[1-3]. In the limit of slow flows of the nematic phase, this highly nonlinear equation generates the Leslie-Ericksen constitutive equation for the stress tensor, linear in the velocity gradient.[4,5] In particular, Semenov[4] obtained the Leslie coefficients by using the Maier-Saupe mean field potential, whereas Kuzuu and Doi[5] used the Onsager excluded volume for polymeric rods. Obviously, the complete Leslie-Ericksen equation[6] (i.e., that embodying Frank elasticity) could not be obtained by these authors because spatial distortions were not included in the original molecular model.

Molecular models of spatial distortions have been considered in statics, mostly with the aim of calculating the constants of Frank elasticity.[7] Once more, the potentials used were either that of Onsager[8] or that of Maier and Saupe.[9,10] By using the latter potential, the large distortions existing within a defect core have also been investigated.[11]

The complete dynamical problem, inclusive of spatial dependencies, has been recently tackled by Doi and coworkers.[12,13] Fluctuations in the isotropic phase were only considered in those works, however,

either to calculate the dynamic structure factor of the concentrated isotropic phase,[12] or to describe the initial stage of the spinodal decomposition.[13] Although both problems refer to "small" deviations from the isotropic state, the nematogenic interaction is properly accounted for; therefore, the general equation laid down by Doi and coworkers is in principle applicable also to the nematic phase.

In this work, the dynamical problem of the nematic phase, inclusive of spatial distortions, is considered. The general equation of Doi and coworkers[12,13] is here specialized by using an extension to distorted nematics of the Maier-Saupe potential, already used in statics.[10,11] Formally, this equation would generate, in the limit of slow flows (and of small distortions as well, see below), the complete Leslie-Ericksen equation. The motivation for the present work is not formal, however. Rather, we are convinced that a conceptual problem exists in slow shear flows of tumbling nematics, as detailed in the following.

From the above-mentioned results on Leslie coefficients,[4,5] as well as from recent nonlinear analyses,[14,15] it is now well established that liquid crystalline polymers (LCPs) are tumbling nematics at low shear rates. It is also well known that, in the shear flow of tumbling nematics, the director "winds up" repeatedly in the gradient direction.[16] These windings become increasingly tighter, i.e., the distortion wants to grow indefinitely, as the distance from the midplane of the sheared layer is increased.[17] An indefinite growth of the distortion is impossible, however, because the molecular level is soon reached, especially in polymeric nematics, and the distortion "saturates".[17] In other words, the Leslie-Ericksen equation may easily "break down" in tumbling LCPs.

Indeed, as previously mentioned, the Leslie-Ericksen equation represents the linear limit of a Smoluchowski equation for molecular models of nematics, such as that of Doi and coworkers. This linear limit is obtained whenever the local distribution function is "very close" (an expansion procedure is here implied) to being axially symmetric; more specifically, when it is very close to the undistorted equilibrium distribution. The symmetry axis (i.e., the director) of this "asymptotically close" uniaxial distribution may vary in space, but the molecular orientational state about the local director remains

close to the undistorted equilibrium distribution everywhere. Thus, linearity is not obtained when that "closeness" breaks down. This event occurs in either one of two possible cases: Either in fast flows or (no matter how slow the flow may be) for large distortions. An example of the latter occurrence can be found even in statics, within the defect cores.[11] Another example is offered by tumbling nematics at low shear rates, in those regions of the sample where the distortion reaches down to the molecular level. The main purpose of this paper is that of laying down the equations which describe this intriguing problem.

THE DOI EQUATION AND THE MEAN FIELD POTENTIAL

The configuration of a rodlike molecule is identified by specifying both its orientation (through a unit pseudo-vector $\underline{u}$) and the position $\underline{R}$ of its center. A single-particle distribution function can be defined in two ways. Doi and coworkers[12,13,18] considered the function $\Psi(\underline{u},\underline{R};t)$ which gives the number density of molecules at $\underline{u}$ and $\underline{R}$, parametric in time. This function automatically accounts for possible changes of density. Indeed, the rod density $\rho(\underline{R};t)$ is obtained from $\Psi(\underline{u},\underline{R};t)$ through integration over $\underline{u}$.

Alternatively, it is possible to define a local orientational distribution function $f(\underline{u};\underline{R},t)$, parametric in both space and time, which gives the probability density of the orientation $\underline{u}$. Needless to say, integration over $\underline{u}$ of f gives unity. Thus, with this choice, information for the rod density distribution is given separately through the function $\rho(\underline{R};t)$. In fact, the overall distribution function $\Psi(\underline{u},\underline{R};t)$ is but the product of $f(\underline{u};\underline{R},t)$ times $\rho(\underline{R};t)$.

Here, as in previous papers,[10,11] we only consider ρ-constant nematics. For such a case, it is convenient to use the orientational distribution function $f(\underline{u};\underline{R},t)$. Because ρ is a constant, f obeys the same Smoluchowski equation written by Doi and coworkers[12,13,18] for the function Ψ. Such an equation accounts for both the rotational and the translational motions of the rodlike molecules in the following way:

$$\partial f/\partial t = \underline{\nabla}\cdot[D_{\parallel}\,\underline{u}\underline{u} + D_{\perp}(\underline{\underline{1}}-\underline{u}\underline{u})]\cdot(\underline{\nabla}f + f\,\underline{\nabla}V) - \underline{\nabla}\cdot(f\,\underline{\underline{\kappa}}\cdot\underline{R}) + \underline{\Omega}\cdot D_r(\underline{\Omega}f + f\,\underline{\Omega}V) - \underline{\Omega}\cdot(f\,\underline{u}\times\underline{\underline{\kappa}}\cdot\underline{u}) \qquad (1)$$

In Eq. (1), $\underline{\nabla}$ is the spatial gradient (at constant $\underline{u}$ and t), $\underline{\Omega}$ is the

rotational operator as defined by Doi, $\underline{\underline{\kappa}}$ is the velocity gradient tensor, and $V(\underline{u},\underline{R},t)$ is the potential (made nondimensional with respect to temperature kT) acting on the $\underline{u}$-oriented test rod at $\underline{R}$, at time t. In Eq. (1), all three diffusion coefficients of a rigid rod are present, i.e., the two translational diffusivities, $D_{\parallel}$ and $D_{\perp}$, and the rotational one D_r. Although these diffusivities are generally variable, it is customary to approximate them by constant parameters. The translational and orientational contributions in Eq. (1) have a similar structure: The terms containing the diffusion coefficient (or coefficients) describe the Brownian motion and the effect of the potential. The terms containing the velocity gradient $\underline{\underline{\kappa}}$ describe "convective" effects due to flow.

For $\underline{\underline{\kappa}}=\underline{\underline{0}}$, Eq. (1) describes the relaxation in time towards an equilibrium distribution $f_0(\underline{u};\underline{R})$. Outside defect cores (and not too close to boundaries), the latter function may be written as $f_{oo}[\underline{u}\cdot\underline{n}(\underline{R})]$, where $\underline{n}(\underline{R})$ is the director field. The function f_{oo} describes the uniaxial equilibrium distribution in the undistorted nematics; it gives the zero-th order term of the expansion alluded to in the last paragraph of the Introduction.

For small $\underline{\underline{\kappa}}$-values, Eq. (1) formally generates the complete Leslie-Ericksen constitutive equation, corresponding to a situation where $f(\underline{u};\underline{R},t)$ differs from $f_{oo}[\underline{u}\cdot\underline{n}(R,t)]$ by terms of order $\underline{\underline{\kappa}}$, a condition always fulfilled in nontumbling nematics. In tumbling nematics, conversely, for a fixed $\underline{\underline{\kappa}}$ (no matter how small), boundary conditions can be envisaged such that $f(\underline{u};\underline{R},t)$ differs considerably from $f_{oo}[\underline{u}\cdot\underline{n}(R,t)]$, at least in some regions of the sample. In a sheared layer, this will occur above a critical layer thickness,[17] when the windings of the director become so tight as to reach down to some characteristic molecular length.

To proceed with the analysis of this problem, the potential $V(\underline{u},\underline{R},t)$ in Eq. (1) needs to be specified. Since we are interested in a flow problem, no external fields will be included in V, which therefore reduces to a mean-field potential only. For rodlike particles, the main part of this potential is "orientational", and is in fact responsible for the very existence of the nematic phase. For the sake of simplicity, in this work we shall use the Maier-Saupe orientational potential. In order to account for spatial distortions, however, one of

the $\underline{R}$-dependent Maier-Saupe forms used in statics[10,11] must be employed here. We shall adopt in particular that choice which, in the Frank elasticity limit, corresponds to the one-constant approximation.[11]

The mean field potential is generally not fully specified by its orientational part. Indeed, a mean field contribution may also exist which is not effective on rotations but only on translations. We thus write:

$$V(\underline{u},\underline{R},t) = V_{or}(\underline{u},\underline{R},t) + V_{tr}(\underline{R},t) \tag{2}$$

In our case, $V_{tr}(\underline{R},t)$ will take care of the constant density constraint.

The mean-field (nondimensional) orientational potential is written as

$$V_{or}(\underline{u},\underline{R},t) = -2U\ \{\underline{u}'\underline{u}'\}:\underline{u}\underline{u} \tag{3}$$

where U is the potential "intensity" (a constant at a given temperature and density), and the $(\underline{R},t)$-dependent "neighborhood" average $\{\underline{u}'\underline{u}'\}$ is defined as:[10,11]

$$\{\underline{u}\underline{u}\} = \int d^2\underline{u}\ \frac{1}{v}\int_v d^3\underline{r}\ \underline{u}\underline{u}\ f(\underline{u};\underline{R}+\underline{r},t) \tag{4}$$

In Eq. (4), v is the volume of a spherical neighborhood centered at $\underline{R}$, scanned by vector $\underline{r}$.

Eqs. (3) and (4) are self-explanatory. In the absence of spatial distortions, the integral in Eq. (4) reduces to the usual, purely orientational average $\langle\underline{u}\underline{u}\rangle$, and Eq. (3) takes the familiar form introduced long ago by Doi.[3] In spatially distorted situations, the average in Eq. (4) is "sensitive" to distortions up to some interaction distance (determined by v). The use of a spherical neighborhood is somehow in conflict with the notion of rodlike molecules, and in fact a more realistic shape of the neighborhood should be used.[10] The spherical shape is simpler, however; as mentioned above, it corresponds to the one-constant approximation of Frank elasticity. Simplifying assumptions are justified here, the aim being that of exploring main

qualitative features only.

Another important simplifying assumption is now made. We will assume that, over the volume v defining the range of the molecular interactions, no large changes of the distribution function $f(\underline{u};\underline{R},t)$ take place. This "gradual variation assumption" was already used in the solution of a static problem,[11] and there proved to hold true in most cases. The assumption allows for an expansion procedure in $\underline{r}$ to be used in the calculation of the integral in Eq. (4). This expansion procedure in $\underline{r}$ should not be mistaken with the expansion about the f_{oo} function. Although f varies little within each neighborhood of size v, it can become very different from f_{oo}. In fact, we are just after a situation where f and f_{oo} are quite distinct. Were not this the case, the usual Leslie-Ericksen limit would be recovered.

It has been shown elsewhere[11] that, by using the gradual variation assumption, Eq. (4) may be rewritten as

$$\{\underline{uu}\} = \underline{\underline{S}} + \frac{1}{2}\ell^2 \Delta\underline{\underline{S}} \tag{5}$$

where

$$\underline{\underline{S}}(\underline{R},t) = \langle\underline{uu}\rangle = \int d^2\underline{u}\ \underline{uu}\ f(\underline{u};\underline{R},t) \tag{6}$$

is a local order parameter tensor (of unit trace). The last term in Eq. (5) accounts for the distortions through the Laplacian of $\underline{\underline{S}}$; the linear size of the interaction neighborhood is ℓ.

From Eqs (3) and (5), the following expression for the orientational mean-field potential is obtained:

$$V_{or}(\underline{u},\underline{R},t) = -2U\ \underline{\underline{S}}:\underline{uu} - U\ \ell^2\ \Delta\underline{\underline{S}}:\underline{uu} \tag{7}$$

The first term in Eq. (7) is the standard Maier-Saupe potential; the second term is the simplest possible way of accounting for spatial distortions.

THE TUMBLING EQUATION IN A SHEAR FLOW

Let us consider a layer of material undergoing a simple shear flow between two parallel plates. A Cartesian coordinate system is used, with the x-axis in the shear direction and the y-axis orthogonal to the

plates, i.e., in the gradient direction.

We will make the following assumptions:

1. At any $\underline{R}$ and t, the distribution function $f(\underline{u};\underline{R},t)$ is symmetric with respect to the xy-plane, and the velocity is parallel to that plane.
2. All space-dependent quantities only vary along the y-coordinate.
3. The shear rate is a constant in both time and space.
4. The system is macroscopically at a steady-state.

The first assumption corresponds to the "in-plane" assumption for the director and velocity fields, usually made in the context of treatments based on the Leslie-Ericksen equation.

The second assumption is also common to all existing solutions (based on a continuum approach) for tumbling nematics. In obtaining these solutions, both stationary[16] and not,[17] the "texture" in the x and z directions was perforce neglected. Assumptions 1 and 2, together with incompressibility and with the boundary conditions on the velocity, also guarantee that the velocity is parallel to the x-axis everywhere, i.e., the flow is a simple shear also locally (and not only in a global sense).

A possible alternative to the third assumption would be that of assuming a constant shear stress instead of a constant shear rate. Both possibilities have been considered in the works just mentioned, a simpler mathematics resulting in fact from the constancy of the shear rate. On the other hand, any texture along x (most probably present, in fact) works in the direction of making the shear rate constant along y as the result of a sort of "x-averaging". Thus, although the x-texture has been (and will be) explicitly ignored in the mathematics, it is somehow recovered in Assumption 3.

We will limit our considerations to a situation where all macroscopic observables (e.g., the stresses) are at a steady state (Assumption 4). This condition does not prohibit that microscopic quantities be time-dependent, though they are expected to be periodic in such a case. Indeed, this latter occurrence, i.e., a situation where the local orientational distribution actually "tumbles" in time,[15,17,19-21] is of interest here.

On the basis of Assumption 2, the $\underline{R}$-dependence of both the distribution function and the mean-field potential reduces to a simple

y-dependence. In the following, therefore, it is understood that we will deal with the functions $f(\underline{u};y,t)$ and $V(\underline{u},y,t)$. The spatial gradient terms (SGT) appearing in Eq. (1) then become

$$\text{SGT} = [D_{\parallel} u_y u_y + D_{\perp}(1-u_y u_y)] \left[\frac{\partial^2 f}{\partial y^2} + \frac{\partial}{\partial y} \left(f \frac{\partial V}{\partial y} \right) \right] \tag{8}$$

It should be noted that the velocity gradient $\underline{\underline{\kappa}}$ is absent in Eq. (8). This is due to the fact that the velocity $\underline{\underline{\kappa}} \cdot \underline{R}$ is along x in our shear flow; because all changes occur along y, the divergence term $\underline{\nabla} \cdot (f \, \underline{\underline{\kappa}} \cdot \underline{R})$ of Eq. (1) is identically zero in our case.

The next simplification arises from the periodic structure of the solution, dictated by Assumption 4 within the context of a situation where the local orientational distribution actually tumbles.[15,17,19-21] The solution is periodic in both time and space; in fact, it has the form of a wave traveling along y with velocity c.[17] This situation is here referred to as the tumbling regime, not to be confused with the winding-up regime discussed by Carlsson.[16] In the latter case, the director is fixed in time and does not actually "tumble".

Let us now consider the order parameter tensor $\underline{\underline{S}}$ defined in Eq. (6). In view of Assumption 1, two principal axes of this symmetric tensor lie in the xy-plane. We call $\underline{n}$ the unit pseudo-vector along one of these axes, specifically the axis which, under equilibrium conditions, reduces to the director. Since $\underline{n}$ belongs to the xy-plane, it is identified by a single angle θ. We choose to measure θ from the shear direction (the x-axis), in the range $-\pi/2 \leq \theta \leq \pi/2$.

The above-mentioned periodicity (or tumbling) shows up, first of all, in a periodicity of $\underline{\underline{S}}$, and therefore of $\underline{n}$, both along y and in time. In terms of the angle θ, tumbling is described by a monotonic decrease of θ from $\pi/2$ to $-\pi/2$, whereupon the cycle repeats itself. The angle θ depends on y and t through their "wave" combination y-ct.[17] Thus, in defining the rate of change of θ, we may write:

$$\omega \equiv \partial\theta/\partial t = -c \, \partial\theta/\partial y \tag{9}$$

(A discussion about the value of the parameter c is postponed to the last section of the paper.) From now on, the angle θ will be used in place of both the space variable y and the time variable t, in the

sense that all functions of y and t will be replaced by functions of θ only. Needless to say, ω itself is regarded as a function of θ.

With the understanding that the same symbols are used for functions which now depend on θ instead of y and t, Eq. (1) becomes

$$\omega \frac{\partial f}{\partial \theta} = (\omega/c^2)\,[D_{\parallel} u_y u_y + D_{\perp}(1-u_y u_y)]\,\frac{\partial}{\partial \theta}\left[\omega\left(\frac{\partial f}{\partial \theta} + f\,\frac{\partial V}{\partial \theta}\right)\right]$$

$$+ \underline{\Omega}\cdot D_r(\underline{\Omega} f + f\,\underline{\Omega} V) - \underline{\Omega}\cdot(f\,\underline{u} \times \underline{\underline{\kappa}}\cdot\underline{u}) \qquad (10)$$

where $f(\underline{u};\theta)$ is the "new" distribution function, and $V(\underline{u},\theta)$ is given by:

$$V(\underline{u},\theta) = -2U\,\underline{\underline{S}}:\underline{u}\underline{u} - (U\ell^2/c^2)\,\omega\,\frac{d}{d\theta}\left(\omega\,\frac{d\underline{\underline{S}}}{d\theta}\right):\underline{u}\underline{u} + V_{tr} \qquad (11)$$

In Eq. (11), only $V_{tr}(\theta)$ needs to be specified from the condition of constant density. Once this specification is made, Eq. (10) describes the tumbling regime completely. It is understood that the value of $\underline{\underline{\kappa}}$, i.e., of the shear rate, must be small enough for this regime to be found.

The solution of Eq. (10) must satisfy the following "periodicity" condition, which replaces boundary and initial conditions:

$$\left.\frac{\partial^n f}{\partial \theta^n}\right|_{\theta=-\pi/2} = \left.\frac{\partial^n f}{\partial \theta^n}\right|_{\theta=\pi/2} \qquad (n = 0,1,\ldots) \qquad (12)$$

At first sight, Eq. (10) contains more than one unknown function. Indeed, together with the "fundamental" unknown $f(\underline{u};\theta)$, the order parameter $\underline{\underline{S}}(\theta)$ enters the problem through the potential of Eq. (11); still more importantly, the rate of change of the "director" $\omega(\theta)$ is also present. It is immediately apparent, however, that $\underline{\underline{S}}(\theta)$ is not an independent unknown, because it is determined by the distribution function through Eq. (6). Much less apparent is the fact that also $\omega(\theta)$ is intimately linked to $f(\underline{u};\theta)$. To demonstrate in the easiest possible way that such is the case, we shall now introduce an additional drastic simplification in the problem.

We shall assume that the translational diffusivities are zero. We

are here carrying to the limit a possibility which is not implausible, i.e., that in our nematics (no longer necessarily made up of rodlike particles) orientational rearrangements of the nematic units occur faster than displacements of these units. It should be immediately emphasized that getting rid of the translational diffusivities does not suppress spatial dependencies in the problem: In Eq. (1), the spatial gradients remain unaltered in the rotational term, where $\underline{\Omega}V$ brings into the picture the spatial distortions. Indeed, the Laplacian term contained in V (see Eq. (7)) is the very term which reduces to Frank elasticity in the linear limit.[10]

In other words, the proposed simplification, though certainly not irrelevant, does not change the nature of the original problem. We are still dealing with a problem of molecular dynamics which, in the linear limit, would give rise to the Leslie-Ericksen equation, complete of the Frank elasticity terms (in the one-constant approximation). We are trying to deal with a difficult nonlinear problem in the simplest possible way, hopefully without destroying the essential physics.

The advantages of the proposed simplification are apparent. Not only a cumbersome term of the equation vanishes. There disappears also the necessity of establishing the translational part of the mean-field potential. In the surviving part of the equation, i.e., in the rotational terms, V_{tr} is indeed ineffective. In the next section, the simplified equation is further elaborated and discussed.

THE SIMPLIFIED EQUATION

With the above discussed simplification, the tumbling equation (in nondimensional form) reduces to:

$$\omega \frac{\partial f}{\partial \theta} = \underline{\Omega}\cdot\underline{\Omega} f - U \left[2\underline{\underline{S}} + \frac{1}{c^2}\,\omega \frac{d}{d\theta}\left(\omega \frac{d\underline{\underline{S}}}{d\theta}\right) \right] : \underline{\Omega}\cdot(f\underline{\Omega}\underline{u}\underline{u}) - \underline{\Omega}\cdot(f\,\underline{u}\times\underline{\underline{\kappa}}\cdot\underline{u}) \tag{13}$$

It should be understood that ω, $\underline{\underline{\kappa}}$, and c appearing in Eq. (13) are nondimensional. They are obtained from the corresponding dimensional quantities by using $1/D_r$ and ℓ as units of time and length, respectively. It is also understood that, in the second term on the

right hand side of Eq. (13), the single dot multiplication affects the $\underline{\underline{Q}}$ operators while the double dot multiplication affects $\underline{\underline{S}}$ and $\underline{u}\underline{u}$. It should be noted that the term in square brackets is $\underline{u}$-independent.

We now perform a change of frame as follows. Instead of the "fixed" frame (fixed with the shear direction x and the gradient direction y), we will adopt a "tumbling" frame, i.e., a frame corotating with the principal directions of tensor $\underline{\underline{S}}$. (Hereafter, the same symbols are used for the same physical quantities in the two frames, with the exception of the velocity gradient.) In the tumbling frame, we will choose a Cartesian coordinate system with axis 1 along $\underline{n}$, and axis 3 coincident with the z-axis of the fixed frame. The "director" $\underline{n}$ is thus fixed in the new frame; with respect to $\underline{n}$, the shear direction forms the angle $-\theta$, counter-rotating with angular velocity $-\omega$.

In the new frame, the velocity gradient $\underline{\underline{\Gamma}}$ is given by

$$\underline{\underline{\Gamma}} = \underline{\underline{Q}} \cdot \underline{\underline{\kappa}} \cdot \underline{\underline{Q}}^T + \dot{\underline{\underline{Q}}} \cdot \underline{\underline{Q}}^T \tag{14}$$

where $\underline{\underline{Q}}$, $\dot{\underline{\underline{Q}}}$ describe the change of frame; their (x,y,z)-matrices are

$$\underline{\underline{Q}} = \begin{Vmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{Vmatrix} \qquad \dot{\underline{\underline{Q}}} = -\omega \begin{Vmatrix} \sin\theta & -\cos\theta & 0 \\ \cos\theta & \sin\theta & 0 \\ 0 & 0 & 0 \end{Vmatrix} \tag{15}$$

and we recall that the (x,y,z)-matrix of $\underline{\underline{\kappa}}$ is ($\dot{\gamma}$ is the shear rate):

$$\underline{\underline{\kappa}} = \begin{Vmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix} \tag{16}$$

By replacing $\underline{\underline{\kappa}}$ with $\underline{\underline{\Gamma}}$, Eq. (13) remains valid in the new frame.

The advantage of working in this new frame is due to the relationship

$$S_{12} = \langle u_1 u_2 \rangle = 0 \tag{17}$$

which automatically holds true for all values of θ, because 1 and 2 are always principal directions. Of course, the average $\langle u_1 u_2 \rangle$ is made by

using the distribution as observed in the new frame. Multiplication of all terms of Eq. (13) by u_1u_2 followed by integration over $\underline{u}$ gives, after some straightforward calculations

$$0 = 4U \left[2\underline{\underline{S}} + \frac{1}{c^2}\,\omega\,\frac{d}{d\theta}\left(\omega\,\frac{d\underline{\underline{S}}}{d\theta}\right) \right] : \langle \underline{u}\underline{u}u_1u_2 \rangle - (\underline{\underline{\Gamma}}\cdot\underline{\underline{S}} + \underline{\underline{S}}\cdot\underline{\underline{\Gamma}}^T)_{12} + 2\,\underline{\underline{\Gamma}} : \langle \underline{u}\underline{u}u_1u_2 \rangle \qquad (18)$$

where use has been made of Eq. (17).

In spite of its apparent complexity, Eq. (18) is but an ordinary first-order differential equation in the function $\omega(\theta)$, subjected to the periodicity condition:

$$\omega(-\pi/2) = \omega(\pi/2) \qquad (19)$$

We recall that in Eq. (18) the function $\omega(\theta)$ is present also inside the "new" velocity gradient $\underline{\underline{\Gamma}}$. The link between $\omega(\theta)$ and the distribution function $f(\underline{u};\theta)$ is provided by the presence in Eq. (18) of the averages $\underline{\underline{S}}$ and $\langle \underline{u}\underline{u}u_1u_2 \rangle$.

To within the approximation resulting from all the assumptions made, the tumbling regime is described by the set of coupled equations, Eq. (13) and Eq. (18), with the boundary conditions given by Eq. (12) and Eq. (19). (We remind that $\underline{\underline{\Gamma}}$ in place of $\underline{\underline{\kappa}}$ must be intended in Eq. (13).)

There remains to discuss the role played by the parameter c appearing in these equations. In analogy with the findings of the previous calculation based on a simple modification of the Leslie-Ericksen theory,[17] we believe that c is automatically determined by Eqs. (12-13,18-19): Once the shear rate is assigned, there should exist a single c-value (when it exists, i.e., for small values of the shear rate) which gives rise to the periodic solution looked for. Of course, only by actually solving these nonlinear equations such a statement will be proved (or disproved). Work is in progress towards this goal.

CONCLUDING REMARKS

We have derived the set of equations describing the tumbling regime in a form which, being the simplest possible, appears amenable to

numerical solution. It is not inconceivable that these equations will explain the nonlinearity observed in most liquid crystalline polymers at low shear rates (known to rheologists as Region I of the viscosity curve[22]). Were this the case, it would be demonstrated that also that behavior is "molecular" in origin, rather than due to complexities of the director and/or velocity fields.

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