

# A theory for flowing nematic polymers with orientational distortion

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## Synopsis

Using a nonlocal nematic potential, we generalize the Doi theory for nematic polymers to include distortional elasticity. We derive an evolution equation for the configuration tensor and a constitutive equation for a nonlocal stress tensor which is consistent with the long-range order in nematic polymers. One of the interesting effects of distortional elasticity is the appearance of a mean-field torque on the molecules as they are forced away by flow from their preferred orientation. This torque gives rise to an antisymmetric part of the stress tensor. With a few molecular parameters, the complete system of equations is capable, we believe, of describing the evolution of the texture and the dynamics of disclinations in flowing nematic polymers. Thus, for the first time, a suitable platform for exploring complex flows of nematic polymers is established. In the limit of weak flows and small distortions, the theory properly reduces to the Leslie–Ericksen theory. The Leslie viscosities are derived in terms of molecular parameters. © 2000 The Society of Rheology. [S0148-6055(00)00705-7]

## I. INTRODUCTION

The prevalent theory for the flow and rheology of nematic polymers is the Doi theory [Doi (1981); Doi and Edwards (1986)], which is based on a statistical mechanical description of the orientation of a suspension of rigid rod-like molecules. The Doi theory takes into account the effects of flow, Brownian motion, and intermolecular forces on the molecular orientation distribution. Thus, it gives a good representation of the *molecular* viscoelasticity. However, it does not include the so-called *distortional* elasticity, which represents the crystalline characteristic of these materials. Since there is no elastic penalty for spatial distortion, the Doi theory is valid only in the limit of spatial homogeneity. It is especially noteworthy that spatial distortion of nematics often takes the form of orientational defects known as disclinations, which are perhaps the most spectacular and significant feature of polymeric and small-molecule nematics. If distortional elasticity is neglected, one may use the Doi theory to simulate inhomogeneous flows but the discli-

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nation dynamics thus obtained is unrealistic. For instance, Feng and Leal (1997); Feng and Leal (1999) and Feng *et al.* (1998) showed that the Doi theory predicts the formation of disclinations due to inhomogeneous director tumbling. However, they are constantly annihilated and reformed. Without distortional elasticity, nothing anchors the disclinations and leads to a steady-state network of disclinations, which seems to arise in reality [Marrucci and Greco (1992)].

For *small-molecule* liquid crystals (SMLCs), distortional elasticity has been formulated in the limit of weak distortion and is known as Frank elasticity. This is one ingredient of the Leslie–Ericksen (LE) theory, a phenomenological theory for the flow of SMLCs [de Gennes and Prost (1993)]. An underlying assumption in the LE theory is that a SMLC has a short relaxation time so that the molecular orientation distribution always retains its uniaxial equilibrium “shape,” even while the axis of symmetry is rotated by flow. Thus, the orientational configuration is completely described by a constant order parameter and a unit vector—the director  $\mathbf{n}$ —which indicates the axis of symmetry. For liquid-crystalline polymers (LCPs), the orientation distribution may be distorted by flow into a nonuniaxial configuration. Thus, the LE theory in general does not apply to LCPs.

Apparently we need a theory that encompasses both the molecular viscoelasticity and the distortional elasticity. Several attempts have been made at such a theory. Ericksen (1991) allowed the order parameter to be a variable but still required the orientation distribution to be uniaxial. Farhodi and Rey (1993) replaced the director vector by a second-order tensor and fashioned a tensor theory after the LE theory. Edwards and Beris (1989) gave an ad hoc generalization of the Frank elasticity in tensorial form. These authors later developed a Hamiltonian formalism that leads to theories for SMLCs and LCPs resembling the LE and Doi theories [Edwards *et al.* (1990); Beris and Edwards (1994)]. More recently, Tsuji and Rey (1997) added distortional elasticity, via the Landau–de Gennes free energy, to the kinetic equation of the Doi theory but did not give a stress tensor. All these approaches are phenomenological in nature, and the resulting theories are unsatisfactory in one way or another. First, they invariably contain a large number of unknown parameters which in general cannot be determined rationally. As pointed out by Greco and Marrucci (1992) and Greco (1996), this causes conceptual difficulties when dealing with spatial distortions, especially the severe distortions near defects. Second, the use of the Landau–de Gennes energy expansion is unjustified in these theories. de Gennes (1969) proposed the energy expansion expressly to describe “short-range-order effects in the isotropic phase.” Katriel *et al.* (1986) further demonstrated that the expansion only converges for very low order parameters. Hence, it is valid only in the neighborhood of the isotropic state and should not be used for the moderately high order parameters typical of real LCP systems. A third drawback of the phenomenological theories is the lack of consistency with existing theories and among themselves. For example, the conformation tensor theory of Edwards *et al.* (1990) does not allow director tumbling for infinitely thin rods as the Doi theory does, and its stress tensor cannot be reduced to the Doi stress. As a consequence, the conformation tensor theory predicts maxima in the shear and normal stresses in simple shear and fails to produce the second change in sign of the normal stress at high flow rates that has been experimentally confirmed. Without a stress tensor, the Tsuji–Rey theory cannot be judged in this regard. But its treatment of the Frank elasticity is at odds with that of Edwards *et al.* (1990). Based on the earlier observations, we believe that a molecular approach would be more advantageous than a phenomenological one.

A molecular theory for distortional elasticity is made possible by Marrucci and Greco (1991) and Marrucci and Greco (1993) who proposed a nonlocal mean-field nematic potential for LCPs which accounts for spatial variations of the molecular orientation

distribution. In the absence of flow, this potential has been used to calculate the static orientational fields corresponding to certain anchoring conditions [Greco and Marrucci (1992); Sigillo *et al.* (1998)]. As far as we are aware, the only attempt so far to apply this potential to a *flow* problem was that of Kupferman *et al.* (2000). Unfortunately, the stress tensor in their theory fails to account for the nonlocal nature of the distortional elasticity and is incomplete. In the present work, we derive a molecularly-based constitutive theory for nematic LCPs which incorporates distortional elasticity via the Marrucci–Greco potential, and therefore lay the foundation for flow simulations of nematic LCPs. We also demonstrate that our molecular theory properly reduces to the Leslie–Ericksen theory in the limit of weak flow and small spatial distortion.

## II. EVOLUTION EQUATION FOR THE POLYMER CONFIGURATION

Similar to the original Doi theory, the new theory will have two major components: a kinetic equation governing the evolution of the polymer configuration and an expression for the stress tensor. The derivation of the evolution equation is rather straightforward; one needs only to substitute the Marrucci–Greco nematic potential for the Maier–Saupe potential in the original Doi theory. We define an orientation distribution function  $\Psi(\mathbf{u}; \mathbf{r})$  that varies in space but neglect the translational diffusion of the molecules. The number density of polymer molecules  $\nu$  is assumed to be constant in space. In this case, the Smoluchowski equation may be written as [Doi and Edwards (1986)]

$$\frac{\partial \Psi}{\partial t} + \mathbf{v} \cdot \nabla \Psi = -\mathfrak{R}(\mathbf{u} \boldsymbol{\kappa} \Psi) + \bar{D}_r \mathfrak{R} \left[ \mathfrak{R} \Psi + \frac{\Psi}{kT} \mathfrak{R} U_{\text{scf}} \right], \quad (1)$$

where  $\mathfrak{R} = \mathbf{u} \times (\partial / \partial \mathbf{u})$  and  $\boldsymbol{\kappa} = (\nabla \mathbf{v})^T$ .  $\bar{D}_r$  is the pre-averaged rotational diffusivity and  $U_{\text{scf}}$  is the mean-field nematic potential. Equation (1) differs from the original Doi theory in that the material derivative of  $\Psi$  appears on the left-hand side instead of the partial time derivative.

The Marrucci–Greco potential represents the energy of molecular interaction in a “gradually varying” orientational field [Greco and Marrucci (1992)]. For simplicity, we use the one-constant approximation of the potential, corresponding to three equal elastic constants in the limit of Frank elasticity

$$U_{\text{MG}}(\mathbf{u}) = -\frac{3}{2} U k T \left( \mathbf{A} + \frac{\mathcal{L}^2}{24} \nabla^2 \mathbf{A} \right) : \mathbf{u} \mathbf{u} = U_{\text{MS}} + \tilde{U}_{\text{MG}}, \quad (2)$$

where  $\mathbf{A}(\mathbf{r}) = \int \Psi(\mathbf{u}; \mathbf{r}) \mathbf{u} \mathbf{u} \, d\mathbf{u} = \langle \mathbf{u} \mathbf{u} \rangle$  is the orientation configuration tensor,  $\mathcal{L}$  is a characteristic length for molecular interaction,  $U$  is a constant representing the nematic strength,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Obviously,  $U_{\text{MG}}$  is a generalization of the Maier–Saupe potential  $U_{\text{MS}} = -\frac{3}{2} U k T \mathbf{A} : \mathbf{u} \mathbf{u}$  to accommodate spatial inhomogeneity. Substituting Eq. (2) for the mean-field potential in Eq. (1) gives us the evolution equation for  $\Psi$  with distortional elasticity.

It is useful to derive an evolution equation for  $\mathbf{A}$  since the stress tensor will be expressed in terms of the moments of  $\Psi$ . Furthermore, solving for the moments is much easier than solving for the distribution function directly [Feng *et al.* (1998)]. Following the Prager procedure, we multiply Eq. (1) by  $\mathbf{u} \mathbf{u}$ , integrate over  $\mathbf{u}$  and obtains

$$\begin{aligned} \frac{\partial \mathbf{A}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{A} - \boldsymbol{\kappa} \cdot \mathbf{A} - \mathbf{A} \cdot \boldsymbol{\kappa}^T = & -6\bar{D}_r \left( \mathbf{A} - \frac{\boldsymbol{\delta}}{3} \right) + 6\bar{D}_r U (\mathbf{A} \cdot \mathbf{A} - \mathbf{A} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle) - 2\boldsymbol{\kappa} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle \\ & + \frac{\bar{D}_r U \mathcal{L}^2}{8} (\nabla^2 \mathbf{A} \cdot \mathbf{A} + \mathbf{A} \cdot \nabla^2 \mathbf{A} - 2\nabla^2 \mathbf{A} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle), \quad (3) \end{aligned}$$

where  $\boldsymbol{\delta}$  is the unit tensor, and  $\langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle = \int \Psi \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \, du$ . The terms involving  $\nabla^2 \mathbf{A}$  represent the effects of spatial distortions. The terms on the left-hand side constitute the upper convected derivative of  $\mathbf{A}$ . Note that  $\langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle$  has to be expressed in terms of  $\mathbf{A}$  via a *closure approximation* for Eq. (3) to be self-contained. We should mention that Eq. (3), in a somewhat different form, was previously derived by Kupferman *et al.* (2000).

### III. THE NONLOCAL STRESS TENSOR

Because of the long-range order in liquid-crystalline polymers, they are not *simple materials*, which, as defined in continuum mechanics, are such that the stress at a material point depends upon the history of the deformation gradient tensor at that point only [see, e.g., Leigh (1968)]. In a LCP, the stress at one point depends on the local deformation history and the polymer configuration, the latter being *globally* determined by distortional elasticity in the entire domain. In this sense the stress tensor is nonlocal and the ellipticity of Eq. (3) is manifest of the nonlocal nature of the polymer dynamics. The original Doi theory requires that the flow and the polymer configuration be spatially homogeneous. This homogeneity avoids nonlocal interference via distortional elasticity and permits the definition of a local stress in the same way as for fluids lacking long-range order such as flexible polymer solutions and melts [Doi and Edwards (1986); p. 70]. Invoking the principle of virtual work, Doi calculated the elastic stress from the reaction of the LCP to a uniform virtual deformation  $\delta \boldsymbol{\epsilon}$ .

According to Doi and Edwards (1986), the polymer stress  $\boldsymbol{\sigma}^{(P)}$  is the sum of the elastic stress  $\boldsymbol{\sigma}^{(E)}$  and a viscous stress  $\boldsymbol{\sigma}^{(V)}$ . The latter arises from the viscous friction on the rigid rod-like molecules and does not depend on the nematic potential. Hence, in going from the Maier–Saupe potential to the Marrucci–Greco potential,  $\boldsymbol{\sigma}^{(V)}$  is unchanged. It is the elastic stress  $\boldsymbol{\sigma}^{(E)}$  that needs to be redefined. To generalize Doi's principle of virtual work to a LCP with inhomogeneous orientation, one imagines freezing a certain volume  $V$  of the material in a stressed state, and applying to it a virtual deformation field  $\delta \boldsymbol{\epsilon}(\mathbf{r}) = [\nabla \delta \mathbf{s}(\mathbf{r})]^T$ , where  $\delta \mathbf{s}$  is the virtual displacement vector. The virtual work that the exterior must do to the material to realize  $\delta \boldsymbol{\epsilon}(\mathbf{r})$  is

$$\delta W = \int_V \boldsymbol{\sigma}^{(E)} : \delta \boldsymbol{\epsilon} \, dV, \quad (4)$$

where  $\boldsymbol{\sigma}^{(E)}$  is the elastic stress tensor being sought. This work is then equated, via the first law of thermodynamics, to the change in free energy of the material within  $V$ . By calculating the change in free energy, one may extract the unknown elastic stress from Eq. (4). Note that by invoking a virtual *deformation*, one defines a Cauchy stress governing the flow of the material. Another stress may be defined by introducing a virtual *rotation* of the molecules without displacement. Such a stress will be analogous to the

Ericksen stress for SMLCs [de Gennes and Prost (1993)] and will not appear in the equations of motion for the material.

For liquid-crystalline materials, this scheme is complicated by the elastic interaction across  $S$ , the boundary of  $V$ . This interaction may be easily visualized by thinking of  $S$  as a solid wall onto which the LCP molecules are anchored. As the virtual deformation in general rotates the molecules on  $S$  against an anchoring torque, the wall does extra work to the LCP which must be incorporated into the energy balance. Accordingly, the change in free energy has to be evaluated for such reorientation of the molecules as respects the anchoring condition. If  $V$  is cut out of a larger domain of LCPs instead of being bounded by walls, the situation remains the same with the anchoring torque replaced by a distortional elastic torque. The upshot is that the ‘‘anchoring condition’’ has to be specified in order that the elastic interaction across  $S$  be accounted for in the energy balance and the elastic stress  $\sigma^{(E)}$  be determined.

In deriving the Leslie–Ericksen theory, de Gennes and Prost (1993) eliminated the surface interactions by requiring the bounding surface to be stationary and the director orientation to be fixed on them. Note that the constitutive equation thus derived is not restricted by those specific boundary conditions; it expresses the stress in terms of the ‘‘local’’ distortion  $\nabla \mathbf{n}$  and is an intrinsic property of the material. We follow a similar approach by requiring that both the molecular orientation and its spatial gradient be fixed on  $S$ . This is equivalent to using a virtual deformation  $\delta \boldsymbol{\varepsilon}$  that vanishes smoothly toward  $S$ . [Alternatively, one may make the volume  $V$  infinitely large such that the virtual deformation causes no disturbance on the boundary. This device was used by Landau and Lifshitz (1986) in treating the deformation of a general elastic body.]

Thus, the anchoring torque does no additional virtual work. The free energy of the LCP is determined by the molecular orientation distribution  $\Psi$  [Doi and Edwards (1986)]

$$A = \nu \int_V dV \int du [kT\Psi \ln \Psi + \frac{1}{2}\Psi U_{\text{scf}}], \quad (5)$$

where  $\nu$  is the number density of the polymer molecules and the factor 1/2 accounts for the fact that the molecular interaction is counted twice when one goes over all the molecules. Substituting the Marrucci–Greco potential  $U_{\text{MG}}$  for  $U_{\text{scf}}$ , we have

$$\delta A = \nu \int_V dV \int du [kT\delta\Psi \ln \Psi + kT\Psi\delta\Psi + \frac{1}{2}\delta(\Psi U_{\text{MS}}) + \frac{1}{2}\delta(\Psi \tilde{U}_{\text{MG}})]. \quad (6)$$

We need to concern ourselves only with the  $\tilde{U}_{\text{MG}}$  term, since the other terms can be treated in formally the same way as in Doi and Edwards (1986) and will produce Doi’s original stress tensor. Hence

$$\begin{aligned}
\delta A_{\text{MG}} &= \frac{\nu}{2} \int_V dV \int \delta(\Psi \tilde{U}_{\text{MG}}) du \\
&= -\frac{\nu U k T \mathcal{L}^2}{32} \int_V dV \int \delta(\Psi \nabla^2 \mathbf{A} : \mathbf{u}\mathbf{u}) du \\
&= -\frac{\nu U k T \mathcal{L}^2}{32} \int_V \delta(\nabla^2 \mathbf{A} : \mathbf{A}) dV \\
&= -\frac{\nu U k T \mathcal{L}^2}{32} \int_V (\nabla^2 \mathbf{A} : \delta \mathbf{A} + \delta \nabla^2 \mathbf{A} : \mathbf{A}) dV. \tag{7}
\end{aligned}$$

The variation  $\delta \mathbf{A} = \int \delta \Psi \mathbf{u}\mathbf{u} du$  involves the change in the polymer orientation distribution due to the virtual deformation.  $\delta \Psi$  can be calculated from Eq. (1) by neglecting the diffusion and nematic terms for a rapid virtual deformation [Doi and Edwards (1986)]

$$\delta \Psi = \left( \frac{\partial \Psi}{\partial t} + \mathbf{v} \cdot \nabla \Psi \right) \delta t = -\mathfrak{R} \cdot (\mathbf{u} \times \delta \boldsymbol{\varepsilon} \cdot \mathbf{u} \Psi). \tag{8}$$

The  $\delta \nabla^2 \mathbf{A}$  term represents the energy penalty for *additional* spatial distortions produced by the virtual strain field  $\delta \boldsymbol{\varepsilon}(\mathbf{r})$ . Because of the inhomogeneity of  $\delta \boldsymbol{\varepsilon}$ , the operators  $\delta$  and  $\nabla^2$  do not commute

$$\delta \nabla^2 \mathbf{A} = \left( \frac{\partial \nabla^2 \mathbf{A}}{\partial t} + \mathbf{v} \cdot \nabla \nabla^2 \mathbf{A} \right) \delta t = \nabla^2 \delta \mathbf{A} - \delta \boldsymbol{\varepsilon} : \nabla \nabla \mathbf{A} - \nabla \cdot (\delta \boldsymbol{\varepsilon} \cdot \nabla \mathbf{A}). \tag{9}$$

Integrating by parts gives

$$\begin{aligned}
\delta A_{\text{MG}} &= -\frac{\nu U k T \mathcal{L}^2}{32} \left[ \int_V (2 \nabla^2 \mathbf{A} : \delta \mathbf{A} - \delta \boldsymbol{\varepsilon} : \nabla \nabla \mathbf{A} : \mathbf{A} + \delta \boldsymbol{\varepsilon} : \mathbf{Q}) dV \right. \\
&\quad \left. + \int_S dS \cdot (\nabla \delta \mathbf{A} : \mathbf{A} - \nabla \mathbf{A} : \delta \mathbf{A} - \delta \boldsymbol{\varepsilon} \cdot \nabla \mathbf{A} : \mathbf{A}) \right], \tag{10}
\end{aligned}$$

where  $Q_{ij} = (\partial A_{kl} / \partial x_i)(\partial A_{lk} / \partial x_j)$ , and contractions in the tensorial expressions apply to adjacent indices, e.g.,  $\delta \boldsymbol{\varepsilon} : \nabla \nabla \mathbf{A} : \mathbf{A} = (\delta \varepsilon_{ij})(\partial^2 A_{lk} / \partial x_i \partial x_j) A_{kl}$ . Now the surface integral, indicating the surface anchoring effect, can be put to zero since  $\delta \boldsymbol{\varepsilon}$ ,  $\delta \mathbf{A}$  and  $\nabla \delta \mathbf{A}$  vanish on  $S$ . The remaining volume integral can be evaluated by using Eq. (8). The procedure consists of integrating by parts and employing the identities given by Bird *et al.* (1987). Finally, the total change in free energy in Eq. (6) is

$$\begin{aligned}
\delta A &= 3\nu k T \int_V \delta \boldsymbol{\varepsilon} : \left[ \mathbf{A} - U(\mathbf{A} \cdot \mathbf{A} - \mathbf{A} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle) \right. \\
&\quad \left. - \frac{U \mathcal{L}^2}{24} \left( \mathbf{A} \cdot \nabla^2 \mathbf{A} - \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle : \nabla^2 \mathbf{A} + \frac{\mathbf{Q} - \nabla \nabla \mathbf{A} : \mathbf{A}}{4} \right) \right] dV. \tag{11}
\end{aligned}$$

Thus, it is clear from Eq. (4) that the elastic stress is

$$\boldsymbol{\sigma}^{(E)} = 3\nu kT \left[ \mathbf{A} - U(\mathbf{A} \cdot \mathbf{A} - \mathbf{A} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle) - \frac{U\mathcal{L}^2}{24} \left( \mathbf{A} \cdot \nabla^2 \mathbf{A} - \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle : \nabla^2 \mathbf{A} + \frac{\mathcal{Q} - \nabla \nabla \mathbf{A} : \mathbf{A}}{4} \right) \right]. \quad (12)$$

The total stress due to the polymer is then

$$\boldsymbol{\sigma}^{(P)} = \boldsymbol{\sigma}^{(E)} + \boldsymbol{\sigma}^{(V)} = \boldsymbol{\sigma}^{(E)} + \frac{\nu}{2} \zeta_r \boldsymbol{\kappa} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle, \quad (13)$$

where  $\zeta_r$  is the rotational friction constant defined in Doi and Edwards (1986).

#### IV. REMARKS ON THE ELASTIC STRESS TENSOR

The elastic stress tensor in Eq. (12) and its derivation present some unusual features that warrant further discussion:

(a) Nonlocality. Adding distortional elasticity changes the nature of the evolution equation [Eq. (3)] from hyperbolic to elliptic. Hence, the polymer configuration is globally determined by distortional elasticity in the entire domain and it depends on the boundary conditions on the entire surface. The elastic stress, being a function of the local deformation history *and* polymer configuration, is therefore also dependent on the evolution of the entire domain. This reflects the long-range order in nematic polymers which makes them nonsimple materials. On the other hand, the *form* of the constitutive equation [Eq. (12)] does not depend on boundary conditions; it expresses the reaction of the LCP to distortions in terms of the *local* polymer configuration, and applies for any anchoring conditions. The nonlocality here is then only an indirect dependence of the stress on distant materials.

(b) Asymmetry. The elastic stress is not symmetric in general, and hence angular momentum is not conserved in the usual sense. This is to be expected since the mean-field potential exerts a torque on the rod-like molecules when they are forced away from their preferred orientational configuration by flow. According to Doi and Edwards (1986; p. 293), the torque on a test molecule oriented along  $\mathbf{u}$  is  $\mathbf{T} = -\mathfrak{R}U_{\text{MG}}(\mathbf{u})$ . Hence, the total torque on a unit volume of the material is

$$\mathbf{t} = \nu \int \Psi \mathbf{T} \, d\mathbf{u} = \frac{3}{24} \nu U k T \mathcal{L}^2 A_{il} \nabla^2 A_{lj} \epsilon_{ijk} \mathbf{e}_k, \quad (14)$$

where  $\epsilon_{ijk}$  is the permutation tensor,  $\mathbf{e}_k$  is the unit vector for the  $k$ th coordinate and summation over repeated indices is implied. This ‘‘body torque’’ can be shown to balance exactly the antisymmetric part of the stress tensor

$$\sigma_{ij}^{(P)} \epsilon_{ijk} + t_k = 0. \quad (15)$$

This balance is required for the conservation of the total angular momentum, which is also known as Cauchy’s second law of motion [Leigh (1968)]. It is worth noting that the body torque is due only to the distortional elasticity. In fact, one may calculate the molecular torque  $\mathbf{T}(\mathbf{u})$  for a spatially *homogeneous* LCP by using the Maier–Saupe potential  $U_{\text{MS}}$ . The average of  $\mathbf{T}$  over  $\mathbf{u}$  vanishes, however. Hence, no body torque results and the stress tensor is symmetric.

(c) Elastic isotropy. We have used the one-constant approximation of the Marrucci–Greco potential [Eq. (2)], which results from neglecting the length of the rods in com-

parison to the length of molecular interaction  $\mathcal{L}$ . If the length of the molecules is taken into account, the nematic potential has an additional term that gives rise to elastic anisotropy [Marrucci and Greco (1991)]. In this general case, the elastic stress can be derived in a similar fashion, and will contain the sixth moment of  $\Psi$  in terms such as  $\int \Psi \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} : \nabla \nabla \mathbf{A} : \mathbf{u} \mathbf{u} \, d\mathbf{u} = \langle u_i u_j u_k u_l u_m u_n \rangle \partial^2 A_{mn} / \partial x_k \partial x_l$ .

(d) Closure approximation. The fourth-moment tensor  $\langle \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \rangle$  appears in the stress tensor and the evolution equation. To formulate a closed theory on the level of the second moment tensor  $\langle \mathbf{u} \mathbf{u} \rangle = \mathbf{A}$ , one needs to relate  $\langle \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \rangle$  to  $\mathbf{A}$  by a closure approximation. Much work has been done on closures for the original Doi theory which can be directly borrowed into the present theory for flow calculations [e.g., Feng *et al.* (1998)].

(e) In the extensive treatise of Doi and Edwards (1986), the elastic stress tensor was derived for a dilute solution of rod-like polymers subjected to an *external* potential (§ 8.6). For nematic solutions, the same expression was used with the external potential replaced by the mean-field nematic potential. This seemingly careless generalization is in fact justified. In the free energy, a factor of 1/2 should be added before the potential energy if it is a mean-field potential [cf. our Eq. (5)]. An extra factor of 2 arises, however, as the virtual deformation changes not only the local molecular distribution but also the mean-field background:  $\int \delta(\Psi U) \, d\mathbf{u} = \int \delta\Psi U \, d\mathbf{u} + \int \Psi \delta U \, d\mathbf{u} = 2 \int \delta\Psi U \, d\mathbf{u}$ . This relationship holds for a  $U$  that depends only on *local* pairwise molecular interactions [Doi and Edwards (1986); p. 355]

$$U(\mathbf{u}) = \int \Psi(\mathbf{u}') \beta(\mathbf{u}, \mathbf{u}') \, d\mathbf{u}'. \quad (16)$$

Such is the case for the Maier–Saupe potential but not for the Marrucci–Greco potential. In fact, the crux of the derivation in Sec. III is to formulate the change in the mean-field background  $\delta U_{\text{MG}}$ . If one were to insert the Marrucci–Greco potential directly into Doi and Edwards' derivation, assuming  $\int \Psi \delta U \, d\mathbf{u} = \int \delta\Psi U \, d\mathbf{u}$ , one would miss the  $(\mathbf{Q} - \nabla \nabla \mathbf{A} : \mathbf{A})$  term of Eq. (12), which, as will be shown in the next section, corresponds to the Ericksen stress in the Leslie–Ericksen theory. This is the term missing from Kupferman *et al.*'s (2000) stress tensor.

## V. THE WEAK FLOW LIMIT

The LE theory is built on the premise that the molecular orientation distribution remains at its uniaxial equilibrium form. This is asymptotically the case when the flow and the spatial distortion are both vanishingly small, a situation often referred to as the weak flow limit. Naturally, one may expect a *molecular* theory to reduce to the LE theory in this limit. Kuzuu and Doi (1983) and Kuzuu and Doi (1984) explored this limit of the original Doi theory and showed that it can be reduced to a form resembling the LE theory. Since the original Doi theory has no distortional elasticity, an external magnetic field had to be introduced to generate an asymmetric stress identifiable with Frank elasticity. The same magnetic field was used to suppress director tumbling so that a steady-state treatment could be applied. Thus, one may consider their work incomplete on those two accounts. We aim to establish rigorously a relationship between our newly developed molecular theory and the LE continuum theory. Time dependence will be assumed at the outset to allow a consistent treatment of director tumbling, and genuine distortional elasticity in our theory will afford a pertinent comparison with Frank elasticity.

### A. Rotation of the director

We first demonstrate that the weak flow limit of our kinetic equation [Eq. (1) or Eq. (3)] can be identified with the LE constitutive equation for the molecular field  $\mathbf{h}$ , which governs the rotation of the director  $\mathbf{n}$ . As Kuzuu and Doi (1983) recognized, the equilibrium state in the absence of flow is degenerate in the sense that the director orientation is indeterminate. A weak flow distorts the “shape” of the orientation distribution  $\Psi$ , whose deviation from the uniaxial state  $\Psi_{\text{eq}}$  then determines the director  $\mathbf{n}$ . In the following, we generalize Kuzuu–Doi’s analysis to allow time dependence and spatial inhomogeneity. Either a weak flow or a mild spatial distortion will perturb  $\Psi$ , and  $\mathbf{n}(t)$  will be determined by the competition of the two effects.

It is convenient to start with the Smoluchowski equation for  $\Psi$ . In view of Eq. (2), we rewrite Eq. (1) as

$$\frac{d\Psi}{dt} = \bar{D}_r \mathfrak{R} \cdot (\mathfrak{R}\Psi + \Psi \mathfrak{R} \bar{U}_{\text{MS}}) - \mathfrak{R} \cdot (\mathbf{\Gamma}\Psi), \quad (17)$$

where  $\bar{U}_{\text{MS}} = U_{\text{MS}}/kT$  and

$$\mathbf{\Gamma} = \mathbf{u} \times \boldsymbol{\kappa} \cdot \mathbf{u} - \frac{\bar{D}_r}{kT} \mathfrak{R} \bar{U}_{\text{MG}} \quad (18)$$

represents the perturbative effects of flow and distortional elasticity. The Leslie–Ericksen theory will therefore correspond to the zeroth-order solution of Eq. (17) for a vanishing  $\mathbf{\Gamma}$ , which may be regarded as the perturbation parameter.

The solution to Eq. (17) can be written as  $\Psi = \Psi_{\text{eq}} + \Psi_1$ , where  $\Psi_{\text{eq}}[\mathbf{u} \cdot \mathbf{n}(t)]$ , the zeroth-order solution, is a uniaxial distribution around the director whose rotation is to be determined, and  $\Psi_1$  is the small deviation in shape from the uniaxial ground state. Substituting this into Eq. (17) and noting that  $d\Psi/dt$  is a small quantity on the same order of magnitude as  $\mathbf{\Gamma}$ , we obtain

$$0 = \mathfrak{R} \cdot (\mathfrak{R}\Psi_{\text{eq}} + \Psi_{\text{eq}} \mathfrak{R} \bar{U}_{\text{MS}}[\Psi_{\text{eq}}]), \quad (19)$$

$$-\bar{D}_r \mathcal{G} \Psi_1 = \frac{d\Psi_{\text{eq}}}{dt} + \mathfrak{R} \cdot (\mathbf{\Gamma}\Psi_{\text{eq}}), \quad (20)$$

where the linear operator  $\mathcal{G}$  is defined by  $\mathcal{G}\phi = -\mathfrak{R} \cdot (\mathfrak{R}\phi + \Psi_{\text{eq}} \mathfrak{R} \bar{U}_{\text{MS}}[\phi] + \phi \mathfrak{R} \bar{U}_{\text{MS}}[\Psi_{\text{eq}}])$ . This perturbation problem is peculiar in that the zeroth-order ground state is degenerate and the equilibrium orientation of the director is indeterminate. The task then is not to determine the first-order perturbation  $\Psi_1$  but to determine the director  $\mathbf{n}(t)$  in the ground state  $\Psi_{\text{eq}}[\mathbf{u} \cdot \mathbf{n}(t)]$  such that the perturbation procedure is self-consistent. The mathematical procedure is outlined in Kuzuu and Doi (1983), and the self-consistency criterion may be visualized for a flow-aligning nematic as follows. If, in the ground state,  $\mathbf{n}$  differs from the preferred orientation, then even a weak flow or distortion would rotate  $\mathbf{n}$  through a finite angle to the preferred orientation because of the degeneracy in the ground state. The change in the distribution function,  $\Psi_1$ , would be finite and the perturbation would fail. Hence, the ground state  $\mathbf{n}$  has to be oriented at the Leslie angle so that it does not rotate as a result of a weak flow or distortion. Then the change in  $\Psi$  is only a small distortion of its shape and the perturbation scheme is

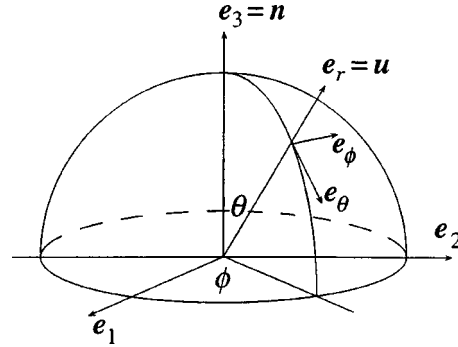


FIG. 1. The spherical coordinate system for Eq. (22).

self-consistent. For a tumbling nematic, the same argument applies although the preferred orientation  $\mathbf{n}(t)$  is now time dependent. In our case, the self-consistency condition may be written as

$$\int \psi_0 \left[ \frac{d\Psi_{\text{eq}}}{dt} + \mathfrak{R} \cdot (\Gamma \Psi_{\text{eq}}) \right] d\mathbf{u} = 0, \quad (21)$$

where  $\psi_0(\mathbf{u})$  is the eigenfunction of the Hermitian conjugate operator of  $\mathcal{G}$  corresponding to the vanishing eigenvalue. Kuzuu and Doi (1983) found a solution in the form of  $\psi_0(\theta, \phi) = \Theta \cdot \mathbf{e}_\phi g(\theta)$ , where  $\Theta$  is an arbitrary constant vector,  $\mathbf{e}_\phi$  is the unit vector for the spherical coordinate  $\phi$  (see Fig. 1) and  $g$  satisfies

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dg}{d\theta} \right) - \frac{g}{\sin^2 \theta} - \frac{dU_0}{d\theta} \frac{dg}{d\theta} = - \frac{dU_0}{d\theta}, \quad (22)$$

where  $U_0 = \bar{U}_{\text{MS}}[\Psi_{\text{eq}}]$  is the Maier–Saupe potential evaluated for the equilibrium distribution function.

The evaluation of the time dependent and distortional terms in Eq. (21) using the eigenfunction  $\psi_0$  is described in the Appendix. In the end, Eq. (21) reduces to an equation governing the rotation of the director  $\mathbf{n}$ . In terms of the rotation relative to the background fluid:  $\mathbf{N} = \dot{\mathbf{n}} - \mathbf{\Omega} \cdot \mathbf{n}$ , this equation can be written as

$$\frac{\nu k T U \mathcal{L}^2 S_2^2}{8} \nabla^2 \mathbf{n} = \frac{2S_2}{\lambda} \bar{\eta} \mathbf{N} - 2S_2 \bar{\eta} \mathbf{D} \cdot \mathbf{n}, \quad (23)$$

where  $\mathbf{\Omega} = (\boldsymbol{\kappa} - \boldsymbol{\kappa}^T)/2$ ,  $\mathbf{D} = (\boldsymbol{\kappa} + \boldsymbol{\kappa}^T)/2$ ,  $S_2 = (3\langle \cos^2 \theta \rangle - 1)/2$  is the order parameter,  $\bar{\eta} = \nu k T / 2\bar{D}_r$  is a nominal viscosity [Doi and Edwards (1986)] and

$$\lambda = 2S_2 \left( \int \Psi_{\text{eq}} g \frac{dU_0}{d\theta} d\mathbf{u} \right)^{-1} = \frac{2S_2}{\langle g (dU_0/d\theta) \rangle} \quad (24)$$

is the tumbling parameter. Equation (23) differs from the result of Kuzuu and Doi (1983) in the distortional elasticity term  $\nabla^2 \mathbf{n}$  and the time dependence of  $\mathbf{n}(t)$ . The tumbling parameter  $\lambda$  was correctly derived by Kuzuu and Doi (1983), and evaluated for the Onsager potential by Kuzuu and Doi (1984).

Comparing Eq. (23) with the LE constitutive equation [de Gennes and Prost (1993)]

$$\mathbf{h} = \gamma_1 \mathbf{N} + \gamma_2 \mathbf{D} \cdot \mathbf{n}, \quad (25)$$

we may identify the molecular field as

$$\mathbf{h} = \left(\frac{1}{8} \nu k T U \mathcal{L}^2 S_2^2\right) \nabla^2 \mathbf{n} = K \nabla^2 \mathbf{n} \quad (26)$$

and the coefficients as

$$\gamma_1 = \frac{2S_2}{\lambda} \bar{\eta}; \quad \gamma_2 = -2S_2 \bar{\eta}. \quad (27)$$

Equation (26) is exactly the molecular field of the LE theory with elastic isotropy [de Gennes and Prost (1993)]. Note that the coefficients of Eq. (23) are determined up to an arbitrary factor; we have chosen  $K$  to be the elastic constant derived from the Marrucci–Greco nematic potential [Marrucci and Greco (1991)].

It should be emphasized that although Eq. (23) does not contain the first-order perturbation  $\Psi_1$ , the director rotation  $\mathbf{n}(t)$  nonetheless depends on how the flow and the spatial inhomogeneity distort the distribution function. Mathematically, this dependence is through the eigenfunction  $\psi_0$  of the transpose operator  $\mathcal{G}^\dagger$ . Physically, any flow or spatial distortion, however weak, distorts  $\Psi$  from its uniaxial equilibrium state, and this distortion modifies the rotation of the director in a subtle way. Ignoring this effect, one could compute a ‘‘Leslie–Ericksen limit’’ of the molecular theory by simply inserting  $\Psi_{\text{eq}}$  into Eq. (1) or, equivalently, by substituting the uniaxial forms of  $\langle \mathbf{u}\mathbf{u} \rangle$  and  $\langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle$  into Eq. (3)

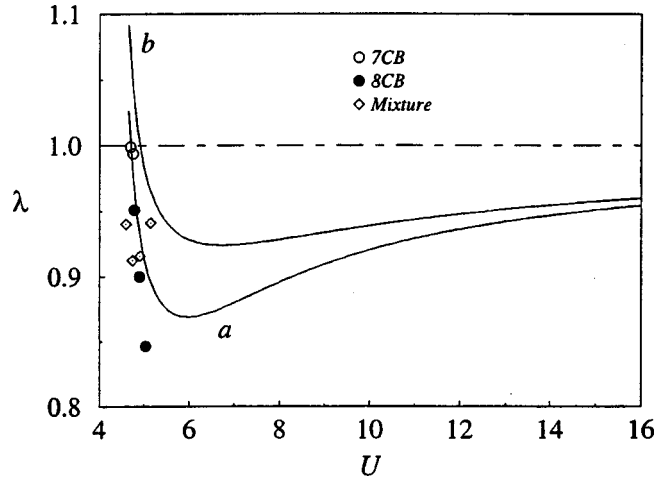
$$\langle u_i u_j \rangle = S_2 n_i n_j + \frac{1-S_2}{3} \delta_{ij}, \quad (28)$$

$$\begin{aligned} \langle u_i u_j u_k u_l \rangle = & S_4 n_i n_j n_k n_l + \frac{S_2 - S_4}{7} (n_i n_j \delta_{kl} + n_k n_l \delta_{ij} + n_i n_k \delta_{jl} + n_j n_l \delta_{ik} \\ & + n_i n_l \delta_{jk} + n_j n_k \delta_{il}) + \frac{7 - 10S_2 + 3S_4}{105} (\delta_{ij} \delta_{kl} + \delta_{jk} \delta_{li} + \delta_{ki} \delta_{jl}), \quad (29) \end{aligned}$$

where  $S_4 = \langle P_4(\cos \theta) \rangle$  is another order parameter,  $P_4$  being the fourth-order Legendre polynomial. This leads to an equation that is similar to Eq. (23) but with a different tumbling parameter

$$\lambda = \frac{14 + 5S_2 + 16S_4}{35S_2}. \quad (30)$$

This would be the tumbling parameter for a nematic that tumbles with its orientation distribution *fixed* at  $\Psi_{\text{eq}}$ —a picture at odds with the molecular theory. Mathematically, this procedure amounts to neglecting the first-order term  $\Psi_1$  (i.e., change in shape of the orientation distribution) in the perturbation scheme while the remaining term  $d\Psi_{\text{eq}}/dt$  (or  $\dot{\mathbf{n}}$ ) is of the same order. Equation (30) was first derived by Archer and Larson (1995), who also recognized its inaccuracy. Figure 2 compares the tumbling parameters according to Eqs. (24) and (30) with the measurements of Ternet *et al.* (1999) for three small-molecule liquid crystals. In Eq. (24),  $g(\theta)$  is calculated by numerically integrating Eq. (22) using the Maier–Saupe potential. The experimental values of  $\lambda$  were measured at different temperatures, which have been converted to values of the nematic strength parameter  $U$  via the Maier–Saupe potential. Equation (24) is clearly superior to Eq. (30)



**FIG. 2.** The tumbling parameter  $\lambda$  as a function of the nematic strength  $U$  for the Maier–Saupe potential. Curve (a) represents the correct  $\lambda$  in Eq. (24) whereas curve (b) corresponds to Eq. (30). The symbols represent experimental data of Ternet *et al.* (1999) for 7CB, 8CB and a commercial mixture (ZLI-3449-100) from EM Industries.

in representing the data. Archer and Larson (1995) performed a similar comparison with previous data that fall mostly in the flow-aligning regime; Eq. (30) appears to fit those data better than the exact  $\lambda$ .

### B. The stress tensor

In the LE theory, the stress is written as the sum of an Ericksen stress, which stems from the Frank elasticity for *static* distortions, and a “viscous stress.” Note that the latter is not genuinely viscous as Doi’s  $\sigma^{(V)}$  is; it is defined as the total stress minus the Ericksen stress and actually contains distortional elasticity. Thus,

$$\sigma^{\text{LE}} = -K\nabla n(\nabla n)^{\text{T}} + \alpha_1 \mathbf{D} : \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} + \alpha_2 \mathbf{n} \mathbf{N} + \alpha_3 \mathbf{N} \mathbf{n} + \alpha_4 \mathbf{D} + \alpha_5 \mathbf{n} \mathbf{n} \cdot \mathbf{D} + \alpha_6 \mathbf{D} \cdot \mathbf{n} \mathbf{n}. \quad (31)$$

With elastic isotropy, the Ericksen stress is symmetric. But the viscous stress is nonsymmetric and it is convenient to write  $\sigma^{\text{LE}}$  as the sum of its antisymmetric and symmetric parts

$$\sigma^{\text{LE}} = \frac{1}{2}(\mathbf{h} \mathbf{n} - \mathbf{n} \mathbf{h}) + \left[ -K\nabla n \cdot (\nabla n)^{\text{T}} + \frac{\alpha_2 + \alpha_3}{2}(\mathbf{n} \mathbf{N} + \mathbf{N} \mathbf{n}) + \alpha_1 \mathbf{D} : \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} + \alpha_4 \mathbf{D} + \frac{\alpha_5 + \alpha_6}{2}(\mathbf{D} \cdot \mathbf{n} \mathbf{n} + \mathbf{n} \mathbf{n} \cdot \mathbf{D}) \right]. \quad (32)$$

The antisymmetric part  $(\mathbf{h} \mathbf{n} - \mathbf{n} \mathbf{h})/2$  manifests its origin in the torque on the director when the flow drives  $\mathbf{n}$  away from its preferred orientation, which is to be collinear with  $\mathbf{h}$  everywhere. The analogy with a suspension of polar particles is obvious [Brenner (1970)].

In reducing the polymer stress tensor to the weak flow limit, one must exercise the same caution as in treating the tumbling parameter. Specifically, the uniaxial equilibrium distribution can be directly inserted only if all terms are uniformly first order. From Eqs.

(12) and (13), the antisymmetric part of  $\boldsymbol{\sigma}^{(P)}$  comes only from the distortional elastic stress and is first order. Hence, it can be reduced directly by using the uniaxial form of  $\mathbf{A}$  in Eq. (28):

$$-\frac{1}{8}\nu kTU\mathcal{L}^2(\mathbf{A}\cdot\nabla^2\mathbf{A}-\nabla^2\mathbf{A}\cdot\mathbf{A})/2 = \frac{1}{8}\nu kTU\mathcal{L}^2S_2^2[(\nabla^2\mathbf{n})\mathbf{n}-\mathbf{n}\nabla^2\mathbf{n}]/2. \quad (33)$$

This is precisely  $(\mathbf{h}\mathbf{n}-\mathbf{n}\mathbf{h})/2$  given the definition of  $\mathbf{h}$  in Eq. (26). Therefore, the antisymmetric part of  $\boldsymbol{\sigma}^{(P)}$  reduces to that of the LE stress in Eq. (32).

With an inconsequential addition of a constant ‘‘pressure,’’ the symmetric part of  $\boldsymbol{\sigma}^{(E)}$  may be written as

$$\begin{aligned} \boldsymbol{\sigma}_s^{(E)} = & 3\nu kT\left[\left(\mathbf{A}-\frac{\boldsymbol{\delta}}{3}\right)-U(\mathbf{A}\cdot\mathbf{A}-\mathbf{A}:\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle)\right. \\ & \left.-\frac{U\mathcal{L}^2}{48}\left(\mathbf{A}\cdot\nabla^2\mathbf{A}+\nabla^2\mathbf{A}\cdot\mathbf{A}-2\nabla^2\mathbf{A}:\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle+\frac{\mathbf{Q}-\nabla\nabla\mathbf{A}:\mathbf{A}}{2}\right)\right]. \end{aligned} \quad (34)$$

It is inappropriate to substitute the uniaxial forms of  $\mathbf{A}$  and  $\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle$  into the earlier equation; the nondistortional terms, representing Doi’s molecular viscoelasticity, would vanish. In reality, these terms make a first-order contribution to the stress due to the distortion of the orientation distribution, while the remaining distortional stress is also of first order. To properly account for this effect, we note that all terms except  $(\mathbf{Q}-\nabla\nabla\mathbf{A}:\mathbf{A})/2$  also appear in the kinetic equation for  $\mathbf{A}$  [Eq. (3)] and can be replaced by the flow terms. With the viscous stress  $\boldsymbol{\sigma}^{(V)}$  added, the symmetric part of the polymer stress  $\boldsymbol{\sigma}^{(P)}$  becomes

$$\begin{aligned} \boldsymbol{\sigma}_s^{(P)} = & -\bar{\eta}\left(\frac{\partial\mathbf{A}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{A}-\boldsymbol{\kappa}\cdot\mathbf{A}-\mathbf{A}\cdot\boldsymbol{\kappa}^T+2\mathbf{D}:\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle\right) \\ & +\eta_0\mathbf{D}:\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle-\frac{\nu kTU\mathcal{L}^2}{32}(\mathbf{Q}-\nabla\nabla\mathbf{A}:\mathbf{A}), \end{aligned} \quad (35)$$

where  $\bar{\eta} = \nu kT/2\bar{D}_r$  and  $\eta_0 = \nu\zeta_r/2$ . Now all terms are explicitly first order in the small perturbation parameter [cf. Eq. (18)]. Inserting the uniaxial forms of  $\mathbf{A}$  and  $\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle$ , the  $\mathcal{L}^2$  terms reduce exactly to the Ericksen stress, and the flow terms transform into the viscous stress terms in Eq. (32):

$$\begin{aligned} \boldsymbol{\sigma}_s^{(P)} = & -K\nabla\mathbf{n}\cdot(\nabla\mathbf{n})^T-S_2\bar{\eta}(\mathbf{n}\mathbf{N}+\mathbf{N}\mathbf{n})+(\eta_0-2\bar{\eta})S_4\mathbf{D}:\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{n} \\ & +\left(\frac{14-20S_2+6S_4}{105}\eta_0+\frac{14-10S_2-4S_4}{35}\bar{\eta}\right)\mathbf{D} \\ & +\left[\frac{2(S_2-S_4)}{7}\eta_0+\frac{3S_2+4S_4}{7}\bar{\eta}\right](\mathbf{D}\cdot\mathbf{n}\mathbf{n}+\mathbf{n}\mathbf{n}\cdot\mathbf{D}). \end{aligned} \quad (36)$$

Therefore, the symmetric part of the polymer stress also reduces to the LE form in the weak flow limit. The six Leslie coefficients can be extracted from comparing Eq. (36) with Eq. (32):

$$\alpha_1 = (\eta_0-2\bar{\eta})S_4, \quad (37)$$

$$\alpha_2 = -S_2 \bar{\eta} \left( 1 + \frac{1}{\lambda} \right), \quad (38)$$

$$\alpha_3 = -S_2 \bar{\eta} \left( 1 - \frac{1}{\lambda} \right), \quad (39)$$

$$\alpha_4 = \frac{14 - 20S_2 + 6S_4}{105} \eta_0 + \frac{14 - 10S_2 - 4S_4}{35} \bar{\eta}, \quad (40)$$

$$\alpha_5 = \frac{2(S_2 - S_4)}{7} \eta_0 + \frac{10S_2 + 4S_4}{7} \bar{\eta}, \quad (41)$$

$$\alpha_6 = \frac{2(S_2 - S_4)}{7} (\eta_0 - 2\bar{\eta}), \quad (42)$$

which satisfy the Parodi relation:  $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$ . Hence, the molecular theory developed here contains the phenomenological LE theory as a limiting case.

The Leslie coefficients differ from those of Kuzuu and Doi (1983) in the  $\eta_0$  terms; they neglected the viscous stress  $\sigma^{(V)}$ . Though the rigid rod is a drastically simplified model of a real LCP molecule, it is nonetheless interesting to see how the predicted viscosities compare with measured values. The predicted  $\alpha$ 's contain three parameters that need to be fitted against measured viscosities. We will use measured values of  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  to determine  $\lambda$ ,  $\eta_0$  and  $\bar{\eta}$ . From  $\lambda$ , the nematic strength  $U$  and, hence, the order parameters  $S_2$  and  $S_4$  can be obtained. Then the theoretical values of  $\alpha_4$ ,  $\alpha_5$  and  $\alpha_6$  can be calculated and compared with the measured ones. Note that  $\eta_0$  can be written as  $\eta_0 = \nu kT/2D_r^0$ , where  $D_r^0$  is the rotational diffusivity of the rods in a *dilute* solution [Doi and Edwards (1986)]. Since  $D_r^0 \gg \bar{D}_r$ , we have  $\eta_0 \ll \bar{\eta}$  and the theory predicts a negative  $\alpha_1$ . This is indeed the case for the PBG solution listed in Larson (1993), whose measured viscosities are (all viscosity values given hereafter are in poise)

$$(\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6) = (-47.24, -69.2, 0.18, 3.48, 69.3, -2.92).$$

The predicted values are:  $(\alpha_4, \alpha_5, \alpha_6) = (9.45, 43.6, -25.4)$ . Despite the rough agreement, an aphysical  $\eta_0 = -127.5$  has to be used to fit  $\alpha_1$ . This is not surprising since  $\alpha_1$  is known to be particularly difficult to measure. In fact, for the flow-aligning small-molecule nematic MBBA, both positive and negative values have been reported for  $\alpha_1$ . O'Neill (1986) showed that  $\alpha_1 = -0.181$  measured by Knepe and Schneider (1981) is more reliable than the value  $\alpha_1 = 0.065$  later cited by Larson (1993). Hence, using the following measured viscosities for MBBA

$$(\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6) = (-0.181, -0.785, -0.012, 0.832, 0.453, -0.344),$$

we have the following predictions:  $(\alpha_4, \alpha_5, \alpha_6) = (0.212, 0.691, -0.105)$ , with the more reasonable values  $\bar{\eta} = 0.795$  and  $\eta_0 = 0.493$ .

## VI. CONCLUDING REMARKS

We have added distortional elasticity to the Doi theory by using the Marrucci–Greco potential. The principal results are the evolution equation for the polymer orientation configuration [Eq. (3)] and the elastic stress tensor [Eq. (12)]. The theory is derived using

the one-constant approximation, but can be readily generalized to incorporate elastic anisotropy. It is the first theory to rationally incorporate both polymer dynamics and distortional elasticity in flowing nematic polymers, and forms a basis for investigating flow-microstructure coupling in LCPs, especially the origin and dynamics of orientational defects. In the limit of weak flow and mild spatial distortion, our molecular theory reduces to the Leslie–Ericksen theory.

A pertinent question is whether the new molecular theory has all the ingredients for predicting disclinations and the polydomain texture in flowing LCPs. Shear-flow experiments of Larson and Mead (1993) suggest that disclinations and texture refinement occur in the aftermath of the roll-cell instability, which itself is due to the interplay between flow and distortional elasticity [Larson (1993)]. The following three factors appear to be essential to this scenario: (a) the effect of flow on polymer orientation; (b) the modification of flow by the polymer stress; and (c) the effects of distortional elasticity on both flow and polymer configuration. Apparently, previous simulations of complex LCP flows failed to produce realistic textures because they did not account for all three factors properly. Using the original Doi theory, Feng and Leal (1997) realized flow-orientation coupling without distortional elasticity. Tsuji and Rey (1997) included a form of Frank elasticity but, for lack of a stress tensor, held the flow field fixed and uncoupled from the polymer orientation. The recent work of Kupferman *et al.* (2000) included both flow-orientation coupling and distortional elasticity. Though their stress tensor is incomplete, the missing ‘‘Ericksen stress’’ has no effect in a unidirectional simple shear so their results are valid. The reason that no realistic textures emerge, it appears, is that the flow and orientation are assumed to be two dimensional. Roll cells are thus prohibited. Evidently, one must have a sound constitutive theory on the one hand and apply it to the appropriate flows on the other. Our new molecular theory contains all the three elements listed earlier, and holds promise for illuminating the issue of LCP textures.

## APPENDIX

We derive Eq. (23) from Eq. (21). Integrating by parts and using the definition of  $\Gamma$  in Eq. (18), we rewrite Eq. (21) as

$$\int \psi_0 \frac{d\Psi_{\text{eq}}}{dt} d\mathbf{u} + \frac{\bar{D}_r}{kT} \langle \mathfrak{R} \bar{U}_{\text{MG}} \cdot \mathfrak{R} \psi_0 \rangle + \boldsymbol{\kappa} \cdot \langle \mathbf{u} (\mathbf{u} \cdot \mathfrak{R} \psi_0) \rangle = 0, \quad (\text{A1})$$

where  $\langle \dots \rangle$  denotes the average of the quantity using the *equilibrium* distribution function  $\Psi_{\text{eq}}$ . The third term was worked out by Kuzuu and Doi (1983)

$$\boldsymbol{\kappa} \cdot \langle \mathbf{u} \mathbf{u} \times \mathfrak{R} \psi_0 \rangle = -\boldsymbol{\Theta} \cdot \mathbf{n} \times \left( S_2 \mathbf{D} \cdot \mathbf{n} + \frac{S_2}{\lambda} \boldsymbol{\Omega} \cdot \mathbf{n} \right), \quad (\text{A2})$$

where  $\lambda$  is the tumbling parameter of Eq. (24). Hence, we only need to calculate the time-dependent term and the distortion term.

### A. Time dependency

The uniaxial distribution  $\Psi_{\text{eq}}[\mathbf{u} \cdot \mathbf{n}(t)]$  depends on time only through the rotating director  $\mathbf{n}(t)$ . If in time  $dt$ ,  $\mathbf{n}$  rotates to  $\mathbf{n}' = \mathbf{n} + d\boldsymbol{\omega} \cdot \mathbf{n}$ , then  $\Psi_{\text{eq}}$  rotates with  $\mathbf{n}$  such that:  $\Psi_{\text{eq}}(\mathbf{u} \cdot \mathbf{n}) = \Psi_{\text{eq}}(\mathbf{u}' \cdot \mathbf{n}')$  where  $\mathbf{u}' = \mathbf{u} + d\boldsymbol{\omega} \cdot \mathbf{u}$ . Hence,

$$\frac{d\Psi_{\text{eq}}}{dt} = \frac{\Psi_{\text{eq}}(\mathbf{u} \cdot \mathbf{n}') - \Psi_{\text{eq}}(\mathbf{u} \cdot \mathbf{n})}{dt} = \frac{\Psi_{\text{eq}}(\mathbf{u} \cdot \mathbf{n}') - \Psi_{\text{eq}}(\mathbf{u}' \cdot \mathbf{n}')}{dt} = -\frac{\partial \Psi_{\text{eq}}}{\partial \mathbf{u}} \cdot \frac{d\mathbf{u}}{dt}. \quad (\text{A3})$$

But  $d\mathbf{u}/dt = d\boldsymbol{\omega}/dt \times \mathbf{u} = (\mathbf{n} \times \dot{\mathbf{n}}) \times \mathbf{u}$ , integration by parts gives

$$\int \psi_0 \frac{d\Psi_{\text{eq}}}{dt} d\mathbf{u} = (\mathbf{n} \times \dot{\mathbf{n}}) \cdot \langle \mathfrak{R}\psi_0 \rangle. \quad (\text{A4})$$

Inserting Kuzuu–Doi's expression  $\psi_0 = \Theta \cdot \mathbf{e}_\phi g(\theta)$  with  $g(\theta)$  determined by Eq. (22), one gets

$$\langle \mathfrak{R}\psi_0 \rangle = \int_0^{2\pi} d\phi \int_0^\pi \Psi_{\text{eq}}(\theta) \sin \theta \left( \frac{dg}{d\theta} \mathbf{e}_\phi \mathbf{e}_\phi + g \mathbf{e}_\theta \mathbf{u} + g \cot \theta \mathbf{e}_\theta \mathbf{e}_\theta \right) \cdot \Theta d\theta. \quad (\text{A5})$$

Integrating the dyads of unit vectors over the azimuthal angle  $\phi$ , one eventually arrives at

$$\int \psi_0 \frac{d\Psi_{\text{eq}}}{dt} d\mathbf{u} = \Theta \cdot (\mathbf{n} \times \dot{\mathbf{n}}) \frac{S_2}{\lambda}. \quad (\text{A6})$$

The final steps of the derivation utilize Eq. (19) for  $\Psi_{\text{eq}}$  and Eq. (22) for  $g$ , and are similar to those in the Appendix to Kuzuu and Doi (1983).

## B. Distortional elasticity

In the weak distortion limit,  $\tilde{U}_{\text{MG}}$  is a small quantity so that the equilibrium form of  $\mathbf{A}$  can be used. From Eqs. (2) and (28):

$$\mathfrak{R}\tilde{U}_{\text{MG}} = -\frac{1}{16}kTU\mathcal{L}^2 \mathfrak{R}(\mathbf{u}\mathbf{u}) : \nabla^2 \mathbf{A} = -\frac{1}{16}kTU\mathcal{L}^2 S_2 \mathfrak{R}(\mathbf{u}\mathbf{u}) : \nabla^2 (\mathbf{n}\mathbf{n}). \quad (\text{A7})$$

Using again  $\psi_0 = \Theta \cdot \mathbf{e}_\phi g(\theta)$  and integrating over  $\phi$ , one gets

$$\frac{\bar{D}_r}{kT} \langle \mathfrak{R}\tilde{U}_{\text{MG}} \mathfrak{R}\psi_0 \rangle = -\frac{1}{8} \bar{D}_r U \mathcal{L}^2 S_2^2 \Theta (\mathbf{n} \nabla^2 \mathbf{n}). \quad (\text{A8})$$

Finally, substituting Eqs. (A2), (A6), and (A8) into Eq. (A1) gives rise to Eq. (23).

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