A hydrodynamic theory for solutions of nonhomogeneous nematic liquid crystalline polymers with density variations

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Abstract

The hydrodynamic theory developed in [31] for solutions of nonhomogeneous nematic liquid crystalline polymers (LCPs) of spheroidal molecular configurations is extended to account for the translational diffusion and related spatial density variation. The new theory augments the effect of the density variation to the intermolecular potential, Smoluchowski equation and the elastic stress. It accounts for the molecular aspect ratio as well as the finite range molecular interaction so that it is applicable to liquid crystals ranging from the rodlike liquid crystal at large aspect ratios to the discotic one at small aspect ratios. It also exhibits enhanced shape effects in the viscous stress and warrants a positive entropy production, thereby, the second law of thermodynamics. Moment averaged, approximate, mesoscopic theories for complex flow simulations are obtained via closure approximations. In weak distortional elasticity, weak translational diffusion, and weak flow limit, the theory yields the torque balance equation of the well-known Ericksen-Leslie theory.

1 Introduction

Nematic phase in liquid crystals is the simplest mesophase in which an orientational order exists, but there is no translational order [1, 2]. Molecules of a variety of molecular configurations may form the simple mesophase at certain concentration or temperature. These include the two drastically different configurations: rodlike and discotic liquid crystals. Most of the hydrodynamical theories formulated for liquid crystal materials are based on the rodlike molecules, which include the well known Leslie-Ericksen (LE) theory [3], suitable to low molar weight liquid crystals, the Doi kinetic theory[4] and a variety of tensor based theories such as the Hand's theory [5], Beris and Edwards' (BE) theory formulated through Poisson brackets [6], and Tsuji and Rey's (TR) phenomenological theory [7], etc., perceived to be applicable to high molar weight liquid crystalline polymers. Although the LE theory was first developed for rodlike liquid crystals, it has also been applied to discotic liquid crystals [8, 9]. Recently, Singh and Rey used the TR theory to model homogeneous flows of discotic liquid crystalline polymers by reversing the sign of a phenomenological "shape parameter" and showed some promising results[10]. This approach appears to be not only convenient, but also reasonable from a molecular point of view. The kinetic theory for spheroidal liquid crystal polymers developed in [31] aimed at providing a rigorous justification for the convenient practice and relating the macroscopic parameters to the microscopic ones.

In the theory, the LCP molecules are modeled as rigid spheroids of equal size so that the theory could be used to model a series of configurations of polymeric liquid crystal molecules in the neighborhood of spheroids. This approach has been undertaken by several pioneers in the past. Isihara studied the effect of the spheroidal shape on the phase transition behavior of colloidal solutions[11]. Takserman-Krozer and Ziabicki studied the behavior of polymer solutions in a velocity field by treating polymer molecules as rigid ellipsoids in dilute solutions[12]. In Helfrich's molecular theory for nematic liquid crystals, the molecules are treated as equally and rigidly oriented ellipsoids[13]. In an effort to address the relationship between the Doi kinetic theory and the Leslie-Ericksen theory, Kuzuu and Doi generalized the Doi theory for homogeneous LCPs to account for the finite aspect ratio of spheroidal molecules[14] and gave the Leslie viscosity coefficients in terms of the uniaxial order parameter and a few physical parameters in the molecular theory, including the aspect ratio of the spheroid. Baalss and Hess also treated liquid crystal molecules as spheroids in their liquid crystal theory[15]. Baalss and Hess' theory predicts the liquid crystal is always flow aligning which has since been proven to be limited since tumbling has been observed in many LC flows. On the other hand, the Kuzuu and Doi theory handles both flow aligning and tumbling at different aspect ratios and polymer concentrations.

The theory developed in [31] extends the Kuzuu and Doi theory to flowing systems of nonhomogeneous liquid crystalline polymers by considering the long range elastic interaction through an extended anisotropic intermolecular potential. It also generalizes the existing Marrucci-Greco theory to a series of spheroidal LCP configurations through a shape parameter. However, the translational diffusion was neglected in the study for highlighting the effect of the molecular shape and the anisotropic elasticity in that paper. As we all know, however, that the spatial nonhomogeneous structure of LCPs is also correlated to the translational diffusion of LCP molecules. So, for completeness, a theory for nonhomogeneous LCPs must also account for the translational diffusion. This paper aims at adding the effect of the translational diffusion to the previous theory to explore the impact of the translational diffusion and the related density variation to the intermolecular potential, Smoluchowski equation, and the stress tensor.

It is shown in [31] that the torque balance equation of the Ericksen-Leslie theory can be recovered from the kinetic theory in the limit of weak flow and weak distortional elasticity while translation diffusion is neglected. In this paper, we will show the same torque balance equation can be derived from the theory only when the translational diffusion is weak. When translational diffusion competes at the same order with the rotary diffusion, the current theory yields a torque balance equation with up to fourth order spatial derivatives, which is indeed an extension of the Ericksen-Leslie theory where only up to second derivatives are present. ,

The rest of the paper consists of the derivation of the intermolecular potential, the Smoluchowski equation, the elastic stress tensor, the proof of the second law of thermodynamic theory and the reduction to Ericksen-Leslie torque balance equation.

2 Kinetic theory for LCPs of spheroidal molecules

We first extend the intermolecular potential developed in [31] that accounts for the intermediate to long range molecular interaction for liquid crystalline polymers of the spheroidal configuration with finite aspect ratios and derive one of its approximations through the gradient expansion of the number density function (defined below) [16] Then, we extend the Smoluchowski equation in the Doi kinetic theory for rodlike LCPs to accommodate the spheroidal shape of the liquid crystalline polymer and translational diffusion, and derive a consistent stress expression using the virtual work principle [2, 4]. Finally, we prove the theory satisfies the second law of thermodynamics in isothermal flows.

2.1 Intermolecular potential

We assume all LCP molecules are of the same spheroidal configuration immersed in viscous solvent. With the axis of revolution of the spheroid identified with the z-axis in the Cartesian coordinate (x, y, z), the surface of the spheroid is represented by:

$$\begin{aligned} x &= c \sin\alpha \cos\beta, \\ y &= c \sin\alpha \sin\beta, \\ z &= b \cos\alpha, \\ 0 &\le \alpha \le \pi, 0 \le \beta < 2\pi, \end{aligned} \tag{1}$$

where b is the length of the semi-axis in the axis of revolution (identified with $\mathbf{e}_z$ now) and c is that in the transverse direction. The aspect ratio of the spheroid is then defined as

$$r = \frac{b}{c}. \tag{2}$$

Let $f(\mathbf{m}, \mathbf{x}, t)$ be the number density function (ndf) of the LCP molecules of the spheroidal shape in their axis of revolution $\mathbf{m}$ ($||\mathbf{m}|| = 1$) with center of mass at location $\mathbf{x}$ and time t. An intermolecular potential for the spheroidal LCPs with finite range molecular interaction was derived in [31]

$$V_i(\mathbf{m}) = \frac{kT}{|S||dV|} \int_S \int_{dV} \int_{||\mathbf{m}'||=1} B(\mathbf{m}, \mathbf{m}') f(\mathbf{m}', \mathbf{x} + \mathbf{s} + \mathbf{r}, t) d\mathbf{m}' d\mathbf{r} d\mathbf{s}, \tag{3}$$

where $\nu = \int_{||\mathbf{m}||=1} f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m}$ is the number density of the LCP molecule per unit volume, the excluded volume formula is given by

$$B(\mathbf{m}, \mathbf{m}') = 2v + 2c^2 br \int_0^\pi \int_0^{2\pi} \frac{\sqrt{(\sin^2\alpha + r^2\cos^2\alpha)}}{(\sin^2\theta' + r^2\cos^2\theta')^2} \sin\alpha d\alpha d\beta, \tag{4}$$

in which v is the volume of the spheroidal LCP with the semi-axes (b, c)[11], S is the surface of the spheroid with the axis of revolution $\mathbf{m}$, dV is a sphere of radius l centered at $\mathbf{0}$,

$$\begin{aligned} \cos\theta' &= \mathbf{w} \cdot \mathbf{m}', \\ \mathbf{w} &= \cos\alpha \mathbf{m} + \sin\alpha \cos\beta \mathbf{e}_1 + c \sin\alpha \sin\beta \mathbf{e}_2, \end{aligned} \tag{5}$$

with $\mathbf{e}_1$ and $\mathbf{e}_2$ the two orthonormal vectors perpendicular to $\mathbf{m}$, $|dV|$ denotes the volume of dV, $|S|$ the surface area of S, k is the Boltzmann constant and T is the absolute temperature. We note that $\mathbf{w}$ is the unit normal of the tangent plane at the contacting point of the two spheroidal molecules of the axis of revolution $\mathbf{m}$ and $\mathbf{m}'$, respectively, and parameterized relative to $\mathbf{m}$.

The intermolecular potential defined by (3) is nonlocal. In particular, the excluded volume given in (4) is too complicated for a hydrodynamical theory of liquid crystals to be used for complex flow simulations. We thus seek an approximate excluded volume expression that would lead to a less complex intermolecular potential.

We seek the Legendre polynomial expansion of the excluded volume (4),

$$B(\mathbf{m},\mathbf{m}') = 2v + B_0(r) - \textstyle\sum_{l=1}^{\infty} B_l(r) P_{2l}(\cos\angle\mathbf{m}\mathbf{m}'), \tag{6}$$

in which $\angle\mathbf{m}\mathbf{m}'$ is the angle between $\mathbf{m}$ and $\mathbf{m}'$.

The first two coefficients B_0 and B_1 are given in the work of Isihara[11],

$$\begin{aligned}
&B_0 = 2\pi bc^2 r[\tfrac{1}{r} + \tfrac{r}{\sqrt{r^2-1}} arcsin(\tfrac{\sqrt{r^2-1}}{r})]\ \ [1 + \tfrac{1}{2r\sqrt{r^2-1}} ln(\tfrac{r+\sqrt{r^2-1}}{r-\sqrt{r^2-1}})],\\
&B_1 = 8\pi c^2 b r h_3(r) h_4(r),\\
&h_3 = \tfrac{1}{4}[\tfrac{arcsin(\sqrt{1-r^2})}{\sqrt{1-r^2}} - \tfrac{3arcsin(\sqrt{1-r^2})}{4\sqrt{1-r^2}^3} + \tfrac{3r}{4(1-r^2)} - \tfrac{r}{2}],\\
&h_4 = \tfrac{5}{2}[\tfrac{3}{2(1-r^2)} + 1 + \tfrac{1-r^2}{r^2} - \tfrac{1}{4\sqrt{1-r^2}}(1 + \tfrac{3}{1-r^2}) ln\tfrac{1+\sqrt{1-r^2}}{1-\sqrt{1-r^2}}].
\end{aligned} \tag{7}$$

Note that

$$\cos^2\angle\mathbf{m}\mathbf{m}' = (\mathbf{m}\cdot\mathbf{m}')^2 = \mathbf{m}\mathbf{m} : \mathbf{m}'\mathbf{m}', \tag{8}$$

where $\mathbf{m}\mathbf{m}$ is the outer (tensor) product of $\mathbf{m}$ with $\mathbf{m}$, "$\cdot$" denotes the contraction operation between two tensors over a pair of indices. In this paper, the number of dots in tensor operations denotes the number of pairs of indices contracted therein. If we truncate series expansion (6) at the second order, the excluded volume is approximated by

$$B(\mathbf{m},\mathbf{m}') \approx 2v + B_0(r) + \tfrac{B_1(r)}{2} - \tfrac{3}{2} B_1(r)\mathbf{m}\mathbf{m} : \mathbf{m}'\mathbf{m}'. \tag{9}$$

With this, we arrive at an approximate intermolecular potential

$$\begin{aligned}
&V_i \approx kT(2v + B_0(r) + \tfrac{B_1(r)}{2})\tfrac{1}{|dV||S|}\textstyle\int_S\int_{dV}\int_{\|\mathbf{m}'\|=1} f(\mathbf{m}',\mathbf{x}+\mathbf{s}+\mathbf{r},t)d\mathbf{m}'d\mathbf{r}d\mathbf{s} -\\
&\tfrac{3}{2}kTB_1\mathbf{m}\mathbf{m} : [\tfrac{1}{|dV||S|}\textstyle\int_S\int_{dV}\int_{\|\mathbf{m}'\|=1} \mathbf{m}'\mathbf{m}' f(\mathbf{m}',\mathbf{x}+\mathbf{s}+\mathbf{r},t)d\mathbf{m}'d\mathbf{r}d\mathbf{s}],
\end{aligned} \tag{10}$$

which extends the intermolecular potential derived in [31] to account for the spatial variation of the ndf. The Legendre polynomial approximation up to the quadratic order given in (9) turns out to be an excellent approximation to (4) for all values of r as shown in [31].

Following Marrucci and Greco's approach[16], we expand the probability density function $f(\mathbf{m}',\mathbf{x}+\mathbf{s}+\mathbf{r},t)$ at $\mathbf{x}$ in its Taylor series,

$$f(\mathbf{m}',\mathbf{x}+\mathbf{s}+\mathbf{r},t) = f(\mathbf{m}',\mathbf{x},t) + \nabla f\cdot(\mathbf{s}+\mathbf{r}) + \tfrac{1}{2}\nabla\nabla f : (\mathbf{s}+\mathbf{r})(\mathbf{s}+\mathbf{r}) + \cdots, \tag{11}$$

where ∇ is the gradient operator and the derivatives are evaluated at $(\mathbf{m}', \mathbf{x}, t)$. Neglecting the terms higher than the second order, we obtain a simplified intermolecular potential for spheroidal LCPs,

$$
\begin{aligned}
&V_{si} = AkT(1 + (\tfrac{l^2}{10} + \tfrac{L_1^2}{8})\Delta + \tfrac{L_2 - L_1}{8}\mathbf{mm} : \nabla\nabla)\nu - \\
&\tfrac{3NkT}{2}[\mathbf{I} + (\tfrac{l^2}{10} + \tfrac{L_1}{8})\Delta + \tfrac{L_2 - L_1}{8}\mathbf{mm} : \nabla\nabla]\langle\mathbf{mm}\rangle : \mathbf{mm},
\end{aligned}
\tag{12}
$$

where

$$
\begin{aligned}
&A = (2v + B_0(r) + \tfrac{B_1(r)}{2}), \\
&N = B_1(r), \\
&D_1 = 1 + \tfrac{r^2}{\sqrt{1-r^2}} arcsinh(\tfrac{\sqrt{1-r^2}}{r}), \\
&L_1 = \tfrac{2bc}{r} - \tfrac{L_2}{2r^2}, \\
&L_2 = \tfrac{2bcr}{D_1}[\tfrac{1}{1-r^2} - \tfrac{r^2}{2(1-r^2)} - \tfrac{r^4}{2(1-r^2)^{3/2}} arcsinh(\tfrac{1-r^2}{r})], \\
&\Delta = \nabla \cdot \nabla, \qquad \text{(Laplacian)}.
\end{aligned}
\tag{13}
$$

The bracket $\langle\rangle$ denotes an average over all possible molecular directions at $(\mathbf{x}, t)$ with respect to the number density function f:

$$\langle(\bullet)\rangle = \int_{||\mathbf{m}||=1} (\bullet) f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m}. \tag{14}$$

Following [31, 16], we introduce two new parameters $\mathcal{L}$ and L, of the unit of length, to denote the finite range of molecular interaction:

$$\mathcal{L} = \sqrt{24[\tfrac{l^2}{10} + \tfrac{L_1}{8}]}, \quad L = \sqrt{3(L_2 - L_1)}. \tag{15}$$

Then,

$$
\begin{aligned}
&V_{si} = AkT(1 + \tfrac{\mathcal{L}^2}{24}\Delta + \tfrac{L^2}{24}\mathbf{mm} : \nabla\nabla)\nu \\
&-\tfrac{3NkT}{2}(\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta + \tfrac{L^2}{24}\mathbf{mm} : \nabla\nabla)\langle\mathbf{mm}\rangle : \mathbf{mm}.
\end{aligned}
\tag{16}
$$

In our definition of the intermolecular potential, we note that $\mathcal{L}$ is still positive even when the length parameter l is assigned zero in (16).

The first term in (16) corresponds to the short and long range elastic effect caused by the spatial variation of the number density. Both A and N approach ∞ as $|a| \to 1^-$ and N equals zero at $a = 0$ since $B(r = 1) = 0$. The behavior of N indicates that the strength of the intermolecular potential weakens as $|a|$ decreases for spheroidal molecules with fixed volumes and constant polymer number density [31].

Notice that both L_1 and L_2 are positive for all values of the aspect ratio r;however, L^2 is positive for $r > 1$ and negative for $0 < r < 1$ [31].

Free energy and the symmetric, effective intermolecular potential

Let's denote a finite volume of the LCP material by G in R^3. The free energy for the volume of LCPs is then given by [4, 14]

$$A[f] = kT \int_G \int_{\|\mathbf{m}\|=1} [f ln f - f + V_H f + \tfrac{1}{2kT} f V_{si}] d\mathbf{m} d\mathbf{x}, \tag{17}$$

where V_H is the potential for the external field. Through integration by part, the free energy can be rewritten into

$$\begin{aligned} A[f] = kT \int_G \int_{\|\mathbf{m}\|=1} [f ln f - f + V_H f + \tfrac{1}{2kT} f V_{ei}] d\mathbf{m} d\mathbf{x} + \tfrac{AkTL^2}{48} [\int_{\partial G} [(\mathbf{M} \cdot \nabla \nu - \\ nu \nabla \cdot \mathbf{M}) \cdot \mathbf{n}_n] ds - \tfrac{NkTL^2}{32} \int_{\partial G} [(\mathbf{M}_4 \vdots \nabla \mathbf{M}) \cdot \mathbf{n}_n - (\nabla \cdot \mathbf{M}_4) \vdots \mathbf{M} \mathbf{n}_n] ds, \end{aligned} \tag{18}$$

where $\mathbf{n}_n$ is the external unit normal of ∂G, the boundary of G, and

$$\begin{aligned} V_{ei} = AkT[(1 + \tfrac{\mathcal{L}^2}{24} \Delta + \tfrac{L^2}{48} \mathbf{mm} : \nabla\nabla) \nu + \tfrac{L^2}{48} \nabla\nabla : \mathbf{M}] - \tfrac{3NkT}{2} [(\mathbf{I} + \tfrac{\mathcal{L}^2}{24} \Delta) \mathbf{M} : \mathbf{mm} + \\ \tfrac{L^2}{48} (\mathbf{mmmm} :: \nabla\nabla\mathbf{M} + \mathbf{mm} \nabla\nabla :: \mathbf{M}_4)], \quad \mathbf{M} = \langle \mathbf{mm} \rangle, \quad \mathbf{M}_4 = \langle \mathbf{mmmm} \rangle, \end{aligned} \tag{19}$$

$\mathbf{M}$ and $\mathbf{M}_4$ are the second and fourth moments of $\mathbf{m}$ with respect to the ndf f, respectively. Neglecting the contribution from the surface integrals, we conclude that the contribution of V_{ei} to the bulk free energy is equivalent to that of V_{si}. However, the symmetrization of the intermolecular potential is essential for a well-posed hydrodynamic theory, in which the positive entropy production and therefore the second law of thermodynamics is warranted. We thus name V_{ei} the effective intermolecular potential and adopt it in the following derivations. In fact, the effective intermolecular potential defines the chemical potential in its usual form:

$$\mu = \frac{\delta A}{\delta f} = kT ln f + V_{ei} + kT V_H. \tag{20}$$

Next, we derive the Smoluchowski equation for the ndf f consistent with the spheroidal LCPs.

2.2 Smoluchowski equation (kinetic equation)

For a rigid spheroidal suspension in a viscous solvent, Jeffrey calculated the velocity of its axis of revolution $\mathbf{m}$ as follows[18]:

$$\dot{\mathbf{m}} = \mathbf{\Omega} \cdot \mathbf{m} + a[\mathbf{D} \cdot \mathbf{m} - \mathbf{D} : \mathbf{mmm}], \tag{21}$$

where, $\mathbf{D}$ and $\mathbf{\Omega}$ are the rate of strain tensor and vorticity tensor, defined by

$$\mathbf{D} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T), \ \mathbf{\Omega} = \frac{1}{2}(\nabla \mathbf{v} - \nabla \mathbf{v}^T), \tag{22}$$

respectively, $\mathbf{v}$ is the velocity vector field for the flowing LCP, $\nabla \mathbf{v} = \frac{\partial \mathbf{v}_i}{\partial \mathbf{x}_j}$ is the velocity gradient, and the superscript T denotes the transpose of a second order tensor; $-1 \leq a \leq 1$ is a *shape parameter* related to the molecular aspect ratio r by

$$a = \frac{r^2 - 1}{r^2 + 1}. \tag{23}$$

$a = 1$: the spheroid degenerates into an infinitely thin rod; $a = 0$: it is a sphere; $a = -1$: it deforms into an infinitely thin disk. Following the development of the Smoluchowski equation for polymer solutions by Doi and Edwards [4] with both the rotary and translational diffusion included and utilizing the result of Jeffrey's (21), we arrive at the Smoluchowski (kinetic) equation for the number density function $f(\mathbf{m}, \mathbf{x}, t)$ for spheroidal LCPs:

$$\begin{aligned} &\tfrac{df}{dt} = \tfrac{\partial}{\partial \mathbf{x}} \cdot [(D_{\|}(a)\mathbf{mm} + D_{\perp}(a)(\mathbf{I} - \mathbf{mm})) \cdot (\tfrac{\partial f}{\partial \mathbf{x}} + \tfrac{f}{kT}\tfrac{\partial V}{\partial \mathbf{x}})] + \\ &\mathcal{R} \cdot [D_r(\mathbf{m}, a)(\mathcal{R} f + \tfrac{1}{kT} f \mathcal{R} V)] - \mathcal{R} \cdot [\mathbf{m} \times \dot{\mathbf{m}} f], \end{aligned} \tag{24}$$

where

$$D_r(\mathbf{m}, a) = \hat{D}_r(a)(\tfrac{1}{\nu^2} \textstyle\int_{\|\mathbf{m}'\|=1} \|\mathbf{m} \times \mathbf{m}'\| f(\mathbf{m}', \mathbf{x}, t) d\mathbf{m}')^{-2} \tag{25}$$

is the rotary diffusivity, inversely proportional to the relaxation time due to molecular rotation, $\hat{D}_r(a)$ a shape-dependent rotary diffusion constant, $D_{\|}(a)$ and $D_{\perp}(a)$ are shape-dependent, translational diffusivities characterizing the translational diffusion in the direction parallel and perpendicular to $\mathbf{m}$, respectively, V is the potential including the intermolecular potential V_{ei} and the external potential (magnetic and/or electric field effect) V_H,

$$V = V_{ei} + \nu k T V_H, \tag{26}$$

$\frac{\partial}{\partial \mathbf{x}} = \nabla$ and $\mathcal{R} = \mathbf{m} \times \frac{\partial}{\partial \mathbf{m}}$ are the spatial and the rotational gradient operator, respectively, and $\frac{d}{dt}(\bullet)$ denotes the material derivative $\frac{\partial}{\partial t}(\cdot) + \mathbf{v} \cdot \nabla(\cdot)$. In the Smoluchowski equation, rotary convection and diffusion as well as spatial (translational) convection and diffusion are all included. Due to the presence of the translational diffusion, the number density ν may no longer be a constant.

By averaging over the configurational space of $\mathbf{m}$ with respect to the ndf f, we have the evolutionary equation for the number density ν:

$$\begin{aligned}
&\tfrac{d\nu}{dt} = D_\perp \Delta\nu + (D_{||} - D_\perp)\nabla_i\nabla_j \mathbf{M}_{ij} + (D_{||} - D_\perp)\nabla_k[A\mathbf{M}_{kl}\nabla_l(\nu + \tfrac{\mathcal{L}^2}{24}\Delta\nu) + \\
&\tfrac{AL^2}{48}(\mathbf{M}_{4klmn}\nabla_l\nabla_m\nabla_n\nu + \mathbf{M}_{kl}\nabla_l\nabla_m\nabla_n\mathbf{M}_{mn}) - \tfrac{3N}{2}(\mathbf{M}_{4klmn}\nabla_l(\mathbf{M}_{mn} + \tfrac{\mathcal{L}^2}{24}\Delta\mathbf{M}_{mn}) + \\
&\tfrac{L^2}{48}(\mathbf{M}_{6klmnij}\nabla_l\nabla_m\nabla_n\mathbf{M}_{ij} + \mathbf{M}_{4klmn}\nabla_l\nabla_i\nabla_j\mathbf{M}_{4mnij}))] + \\
&D_\perp\nabla_k[A\nu\nabla_k((1 + \tfrac{\mathcal{L}^2}{24}\Delta)\nu) + \tfrac{AL^2}{48}(\mathbf{M}_{mn}\nabla_k\nabla_m\nabla_n\nu + \nu\nabla_k\nabla_m\nabla_n\mathbf{M}_{mn}) - \\
&\tfrac{3N}{2}(\mathbf{M}_{mn}\nabla_k(\mathbf{M}_{mn} + \tfrac{\mathcal{L}^2}{24}\Delta\mathbf{M}_{mn}) + \tfrac{L^2}{48}(\mathbf{M}_{4mnij}\nabla_k\nabla_m\nabla_n\mathbf{M}_{ij} + \\
&\mathbf{M}_{mn}\nabla_k\nabla_i\nabla_j\mathbf{M}_{4mnij}))],
\end{aligned} \tag{27}$$

where

$$\mathbf{M}_6 = \langle\mathbf{mmmmmm}\rangle \tag{28}$$

is the sixth moment of $\mathbf{m}$ with respect to the ndf and indices are used wherever necessary for clarity.

Like in most kinetic theories, the mesoscopic, or average, internal orientational properties of nematic liquid crystals are defined in terms of the moments of $\mathbf{m}$ with respect to the probability density function $\frac{1}{\nu}f$ (normalized ndf) [4]. Often, one uses the normalized second moment $\frac{1}{\nu}\mathbf{M}$ or its deviatoric part $\mathbf{Q}$ (a second order, symmetric, traceless tensor $\mathbf{Q}$) known as the orientation tensor (or structure tensor):

$$\mathbf{Q} = \tfrac{1}{\nu}\langle\mathbf{mm}\rangle - \mathbf{I}/3. \tag{29}$$

Taking the second moment of $\mathbf{m}$ in the configurational space of $\mathbf{m}$ with respect to the ndf governed by the kinetic equation (24), we arrive at the mesoscale *orientation tensor equation*

$$
\begin{aligned}
&\{\tfrac{d}{dt}\mathbf{M} - \Omega\cdot\mathbf{M} + \mathbf{M}\cdot\Omega - a[\mathbf{D}\cdot\mathbf{M} + \mathbf{M}\cdot\mathbf{D}]\}_{\alpha\beta} = \{-2a\mathbf{D}:\mathbf{M}_4 - 6D_r^0[\mathbf{M} - \tfrac{\nu}{3}\mathbf{I} - \\
&\tfrac{1}{6kT}(\langle\mathbf{m}\times\mathcal{R}V\mathbf{m}\rangle + \langle\mathbf{mm}\times\mathcal{R}V\rangle)] + (D_{||} - D_\perp)\nabla\nabla:\mathbf{M}_4 + D_\perp\Delta\mathbf{M}\}_{\alpha\beta} + \\
&\tfrac{1}{kT}(D_{||} - D_\perp)\nabla_i\langle\mathbf{m}_\alpha\mathbf{m}_\beta\mathbf{m}_i\mathbf{m}_j\nabla_j V\rangle + \tfrac{1}{kT}D_\perp\nabla_i\langle\mathbf{m}_\alpha\mathbf{m}_\beta\nabla_i V\rangle \\
&= \{-2a\mathbf{D}:\mathbf{M}_4 - 6D_r^0[\mathbf{M} - \tfrac{\nu}{3}\mathbf{I} - \tfrac{N}{2}((\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M}\cdot\mathbf{M} + \mathbf{M}\cdot(\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M}) + \\
&N(\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M}:\mathbf{M}_4 - \tfrac{NL^2}{96}((\nabla\nabla\mathbf{M})\vdots\mathbf{M}_4 + ((\nabla\nabla\mathbf{M})\vdots\mathbf{M}_4)^T + \\
&\mathbf{M}_4\vdots\nabla\nabla\mathbf{M} + (\mathbf{M}_4\vdots\nabla\nabla\mathbf{M})^T + \mathbf{M}\nabla\nabla\vdots\mathbf{M}_4 + (\mathbf{M}\nabla\nabla\vdots\mathbf{M}_4)^T - \\
&4\mathbf{M}_6::\nabla\nabla\mathbf{M} - 2\mathbf{M}_4\nabla\nabla::\mathbf{M}_4) + \tfrac{AL^2}{144}(\nabla\nabla\nu\cdot\mathbf{M} + \mathbf{M}\cdot\nabla\nabla\nu - 2\nabla\nabla\nu:\mathbf{M}_4]\}_{\alpha\beta} + \\
&(D_{||} - D_\perp)\nabla_i\nabla_j\mathbf{M}_{4ij\alpha\beta} + D_\perp\Delta\mathbf{M}_{\alpha\beta} + (D_{||} - D_\perp)\nabla_i[A(\mathbf{M}_{4\alpha\beta ij}(1 + \tfrac{\mathcal{L}^2}{24}\Delta)\nabla_j\nu + \\
&\tfrac{L^2}{48}(\mathbf{M}_{4\alpha\beta ij}\nabla_j\nabla_k\nabla_l\mathbf{M}_{kl} + \mathbf{M}_{6\alpha\beta ijkl}\nabla_j\nabla_k\nabla_l\nu)) - \tfrac{3N}{2}(\mathbf{M}_{6\alpha\beta ijkl}\nabla_j(1 + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M}_{kl} + \\
&\tfrac{L^2}{48}\mathbf{M}_{8\alpha\beta ijklmn}\nabla_j\nabla_m\nabla_n\mathbf{M}_{kl} + \mathbf{M}_{6\alpha\beta ijkl}\nabla_j\nabla_m\nabla_n\mathbf{M}_{4klmn})] + \\
&D_\perp\nabla_i[A(\mathbf{M}_{\alpha\beta}(1 + \tfrac{\mathcal{L}^2}{24}\Delta)\nabla_i\nu + \tfrac{L^2}{48}(\mathbf{M}_{\alpha\beta}\nabla_i\nabla_k\nabla_l\mathbf{M}_{kl} + \mathbf{M}_{4\alpha\beta kl}\nabla_i\nabla_k\nabla_l\nu)) - \\
&\tfrac{3N}{2}(\mathbf{M}_{4\alpha\beta kl}(1 + \tfrac{\mathcal{L}^2}{24}\Delta)\nabla_i\mathbf{M}_{kl} + \tfrac{L^2}{48}(\mathbf{M}_{6\alpha\beta klmn}\nabla_i\nabla_k\nabla_l\mathbf{M}_{mn} + \\
&\mathbf{M}_{4\alpha\beta kl}\nabla_i\nabla_m\nabla_n\mathbf{M}_{4klmn}))] + D_r^0[\langle\mathbf{m}\times\mathcal{R}V_H\mathbf{m}\rangle + \langle\mathbf{mm}\times\mathcal{R}V_H\rangle].
\end{aligned}
\tag{30}
$$

where D_r^0 is an averaged rotary diffusivity resulted from the averaging process[4], which is assumed a shape dependent constant in this study. We remark that the averaged rotary diffusivity is also possibly orientation dependent; then the "tube-dilation" effect can be modeled by replacing the constant rotary diffusivity D_r^0 by[4]

$$\frac{D_r^0}{(1 - \frac{3}{2}\mathbf{Q}:\mathbf{Q})^2}. \tag{31}$$

We note that in the equation of ν up to sixth order tensors are included. Up to eighth order tensors are present in the orientation tensor equation for $\mathbf{M}$. If we were to choose the fundamental variables to be ν and $\mathbf{M}$, closure approximation would have to be employed to represent the higher moments in terms of the zeroth and second moment. With the kinetic equation, we next derive the consistent stress tensor.

2.3 Derivation of the stress tensor

We treat the LCP system as incompressible. Then, the stress tensor consists of three parts: the pressure $-p\mathbf{I}$, the viscous stress τ^v and the elastic stress τ^e. We derive the elastic stress first by applying the virtual work principle [2, 4] on a finite volume of the LCP material denoted by G called control volume. In order to take into account the nonlocal effect of the intermolecular potential (19), the virtual deformation field $\delta\epsilon = \delta\nabla\mathbf{x}$, the variation of all tensor fields and their first order derivatives are assumed zero at the boundaries of the control volume [19].

The free energy of the LCP system in the material volume is given by (18). Consider a virtual deformation $\delta\epsilon$ of the material in G. According to the virtual work principle[4], the virtual work that the exterior must do to the material to realize $\delta\epsilon$ is

$$\delta W = \int_G \tau^e : \delta\epsilon d\mathbf{x}, \tag{32}$$

where τ^e is the elastic part of extra stress. In response to the virtual deformation $\delta\epsilon$, the variation of f is calculated from the kinetic equation by neglecting all terms except for the convection terms [4]:

$$\delta f = \frac{df}{dt}\delta t = -\mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f)\delta t. \tag{33}$$

The change in the free energy must then equal the work done to the material, i.e.,

$$\delta A = \delta W. \tag{34}$$

This equation yields the elastic stress,

$$\begin{aligned}
&\tau^e = 3akT[\mathbf{M} - \tfrac{\nu}{3}\mathbf{I} - \tfrac{1}{6kT}(\langle\mathbf{m}\times\mathcal{R}(V)\mathbf{m}\rangle + \langle\mathbf{mm}\times\mathcal{R}(V)\rangle)] - \tfrac{1}{2}[\langle\mathbf{m}\times\mathcal{R}(V)\mathbf{m}\rangle - \\
&\langle\mathbf{mm}\times\mathcal{R}(V)\rangle] + \tfrac{AkT}{2}[\tfrac{\mathcal{L}^2}{24}(\nabla_\alpha\nu\nabla_\beta\nu - \nu\nabla_\alpha\nabla_\beta\nu) + \tfrac{L^2}{48}(\nabla_\alpha\mathbf{M}_{\mu\beta}\nabla_\mu\nu - \nu\nabla_\alpha\nabla_\mu\mathbf{M}_{\mu\beta} + \\
&\nabla_\alpha\nu\nabla_\mu\mathbf{M}_{\mu\beta} - \nabla_\alpha\nabla_\mu\nu\mathbf{M}_{\mu\beta})] - \tfrac{3NkT}{4} \\
&[\tfrac{\mathcal{L}^2}{24}(\nabla_\alpha\mathbf{M}_{\mu\gamma}\nabla_\beta\mathbf{M}_{\mu\gamma} - \nabla_\alpha\nabla_\beta\mathbf{M}_{\mu\gamma}\mathbf{M}_{\mu\gamma}) + \tfrac{L^2}{48}(\nabla_\alpha\mathbf{M}_{4i\beta\mu\gamma}\nabla_i\mathbf{M}_{\mu\gamma} - \\
&\nabla_\alpha\nabla_i\mathbf{M}_{4\beta i\mu\gamma}\mathbf{M}_{\mu\gamma} + \nabla_\alpha\mathbf{M}_{\mu\gamma}\nabla_i\mathbf{M}_{4i\beta\mu\gamma} - \nabla_\alpha\nabla_i\mathbf{M}_{\mu\gamma}\mathbf{M}_{4\beta i\mu\gamma})].
\end{aligned} \tag{35}$$

The details of the derivation is given in Appendix. The antisymmetric part of the elastic stress is

$$\begin{aligned}
&\tau^e_a = \tfrac{1}{2}[\langle\mathbf{m}\times\mathcal{R}V\mathbf{m}\rangle - \langle\mathbf{mm}\times\mathcal{R}V\rangle] + \tfrac{AkT}{2}[\tfrac{L^2}{48}(\nabla_\alpha\mathbf{M}_{\mu\beta}\nabla_\mu\nu - \nu\nabla_\alpha\nabla_\mu\mathbf{M}_{\mu\beta} + \\
&\nabla_\alpha\nu\nabla_\mu\mathbf{M}_{\mu\beta} - \nabla_\alpha\nabla_\mu\nu\mathbf{M}_{\mu\beta})] - \tfrac{3NkT}{4}[\tfrac{L^2}{48}(\nabla_\alpha\mathbf{M}_{4i\beta\mu\gamma}\nabla_i\mathbf{M}_{\mu\gamma} - \\
&\nabla_\alpha\nabla_i\mathbf{M}_{4\beta i\mu\gamma}\mathbf{M}_{\mu\gamma} + \nabla_\alpha\mathbf{M}_{\mu\gamma}\nabla_i\mathbf{M}_{4i\beta\mu\gamma} - \nabla_\alpha\nabla_i\mathbf{M}_{\mu\gamma}\mathbf{M}_{4\beta i\mu\gamma})].
\end{aligned} \tag{36}$$

For the viscous stress, we use the results of Jeffrey's[18], Batchelor's[20] and Hinch and Leal's [21, 22, 23] on spheroidal suspensions in viscous solvent to arrive at:

$$\tau^v = 2\eta_s \mathbf{D} + 3kT[\zeta_1(a)(\mathbf{D}\cdot\mathbf{M} + \mathbf{M}\cdot\mathbf{D}) + \zeta_2(a)\mathbf{D} : \langle\mathbf{mmmm}\rangle)], \tag{37}$$

where

$$\begin{aligned}
&\eta_s = \eta + \tfrac{3}{2}\nu kT\zeta_3(a),\\
&\zeta_3(a) = \tfrac{\zeta^{(0)}}{I_1}, \qquad \zeta_1(a) = \zeta^{(0)}(\tfrac{1}{I_3} - \tfrac{1}{I_1}),\\
&\zeta_2(a) = \zeta^{(0)}[\tfrac{J_1}{I_1 J_3} + \tfrac{1}{I_1} - \tfrac{2}{I_3}],\\
&I_1 = 2r\int_0^\infty \tfrac{dx}{\sqrt{(r^2+x)(1+x)^3}}, \qquad I_3 = r(r^2+1)\int_0^\infty \tfrac{dx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}},\\
&J_1 = r\int_0^\infty \tfrac{xdx}{\sqrt{(r^2+x)(1+x)^3}}, \qquad J_3 = r\int_0^\infty \tfrac{xdx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}},\\
&r = \tfrac{1+a}{1-a},
\end{aligned} \tag{38}$$

η is the solvent viscosity, $\zeta_{1,2,3}(a)$ are three friction coefficients. $3\nu kT\zeta_i(a), i = 1, 2, 3$ are identified as two shape-dependent viscosity parameters due to the polymer-solvent interaction. The total extra stress is given in the *constitutive equation for the extra stress*

$$\tau = \tau^e + \tau^v. \tag{39}$$

From [21, 22], it follows that

$$\begin{aligned}
&\lim_{a\to 1}\zeta_1(a) = 0, \qquad \lim_{a\to 1}\zeta_2(a) = \infty,\\
&\lim_{a\to -1}\zeta_1(a) = -\infty, \qquad \lim_{a\to -1}\zeta_2(a) = \infty.
\end{aligned} \tag{40}$$

So, the formulae are not meant to be applied to the two extremes $a = -1$ and $a = 1$ at all. To obtain the viscous stress in practice, one should calibrate the coefficients at a fixed aspect ratio $0 < r = r_0 < \infty$ and then extrapolate the formulae to all the other finite values of r since after all the friction coefficients need to be experimentally determined. In the range of $a \approx 1$ though, the stress contribution from the term $\mathbf{D}\cdot\mathbf{M} + \mathbf{M}\cdot\mathbf{D}$ is negligible, consistent with the Doi theory for rodlike molecules[4].

As shown in [31], when $a > 0$, all are positive and $\zeta_1(a)$ is smaller than $\zeta_2(a)$ as well as $\zeta_3(a)$; $\zeta_1(a)$ becomes negligibly small as a approaches 1 while $\zeta_2(a)$ goes to infinity and $\zeta_3(a)$ settles at a finite positive value; for $a < 0$, $\zeta_1(a)$ becomes negative and comparable in magnitudes to $\zeta_2(a)$, giving rise to a non-negligible "shape-induced-antidrag" to the total stress from the term $\mathbf{D}\cdot\mathbf{M}+\mathbf{M}\cdot\mathbf{D}$. This indicates that the oblate spheroidal molecule has the tendency to weaken the viscous stress due to the shape-induced polymer-solvent interaction. However, this will by no means change the dissipative nature of the stress. As shown in [31], the viscous stress part due to the polymer-solvent interaction is indeed dissipative for all values of $a \in (-1, 1)$ and all possible orientation despite $\zeta_1(a) < 0$ at $a < 0$.

The kinetic equation (24), orientation tensor equation (30) and (27), constitutive equation for the extra stress (39), balance of linear momentum (41) and the continuity equation (42), both given next, constitute the hydrodynamical model for spheroidal LCPs.
Balance of linear momentum

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot (-p\mathbf{I} + \tau) + \mathbf{f}, \tag{41}$$

where ρ is the fluid density, p is the scalar pressure and $\mathbf{f}$ the external force. Corresponding to the incompressibility, $\mathbf{v}$ satisfies the
continuity equation

$$\nabla \cdot \mathbf{v} = 0. \tag{42}$$

Balance of angular momentum and the anisotropic elasticity

Finally, we want to make sure that the derived theory obeys the balance of angular momentum. From [4], we know that the torque on a test molecule oriented along $\mathbf{m}$ is given by

$$\mathbf{T} = -\mathcal{R} V_{ei}, \tag{43}$$

absence of external effects. In this mesoscopic theory, the material point is implicitly (tacitly) defined as a sphere in which the velocity gradient is assumed constant and all LCP molecules convect spatially in an identical manner within the sphere. Due to the anisotropic elasticity from the intermolecular potential, there exists an additional torque associated to the spatial convection on the "material points". Then, the total torque on a unit volume of the material is

$$\begin{aligned} \mathbf{t}_k = {} & \textstyle\int_{\|\mathbf{m}\|=1} \mathbf{T}_k f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m} + \frac{AkT}{2} [\frac{L^2}{48} (\nabla_\alpha \mathbf{M}_{\mu\beta} \nabla_\mu \nu - \nu \nabla_\alpha \nabla_\mu \mathbf{M}_{\mu\beta} + \\ & \nabla_\alpha \nu \nabla_\mu \mathbf{M}_{\mu\beta} - \nabla_\alpha \nabla_\mu \nu \mathbf{M}_{\mu\beta})] - \tfrac{3NkT}{4} [\tfrac{L^2}{48} (\nabla_\alpha \mathbf{M}_{4i\beta\mu\gamma} \nabla_i \mathbf{M}_{\mu\gamma} - \\ & \nabla_\alpha \nabla_i \mathbf{M}_{4\beta i\mu\gamma} \mathbf{M}_{\mu\gamma} + \nabla_\alpha \mathbf{M}_{\mu\gamma} \nabla_i \mathbf{M}_{4i\beta\mu\gamma} - \nabla_\alpha \nabla_i \mathbf{M}_{\mu\gamma} \mathbf{M}_{4\beta i\mu\gamma})] \epsilon_{\alpha\beta k}, \end{aligned} \tag{44}$$

where $\epsilon_{\alpha\beta k}$ is the alternator tensor[17]. Integrating over the control volume G and applying integration by part whenever necessary, our calculations end up with

$$\int_G \tau_{ij} \epsilon_{ijk} d\mathbf{x} = \int_G \mathbf{t}_k d\mathbf{x}. \tag{45}$$

This equality indicates that the body torque balances the antisymmetric part of the stress tensor on the control volume G, confirming that the balance of angular momentum is maintained[2]. We note that the balance of the angular momentum is achieved on the entire control volume G subject to the assumptions on the zero boundary conditions alluded to earlier rather than in a pointwise sense due to the nonlocality of the intermolecular potential. The presence of the anisotropic elasticity is due to the long-range anisotropic molecular interaction. It is the interaction between the spatial convection and the long-range anisotropic molecular interaction that causes the additional torque on the material point. The role of the anisotropic elasticity needs to be investigated further.

2.4 Entropy production and energy dissipation

In an isothermal process, the entropy production or (energy dissipation) is equal to the decrease in the total energy[2]

$$T\dot{S} = -\frac{d}{dt}[\int_G (\frac{1}{2}\rho \mathbf{v}\cdot\mathbf{v})dx + A[f]], \tag{46}$$

where S denotes the entropy of the control volume G. It is shown that

$$\begin{aligned} T\dot{S} = &\textstyle\int_G \langle D_r(\mathbf{m},a)\|\mathcal{R}(lnf + \frac{1}{kT}V_{ei})\|^2\rangle d\mathbf{x} + \int_G \langle \nabla(lnf + \frac{1}{kT}V_{ei})\cdot (D_{||}(a)\mathbf{mm} + \\ &\textstyle D_\perp(a)(\mathbf{I}-\mathbf{mm}))\cdot\nabla(lnf + \frac{1}{kT}V_{ei})\rangle d\mathbf{x} + \int_G D_{vdisp} d\mathbf{x}, \end{aligned} \tag{47}$$

where

$$D_{vdisp} = 2\eta\mathbf{D}:\mathbf{D} + 3\nu kT(\zeta_3\mathbf{D} + \zeta_1(\mathbf{M}\cdot\mathbf{D} + \mathbf{D}\cdot\mathbf{M}) + \zeta_2\mathbf{D}:\langle\mathbf{mmmm}\rangle):\mathbf{D} \tag{48}$$

is nonnegative definite[31]. It is nonnegative definite provided the translational diffusion coefficient matrix

$$(D_{||}(a)\mathbf{mm} + D_\perp(a)(\mathbf{I}-\mathbf{mm})) \tag{49}$$

is, which is warranted provided $D_{||}(a)$ and $D_\perp(a)$ are nonnegative as implicitly assumed. This indicates the theory warrants a positive entropy production and thereby obeys the second law of thermodynamics.

2.5 Approximate theory

The equation for the orientation tensor and the stress expression both contain up to eighth order tensors, indicating a strong coupling to the kinetic equation. To decouple the kinetic equation, which often yields a much simpler governing equation system for LCPs, one has used a variety of decoupling or closure approximations [23, 24, 25, 26, 27]. The simplest among all the choices of the closure approximations is given in the following

$$\begin{aligned}
&\langle \mathbf{mmmm} \rangle \approx \tfrac{1}{\nu} \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle, \\
&\langle \mathbf{mmmmmm} \rangle \approx \tfrac{1}{\nu^2} \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle, \\
&\langle \mathbf{mmmmmmmm} \rangle \approx \tfrac{1}{\nu^3} \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle.
\end{aligned} \tag{50}$$

These are exact when the orientation is perfect. The orientation tensor equation and the stress expression are given by (30) and (39), respectively, after the above substitutions. These equations along with the momentum and continuity equation constitute the approximate theory for spheroidal LCPs.

An improved approximate theory may be obtained if we use both $\mathbf{M}$ and $\mathbf{M}_4$ as orientational variables and approximate sixth order and eighth order tensors by

$$\begin{aligned}
&\langle \mathbf{mmmmmm} \rangle \approx a_1^{(1)} \langle \mathbf{mm} \rangle \langle \mathbf{mmmm} \rangle + \\
&a_2^{(1)} \langle \mathbf{mmmm} \rangle \langle \mathbf{mm} \rangle + \\
&a_3^{(1)} \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle, \\
&a_1^{(1)} + a_2^{(1)} + a_3^{(1)} = \tfrac{1}{\nu}, \\
&\langle \mathbf{mmmmmmmm} \rangle \approx a_1^{(2)} \langle \mathbf{mmmm} \rangle \langle \mathbf{mmmm} \rangle \\
&+ a_2^{(2)} \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mmmm} \rangle \\
&a_3^{(2)} \langle \mathbf{mmmm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle + \\
&a_4^{(2)} \langle \mathbf{mm} \rangle \langle \mathbf{mmmm} \rangle \langle \mathbf{mm} \rangle, \\
&a_1^{(2)} \nu + a_2^{(2)} + a_3^{(2)} + a_4^{(2)} = \tfrac{1}{\nu^2}.
\end{aligned} \tag{51}$$

The specific values of the weight parameters $a_j^{(i)}$ can be calibrated based on the flow types. Of course, more sophisticated closures may be employed to improve the approximation given here [6, 7, 23, 24]. Most of the closures are flow-type dependent so that their performance in different types of flows may vary widely [24, 25, 26, 27]. Unless a specific flow problem is identified, we don't see the need for enumerating all the closure approximations here.

3 Reduction to the Ericksen-Leslie theory

In [31], we showed the kinetic theory of Wang yields the torque balance equation in the Ericksen-Leslie theory in the limit of weak flow, weak distortional elasticity, and long time. Here we extend the asymptotic analysis to include a weak translational diffusion and show that the asymptotic limit of the torque balance equation of the theory remains.

We introduce a dimensionless small parameter $0 < \epsilon << 1$ to quality the weak effects mentioned above explicitly. Let

$$D_{||} = \epsilon \tilde{D_{||}}, D_{\perp} = \epsilon \tilde{D_{\perp}}, \tilde{t} = t\epsilon, \mathbf{D} = \epsilon \tilde{\mathbf{D}}, \Omega = \epsilon \tilde{\Omega}, \mathcal{L}^2 = \epsilon \tilde{\mathcal{L}}^2, L^2 = \epsilon \tilde{L}^2. \tag{52}$$

Dropping the tildes, the kinetic equation becomes

$$\begin{aligned} \epsilon \tfrac{df}{dt} = \epsilon \tfrac{\partial}{\partial \mathbf{x}} \cdot [(D_{||}(a)\mathbf{mm} + D_{\perp}(a)(\mathbf{I} - \mathbf{mm})) \cdot (\tfrac{\partial f}{\partial \mathbf{x}} + \tfrac{f}{kT}\tfrac{\partial V_0}{\partial \mathbf{x}})] + \\ \mathcal{R} \cdot [D_r(\mathbf{m}, a)(\mathcal{R}f + \tfrac{1}{kT} f \mathcal{R} V_0)] - \epsilon \mathcal{R} \cdot [\mathbf{m} \times \dot{\mathbf{m}} f - D_r f \mathcal{R} \tfrac{V_e}{kT}], \end{aligned} \tag{53}$$

where

$$V_0 = AkT\nu - \frac{3N}{2} kT \mathbf{M} : \mathbf{mm}, V_e = V_{is} - V_0. \tag{54}$$

We seek an asymptotic expansion of the probability density function

$$f = \sum_{n=0}^{\infty} \epsilon^n f_n(\mathbf{m}, \mathbf{x}, t). \tag{55}$$

Substituting the ansatz (55) into the Smoluchowski equation, we obtain at leading order ($O(1)$)

$$\mathcal{R} \cdot [Dr(\mathcal{R} f_0 + f_0 \mathcal{R} \frac{V_0[f_0]}{kT}] = 0. \tag{56}$$

Clearly, f_0 at leading order is a steady state solution of the Smoluchowski equation with the Maier-Saupe intermolecular potential. A solution of the leading order equation is given by the integral equation

$$f_0 = \rho e^{-\frac{V_0[f_0]}{kT}}, \tag{57}$$

where $\rho = \rho(\mathbf{x}, t)$. In this paper, we assume $\rho = const.$ So, it is the normalizing factor for f_0. Without loss of generality, we also assume

$$\nu = \int_{||\{\mathbf{m}||=\mathbf{1}\}} f_0 d\mathbf{m} = 1. \tag{58}$$

This assumption is equivalent to

$$ln f_0 + \frac{V[f_0]}{kT} = const, \tag{59}$$

where $V_0[f_0]$ indicates the potential is evaluated at f_0. Assuming uniaxial symmetry in the base state f_0, i.e.,

$$\mathbf{M} = s\mathbf{nn} - \frac{1-s}{3}\mathbf{I}, \tag{60}$$

where n is the distinguished major director direction of the second moment tensor, we find a steady state solution of f_0 given by

$$\begin{aligned} f_0 &= f_0(\cos\theta) \\ \tfrac{df_0}{d\xi} &= 3sN\cos\theta f_0(\xi), \end{aligned} \tag{61}$$

where $\xi = \cos\theta = \mathbf{n}\cdot\mathbf{m}$. The uniaxial director $\mathbf{n}$ is arbitrary since the leading order equation does not tell us how $\mathbf{n}$ varies in time and space. This is the well-known degeneracy of the steady kinetic equation in equilibrium [4]. Let

$$\mathbf{n} = \mathbf{n}(\mathbf{x}, t). \tag{62}$$

We then derive its governing equation using higher order equations.

At the next order ($O(\epsilon)$), we have

$$\begin{aligned} &\tfrac{df_0}{dt} = \mathcal{R}\cdot Dr[\mathcal{R}f_1 + f_1\mathcal{R}V_0[f_0] + f_0\mathcal{R}V_0[f_1]] - \mathcal{R}\cdot[(\mathbf{m}\times\dot{\mathbf{m}}f_0 - D_r f_0(\mathcal{R}\tfrac{V_e[f_0]}{kT})]+ \\ &\nabla\cdot(D_{||}\mathbf{mm} + D_\perp(\mathbf{I}-\mathbf{mm})\cdot(\nabla f_0 + \tfrac{f_0}{kT}\nabla V_0[f_0])). \end{aligned} \tag{63}$$

The term corresponding to the translational diffusion vanishes because

$$(\nabla f_0 + \frac{f_0}{kT}\nabla V_0[f_0]) = f_0\nabla(lnf_0 + \frac{V_0[f_0]}{kT}) = f_0\nabla const = 0. \tag{64}$$

Thus, (63) reduces to

$$\tfrac{df_0}{dt} = \mathcal{R}\cdot D_r[\mathcal{R}f_1 + f_1\mathcal{R}V_0[f_0] + f_0\mathcal{R}V_0[f_1]] - \mathcal{R}\cdot[(\mathbf{m}\times\dot{\mathbf{m}}f_0 - D_r f_0(\mathcal{R}\tfrac{V_e[f_0]}{kT})]. \tag{65}$$

From the solvability condition of (65), detailed in [31], we obtain the torque balance equation for the uniaxial director $\mathbf{n}$

$$-\gamma\mathbf{n} + \frac{as}{\lambda}\frac{\nu kT}{D_r^0}\mathbf{N} - as\frac{\nu kT}{D_r^0}\mathbf{D}\cdot\mathbf{n} - \mathbf{h} = 0, \tag{66}$$

where γ is a Lagrangian multiplier,

$$\mathbf{N} = \frac{d\mathbf{n}}{dt} - \Omega\cdot\mathbf{n}, \tag{67}$$

$\mathbf{h}$ is the elastic field [2]

$$\begin{aligned} &\mathbf{h} = \tfrac{\nu NkTs}{8}[(s\mathcal{L}^2 + \tfrac{s-s_4}{7}L^2)\Delta\mathbf{n} + \tfrac{2(s-s_4)}{7}L^2\nabla(\nabla\cdot\mathbf{n})+ \\ &\tfrac{2s+5s_4}{7}L^2((\nabla\cdot\mathbf{n})\mathbf{n}\cdot\nabla\mathbf{n} + (\mathbf{n}\cdot\nabla\mathbf{n})\cdot\nabla\mathbf{n} + \mathbf{nn}:\nabla\nabla\mathbf{n} - \mathbf{n}\cdot\nabla\mathbf{n}\cdot\nabla\mathbf{n}^T)], \end{aligned} \tag{68}$$

and

$$\lambda = 2as(\int_{\|\mathbf{m}\|=1} f_{ms} g(\theta) \frac{dV_{ms}}{d\theta} d\mathbf{m})^{-1} \tag{69}$$

is the "tumbling parameter" [14]. This is exactly the torque balance equation in the Ericksen-Leslie theory with the Frank elastic energy given by

$$\begin{aligned} F = \tfrac{1}{2}[\tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{3L^2}{7}(s-s_4))(\nabla\cdot\mathbf{n})^2 + \tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{L^2}{7}(s-s_4))(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + \\ \tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{L^2}{7}(3s+4s_4))\|\mathbf{n}\times\nabla\times\mathbf{n}\|^2]. \end{aligned} \tag{70}$$

The stress tensor evaluated at the leading order solution f_0 yields the identical expression as the one in [31]. Therefore, the stress expression does not reduce to that in the Ericksen-Leslie theory; however, it does contain every term in the Ericksen-Leslie stress expression. The Frank elastic constants and the Leslie viscosity coefficients are identical to the ones in [31]. Hence, the inclusion of a weak translational diffusion does not change the asymptotic dynamics in the limit of the weak flows and weak distortional elasticity.

When the translational diffusion competes with the rotary diffusion at the same order, the torque balance equation contains additional gradient terms with up to fourth order spatial derivatives. The asymptotic limit certainly extends the Ericksen-Leslie torque balance to higher orders. The details are cumbersome and therefore omitted.

4 Conclusion

We have developed a hydrodynamic theory for nonhomogeneous liquid crystalline polymers of spheroidal configurations generalizing the kinetic theory of Kuzuu and Doi for homogeneous liquid crystal polymers as well as that of Wang for nonhomogeneous LCPs to account for translational diffusion and density variation in space. The theory is applicable to flows of rodlike liquid crystal polymers at the large aspect ratios and to those of discotic liquid crystal polymers at small aspect ratios. It also accounts for the molecular configurational effect in the viscous stress due to polymer-solvent interaction. The theory is shown to satisfy the second law of thermodynamics and thereby warrants a positive entropy production. Therefore, it is a well-posed kinetic theory for flows of LCPs. In the asymptotic limit of weak flow, weak distortional elasticity, weak translational diffusion, and long time, the theory yields at leading order the torque balance equation of the Ericksen-Leslie theory. Otherwise, it is a bona fide extension of the Ericksen-Leslie theory to include higher order spatial gradients.

Acknowledgment and Disclaimer

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Appendix

Derivation of the elastic stress tensor using virtual work principles

We calculate the variation of the free energy $A[f]$ with respect to the variation of the probability density function defined by

$$\delta f = \frac{df}{dt}\delta t = -\mathcal{R} \cdot (\mathbf{m} \times \dot{\mathbf{m}} f)\delta t. \tag{71}$$

This indicates that not only the rotational configuration of the spheroidal molecule, but also its mass of center are perturbed along the moving trajectory of the material point $\mathbf{x}$. Then,

$$\delta A[f] = kT \int_G \int_{||\mathbf{m}||=1} [(lnf + \tfrac{V}{kT})\delta f + \tfrac{1}{2kT}(f\delta V - V\delta f)]d\mathbf{m}d\mathbf{x}. \tag{72}$$

Assuming the deformation tensor $\mathbf{K}\delta t$ and its derivatives vanish at ∂G and applying integration by part, we have

$$\begin{aligned}&\textstyle\int_G \int_{||\mathbf{m}||=1}[(lnf + \frac{V}{kT})\delta f]d\mathbf{m}d\mathbf{x} = \int_G \mathbf{K}_{\alpha\beta}\delta t : \{3a(\mathbf{M} - \frac{\mathbf{I}}{3}) - \frac{a}{2}[\langle(\mathbf{m} \times \mathcal{R}V)\mathbf{m}\rangle + \\ &\textstyle\langle \mathbf{m}(\mathbf{m} \times \mathcal{R}V)\rangle] - \frac{1}{2}[\langle(\mathbf{m} \times \mathcal{R}V)\mathbf{m}\rangle - \langle \mathbf{m}(\mathbf{m} \times \mathcal{R}V)\rangle]\}_{\alpha\beta}d\mathbf{x},\end{aligned} \tag{73}$$

and

$$\begin{aligned}&\textstyle\int_G \int_{||\mathbf{m}||=1}[\frac{1}{2kT}(f\delta V - V\delta f)]d\mathbf{m}d\mathbf{x} = -\int_G \mathbf{K}_{\alpha\beta}\delta t\{\frac{AkT}{2}[\frac{\mathcal{L}^2}{24}(\nabla_\alpha\nu\nabla_\beta\nu - \nu\nabla_\alpha\nabla_\beta\nu) + \\ &\textstyle\frac{L^2}{48}(\nabla_\alpha\mathbf{M}_{\mu\beta}\nabla_\mu\nu - \nu\nabla_\alpha\nabla_\mu\mathbf{M}_{\mu\beta} + \nabla_\alpha\nu\nabla_\mu\mathbf{M}_{\mu\beta} - \nabla_\alpha\nabla_\mu\nu\mathbf{M}_{\mu\beta})] - \\ &\textstyle\frac{3NkT}{4}[\frac{\mathcal{L}^2}{24}(\nabla_\alpha\mathbf{M}_{\mu\gamma}\nabla_\beta\mathbf{M}_{\mu\gamma} - \\ &\textstyle\nabla_\alpha\nabla_\beta\mathbf{M}_{\mu\gamma}\mathbf{M}_{\mu\gamma}) + \frac{L^2}{48}(\nabla_\alpha\mathbf{M}_{4i\beta\mu\gamma}\nabla_i\mathbf{M}_{\mu\gamma} - \nabla_\alpha\nabla_i\mathbf{M}_{4\beta i\mu\gamma}\mathbf{M}_{\mu\gamma} + \nabla_\alpha\mathbf{M}_{\mu\gamma}\nabla_i\mathbf{M}_{4i\beta\mu\gamma} - \\ &\nabla_\alpha\nabla_i\mathbf{M}_{\mu\gamma}\mathbf{M}_{4\beta i\mu\gamma})]\}d\mathbf{x}.\end{aligned} \tag{74}$$

In arriving at the above expression, we have used the following identities

$$\begin{aligned}&\nabla \cdot \mathbf{v} = 0, \\ &\nabla_i\nabla_j(\mathbf{v}_\mu\nabla_\mu) = \mathbf{v}_\mu\nabla_\mu\nabla_j\nabla_i + \nabla_i(\mathbf{K}_{\mu j}\nabla_\mu) + \mathbf{K}_{\mu i}\nabla_\mu\nabla_j.\end{aligned} \tag{75}$$

The extra terms given by (74) are resulted from the interaction of the long range elastic potential and the spatial convection, which contributes additional elastic torque to the macroscopic motion of the material.