A hydrodynamic theory for solutions of nonhomogeneous nematic liquid crystalline polymers of different configurations

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Abstract

A hydrodynamic theory is developed for solutions of nonhomogeneous nematic liquid crystalline polymers (LCPs) of a variety of molecular configurations in proximity of spheroids, extending the Doi kinetic theory for rodlike molecules. The new theory 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. When restricted to uniaxial symmetry in the weak flow limit, the theory recovers the director equation of the Leslie-Ericksen (LE) theory, but the stress tensor contains excessive gradient terms in addition to the LE stress tensor. The theory predicts that the elastic moduli K_1, K_2 and K_3 obey the ordering $K_3 < K_1 < K_2$ for stable, discotic (oblate spheroidal) LCPs in the weak flow limit. The ordering is reversed for rodlike (prolate spheroidal) LCPs. It yields a positive Leslie viscosity α_2 (α_3) in the flow-aligning (tumbling) regime for oblate (prolate) spheroidal LCPs. Moment averaged, approximate, mesoscopic theories for complex flow simulations are obtained via closure approximations.

1 Introduction

The nematic phase is one of the "simplest" liquid crystal phases known so far, in which an orientational order, but no translational order, exists[1,2]. Liquid crystals of variety of molecular configurations may form the nematic phase, which include the two drastically different configurations: rodlike and discotic liquid crystals. Most of the hydrodynamical theories formulated for liquid crystal materials are prototyped 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. However, a rigorous justification seems to be lacking in adopting the convenient practice. This paper is hence motivated to address the concerns.

We intend to develop a theory for nonhomogeneous flows of liquid crystalline polymers with a few adjustable parameters that could model a variety of configurations of polymeric liquid crystal molecules. We find the rigid spheroidal description of polymer molecule can best serve the purpose. This approach has been undertaken by several pioneers so far. 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.

Our theory can be viewed as an extension of the Kuzuu and Doi theory to flowing systems of nonhomogeneous liquid crystalline polymers. We model the LCP molecules as spheroids of equal shapes and sizes. We will derive an intermolecular potential that is valid for all values of the aspect ratios of the spheroids and a corresponding Smoluchowski equation for the orientational probability density function. Aimed at developing a theory that would be practical in complex flow simulations, we then approximate the intermolecular potential with an approximate potential. At this level of approximation, we will show that the approximate theory extends the Doi kinetic theory with the Marrucci-Greco potential[16] to include a symmetric intermolecular potential to guarantee a positive entropy production, which is required for a well-posed hydrodynamic theory. Our theory relates the physical parameters in the model to the molecular geometry, which provides invaluable insights into the interconnection between the molecular shape and its effect to mesoscopic material properties. In addition, the length parameters for the finite range of molecular interaction resulted from our different averaging procedure[16] differ from those in the Marrucci-Greco's potential. By absorbing the aspect ratio into the dimensionless concentration (defined later in the next section), the intermolecular potential indeed looks like the Maier-Saupe potential in the case of homogeneous liquid crystal materials, justifying the convenient use of the liquid crystal theories developed for rodlike molecules in the context of homogeneous discotic liquid crystals by Singh and Rey[10]. In addition, our theory exploits the influence of the molecular shape on the distortional elasticity for the first time, which undoubtedly will shed new lights on how to generalize other tensor theories of nonhomogeneous liquid crystals to nonhomogeneous discotic LCs. The most relevant theories among them perhaps would be the BE and TR theory.

The rest of the paper is divided into two sections. In the section to follow immediately, we derive the kinetic theory, stress expressions, and its approximate forms; show the theory satisfy the second law of thermodynamics in isothermal flows to establish the well-posedness of the theory. In the last section, we discuss some preliminary properties of the important physical parameters in the theory by establishing the connection to the LE theory in the limit of weak flows. More detailed rheological evaluations of the model are postponed to a sequel.

2 Kinetic theory for LCPs of spheroidal molecules

We first propose an intermolecular potential that accounts for the intermediate 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 probability 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 derive a consistent stress expression using the virtual work principle[2,4].

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 probability density function (pdf) corresponding to the probability that an arbitrary LCP molecule of the spheroidal shape is in its axis of revolution $\mathbf{m}$ ($||\mathbf{m}|| = 1$) at location $\mathbf{x}$ and time t. The material point at location $\mathbf{x}$ is assumed a sphere, whose radius is sufficiently large relative to the LCP molecule and small relative to the experimental apparatus, and the macroscopic velocity gradient in the sphere is assumed a constant provided it exists. For spheroidal molecules, the excluded volume has been calculated by Isihara in his work on phase transition behavior of colloidal solutions[11]. Using his excluded volume, we then propose the following form of the intermolecular potential with finite range molecular interaction, extending the work of Marrucci and Greco for rodlike molecules[16],

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

Here ν 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 and $|S|$ the surface area of S. 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 a nonlocal potential. Moreover, from a practical point of view, 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),

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

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

As shown by Isihara[11], the first two coefficients B_0 and B_1 are

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

We remark that formulae in Isihara's paper[11] for the case of $r > 1$ are erroneous.

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 $\mathbf{m}$, "·" 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 in the operation[17]. 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

$$V_i \approx -\frac{3}{2}\nu k T B_1 \mathbf{m}\mathbf{m} : [\frac{1}{|dV||S|}\int_S \int_{dV} \int_{||\mathbf{m}'||=1} \mathbf{m}'\mathbf{m}' f(\mathbf{m}', \mathbf{x}+\mathbf{s}+\mathbf{r}, t) d\mathbf{m}' d\mathbf{r} d\mathbf{s}] + const, \tag{10}$$

which resembles the intermolecular potential that Marrucci and Greco proposed for rodlike molecules [16] except that our first integral is over a spheroid in stead of along the direction of $\mathbf{m}$. 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. Figure 1 demonstrates a very good agreement between the excluded volume given in (4) less $2v$, normalized by $\frac{1}{2\pi bc^2}$, and its second order Legendre polynomial approximation at $r = 3$. At $r = 4$ and $r = 1/4$, for example, the two curves become nearly indistinguishable (not shown in Figure 1 though).

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,

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

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,

$$V_{si} = -\frac{3NkT}{2}[\mathbf{I} + (\frac{l^2}{10} + \frac{L_1}{8})\Delta + \frac{L_2 - L_1}{8}\mathbf{mm} : \nabla\nabla]\langle\mathbf{mm}\rangle : \mathbf{mm} + const, \tag{12}$$

where

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

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

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

We can rewrite the potential in the same form as that of Marrucci-Greco's by introducing 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,

$$V_{si} = -\frac{3NkT}{2}(\mathbf{I} + \frac{\mathcal{L}^2}{24}\Delta + \frac{L^2}{24}\mathbf{mm} : \nabla\nabla)\langle\mathbf{mm}\rangle : \mathbf{mm} + const, \tag{16}$$

which is identical to the Marrucci-Greco potential for rodlike molecules formally[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), which distinguish (16) from the Marrucci-Greco potential[16]. We remark that the form of the potential given in (16) is independent of the choice of the surface S on which the average is calculated so long as the surface is smooth and symmetric about the axis of revolution $\mathbf{m}$ although the shape as well as the size of S affect the numerical values of L_1 and L_2. This observation suggests that the potential may be generalized to more complex molecular configurations other than spheroids. But, we will not pursue it here.

The first term in (16) corresponds to the homogeneous excluded-volume interaction of the Maier-Saupe type while the second and third term model the effect of the long-range distortional elasticity. N is a dimensionless polymer number density ν which also characterizes the strength of the intermolecular potential and varies with respect to the aspect ratio r and so the shape parameter a (defined later). Figure 2 depicts the dependence of $N/(8\pi c^2 b\nu)$ as a function of the shape parameter a. It approaches ∞ as $|a| \to 1^-$ and equals zero at $a = 0$ since $B(r = 1) = 0$. The behavior of $N/(8\pi c^2 b\nu)$ indicates that the strength of the intermolecular potential weakens as $|a|$ decreases for spheroidal molecules with fixed volumes and fixed polymer number density. So, *the critical number density at which phase transition takes place increases as shape parameter $|a|$ decreases, i.e., the closer the spheroid is to the sphere, the higher the critical number density is.* (16) also illustrates that the Marrucci-Greco potential is valid for spheroidal LCPs approximately, rectifying the use of the Maier-Saupe type potential for homogeneous discotic LCPs[10].

Notice that both L_1 and L_2 are positive for all values of the aspect ratio r;however, L is positive for $r > 1$ and negative for $0 < r < 1$. In fact, L/bc is an odd function of the shape parameter a via (23). Figure 3 portraits the variation of $L_1/bc, L_2/bc$ and L/bc with respect to a, respectively.

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]

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

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

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

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

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

$\mathbf{M}$ and $\mathbf{M}_4$ are the second and fourth moments of $\mathbf{m}$ with respect to the probability density function 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 crucial for a well-posed hydrodynamic theory, in which the positive entropy production and therefore the second law of thermodynamics is warranted. *We will show later that the symmetric V_{ei} respect the second law of thermodynamics at this level of approximation.* 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:

$$\mu = \frac{\delta A}{\delta f} = kTlnf + V_{ei} + kTV_H. \qquad (20)$$

Next, we derive the Smoluchowski equation for the probability density function f consistent with the spheroidal LCPs.

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]:

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

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

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

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; $-1 \le a \le 1$ is a *shape parameter* related to the molecular aspect ratio r by

$$a = \frac{r^2 - 1}{r^2 + 1}. \qquad (23)$$

$a = 1$: 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 probability 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 $D_r(\mathbf{m}, a) = \hat{D}_r(a)(\int_{\|\mathbf{m}'\|=1} \|\mathbf{m} \times \mathbf{m}'\| f(\mathbf{m}', \mathbf{x}, t) d\mathbf{m}')^{-2}$ 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, k is the Boltzmann constant, T is the absolute temperature, V is the potential including the intermolecular potential V_{ei} and the external potential (magnetic and/or electric field effect) V_H,

$$V = V_{ei} + \nu k T V_H, \tag{25}$$

$\frac{\partial}{\partial \mathbf{x}} = \nabla$ 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. In the following, we will assume the translational diffusion is weak and thus neglected.

Like in most kinetic theories, the macroscopic, 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 f[4]. Often, one uses the second moment $\mathbf{M}$ or its deviatoric part $\mathbf{Q}$ (a second order, symmetric, traceless tensor $\mathbf{Q}$) known as the orientation tensor (or structure tensor):

$$\mathbf{Q} = \langle \mathbf{mm} \rangle - \mathbf{I}/3. \tag{26}$$

Taking the second moment of $\mathbf{m}$ in the 3-dimensional space of $\mathbf{m}$ with respect to the probability density function governed by the kinetic equation (24), we arrive at the mesoscale *orientation tensor equation*

$$\left\{\begin{array}{l}
\frac{d}{dt}\mathbf{M} - \Omega \cdot \mathbf{M} + \mathbf{M} \cdot \Omega - a[\mathbf{D} \cdot \mathbf{M} + \mathbf{M} \cdot \mathbf{D}] = -2a\mathbf{D} : \langle \mathbf{mmmm} \rangle - \\
6D_r^0[\mathbf{M} - \frac{\mathbf{I}}{3} - \frac{1}{6kT}(\langle \mathbf{m} \times \mathcal{R}V\mathbf{m} \rangle + \langle \mathbf{mm} \times \mathcal{R}V \rangle)] = \\
\frac{2a}{3}\mathbf{D} - 2a\mathbf{D} : \mathbf{QM} - 6D_r^0[\mathbf{Q} - \frac{N}{2}((\mathbf{I} + \frac{\mathcal{L}^2}{24}\Delta)\mathbf{M} \cdot \mathbf{M} + \mathbf{M} \cdot (\mathbf{I} + \frac{\mathcal{L}^2}{24}\Delta)\mathbf{M}) + \\
N(\mathbf{I} + \frac{\mathcal{L}^2}{24}\Delta)\mathbf{M} : \langle \mathbf{mmmm} \rangle - \frac{NL^2}{96}((\nabla\nabla\mathbf{M}) \vdots \mathbf{M}_4 + ((\nabla\nabla\mathbf{M}) \vdots \mathbf{M}_4)^T + \\
\mathbf{M}_4 \vdots \nabla\nabla\mathbf{M} + (\mathbf{M}_4 \vdots \nabla\nabla\mathbf{M})^T + \mathbf{M}\nabla\nabla \vdots \mathbf{M}_4 + (\mathbf{M}\nabla\nabla \vdots \mathbf{M}_4)^T - \\
4\langle \mathbf{mmmmmm} \rangle :: \nabla\nabla\mathbf{M} - 2\mathbf{M}_4\nabla\nabla :: \mathbf{M}_4)] + \\
D_r^0\nu[\langle \mathbf{m} \times \mathcal{R}V_H\mathbf{m} \rangle + \langle \mathbf{mm} \times \mathcal{R}V_H \rangle].
\end{array}\right. \tag{27}$$

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 for rodlike LCPs or the analogous effect for disklike LCPs, perhaps should be termed "disk-expansion" effect, can be modeled by replacing the constant rotary diffusivity D_r^0 by[4]

$$\frac{D_r^0}{(1 - \frac{3}{2}\mathbf{Q} : \mathbf{Q})^2}. \tag{28}$$

The translational diffusion can be easily incorporated into the orientation tensor equation once it is identified as significant. In that case, an additional variable for the polymer density would have to be introduced along with its governing equation resulted from the averaging of the kinetic equation. In the above, we have chosen not to include it in the orientation tensor equation for the sake of simplicity, which is also consistent with the customary practice in this field.

Analogous to the derivation of orientation tensor equation, we can also obtain an evolutionary equation for $\mathbf{M}_4$ from the kinetic equation:

$$\begin{array}{l}
\frac{d}{dt}(\mathbf{M}_4)_{ijkl} - [\Omega_{im}\mathbf{M}_{4,mjkl} - \mathbf{M}_{4,ijkm}\Omega_{ml} - \mathbf{M}_{4imkl}\Omega_{mj} - \mathbf{M}_{4ijml}\Omega_{mk}] - \\
a[\mathbf{D}_{im}\mathbf{M}_{4mjkl} + \mathbf{M}_{4imkl}\mathbf{D}_{mj} + \mathbf{M}_{4ijml}\mathbf{D}_{mk} + \mathbf{M}_{4ijkm}\mathbf{D}_{ml}] = -4a\mathbf{M}_{6ijklmn}\mathbf{D}_{mn} - \\
20\bar{D}_r[\mathbf{M}_{4ijkl} - \frac{1}{10}(\langle \delta_{ij}\mathbf{m}_k\mathbf{m}_l \rangle + \langle \delta_{ik}\mathbf{m}_j\mathbf{m}_l \rangle + \langle \delta_{il}\mathbf{m}_j\mathbf{m}_k \rangle + \langle \mathbf{m}_i\delta_{jk}\mathbf{m}_l \rangle + \\
\langle \mathbf{m}_i\delta_{jl}\mathbf{m}_k \rangle + \langle \mathbf{m}_i\mathbf{m}_j\delta_{kl} \rangle) - \frac{1}{20kT}(\langle \mathbf{m} \times \mathcal{R}V\mathbf{mmm} \rangle_{ijkl} + \langle \mathbf{mm} \times \mathcal{R}V\mathbf{mm} \rangle_{ijkl} + \\
\langle \mathbf{mmm} \times \mathcal{R}V\mathbf{m} \rangle_{ijkl} + \langle \mathbf{mmmm} \times \mathcal{R}V \rangle_{ijkl})],
\end{array} \tag{29}$$

where $\bar{D}_r$ is another averaged rotary diffusivity resulted from the averaging process, which is assumed equal to D_r^0 for simplicity in the following, and indices are used to clarify the tensor products. The equation of $\mathbf{M}$ contains the fourth and sixth order moments and that of $\mathbf{M}_4$ includes even eighth order moments, posing a closure problem typical to kinetic theories[4].

With the kinetic equation, we next derive the consistent stress tensor.

Derivation of the stress tensor

We treat the LCP system as incompressible. Then, the stress tensor consists of three parts: the presure $-p\mathbf{I}$, 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

$$\delta W = \int_G \tau^e : \delta\epsilon d\mathbf{x}, \tag{30}$$

where τ^e is the elastic stress 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 rotational convection term[4]:

$$\delta f = \frac{df}{dt}\delta t = -\mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f)\delta t. \tag{31}$$

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

$$\delta A = \delta W. \tag{32}$$

This equation yields the elastic stress,

$$\begin{aligned}
&\tau^e = 3a\nu kT[\mathbf{M} - \tfrac{\mathbf{I}}{3} - \tfrac{1}{6kT}(\langle\mathbf{m}\times\mathcal{R}(V)\mathbf{m}\rangle + \langle\mathbf{mm}\times\mathcal{R}(V)\rangle)] - \\
&\tfrac{\nu}{2}[\langle\mathbf{m}\times\mathcal{R}(V)\mathbf{m}\rangle - \langle\mathbf{mm}\times\mathcal{R}(V)\rangle] - \tfrac{\nu NkT\mathcal{L}^2}{32}[\nabla\mathbf{M}:\nabla\mathbf{M} - (\nabla\nabla\mathbf{M}):\mathbf{M}] + \\
&\tfrac{\nu kTNL^2}{64}[\nabla\nabla\mathbf{M}\,\vdots\,\mathbf{M}_4 + (\nabla\nabla\cdot\mathbf{M}_4):\mathbf{M} - \nabla\mathbf{M}:(\nabla\cdot\mathbf{M}_4) - \nabla\mathbf{M}_4\,\vdots\,\nabla\mathbf{M}],
\end{aligned} \tag{33}$$

where

$$(\nabla\mathbf{M}:\nabla\mathbf{M})_{ij} = \nabla_i\mathbf{M}_{kl}\nabla_j\mathbf{M}_{kl}. \tag{34}$$

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

$$\begin{aligned} &\tau_a^e = -\tfrac{\nu}{2}[\langle \mathbf{m} \times \mathcal{R}V\mathbf{m}\rangle - \langle \mathbf{mm} \times \mathcal{R}V\rangle] + \\ &\tfrac{\nu kTNL^2}{64}[\nabla\nabla\mathbf{M}\vdots\mathbf{M}_4 + (\nabla\nabla \cdot \mathbf{M}_4) : \mathbf{M} - \nabla\mathbf{M} : (\nabla \cdot \mathbf{M}_4) - \nabla\mathbf{M}_4\vdots\nabla\mathbf{M}]_a, \end{aligned} \tag{35}$$

where the subscript a indicate the antisymmetric part of the second order tensor.

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:

$$\tau^v = 2\eta_s\mathbf{D} + 3\nu kT[\zeta_1(a)(\mathbf{D} \cdot \mathbf{M} + \mathbf{M} \cdot \mathbf{D}) + \zeta_2(a)\mathbf{D} : \langle\mathbf{mmmm}\rangle)], \tag{36}$$

where

$$\begin{aligned} &\eta_s = \eta + \tfrac{3}{2}\nu kT\zeta_3(a), \\ &\zeta_3(a) = \tfrac{\zeta^{(0)}}{I_1}, \qquad \zeta_1(a) = \zeta^{(0)}(\tfrac{1}{I_3} - \tfrac{1}{I_1}), \qquad \zeta_2(a) = \zeta^{(0)}[\tfrac{J_1}{I_1 J_3} + \tfrac{1}{I_1} - \tfrac{2}{I_3}], \\ &I_1 = 2r\int_0^\infty \tfrac{dx}{\sqrt{(r^2+x)(1+x)^3}}, \qquad I_3 = r(r^2+1)\int_0^\infty \tfrac{dx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}, \\ &J_1 = r\int_0^\infty \tfrac{xdx}{\sqrt{(r^2+x)(1+x)^3}}, \qquad J_3 = r\int_0^\infty \tfrac{xdx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}, \\ &r = \tfrac{1+a}{1-a}, \end{aligned} \tag{37}$$

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*

$$\tau = \tau^e + \tau^v. \tag{38}$$

Expanding the terms in (33), we obtain the extra stress tensor expression explicitly:

$$\begin{aligned} &\tau = 2\eta_s\mathbf{D} + 3a\nu kT[\mathbf{M} - \tfrac{\mathbf{I}}{3} - \tfrac{N}{2}((\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M} \cdot \mathbf{M} + \mathbf{M} \cdot (\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M} \\ &-2(\mathbf{I} + \tfrac{\mathcal{L}^2}{24}\Delta)\mathbf{M} : \langle\mathbf{mmmm}\rangle)] - \tfrac{\nu kTN\mathcal{L}^2}{16}(\Delta\mathbf{M} \cdot \mathbf{M} - \mathbf{M} \cdot \Delta\mathbf{M}) + \\ &\tfrac{a\nu kTNL^2}{32}[4\mathbf{M}_6 :: \nabla\nabla\mathbf{M} + 2\mathbf{M}_4\nabla\nabla :: \mathbf{M}_4 - \nabla\nabla\mathbf{M}\vdots\mathbf{M}_4 - (\nabla\nabla\mathbf{M}\vdots\mathbf{M}_4)^T - \\ &\mathbf{M}_4\vdots\nabla\nabla\mathbf{M} - (\mathbf{M}_4\vdots\nabla\nabla\mathbf{M})^T - (\mathbf{M}\nabla\nabla\vdots\mathbf{M}_4)^T - \mathbf{M}\nabla\nabla\vdots\mathbf{M}_4] - \tfrac{\nu kTNL^2}{32}[\nabla\nabla\mathbf{M}\vdots\mathbf{M}_4 - \\ &(\nabla\nabla\mathbf{M}\vdots\mathbf{M}_4)^T - \mathbf{M}_4\vdots\nabla\nabla\mathbf{M} + (\mathbf{M}_4\vdots\nabla\nabla\mathbf{M})^T - \mathbf{M}\nabla\nabla\vdots\mathbf{M}_4 + (\mathbf{M}\nabla\nabla\vdots\mathbf{M}_4)^T] \\ &+3\nu kT[\zeta_1(a)(\mathbf{DM} + \mathbf{MD}) + \zeta_2(a)\mathbf{D} : \langle\mathbf{mmmm}\rangle] - \\ &\tfrac{\nu kT}{2}[a(\langle\mathbf{m} \times \mathcal{R}(V_H)\mathbf{m}\rangle + \langle\mathbf{mm} \times \mathcal{R}(V_H)\rangle) - (\langle\mathbf{m} \times \mathcal{R}(V_H)\mathbf{m}\rangle - \mathbf{mm}\mathcal{R}(V_H)\rangle)]. \end{aligned} \tag{39}$$

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 coefficient 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].

Figure 4. depicts the three friction coefficients $\zeta_i(a), i = 1,2,3$ as functions of the shape parameter a. 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 the appendix, 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 (27) and (29), 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. Correponding 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 Doi and Edwards' book[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

$$\begin{aligned}\mathbf{t}_k = \nu \textstyle\int_{\|\mathbf{m}\|=1} \mathbf{T}_k f(\mathbf{m},\mathbf{x},t) d\mathbf{m} + \frac{\nu NkTL^2}{32}[\mathbf{M}_{4ij\alpha\mu}\nabla_\mu\nabla_\beta\mathbf{M}_{ij} + \mathbf{M}_{ij}\nabla_\mu\nabla_\beta\mathbf{M}_{4\alpha\mu ij} - \\ \nabla_\mu\mathbf{M}_{4ij\mu\beta}\nabla_\alpha\mathbf{M}_{ij} - \nabla_\mu\mathbf{M}_{ij}\nabla_\alpha\mathbf{M}_{4\mu\beta ij}]\epsilon_{\alpha\beta k},\end{aligned} \tag{44}$$

where $\epsilon_{\alpha\beta k}$ is the alternator tensor[17]. Integrating over the control volume G and applying integration by parts 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 in more details.

Entropy production and energy dissipition

In an isothermal process, the entropy production or (energy dissipition) 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. As it is demonstrated in Appendix A that

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

where

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

It is nonnegative definite provided the translational diffusion coefficient matrix

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

is nonnegative definite, 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 abeys the second law of thermodynamics.

Approximate theory

The equation for the orientation tensor and the stress expression both contain fourth and sixth 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 the quadratic closure for fourth order tensors and cubic closure for sixth order tensors given below

$$\begin{aligned} &\langle \mathbf{mmmm} \rangle \approx \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle, \\ &\langle \mathbf{mmmmmm} \rangle \approx \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle \langle \mathbf{mm} \rangle. \end{aligned} \tag{50}$$

The orientation tensor equation and the stress expression are given by (27) 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

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

The specific values of the weight parameters $a_j^{(i)}$ can be caliberated 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 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.

Given the theory outlined above, we next discuss some of its preliminary properties in the limit of weak flows and leave the rheological evaluations to a forthcoming paper.

3 Reduction to the Leslie-Ericksen theory in the weak flow limit

Owing to historical reasons, one likes to interpret phenomena in liquid crystals using the language developed in the Leslie-Ericksen theory[3]. Without being an exception, we would therefore like to see how this theory relates to the well known LE theory in the limit of weak flows and weak distortional elasticity. To establish the connection, we need to restrict $\mathbf{Q}$ and $\mathbf{M}_4$ to their uniaxial forms in equilibrium,

$$\begin{aligned}
&\mathbf{Q} = s(\mathbf{nn} - \tfrac{\mathbf{I}}{3}), \quad \mathbf{M} = \mathbf{Q} + \tfrac{\mathbf{I}}{3}, \\
&\mathbf{M}_{4ijkl} = s_4\mathbf{n}_i\mathbf{n}_j\mathbf{n}_k\mathbf{n}_l + \tfrac{s-s_4}{7}(\mathbf{n}_i\mathbf{n}_j\delta_{kl} + \mathbf{n}_k\mathbf{n}_l\delta_{ij} + \mathbf{n}_i\mathbf{n}_k\delta_{jl} + \mathbf{n}_j\mathbf{n}_l\delta_{ik} + \\
&\mathbf{n}_i\mathbf{n}_l\delta_{jk} + \mathbf{n}_j\mathbf{n}_k\delta_{il}) + \tfrac{7-10s+3s_4}{105}(\delta_{ij}\delta_{kl} + \delta_{jk}\delta_{il} + \delta_{ik}\delta_{jl}), \\
&s = \langle P_2(\mathbf{m}\cdot\mathbf{n})\rangle, \quad s_4 = \langle P_4(\mathbf{m}\cdot\mathbf{n})\rangle,
\end{aligned} \tag{52}$$

where s and s_4 are uniaxial order parameters in equilibrium, $P_2(x)$ and $P_4(x)$ are the Legendre polynomial of order 2 and 4, respectively, and $\mathbf{n}$ is the corresponding, distinguished director of $\mathbf{Q}$[4]. Assuming s and s_4 constants and $\mathbf{n}$ a function of $\mathbf{x}$, inserting (52) to the free energy given by (18), we have

$$\begin{aligned}
&A[f] = \nu kT \int_G \langle lnf - 1 + V_H + \tfrac{1}{2kT}V_{ei}\rangle d\mathbf{x} - \tfrac{\nu NkTL^2}{32}\int_{\partial G}[(\mathbf{M}_4\vdots\nabla\mathbf{M})\cdot\mathbf{n}_n - (\nabla\cdot\mathbf{M}_4)\vdots\mathbf{M}\mathbf{n}_n]ds \\
&= \nu kT \int_G \langle lnf - 1 + V_H + \tfrac{1}{2}V_{ms}\rangle d\mathbf{x} - \tfrac{\nu NkTL^2}{32}\int_{\partial G}[(\mathbf{M}_4\vdots\nabla\mathbf{M})\cdot\mathbf{n}_n - (\nabla\cdot\mathbf{M}_4)\vdots\mathbf{M}\mathbf{n}_n]ds + \\
&\int_G\{\tfrac{\nu NkT}{8}s[(\mathcal{L}^2 s + \tfrac{s-s_4}{7}L^2)\|\nabla\mathbf{n}\|^2 + \tfrac{2(s-s_4)}{7}L^2(\nabla\cdot\mathbf{n})^2 + \tfrac{2s+5s_4}{7}L^2\|\mathbf{n}\cdot\nabla\mathbf{n}\|^2] - \\
&\tfrac{\nu NkT}{32}L^2 s[\tfrac{49-40s+12s_4}{21}\nabla\cdot(\mathbf{n}\nabla\cdot\mathbf{n}) + \tfrac{49-64s+36s_4}{21}\nabla\cdot(\mathbf{n}\cdot\nabla\mathbf{n})]\} \\
&= \nu kT \int_G \langle lnf - 1 + V_H + \tfrac{1}{2}V_{ms}\rangle d\mathbf{x} - \tfrac{\nu NkTL^2}{32}\int_{\partial G}[(\mathbf{M}_4\vdots\nabla\mathbf{M})\cdot\mathbf{n}_n - (\nabla\cdot\mathbf{M}_4)\vdots\mathbf{M}\mathbf{n}_n]ds + \\
&\underline{\int_G\{\tfrac{\nu NkT}{8}s[(\mathcal{L}^2 s + \tfrac{s-s_4}{7}L^2)\|\nabla\mathbf{n}\|^2 + \tfrac{2(s-s_4)}{7}L^2(\nabla\cdot\mathbf{n})^2 + \tfrac{2s+5s_4}{7}L^2\|\mathbf{n}\cdot\nabla\mathbf{n}\|^2]\}} - \\
&\int_{\partial G}\{\tfrac{\nu NkT}{32}L^2 s[\tfrac{49-40s+12s_4}{21}(\mathbf{n}\nabla\cdot\mathbf{n})\cdot\mathbf{n}_n + \tfrac{49-64s+36s_4}{21}(\mathbf{n}\cdot\nabla\mathbf{n})\cdot\mathbf{n}_n]\},
\end{aligned} \tag{53}$$

where $kTV_{ms} = -\frac{3NkT}{2}M : \mathbf{mm}$ is the Maier-Saupe intermolecular potential.

Comparing the bulk distortional free energy (underlined above) with that in the LE theory, we can identify the three Frank elastic constants as follows:

$$\begin{aligned} K_1 &= \tfrac{\nu NkT}{8}(\mathcal{L}^2 s^2 + \tfrac{3s(s-s_4)}{7}L^2), \\ K_2 &= \tfrac{\nu NkT}{8}(\mathcal{L}^2 s^2 + \tfrac{s(s-s_4)}{7}L^2), \\ K_3 &= \tfrac{\nu NkT}{8}(\mathcal{L}^2 s^2 + \tfrac{s(3s+4s_4)}{7}L^2). \end{aligned} \tag{54}$$

These can be written into self-contained forms for easy calculations following Marrucci and Greco[16]

$$\begin{aligned} K_1 &= \tfrac{\nu kTNS^2}{8}[\mathcal{L}^2 + 3L^2\chi_1], \\ K_2 &= \tfrac{\nu kTNS^2}{8}[\mathcal{L}^2 + L^2\chi_1], \\ K_3 &= \tfrac{\nu kTNS^2}{8}[\mathcal{L}^2 + L^2\chi_2], \end{aligned} \tag{55}$$

where

$$\begin{aligned} \chi_1 &= \tfrac{1}{4(G_0-3G_2)}[G_0 - 6G_2 + 5G_4], \\ \chi_2 &= \tfrac{3G_2-5G_4}{(G_0-3G_2)}, \\ s &= \tfrac{3G_2}{2G_0} - \tfrac{1}{2}, \\ G_k &= \textstyle\int_0^1 x^k exp(3N/2sx^2)dx. \end{aligned} \tag{56}$$

In the following, we will derive the governing equation for the director $\mathbf{n}$ using Kuzuu and Doi's perturbation scheme[14], extended recently by Feng et al.[19] to the nonlocal intermolecular potential to establish a direct link to the LE theory and confirm the relations between the elastic moduli and the parameters in the new theory. In this perturbation scheme, we assume the rotary diffusivity is a constant and formally assume the distortional elasticity and the flow effect are both weak (small) and of the same order of magnitudes, i.e.,

$$O(\|\dot{\mathbf{m}}\|, \|\mathcal{R}V_e\|) << 1, \tag{57}$$

where $kTV_e = V_{ei} - kTV_{ms}$. We then seek an asymptotic expansion of the probability density function

$$f = f_{ms} + f_1 + f_2 + \cdots, \tag{58}$$

where f_{ms} is a function of order $O(1)$ and its material derivative scales with the small velocity gradient and the bulk distortional free energy, i.e.,

$$\frac{df_{ms}}{dt} \approx O(\|\dot{\mathbf{m}}\|, \|\mathcal{R}V_e\|), \tag{59}$$

f_1 is a function of order $O(\|\dot{\mathbf{m}}\|, \|\mathcal{R}V_e\|)$, f_2 is a function of higher order, etc.. Substituting the ansatz (58) into the Smoluchowski equation, we have at leading order ($O(1)$)

$$\mathcal{R} \cdot [Dr(\mathcal{R}f_{ms} + f_{ms}\mathcal{R}V_{ms})] = 0. \tag{60}$$

Clearly, f_{ms} at leading order is a steady state solution of the Smoluchowski equation with the Maier-Saupe intermolecular potential. At the next order, we have

$$\frac{df_{ms}}{dt} = \mathcal{R} \cdot Dr[\mathcal{R}f_1 + f_1\mathcal{R}V_{ms}[f_{ms}] + f_{ms}\mathcal{R}V_{ms}[f_1]] - \mathcal{R} \cdot [(\mathbf{m} \times \dot{\mathbf{m}} - Dr\mathcal{R}V_e[f_{ms}])f_{ms}]. \tag{61}$$

We denote

$$\mathcal{G}\phi = \mathcal{R} \cdot (\mathcal{R}\phi + \phi\mathcal{R}V_{ms}[f_{ms}] + f_{ms}\mathcal{R}V_{ms}[\phi]). \tag{62}$$

Let ψ_0 be the eigenvector of the Hermitian operator $\mathcal{G}^*$ corresponding to the zero eigenvalue of $\mathcal{G}$ [14]. Then, it follows from (61) that

$$\begin{aligned} &\textstyle\int_{\|\mathbf{m}\|=1} \psi_0[\frac{df_{ms}}{dt} + \mathcal{R} \cdot [(\mathbf{m} \times \dot{\mathbf{m}} - Dr\mathcal{R}V_e[f_{ms}])f_{ms}]]d\mathbf{m} = \\ &\textstyle\int_{\|\mathbf{m}\|=1} \{\psi_0\frac{df_{ms}}{dt} - \mathcal{R}\psi_0 \cdot [(\mathbf{m} \times \dot{\mathbf{m}} - Dr\mathcal{R}V_e[f_{ms}])f_{ms}]\}d\mathbf{m} = 0. \end{aligned} \tag{63}$$

This is the solvability condition at the second order in the perturbation scheme, which yields the governing equation for the director $\mathbf{n}$. Kuzuu and Doi found that the left eigenvector $\psi_0 = \mathbf{b} \cdot \mathbf{e}_\phi g(\theta)$ with $g(\theta)$ the solution of the steady state equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{dg}{d\theta}) - \frac{g}{\sin^2\theta} - \frac{dV_{ms}}{d\theta}\frac{dg}{d\theta} = -\frac{dV_{ms}}{d\theta} \tag{64}$$

and $\mathbf{b}$ an arbitrary constant vector[14]. Since $V_{ms}[f_{ms}] = -\frac{3Ns}{2}(\mathbf{n}\cdot\mathbf{m})^2 + const$, $f_{ms} = f_{ms}(\mathbf{n}\cdot\mathbf{m})$. Using the fact $\mathbf{m} \times \mathcal{R}_m f_{ms}(\mathbf{n} \cdot \mathbf{m}) = -\mathbf{n} \times \mathcal{R}_n f_{ms}(\mathbf{n} \cdot \mathbf{m})$ and $\mathcal{R}f_{ms} = -f_{ms}\mathcal{R}V_{ms}[f_{ms}]$, we find

$$\int_{\|\mathbf{m}\|=1} \psi_0\frac{df_{ms}}{dt}d\mathbf{m} = \frac{as}{\lambda}\mathbf{b} \cdot (\mathbf{n} \times \dot{\mathbf{n}}), \tag{65}$$

where

$$\lambda = 2as(\textstyle\int_{\|\mathbf{m}\|=1} f_{ms}g(\theta)\frac{dV_{ms}}{d\theta}d\mathbf{m})^{-1} \tag{66}$$

is the "tumbling parameter"[14] (We note that Feng et al. obtained the same result using a different approach[19]). Kuzuu and Doi calculated[14]:

$$\int_{\|\mathbf{m}\|=1} \mathcal{R}\psi_0 \cdot (\mathbf{m} \times \dot{\mathbf{m}}f_{ms})d\mathbf{m} = \mathbf{b} \cdot (\mathbf{n} \times (as(\mathbf{D}\mathbf{n} + \frac{1}{\lambda}\Omega\mathbf{n}))). \tag{67}$$

We calculate the remaining terms and list them as follows:

$$\int_{||\mathbf{m}||=1} D_r \mathcal{R}(V_e) \cdot \mathcal{R}\psi_0 f_{ms} d\mathbf{m} = -\mathbf{b} \cdot (\mathbf{n} \times \mathbf{h}) \tfrac{D_r^0}{\nu kT}, \tag{68}$$

where $\mathbf{h}$ is given by

$$\begin{gathered}\mathbf{h} = \tfrac{\nu NkTs}{8}[(s\mathcal{L}^2 + \tfrac{s-s_4}{7}L^2)\Delta\mathbf{n} + \tfrac{2(s-s_4)}{7}L^2\nabla(\nabla\cdot\mathbf{n}) + \\ \tfrac{2s+5s_4}{7}L^2((\nabla\cdot\mathbf{n})\mathbf{n}\cdot\nabla\mathbf{n} + (\mathbf{n}\cdot\nabla\mathbf{n})\cdot\nabla\mathbf{n} + \mathbf{nn}:\nabla\nabla\mathbf{n} - \mathbf{n}\cdot\nabla\mathbf{n}\cdot\nabla\mathbf{n}^T)],\end{gathered} \tag{69}$$

where

$$(\mathbf{n}\cdot\nabla\mathbf{n}\cdot\nabla\mathbf{n}^T)_\alpha = \mathbf{n}_i \mathbf{n}_{j,i} \mathbf{n}_{j,\alpha}. \tag{70}$$

Combining the results of Kuzuu and Doi[14], Feng et al.'s[19] and (69), we arrive at the governing equation for the director $\mathbf{n}$:

$$\mathbf{n} \times [\tfrac{as}{\lambda}\tfrac{\nu kT}{D_r^0}\mathbf{N} - as\tfrac{\nu kT}{D_r^0}\mathbf{D}\cdot\mathbf{n} - \mathbf{h}] = 0, \tag{71}$$

where

$$\mathbf{N} = \frac{d\mathbf{n}}{dt} - \Omega\cdot\mathbf{n}, \tag{72}$$

and $\mathbf{h}$ is the elastic field[2,14]. This is equivalent to

$$-\gamma\mathbf{n} + \frac{as}{\lambda}\frac{\nu kT}{D_r^0}\mathbf{N} - as\frac{\nu kT}{D_r^0}\mathbf{D}\cdot\mathbf{n} - \mathbf{h} = 0, \tag{73}$$

which is the director field equation in the LE theory[1] with the Lagrangian multiplier γ.

Finally, the bulk distortional free energy density in the weak flow limit can be written into the familiar form:

$$\begin{gathered}F = \tfrac{1}{2}[\tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{3L^2}{7}(s-s_4))(\nabla\cdot\mathbf{n})^2 + \tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{L^2}{7}(s-s_4))(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + \\ \tfrac{\nu kTNs}{8}(s\mathcal{L}^2 + \tfrac{L^2}{7}(3s+4s_4))||\mathbf{n}\times\nabla\times\mathbf{n}||^2].\end{gathered} \tag{74}$$

We note that we have employed the following identity throughout our derivations:

$$\mathbf{n}\cdot\nabla\mathbf{n} = 0. \tag{75}$$

From (55), we observe that all the elastic moduli contain the equilibrium order parameter s as a factor. Recall the equilibrium phase diagram of the Doi model with Maier-Saupe potential[27], reproduced in Figure 5., we note that the isotropic phase $s = 0$ is the unique phase in the range of $N < N_b \approx 4.49$; two additional nematic ones emerge in the range of $N > N_b$, one is a highly aligned prolate one, which is linear stable, and the other is an unstable prolate equilibrium at $N < N_c$ and oblate one at $N > N_c$, where $N_c = 5$ is the phase transition concentration. At the isotropic phase, all the elastic moduli vanish according to (55). At the highly aligned prolate equilibrium for rodlike molecules, Marrucci and Greco showed that above the phase transition concentration[16]

$$K_2 < K_1 < K_3. \tag{76}$$

In our calculations, we confirm Marrucci and Greco's results with our potential for LCPs of prolate spheroidal configurations ($a > 0$). In addition, if we let $\mathcal{L} = 0$ in the intermolecular potential, we observe that $K_1/K_2 \to 3$ as the aspect ratio $r \to \infty$[28].

We also evaluate the three elastic moduli along the second nematic equilibrium as shown in Figure 5. Their magnitudes depends strongly on the dimensionless concentration N. Specifically,

$$\begin{cases} K_2 < K_1 < K_3, & 4.49 < N < N_c = 5, \\ K_2 < K_3 < K_1, & N_c < N < N_d, \\ K_3 < K_2 < K_1, & N > N_d, \end{cases} \tag{77}$$

where N_d is a second critical concentration related to the molecular shape parameter a. The variation of the three elastic moduli with respect to the dimensionless concentration N for $a = 0.8$ is depicted in Figure 6, where the critical concentration value $N_d \approx 10.29$.

When $a < 0$, the spheroidal molecule exhibits an oblate symmetry so that the parameter $L^2 < 0$, nevertheless, $\mathcal{L}^2 > |L^2|$ and all elastic moduli are nonnegative. However, the ordering of their magnitudes are in complete reversal of the case for $a > 0$; namely,

$$K_3 < K_1 < K_2 \tag{78}$$

for all $N > 4.49$ along the highly aligned prolate equilibrium; for the second nematic phase,

$$\begin{cases} K_3 < K_1 < K_2, & 4.49 < N < N_c = 5, \\ K_1 < K_3 < K_2, & N_c < N < N_d, \\ K_1 < K_2 < K_3, & N_d < N, \end{cases} \tag{79}$$

where N_d is a critical concentration value related to the molecular shape. Figure 7 depicts the three elastic moduli as functions of concentration N for $a = -0.8$, in which $N_d \approx 10.49$.

Reducing the extra stress tensor expression using (52), we obtain the antisymmetric part of the stress tensor

$$\tau^a = -\frac{1}{2}(\mathbf{nh} - \mathbf{hn}) + \text{extra gradient terms} , \tag{80}$$

where the "extra gradient terms" are associated with the torque exerted on the material point due to the spatial convection given in (44). Inserting (71) via (80) into the stress expression (39) and comparing the "viscous" stress in the limit, we obtain

$$\begin{aligned}
&\alpha_1 = (3\nu kT\zeta_2 - \tfrac{a^2\nu kT}{D_r^0})s_4,\\
&\alpha_2 = -\tfrac{a\nu kT}{2D_r^0}s(1+\tfrac{1}{\lambda}),\\
&\alpha_3 = -\tfrac{a\nu kT}{2D_r^0}s(1-\tfrac{1}{\lambda}),\\
&\alpha_4 = 2\eta_s + 2(1-s)\nu kT\zeta_1 + \nu kT\zeta_2\tfrac{14-20s+6s_4}{35} + \tfrac{a^2\nu kT}{D_r^0}\tfrac{7-10s+3s_4}{35},\\
&\alpha_5 = 3\nu kT\zeta_1 s + \tfrac{6}{7}(s-s_4)\nu kT\zeta_2 + \tfrac{a\nu kT}{2D_r^0}(\tfrac{a}{7}(3s+4s_4)+s),\\
&\alpha_6 = 3\nu kT\zeta_1 s + \tfrac{6}{7}(s-s_4)\nu kT\zeta_2 + \tfrac{a\nu kT}{2D_r^0}(\tfrac{a}{7}(3s+4s_4)-s).
\end{aligned} \tag{81}$$

These coefficients reduce to those obtained by Kuzuu and Doi[14] while η_s, ζ_1 and ζ_2 are assigned zero.

In addition to all the stress terms in the LE theory, the stress expression (39) in the weak flow limit also contains a number of "excessive" gradient terms, some of which are surface terms while others are not. So, they are indeed excessive relative to the LE theory. Thereby, the extra stress expression in our theory does not reduce to that of the LE theory exactly. It does include the LE stress tensor however. Since the terms are tediously long and not illuminating, we will not list them here. The "excessive" terms in our stress expression are due to the second order derivative terms in the intermolecular in the stress expression while LE theory only contains first order derivative terms. The LE theory is therefore a lower order truncated theory for small deformations.

Examining the Leslie viscosity α_2 and α_3, we notice that $\alpha_2 < 0$ as $a > 0$ while $\alpha_3 > 0$ as $1 - \frac{1}{\lambda} < 0$ and $\alpha_3 < 0$ otherwise along the stable, prolate nematic equilibrium. When $a < 0$, however, $\alpha_3 > 0$, but $\alpha_2 > 0$ provided $1 + \frac{1}{\lambda} > 0$ and $\alpha_2 < 0$ otherwise. It is known that the tumbling regime of the LCP is quantified by $|\lambda| < 1$ in the LE theory; the flow aligning regime is characterized by $|\lambda| > 1$. Applying this to α_2 (α_3), we conclude that the positive value of α_2 (α_3) can only be reached when the oblate (prolate) spheroidal LCP is in the flow-aligning (tumbling) regime. This is consistent with the observation of Carlsson and his coworkers' on discotic LCs using the LE theory[8,29].

Finally, we point out that the Parodi relation[30]

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \tag{82}$$

is satisfied by the Leslie viscosity coefficients given in (81).

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. 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 flows and weak elasticity, it recovers the director equation of the Leslie-Ericksen theory and predicts that the magnitudes of the three elastic moduli obey the following order $K_3 < K_1 < K_2$ in the stable nematic phase for discotic lcps and the reversed ordering for rodlike liquid crystals. The Leslie viscosity coefficient α_2 (α_3) in the asymptotic limit is positive in the flow-aligning (tumbling) regime for discotic (rodlike) LCPs. However, the stress in the asymptotic limit does not reduce to that in the LE theory due to the presence of higher order derivatives in the effective intermolecular potential.

Further rheological evaluations of the new theory for discotic liquid crystals in simple flows as well as orientational structures emerged due to flow orientation coupling will be reported in a forthcoming paper.

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Appendix

A.Energy dissipation

Here we first examine the dissipation caused by the viscous stress due to polymer-solvent interaction and viscous solvent. The dissipation is given by

$$D_{vdisp} = 2\eta \mathbf{D} : \mathbf{D} + 3\nu kT(\zeta_3 \mathbf{D} + \zeta_1(\mathbf{M} \cdot \mathbf{D} + \mathbf{D} \cdot \mathbf{M}) + \zeta_2 \mathbf{D} : \langle \mathbf{mmmm} \rangle) : \mathbf{D}. \tag{83}$$

(83) can be rewritten as

$$D_{vdisp} = 2\eta \mathbf{D} : \mathbf{D} + 3\nu kT \langle [\zeta_3 \mathbf{D} : \mathbf{D} + 2\zeta_1 \mathbf{m} \cdot \mathbf{D} \cdot \mathbf{D} \cdot \mathbf{m} + \zeta_2 (\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})^2] \rangle. \tag{84}$$

When all $\zeta_i > 0$, this is certainly positive.

While $\zeta_1 < 0$, we have to rewrite the expression using the identities:

$$\begin{aligned} &\mathbf{m} \cdot \mathbf{D}^2 \cdot \mathbf{m} = \|\mathbf{P} \cdot \mathbf{D} \cdot \mathbf{m}\|^2 + (\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})^2, \\ &\|\mathbf{D}\|^2 = \|\mathbf{D}_0\|^2 + \tfrac{3}{2}(\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})^2 + 2\|\mathbf{P} \cdot \mathbf{D} \cdot \mathbf{m}\|^2, \end{aligned} \tag{85}$$

where

$$\begin{aligned} &\mathbf{P} = \mathbf{I} - \mathbf{mm}, \\ &\mathbf{D}_0 = \mathbf{D} - \tfrac{1}{2}(\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})\mathbf{I} - \mathbf{mP} \cdot \mathbf{D} \cdot \mathbf{m} - \mathbf{P} \cdot \mathbf{D} \cdot \mathbf{mm} - \tfrac{3}{2}(\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})\mathbf{mm}. \end{aligned} \tag{86}$$

With these, we reduce (84) to

$$\begin{aligned} &D_{vdisp} = 2\eta \mathbf{D} : \mathbf{D} + 3\nu kT \langle [2(\zeta_3 + \zeta_1)\|\mathbf{P} \cdot \mathbf{D} \cdot \mathbf{m}\|^2 + \\ &(\zeta_2 + \tfrac{3}{2}\zeta_3 + 2\zeta_1)(\mathbf{m} \cdot \mathbf{D} \cdot \mathbf{m})^2 + \zeta_3 \mathbf{D}_0 : \mathbf{D}_0] \rangle. \end{aligned} \tag{87}$$

Notice that

$$\begin{aligned} &\zeta_1 + \zeta_3 = \tfrac{1}{I_3}, \\ &2\zeta_1 + \zeta_2 + \tfrac{3}{2}\zeta_3 = \tfrac{J_1}{I_1 J_3} + \tfrac{1}{2I_1}, \end{aligned} \tag{88}$$

and both are positive. So, $D_{vdisp} \geq 0$ even though $\zeta_1 < 0$ for $a < 0$. This demonstrates that the viscous stress derived in the theory due to polymer-solvent interaction and viscous solvent is dissipative for all aspect ratios.

We then show that the total energy is dissipative in the theory in isothermal flows. In the isothermal state, the entropy production is defined as follows[2]

$$T\dot{S} = -\frac{d}{dt}[\int_G (\frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v}) d\mathbf{x} + A[f]]. \tag{89}$$

Applying the kinetic equation and integration by part, we deduce that

$$\begin{aligned}
&\tfrac{d}{dt}[\textstyle\int_G (\tfrac{1}{2}\rho\mathbf{v}\cdot\mathbf{v})d\mathbf{x} + A[f]] = \\
&\textstyle\int_G\{-K:\tau + \nu kT\int_{||m||=1}[(lnf+\tfrac{1}{kT}V)\tfrac{d}{dt}f + \tfrac{1}{2kT}(f\tfrac{d}{dt}V - V\tfrac{d}{dt}f)]d\mathbf{m}\}d\mathbf{x} = \\
&\textstyle\int_G\{-K:\tau^v + \nu kT\int_{||m||=1}[(lnf+\tfrac{1}{kT}V)(\mathcal{R}\cdot D_r(\mathcal{R}f+\tfrac{f}{kT}\mathcal{R}V)+ \\
&\nabla\cdot(D_{||}(a)\mathbf{mm}+D_{\perp}(a)(\mathbf{I}-\mathbf{mm}))\cdot(\nabla f+\tfrac{f}{kT}\nabla V)) + \tfrac{1}{2kT}(f\tfrac{d^*}{dt}V - V\tfrac{d^*}{dt}f)]d\mathbf{m}\}d\mathbf{x} = \\
&-\textstyle\int_G\{D_{vdisp}+\nu kT[\langle\mathcal{R}(lnf+\tfrac{1}{kT}V)\cdot D_r\mathcal{R}(lnf+\tfrac{1}{kT}V)\rangle+ \\
&\langle\nabla(lnf+\tfrac{1}{kT}V)\cdot(D_{||}(a)\mathbf{mm}+D_{\perp}(a)(\mathbf{I}-\mathbf{mm}))\cdot\nabla(lnf+\tfrac{1}{kT}V)\rangle]\}d\mathbf{x}+ \\
&\textstyle\int_{\partial G}\text{surface terms}ds,
\end{aligned}\tag{90}$$

where

$$\frac{d^*}{dt} = \mathcal{R}\cdot D_r(\mathcal{R}f+\frac{f}{kT}\mathcal{R}V) + \nabla\cdot(D_{||}(a)\mathbf{mm}+D_{\perp}(a)(\mathbf{I}-\mathbf{mm}))\cdot(\nabla f+\frac{f}{kT}\nabla V), \tag{91}$$

representing the rotary and translational diffusion in the kinetic equation. Assuming the derivatives of f and its moments are all zero on the boundary ∂G, we arrive at

$$\begin{aligned}
&T\dot{S} = \textstyle\int_G\{D_{vdisp}+\nu kT[\langle\mathcal{R}(lnf+\tfrac{1}{kT}V)\cdot D_r\mathcal{R}(lnf+\tfrac{1}{kT}V)\rangle+ \\
&\langle\nabla(lnf+\tfrac{1}{kT}V)\cdot(D_{||}(a)\mathbf{mm}+D_{\perp}(a)(\mathbf{I}-\mathbf{mm}))\cdot\nabla(lnf+\tfrac{1}{kT}V)\rangle]\}d\mathbf{x}.
\end{aligned}\tag{92}$$

The entropy production is positive provided

$$D_r > 0 \quad \text{and} \quad (D_{||}(a)\mathbf{mm}+D_{\perp}(a)(\mathbf{I}-\mathbf{mm})) > 0. \tag{93}$$

So the energy is dissipative, consistent with the second law of thermodynamics.

B. **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

$$\delta f = \frac{df}{dt}\delta t = -\mathcal{R}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f)\delta t. \tag{94}$$

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,

$$\delta A[f] = \nu kT\int_G\int_{||\mathbf{m}||=1}[(lnf-1+\frac{V}{kT})\delta f + \frac{1}{2kT}(f\delta V - V\delta f)]d\mathbf{m}d\mathbf{x}. \tag{95}$$

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

$$\begin{aligned}
&\textstyle\int_G \int_{\|\mathbf{m}\|=1} [(lnf - 1 + \frac{V}{kT})\delta f] d\mathbf{m} d\mathbf{x} = \\
&\textstyle\int_G \mathbf{K}_{\alpha\beta}\delta t : \{3a(\mathbf{M} - \frac{\mathbf{I}}{3}) - \frac{a}{2}[\langle(\mathbf{m} \times \mathcal{R}V)\mathbf{m}\rangle + \langle\mathbf{m}(\mathbf{m} \times \mathcal{R}V)\rangle] - \\
&\textstyle\frac{1}{2}[\langle(\mathbf{m} \times \mathcal{R}V)\mathbf{m}\rangle - \langle\mathbf{m}(\mathbf{m} \times \mathcal{R}V)\rangle]\}_{\alpha\beta} d\mathbf{x},
\end{aligned} \tag{96}$$

and

$$\begin{aligned}
&\textstyle\int_G \int_{\|\mathbf{m}\|=1} [\frac{1}{2kT}(f\delta V - V\delta f)] d\mathbf{m} d\mathbf{x} = -\int_G \{\mathbf{K}_{\alpha\beta}\delta t : (\frac{N\mathcal{L}^2}{32})[\nabla_\alpha \mathbf{M}_{ij} \nabla_\beta \mathbf{M}_{ij} - \\
&\textstyle\nabla_\alpha \nabla_\beta \mathbf{M}_{ij} \mathbf{M}_{ij}] + \mathbf{K}_{\alpha\beta}\delta t : (\frac{NL^2}{64})[\nabla_\mu \mathbf{M}_{4ij\mu\beta} \nabla_\alpha \mathbf{M}_{ij} - \\
&\textstyle\mathbf{M}_{4ij\beta\mu} \nabla_\mu \nabla_\alpha \mathbf{M}_{ij} + \nabla_\mu \mathbf{M}_{ij} \nabla_\alpha \mathbf{M}_{4\mu\beta ij} - \mathbf{M}_{ij} \nabla_\mu \nabla_\alpha \mathbf{M}_{4\beta\mu ij}]\} d\mathbf{x} \\
&\textstyle= -\int_G \{\mathbf{K}_{\alpha\beta}\delta t : (\frac{N\mathcal{L}^2}{32})[\nabla_\alpha \mathbf{M}_{ij} \nabla_\beta \mathbf{M}_{ij} - \nabla_\alpha \nabla_\beta \mathbf{M}_{ij} \mathbf{M}_{ij}] - \\
&\textstyle\mathbf{K}_{\alpha\beta}\delta t : (\frac{NL^2}{32})[\mathbf{M}_{4ij\beta\mu} \nabla_\mu \nabla_\alpha \mathbf{M}_{ij} + \mathbf{M}_{ij} \nabla_\mu \nabla_\alpha \mathbf{M}_{4\beta\mu ij}]\} d\mathbf{x}.
\end{aligned} \tag{97}$$

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

$$\begin{aligned}
&\nabla \cdot \mathbf{v} = 0, \\
&\nabla_i \nabla_j (\mathbf{v}_\mu \nabla_\mu) = \mathbf{v}_\mu \nabla_\mu \nabla_j \nabla_i + \nabla_i (\mathbf{K}_{\mu j} \nabla_\mu) + \mathbf{K}_{\mu i} \nabla_\mu \nabla_j.
\end{aligned} \tag{98}$$

The extra terms given by (97) 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.

Figure Captions

Figure 1. Comparison between the excluded volume and its approximate form at $r = 3$, where $Bq = \frac{1}{2\pi bc^2}(B - 2v)$ and $q = \cos\angle\mathbf{mn}$. The solid curve represents the excluded volume defined in (4) less $2v$, normalized by $\frac{1}{2\pi bc^2}$, and the dotted curve does its corresponding Legendre polynomial approximation up to the second order.

Figure 2. $N_n = \frac{N(a)}{8\pi bc^2\nu}$ as a function of the shape parameter a. $\lim_{|a|\to 1^-} N_n(a) = \infty$.

Figure 3. (a). L_1/bc and L_2/bc as functions of a. The dotted curve represents L_2/bc and the solid one L_1/bc. (b). L^2/bc as a function of a.

Figure 4. (a). $\frac{\zeta_i(a)}{\zeta_0}, i = 1, 2, 3$ as functions of a. The solid curve represents $\frac{\zeta_2(a)}{\zeta_0}$, the dashed one $\frac{\zeta_1(a)}{\zeta_0}$, and the dotted one $\frac{\zeta_3(a)}{\zeta_0}$. $\zeta_1(1) = 0$ and $\lim_{a\to 1^-} \zeta_2(a) = +\infty$. (b). $|\frac{\zeta_i(a)}{\zeta_0}|, i = 1, 2, 3$ as functions of a. ζ_1 and ζ_2 are comparable in magnitudes in the range of $a < 0$ while ζ_3 is slightly larger than both.

Figure 5. The bifurcation diagram of the homogeneous equilibria with the Maier-Saupe potential. The solid curves denote the stable equilibria and the dotted ones the unstable ones. The critical concentration where the two nematic phases are first born is $N_b \approx 4.49$ and the second critical concentration is $N_c = 5$ beyond which the isotropic phase loses stability.

Figure 6. The elastic moduli K_i for rodlike liquid crystals (prolate spheroidal LCs, $a > 0$), with $K_i' = \frac{8}{\nu kTs^2N}K_i, i = 1, 2, 3$, as functions of the dimensionless concentration N along the highly aligned, stable, prolate equilibrium ((a) and (b)) and along the unstable less aligned nematic equilibrium ((c) and (d)), respectively. The solid curve denotes K_1, the thin dotted one K_2 and the thick dotted one K_3. The parameter values used are $a = 0.8, l = 1, c = 0.15, b = cr$. We remark that the magnitudes of l and c do not alter the order of the elastic moduli.

Figure 7. The elastic moduli K_i for discotic liquic crystals (oblate spheroidal LCs, $a < 0$), with $K_i' = \frac{8}{\nu kTs^2N}K_i, i = 1, 2, 3$, as functions of the dimensionless concentration N along the highly aligned, stable, prolate equilibrium ((a) and (b)) and along the unstable less aligned nematic equilibrium ((c) and (d)), respectively. The solid curve denotes K_1, the thin dotted one K_2 and the thick dotted one K_3. The parameter values used are $a = -0.8, l = 1, c = 0.45, b = cr$. We remark that the magnitudes of l and c do not alter the order of the elastic moduli.

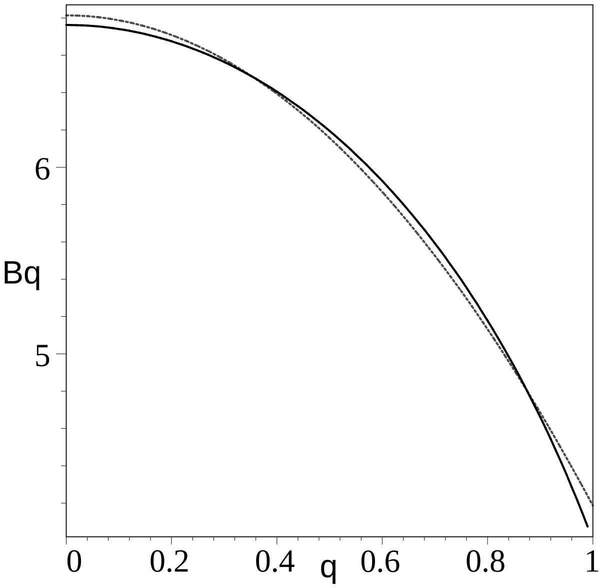


Figure 1:

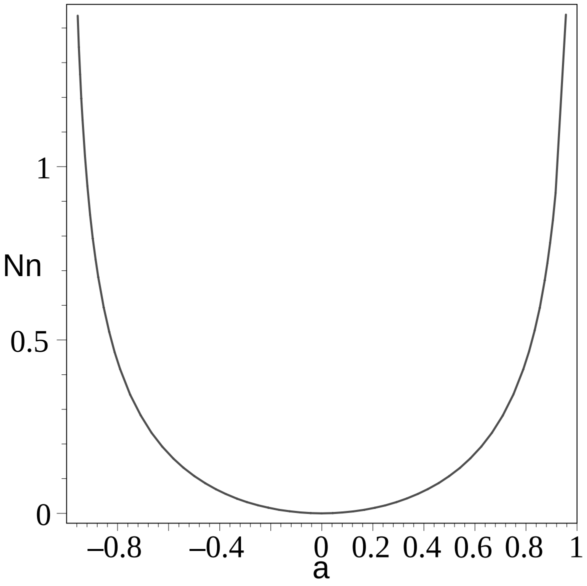
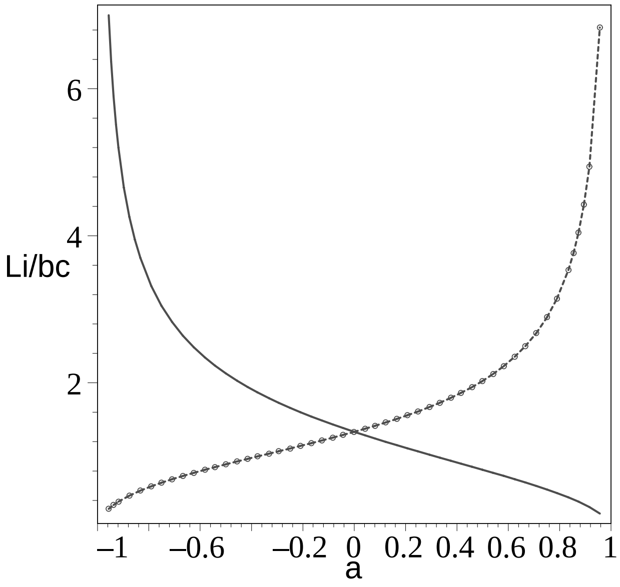
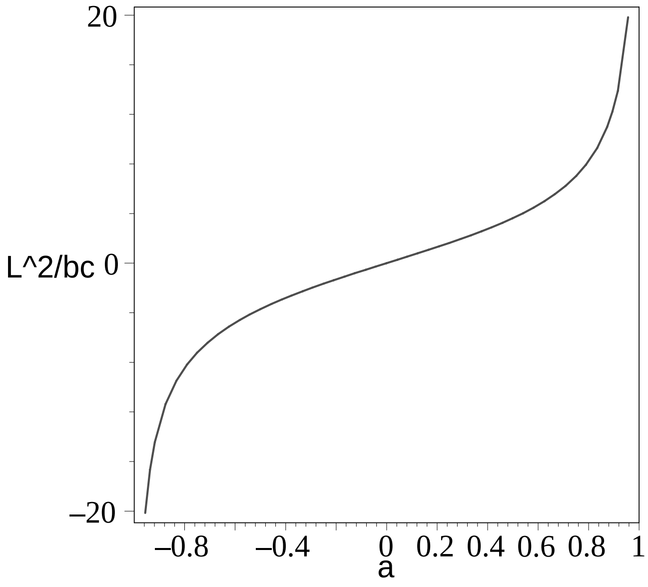


Figure 2:

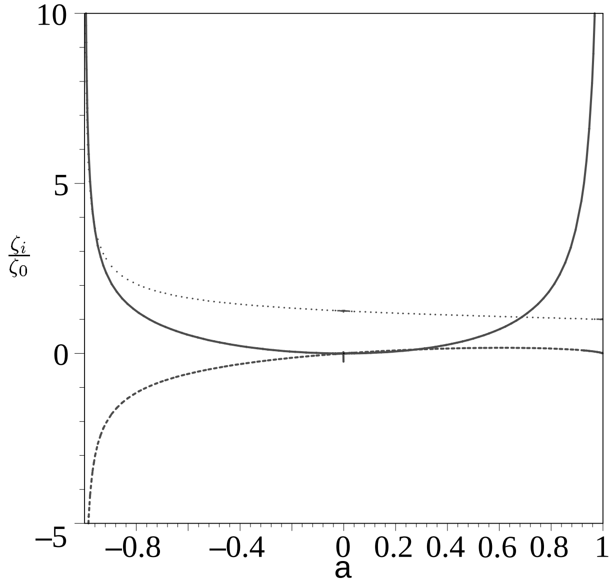


(a)

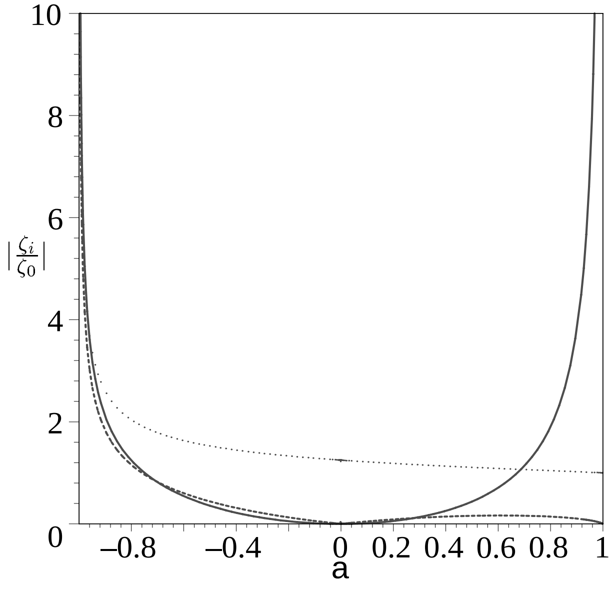


(b)

Figure 3:


10
5
0
–5
$\frac{\zeta_i}{\zeta_0}$
–0.8
–0.4
0
0.2
0.4
0.6
0.8
1
a

(a)


10
8
6
4
2
0
$|\frac{\zeta_i}{\zeta_0}|$
–0.8
–0.4
0
0.2
0.4
0.6
0.8
1
a

(b)

Figure 4:

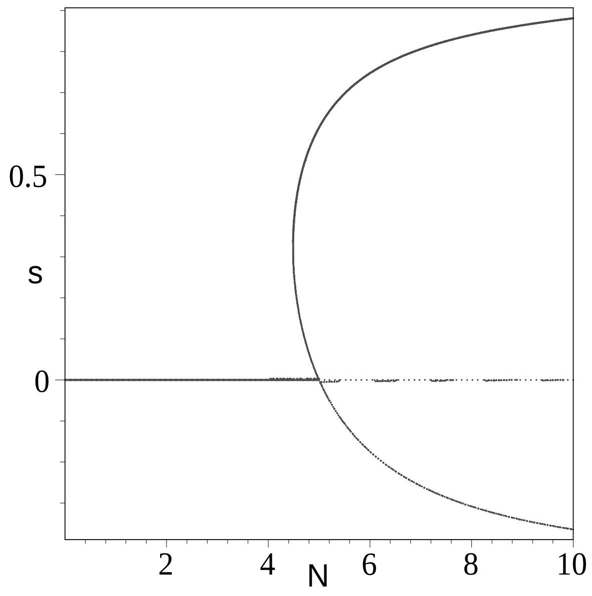
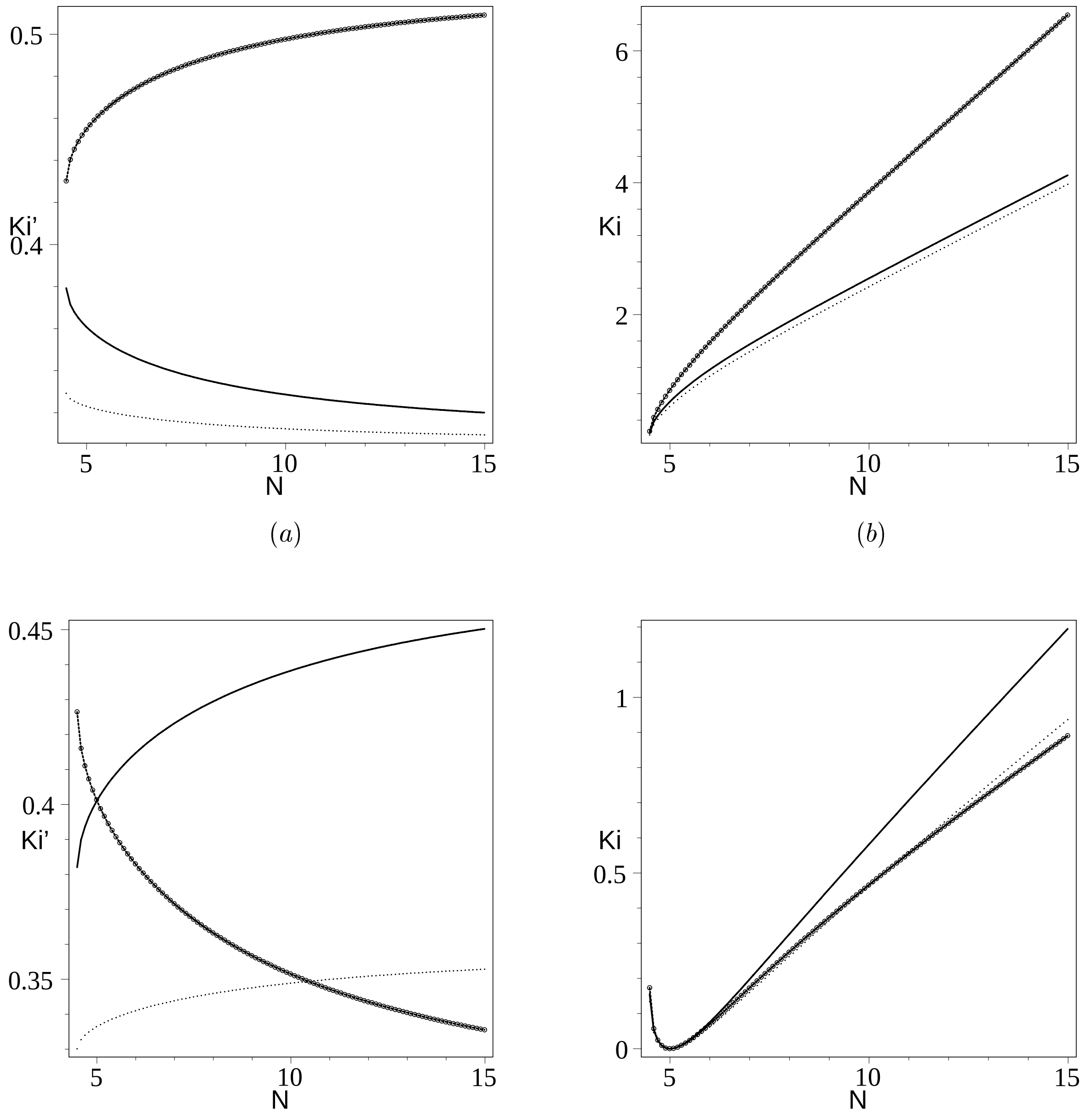


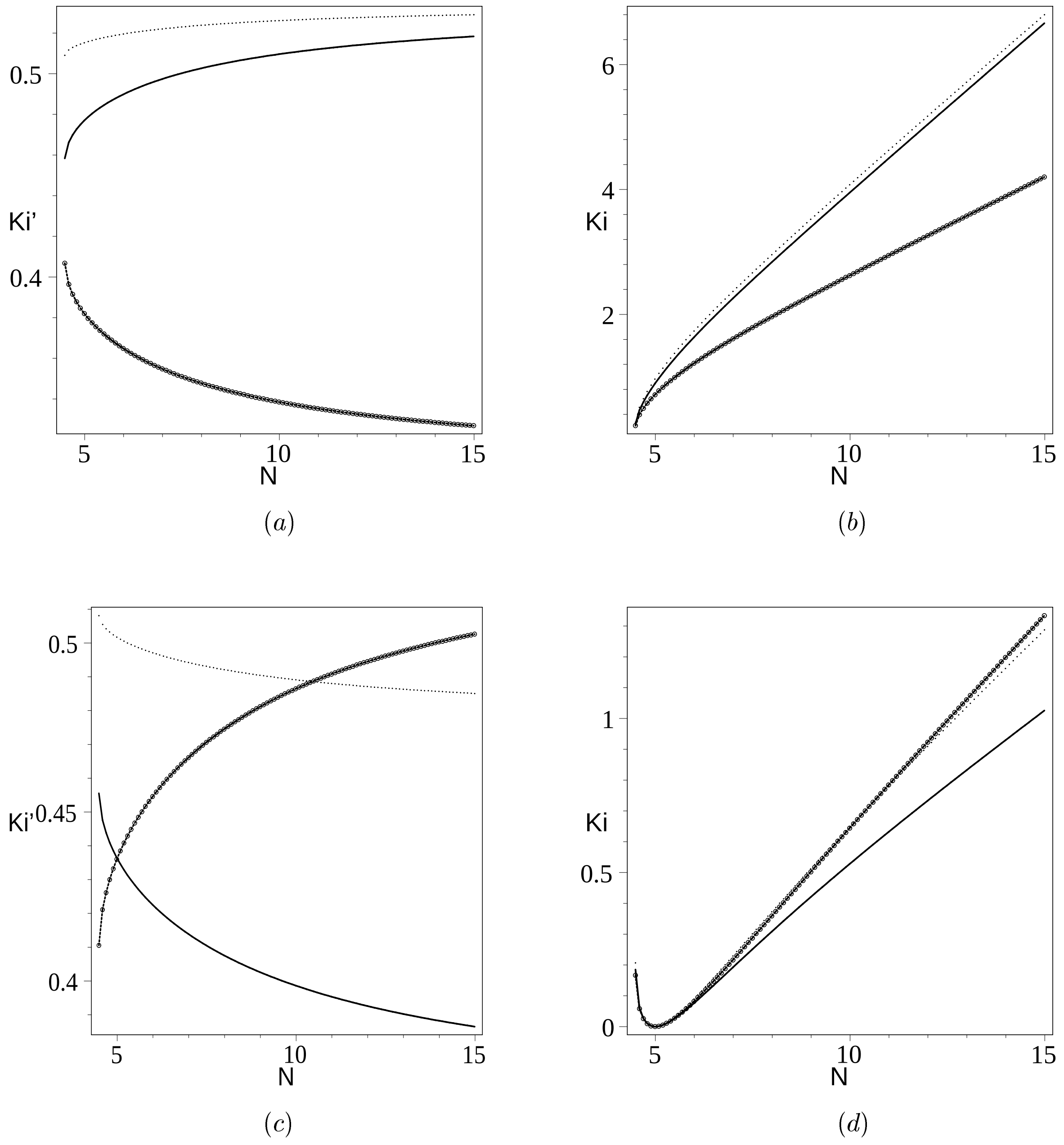
Figure 5:



(*a*) (*b*)

(*c*) (*d*)

Figure 6:



(a) (b)

(c) (d)

Figure 7: