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Proceedings of IMECE2002
ASME International Mechanical Engineering Congress & Exposition
November 17–22, 2002, New Orleans, Louisiana

IMECE2002-32185

EXPLICIT FLOW-ALIGNED ORIENTATIONAL DISTRIBUTION FUNCTIONS FOR DILUTE NEMATIC POLYMERS IN WEAK SHEAR

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ABSTRACT

Flow-alignment of sheared nematic polymers occurs in various flow-concentration regimes. Analytical descriptions of shear-aligned nematic monodomains have a long history across continuum, mesoscopic and mean-field kinetic models, sacrificing precision at each finer scale. Continuum Leslie-Ericksen theory applies to highly concentrated, weak flows of small molecular weight polymers, giving an explicit macroscopic alignment angle formula dependent only on Miesowicz viscosities. Mesoscopic tensor models apply at all concentrations and shear rates, but explicit "Leslie angle" formulas exist only in the weak shear limit (Cocchini *et. al*, 90; Bhave *et. al*, 93; Wang, 97; Rienacker and Hess, 99; Maffettone *et. al*, 00; Forest and Wang, 02; Forest *et. al*, 02c; Grecov and Rey, 02), with distinct behavior in dilute versus concentrated regimes. Exact probability distribution functions (pdf's) of kinetic theory do not exist for highly concentrated nematic states, even without flow, although appealing flow-aligned approximations have been derived (Kuzuu and Doi, 83; Kuzuu and Doi, 84; Semenov, 83; Semenov, 86; Archer and Larson, 95; Kroger and Seller, 95), which offer a molecular theory basis for the Leslie alignment angle. A simpler problem concerns the dilute concentration regime where the unique quiescent equilibrium is isotropic, corresponding to a constant pdf, and whose weak shear deformation is robust to mesoscopic closure approximation (Forest and Wang, 02; Forest *et. al*, 02c): steady, flow-aligning, weakly anisotropic, and biaxial. The purpose of this paper is to explicitly construct the weakly anisotropic branch of stationary pdf's by a weak-shear asymptotic expansion of kinetic theory. A second-moment pdf projection confirms mesoscopic model predictions, and further yields explicit Leslie angle and degree of alignment formulas in terms of molecular parameters and normalized shear rate.

1 Introduction

A classical benchmark of continuum, mesoscopic, and molecular theory for nematic polymers is the ability to predict conditions under which monodomain flow-alignment occurs, the resultant most probable direction of alignment (the "major director"), and to parametrize these properties in terms of model parameters. As one passes down from larger to smaller scale models, the ability to do explicit analysis is compromised. Leslie-Ericksen (L-E) continuum theory gives an explicit in-plane alignment condition and Leslie angle formula, which depend only on Miesowicz viscosities, independent of shear rate. These results apply only to strongly nematic, small-molecular-weight liquids (liquid crystals), so that continuum theory gives no information for dilute concentrations of nematic polymers; indeed, there is no concentration parameter in the theory.

Quiescent nematic polymers have multiple stable phases (isotropic in the dilute regime, nematic at high concentrations, with bistability in an overlap regime). When sheared, steady alignment sometimes occurs, and it is a challenge of mesoscopic or kinetic theory to predict a most probable alignment angle in terms of model parameters. This analog of the Leslie alignment angle is known to vary with shear rate and concentration, and there is ample theoretical evidence for strong dependence on molecular aspect ratio at nematic concentrations (Archer and Larson, 95; Kroger and Seller, 95; Forest and Wang, 02; Forest *et. al*, 02c). Mesoscopic models describe shear-aligned steady states, but explicit formulas are only available in the weak shear limit (Cocchini *et. al*, 90; Bhave *et. al*, 93; Wang, 97; Rienacker and Hess, 99; Maffettone *et. al*, 00; Forest and Wang, 02; Forest *et. al*, 02c; Grecov and Rey, 02). In this limit, the in-plane Leslie angle depends explicitly upon molecular aspect ratio and concentration, whereas shear rate dependence requires higher order asymptotic analysis (Forest *et. al*, 02c) or direct numerical simulation. Furthermore, the Leslie angle of stable states varies abruptly for dilute vs. concentrated nematics, as expected since the flow-aligned solution branches arise from two distinct quiescent states (the isotropic and the nematic).

In kinetic theory, exact expressions for the orientational probability distribution function in shear flow are not yet available, although several useful approximations have been derived (Kuzuu and Doi, 83; Kuzuu and Doi, 84; Semenov, 83; Semenov, 86; Archer and Larson, 95; Kroger and Seller, 95). The difficulty is not surprising, since exact pdf solutions do not even exist without flow for the nematic branch of solutions, which numerically are shown (Larson and Ottinger, 91; Faraoni *et. al*, 99) to have significant high-order spherical harmonic amplitudes. On the other hand, the isotropic branch is trivial (constant) for kinetic theory as well as mesoscopic theory, so one might expect to be able to carry out a weak-shear asymptotic analysis for this deformed isotropic branch. Such an analysis is relevant experimentally only in the dilute regime below the "clearing transition", where quiescent nematic polymers are isotropic. Imposed shear flows are known to induce weak birefringence, with peaks in the orientational distribution focused in the shear plane, at the Leslie alignment angle, as predicted from essentially all mesoscopic models (Forest and Wang, 02; Forest *et. al*, 02c). Our goal in this paper is to establish these analytical properties directly from kinetic theory in the weak shear limit, and to see how the alignment angle and degrees of alignment scale with molecular parameters and normalized shear rate.

We employ the Doi kinetic theory, extended to include a finite aspect ratio of spheroidal molecules (Wang 02); we then develop a weak-shear asymptotic expansion of the probability distribution function (f). At leading order, the quiescent equilibrium distribution functions consist of: the isotropic state ($f = \frac{1}{4\pi}$) for all concentrations, which is stable only for $0 < N < N_2 = 5$; and, a pair of nematic equilibria above a critical concentration $N_1 \approx 4.49$. Since analytical formulas for the quiescent nematic equilibria do not exist, their weak shear asymptotic corrections are inaccessible to our analysis. We are nonetheless motivated by the approximations predicted by Archer and Larson (1995) and Kroger and Sellers (1995) for the shear-aligned nematic steady state, which provide an expression for the Leslie tumbling parameter, λ,

$$\lambda = a\frac{5P_2 + 16P_4 + 14}{35P_2}, \tag{1}$$

where $a = \frac{1-r^2}{1+r^2}$, r is the molecular aspect ratio, and P_2, P_4 are equilibrium values of the second and fourth moments of the pdf f, given in terms of Legendre polynomials. The Leslie alignment angle ϕ for flow-aligning nematics is then given by

$$\cos(2\phi) = \lambda^{-1}. \tag{2}$$

This formula yields a molecular origin for the Leslie "tumbling parameter", which implies important shear-induced features. Since the L-E theory describes only the nematic states, one of the main predictions was the alignment-to-tumbling transition of the nematic phase. (As we shall confirm below, the kinetic theory analog of the Leslie tumbling parameter for the isotropic branch in weak shear should be a "flow-aligning parameter", since dilute concentrations of nematic polymers are not known to tumble.) According to (1), flow-alignment occurs only when $|\lambda| \geq 1$. The moments $P_{2,4}$ are concentration-dependent, and can be computed numerically as functions of N; therefore if $|a| = 1$, the Leslie angle and unsteady transition can be tabulated versus N. The molecular geometry parameter a lies between $a = -1$ for infinitely thin discs, $a = 0$ for spherical molecules, and $a = +1$ for infinitely thin rods; $|a|$ decreases monotonically from 1 to 0 from extreme aspect ratios to the spherical molecule limit. From (1), as noted by Archer and Larson, the effect of reducing the aspect ratio, e.g. from $a = 1$ to $a = .8$ ($r = 3$), can be quite significant. If the $a = 1 (r = \infty)$ nematic liquid is tumbling, lowering aspect ratio will only enhance the tumbling, i.e., shorten the period. However, a flow-aligned infinite aspect ratio liquid is transformed by lowering aspect ratio to *either* reduce the Leslie angle downward (toward the flow axis) *or* cause a tumbling transition. This effect due to aspect ratio has been explored in (Forest and Wang, 02) for a variety of mesoscopic closure approximations to the Doi theory, and in (Forest *et. al*, 02c) from an analytical tensor method which yields precise curves $N(a)$ along which the steady-unsteady transition occurs. These phenomena are specific to the nematic state in weak shear, and rigorous analysis only exists from mesoscopic tensor models in the weak shear limit.

By focusing on the weak-shear continuation of the isotropic state, at low and high concentrations, we will derive explicit kinetic theory formulas of the form (1). They are only relevant to experimental observations in the dilute regime where these are the unique attracting monodomain states. Nonetheless, we are able to affirm the validity of such exact kinetic theory expressions, and to deduce detailed mesoscopic alignment properties of the attracting state by projection of the pdf onto the second-moment tensor. The results are applicable up to the nematic transition where the isotropic state destabilizes. The formulas persist into the unstable, nearly isotropic regime, but the states are not physically realizable. We note, as a curiosity, that nearly isotropic monodomains are transiently observed in numerical simulations of structure formation in shear cells (Tesuji and

Rey, 98; Feng *et. al*, 00), associated with local defects that mediate neighboring incompatible orientational patterns.

2 Kinetic theory for LCPs of spheroidal molecules

Let $f(\mathbf{m},t)$ be the orientational probability distribution function for rod-like molecules with axis of symmetry $\mathbf{m}$ on the unit sphere S^2. The Smoluchowski (kinetic) equation for $f(\mathbf{m},t)$ is given by (Wang 02):

$$\begin{aligned} \frac{Df}{Dt} &= \mathcal{R}\cdot[D_r(\mathbf{m})(\mathcal{R}f+\tfrac{1}{kT}f\mathcal{R}V)]-\mathcal{R}\cdot[\mathbf{m}\times\dot{\mathbf{m}}f], \\ \dot{\mathbf{m}} &= \omega\cdot\mathbf{m}+a[\mathbf{D}\cdot\mathbf{m}-\mathbf{D}:\mathbf{mmm}], \end{aligned} \tag{3}$$

where $D_r(\mathbf{m})$ is the rotary diffusivity which we hold constant, $D_r(\mathbf{m}) = D_r^0$, to make connection with (Faraoni *et. al*, 99) and (Grosso *et. al*, 01); k is the Boltzmann constant, T is the absolute temperature. $\mathcal{R} = \mathbf{m}\times\frac{\partial}{\partial\mathbf{m}}$ is the rotational gradient operator, and $\frac{D}{Dt}(\bullet)$ denotes the material derivative $\frac{\partial}{\partial t}(\cdot)+\mathbf{v}\cdot\nabla(\cdot)$. In (3), the second moment of $\mathbf{m}$,

$$\mathbf{M} = \langle\mathbf{mm}\rangle = \int_{\|\mathbf{m}\|=1}\mathbf{mm}f(\mathbf{m},t)\,d\mathbf{m}, \tag{4}$$

enters through the mean-field Maier-Saupe excluded-volume potential V,

$$V = -\frac{3}{2}NkT\,\mathbf{mm}:\mathbf{M}. \tag{5}$$

The mesoscopic orientation tensor $\mathbf{Q}$ is the traceless form of $\mathbf{M}$, whose eigenvalues and eigenvectors provide the mesoscopic order parameters and directors:

$$\mathbf{Q} = \mathbf{M}-\tfrac{1}{3}\mathbf{I}. \tag{6}$$

At issue here is the Smoluchowski kinetic equation for an imposed simple shear flow, given in Cartesian coordinates (x,y,z) by

$$\mathbf{v} = \dot{\gamma}(y,0,0), \tag{7}$$

where $\dot{\gamma}$ is the shear rate, assumed constant. The *Peclet number*, $Pe = \dot{\gamma}/D_r^0$, is the normalized shear rate. The corresponding rate-of-strain and vorticity tensors are:

$$\mathbf{D} = \frac{1}{2}\dot{\gamma}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}, \quad \omega = \frac{1}{2}\dot{\gamma}\begin{pmatrix}0&1&0\\-1&0&0\\0&0&0\end{pmatrix}. \tag{8}$$

3 Important expansions

We employ spherical harmonic expansions (Larson and Ottinger, 91; Faraoni *et. al*, 99) with the basis $Y_l^m(\theta,\phi)$, defined by

$$Y_l^m(\theta,\phi) = P_l^m(\cos\theta)e^{im\phi}, \tag{9}$$

where $P_l^m(\cos\theta)$ are normalized Legendre polynomials. We now develop expansion formulas for the various terms in the Smoluchowski equation (3), which we will then combine to derive the weak shear construction of f.

3.1 Maier-Saupe potential

For any function $g = g(\theta,\phi)$, define T_g as

$$T_g = \mathbf{mm}:\langle\mathbf{mm}\rangle_g \tag{10}$$

with

$$\langle\mathbf{mm}\rangle_g = \int_{\|\mathbf{m}\|=1}\mathbf{mm}g\,d\mathbf{m}. \tag{11}$$

One can write T_g as an expansion with only 6 terms:

$$T_g = \frac{4\pi}{3}\langle Y_0^0\rangle_g Y_0^0+\frac{8\pi}{15}\sum_{m=-2}^{2}(-1)^m\langle Y_2^{-m}\rangle_g Y_2^m. \tag{12}$$

From this expansion, by the orthogonality property of the harmonics, we immediately find

$$\begin{cases} T_{Y_0^0} = \frac{4\pi}{3}Y_0^0 \\ T_{Y_2^m} = \frac{8\pi}{15}Y_2^m, \quad m=-2,-1,0,1,2, \\ T_{Y_l^m} = 0, \quad \text{otherwise}. \end{cases} \tag{13}$$

We note that T_g is a linear function of g.

The Maier-Saupe potential for the distribution function f is then given by

$$\begin{aligned} V_{MS} &= -\frac{3}{2}kTN\mathbf{mm}:\langle\mathbf{mm}\rangle \\ &= \frac{4\pi}{3}\langle Y_0^0\rangle_f Y_0^0+\frac{8\pi}{15}\sum_{m=-2}^{2}(-1)^m\langle Y_2^{-m}\rangle_f Y_2^m. \end{aligned} \tag{14}$$

3.2 Shear flow

The last term in (3) is the shear flow contribution, which can be written as

$$
\begin{aligned}
&\mathcal{R}\cdot[\mathbf{m}\times\dot{\mathbf{m}}f] \\
&= -\frac{1}{2}\dot{\gamma}\left[(1+a\cos 2\phi)\frac{\partial f}{\partial\phi}+\frac{1}{2}a\sin 2\theta\sin 2\phi\frac{\partial f}{\partial\theta}\right] \\
&+\frac{3}{2}a\dot{\gamma}(\sin^2\theta\sin 2\phi)f \\
&= -\frac{1}{2}\dot{\gamma}G(f),
\end{aligned}
\tag{15}
$$

where the linear function $G(f)$ can be expressed as

$$
\begin{aligned}
G(f) = a\sqrt{\frac{8\pi}{15}}&\left(\frac{1}{2}(Y_2^1-Y_2^{-1})\mathcal{R}_x f+\frac{1}{2}i(Y_2^1+Y_2^{-1})\mathcal{R}_y f\right. \\
&\left.+(Y_2^2+Y_2^{-2})\mathcal{R}_z f\right) \\
&+\mathcal{R}_z f-3\sqrt{\frac{8\pi}{15}}ia(Y_2^2-Y_2^{-2})f.
\end{aligned}
\tag{16}
$$

$\mathcal{R}_x$, $\mathcal{R}_y$ and $\mathcal{R}_z$ are three components of the operator $\mathcal{R}$ in Cartesian coordinates. Applied to the spherical harmonics, we have

$$
\begin{aligned}
&\frac{1}{i}G(Y_l^m) \\
&= mY_l^m + a\left(\sum_{p=-2}^{2}\alpha_{l,m,p}Y_{l+p}^{m-2}+\sum_{p=-2}^{2}\alpha_{l,-m,p}Y_{l+p}^{m+2}\right),
\end{aligned}
\tag{17}
$$

where the coefficients are determined by

$$
\begin{cases}
\alpha_{l,m,-2} = \frac{(l-2)\sqrt{(-3-4l+4l^2)(-3+l+m)(-2+l+m)(-1+l+m)(l+m)}}{2(-3+2l)(-1+2l)(1+2l)} \\
\alpha_{l,m,0} = \frac{3(1+2l)\sqrt{(1+l-m)(2+l-m)(-1+l+m)(l+m)}}{2(-1+2l)(1+2l)(3+2l)} \\
\alpha_{l,m,2} = -\frac{(3+l)\sqrt{(5+12l+4l^2)(1+l-m)(2+l-m)(3+l-m)(4+l-m)}}{2(1+2l)(3+2l)(5+2l)} \\
\alpha_{l,m,p} = 0, \quad \text{if } p\neq -2,0,2.
\end{cases}
\tag{18}
$$

3.3 The Smoluchowski equation for steady states

Steady states of (3) satisfy

$$
\begin{aligned}
\mathcal{R}\cdot\mathcal{R}f-\frac{3}{2}N\mathcal{R}\cdot(f\mathcal{R}T_f)& \\
+\frac{1}{2}PeG(f) = 0,.&
\end{aligned}
\tag{19}
$$

An important property for the rotational gradient operator $\mathcal{R}$ is that

$$
\mathcal{R}\cdot\mathcal{R}Y_l^m = -l(l+1)Y_l^m. \tag{20}
$$

4 Approximate steady solutions in weak shear

We expand f in the Peclet number Pe:

$$
f=\frac{1}{\sqrt{4\pi}}\left(f_0+Pef_1+Pe^2f_2+Pe^3f_3+\cdots\right), \tag{21}
$$

and the goal is to determine $f_0, f_1, f_2, \cdots$ associated with the isotropic quiescent state, $f_0 = \frac{1}{4\pi}$. If we insert this expansion into (19), we have

$$
\begin{aligned}
&\mathcal{R}\cdot\mathcal{R}f-\frac{3}{2}N\mathcal{R}\cdot(f\mathcal{R}T_f)+\frac{1}{2}PeG(f) \\
&= \frac{1}{\sqrt{4\pi}}\left\{\sum_{k=0}Pe^k\mathcal{R}\cdot\mathcal{R}f_k-\frac{3N}{4\sqrt{\pi}}\sum_{k_1=0}\sum_{k_2=0}Pe^{k_1+k_2}\mathcal{R}\cdot\left(f_{k_1}\mathcal{R}T_{f_{k_2}}\right)\right. \\
&\left.\quad+\frac{1}{2}Pe\sum_{k=0}Pe^kG(f_k)\right\}.
\end{aligned}
\tag{22}
$$

4.1 Leading order terms

The terms independent of Pe give the quiescent Smoluchowski equation for f_0,

$$
\mathcal{R}\cdot\mathcal{R}f_0-\frac{3N}{4\sqrt{\pi}}\mathcal{R}\cdot(f_0\mathcal{R}T_{f_0}) = 0. \tag{23}
$$

With the normalization

$$
\int_{||\mathbf{m}||=1} f\,d\mathbf{m} = 1, \tag{24}
$$

the *isotropic solution* is

$$
f_0 = Y_0^0 = \frac{1}{\sqrt{4\pi}}. \tag{25}
$$

The nematic branch is computed numerically in (Larson and Ottinger, 91; Faraoni *et. al*, 99; Forest *et. al*, 02b), and several valiant attempts have been made to characterize this branch of solutions analytically. Without analytical control on the quiescent nematic branch, we restrict hereafter to the isotropic branch. If we had an explicit expansion for the nematic pdf, we could analyze the solvability conditions derived below.

4.2 First order terms

The terms of order Pe determine a non-homogeneous equation for f_1:

$$\mathcal{R}\cdot\mathcal{R}f_1 - \frac{3N}{4\sqrt{\pi}}\left(\mathcal{R}\cdot(f_0\,\mathcal{R}T_{f_1}) + \mathcal{R}\cdot(f_1\,\mathcal{R}T_{f_0})\right) + \frac{1}{2}G(f_0) = 0 \tag{26}$$

Since

$$T_{f_0} = T_{Y_0^0} = \frac{4\pi}{3}Y_0^0, \tag{27}$$

which is constant, and

$$G(f_0) = \sqrt{\frac{6}{5}}\,ai\,(Y_2^2 - Y_2^{-2}), \tag{28}$$

(26) reduces to

$$\mathcal{R}\cdot\mathcal{R}f_1 - \frac{3N}{8\pi}\mathcal{R}\cdot\mathcal{R}T_{f_1} + \sqrt{\frac{3}{10}}\,ai\,(Y_2^2 - Y_2^{-2}) = 0. \tag{29}$$

The normalization condition (24) together with (25) imply

$$\int_{\|\mathbf{m}\|=1} f_1\,d\mathbf{m} = 0. \tag{30}$$

Therefore, the first order correction to the isotropic state is explicitly solvable:

$$f_1 = \frac{i}{2}\sqrt{\frac{5}{6}}\,\frac{a}{N-5}\,(Y_2^2 - Y_2^{-2}), \tag{31}$$

which is real since Y_2^{-2} is the complex conjugate of Y_2^2.

4.3 Second order terms

The second order terms give

$$\mathcal{R}\cdot\mathcal{R}f_2 - \frac{3N}{4\sqrt{\pi}}\left[\mathcal{R}\cdot(f_0\,\mathcal{R}T_{f_2}) + \mathcal{R}\cdot(f_1\,\mathcal{R}T_{f_1}) + \mathcal{R}\cdot(f_2\,\mathcal{R}T_{f_0})\right] + \frac{1}{2}G(f_1) = 0, \tag{32}$$

or equivalently,

$$\mathcal{R}\cdot\mathcal{R}f_2 - \frac{3N}{8\pi}\mathcal{R}\cdot\mathcal{R}T_{f_2} = \frac{3N}{8\pi}\mathcal{R}\cdot(f_1\,\mathcal{R}T_{f_1}) - \frac{1}{2}G(f_1). \tag{33}$$

Denote

$$\alpha_1 = \frac{1}{2}\sqrt{\frac{5}{6}}\,\frac{a}{N-5}, \tag{34}$$

then we have

$$f_1 = i\alpha_1\,(Y_2^2 - Y_2^{-2}) \tag{35}$$

$$T_{f_1} = i\alpha_1\,(T_{Y_2^2} - T_{Y_2^{-2}}) = i\frac{8\pi}{15}\alpha_1\,(Y_2^2 - Y_2^{-2}) \tag{36}$$

Now we expand the right hand side of (33) in spherical harmonics. The following formulas are needed:

$$(\mathcal{R}f_1)\cdot(\mathcal{R}T_{f_1}) = -\frac{8\pi}{15}\alpha_1^2\,\mathcal{R}(Y_2^2 - Y_2^{-2})\cdot\mathcal{R}(Y_2^2 - Y_2^{-2}) = \frac{16\sqrt{\pi}}{105}\alpha_1^2\left(21Y_0^0 - 3\sqrt{5}Y_2^0 - 2Y_4^0 + \sqrt{70}(Y_4^4 + Y_4^{-4})\right) \tag{37}$$

$$\begin{aligned} & f_1\,(\mathcal{R}\cdot\mathcal{R}T_{f_1}) \\ &= -\frac{8\pi}{15}\alpha_1^2\,(Y_2^2 - Y_2^{-2})\mathcal{R}\cdot\mathcal{R}\,(Y_2^2 - Y_2^{-2}) \\ &= \frac{48\pi}{15}\alpha_1^2\,(Y_2^2 - Y_2^{-2})^2 \\ &= \frac{8\sqrt{\pi}}{35}\alpha_1^2\left(-14Y_0^0 + 4\sqrt{5}Y_2^0 - 2Y_4^0 + \sqrt{70}(Y_4^4 + Y_4^{-4})\right) \end{aligned} \tag{38}$$

which give

$$\mathcal{R}\cdot(f_1\,\mathcal{R}T_{f_1}) = (\mathcal{R}f_1)\cdot(\mathcal{R}T_{f_1}) + f_1\,(\mathcal{R}\cdot\mathcal{R}T_{f_1}) = \frac{8\sqrt{\pi}}{105}\alpha_1^2\left(6\sqrt{5}Y_2^0 - 10Y_4^0 + 5\sqrt{70}(Y_4^4 + Y_4^{-4}))\right). \tag{39}$$

We also expand $G(f_1)$

$$\begin{aligned} G(f_1) &= i\alpha_1\,\left(G(Y_2^2) - G(Y_2^{-2})\right) \\ &= -\alpha_1\left(2(Y_2^2 + Y_2^{-2}) + \frac{a}{7}\sqrt{\frac{2}{15}}\left[6\sqrt{5}\,Y_2^0 - 10\,Y_4^0 + 5\sqrt{70}\,(Y_4^4 + Y_4^{-4})\right]\right) \end{aligned} \tag{40}$$

Therefore, the solution to (33) has the form

$$f_2 = f_2^{(1)}(Y_2^0, Y_2^2, Y_2^{-2}) + f_2^{(2)}(Y_4^0, Y_4^4, Y_4^{-4}), \tag{41}$$

where $f_1^{(1)}$ is a linear function of Y_2^0, Y_2^2, Y_2^{-2}, $f_2^{(2)}$ is a linear function about Y_4^0, Y_4^4, Y_4^{-4}. By formula (13), (33) reduces to

$$-\frac{6}{5}(5-N)f_1^{(1)} - 20f_2^{(2)} = \frac{3N}{8\pi}\mathcal{R}\cdot(f_1\,\mathcal{R}T_{f_1}) - \frac{1}{2}G(f_1). \tag{42}$$

Then from (39) and (40), *we finally arrive at the explicit formulas to construct the second-order term f_2 in the expansion of f*:

$$f_2^{(1)} = \frac{5\alpha_1}{6(N-5)}\left\{\left(\frac{6\sqrt{5}N}{35\sqrt{\pi}}\alpha_1 + \frac{a\sqrt{6}}{7}\right)Y_2^0 + (Y_2^2 + Y_2^{-2})\right\} \tag{43}$$

$$f_2^{(2)} = \frac{\alpha_1}{140}\left(\frac{\alpha_1 N}{5\sqrt{\pi}} + \frac{a}{\sqrt{30}}\right)\left(10Y_4^0 - 5\sqrt{70}(Y_4^4 + Y_4^{-4})\right) \tag{44}$$

5 Alignment properties from the pdf construction

The explicit formula constructed above,

$$f \approx \frac{1}{\sqrt{4\pi}}\left(f_0 + Pe f_1 + Pe^2 f_2\right), \tag{45}$$

is now used to infer properties of the shear-perturbed isotropic branch. We first note that the construction of f contains only Y_l^m with *m even*. In (Forest *et. al*, 02a), we showed that if f has zero projections onto Y_l^m for all m odd, then f is an *in-plane* solution of the shear-driven Smoluchowski equation. This notion extends to kinetic theory the traditional definition of in-plane L-E configurations and mesoscopic orientation tensors, discussed shortly. We note at this point that through $O(Pe^2)$, we have established *the weak-shear deformation of the isotropic branch persists as a steady distribution, and aligns in-plane.* We now extract more detailed information about the alignment properties, both in the dilute and concentrated regimes.

The traditional measure of in-plane orientation is to project f onto the second-moment tensor **Q** (Forest *et. al*, 02a):

$$Q_{xx} = -\frac{2}{3}\sqrt{\frac{\pi}{5}}a_{2,0} + \sqrt{\frac{8\pi}{15}}Re(a_{2,2}) \tag{46}$$

$$Q_{yy} = -\frac{2}{3}\sqrt{\frac{\pi}{5}}a_{2,0} - \sqrt{\frac{8\pi}{15}}Re(a_{2,2}) \tag{47}$$

$$Q_{xy} = -\sqrt{\frac{8\pi}{15}}Im(a_{2,2}) \tag{48}$$

$$Q_{xz} = -\sqrt{\frac{8\pi}{15}}Re(a_{2,1}) \tag{49}$$

$$Q_{yz} = \sqrt{\frac{8\pi}{15}}Im(a_{2,1}), \tag{50}$$

where we recall

$$a_l^m = (-1)^m \langle Y_l^{-m}\rangle_f, \tag{51}$$

and $Re(\cdot)$ and $Im(\cdot)$ represent the real and the imaginary part, respectively. Note this projection suppresses the influence of Y_l^m with $m > 2$, because of the orthogonality properties of the spherical harmonics. Therfore **Q** does not dependent on P_4. From the exact expansions through $O(Pe^2)$ we deduce

$$\langle Y_2^0\rangle_f = \frac{5\alpha_1}{6(N-5)}\left(\frac{6\sqrt{5}N}{35\sqrt{\pi}}\alpha_1 + \frac{a\sqrt{6}}{7}\right) \tag{52}$$

$$\langle Y_2^1\rangle_f = 0 \tag{53}$$

$$\langle Y_2^2\rangle_f = \alpha_1 Pe\left(\frac{5}{6(N-5)}Pe - i\right), \tag{54}$$

which now gives the explicit second-moment of f:

$$\mathbf{Q} = \mathbf{0} + Pe\frac{a}{6(5-N)}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix} + Pe^2\frac{a\alpha_1}{6(5-N)}\left[\gamma_1\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix} + \gamma_2\begin{pmatrix}1&0&0\\0&-1&0\\0&0&0\end{pmatrix}\right] \tag{55}$$

where

$$\gamma_1 = \frac{\sqrt{30}a}{21}\left(\frac{1}{2\sqrt{\pi}}\frac{N}{N-5} + 1\right), \tag{56}$$

$$\gamma_2 = -\sqrt{\frac{10}{3}}. \tag{57}$$

We can now explicitly provide the eigenvalues and eigenvectors of **Q** to determine the mesoscopic alignment properties.

The eigenvalues of **Q** through $O(Pe)$ are distinct, in descending order,

$$\lambda_1 = \frac{Pe}{6}\left|\frac{a}{5-N}\right|, \quad \lambda_2 = 0, \quad \lambda_3 = -\frac{Pe}{6}\left|\frac{a}{5-N}\right|. \tag{58}$$

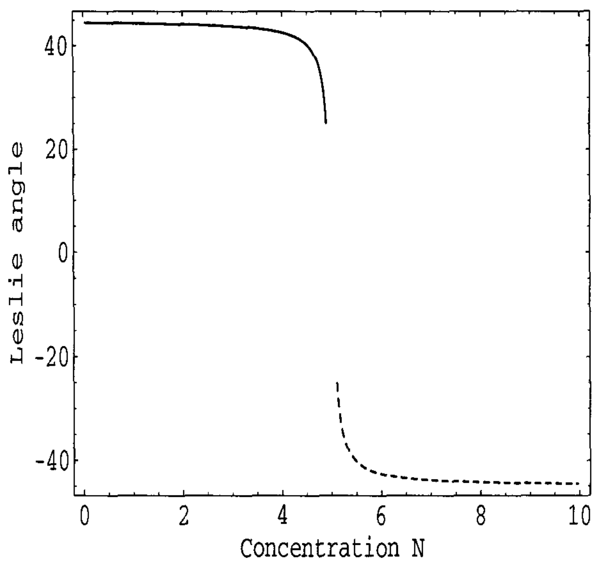

Figure 1. Leslie angle for $Pe = 0.1$ and $a = 1$. Solid line indicates stable solutions, dashed line unstable solutions.

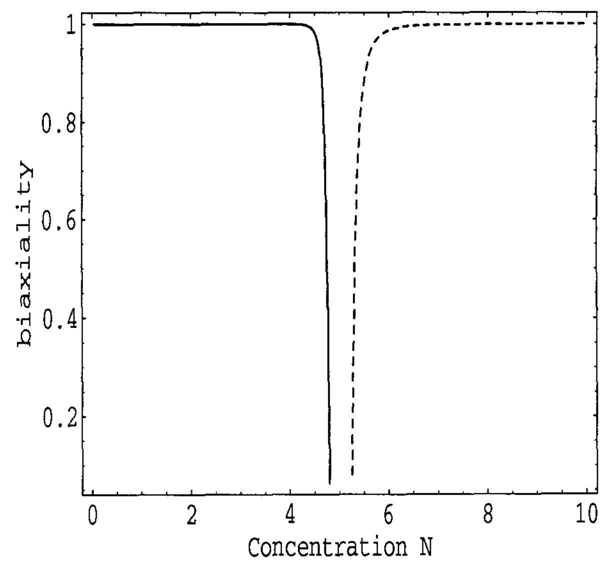

Figure 2. Biaxiality parameter b for $Pe = 0.1, a = 1$.

We deduce $\mathbf{Q}$ is *biaxial.* The *degree of biaxiality*, $0 \le b \le 1$, (Rienacker and Hess, 99) is defined by

$$b = \sqrt{1 - \frac{6\,Tr(\mathbf{Q}^3)^2}{Tr(\mathbf{Q}^2)^3}}, \tag{59}$$

which is depicted in Figure 2 versus N using the $O(Pe^2)$ eigenvalue formulas. This is one measure of the relative focusing of the distribution function with respect to the three director axes, with $b = 1$ corresponding to maximum biaxiality.

The intermediate eigenvalue, $\lambda_2 = 0$ through $O(Pe)$, has director $\mathbf{n}_2 = (0,0,1)$, aligned with the vorticity axis. Thus, the isotropic state can never become "logrolling", with peak orientation orthogonal to the shearing plane. Indeed, at leading order in Pe, there is no focusing of the distribution function along the vorticity axis.

The *major director* $\mathbf{n}_1 = (\cos\phi, \sin\phi, 0)$ (associated with the largest degree of order λ_1) always lies in the shear plane with $\mathbf{n}_3 \perp \mathbf{n}_1$ also in-plane. The formulae for λ_i indicate that the LCP molecules break their random orientation by shifting primary alignment completely within the shearing plane. The "mesoscopic ellipsoid" is an in-plane disc at $O(Pe)$, and opens into a full ellipsoid at $O(Pe^2)$.

The *major director* $\mathbf{n}_1$ is parallel to

$$\left(Q_{xx} - Q_{yy} + \sqrt{(Q_{xx} - Q_{yy})^2 + 4Q_{xy}^2},\, 2Q_{xy},\, 0\right), \tag{60}$$

so that the *Leslie alignment angle* ϕ *takes the explicit form through* $O(Pe^2)$:

$$\cos 2\phi = \frac{\frac{5Pe}{5-N}}{\sqrt{\left(\frac{5Pe}{5-N}\right)^2 + 36}} = \frac{1}{\lambda}. \tag{61}$$

This expression shows several important features:

- Flow-alignment always occurs for stable ($N < 5$) *and* unstable ($N > 5$) nearly isotropic states, i.e., $\lambda \ge 1$. *Tumbling is impossible for the shear perturbed isotropic branch.*
- The stable alignment angle in the weak shear limit, $Pe \to 0$, is 45^o, independent of both molecular aspect ratio and concentration N.
- The Leslie angle through $O(Pe^2)$ is independent of aspect ratio, depicted versus N in Figure 1 for fixed $Pe = 0.1$.

The shear-induced flow birefringence is measured by the differences in eigenvalues of $\mathbf{Q}$, which from the $O(Pe)$ formulas for λ_i are:

$$\lambda_1 - \lambda_2 = \left|\frac{a}{5-N}\right|\frac{Pe}{6}, \qquad \lambda_3 - \lambda_2 = -\left|\frac{a}{5-N}\right|\frac{Pe}{6}. \tag{62}$$

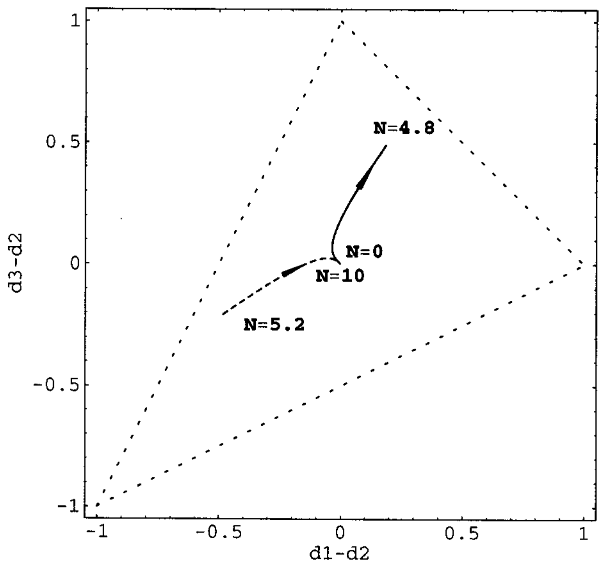

Figure 3. Order parameters for $Pe = 0.1$ and $a = 1$.

These are depicted in Figure 3 versus N for $Pe = 0.1$ using the $O(Pe^2)$ formulas.
The asymptotic analysis breaks down in an $O(Pe)$ neighborhood of the critical concentration $N = 5$ where the isotropic state becomes unstable. Indeed, we cannot satisfy the solvability conditions in this neighborhood, and the analysis suggests the isotropic branch fails to persist. This result is consistent with mesoscopic second-moment tensor analysis (Forest *et. al*, 02c) and numerical simulations of both kinetic theory (Faraoni *et. al*, 99; Forest *et. al*, 02b) and mesoscopic tensor models (Bhave *et. al*, 93; Forest and Wang, 02).

6 Rheological properties

The extra stress in dimensionless form is given by (Wang 02)

$$\tau = (\tfrac{2}{Re} + 3\nu kT\zeta_3(a))\mathbf{D} + 3a\nu kT[\mathbf{Q} - N(\mathbf{Q} + \tfrac{\mathbf{I}}{3})\mathbf{Q} + N\mathbf{Q} : \langle\mathbf{mmmm}\rangle]$$
$$+3\nu kT[\zeta_1(a)(\mathbf{DM} + \mathbf{MD}) + \zeta_2(a)\mathbf{D} : \langle\mathbf{mmmm}\rangle], \qquad (63)$$

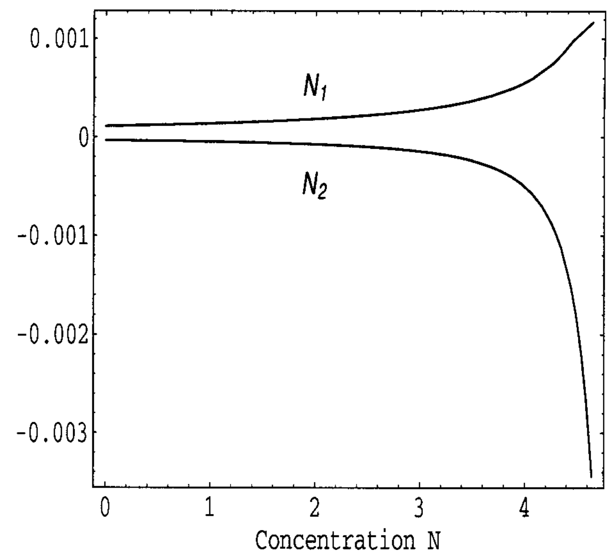

Figure 4. Normal stress differences for $Pe = 0.1$ and $a = 1$.

where

$$\zeta_3 = \frac{\zeta^{(0)}}{I_1}, \quad \zeta_1 = \zeta^{(0)}(\frac{1}{I_3} - \frac{1}{I_1}), \quad \zeta_2 = \zeta^{(0)}[\frac{J_1}{I_1 J_3} + \frac{1}{I_1} - \frac{2}{I_3}],$$
$$r = \sqrt{\frac{1+a}{1-a}}, \quad I_1 = 2r\int_0^\infty \frac{dx}{\sqrt{(r^2+x)(1+x)^3}},$$
$$I_3 = r(r^2+1)\int_0^\infty \frac{dx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}, \qquad (64)$$
$$J_1 = r\int_0^\infty \frac{xdx}{\sqrt{(r^2+x)(1+x)^3}}, \quad J_3 = r\int_0^\infty \frac{xdx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}.$$

where, ν is the number density of LCP molecules per unit volume. The steady shear stress η, the first normal stress difference N_1, and the second normal stress difference N_2 are then computed as

$$N_1 = \tau_{xx} - \tau_{yy}, \qquad (65)$$
$$N_2 = \tau_{yy} - \tau_{zz}, \qquad (66)$$
$$\eta = \tau_{xy}/Pe. \qquad (67)$$

Through $O(Pe^2)$, expansions for these rheological properties are:

$$N_1 = \frac{\nu kT}{6(5-N)} a^2 Pe^2 + O(Pe^3),$$
$$N_2 = 3\nu kT \frac{3a^2(N - 10\sqrt{\pi}) - (5-N)\sqrt{\pi}(14a - 24\zeta_2)}{504(5-N)^2\sqrt{\pi}} aPe^2,$$

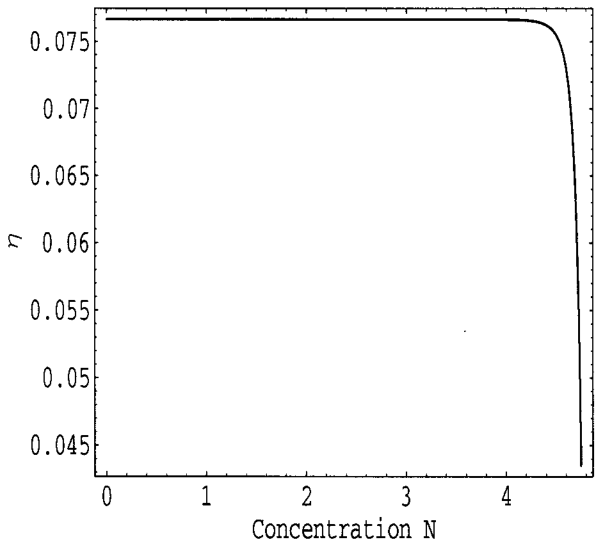

Figure 5. Shear stress for $Pe = 0.1$ and $a = 1$.

$$\eta = \frac{1}{10}\left(\nu kT(a+2\zeta_2) + 10(\frac{2}{Re} + \alpha\zeta_3)\right) + O(Pe)^2.$$

After scaling by $3\nu kT$, they are plotted in Figures 4 and 5, respectively. N_1 is clearly positive for $N \in (0, 5-\delta)$ with $\delta = O(Pe)$. N_2 does not change sign for parameter chosen here. The shear stress is nearly constant for $0 < N < 4.5$, and then exhibits shear thinning as the concentration increases towards the nematic transition.

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