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ORIGINAL CONTRIBUTION

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A classical problem revisited: rheology of nematic polymer monodomains in small amplitude oscillatory shear

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Abstract We revisit the classical problem of the viscoelastic response of nematic (liquid crystal) polymers to small amplitude oscillatory shear. A multiple time scale perturbation analysis is applied to the Doi–Hess mesoscopic orientation tensor model to describe key features observed of longtime experiments, both physical (Moldenaers and Mewis, J Rheol, 30:567–584, 1986; Larson and Mead, J Rheol, 33:1251–1281, 1989b) and numerical (herein). First, there is a very slow time scale drift in the envelope of oscillations of the major director; we characterize the mean director angle and the envelope of oscillation. Second, there are bistable asymptotic orientational states, distinguished in that they are precisely the zero-stress orientational distributions noted in Larson and Mead (J Rheol, 33:185–206, 1989a). Third, the drift dynamics and asymptotic mean director angle are determined by the initial orientation of the director, not by material properties; we characterize the domain of attraction of each bistable state. Finally, the director drift leads to a predicted longtime decrease in the storage and loss moduli, consistent with experimental observations.

Introduction

A solution of nematic liquid crystal polymers (LCPs) undergoes a spontaneous isotropic-to-nematic first-order phase transition, driven by either an increase in concentration or a decrease in temperature. In the nematic phase, the concentration and temperature determine the degree to which the solution is oriented, as described by the Flory order parameter. However, in the absence of an externally imposed field, the principal axis of the equilibrium distribution is arbitrary. In Russo and Maffettone (2003), this orientational degeneracy is broken by a strong steady shear flow component, which provides the background for an investigation of a superimposed weak oscillatory shear perturbation. In this paper, we examine the importance of this orientational degeneracy when small amplitude oscillatory shear flow is applied to a nematic monodomain at quiescent equilibrium.

We employ multiple time scale perturbation analysis of the Doi–Hess mesoscopic tensor model, which couples order parameter variations to the director dynamics. Though tractable only for in-plane orientational distributions, we predict very slow director drift dynamics that were not previously analyzed and we show that the drift depends strongly on the initial director orientation. Indeed, there are bistable longtime asymptotic states, each with a basin of attraction dictated by initial director orientation.

Armed with this multiple time scale analysis, we revisit this classical problem in rheology: the prediction of the storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli in response to imposed, small amplitude oscillatory shear. The seminal papers on linear viscoelasticity for LCPs are by Moldenaers and Mewis (1986) and Larson and Mead (1989a,b). Their work predated the wealth of understanding of the role of orientational degeneracy for LCP monodomains in imposed steady shear, i.e., the low frequency limit, $G'(0)$ and $G''(0)$, which yields steady and unsteady responses depending on molecular aspect ratio and number density. Our results share much in common with those of Larson and Mead (1989a) with the exception of our slow time scale dynamics; in fact, we recover many of their acute observations.

We begin with a brief discussion of the two types of monodomain responses (flow aligning and tumbling) to weak steady shear. For in-plane orientational configurations, the arbitrariness of the initial value of the alignment angle plays a minor role, affecting transients and not the longtime attractor. (We refer the interested reader to Van Horn et al. 2003; Zheng et al. 2005 for experiments and modeling of the role of initial director orientation in steady shear.) Then we turn to small amplitude oscillatory shear flow: We find that the director angle begins by oscillating around its initial value but the small oscillations of the order parameters induce a slow migration (with time scale proportional to the square of the shear rate) of the mean of the director oscillation. The mean director drifts toward either the flow or flow-gradient axis, depending on the initial value of the director angle. The envelope of the fast oscillations is likewise characterized. We also predict a slow decay in the amplitudes of oscillation of the order parameters.

Finally, we look at the associated stress tensor and various rheological properties. In their classical paper, Moldenaers and Mewis (1986) investigate a solution of poly-γ-benzyl-L-glutamate (PBLG) in *m*-cresol subjected to small amplitude oscillatory shear flow. They observe a decrease in the dynamic moduli occurring on a very slow time scale, results that were then verified by Larson and Mead (1989b). In both cases, the authors lamented that the Doi–Hess tensor models did not seem sufficient to predict this decay. We show with a weakly nonlinear, multiple time scale analysis that a decay phenomenon can be predicted theoretically from Doi–Hess theory.

Theoretical background

A dynamical equation for the symmetric, traceless mesoscopic orientation tensor $\mathbf{Q}$ in linear oscillatory shear flow is (Doi and Edwards 1986; Hess 1976; Wang 2002)

$$\begin{aligned}\frac{\partial}{\partial t}\mathbf{Q} =& -6D_{r0}\Lambda(\mathbf{Q})\left(\mathbf{Q}-N\left(\mathbf{Q}+\frac{\mathbf{I}}{3}\right)\cdot\mathbf{Q}+N\mathbf{Q}:\mathbf{Q}\left(\mathbf{Q}+\frac{\mathbf{I}}{3}\right)\right)\\ &+\Omega\cdot\mathbf{Q}-\mathbf{Q}\cdot\Omega+a(\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D})\\ &+\frac{2}{3}a\mathbf{D}-2a\mathbf{D}:\mathbf{Q}\left(\mathbf{Q}+\frac{\mathbf{I}}{3}\right),\end{aligned} \tag{1}$$

where the molecular geometry parameter $a=\frac{r^2-1}{r^2+1}$ is a function of aspect ratio r of the rod-like spheroidal molecules; the dimensionless concentration parameter N characterizes the strength of the Maier–Saupe intermolecular potential; rotational diffusion of an ensemble of rods is captured by a bulk rate D_{r0} and a prefactor for the orientational dependence $\Lambda(\mathbf{Q})=\left(1-\frac{3}{2}\mathbf{Q}:\mathbf{Q}\right)^{-2}$; and

$$\mathbf{D}=\frac{\dot\gamma\cos\omega t}{2}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix},\ \Omega=\frac{\dot\gamma\cos\omega t}{2}\begin{pmatrix}0&1&0\\-1&0&0\\0&0&0\end{pmatrix},$$

are the rate-of-strain and vorticity tensors for the imposed linear two-dimensional oscillatory shear velocity field $\mathbf{v}=(\mathbf{D}+\mathbf{\Omega})\cdot\mathbf{x}$ with shear rate $\dot\gamma$.

To make contact with previous analysis, we assume the major director $\mathbf{n}_1$ lies in the shearing plane, which is equivalent to imposing $Q_{xz}=Q_{yz}=0$.[1] This allows a convenient representation of $\mathbf{Q}$ in terms of the in-plane director angle ξ and the scalar order parameters s and β as

$$\mathbf{Q}=s\left(\mathbf{n}_1\mathbf{n}_1-\frac{\mathbf{I}}{3}\right)+\beta\left(\mathbf{n}_2\mathbf{n}_2-\frac{\mathbf{I}}{3}\right)$$
$$\mathbf{n}_1=(\cos\xi,\sin\xi,0),\ \mathbf{n}_2=(-\sin\xi,\cos\xi,0).$$

This is a standard “spectral representation” of the orientation tensor where $\mathbf{n}_1$ and $\mathbf{n}_2$ are eigenvectors and $s=\lambda_1-\lambda_2$ and $\beta=\lambda_2-\lambda_3$ are differences of the eigenvalues λ_i of $\mathbf{Q}$. This s is the traditional Flory order parameter, whereas β is a biaxiality order parameter because $\beta=0$ corresponds to a uniaxial phase. This representation turns Eq. 1 into the dynamical system (Forest and Wang 2003):

$$\begin{aligned}\frac{ds}{dt}=&-\Lambda(s,\beta)\left(U(s)-\frac{2Ns\beta}{3}(s-\beta-1)\right)\\ &+\frac{a}{3}Pe\cos\omega t\left(1-\beta+2s+3s\beta-3s^2\right)\sin2\xi,\\ \frac{d\beta}{dt}=&-\Lambda(s,\beta)\left(U(\beta)-\frac{2Ns\beta}{3}(\beta-s-1)\right)\\ &-\frac{a}{3}Pe\cos\omega t\left(1+2\beta-s+3s\beta-3\beta^2\right)\sin2\xi,\\ \frac{d\xi}{dt}=&-\frac{1}{2}Pe\cos\omega t\left(1-\frac{a}{3}\frac{s+\beta+2}{s-\beta}\cos2\xi\right),\end{aligned} \tag{2}$$

where $U(s)=s\left(1-\frac{N}{3}(1-s)(2s+1)\right)$, $\Lambda(s,\beta)=\frac{\left(1-s_+^2\right)^2}{\left(1-s^2+s\beta-s\beta^2\right)^2}$, and where we measure time in terms of the relaxation time $t_r=\frac{\left(1-s_+^2\right)^2}{6D_{r0}}$ and appropriately redefine ω so that it is now dimensionless, and the shear rate is normalized in terms of the dimensionless, Peclet number, $Pe=\frac{\dot\gamma\left(1-s_+^2\right)^2}{6D_{r0}}$.

[1] The generalization of this analysis to full tensor degrees of freedom leads to a five-dimensional dynamical system, which was not yet analytically solved.

When there is no flow (Pe=0) and the concentration is sufficiently high ($N>3$), the order parameters relax to the stable uniaxial nematic equilibrium (s, β)=(s_+, 0) where $s_+ = \frac{1}{4}\left(1+3\sqrt{1-\frac{8}{3N}}\right)$. (This phase also exists for $\frac{8}{3} < N < 3$, but it is bistable with the isotropic phase.) However, this equilibrium has no preferred orientation of the director; any constant value $\xi \equiv \Xi_0$ (mod π) yields an equilibrium solution. This degree of freedom in the equilibrium rest state for N>3 parameterizes the initial conditions for the analysis to follow. Several authors (cf. Marrucci and Greco 1993; Rienäcker and Hess 1999; Rienäcker et al. 2002a,b; Forest and Wang 2003; Vicente Alonso et al. 2003; Forest et al. 2003; Hess and Kröger 2004; Lee et al. 2006) have explored the role of orientational degeneracy in steady shear.

Weak flow-rate limit for steady shear

In weak steady shear (Pe<<1 with ω=0 in Eq. 2), we employ "two-timing" asymptotic analysis similar to that used in Vicente Alonso et al. (2003) for a Landau-de Gennes model. The utility of this asymptotic analysis is that one can effectively diagonalize the fast and slow response of the director and order parameters and thereby solve the system in Eq. 2 in a hierarchy of simpler, lower dimensional equations. The molecular relaxation time scale T_0=t dominates the order parameter Eqs. 2a and 2b while the director angle Eq. 2c is on the slower shear flow time scale T_1=$Pe\,t$. We treat the initial slow time as zero, but we allow for the initial value of the fast time T_{00}=t_0 to be a free parameter, the role of which will be discussed below. We use the expansions

$$s = s_+ + Pe\, s_1^{ss}(T_0, T_1) + O\left(Pe^2\right),$$
$$\beta = 0 + Pe\beta_1^{ss}(T_0, T_1) + O\left(Pe^2\right),$$
$$\xi = \xi_0^{ss}(T_0, T_1) + Pe\xi_1^{ss}(T_0, T_1) + O\left(Pe^2\right),$$

where the superscript ss denotes steady shear.

At zeroth order in Pe, we quickly see that $\frac{\partial \xi_0^{ss}}{\partial T_0} = 0$ and so at first order, Eq. 2c yields

$$\frac{\partial \xi_1^{ss}}{\partial T_0} = -\frac{d\xi_0^{ss}}{dT_1} - \frac{1}{2}\left(1 - \lambda_0 \cos 2\xi_0^{ss}(T_1)\right), \tag{3}$$

where we define the *Leslie tumbling parameter* λ_0=$\lambda(s_+, 0)$ with $\lambda(s, \beta) = \frac{a}{3}\frac{2+s+\beta}{s-\beta}$. The solvability condition that ξ_1^{ss} remains bounded as a function of T_0 yields

$$\frac{d\xi_0^{ss}}{dT_1} = -\frac{1}{2}\left(1 - \lambda_0 \cos 2\xi_0^{ss}\right).$$

Thus, one recovers the well-known director angle equation from Leslie–Ericksen (LE) theory. It is separable and can be integrated in closed form, which we represent by $\xi_0^{ss}(T_1) = \Xi(T_1 + \phi_0)$ where

$$\Xi(x) = \begin{cases} \tan^{-1}\left(\frac{\sqrt{1-\lambda_0^2}}{1+\lambda_0}\tan\left(-\frac{\sqrt{1-\lambda_0^2}}{2}x\right)\right), \text{if } |\lambda_0| < 1, \\ \tan^{-1}\left(\tan\xi_L \tanh\left(\frac{\sqrt{\lambda_0^2-1}}{2}x\right)\right), \text{if } |\lambda_0| > 1 \text{ and } |\Xi_0| < |\xi_L|, \\ \tan^{-1}\left(\tan\xi_L \coth\left(\frac{\sqrt{\lambda_0^2-1}}{2}x\right)\right), \text{if } |\lambda_0| > 1 \text{ and } |\xi_L| < |\Xi_0| < \frac{\pi}{2}, \end{cases} \tag{4}$$

where $\xi_L = \tan^{-1}\left(\frac{\sqrt{\lambda_0^2-1}}{\lambda_0+1}\right)$ is the classical Leslie angle and

$$\phi_0 = \begin{cases} -\frac{2}{\sqrt{1-\lambda_0^2}}\tan^{-1}\left(\frac{1+\lambda_0}{\sqrt{1-\lambda_0^2}}\tan\Xi_0\right), \text{if } |\lambda_0| < 1, \\ \frac{2}{\sqrt{\lambda_0^2-1}}\tanh^{-1}\left(\frac{\tan\Xi_0}{\tan\xi_L}\right), \text{if } |\lambda_0| > 1 \text{ and } |\Xi_0| < |\xi_L|, \\ \frac{2}{\sqrt{\lambda_0^2-1}}\coth^{-1}\left(\frac{\tan\Xi_0}{\tan\xi_L}\right), \text{if } |\lambda_0| > 1 \text{ and } |\xi_L| < |\Xi_0| < \frac{\pi}{2}. \end{cases} \tag{5}$$

Thus, if $|\lambda_0| < 1$, then $\xi_0^{ss}(Pe\,t)$ is periodic with period $T^{ss} = \frac{2\pi}{Pe\sqrt{1-\lambda_0^2}}$, meaning that the director tumbles. However, if $|\lambda_0| > 1$, then the director aligns relative to the flow with $\xi_0^{ss}(Pe\,t)$ decaying to the Leslie alignment angle ξ_L.

To our knowledge the exact role of the initial director angle Ξ_0 has not been previously amplified. It is often hidden in a generic constant of integration and sometimes taken to be zero. This is understandable because the qualitative effect of Ξ_0 on ξ_0^{ss} is not significant, introducing only a phase shift in the tumbling regime and in the flow-aligning case only affecting the direction from which the director approaches the Leslie angle via the choice of either hyperbolic tangent or hyperbolic cotangent in Eq. 4. We shall show below, however, that the effect of Ξ_0 is qualitatively significant for oscillatory shear.

Using $\xi_0^{ss}(T_1)$, the $O(Pe)$ order parameter terms can be found exactly by quadrature:

$$\begin{aligned} \beta_1^{ss}(T_0,T_1) &= a\sin 2\xi_0^{ss}(T_1)\frac{a_4}{a_1}\left(1-e^{a_1(T_{00}-T_0)}\right), \\ s_1^{ss}(T_0,T_1) &= a\sin 2\xi_0^{ss}(T_1)\left(\frac{a_3a_4+a_5a_1}{a_1a_2}-\frac{a_4}{2a_1}e^{a_1(T_{00}-T_0)}+\frac{a_4-2a_5}{2a_2}e^{a_2(T_{00}-T_0)}\right), \end{aligned} \tag{6}$$

where $a_1 = Ns_+$, $a_2 = \frac{N}{3}\left(s_+ + 2 - \frac{6}{N}\right)$, $a_3 = \frac{1}{2}(a_2 - a_1)$, $a_4 = \frac{1}{3}(s_+ - 1)$ and $a_5 = \frac{1}{6}\left(s_+ - 1 + \frac{9}{N}\right)$. The two order parameter relaxation rates a_1 and a_2 are the same rates identified in Larson and Mead (1989a). In the nematic region, $N > 3$, $a_1 > a_2 > \frac{1}{2}$. However, in the bistable region, $\frac{8}{3} < N < 3$, $a_2 \to 0$ as $N \to \frac{8}{3}$.

Thus, for steady shear at leading order, the tensor model predicts the same director behavior as LE theory coupled with order parameters that decay exponentially to the quiescent uniaxial values modified by $O(Pe)$ corrections that are proportional to $\sin 2\xi_0^{ss}$. The main parameter in determining qualitative behavior is the Leslie "material parameter" λ_0, which is identified for nematic polymers as dependent on aspect ratio through a and concentration through s_+ (Forest and Wang 2003).

Weak oscillatory shear: asymptotics and slow drift

Anticipating a similar relationship between the tensor and LE models for the more complicated dynamics of oscillatory shear, we begin our investigation of oscillatory shear with the nonautonomous generalization of the LE director angle equation,

$$\frac{d\xi_{LE}}{dt} = -\frac{1}{2}Pe\cos\omega t(1-\lambda_0\cos 2\xi_{LE}). \tag{7}$$

This equation can also be solved exactly: $\xi_{LE}(t) = \Xi\left(Pe\frac{\sin\omega t - \sin\omega t_0}{\omega} + \phi_0\right)$ where the function Ξ is defined by Eq. 4. This solution predicts an oscillatory response for both "tumbling" and "flow-aligning" nematic liquids as classified based on their steady shear response. This oscillatory behavior is a consequence of the "internal clock," $\frac{Pe}{\omega}\sin\omega t$, which oscillates between $\pm\frac{Pe}{\omega}$ on which the function Ξ is evaluated. Thus, the director angle oscillates about the initial angle Ξ_0.

Figure 1 compares ξ_{LE} to a numerical solution of Eq. 2 where ξ, s, and β are coupled. We observe that ξ_{LE} accurately captures the oscillatory nature of the director angle *for small times*, a few dozen periods of the plates. However, for larger times, a slow drift of the mean director angle of the tensor model emerges and furthermore, the drift dynamics are sensitive to initial data.

More complete numerical studies show the asymptotic value of the mean angle is parallel to the plates when $|\Xi_0| < \frac{\pi}{4}$ or perpendicular to the plates when $\frac{\pi}{4} < |\Xi_0| < \frac{\pi}{2}$. For the LE model, the asymptotic value of the mean is simply Ξ_0, independent of the initial data *and* independent of the Leslie parameter λ_0.

Before using multiple time scale perturbation analysis, we must briefly discuss the additional time scale introduced when $\omega \neq 0$. We limit the present discussion to relatively fast plate oscillation or $\omega >> Pe$ and use $\cos\,\omega t = \cos\omega T_0$ when time appears explicitly in Eq. 2. In addition, we note that we have used the term "mean" loosely for indeed, $\frac{\omega}{2\pi}\int_{t-\frac{\pi}{\omega}}^{t+\frac{\pi}{\omega}}\xi_{LE}(t')dt' \neq \Xi_0$ (unless Ξ_0=0), but instead $\int_{t-\frac{\pi}{\omega}}^{t+\frac{\pi}{\omega}} sgn(\xi_{LE}(t') - \Xi_0)dt' = 0$. For the remainder of the paper, we use "mean" to refer to integrating with respect to T_0 only over one period.

If the two-timing argument from Section 3 is followed again for oscillatory shear, we still have $\frac{\partial \xi_0}{\partial T_0} = 0$ so that $\xi_0(T_0, T_1) \equiv \tilde{\xi}_0(T_1)$, but Eq. 3 becomes $\frac{\partial \xi_1}{\partial T_0} = -\frac{d\tilde{\xi}_0}{dT_1} - \frac{1}{2}\cos\omega T_0\left(1 - \lambda_0 \cos 2\tilde{\xi}_0(T_1)\right)$. After integration with respect to T_0, one finds

$$\xi_1(T_0, T_1) = -T_0 \frac{d\tilde{\xi}_0}{dT_1} - \frac{\sin\omega T_0 - \sin\omega T_{00}}{2\omega}\left(1 - \lambda_0 \cos 2\tilde{\xi}_0\right) + \tilde{\xi}_1(T_1). \tag{8}$$

Thus, the solvability condition for ξ_1 to remain bounded as a function of T_0 is now $\frac{d\tilde{\xi}_0}{dT_1} = 0$, implying that $\xi_0(T_0, T_1) \equiv \Xi_0$, which clearly does *not* capture the longtime dynamics of the numerical solutions shown in Fig. 1. We shall see that, in fact, this longtime drift of the mean of the oscillation arises from the emergence of higher harmonics in the $O(Pe^2)$ balance, arising precisely through the small amplitude oscillations of the tumbling parameter $\lambda(s, \beta)$. Thus, LE theory cannot yield this effect. Instead of $\xi_0(T_0, T_1) \equiv \Xi_0$, we allow $\xi_0(T_0, T_1, T_2) \equiv \tilde{\xi}_0(T_2)$ for a new slower time $T_2 = Pe^2 t$ where $\tilde{\xi}_0(T_2)$ is to be determined and replace $\tilde{\xi}_1(T_1)$ in Eq. 8 with $\tilde{\xi}_1(T_1, T_2)$.

We can determine the first-order corrections for the order parameters by quadrature as in the steady shear case, but now they quickly decay to sinusoidal states:

$$\begin{aligned}\beta_1(T_0, T_2) &= a \sin 2\tilde{\xi}_0(T_2)\left(a_{\beta_1}\cos\omega T_0 + b_{\beta_1}\sin\omega T_0 + c_{\beta_1} e^{a_1(T_{00}-T_0)}\right)\\ s_1(T_0, T_2) &= a \sin 2\tilde{\xi}_0(T_2)\left(a_{s_1}\cos\omega T_0 + b_{s_1}\sin\omega T_0 + \frac{c_{\beta_1}}{2} e^{a_1(T_{00}-T_0)} + c_{s_1} e^{a_2(T_{00}-T_0)}\right),\end{aligned} \tag{9}$$

where $a_{\beta_1} = \frac{a_1 a_4}{a_1^2+\omega^2}$, $b_{\beta_1} = \frac{\omega a_4}{a_1^2+\omega^2}$ $c_{\beta_1} = -a_{\beta_1}\cos\omega T_{00} - b_{\beta_1}\sin\omega T_{00}$, $a_{s_1} = \frac{a_3\left(a_2 a_{\beta_1} - \omega b_{\beta_1}\right) + a_5 a_2}{a_2^2+\omega^2}$, $b_{s_1} = \frac{a_3\left(\omega a_{\beta_1} + a_2 b_{\beta_1}\right) + a_5\omega}{a_2^2+\omega^2}$, $c_{s_1} = -a_{s_1}\cos\omega T_{00} - b_{s_1}\sin\omega T_{00} - \frac{c_{\beta_1}}{2}$. We briefly pause to note that we have the freedom to add functions of T_1 and T_2 to c_{β_1} and c_{s_1}, but we will suppress these terms because they would be quickly killed by the exponentially decaying factors. We also observe that judiciously fine tuning T_{00} can make either $c_{\beta_1} = 0$ or $c_{s_1} = 0$, thereby eliminating our choice of terms that decay exponentially with rates a_1 or a_2, leaving us with only one decay rate in the first-order terms.

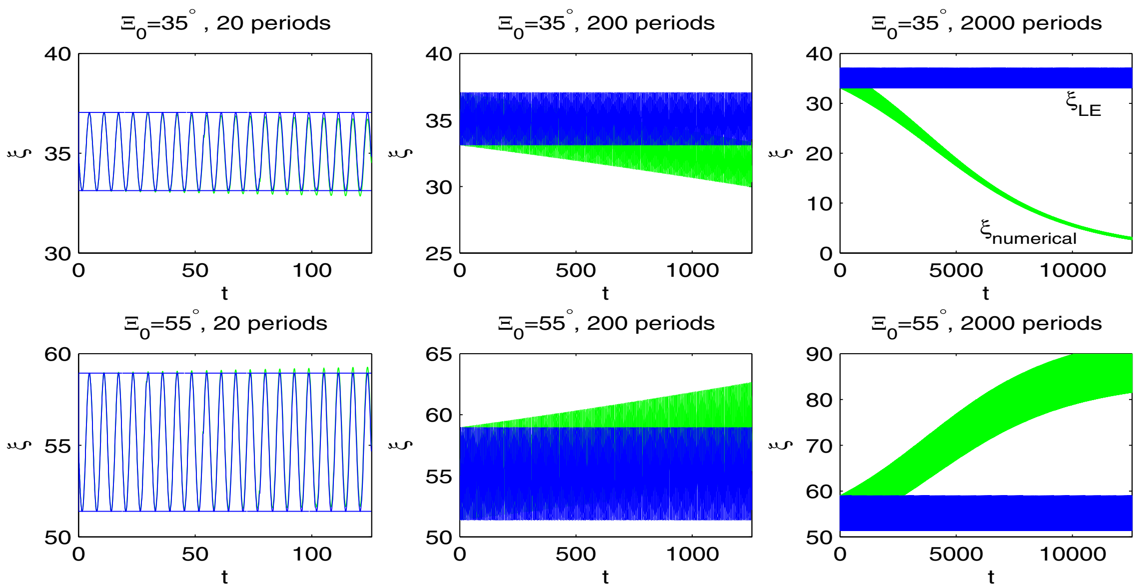

Fig. 1 The LE theory prediction (*dark band*) of oscillation around the initial value Ξ_0 coincides with the numerical solution (*light band*) for the first few plate oscillations, but the mean slowly drifts toward either 0° (if $|\Xi_0|<45°$) or ±90° (if $45° < |\Xi_0| < 90°$). N=6, a=0.8 (λ_0=0.926), Pe=0.1, and ω_0=1 for Ξ_0=35° and Ξ_0=55°

We can now better approximate $\lambda(s, \beta)$ by $\lambda(s_+ + Pes_1, Pe\beta_1) = \lambda_0 + Pe\lambda_1 + O(Pe^2)$ with

$$\begin{aligned}\lambda_1 &= \frac{2a}{3s_+^2}((1+s_+)\beta_1 - s_1)\\ &= 2\sin 2\tilde{\xi}_0(T_2)(B_1\cos\omega T_0 + B_2\sin\omega T_0)\end{aligned}$$

where $B_1 = \frac{a^2}{3s_+^2}\left((1+s_+)a_{\beta_1} - a_{s_1}\right)$, $B_2 = \frac{a^2}{3s_+^2}((1+s_+)b_{\beta_1} - b_{s_1})$ and terms that decay exponentially with T_0 are dropped. It can be shown that $B_1<0$ for all $N > \frac{8}{3}$ and $\omega>0$.

Thus, at second order, Eq. 2c simplifies to

$$\begin{aligned}\frac{\partial\xi_2}{\partial T_0} + \frac{\partial\tilde{\xi}_1}{\partial T_1} + \frac{d\tilde{\xi}_0}{dT_2} &= \frac{1}{2}\cos\omega T_0\left(-2\lambda_0\xi_1\sin 2\tilde{\xi}_0 + \lambda_1\cos 2\tilde{\xi}_0\right)\\ &= \frac{\sin 2\tilde{\xi}_0\cos 2\tilde{\xi}_0}{2}(B_1 + B_1\cos 2\omega T_0 + B_2\sin 2\omega T_0) - \cos\omega T_0\lambda_0\xi_1\sin 2\tilde{\xi}_0.\end{aligned}$$

In order for ξ_2 and $\tilde{\xi}_1$ to be bounded functions of T_0 and T_1, respectively, we impose the solvability condition $\frac{d\tilde{\xi}_0}{dT_2} = \frac{B_1}{2}\sin 2\tilde{\xi}_0\cos 2\tilde{\xi}_0$. This is separable and can be integrated in closed form to get

$$\begin{aligned}\tilde{\xi}_0(T_2) =& \frac{1}{2}\tan^{-1}\left(e^{B_1T_2}\tan 2\Xi_0\right)\\ &+ \frac{\pi(sgn(\Xi_0) - sgn(\tan 2\Xi_0))}{4},\end{aligned} \tag{10}$$

where the $sgn(\Xi_0)-sgn(\tan 2\Xi_0)$ term is included to allow $\frac{1}{2}\tan^{-1}$ to return values onto the intervals $\left(-\frac{\pi}{2}, -\frac{\pi}{4}\right)$ and $\left(\frac{\pi}{4}, \frac{\pi}{2}\right)$ when appropriate.

Returning to Eq. 8, the dependence of $\tilde{\xi}_1$ on T_2 can be determined from a third order calculation, but we will treat it as though it were 0 ($\tilde{\xi}_1 \equiv 0$ if we choose $T_{00}=0$), and so we can now express ξ to first order as

$$\xi(T_0, T_2) = \begin{cases} -\frac{\pi}{2} + \frac{1}{2}\tan^{-1}\left(e^{B_1T_2}\tan 2\Xi_0\right) - Pe\left(1 + \frac{\lambda_0}{\sqrt{1+e^{2B_1T_2}\tan^2 2\Xi_0}}\right)\frac{(\sin\omega T_0 - \sin\omega T_{00})}{2\omega}, & \text{if } -\frac{\pi}{2} < \Xi_0 < -\frac{\pi}{4},\\ \frac{1}{2}\tan^{-1}\left(e^{B_1T_2}\tan 2\Xi_0\right) - Pe\left(1 - \frac{\lambda_0}{\sqrt{1+e^{2B_1T_2}\tan^2 2\Xi_0}}\right)\frac{(\sin\omega T_0 - \sin\omega T_{00})}{2\omega}, & \text{if } -\frac{\pi}{4} < \Xi_0 < -\frac{\pi}{4},\\ \frac{\pi}{2} + \frac{1}{2}\tan^{-1}\left(e^{B_1T_2}\tan 2\Xi_0\right) - Pe\left(1 + \frac{\lambda_0}{\sqrt{1+e^{2B_1T_2}\tan^2 2\Xi_0}}\right)\frac{(\sin\omega T_0 - \sin\omega T_{00})}{2\omega}, & \text{if } \frac{\pi}{4} < \Xi_0 < \frac{\pi}{2}.\end{cases} \tag{11}$$

This predicts fast-time oscillations with mean and amplitude controlled by the slow time T_2. We immediately predict the envelope of the oscillations by restricting the fast time scale at the maximum and

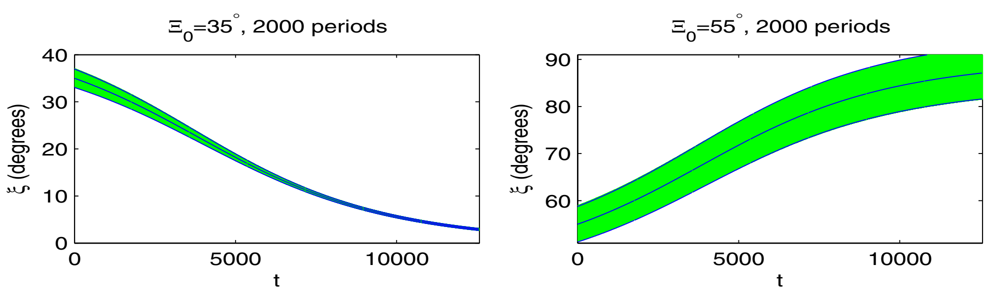

Fig. 2 The oscillating numerical solution compared with our predicted envelope $\xi_\pm$ and predicted mean ξ_0 for the same parameters as Fig. 1. Note that ξ_+ is actually the bottom edge of the envelope

minimum values, leaving the T_2 time scale dynamics of the envelope: $\xi_\pm(T_2) = \xi\left(\pm\frac{\pi}{2\omega}, T_2\right)$. The asymptotic values of $\xi_\pm$ are $-\frac{Pe}{2\omega}(1-\lambda_0)(\pm 1 - \sin\omega T_{00})$ if $|\Xi_0| < \frac{\pi}{4}$, but $-\frac{\pi}{4} - \frac{Pe}{2\omega}(1+\lambda_0)(\pm 1 - \sin\omega T_{00})$ if $-\frac{\pi}{2} < \Xi_0 < -\frac{\pi}{4}$ or $\frac{\pi}{4} - \frac{Pe}{2\omega}(1+\lambda_0)(\pm 1 - \sin\omega T_{00})$ if $\frac{\pi}{4} < \Xi_0 < \frac{\pi}{2}$. Figure 2 shows $\xi_\pm(T_2)$ and $\xi_0(T_2)$ plotted on top numerical solutions for ξ when $|\lambda_0| < 1$.

It is interesting to compare this to the response to steady shear. In steady shear, the dominant parameter in determining the nature of the response is the tumbling parameter λ_0, a material parameter that depends on the concentration N and molecular shape parameter a. However, in oscillatory shear, the initial value of the director angle Ξ_0 determines the longtime asymptotic response.

The qualitative dependence on λ_0 in oscillatory shear is much more subtle. First, consider $|\lambda_0| > 1$ so that the steady shear alignment angle ξ_L is defined. For rods, suppose $\xi_L < |\Xi_0| < \frac{\pi}{4}$, (or for disks with $\lambda_0 < -1$ when $\frac{\pi}{4} < |\Xi_0| < -\xi_L$). Then, there is a moment when $\xi_0(T_2)$ passes through $\pm\xi_L$ so that the envelope pinches with $\xi_+ = \xi_- = \pm\xi_L$, as illustrated in Fig. 3. The close-up shows that our predicted envelope may slightly overestimate the value of the angle but the amplitude of the numerical solution is at its minimum near ξ_L. No such behavior occurs for other values of Ξ_0 if $|\lambda_0| > 1$ or for any value of Ξ_0 if $|\lambda_0| < 1$.

Figure 4 demonstrates the effect that Ξ_0 has on $\xi_0(T_2)$ and the order parameters after several plate oscillations. In $s{-}\beta$ phase space, the size of the elliptical orbit is proportional to $\sin 2\xi_0$ and therefore decreases with increasing T_2. The fluctuations of β from zero are very small, indicating that the shear-induced biaxiality is a weak effect.

These decay effects are much less dramatic for rapid oscillations as shown in Fig. 5. We noted earlier that B_1 is negative; however, B_1 is $O(\omega^{-2})$ as $\omega\to\infty$, an effect further compounded by the fact that the time required to reach a set number of periods is $O(\omega^{-1})$.

The preceding derivation can be seen from a different point of view as taking $\xi_{LE}(T_0) = \Xi\left(Pe\frac{\sin\omega T_0 - \sin\omega T_{00}}{\omega} + \phi_0\right)$ but instead of using the constant ϕ_0 of Eq. 5, we now allow it to be an unknown function of T_2. Once $\phi_0(T_2)$ is determined, the approximation $\xi(T_0, T_2) = \Xi(\phi_0(T_2)) + Pe\,\Xi'(\phi_0(T_2))\frac{\sin\omega T_0 - \sin\omega T_{00}}{\omega}$ is equal to Eq. 11.

Slow decay of the stress tensor and linear viscoelasticity

From Doi and Edwards (1986), Larson (1999), and Wang (2002), the stress tensor consists of a sum of the pressure $-p\mathbf{I}$ and the extra stress $\tau = \tau^e + \tau^\upsilon$. In this decomposition, τ^e is the purely elastic stress, which is zero in nematic equilibrium, and τ^υ is the viscous stress including a pure viscous stress and a viscoelastic coupled stress. We nondimensionalize by the characteristic stress $\tau_0 = 3ck_BT$ where c is the number density of LCP molecules per unit volume and the formulas are

$$\tau^e = a\left(\mathbf{Q} - N\left(\mathbf{Q} + \frac{\mathbf{I}}{3}\right)\cdot\mathbf{Q} + N\mathbf{Q}:\mathbf{Q}\left(\mathbf{Q} + \frac{\mathbf{I}}{3}\right)\right),$$

$$\tau^\upsilon = \frac{2}{Re}\mathbf{D} + \varsigma_3\mathbf{D} + \varsigma_1\left(\mathbf{D}\cdot\mathbf{Q} + \mathbf{Q}\cdot\mathbf{D} + \frac{2}{3}\mathbf{D}\right) + \varsigma_2\mathbf{D}:\mathbf{Q}\left(\mathbf{Q} + \frac{\mathbf{I}}{3}\right),$$

where $Re = \frac{\tau_0\left(1-s_+^2\right)^2}{6D_{r0}\eta_0}$ is the solvent Reynolds number, η_0 is the solvent viscosity, and $\varsigma_1 = \varsigma^{(0)}\left(\frac{1}{I_3} - \frac{1}{I_1}\right)$, $\varsigma_2 = \varsigma^{(0)}\left(\frac{J_1}{I_1 J_3} + \frac{1}{I_1} - \frac{2}{I_3}\right)$, $\varsigma_3 = \frac{\varsigma^{(0)}}{I_1}$, $I_1 = 2r\int_0^\infty \frac{dx}{\sqrt{(r^2+x)(1+x)^3}}$, $I_3 = r(r^2+1)\int_0^\infty \frac{dx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}$, $J_1 = r\int_0^\infty \frac{xdx}{\sqrt{(r^2+x)(1+x)^3}}$, $J_3 = r\int_0^\infty \frac{xdx}{\sqrt{(r^2+x)(1+x)^2(r^2+x)}}$ where r is the aspect ratio, $\varsigma^{(0)}$ is a free parameter to be experimentally characterized, and the quadratic Doi second moment closure rule was used. To $O(Pe)$, τ^υ can be computed using just s_+ and the mean major director $\overline{\mathbf{n}}_1(T_2) = (\cos\xi_0(T_2), \sin\xi_0(T_2), 0)$, so

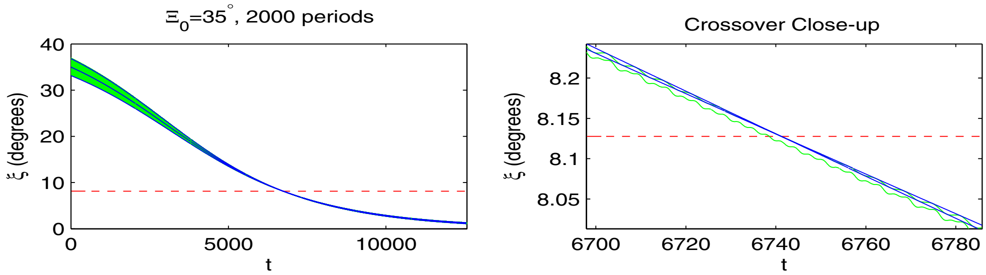

Fig. 3 When $|\lambda_0| > 1$, the predicted envelope edges cross if ξ passes through $|\xi_L|$. The *dashed line* is ξ_L=8.128° for λ_0=1.04. N=6, a=0.9, Pe=0.1, ω=1, and Ξ_0=35°

that only the oscillations of $\mathbf{D}$ enter with those of both the director and the order parameters entering at $O(Pe^2)$. The leading order elastic stress depends on the order parameter but not the director oscillations: $\tau^e = aPe((a_2 s_1 - a_3\beta_1)\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1 + a_1\beta_1\overline{\mathbf{n}}_2\overline{\mathbf{n}}_2)$ where $\overline{\mathbf{n}}_2(T_2)$=−sin$\xi_0$ (T_2), cos$\xi_0(T_2)$, 0) is the mean minor director and isotropic terms are now included in the pressure. Because both s_1 and β_1 are proportional to sin $2\xi_0$, we observe that there are two orientations, ξ_0=0 and $\xi_0 = \pm\frac{\pi}{2}$, which generate no elastic stress. This observation is also made in Larson and Mead (1989a); however with our slow time dependence of ξ_0, we are now able to predict that the director slowly migrates toward small amplitude oscillations about one of these zero-stress states!

To make contact with the complex linear viscoelastic modulus, we equivalently express the extra stress to order Pe using an integral, $\tau = \int_{T_{00}}^{T_0} G(T_0 - T_0')\mathbf{D}(T_0')dT_0'$, which identifies the relaxation modulus

$$\mathbf{G}(u)(\cdot) = a^2((a_1a_4e^{-a_1u} + a_2(2a_5 - a_4)e^{-a_2u})((\cdot):\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1)\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1 - 2a_1a_4e^{-a_1u}((\cdot):\overline{\mathbf{n}}_2\overline{\mathbf{n}}_2)\overline{\mathbf{n}}_2\overline{\mathbf{n}}_2)$$
$$+\delta(u)\left(\left(\frac{2}{Re} + \varsigma_3 + \frac{2}{3}\varsigma_1\right)(\cdot) + \varsigma_1 s_+ + ((\cdot)\cdot\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1 + \overline{\mathbf{n}}_1\overline{\mathbf{n}}_1\cdot(\cdot)) + \varsigma_2 s_+^2((\cdot):\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1)\overline{\mathbf{n}}_1\overline{\mathbf{n}}_1\right).$$

In the limit a=1, if the viscous terms are dropped, then the e^{-a_2u} term is the same as the one in Larson and Mead (1989a) restricted to the in-plane case. The e^{-a_1u} terms may be shown to be equivalent up to diagonal terms through the identity $\overline{\mathbf{n}}_2\overline{\mathbf{n}}_2 = \mathbf{I} - \overline{\mathbf{n}}_1\overline{\mathbf{n}}_1 - \overline{\mathbf{n}}_3\overline{\mathbf{n}}_3$.

Shear stress and storage and loss moduli

The dynamic moduli of PBLG were shown to exhibit a very slow decay if oscillatory shear is continued for a long time (Moldenaers and Mewis 1986; Larson and Mead 1989b). From the multiple time scale perturbation analysis above, we can derive formulas for the (nondimensional) storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ (the parts of the shear stress that are respectively in-phase and out-of-phase with the imposed strain), which reproduce this longtime behavior.

If we take the temporal integrations in the definitions of $G'(\omega)$ and $G''(\omega)$ to be with respect to T_0 only and wait until the transient terms in Eq. 9 have decayed, then the integrals can be calculated explicitly. This yields storage and loss moduli, which are functions of the plate frequency ω, but which also retain a dependence on the slow time T_2:

$$G'(\omega, T_2) = \frac{\omega^2}{\pi Pe}\int_{\frac{-\pi}{\omega}}^{\frac{\pi}{\omega}} \tau_{12}(T_0, T_2)\sin\omega T_0 dT_0 = C_1(\omega)\sin^2 2\xi_0(T_2),$$
$$G''(\omega, T_2) = \frac{\omega^2}{\pi Pe}\int_{\frac{-\pi}{\omega}}^{\frac{\pi}{\omega}} \tau_{12}(T_0, T_2)\cos\omega T_0 dT_0 = \omega\widehat{\eta} + C_2(\omega)\sin^2 2\xi_0(T_2),$$

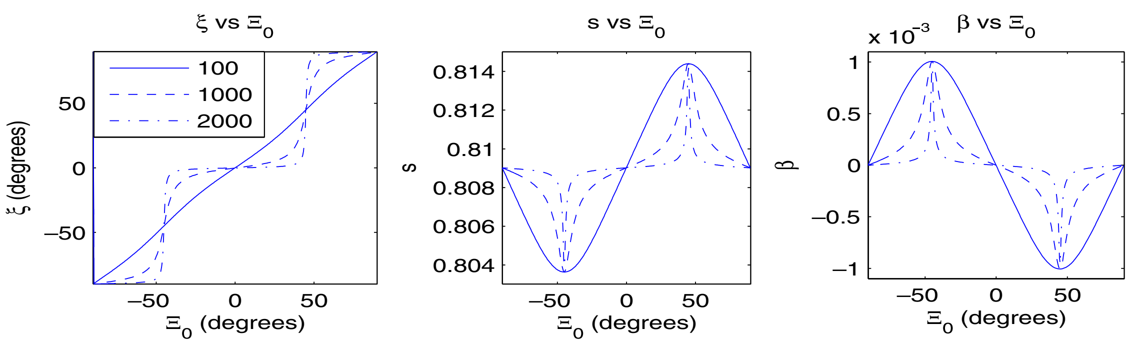

Fig. 4 The effect that the initial value of the director angle Ξ_0 has on ξ, s and β after 100, 1,000, and 2,000 plate oscillations. N=6, a=0.8, Pe=0.1, and ω=1

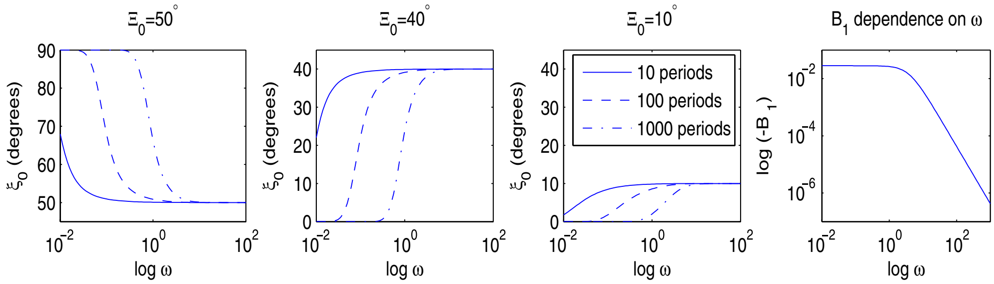

Fig. 5 The effect of ω on ξ_0 after 10, 100, and 1,000 plate oscillations for Ξ_0=50, 40, and 10°. For larger values of ω, the decay of ξ_0 is not noticeable due the dependence of the decay rate B_1 on ω. N=6, a=0.8, and Pe=0.1

where $\widehat{\eta} = \frac{1}{Re} + \varsigma_1\frac{2+s_+}{6} + \frac{1}{2}\varsigma_3$, $C_1(\omega) = \frac{\omega a^2}{2}(a_2 b_{s_1} - (a_3 + a_1)b_{\beta_1})$ and $C_2(\omega) = \frac{\omega s_+^2}{4}\varsigma_2 + \frac{\omega^2}{a}2(a_2 a_{s_1} - (a_3 + a_1)a_{\beta_1})$.

Note first that we recover the formulas in Larson and Mead (1989a) if we drop all viscous terms ($\widehat{\eta}_0 \equiv 0$ and $\zeta_2 \equiv 0$), set a=1, and suppress slow-time behavior of the director. From the slow time characterization in Eq. 10, the key factor in G' and G'' becomes explicit:

$$\sin^2 2\xi_0(T_2) = \frac{e^{2B_1T_2}\tan^2 2\Xi_0}{1 + e^{2B_1T_2}\tan^2 2\Xi_0}. \tag{12}$$

We immediately deduce that the dynamic moduli G' and G'' obey a logistic longtime decay law; Fig. 6 illustrates this property for three different values of Ξ_0. This prediction is consistent with experimental data in Moldenaers and Mewis (1986) and Larson and Mead (1989b) for G''; features of G' are consistent except the model does not predict the long time upturn reported for some data (Larson and Mead 1989b).

The initial data in our "theoretical experiment" differs from laboratory experiments in Moldenaers and Mewis (1986) and Larson and Mead (1989b), which begin with a lengthy period of sufficiently strong steady shear to prealign the monodomains. This implies that the order parameters do not start at their zero-shear equilibrium values as we have assumed. This preshearing protocol will have two effects: First, the transient dynamics will be modified and second, because this presheared alignment angle will be very close to zero, this will prejudice the response in favor of the asymptotic state parallel to the plates.

In addition, it was experimentally observed that t_c, the characteristic time required for the dynamic moduli to complete one-third of their decay, was inversely proportional to the shear rate of the prealigning shear. Because our set-up has no prealigning shear rate, we cannot speak directly to this; however, we can compute the characteristic decay time for quiescent initial data and find that $t_c = \frac{1}{2B_1 Pe^2}\ln\frac{2}{3+\tan^2 2\Xi_0}$. One can interpret this result to predict consistency with presheared states in the following sense. The preshear moves the order parameters away from their quiescent equilibrium by an increment proportional to the preshear rate. We observe that B_1 is a linear combination of a_{s_1} and a_{β_1}, the coefficients of the $\cos\omega t$ terms in s_1 and β_1, respectively. Thus, B_1, which is inversely proportional to t_c, is also proportional to the leading order distance of the order parameters from their quiescent equilibrium values and hence, the preshear rate.

For rods, the dependence of G' and G'' vs ω is shown in Figs. 7 and 8. The decay is greatly diminished for larger ω because B_1 is $O(\omega{-2})$ as ω becomes large (see Fig. 5d).

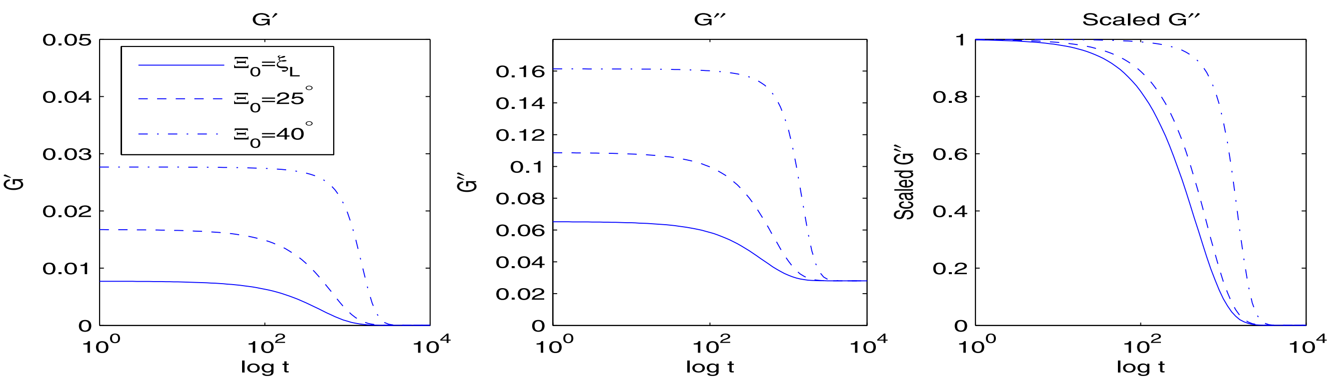

Fig. 6 G', G'', and the scaled $G = \frac{G''(t=\infty)-G''(t)}{G''(t=\infty)-G''(t=0)}$ for N=6, a=0.9 (ξ_L=8.128°), for Ξ_0=ξ_L, Ξ_0=25° and Ξ_0=40°. Pe=0.2, ω=1, and $\zeta^{(0)}$=0.05

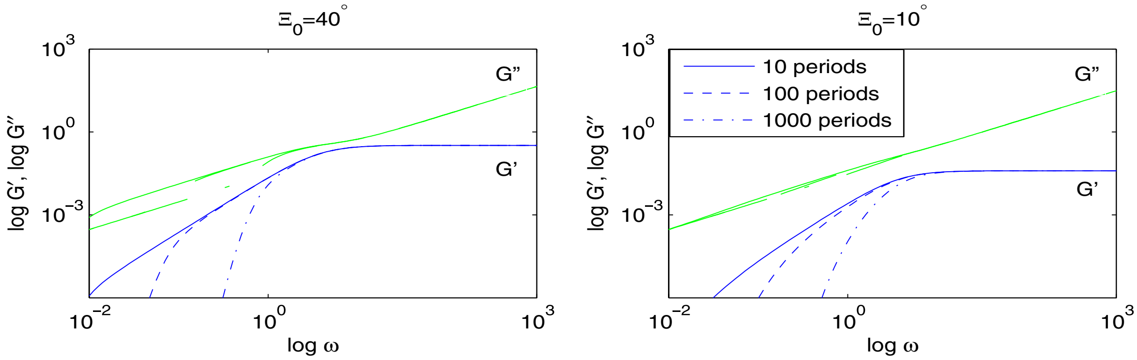

Fig. 7 The storage modulus G' and the contribution to the loss modulus from the nematic, $G''-\frac{\omega}{Re}$, for Ξ_0=40° and Ξ_0=10° for 10, 100, and 1,000 plate oscillations highlighting the slow time dependence. N=6, a=0.8, Pe=0.1, and $\zeta^{(0)}$=0.05

First and second normal stress differences

In oscillatory shear, the normal stress differences assume the forms

$$N_1 = \tau_{11} - \tau_{22} = Pe \sin 2\xi_0(T_2) \cos 2\xi_0(T_2)(D_1 \cos \omega T_0 + D_2 \sin \omega T_0),$$
$$N_2 = \tau_{22} - \tau_{33} = Pe \sin 2\xi_0(T_2)((D_3 + D_4 \cos 2\xi_0(T_2)) \cos \omega T_0 + (D_5 + D_6 \cos 2\xi_0(T_2)) \sin \omega T_0)$$

where $D_1 = \frac{\varsigma_2 s_+^2}{2} + a^2\left(a_2 a_{s_1} - (a_3 + a_1)a_{\beta_1}\right)$, $D_2 = a^2\left(a_2 b_{s_1} - (a_3 + a_1)b_{\beta_1}\right)$, $D_3 = \frac{\varsigma_1 s_+}{2} + \frac{\varsigma_2 s_+^2}{4} + \frac{a^2}{2}(a_2 a_{s_1} + (a_1 - a_3)a_{\beta_1})$, $D_4 = -\frac{\varsigma_2 s_+^2}{4} + \frac{a^2}{2}\left(-a_2 a_{s_1} + (a_3 + a_1)a_{\beta_1}\right)$, $D_5 = \frac{a^2}{2}\left(a_2 b_{s_1} + (a_1 - a_3)b_{\beta_1}\right)$, $D_6 = \frac{a^2}{2}\left(-a_2 b_{s_1} + (a_3 + a_1)b_{\beta_1}\right)$, and exponential terms were ignored. Both N_1 and N_2 oscillate with a small amplitude about zero; however, only the envelope behavior of N_2 is qualitatively sensitive to the initial angle Ξ_0. Graphs of N_1 and N_2 for the same parameters as those in Fig. 1 are depicted in Fig. 9.

Conclusion

We have examined the mesoscopic monodomain in-plane Doi–Hess tensor model for a nematic liquid crystal polymer subjected to an imposed small amplitude oscillatory shear flow. A multiple time scale perturbation analysis predicts sensitivity in the director angle and storage and loss moduli to initial value of the director angle Ξ_0 that is experimentally relevant on long time scales. This analysis was motivated by a return to the classical papers of Moldenaers and Mewis (1986) and Larson and Mead

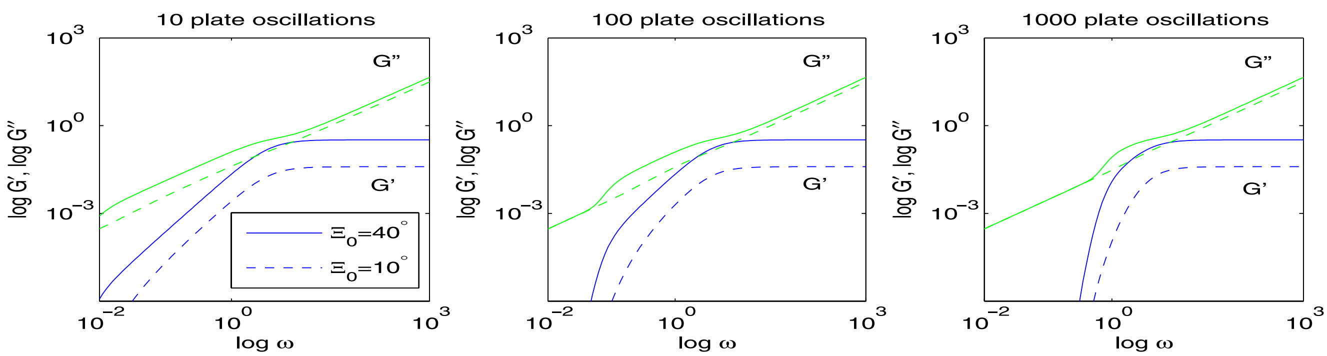

Fig. 8 The same data as Fig. 7 highlighting the effect of differing initial angles Ξ_0=40° and Ξ_0=10°, which can be up to an order of magnitude

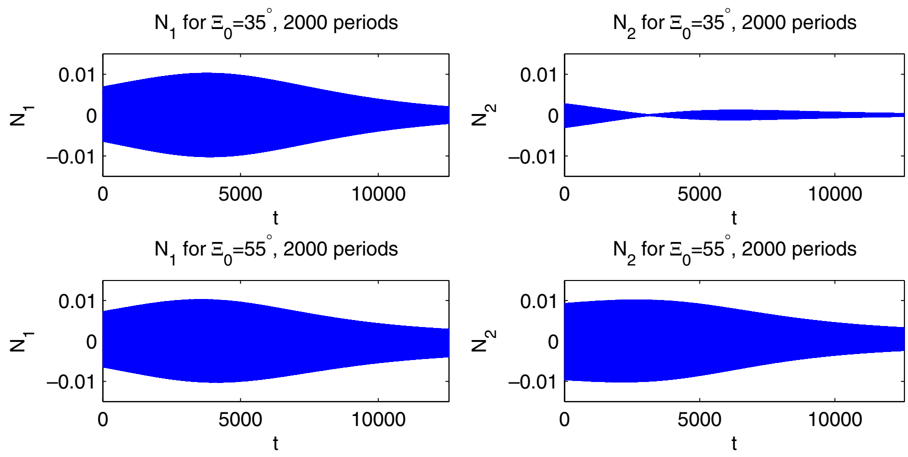

Fig. 9 The first (N_1) and second (N_2) normal stress differences for oscillatory shear for Ξ_0=35° and Ξ_0=55°. N=6, a=0.8, Pe=0.1, ω=1, and $\zeta^{(0)}$=0.05

(1989a) on linear viscoelasticity of nematic polymers, armed with current analytical understanding of the role of orientational degeneracy of nematic equilibria in simple shear.

The behavior of sheared nematic polymers in small amplitude steady shear was extensively analyzed with kinetic and mesoscopic models by many authors in recent years and the behavior with a strong steady shear component coupled with small amplitude oscillatory shear was reported recently by Russo and Maffettone (2003). This paper is a contribution toward filling the gap in the current literature on behavior of nematic rod suspensions in small amplitude oscillatory shear. The analysis is restricted to a simple model of monodomains with in-plane orientation; the extension to full orientation tensors or kinetic theory seems intractable. Nonetheless, our analysis reveals explicit analytical predictions of linear viscoelastic phenomena that are consistent with classical experiments.

Specifically, we predict a slow drift dynamics of the major director of the orientational distribution. The drift phenomenon is due to the coupling of the director to order parameter fluctuations and thus would not be observed in small molecule liquid crystals and the LE model. The envelope and mean of the drift dynamics is explicitly characterized, which predicts bistable longtime asymptotic orientational states, one with the major director along the flow axis and the other along the flow-gradient axis. These states are distinguished in that they are the minima of the purely elastic shear stress component as noted in Larson and Mead (1989a). Remarkably, the basins of attraction of the bistable longtime states do not depend on material parameters (e.g., the Leslie tumbling parameter, which determines tumbling vs flow-alignment in simple steady shear); rather, the initial director orientation angle alone determines the two drift dynamic routes and final states. These results are then converted into predictions of the storage and loss moduli, which are predicted to obey a logistic long-time decay law consistent with experimental observations of Moldenaers and Mewis (1986). The bistable drift dynamics yield the same order of magnitude loss modulus, yet an order of magnitude difference in storage modulus, which is due solely to the initial director orientation angle. Experiments, which bias the initial director of the nematic sample as with steady preshear, would thereby not observe this sensitivity in storage modulus.

We close with brief remarks on the robustness of these drift phenomena to closure approximation. The two other algebraic closures addressed in Forest and Wang (2003) [those of Tsuji–Rey (Tsuji and Rey 1997) and Hinch–Leal 1 (Hinch and Leal 1976)] produce the same qualitative behavior as the Doi closure presented here: the same two stress-free asymptotic states with the same basins of attraction independent of closure and the long-time decrease of the dynamic moduli. The nonalgebraic Hinch–Leal 2 closure yields similar behavior for sufficiently low nematic concentrations. However, at higher concentrations, it predicts different bistable asymptotic states where $\xi_0(T_2)$ drifts toward $\pm\frac{\pi}{4}$, which are not stress-free, and it predicts a long-time increase in the dynamic moduli. These modified properties appear to be a nonphysical closure artifact.

The monodomain predictions of linear viscoelastic properties in oscillatory shear are a precursor to structure-dependent properties of nematic polymers and rigid rod suspensions. The present monodomain results predict that the loss modulus dominates the storage modulus at essentially all frequencies. On the other hand, defect-ridden nematic polymer suspensions were observed to obey the opposite extreme with nearly solid-like linear viscoelastic response (Colby et al. 2002). It remains to be determined how structure-dependence modifies $G'(\omega)$ and $G''(\omega)$.

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