

# Research Statement

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My research interests center on mathematical modeling of complex fluids, and specifically on the flow, orientation, and rheological properties of solutions of nematic liquid crystal polymers. In this research statement, I will briefly introduce nematic liquid crystal polymers (LCPs) and how they have been modeled, review my previous and current research into refining and extending these models, and then discuss problems that I anticipate studying in the near future.

In the 1880s, Reinitzer and Lehmann discovered substances for which the transition from solid to liquid is anything but simple. Intermediate mesophases were found in which to varying degrees, the molecules lost the rigid positional ordering of the solid phase, but they retained an orientational order. That is, they flowed like a liquid, but the molecules, which we idealize as rigid, high aspect ratio spheroids in a Newtonian solvent, still had a preferred direction and refracted light like a crystal, prompting Lehmann to call them *liquid crystals*. In *smectic* phases, the molecules retain positional ordering in one or two dimensions, but my research has focused on the *nematic* phase, in which there is no positional ordering. The orientation of such fluids can be controlled by flows and electromagnetic fields, and they have become commonplace in laptop and television displays. More details on liquid crystals and the foundations of much of the following can be found in [6].

To model such an anisotropic fluid, in addition to the fluid velocity  $\mathbf{v}$ , a variable is required to describe the microstructure and its orientation, which generate stresses that couple to the flow. In the 1960s, Leslie and Ericksen (LE) developed a theory to predict the preferred direction of molecular alignment, the so-called *major director*  $\mathbf{n}_1$ . The degree to which the molecules align with  $\mathbf{n}_1$  was assumed to be constant. For small-molecule nematics such as those used in liquid crystal displays, this works fairly well; however, for the larger macromolecules of high performance materials, variations in the degree of order become important.

In the 1970s, Doi and Hess independently proposed a kinetic theory for the probability distribution function  $f(\mathbf{m}, \mathbf{x}, t)$  that gives the probability that a spheroidal molecule has its axis of symmetry aligned with the unit vector  $\mathbf{m}$ . The nonlinear Smoluchowski equation for  $f$  is [7]

$$\frac{Df}{Dt} = D_r \frac{\partial}{\partial \mathbf{m}} \cdot \left( \frac{\partial f}{\partial \mathbf{m}} + \frac{1}{kT} f \frac{\partial V}{\partial \mathbf{m}} \right) - \frac{\partial}{\partial \mathbf{m}} \cdot [(\boldsymbol{\Omega} \cdot \mathbf{m} + a(\mathbf{D} \cdot \mathbf{m} - \mathbf{D} : \mathbf{m}\mathbf{m}))f], \quad (1)$$

for the Boltzmann constant  $k$ , the temperature  $T$ , the molecular shape parameter  $a = \frac{r^2-1}{r^2+1}$  for the molecular aspect ratio  $r$ , and the orientational diffusion rate  $D_r$ . The nonlinearity of (1) arises from the excluded volume potential  $V$ , which depends on  $f$  through the second moment tensor  $\mathbf{M}(f)$ :

$$V(f) = -\frac{3}{2}NkT \left( 1 + \frac{\mathcal{L}^2}{24}\Delta \right) \mathbf{M} : \mathbf{m}\mathbf{m}, \text{ for } \mathbf{M} = \langle \mathbf{m}\mathbf{m} \rangle = \int_{\|\mathbf{m}\|=1} \mathbf{m}\mathbf{m} f(\mathbf{m}) d\mathbf{m}, \quad (2)$$

where  $N$  is the dimensionless concentration parameter and  $\mathcal{L}$  is the penetration depth of the distortional elasticity potential. The second term in (1) contains the effect of the fluid velocity

through for the rate-of-strain tensor  $\mathbf{D} = \frac{1}{2}(\nabla\mathbf{v} + \nabla\mathbf{v}^T)$  and the vorticity tensor  $\mathbf{\Omega} = \frac{1}{2}(\nabla\mathbf{v} - \nabla\mathbf{v}^T)$ . Most of my research has dealt with one-dimensional flows between two parallel plates in which  $v_x(y)$  is the only non-zero fluid velocity component. This dimensional reduction is upheld in rheometers, where indeed most previous modeling has been restricted to linear shear instead of arbitrary shear.

My research has primarily used the equation for the second moment tensor, which can be obtained from (1) by multiplying by  $\mathbf{mm}$  and then integrating with respect to  $\mathbf{m}$ :

$$\begin{aligned} \frac{D}{Dt}\mathbf{M} = & -6D_r \left[ \mathbf{M} - \frac{\mathbf{I}}{3} - N(\mathbf{M} \cdot \mathbf{M} - \mathbf{M} : \mathbf{M}_4) - \frac{N\mathcal{L}^2}{48}(\Delta\mathbf{M} \cdot \mathbf{M} + \mathbf{M} \cdot \Delta\mathbf{M} - 2\Delta\mathbf{M} : \mathbf{M}_4) \right] \\ & + \mathbf{\Omega} \cdot \mathbf{M} - \mathbf{M} \cdot \mathbf{\Omega} + a(\mathbf{D} \cdot \mathbf{M} + \mathbf{M} \cdot \mathbf{D} - 2\mathbf{D} : \mathbf{M}_4). \end{aligned} \quad (3)$$

This equation is, however, not closed on  $\mathbf{M}$  due to the appearance of the fourth moment tensor  $\mathbf{M}_4 = \langle \mathbf{mmmm} \rangle$ . We have explored various approximations of  $\mathbf{M}_4$  as a function of  $\mathbf{M}$  to close the system. The major director can be identified from  $\mathbf{M}$  as the eigenvector corresponding to its unique largest eigenvalue, which is the point of contact with the liquid crystal theory noted above.

This couples to the velocity through a linear momentum balance with the stress tensor [7]

$$\begin{aligned} \boldsymbol{\tau} = & \mu_1(\mathbf{D} \cdot \mathbf{M} + \mathbf{M} \cdot \mathbf{D}) + \mu_2\mathbf{D} : \mathbf{M}_4 + \mu_3\mathbf{D} + 3\nu kT \left[ a \left[ \mathbf{M} - \frac{\mathbf{I}}{3} - N(\mathbf{M} \cdot \mathbf{M} - \mathbf{M} : \mathbf{M}_4) \right] \right. \\ & \left. - \frac{N\mathcal{L}^2}{48} \left[ (1+a)\Delta\mathbf{M} \cdot \mathbf{M} - (1-a)\mathbf{M} \cdot \Delta\mathbf{M} - 2a\Delta\mathbf{M} : \mathbf{M}_4 + \frac{1}{2}(M_{kl,i}M_{kl,j} - \mathbf{M} : \nabla\nabla\mathbf{M}) \right] \right], \end{aligned} \quad (4)$$

for the LCP number density  $\nu$  and three molecular shape-dependent viscosities  $\mu_i$ .

If you open any book on polymeric liquids, the primary focus of liquid crystal polymers and theory is on linear viscoelastic characterization. Viscoelastic materials have a shear viscosity  $\eta'$  and a storage modulus  $G'$  that depend, often dramatically, on the frequency of the forcing. These properties are called the dynamic moduli. For nematic LCPs, linear viscoelastic characterization has been in a state of confusion, which my thesis and subsequent research has aimed to clean up.

Since  $\mathbf{M}$  is symmetric and has trace 1, it has five independent components; however, (3) contains a three-dimensional subspace that corresponds to fixing one eigenvector of  $\mathbf{M}$  to be parallel to the vorticity axis in the coordinate system of a parallel-plate shear cell. In this reduction, the orientational dynamics are confined to the flow-flow gradient plane. We express these degrees of freedom using the spectral representation

$$\mathbf{M} = s(\mathbf{n}_1\mathbf{n}_1 - \frac{\mathbf{I}}{3}) + \beta(\mathbf{n}_2\mathbf{n}_2 - \frac{\mathbf{I}}{3}) + \frac{\mathbf{I}}{3}, \quad (5)$$

$$\mathbf{n}_1 = (\cos\psi, \sin\psi, 0)^T, \quad \mathbf{n}_2 = (-\sin\psi, \cos\psi, 0)^T, \quad (6)$$

where the *director angle*  $\psi$  parameterizes the eigenvectors  $\mathbf{n}_i$  of  $\mathbf{M}$ , and the scalar *order parameters*  $s = d_1 - d_3$  and  $\beta = d_2 - d_3$  are the differences of the eigenvalues  $d_i$ .

In [2], we analyzed the so-called *monodomain* limit, in which  $\mathbf{M}$  is assumed to have no spatial gradients, for the imposed small amplitude oscillatory shear flow  $v_x = De y \cos\omega t$ . The nondimensional *Deborah number* is  $De = \dot{\gamma}(6D_r)^{-1} \ll 1$ , where  $\dot{\gamma}$  is the macroscopic strain-rate. The

resulting system of ODEs for the spectral variables is

$$\begin{aligned}\dot{s} &= -U(s) + \frac{2Ns\beta}{3}(s - \beta - 1) + \frac{a}{3}De \cos \omega t(1 - \beta + 2s + 3s\beta - 3s^2) \sin 2\psi, \\ \dot{\beta} &= -U(\beta) + \frac{2N\beta s}{3}(\beta - s - 1) - \frac{a}{3}De \cos \omega t(1 + 2\beta - s + 3s\beta - 3\beta^2) \sin 2\psi, \\ \dot{\psi} &= -\frac{1}{2}De \cos \omega t \left(1 - \frac{a}{3} \frac{s+\beta+2}{s-\beta} \cos 2\psi\right)\end{aligned}\quad (7)$$

for  $U(s) = s(1 - \frac{N}{3}(1 - s)(1 + 2s))$ .

This system possesses an interesting degenerate no-flow equilibrium. If  $De = 0$ , then if  $N$  is sufficiently high ( $N > 3$ ), the order parameters lie at the stable nematic equilibrium  $(s, \beta) = (s_0, 0)$  where  $s_0 = \frac{1}{4} \left(1 + 3\sqrt{1 - \frac{8}{3N}}\right)$ . (This solution exists for  $\frac{8}{3} \leq N \leq 3$ , but it is bistable with the isotropic solution  $(s, \beta) = (0, 0)$ .) However, any constant angle  $\psi \equiv \psi_0 \pmod{\pi}$  is a solution. That is, the molecules have a preferred degree of order but no preferred direction for this order. We used this order parameter equilibrium and arbitrary director angle as the initial conditions for (7), and we found that this angle degeneracy plays an important role if the system is allowed to run for long times. In numerical solutions, we found that for short times, the angle  $\psi$  oscillates round  $\psi_0$ , but the mean of the oscillation slowly drifts to the nearest elastic stress free state, which is 0 if  $|\psi_0| < \frac{\pi}{4}$  or  $\pm\frac{\pi}{2}$  if  $\frac{\pi}{4} < |\psi_0| < \frac{\pi}{2}$ .

We used a multiple timescale perturbation analysis with the fast time  $T_0 = t$  and slow time  $T_2 = De^2t$  and captured this effect quite well. We found that to leading order

$$\psi(T_0, T_2) = \frac{1}{2} \tan^{-1}(e^{B_1 T_2} \tan 2\psi_0) - De \left(1 \mp \frac{\lambda_0}{\sqrt{1 + e^{2B_1 T_2} \tan^2 2\psi_0}}\right) \frac{\sin \omega T_0}{2\omega}, \quad (8)$$

where  $B_1$  is a negative constant,  $\lambda_0 = \frac{a(s_0+2)}{3s_0}$ , and  $\mp$  is  $-$  for  $|\psi_0| < \frac{\pi}{4}$  and  $+$  for  $\frac{\pi}{4} < |\psi_0| < \frac{\pi}{2}$ . Figure 1 compares our prediction of the envelope of the oscillation to a numerical solution of  $\psi$  from (7) for 2000 periods of oscillation.

Furthermore, we were able to show that from (4), the dynamic moduli exhibit logistic decay with the slow time  $T_2$ , consistent with experimental results. Previously, it had been assumed that this long-time decay in the stress must be caused by spatial gradients.

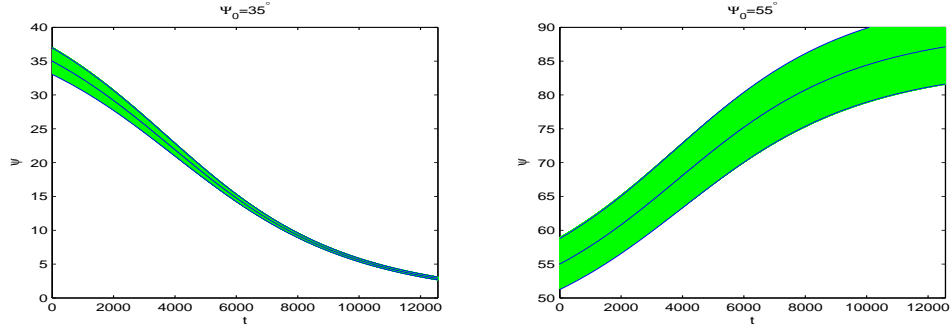


Figure 1: Our predicted envelope and mean compared to numerical solutions of the director angle  $\psi$  from (7) for  $\omega = 1$  and  $De = 0.1$  for 2000 plate oscillation for two different initial angles.

I then turned my attention to the prediction of the dynamic moduli when  $\mathbf{M}$  is allowed to have spatial gradients, focusing again on the role of the director angle degeneracy. One important issue in comparing theory with experiments is that from a mathematical perspective, it is most natural to impose boundary conditions on the velocity since it is one of the unknowns in the problem. However, on the lab bench, it is more common to impose the stress on the plates in oscillatory shear, not their velocity. We showed that the solutions with imposed stress boundary conditions and with imposed velocity boundary conditions are equivalent up to a phase shift and a rescaling, and this means the moduli predictions, which come from the stress-strain relationship, are independent of the choice of velocity or stress boundary conditions.

When spatial gradients in the orientation are included, the orientational degeneracy  $\psi_0$  now becomes an anchoring condition on the plates, which establishes a homogeneous solution that our small amplitude shear flow drives a heterogeneous frequency-locked oscillation around. In [1], we analyzed the effects of these spatial gradients when  $\psi_0 = 0$  or  $\frac{\pi}{2}$ . That is, when the major director  $\mathbf{n}_1$  is either tangential or normal to the plates. We found that the equations for the order parameters decouple from the equations for the director angle and the velocity at leading order, which effectively recovers analytically solvable LE-like behavior. The dependence of the moduli on the anchoring condition  $\psi_0$  is quite striking, particularly in the storage modulus, which for normal anchoring can be two-to-three orders of magnitude larger than for tangential anchoring.

In [3], we filled in the oblique angles between tangential and normal anchoring where the order parameters do not decouple. Figure 2 shows numerical predictions of the moduli. The viscosity shows a symmetry between  $\psi_0$  and  $\frac{\pi}{2} - \psi_0$  for high frequencies, but this is not seen for low frequencies. For the storage modulus, we predict  $O(\omega^2)$  behavior for low frequencies, and  $O(\sqrt{\omega})$  behavior

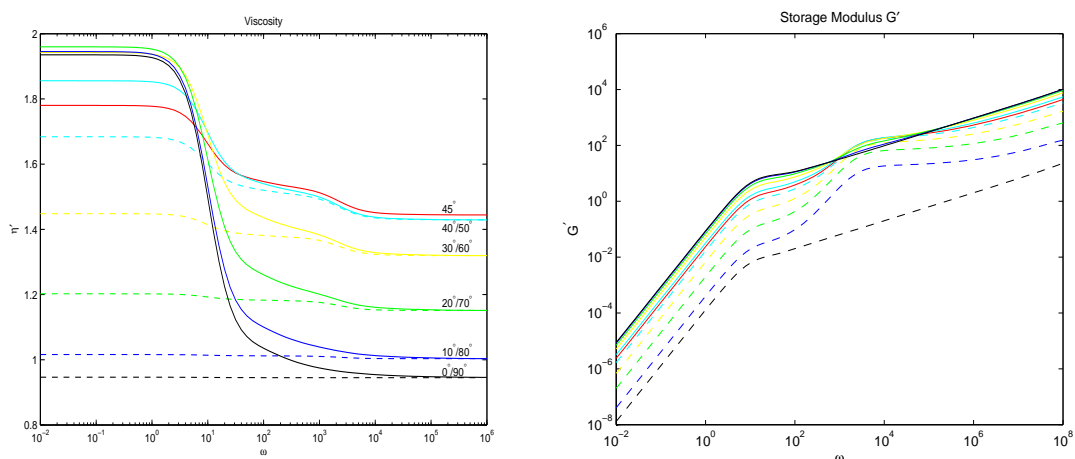


Figure 2: The viscosity and storage modulus for different values of the director anchoring angle  $\psi_0$ .

for high frequencies. These extremes are the same scalings as LE theory. However, for moderately high frequencies, we find a secondary plateau in both moduli for angles near  $\pm\frac{\pi}{4}$ , which is not predicted by LE theory. For low and high frequencies, the largest value of the storage modulus is for normal anchoring; however, in this plateau, its largest value is for an angle near  $\pm\frac{\pi}{4}$ . We captured this behavior quite nicely with a simple linear superposition of the corresponding LE prediction and the monodomain prediction, with the monodomain prediction corresponding to the secondary plateau. This indicates that the stresses from the order parameters being out of their preferred equilibrium persist to higher frequencies than those generated by the oscillations of the major director.

The next step in this direction is to examine what happens when the out-of-plane restriction is lifted and the molecules are anchored to lie parallel to the plates, but the flow can be aligned in this direction or perpendicular to it, which is called a logrolling state. Figure 3 shows some of our preliminary work on this problem and indicates that unlike parallel anchoring, the viscosity for logrolling anchoring exhibits noticeable shear-thinning for high frequencies. Also, the storage modulus for parallel anchoring is slightly larger for low frequencies, but logrolling is orders of magnitude larger for high frequencies.

In the future, I hope to extend these heterogenous results in two different directions, allowing for two- and three-dimensional heterogeneity and also examining the effect of different anchoring angles on the top and bottom plates.

Another class of problems that interests me is the identification of correspondence principles between combinations of molecular geometry and flow types that map onto the same orientational distribution as a flow of a simpler form. For example, in [5], we found that for a monodomain subjected to a linear planar flow with both extensional and shear components, the extensional part

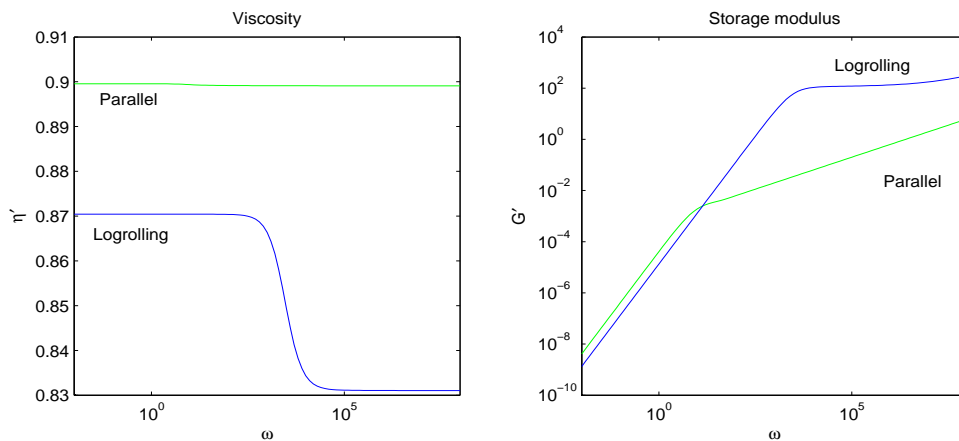


Figure 3: The viscosity and storage modulus for logrolling and parallel anchoring.

can be absorbed into a modified scaling of the molecular shape parameter  $a$  so that an existing numerical code built to solve shear flow problems could now be extended to solve the problem for any type of planar linear flow except for pure extensional flow. I want to revisit this problem looking at general linear flows that are not confined to a plane but are fully three-dimensional.

In [4], we looked at a different type of problem. We observed two different ways in which *defect phases* arise in monodomains. These are situations in which no major director can be defined, meaning that the molecules have no preferred direction. One success of LE theory was its ability to predict discontinuities in the director field, which correspond to defects. However, these require spatial gradients. We examined non-topological defects of the monodomain model in which the system has no well defined major director because  $\mathbf{M}$  does not have a unique largest eigenvalue. We found situations in which transient solutions must pass through the defect set in solution space to get to their stable equilibria, and we also observed that at the bifurcation between two different types of periodic solutions, there is a solution that passes through a defect state periodically.

I am also interested extending some preliminary work on the nematic response to a rotating magnetic field which exhibits an interesting sequence of bifurcations with increasing frequency. I would also like to examine different types of flow, including spin coating, which would also focus on the behavior of disk-shaped nematics. Also, on the modeling front, a flaw in our current work is the use the no-flow monodomain equilibrium values as a boundary condition for the order parameters. Determining a more appropriate boundary condition for the order parameters is a problem I wish to address in the near future. The issues worth pursuing here are the transition from hard to soft anchoring and the role that these boundary conditions have on the dynamic moduli and flow feedback.

## References

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