LCP droplet dispersions: a two-phase, diffuse-interface kinetic theory and global droplet defect predictions

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Advanced, predictive numerical tools for liquid crystalline polymers (LCPs) are well established. These tools yield descriptive features (steady and unsteady behavior, gradient morphology) of LCPs in the bulk and in confined geometries; some are applicable to LCP hydrodynamics. Our goal here is to expand the hydrodynamic toolkit (a predictive theory, algorithms, and simulations) to two-phase fluids consisting of an immiscible LCP phase (initialized as droplets) dispersed in a viscous or polymeric phase. To do so, we bridge the modeling and simulation gap between molecular dynamics and Monte Carlo discrete lattice models for polymer-dispersed liquid crystal (LC) droplets and continuum scale, diffuse interface methods for LC droplets in viscous fluids. We give a brief overview of molecular-to-continuum scales of modeling and simulations for single LCP phases, and of their relative benefits and limitations. We likewise recall the sharp versus diffuse interface methods for coupling of two immiscible fluid phases in a hydrodynamic theory. From this assessment, we present a kinetic scale, diffuse interface strategy for hydrodynamic simulations of LCP droplet dispersions. The Fokker–Planck or Smoluchowski equation due to Doi and Hess for the orientational distribution function of the LCP phase is generalized to a two-phase, energy-based theory. Although feasible for simulations by adaptation of existing kinetic solvers, we first put the two-phase kinetic model through analogous preliminary benchmarks that were applied to the Doi–Hess theory for LCPs. We project onto the scalar zeroth moment and tensorial second-moment of the rod number density function to achieve a generalized Landau-deGennes two-phase model for equilibria and imposed shear of LCP droplets in a viscous fluid. A numerical algorithm in two space dimensions is developed and implemented to study global droplet defect structure versus interfacial anchoring energy. Simulations reveal topological defects (surface boojums for tangential anchoring and interior degree 1/2 or radial defects for normal anchoring) and details of their respective cores. These predictions support the hypothesis in [I. Lin et al., Science, 2011, 332, 1297–1300] that anchoring boundary conditions between the LCP and surrounding fluid phase can be satisfied by the formation of extremely localized defect cores which self-organize the orientational order external to the cores, without the need for bend-splay-twist mediated, continuous elastic strain.

1 Introduction

This paper takes aim at the hydrodynamics of liquid crystal polymer (LCP) droplets dispersed in another (possibly polymeric) fluid phase. To approach this target, we pull together advances in liquid crystal, LCP and two-phase fluid modeling, and assess alternative modeling and numerical strategies. We give the rationale for, and then present, an energy-based, diffuse interface model at the kinetic scale (of the rod molecule orientational probability distribution function). This approach embeds the Doi–Hess kinetic theory for homogeneous LCP equilibria and hydrodynamics into a two-phase complex fluid modeling framework, relying on results of the authors as well as the diffuse interface framework for complex fluids. We benchmark the two-phase kinetic theory in two relatively simple situations: equilibrium LCP droplet dispersions in a viscous, immiscible fluid, followed by the perturbed droplet shape and internal nematic structure in imposed shear. Ultimately, our goal is a predictive theory for strong shear or extensional flows of LCP droplets in a polymeric host phase, where the droplets rupture and saturate in stationary daughter droplets. A specific goal, which lies ahead of present capabilities, is to use this modeling framework to tune satellite droplet size distributions,
starting from bulk LCP droplets of microns or larger diameter, by shear or extensional flow processes. There are myriad applications, from optical to acoustic wave propagation, which lead one to explore the limits of LC and LCP droplet size and droplet arrays that can be achieved by controlled flow conditions. We refer the reader to the review for optical applications of polymer-dispersed liquid crystals and to papers by Smalyukh and colleagues for additional applications.

We are especially interested in how the internal nematic defect structure and rupture dynamics vary with surface orientational anchoring at the LCP-host fluid interface. Recent experimental results of the Abbott lab have used lipids at varying concentrations to tune tangential versus normal anchoring boundary conditions at the LCP-host interface. These results provide a blind test of our theory, especially with regard to their seminal hypothesis regarding the mechanism that nematics employ to satisfy boundary anchoring conditions at interfaces. Namely, Abbott et al. hypothesize that highly localized defect cores form, that are themselves capable of self-organizing the global nematic morphology to satisfy boundary anchoring conditions. This is a stark alternative to the accepted mechanism of Oseen–Frank distortional elasticity, which employs bend, splay and twist continuous strain fields in such a way that energy is minimized with the imposed constraint of interfacial anchoring conditions. In this traditional mechanism, defect cores arise to resolve topological singularities of the global director field. Our numerical results section confirms the Abbott hypothesis is indeed possible by simply not including a distortional energy and yet capturing the defects selected by tangential versus normal interfacial anchoring. The authors and collaborators have recently presented results from a two-phase continuum-scale model of LC droplet rupture while being sheared in a viscous fluid. That is, the LC phase is modeled with the Leslie–Ericksen–Frank director theory which is blind to the cores of topological singularities, and which employs one constant Oseen–Frank distortional elasticity as the organizing mechanism to satisfy anchoring conditions at LC-viscous fluid interfaces. This continuum scale theory also predicts global nematic drop topology is tuned by the interfacial anchoring condition and Oseen–Frank continuous strain, but the theory is singular in defect cores and an artificial regularization of the core has to be imposed.

The present paper aims for more detailed physics (excluded volume potential, a non-singular orientational distribution function, and anchoring energy); these extensions are necessary to self-consistently determine the nematic defect core structure in LCP droplets. Our multiscale approach follows analogous historical developments for flow simulations of single-phase nematic fluids, starting first with continuum modeling of the nematic director, followed by modeling at the mesoscopic (second moment orientation tensor) scale of Landau-deGennes model, then at the kinetic (full orientational distribution function) scale.

For this paper, we define the LCP phase as a melt or aqueous dispersion of rigid, high aspect ratio, high molecular weight, macromolecular rods or platelets. The single-phase predictive tools that have been developed span diverse scales, including molecular dynamics (MD) algorithms with individual particle resolution (cf. and the Zannoni references above), Monte Carlo lattice models (cf.), Fokker–Planck (FP) equation solvers for the particle orientational probability distribution function (cf.), Landau-deGennes (LdG) mesoscopic model solvers for the second-moment tensor of the particle PDF (cf.), and Leslie–Ericksen–Frank (LEF) continuum model solvers for the nematic director (cf.). These tools were historically developed and successfully benchmarked from the continuum to successively finer scales; furthermore, at each level of fine scale, it is clear how to coarse-grain up in the hierarchy, revealing what the coarser scale model both captures and misses, and often giving physical meaning to coarser model parameters. There have been decades of development of nematic fluid theory and modeling for which our brief remarks cannot do justice. The task of downscaling from a coarse model to a finer scale is an ill-posed problem, which is one reason that theorists pushed the tools down to finer scales to reveal deeper insights into nematic structure, and defects in particular. The fine-scale MD, Monte Carlo and FP solver data nonetheless require upscaling to compare with experimentally measurable, statistical features of the rod or platelet ensemble, the coarsest being the nematic director (the object of LEF continuum theory), followed by the scalar order parameters (which detect defects, uniaxial or biaxial phases) of the second-moment tensor of LdG theory, then higher moment information. These studies have produced numerically efficient defect detection and tracking metrics which we will employ here. The full spectrum of multiscale numerical tools has been implemented and benchmarked for liquid crystals and LCPs in bulk equilibrium homogeneous phases (independent of physical confinement) and for heterogeneous equilibria in the presence of physical confinement with solid boundaries. Only the FP, LdG and LEF models are amenable to nematic hydrodynamics applications. The LEF continuum theory has well-known limitations yet it is easiest to solve numerically, while the FP kinetic theory is computationally feasible so far in 1 and 2 physical space dimensions, albeit using supercomputers; LdG theory and related second-moment tensor models reside at the scale, at least so far, that strikes the best compromise between resolution of important physics and computational cost. The LdG mesoscopic scale is also the established level of approximation for testing of kinetic models, with a large body of work devoted to optimal closure approximations to avoid the significant complexity of FP solvers in orientation and physical space.

The theoretical framework given here generalizes diffuse-interface modeling and studies of small-molecule liquid crystal (LC) droplet dispersions at the continuum scale (Leslie–Ericksen–Frank theory for the nematic director) to larger molar mass LCPs at the kinetic scale (Doi–Hess theory for the full orientational distribution function, whose peak probability direction is the nematic director). In this way, the advances and gains in kinetic scale and mesoscopic scale (moment-averaged) descriptions of LCPs, including flow-nematic solvers and enhanced defect diagnostics, can be brought to bear on LCP droplet dispersions. A kinetic description of the molecular orientational distribution function is chosen over molecular-scale potentials and molecular dynamics simulations, which have been highly successful for near-equilibrium single and two-phase nematic studies (cf.), precisely to make hydrodynamic and unsteady simulations feasible. This modeling approach is based on an energy formulation that naturally incorporates the bulk free energy, short and long range particle interaction
potentials, rotational and translational diffusion of the LCP phase, flow torques, and the interfacial de-mixing and orientational anchoring energies in the diffuse interfacial domains where the LCP and viscous phases come into contact. This approach thereby encodes the full physics of both phases, energetics of their interaction, and hydrodynamics. Indeed, an energy formulation can be posed at the molecular, kinetic, mesoscopic, or continuum scale with the appropriate energy functionals, and our goal here is to develop the kinetic scale formulation. For this paper, we simulate equilibrium LCP droplets in a viscous fluid and their perturbations under imposed shear, with a focus on global droplet defect structure when the orientational anchoring energy is biased toward parallel or orthogonal rod alignment at fluid–fluid interfaces. To do so, we project the full kinetic model onto the first two non-trivial moments of the LCP distribution function, then develop and implement a numerical method in two space dimensions with full orientational degrees of freedom. We test the Abbott et al. hypothesis by suppressing Oseen–Frank distortional elasticity, and explore the global topology and defect structure versus anchoring conditions at LCP-viscous fluid interfaces.

There are related two-fluid systems for which accurate modeling and numerical tools have been developed and compared with experiments, such as polymeric filaments in air and studies of the mechanisms of filament breakup. For nematic fluid droplets dispersed in an immiscible solvent, the Zannoni group has developed molecular dynamics codes for equilibrium behavior that give far greater resolution of the defect structure than our approach can. However, we target non-equilibrium and unsteady flow simulations, for which molecular dynamics codes are not computationally feasible. We have to therefore coarse grain from the particle scale to some ensemble description, either for the particle orientational PDF (kinetic theory) or low moments of the PDF (mesoscopic, Landau-deGennes theory) or the nematic director (continuum theory). In either of these scales, two general approaches are feasible: sharp interface methods and diffusive interface methods. Sharp interface methods rely on some type of explicit front tracking method, have advantages in accuracy, yet require significant “surgical” overhead costs when there are strong topological changes in interfaces. Since we are ultimately interested in droplets and their potential rupture in strong extensional or shear flows, we have adopted the diffuse interface approach, previously at the continuum scale of Leslie–Erickson–Frank theory, and here at the kinetic scale of Doi–Hess theory. In this approach, one introduces a thin mixing layer and a scalar field, traditionally called a phase field variable, that captures the physics in the thin mixing layer between the distinct fluid phases. The dynamics of the scalar field penalizes mixing of immiscible fluids, with an energy function that recovers classical surface tension in the sharp interface limit. In addition, for nematic fluids there is an additional energy contribution to enforce orientational anchoring of the LCP phase in the interphase mixing layer. This energy penalizes variations away from the orientational bias of the LCP molecules to align tangentially or normally with the other fluid. We note that the Doi–Hess kinetic theory for LCPs is an energy-based formulation, and therefore compatible with a diffuse interface approach to two-phase fluids.

## 2 Kinetic model and moment-closure approximations for immiscible LCP mixtures

In a spatially homogeneous liquid crystal polymer solution where the number density of LCP molecules is constant, a probability distribution function (PDF) for molecular (rod) orientation can then be used to describe the orientational distribution, as assumed in the seminal papers by Kuzuu–Doi and Hess. This PDF is obtained from the number density distribution function at spatial location \( x \) with molecular orientation \( m \) at time \( t \) by normalization with respect to the constant number density of rod molecules. For a spatially heterogeneous LCP system, however, the rod molecule number density varies. We want to generalize the number density for these purposes, while also identifying how to reduce to the LCP theory of homogeneous systems. We introduce a normalized number density distribution function (NND) \( f(x, m, t) \) with respect to a characteristic rod number density to describe the distribution of rigid rod macromolecules at spatial location \( x \) with orientation direction \( m \) at time \( t \). The characteristic rod number density can be the average number density or the number density at a particular location \( x_0 \) and time \( t_0 \). In the latter case, the NND at \( (x_0, t_0) \) is a PDF.

The easiest way to see the relationship between homogeneous and heterogeneous LCPs is through properties of moments of the NND. We denote the zeroth moment of the NND with respect to \( m \) on the sphere by \( \phi = (1) \) and the second moment by \( M = (mm) \), where

\[
\langle \Phi \rangle = \int \frac{\Phi \text{d}m}{|m|^{n-1}}
\]

By definition, \( \phi \) describes the spatial concentration of the rod ensemble normalized relative to a characteristic number density while \( M(x, t) \) is proportional to the nematic tensor order parameter of Landau-deGennes theories for LCPs with scalar proportionality \( \phi \), i.e., \( tr(M) = \phi \). Therefore, since \( \phi = 0 \) in the purely viscous phase, the second moment vanishes \( M = 0 \). In regions where \( \phi \neq 0 \) (in the pure LCP phase and most of the diffuse interface region) a rank 2 orientation tensor \( Q = \frac{1}{\phi} M - \frac{1}{3} I \) can then be defined. This orientation tensor \( Q \) is identical to the trace 0 orientation tensor of Landau-deGennes and Doi–Hess theory for LCPs when \( \phi = 1 \). The second moment tensor or its equivalence \( \phi Q \) generalizes the notion of orientation tensor to the diffuse interface domain as well as the viscous phase where \( M \) vanishes identically by definition. We are careful not to numerically impose this normalization except where \( \phi \) is bounded away from 0. This generalized NND is defined throughout the two-phase fluid system. For immiscible LCP mixtures, we assume the condition \( \phi(x_0, t_0) = 1 \) at some \( (x_0, t_0) \), corresponding to a pure LCP phase. This is equivalent to normalizing the NND using the number density at \( (x_0, t_0) \).

For heterogeneous LCP-viscous fluid mixtures, the zero moment of \( f, \phi(x, t) \), serves as the labeling function, or phase variable, of diffuse interface theory! The condition \( \phi(x, t) = 0 \) defines the purely viscous fluid phase with zero rod number density. We have the representation of \( M \) in terms of principal values and directions,
\[ M = \sum_{i=1}^{3} d_i n_i n_i, \]

where \( 0 \leq d_i \leq \phi \) are the eigenvalues of \( M \) and \( n_i \) are the corresponding unit eigenvectors, yet \( \sum_{i=1}^{3} d_i = \phi \). These \( d_i \) are proportional to the standard scalar order parameters in the pure LCP phase as well as in the thin diffuse interface region, where they are scaled by the normalized density number. Clearly, the eigenvectors are defined uniquely only in the region where \( \phi > 0 \). We order the eigenvalues as follows: \( d_1 \leq d_2 \leq d_3 \leq \phi \). If \( d_1 > d_2 \), \( n_1 \) is uniquely specified, called the major director; if in addition \( d_2 = d_3 \), the local nematic phase is uniaxial and otherwise biaxial. The condition \( d_1 = d_2 > d_3 \) defines an oblate defect phase or core, which is partially disordered since \( n_1 \) lies anywhere on the circle orthogonal to the unique director \( n_3 \). The isotropic (fully disordered) defect phase or core is defined by the condition \( d_1 = d_2 = d_3 \). Extending our previous defect diagnostics,\(^{36,37,42}\) we utilize the metrics \( d_1-d_2 \), the oblate defect metric, and \( d_3-d_2 \), the isotropic defect metric, in domains where \( \phi \) is bounded away from 0. Since \( \phi \) vanishes smoothly, these metrics reveal a smooth transition to a completely isotropic fluid in the viscous fluid domain.

For the LCP phase, we model short-range excluded volume interactions by the extended Maier–Saupe potential

\[ U = A\phi - \frac{3N}{2}M:mm, \]  

where \( A \) and \( N \) are derived in ref. 1 based on spheroidal rods of major axis \( b \), minor axis \( a \) and aspect ratio \( \alpha = bc \), and given in the Appendix. The ratio \( A/N \) is an even function of the geometric parameter \( a = a^2 - 1 \). We denote \( A = \frac{3}{2}H(a) \). We will impose \( a = 0.8 \) such that \( H(a) = 3.1 \) to make contact with our previous studies of sheared LCP monodromains. Recall \( \phi \) represents a homogeneous LCP domain while \( \phi = 0 \) indicates a viscous fluid domain. Between the two immiscible liquids, there exists an interfacial region known as the mixing layer or diffuse interface layer, in which the LCP mixes with the viscous fluid. In the mixing layer, the NNDF \( f \) is a smooth function with \( 0 < \phi < 1 \). With this extension, the NNDF \( f \) is defined everywhere in the immiscible mixture. The zeroth moment in the mixing layer yields a relative measure of the number density with respect to the number density in the homogeneous bulk LCP region.

For this mixture, we consider the interaction between the liquid crystal polymer phase, mixing between the viscous and LCP phase, and anchoring energy at the LCP-solvent interface. We thus propose the free energy density for the mixture as follows

\[ \mathcal{A} = F_{\text{LCP}} + F_{\text{mix}} + F_{\text{anch}}, \]

\[ F_{\text{LCP}} = c_kT \int \left[ f \ln f - f + \frac{U}{2} f \right] dm dx, \]

\[ F_{\text{mix}} = c_kT \int \left[ \frac{1}{2} \| \nabla \phi \|^2 + b(\phi) \right] dx, \]

\[ F_{\text{anch}} = c_kT \int \left[ h \left( m \nabla \phi, \| \nabla \phi \|^2 \right) \right] f dm dx, \]

where \( c \) is the LCP concentration (number density) in the pure source phase at \( (x_0, t_0) \), \( c_k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( U \) is the potential in the pure LCP phase which generally has both short-range excluded volume and long-range distortional elasticity contributions, \( b(\phi) \) is the mixing free energy that governs physics of the two fluid phases in the diffuse mixing layer, and \( h(x, y) \) specifies the interfacial anchoring energy by penalizing variations from a preferred orientation of the rod molecules at the viscous fluid interface. The LCP free energy \( F_{\text{LCP}} \) is adopted from the Doi–Hess theory for this paper, which resolves a Maier–Saupe-like nematic ordering potential yet suppresses the long-range Frank elasticity contributions introduced later by Marrucci and Greco.\(^4\) The mixing free energy \( F_{\text{mix}} \) includes conformational entropy. The anchoring energy is new, extending analogous formulations at the continuum scale.\(^4\) For the above free energy density, the chemical potential is given by

\[ \mu = \frac{\delta \mathcal{A}}{\delta f} = k_B T \left[ \ln f + U - \lambda_1 \nabla^2 \phi + \frac{\delta b(\phi)}{\delta \phi} \right. \]

\[ \left. + h - \nabla (m h) - 2 \nabla \left( \langle h \rangle \nabla \phi \right) \right], \]

where \( h, h \) denote partial derivatives of \( h \) with respect to the indicated arguments.

With these choices of energy density contributions, the LCP droplet dispersion is dominated by spatial or translational diffusion and mixing in the diffuse interface. These choices essentially embed the original Doi–Hess kinetic theory into a diffuse interface two-phase fluid model; for single LCP phases, Doi and Hess suppressed translational diffusion relative to rotational diffusion of the rod macromolecular ensemble, whereas in the mixing layer, these two diffusive mechanisms are comparable. Again we emphasize that for the first proof-of-principle predictions, we are suppressing Frank distortional elasticity in the free energy. From a mathematical structure perspective however, long range interaction analogous to Frank distortional elasticity is present in this theory for the orientational dynamics due to the spatial diffusion operator, but not in the hydrodynamics (stress constitutive equation).\(^2\) We note that, in a linearization of the theory near a constant state in the limit of weak shear and weak spatial diffusion, this theory reduces to the well-known Ericksen–Leslie director theory for nematic liquid crystals without Frank elasticity.\(^2\) The translational diffusion provides the source for the long-range interaction among LCP molecules nonetheless. Consistent with these assumptions, the transport equation for the normalized number density function \( f \) is the generalized Doi–Hess Smoluchowski equation,

\[ \frac{df}{dt} + \nabla (vf) = \nabla \left( \frac{D_i}{k_B T} \nabla f \right) + \nabla \left( \frac{D_{r} h}{k_BT} \nabla h \right) - \nabla \left( m \times mf \right), \]

\[ m = Wm + a (Dm - D:mmm), \]

where \( D_i \) is a spatial diffusion matrix operator defined below, \( D_r \) is the rotational diffusion coefficient, \( \nabla \) is the spatial gradient operator, \( R \) is the rotational gradient operator, \( v \) is the average velocity, \( W = \frac{1}{2} \left( \nabla v - \nabla v^T \right) \) is the vorticity tensor and \( D = \frac{1}{2} \left( \nabla v + \nabla v^T \right) \) is the rate-of-strain tensor. The spatial diffusion matrix is
where $D_\parallel$ is the diffusion coefficient aligned with the nematic orientation tensor of the LCP while $D_\perp$ is the transverse diffusion coefficient. We assume $D_1 = D_\perp = D_\parallel$, which suppresses translational anisotropic diffusion in this paper.

Taking the zeroth moment of the Smoluchowski equation, we arrive at the transport equation for the zeroth moment ($\phi$) of $f$:

$$
\frac{\partial f}{\partial t} + \nabla \cdot (\nabla \phi f) = D_\parallel \int_{|\mathbf{m}|=1} \nabla (\nabla \mu f) \, d\mathbf{m} - D_\perp \int_{|\mathbf{m}|=1} \nabla (\nabla \mu f) \, d\mathbf{m} - \nabla \cdot \left( \nabla \phi (\nabla (h_f)) \right).
$$

Thus the transport equation for the phase variable of LCPs for the mixture is given by:

$$
\frac{\partial \phi}{\partial t} + \phi \nabla \cdot f = D_\parallel \nabla \phi - \frac{3N}{4} \nabla \left( \text{tr}(M^2) \right)
+ \phi \nabla \left( - \lambda_1 \nabla^2 \phi + \beta (\phi) \right)
+ (\nabla h) - \phi \nabla (\nabla (h_f))
- 2\phi \nabla (\nabla (h_f)),
$$

The translational flux embedded in the above equation contains contributions from both the normalized volume fraction variable and the second moment structure tensor $M$.

Taking the second moment of the Smoluchowski equation with respect to $f$,

$$
M = \frac{\partial M}{\partial t} + \nabla \cdot (\nabla M) - WM + MW - \alpha_1 [\text{DM} + \text{MD}]
= -2\alpha_1 D_\parallel A_{44} \nabla \phi + D_\parallel \nabla^2 M + D_\parallel A_{44} \nabla \phi M
- \frac{3ND_\parallel}{2} \nabla \cdot [\nabla (M_{44})] + D_\parallel \nabla \cdot \left( M \nabla \frac{\partial F_{\text{mix}}}{\partial \phi} \right)
+ D_\parallel \nabla \cdot [\nabla (M_{44})] - D_\parallel \nabla \cdot [\nabla (M_{44})] M
- 2D_\parallel \nabla \cdot [\nabla (h_f) \nabla \phi M].
$$

For the anchoring energy, we propose the following kernel

$$
h(x,y) = \alpha_1 x^2 + \alpha_2 (y - x^2),
$$

where $\alpha_1$, $\alpha_2 \geq 0$ parametrize the two prominent anchoring conditions: tangential and homeotropic anchoring. If $\alpha_1 = 0$, the anchoring energy favors a tangential anchoring; if $\alpha_2 = 0$, the anchoring energy favors a homeotropic anchoring. The derivatives of the function with respect to its arguments are given by

$$
h_x = 2(\alpha_1 - \alpha_2)x, \quad h_y = \alpha_2.
$$

Notice that the transport equation for the zeroth moment, by nonlinearity, couples to the second moment tensor; likewise, the second moment transport equation couples to the fourth moment. As with all moment equations for nonlinear PDEs, the equations for $\phi$ and $M$ are not closed, and so a closure approximation is needed to truncate the infinite system of coupled moment equations. Since Landau-deGennes theory is posited at the scale of the second-moment tensor, and the Onsager isotropic-nematic phase diagram is uniquely specified by projection onto the second-moment tensor, most closure rules for LCP kinetic theory have approximated the fourth moment in terms of lower moments. We adopt the following closure rule consistent with our earlier work, where closure parameters are chosen to match bifurcations in the Onsager isotropic-nematic equilibrium phase diagram,

$$
M_{44} = \alpha_1 M_{M:B} B + \frac{1 - \alpha_1}{2} (MB + BM),
$$

and $0 \leq \alpha_1 \leq 1$ is a closure parameter that can be chosen to match key equilibrium features with experimental data.

Before solving the zeroth and second moment equations, we non-dimensionalize the system with a characteristic time scale $t_0$ and length scale $x_0$. The dimensionless equations (before the closure is applied) are given by

$$
\frac{d\phi}{dt} + \phi \nabla \cdot f = D_{\parallel} \nabla^2 \phi + A \nabla (\phi \nabla \phi) - \frac{3N}{4} \nabla \cdot (\text{tr}(M^2))
+ \nabla \left( \phi \nabla \left( - \alpha_1 \nabla^2 \phi + \frac{1}{\epsilon^2} \beta (\phi) (1 - 2\phi) \right) \right)
- \alpha_1 \nabla \cdot (\nabla (h_f)) + \alpha_2 \nabla \phi \nabla \phi M_{44}
- 2\alpha_2 \nabla \phi \nabla \phi M.
$$

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where the dimensionless parameters are defined by
\[ A_1 = \frac{\lambda_1}{\lambda_0}, \beta = \frac{2(\alpha_1 - \alpha_2)}{\alpha_0^2}, \tilde{a}_2 = \frac{\alpha_2}{\alpha_0}, \tilde{D}_2 = \frac{h_0}{\lambda_0} D_2, \tilde{D}_c = \frac{1}{6\tilde{D}_c}, \]
(18)

\( A_1 \) is the dimensionless parameter measuring the persistence length in the conformational entropy, \( \beta \) and \( \tilde{a}_2 \) are dimensionless parameters which determine the bias in LCP anchoring at a fluid interface, \( \tilde{D}_2 \) is the dimensionless translational diffusion coefficient, and \( \tilde{D}_c \) is the standard Deborah number for the LCP phase if \( h_0 \) is a characteristic flow time scale. In equilibrium, the choice of the characteristic length and time scale is internal, e.g., \( 6\tilde{D}_c \tilde{D}_2 = 1 \), so \( \tilde{D}_c = 1 \), and then \( \tilde{a}_2 \) is chosen so that either \( A_1 \) or \( \tilde{D}_2 = 1 \). When flow boundary conditions are given, the choice of the characteristic scales are typically chosen by the driving conditions and geometry. We will specify these choices in the numerical results section. The second moment equation in closure form is given by

\[
\frac{dM}{dt} + M\nabla v - WM + MW - a_1[DM + MD] = 0
\]

\[
-2a_{a_1}D_{MM}M - \frac{1}{De} \left[ M - \frac{\phi}{3} - a_1NM^2 + \frac{a_1}{\phi} MM:MM \right]
\]

\[
-\frac{\beta}{6De} \left[ a_1M \phi \nabla \phi + a_1 \nabla \phi \nabla \phi M + 2a_{a_1}MM: \nabla \phi \nabla \phi \right]
\]

\[
+ \tilde{D}_2 \left( \nabla^2 M + \tilde{A} \nabla \phi (\nabla \phi M) \right)
\]

\[
- \frac{3N\tilde{D}_2}{2} \left[ a_1 \nabla \left( \frac{1}{\phi} \nabla \nabla \phi (M^2) M \right) + \frac{1}{2} \nabla \phi^2 M^2 \right]
\]

\[
+ \tilde{D}_2 \nabla \left( \phi M, - A_1 \nabla^2 \phi + \phi (\nabla \phi) \right)
\]

\[
+ \beta \tilde{D}_2 \tilde{a}_2 \tilde{D}_2 \left[ \frac{a_1}{\phi} \tilde{d}_\phi \phi \tilde{d}_\phi \phi \nabla \phi (M_{\mu\nu} M_{\sigma\delta}) + \frac{1}{2} \tilde{d}_\phi \phi \nabla \phi (M_{\mu\nu} M_{\sigma\delta}) \right]
\]

\[
- \beta \tilde{D}_2 \tilde{a}_2 \left[ \nabla \phi (\tilde{d}_\phi \phi (M_{\mu\nu} \nabla \phi)) M \right]
\]

\[
-2\tilde{a}_2 \tilde{D}_2 \tilde{a}_2 \left[ \nabla \phi (\tilde{d}_\phi \phi (\nabla \phi \phi)) M \right].
\]

(19)

We note that the transport equation for the volume fraction is a modified Cahn–Hilliard equation with a fourth order dissipation in \( \phi \); the equation for \( M \) is a possibly singular third order equation. In the regime where \( \phi \) is constant (the pure LCP or pure viscous phases), the second moment transport equation is dissipative, whereas the highest order derivatives are dispersive when \( \nabla \phi \neq 0 \). We turn next to the zeroth moment transport equation in closure form.

### 2.1 Enforcing immiscibility of the two liquid phases: choice of \( h(\phi) \)

Recall that \( \phi \) is the volume fraction of LCP phase in the two-phase fluid, which will vanish in the pure viscous phase and grow to unity in the pure LCP phase. We have the freedom within the diffuse interface formulation to impose miscibility or immiscibility of the two fluid phases; since we are interested in immiscible LCP-viscous fluid mixtures, we choose the bulk energy that favors phase separation:

\[ h(\phi) = \frac{1}{\varepsilon} \phi^2 (1 - \phi)^2 + B_1 \phi + B_2. \]

(20)

where \( \varepsilon \) is a parameter whose reciprocal measures the strength of the phobic bulk mixing energy, \( B_1 \) is the free energy density for the viscous fluid and \( B_2 \) is the free energy difference between the LCP and the viscous fluid. For the current model, this linear term does not have any effect on the dynamics of the system, so we drop it from the bulk energy from now on. These transport equations for the zeroth and the second moment of \( m \) with respect to the normalized number density provide some internal order variables for the mesoscopic structure of the mixture. These need to be coupled to the mass and momentum balance to arrive at a complete hydrodynamic theory for the mixture fluid system.

#### 2.2 Balance of mass and momentum

We denote the density of the incompressible viscous fluid by \( \rho_v \) and that of the incompressible LCP by \( \rho_c \). The total mass density of the mixture is defined as

\[ \rho = \rho_v (1 - \phi) + \rho_c \phi. \]

(21)

Mass conservation implies

\[ \frac{\partial \rho}{\partial t} + \nabla (\rho v) = 0. \]

(22)

The momentum balance leads to

\[ \rho \left( \frac{\partial v}{\partial t} + v \nabla v \right) = \nabla (-pI + \tau) + F_v, \]

(23)

where \( p \) is the hydrodynamic pressure, \( \tau \) is the total extra stress, and \( F_v \) is the external force including the elastic force due to material inhomogeneity. The mass conservation equation (or the continuity equation) coupled with the transport equation for \( \phi \) leads to

\[ \nabla \phi = \frac{\rho_v - \rho_c}{\rho_v} \left[ \frac{\partial \phi}{\partial t} + \nabla (\phi v) \right]. \]

(24)

With this, the transport equation for \( \phi \) reduces to

\[ \frac{\partial \phi}{\partial t} + \nabla (\phi v) = \frac{\rho_v - \rho_c}{\rho_v} \nabla v. \]

(25)

In the region of a single phase, either the viscous fluid or the LCP, the right hand side of (24) vanishes. So, the divergence of the velocity can be non-zero only in the mixed region.

In this paper, we focus only on the equilibrium phase in quiescent states and flow-imposed deformation of LCP droplets, so we suppress the details of the pressure, extra stress and external force.

### 3 Numerical methods

Ignoring the feedback to flow in the simulations, we focus on the equilibrium configuration of the droplets and their internal orientational microstructure in equilibrium and in the presence...
of imposed weak shear flows. This reduces the full flow-nematic system to the transport equations for the LCP volume fraction and second-moment tensor. We will solve these equations in two space dimensions, building a numerical method that we now describe. First, we rewrite the eqn (17) in a form that reveals the basic mathematical structure,

\[
\begin{aligned}
\frac{\partial M}{\partial t} - \bar{D}_s \Delta M &= f(M, \phi), \\
\partial_n M |_{\partial D} &= 0; \\
\frac{\partial \phi}{\partial t} - \bar{D_i} \nabla (\nabla (-A_1 \Delta \phi)) - \bar{D}_s \Delta \phi &= g(M, \phi), \\
\partial_n \phi |_{\partial D} &= 0, \quad \partial_n \Delta \phi |_{\partial D} = 0,
\end{aligned}
\tag{26}
\]

where \(f(M, \phi)\) and \(g(M, \phi)\) contain all corresponding nonlinear terms in the transport equations, and \(\Omega\) is the computational domain. The Neumann boundary conditions are consistent with the zero-flux condition for the normalized number density function.

We denote \(\phi^k\) and \(\mathbf{M}^k\) as the numerical approximation of \(\phi\) and \(M\) at time \(t = k\Delta t\), respectively, where \(\Delta t\) is the discrete time step. The first-order (in time) discrete scheme for \(\mathbf{M}\), \(\phi\) is:

\[
\begin{aligned}
\frac{\mathbf{M}^{k+1} - \mathbf{M}^k}{\Delta t} &= f(M^k, \phi^k), \\
\partial_n M^{k+1} |_{\partial D} &= 0, \\
\frac{\phi^{k+1} - \phi^k}{\Delta t} &= \Delta \mathbf{M}^{k+1} + A_1 \Delta \phi (\phi^{k+1} - \phi^k) \\
\frac{-\gamma}{\varepsilon^2} \Delta (\phi^{k+1} - \phi^k) &= \nabla \nabla (-A_1 \Delta \phi^k) + g(M^k, \phi^k), \\
\partial_n \phi^{k+1} |_{\partial D} &= 0, \quad \partial_n \Delta \phi^{k+1} |_{\partial D} = 0.
\end{aligned}
\tag{27}
\]

Here, we introduce a dissipative term \(-\frac{\gamma}{\varepsilon^2} \Delta (\phi^{k+1} - \phi^k)\) in the equation for \(\phi\), of order \(s \Delta t / \varepsilon^2\), to improve the stability of the scheme. The parameter \(s\) is proportional to the amount of artificial dissipation added in the numerical scheme. Larger \(s\) imposes more stability but less accuracy. In our numerical simulations, we use \(s = 2\) which appears to provide a good balance between stability and accuracy. Details of stability and error analysis of this stabilized semi-implicit scheme can be found in ref. 66–68.

Note that in (27), the fourth-order term involves a non-constant coefficient \(\phi^k\). Notice that \(\phi \sim 0\) in the exterior of the drop. Hence, \(\phi\) may become negative at some grid points and may render an iterative method like Conjugate Gradient to diverge. Therefore, we use a standard approximation of the fourth-order operator with variable coefficients by one with constant coefficients in (27), which is equivalent to stabilizing the scheme by yet another first order term; see ref. 69.

To summarize, at each time step, the above scheme leads to a sequence of Poisson-type equations for \(\mathbf{M}^{k+1}\) and \(\phi^{k+1}\). Since these equations have constant coefficients and the domain is regular, they can be efficiently and accurately solved by using a high order spectral-Galerkin method.\textsuperscript{39,40} Specifically, we consider the computational domain as a two-dimensional rectangular domain \(\Omega = \{(x, y) | x \in [0, L_x], y \in [0, L_y]\}\) with periodic boundary conditions in \(x\) and Neumann boundary conditions in the \(y\)-direction. We apply a Fourier spectral method in \(x\) and the Legendre–Galerkin spectral method\textsuperscript{10} in the \(y\)-direction. We note in particular that, in order to reduce the computational complexity, we use the basis functions which satisfy exactly the Neumann boundary condition for \(\mathbf{M}^{k+1}\), as well as the typical boundary conditions for the Cahn–Hilliard type eqn (27).\textsuperscript{70} For these basis functions, the resultant linear systems from the scheme are all sparse with compact bandwidth.

### 4 Numerical results and discussion

We implement the numerical scheme above in two space dimensions, first to study equilibrium orientational morphology of 2D LCP droplets immersed in viscous fluids under two typical anchoring situations: tangential and homeotropic anchoring at the interface. Recall that the actual 3D LCP geometry is a cylinder, since we assume uniformity in the direction normal to the 2D domain. The defect structures are likewise extended along the \(z\)-axis, so that topological point defects correspond to line defects, and defect cores correspond to threads. After analyzing these structures, we perturb droplet equilibria by imposing a linear shear flow on the computational domain. The parameters used for the simulations are listed in Table 1. For tangential anchoring, \(\beta = -0.05\) and \(\tilde{a}_2 = 0.025\); for homeotropic anchoring, \(\beta = 0.05\) and \(\tilde{a}_2 = 0\).

#### 4.1 Droplet morphology metrics and figures: defect cores, defect topology, and “3D” graphics

For each simulation, we employ a portfolio of three figures to give a comprehensive explanation of LCP morphology in the droplet interior and diffuse interface. The figures are generated from the eigenvalues \(d_i\) and frame of eigenvectors \(\mathbf{n}_i\) of the second moment tensor \(\mathbf{M}\) (which is symmetric and positive semi-definite) together with the LCP volume fraction \(\phi\) across the 2D computational domain. Orientation tensor diagnostics were previously developed for static LC molecular dynamics simulations\textsuperscript{43,44} and dynamic flow simulations\textsuperscript{45,46,47} of single phase LCPs, which we integrate with the LCP volume fraction \(\phi\) over the 2D \(x, y\) domain to provide new perspectives on LCP droplet dispersions that expose the cores of surface and interior defects. The three figures represent a protocol for morphology classification, starting with defect core detection and classification, then traditional director-based topological classification, and finally an integrated morphology depiction based on the unique 3D ellipsoid representation of the second-moment tensor \(\mathbf{M}\).

#### Table 1 Parameter values

<table>
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<th>Value</th>
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<td>(M)</td>
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methods, and then builds out from the cores to the surrounding topological structure.

We now describe the construction of these three figures prior to their implementation for numerical data.

**First figure: defect core metrics.** The first element of morphology characterization is determined from the ordered principal values $d_i$ of $M$, which obey the inequalities: $1 \geq d_1 \geq d_2 \geq d_3 \geq 0$, where $tr(M) = \phi$. In the pure LCP phase, $tr(M) = \phi = 1$, whereas in the pure viscous phase, $tr(M) = \phi = 0$. Defect cores correspond to domains of disorder where the director $n_1$ is not well-defined. Partial disorder arises when $d_1$ has multiplicity 2 and the defect core is called oblate because the triaxial ellipsoid uniquely specified by $M$ is an oblate spheroid (platelet-shaped). When $d_1$ has multiplicity 3 the defect core is isotropic, and the ellipsoid defined by $M$ is a sphere of radius $\phi$. Defect cores are numerically detected by the zero level sets of the oblate defect core metric $d_1$ and the isotropic defect core metric $d_1$–$d_3$. Panels $a$ and $b$ give the color map of the oblate and isotropic defect core metrics over the 2D domain, with the zero level set colored dark blue, and the maximum value (corresponding to strongest nematic phase) colored dark red. The pertinent information from these metrics and figures resides within the LCP drop and the diffuse interface (“in the surface”).

Note that both metrics must be analyzed. If the isotropic defect core metric yields a positive test, obviously so will the oblate metric. Yet a positive test for an oblate defect core can and does often arise while the isotropic defect metric is bounded away from zero. On mathematical and physical grounds, since both defect phases are unstable at the nematic concentrations inside the pure LCP phase considered here, the oblate phase is preferred over the isotropic phase in order to resolve the core of a topological defect. There are geometric constraints which can force an isotropic core, which we illustrate in the final simulation. Thus panels $a$ and $b$ immediately reveal the presence, location, type and extent of defect cores. Panels $c$ and $d$ blow up a selected defect core domain to gain more amplified resolution of the core domain; different anchoring conditions yield quite different defect core domains. Panels $e$ and $f$ give the surface plots (topographic maps) of $d_1$–$d_2$ and $d_1$–$d_3$ superimposed with their level set color map in panels $a$ and $b$, providing a more enhanced perspective of the defect core domains (local wells) amid highly ordered domains (high plateaus). Panels $g$ and $h$ represent a shift from differences in the $d_i$ to individual plots of $d_1$, $d_2$, $d_3$ along cross-sections of a chosen defect core. Collisions of $d_1$ with $d_2$ identify a defect core, and $d_3$ either lies below (oblate) or coincides (isotropic), collisions of $d_2$ and $d_3$ with $d_1$ above specifies uniaxial nematic phases, and regions where all $d_i$ are distinct correspond to biaxial nematic phases.

The first figure for each simulation therefore gives an exhaustive detection and classification protocol for the defect cores.

**Second figure: director fields and defect topology.** Panels $a$ and $b$ map the director field $n_1$ where defined, i.e., outside defect cores, over the LCP droplet and diffuse interface 2D domains. Panels $c$ and $d$ blow up the director field surrounding the identified defect cores; we use rectangles to denote degree $+1/2$ defects and ovals to denote degree $-1/2$ defects. An isotropic core is unique to the final simulation. Panels $a$ and $c$ use color maps of the oblate metric so that one can locate topology over the defect core where the director becomes ill-defined. Panels $b$ and $d$ superimpose color maps of the LCP volume fraction $\phi$ to locate topology relative to the pure LCP phase (“inside the droplet”) or within the diffuse interface (“in the surface”).

**Fig. 1** Equilibrium droplet morphology with tangential anchoring. (a) Color map of the oblate defect core metric $d_1$–$d_2$. (b) Color map of the isotropic defect core metric $d_1$–$d_3$. (c) Blow-up of (a) around defect core. (d) Blow-up of (b) around defect core. (e) Principal values $d_i$ of $M$ along the horizontal slice $y = 0.5$ through the droplet center. (f) Principal values $d_i$ along a vertical slice $x = 0.25$ through the left defect core. (g) The surface mesh of $d_1$–$d_2$ around defect core. (h) The surface mesh of $d_1$–$d_3$ around defect core.
Fig. 2 Equilibrium droplet morphology with tangential anchoring. (a) The blow up of the director field around defect core with color map of the oblate defect core metric \(d_1 - d_2\). (b) The blow up of the director field around defect core with color map of phase field \(\phi\). (c) The whole domain of (a). (d) The whole domain of (b).

Fig. 3 Equilibrium droplet morphology with tangential anchoring. (A) The 3d ellipsoids \(\left(\frac{d_1}{\phi}, \frac{d_2}{\phi}, \frac{d_3}{\phi}\right)\) around defect core, with color map of \(\frac{d_1}{\phi} - \frac{d_2}{\phi}\) through three different view perspective. (B) The 3d ellipsoids \((d_1, d_2, d_3)\) around defect core, with color map of \(d_1 - d_2\) through three different view perspective.
Fig. 4  Equilibrium droplet morphology with homeotropic anchoring. (a) Color map of the oblate defect core metric $d_1 - d_2$. (b) Color map of the isotropic defect core metric $d_1 - d_3$. (c) Blow-up of a) around defect core. (d) Blow-up of b) around defect core. (e) Principal values $d_i$ of $M$ along the vertical slice $x = 0.5$ through the droplet center. (f) Principal values $d_i$ along a horizontal slice $y = 0.2716$ through the interior defect core at the north pole. (g) The surface mesh of $d_1 - d_2$ around defect core. (h) The surface mesh of $d_1 - d_3$ around defect core.
This second figure therefore recovers the traditional topological defect characterization of continuum modeling, while simultaneously locating topology relative to the core structure. It will be shown that the LCP drop topology-core structure differs dramatically for parallel and normal anchoring conditions. Indeed, these modeling tools allow a tuning of the anchoring preference from parallel to homeotropic, and therefore an anchoring-induced morphology transition; such a study is deferred to future applications.

Third figure: tensorial 3D graphics of order and disorder. Finally, we apply the full graphical power of data for \( M \) and \( \phi \). We image the spatial field of 3D triaxial ellipsoids uniquely defined by \( M \) where \( \phi > 0 \). The ellipsoid shape visually conveys the principal directions \( n_i \) and degrees \( d_i \) of orientational order at each spatial location, which we further reinforce with the oblate defect color map (dark red for strongly ordered phases and dark blue for the oblate defect phase). In ordered locations where \( d_1 \) is simple (\( d_1 \gg d_2 \)), the ellipsoid is a red prolate spheroid (a thin rod) with major axis \( n_1 \). In oblate cores where \( d_1 \) has multiplicity two (\( d_1 = d_2 > d_3 \)), the ellipsoid is a dark blue oblate spheroid (discotic) with normal axis \( n_3 \). In isotropic cores where \( d_1 \) has multiplicity three, the ellipsoid is a dark blue sphere. Since \( M \) has trace \( \phi \), the unscaled ellipsoids shrink in the diffuse interface (given in the right column). The traditional ellipsoids of the second-moment tensor of a PDF have semi-axes lengths \( d_i/\phi \) that sum to 1 (given in the left column). The top row shows the color-coded ellipsoids over a defect core area, while the next two rows blow up the defect core from two different angles. These perspectives are necessary since local ellipsoids that are discotic will appear as rods from one perspective and spheres from another.

4.2 Equilibrium LCP droplets with tangential anchoring: bipolar surface boojums with oblate defect cores spanning the diffuse interface

The equilibrium morphology of a 2D LC droplet in a viscous fluid with tangential anchoring was studied previously in ref. 3 with a continuum diffuse interface model. The numerical results yield circular 2D drops with an internal homogeneous director orientation and a bipolar defect structure, with surface topological defects of degree +1/2 at opposite poles of the drop, called boojums. The same global droplet structure arises in 2D satellite drops that form in the breakup of a LC thread, also using phase field continuum modeling,\(^71,72\) and in 2D satellite drops that form in the shear rupture of a LC droplet.\(^5\) The fundamental limitation of these LC-viscous continuum models is that the core structure is invisible to the nematic director. The major advance provided by the present diffuse interface tensor model, by virtue of the eigenvalues and full set of eigenvectors of \( M \), is the ability to resolve the defect core structure associated with a topological defect. We follow the figure protocol described just above to provide these enhancements of continuum LC modeling.
Fig. 1 describes drop-interface morphology on the basis of order parameters $d_i$. Fig. 1a and b give the color maps of the oblate and isotropic defect metrics, revealing uniform equilibrium nematic order within the droplet with the exception of two surface oblate defect domains at the east and west poles. (Note: the isotropic defect metric test fails.) The east-west poles of the oblate defects are arbitrary; this structure is rotationally invariant and we have broken rotational symmetry by the initial data, which is a uniform nematic equilibrium with director along the $x$ axis. If we rotate the initial data with principal axis at any angle, this structure simply rotates by the same angle.

Fig. 1c and d blow up Fig. 1a and b around the west oblate defect core, revealing a disordered 2D domain where both metrics have apparent gradients within the diffuse interface. The oblate core spans the thin diffuse interface east-to-west while stretching along the tangential direction within the diffuse interface. This simulation is a perfect illustration of a diffuse interface characterization of a “surface defect”.

Fig. 1e and f drill deeper into the $M$ tensor degeneracy with horizontal (e) and vertical (f) slices of the entire computational domain, plotting all three $d_i$ together along these lines. The $y = 0.5$ slice cuts along the east-west axis and therefore through both defect cores, while the $x = 0.2431$ slice cuts through the west oblate core. These graphs confirm the defect cores are oblate and 2D, with nematic order recovery around the oblate core. The surprising part of this result is the “nematic rebound” going westward from the core even as the LCP volume fraction is falling toward zero. The vertical cross-section shows a more gradual “well” in $d_i$ as one traverses upward within the diffuse interface. The $x = 0.2431$ graphs clearly show a transition from oblate defect degeneracy to a fully biaxial phase ($d_1 > d_2 > d_3$) and then a uniaxial nematic phase ($d_1 > d_2 = d_3$) until the viscous fluid is reached. A blow-up of the $y = 0.5$ graph (not shown) confirms the same nematic phase transition sequence with sharper gradients.

Fig. 1g and h provide a level-set surface topography of the oblate and isotropic defect metrics that enhances the color maps $a–d$, revealing a “well” in the oblate metric over the oblate core that drops down to ground level, and a shallow well in the isotropic defect metric surface.

Fig. 2 reveals defect topology surrounding the west (left) oblate core, which is identical to the east core. We print the traditional “director map” of $n_1$ where it is defined (where $d_i$ is simple), on the left with background color map from the oblate metric and on the right with color map from the LCP volume fraction. Each oblate core has a pair of degree $+1/2$, $-1/2$ topological defects, with the $+1/2$ degree structures in the interior of the $\phi = 0.5$ level set and the $-1/2$ degree structures in the exterior of the $\phi = 0.5$ level set, still within the diffuse interface. Note the feature of two topological degree defects sharing the same oblate core is consistent with Fig. 1e–h where nematic order surrounds the oblate core, even though the entire structure lies within the diffuse interface! Our group has seen similar topology-core behavior in single phase LCP hydrodynamic simulations with two opposite-signed half-integer defects sharing a single oblate defect core. However, if this droplet defect morphology is physical, it is unclear the $-1/2$ degree structures closest to the viscous fluid are experimentally visible.
Fig. 7 A moderately sheared LCP droplet favoring tangential interfacial anchoring. (a) Color map of the oblate defect core metric $d_1 - d_2$. (b) Color map of the isotropic defect core metric $d_1 - d_3$. (c) Principal values $d_i$ of $M$ along the vertical slice $x = 0.7809$ through the droplet center. (d) Principal values $d_i$ along a horizontal slice $y = 0.5789$ through the northeast defect core. (e) The surface mesh of $d_1 - d_2$ around defect core. (f) The surface mesh of $d_1 - d_3$ around defect core.

Fig. 8 A moderately sheared LCP droplet favoring tangential interfacial anchoring. (a) The blow up of the director field around defect core with color map of the oblate defect core metric $d_1 - d_2$. (b) The blow up of the director field around defect core with color map of phase field $\phi$. 

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Are these surface defects identical to the traditional picture of boojums? Yes and No. If we restrict attention only to the $+1/2$ degree topology inside the $\phi = 1/2$ level set in the diffuse interface, and suppress the $-1/2$ degree topological structure outside the $\phi = 1/2$ level set, toward the outer edges of the diffuse interface, then we recover the traditional picture of surface boojums at the east and west poles of the LCP drop. This “partially blind perspective” agrees with continuum director modeling results for LC drops in equilibrium, satellite drops that form after shear rupture and after LC fiber pinch-off; each of these simulations employ a diffuse interface approach and tangential anchoring. In each of these diverse conditions, a bipolar boojum structure resides on the interior side of the LC drop interface; each polar boojum has degree $+1/2$ and therefore the drop does not conserve topological degree neutrality, locally or globally. These director models do not have the degrees of freedom afforded by the scalar order parameters nor the physics that would dictate their behavior in the diffuse interface. Our model, with tensorial resolution throughout the defect core, fills in the missing features of both the local and global topology, and of the structure of boojums. We find that topological degree neutrality is conserved locally for each oblate defect core, and therefore globally, in equilibrium LCP drops. Boojums in our model still have degree $+1/2$ topology at the “inner interface” of the pure LCP drop, but there is a degree $-1/2$ defect sharing the same defect core at the “outer interface” closest to the viscous phase. Thus our model predicts that boojums have a more complex structure than previously thought. We are interested in extending these mesoscopic model predictions to include the kinetic nonlinear analog of Frank elastic energy to confirm the predictions made here which are equivalent to identical bend, splay, twist linear elasticity constants. We emphasize that our model and results are consistent with the hypothesis of the Abbott lab. Their studies indicate that anchoring boundary conditions on the LC phase can be met by the formation of local defect cores (small domains of disorder) which self-organize the surrounding orientational morphology. This is precisely what our model predicts, since we have suppressed Frank elasticity which would be necessary to resolve a continuous strain via bend, splay and twist distortions as the primary mechanism to satisfy anchoring conditions.

Fig. 3 compiles the above information into the $M$ tensor ellipsoid morphology over the 2D oblate core at the west pole. The left column employs pure orientational ellipsoids whose semi-axes lengths $d_i/d_\phi$ sum to 1, while the right column ellipsoids scale down with $d_\phi$ and disappear on the outskirts of the LCP droplet interface. The oblate defect color scale (dark red for strongly ordered, dark blue for oblate cores) helps distinguish ambiguities due to perspective. The second and third rows blow up a small oblate core domain with two different angles of view to further distinguish ambiguities. The interior orientation is along the $x$ axis, which strongly conflicts with tangential anchoring at the east and west poles. The prediction is that the minimum energy configuration that resolves this conflict is a partially ordered, oblate phase whose minor axis aligns with the interior and the circle of directions associated with $d_1 = d_2$ satisfies tangential anchoring “weakly”. Visually this
corresponds to dark blue oblate spheroids (thin discs) spanning the diffuse interface with normal to the discs along the x-axis. To accomplish a smooth transition leaving the center of the diffuse interface, the ellipsoids become triaxial (an unfortunate terminology, equivalent to a biaxial LCP phase), meaning the \( d_i \) separate from one another, allowing the principal axis associated with \( d_1 \) to sharply transition to tangential anchoring and restore the uniaxial phase with \( d_1 > d_2 = d_3 \). This oblate to biaxial to uniaxial phase transition occurs sharply across the diffuse interface and more gradually along the vertical y direction, consistent with the results in Fig. 1.

### 4.3 Equilibrium 2D LCP droplets with homeotropic anchoring: splitting of oblate cores with half-integer defects separated by a nematic diffuse interface

From uniform initial data with horizontal (x-aligned) nematic order, a steady state LCP droplet structure is reached. The initial data breaks rotational symmetry as in the tangential anchoring case, and the numerical results are invariant under rotation. With normal anchoring and horizontal initial alignment, the orientational incompatibility is at the north and south poles.

Fig. 4a and b indicate oblate defect cores have shifted inside the drop relative to tangential anchoring. The blow-up in Fig. 4c and d confirms the southern oblate core has shifted to the interior while further indicating a nematic phase in the diffuse interface. Fig. 4e indicates a double oblate phase slicing vertically through the center of the defect domain, while Fig. 4f slices horizontally, piercing one oblate domain. Remarkably, the nematic order between the two oblate domains is stronger than the equilibrium order in the center of the drop. Fig. 4g and h reveal the nearby double wells in the oblate metric. We note that the degree of disorder is not complete as in the tangential anchoring case, in that \( d_1 \) approaches \( d_2 \) but does not intersect. The phase transitions with normal anchoring surrounding the defect core are more complex as seen from Fig. 4e and f with a transition from a uniaxial nematic interior of the drop to two oblate transitions separated by biaxial and uniaxial transitions as the viscous phase is approached. Such strong gradients in the order parameters are apparently the lowest energy resolutions of the anchoring conflict at the north-south poles with interior horizontal orientation.

Fig. 5 shows that the defect topology is identical to the tangential anchoring case, except that now the +1/2 defects surround the interior oblate domain at each pole and the −1/2 defects follow the oblate domain toward the outer edge of the diffuse interface. With tangential anchoring, the model predicts single polar oblate domains with a pair of opposite degree half-integer defects; with normal anchoring, the oblate domain at each pole is split in two with each single oblate domain carrying one topological defect.

Fig. 6 reveals the full 3D orientational morphology around the southern pole of the droplet. The perspective is looking down on the x–y plane from the z-axis. These figures reveal that the resolution of the anchoring conflict from horizontal interior orientation to normal south pole orientation is accomplished quite simply. The “recessive” eigenvector \( n_1 \) of \( \mathbf{M} \) associated with \( d_1 \) remains along the z-axis. Moving along the \( x = 0.5 \) line, the principal eigenvector \( n_1 \) remains along the y-axis in the middle of the diffuse interface while \( d_1 \) and \( d_3 \) approach a collision. The degeneracy allows \( n_1 \) to choose any direction coming out of the degeneracy moving north, which is taken as the x-axis to match the interior. If one takes vertical slices to the right or left of \( x = 0.5 \), the same scenario unfolds except with a slight tilt in \( n_1 \).

### 4.4 Weakly sheared LCP droplets: robustness of the global LCP droplet defect morphology

We next examine how a weak, imposed linear shear (moving the top boundary from left to right, and the bottom boundary from...
right to left, at equal speeds) perturbs the two equilibrium droplet defect structures discussed above. We restrict these studies to moderate shear where the drops deform but do not rupture and it is reasonable to suppress flow generation. Fig. 7–9 (respectively Fig. 10–12) reveal the effects of a weak shear applied to the equilibrium LCP droplet with tangential (respectively normal) anchoring described in Fig. 1–3 (respectively Fig. 4–6). The droplet shapes are tilted and elongated, and the oblate polar domains have rotated yet remain in similar relative positions with respect to the diffuse interface and droplet interior. The quantitative defect metrics in Fig. 7c–f and 10c–f show that the defect domains are sheared, with asymmetry of $d_i$ in the cross-sections and an asymmetry in the oblate and isotropic metric surfaces. Fig. 8 and 11 shows the topological degree and position of $+1/2$ and $-1/2$ defects are robust. Fig. 9 and 12 likewise show the ellipsoid morphology surrounding the oblate cores are a sheared version of the equilibrium structures.

**Fig. 11** A moderately sheared LCP droplet favoring normal interfacial anchoring. (a) The blow up of the director field around defect core with color map of the oblate defect core metric $d_1$–$d_2$. (b) The blow up of the director field around defect core with color map of phase field $\phi$.

**Fig. 12** Equilibrium droplet morphology with normal anchoring. (A) The 3d ellipsoids of $d_1$, $d_2$, $d_3$ around defect core, with color map of $\frac{d_1}{\phi}$–$\frac{d_2}{\phi}$ through three different view perspective. (B) The 3d ellipsoids of $d_1$, $d_2$, $d_3$ around defect core, with color map of $d_1$–$d_2$ through three different view perspective.
4.5 Radial orientational symmetry of initial data: a bi-stable steady 2D droplet equilibrium with normal anchoring

In Fig. 13, we close with a simulation that recovers the 2D analog of a hedgehog defect and confirms that the defect core at the droplet interior is a highly localized isotropic core. Recall in Fig. 4–6 we imposed normal anchoring and homogeneous nematic equilibrium initial data. The model converges to the steady state conveyed in the figures. It is reasonable to ask whether this steady structure is unique, independent of initial data. Clearly, the most natural structure self-consistent with normal anchoring of an LCP circular 2D droplet is a radial orientational structure. We therefore impose radial initial data, and the model converges to the structure shown in Fig. 13. This result recovers the radial 2D structure from previous continuum diffuse-interface modeling, and furthermore resolves the isotropic defect core in the center of the droplet. This result shows the energy-based diffuse interface theory is capable of convergence to multiple energy minima if the initial data is sufficiently close (i.e., in the domain of attraction). We have not done so, but it would be possible to calculate the energy of each of these bi-stable equilibria to determine which is lower energy.

5 Concluding remarks

We have developed a hydrodynamic diffuse interface kinetic theory for immiscible liquid crystalline polymer droplets in viscous fluids. The physics we have focused on for this initial study includes steric interactions in the LCP phase, interfacial orientational anchoring, interfacial conformational entropy and a de-mixing free energy to maintain immiscibility of the fluids. Frank elasticity is considered weak as hypothesized by Abbott et al., for micron or sub-micron droplets, and instead we instantiate a global communication between interfacial and interior LCP orientational distributions by translational diffusion. These physical balances select global defect structures for each anchoring condition which are perturbed yet preserved by moderate shear. A high order spectral method is developed to solve the governing system of partial differential equations for low moments of the normalized number density NNDF of LCP molecules in two space dimensions. We apply the code for equilibrium drops and their perturbation under imposed shear for this paper. The zeroth moment yields the LCP volume fraction whose level sets resolve the LCP droplet domain, viscous phase and the diffuse interface layer. The second moment yields the orientation tensor weighted by the LCP volume fraction. The data for these moments reveal LCP droplet shapes and global defect structure for interfacial anchoring energies that favor tangential versus homeotropic orientation.

As expected, the 2D equilibrium drop shapes are circular, and then elongated and tilted in shear. The novel predictions of the model and simulations pertain to the resolution of the cores of half-integer defects, their positions relative to the diffuse interface and droplet interior, and the order-disorder phase transitions that arise in the core domains. Level sets of the zeroth moment \( \phi \) of the nano-rod number density function (NNDF) label the diffuse interface “annulus” separating the LCP and

![Fig. 13](image-url) Another equilibrium droplet morphology with normal anchoring. (A) \( d_1 - d_3 \); (B) The 3d ellipsoids \((d_1, d_2, d_3)\), with color map of \(d_1-d_2\); (C) blow up of (B); (D) the isotropic defect in the center; (E) The director field with contour line of \(\phi = \frac{1}{2}\); (F) Principal values \(d_i\) along a horizontal slice \(y = 0.5\) through central isotropic defect (where \(d_2 = d_3\), thus only one curve is visible).
viscous phases. The second moment tensor $M$ of the NNDF provides a suite of defect core metrics, topological degree metrics, and a 3D graphical realization of the orientational morphology. From uniform nematic initial data, the droplet morphology converges to a bipolar structure which differs in significant ways for tangential and normal anchoring. Generally speaking, tangential anchoring selects bipolar surface defects called boojums which are degree $+1/2$ defects on an oblate phase sharing the diffuse interface. We find that the boojums also have a nearby degree $-1/2$ topological defect sharing the same oblate core domain. Thus, our model predicts that the local topological degree is neutral and therefore the global degree is neutral. This topology agrees with recent data from the Abbott lab,$^{12,73}$ but to our knowledge the defect core structure is an open question. For normal anchoring, the polar oblate cores split into two oblate domains, one inside the droplet and one closer to the viscous boundary, with a nematic order in the middle of the diffuse interface that separates the oblate defect cores. Furthermore, each of the nearby cores has a half-integer topological defect associated with it. Once again, the local and global topological degree is neutral. These topological features likewise agree with the Abbott lab results,$^{12,73}$ while the defect core structure remains an open question. These core features and topological degree conservation are new information beyond that afforded by the continuum director theory predictions which also employ diffuse interface methods. We further show that these equilibrium global droplet morphologies are perturbed by an imposed simple shear, but the basic features are preserved.

These benchmarks lay the foundation for future studies with fully coupled hydrodynamics and droplet rupture in shear or extensional free surface flows in two and three space dimensions. We also seek to determine the geometric conditions (e.g., droplet diameter) or other physics which would favor the traditional Oseen–Frank versus Abbott et al. mechanism for satisfying hard anchoring conditions at LCP-fluid interfaces.

6 Appendix

For a spheroid with semiaxes $(a, b, c)$ and aspect ratio $r = b/c$, the excluded volume is approximated by a leading order Legendre polynomial approximation:

$$B(m, m') = A - \frac{3N}{2\phi} M_{mm},$$

where the parameters are defined by

$$A = \left[2 + B_0 + B_1/2\right], N = B_1, 2v = \frac{8\pi}{3} bc^2$$

$$B_0 = 2\pi bc^2 \left[1 + \frac{r}{\sqrt{r^2 - 1}} \arcsin \left(\frac{\sqrt{r^2 - 1}}{r}\right)\right]$$

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