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Rheological phase diagrams for nonhomogeneous flows of rodlike liquid crystalline polymers

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ABSTRACT

The rheological phase diagrams for solutions of rigid rod molecules are computed for planar Couette and Poiseuille flow as a function of Deborah number, initial orientation, and wall separation; this analysis extends the seminal work of Larson and Öttinger [R.G. Larson, H.C. Öttinger, Effect of molecular elasticity on out-of-plane orientations in shearing flows of liquid-crystalline polymers, Macromolecules 24 (1991) 6270–6282] to nonhomogeneous flows. The Doi diffusion equation is solved by using a finite-element discretization of the rod distribution function and Onsager interaction potential. Simulations of planar Couette flow show the familiar logrolling–tumbling–wagging–flow-aligning cascade as Deborah number increases, and the critical Deborah numbers associated with transitions between states vary with wall separation. Defects are caused solely by wall interactions rather than artificial anchoring conditions. Simulations of planar Poiseuille flow show that the system tends toward either logrolling states or composite flow-aligning/logrolling attractors depending on the Deborah number, wall separation, and initial orientation.

1. Introduction

Rodlike liquid crystalline polymers (LCPs) have been the subject of many experimental and theoretical studies in recent decades because of their physically interesting phase behavior and rheology and also because of the industrially useful properties of LCP-based products. One of the most complex and challenging aspects of LCP research is the coupled evolution of structure and stress during flow, and a variety of theoretical models have been developed with this problem in mind. These models include continuum expressions such as the Leslie Ericksen (LE) theory [2–6], micromechanical kinetic theories such as the Doi diffusion equation [7,8], and tensor-based phenomenological expressions for structure evolution with empirical parameters.

In the LE theory, the system is locally described by a nematic director, which gives the average rod orientation at a given point in space; stresses in the fluid are related to Frank elasticity, as measured by gradients in the director. A number of studies have used the LE theory to model structure coarsening, banded textures, and roll cells [10]. However, the LE theory is only valid in the limit of weak shear flow, and the director-based formalism prevents the theory from describing the fine-scale gradients in density or structure that are prevalent in polydomain LCP systems. Additionally, the LE theory requires the use of a number of empirical parameters.

The original Doi diffusion equation [7] for the rod orientation distribution function f is based on a kinetic theory description of spatially homogeneous flows of rods interacting through the Onsager excluded-volume potential. This homogeneous formulation has been used to compute the rheological behavior of rigid rod solutions in simple flows. Semenov [11] and later Doi and Kuzuu [12] predicted that rods in homogeneous shear flow would undergo continuous tumbling; Doi and Kuzuu also showed that the cessation of tumbling is associated with the unusual negative first normal stress differences frequently observed in experimental LCP systems. Marrucci and Maffettone simulated the Doi diffusion equation in planar shear flow in a two-dimensional geometry (constrained to a single dimension in orientation space), and they demonstrated that tumbling is suppressed at high shear rates and gives rise to wagging and flow-aligning states [13,14]. Larson and Öttinger [1,15] generalized these results by expanding the Doi diffusion equation in spherical harmonic functions and by computing a sequence of states – logrolling, kayaking, tumbling, wagging, flow-aligning – that occur sequentially as a function of shear rate and initial director orientation relative to the shear plane. They mapped these states onto rheological phase diagrams for given values of the dimensionless rod concentration.

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The most natural extension of Larson and Öttinger's results is the characterization of nonhomogeneous states, where orientation and rod density vary in space either because of wall–rod interactions or because of spatially varying shear rate. However, until recently, the nonhomogeneous formulation of the Doi diffusion equation [16] was used only in its linearized form for linear stability analysis of spinodal decomposition [17–19], because the equation is numerically unwieldy. The nonhomogeneous theory presents two major numerical challenges. First, the evolution of f in both physical and orientation space is difficult, because of the large number of unknowns; second, the computation of gradients in the exact "long range" contribution to the excluded-volume potential is numerically intensive. (Note that the term "long range contributions" is something of a misnomer. These terms capture the same physical forces as those in the local potential and describe the influence of gradients in structure.)

A number of studies have attempted to circumvent both of these challenges by neglecting translational diffusion and by averaging the diffusion equation over orientation space to give an evolution equation for the structure tensor $\mathbf{S}$. This latter simplification requires the use of closure approximations and the replacement of the exact Onsager potential with tensor-based approximations such as the Maier-Saupe [20] or the Marrucci–Greco potentials [21–23]. The Maier-Saupe potential can be classified as a purely "local" nematic potential, whereas the Marrucci–Greco potential contains phenomenological elastic terms similar to the first "non-local" contribution to the Taylor series expansion of the original Onsager potential. These tensor-based simplifications of the Doi theory [24–27] are mathematically similar to the broad class of phenomenological, tensor-based theories of LC dynamics [28–30], because both types of theories incorporate the same physical forces in the texture evolution equations. Both sets of theories also suffer the same drawbacks: (1) they require the assumption of constant-density, even in defects and interfaces; (2) they require closure approximations, which can be extremely imprecise; (3) they require artificial anchoring boundary conditions and (4) they lack the ability to resolve interfaces and defects on the length scale of an individual rod. This is the case because the approximate potentials are constructed as Taylor expansions of the original Onsager excluded-volume potential and lose accuracy in the presence of sharp gradients in the distribution function. Although tensor-based models have been used extensively in the study of nonhomogeneous LCP flows, they cannot accurately capture the true behavior of rigid rods in defect-laden systems because of the simplifying assumptions inherent in the models.

Due to advances in computational power and numerical methods, several recent studies have attempted to solve the nonhomogeneous Doi diffusion in simple geometries. Zhou et al. [31,32] used a numerical scheme that coupled a finite difference discretization in physical space with spherical harmonics in orientation space in order to simulate the Doi diffusion equation with Marrucci–Greco elasticity in planar Couette flow. Yu and Zhang [33] followed this work by simulating the full nonhomogeneous Doi diffusion equation with the Onsager potential; their simulations invoked the simplifying constraint that rod orientations be restricted to the plane of shear with no logrolling or kayaking states allowed. This constraint is similar to the planar constraint invoked by Marrucci and Maffettone and effectively reduces orientation space to a single dimension θ. Other simplifications included further approximations to the Onsager intermolecular potential and the use of nematic anchoring conditions at the walls. They also simulated a very weak coupling between flow and texture evolution by assuming that the rod concentration was so dilute that any deviations from Newtonian flow were small.

Their results for simple wall-driven shear flow show an extension of the tumbling–wagging–flow-aligning cascade seen in the homogeneous system. These states include: (a) *the in-plane elastic-driven steady-state* (IE) at low shear rates where no time-periodic behavior is present, (b) *the tumbling state* (IT) where tumbling occurs in the bulk of the system bounded by flow-aligned boundary layers with time-periodic defects separating the boundary layers from the bulk, (c) *the in-plane wagging state* (IW) where wagging occurs in the bulk of the system with two flow-aligned boundary layers at the walls, and (d) *the viscous-driven steady-state* (IV, flow-aligning). They also predicted three new flow modes: (e) *the tumbling–wagging composite region* (TW) which acts as a transition between the IT and IW mode, (f) *the tumbling state with inside defects* (ITD) where inner defects arise in the midst of tumbling at high values of the wall separation b, and (g) *the tumbling–wagging composite region with inside defects* (TWD) where inner defects appear in the midst of the TW mode at high values of b. (Note that Tsuji and Rey also report four twisting out-of-plane states in their qualitative rheological phase diagram based on a phenomenological tensor-based theory, but the complex structures found in these states are chiefly caused by the wall anchoring conditions [29].) Yu and Zhang present a rheological phase diagram (their Fig. 3) for planar Couette flow that shows the regions of stability for the various states as a function of wall separation and Deborah number. However, this phase diagram is only qualitative and has no numerical delineation of the boundaries between the various states.

Also, quasi-periodic flows with complex defect patterns were predicted by Yu and Zhang for pressure-driven flows when the effects of viscosity and molecular interactions were comparable. No phase diagram for pressure-driven flow was given.

In a previous letter, we described a finite-element-based numerical method for evolving the nonhomogeneous Doi diffusion equation in a single spatial dimension and full orientation space [34]. The method was applied to planar Couette flow and planar Poiseuille flow with strong coupling between the flow and texture evolution. These simulation results showed that nematic anchoring conditions at walls can suppress the out-of-plane instabilities that arise during tumbling at low shear rates. We also characterized the periodic defects that occur in tumbling as low-density, low-order parameter regions of finite size; this stands in contrast to previous descriptions of defects as singularities or constant-density, abnormal nematic states [28]. We also demonstrated the existence of a composite flow-aligning/logrolling state caused by the spatially varying shear rate in pressure-driven flow, with flow-aligning regions near the wall (where the shear rate is high) and a logrolling region in the channel center (where the shear rate is low). These results sharply differed from those of Yu and Zhang because of the unrestricted orientation space, the lack of nematic anchoring conditions, and the high polymeric viscosity and subsequent coupling between flow and texture.

In the present work, we generalize the numerical results of the previous paper and show quantitative rheological phase diagrams for concentrated LCP solutions in both planar Couette flow and planar Poiseuille flow with no nematic anchoring at channel walls. These diagrams represent the first quantitative extension of Larson and Öttinger's phase diagrams for homogeneous flows to phase diagrams for nonhomogeneous flows with the full Doi diffusion equation and Onsager potential.

2. Formulation

A solution of rigid rodlike molecules of diameter d and length L is described by the distribution function $f(\mathbf{r}, \mathbf{u}, t)$, which gives the probability that a rod will have a center-of-mass location $\mathbf{r}$ and orientation $\mathbf{u}$ at time t. Integrating f over all orientations $\mathbf{u}$ gives