Spatial coherence, rheological chaotic dynamics, and hydrodynamic feedback of nematic polymers in plate-driven shear

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July 28, 2005
Abstract

Rheochaos arising from bulk orientational dynamics of nematic (liquid crystalline) polymers in simple shear is well established [1-4]. Here we address the persistence of chaotic phenomena in the presence of spatial gradient morphology in the rigid rod ensemble and flow field. We simulate the Doi-Hess kinetic theory with a Marrucci-Greco distortional elasticity potential, and hydrodynamic feedback [5]. Opposing parallel plate speeds are chosen to resonate bulk rheochaos, and elasticity constants are selected so that the nematic suspension cannot store plate-generated stresses, staging an unsteady experiment. We are motivated by spatio-temporal chaos [6] with a second-moment tensor (5 component) nematic liquid model with imposed simple shear, extended here to 65 component resolution of the orientational distribution with flow coupling. We find a spatially coherent, temporally chaotic attractor with: an interior layer with chaotic orientational dynamics and velocity fluctuations at each gap height; layers buffering the plates with regular kayaking orbits at each location; spatial coherence and laminar structure at every timestep in all features (flow, orientational distribution, and stresses).
Chaotic behavior of sheared nematic polymers has been reported in various laboratory experiments (cf. [7, 8, 9, 10]). Historically, the rapid emergence of turbidity from pristine samples in shear experiments was posited as "director turbulence" [11]. Chaotic dynamics of bulk sheared mesophases has been established through careful numerical simulations and bifurcation software in both kinetic [3, 4, 12, 13] and mesoscopic models [1, 2, 14]. Using the kinetic theory of Doi [15, 16] and Hess [17], for thin rods or platelets in planar linear flows, the authors [19, 20, 18, 4] have established a certain robustness of chaotic monodomain responses: to variations in shear rate, to extensional flow perturbations, and to finite aspect ratio of the nematogens. This implies that moderate spatial gradients in local shear rate due to flow feedback are not sufficient by themself to arrest chaotic monodomain dynamics. Our goal here is to study the persistence of chaotic orientational dynamics during structure formation, allowing for wall anchoring conditions, an anisotropic distortional elasticity potential specialized to rigid rod polymers, and hydrodynamic feedback. In particular, we are interested in how chaotic longwave dynamics injects energy from plate motion into morphology of the molecular orientational distribution, stored stresses, and flow field. We explore whether spatial degrees of freedom are sufficient to saturate longwave irregular dynamics, whether spatial features are coherent or chaotic (broad banded), and the extent of shear banding (motivated by theoretical and experimental work on sheared wormlike micellar solutions [21, 24, 23, 22, 25]).

We consider nematic (rigid rod) suspensions between two plates which move at the same speed in opposite directions. Let $f(m, x, t)$ be the orientational probability distribution function (PDF) for rod-like, rigid, high-aspect-ratio spheroidal molecules with axis of symmetry $m$ on the unit sphere. The Smoluchowski equation with flow field $v$ is written in the internal timescale of the pure nematic liquid, $t = \tilde{t} D_r$, where $\tilde{t}$ is the laboratory time, and $D_r$ is the average rotational diffusivity of the nematic liquid:

$$\frac{Df}{Dt} = \mathcal{R} \cdot [(Rf + \frac{3N}{2} fRV)] - \mathcal{R} \cdot [m \times mf],$$

$$\dot{m} = \Omega \cdot m + a[D \cdot m - D : mmm],$$

where $D/Dt$ is the material derivative $\partial/\partial t + v \cdot \nabla$, $\mathcal{R}$ is the rotational gradient operator:

$$\mathcal{R} = m \times \frac{\partial}{\partial m},$$

$D$ and $\Omega$ are the dimensionless rate of strain and vorticity tensors, $N$ is a dimensionless volume fraction of spheroids, and $a = \frac{r^2 - 1}{r^2 + 1}$, where $r$ is the aspect ratio of the spheroids. The Doi-Marrucci-Greco potential is

$$V = -[(I + \frac{1}{3D_r} \Delta)M : mm + \frac{\theta}{3D_r}(mm : (\nabla \nabla \cdot m))].$$
where \( \theta > 0 \) for rods, with bend constant greater than equal splay, twist constants; the Ericksen number \( Er \) measures short range nematic potential strength relative to long range distortional elasticity strength, and \( M \) is the second moment tensor of \( f \),

\[
M = M(f) = \int_{||m||=1} m^m f(m, x, t) \, dm. \tag{4}
\]

\( M \) is the traditional descriptive variable from which mesoscopic features of the orientational distribution are defined and connected to laboratory measurements. The eigenvectors \( n_i, i = 1, 2, 3 \) of \( M \) are the nematic directors, with corresponding ordered eigenvalues \( 0 \leq d_3 \leq d_2 \leq d_1 \leq 1, d_1 + d_2 + d_3 = 1 \). The differences \( s = d_1 - d_2 \) and \( \beta = d_2 - d_3 \) are called the Flory and biaxiality order parameters, respectively, indicating relative degrees of orientation along the director axes. The peak orientation director, \( n_1 \), is called the major director.

The Deborah number \( De = v_0 \frac{h}{D_r} \) is the gap shear rate normalized by the molecular relaxation rate \( D_r \), \( \pm v_0 \) are the plate speeds, and \( 2h \) is the gap width.

The dimensionless forms of the balance of linear momentum, stress constitutive equation, and continuity equation are

\[
\frac{dv}{dt} = \nabla \cdot (-pI + \tau), \tag{5}
\]

\[
\tau = (2/Re + \mu_3(a))D + [\mu_1(a)(D \cdot M + M \cdot D) + \mu_2(a)D : M_4] + a\alpha(\mathbf{M} - \frac{1}{3}I - N \mathbf{M} \cdot \mathbf{M} + N \mathbf{M} : \mathbf{M}_4)
- \frac{a}{6Er}(\Delta \mathbf{M} \cdot \mathbf{M} + \mathbf{M} \cdot \Delta \mathbf{M} - 2 \Delta \mathbf{M} : \mathbf{M}_4)
- \frac{a}{12Er}[2(\Delta \mathbf{M} \cdot \mathbf{M} - \mathbf{M} \cdot \Delta \mathbf{M}) + \mathbf{M}_c]
- \frac{a\theta}{12Er}[\mathbf{M} \cdot \mathbf{M}_d + \mathbf{M}_d \cdot \mathbf{M} - 4(\nabla \nabla \cdot \mathbf{M}) : \mathbf{M}_4]
- \frac{a\theta}{12Er}[\mathbf{M}_d \cdot \mathbf{M} - \mathbf{M} \cdot \mathbf{M}_d - \mathbf{M}_e], \tag{6}
\]

\[
\nabla \cdot \mathbf{v} = 0, \tag{7}
\]

where

\[
M_c = (\nabla \mathbf{M} : \nabla \mathbf{M} - (\nabla \nabla \mathbf{M}) : \mathbf{M}), \tag{8}
\]

\[
M_d = \nabla \nabla \cdot \mathbf{M} + (\nabla \nabla \cdot \mathbf{M})^T, \tag{9}
\]

\[
M_e = (\nabla \nabla \cdot \mathbf{M}) \cdot \mathbf{M} - M_{j\alpha} M_{ij,j}, \tag{10}
\]

\[
M_4 = \int_{||m||=1} m^m m^m m^m f(m, x, t) \, dm. \tag{11}
\]

Following simulations in [5, 26], we select \( Re = \infty, \mu_1 = 0.0004, \mu_2 = 0.15, \mu_3 = 0.01, \alpha = 0.5, \theta = 2 \), corresponding to nominal values of a rod-like nematic polymer dispersion.
From our studies of chaotic monodomain dynamics [18], we select $N$ and $De$ to resonate chaotic orientational response to pure shear: $N = 5.2$, which corresponds to a 1% volume fraction of rod-like nematogens of diameter 2 nm and length 200 nm, for which the geometry parameter $a \approx 1$; and $De = 4.04$, which lies inside the chaotic range, $2.69 < De < 4.10$ [4]. Next we pick the strength of the distortional elasticity potential by fixing $Er = 500$. For sufficiently low $Er$, the material is highly elastic and can store all stresses generated by the plate motion, leading to a steady state structure [27, 28]. At some critical $Er$, the nematic liquid cannot store the plate-generated stresses and a transition to dynamic structure evolution arises [30, 29, 26].

We label the flow direction the $x$-axis, flow-gradient direction the $y$-axis, and $z$ the vorticity axis. The polar angle $\theta$ is the angle between the major director $n_1$ and the vorticity axis, and the azimuthal angle $\phi$ is the angle between the $x$-axis and the projection of the major director on the $xy$-plane. Thus, $n_1 = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. At the plates, the liquid is in the uniaxial nematic phase ($s = 0.75, \beta = 0$) for $N = 5.2$, and rotational invariance of the PDF is broken by the anchoring condition on $n_1$: $\theta = \phi = 60^\circ$.

We begin with temporal statistics in flow-orientation-stress variables at four fixed gap heights, $y = 0.9, 0.6, 0.3, 0.0$, where $y = 1$ is the top plate, and $y = 0$ is the mid-gap. Figures 1-3 represent post-processed data from fully resolved space-time simulations, with simultaneous dynamics over dimensionless time 1400 through 2500. Figure 1 depicts the orbit of the major director $n_1(M(f))$ on the unit sphere (left column) and the order parameter $s$ (right column). At interior locations $y = 0.6, 0.3, 0.0$, one finds chaotic orbits typical of sheared monodomains [1, 2, 3, 4, 14, 31]: the major director exhibits a random jump between a kayaking limit cycle ($K_1$) where $n_1$ oscillates around the vorticity axis, and a symmetric pair of tilted kayaking orbits ($K^\pm_2$) where $n_1$ oscillates around an axis tilted between the vorticity axis and shearing ($x$-$y$) plane. Near the plates, e.g. $y = 0.9$, the orbits regularize to a tight $K_2$ limit cycle, with axis of symmetry close to the flow direction. There is a thin boundary layer, inside of which the PDF sharply transitions to the plate anchoring condition. The order parameter $s$, Figure 1, exhibits slight fluctuations about .67 at $y = 0.9$, indicating 10% defocusing from the plate condition, then random time series with large deviations about even lower mean values within the chaotic layer. We call attention to intermittent strong defocusing events in the chaotic layer, where $s$ spikes toward 0, indicating local defect events which are spatially uncorrelated on this sampling scale.

Figure 2 shows irregular velocity (left) and velocity-gradient (right) time series at each fixed gap height, except the symmetry-constrained zero velocity at the mid-gap. There is strong flow feedback, and thereby strong momentum and energy transfer between the solvent and rod ensemble. Note the local Deborah number, $De^{loc} = \partial v_x / \partial y$, exhibits irregular time
Figure 1: Orbit of the major director (left column) and time series of the Flory order parameter $s = d_1 - d_2$ (right column), at 4 fixed height locations, $y = 0.9, 0.6, 0.3, 0.0$. ($y = 0$ is the mid-gap, $y = 1$ is the top plate.) On the sphere, the center dot is the vorticity axis, the right dot is the flow direction, and the large dot is the plate anchoring condition. Time runs between $t = 1400$ and 2500.
Figure 2: Time series of the normalized primary velocity $v_x$ (left) and local shear rate $\partial v_x / \partial y$ (right) at the same 4 heights and time interval of Figure 1.
series at each gap height, with amplitude fluctuations that grow with distance from the plates. Further evidence appears in Figure 3, showing time series of the first normal stress difference \( N_1 = \tau_{xx} - \tau_{yy} \) (left) and shear stress \( \tau_{xy} \) (right) at the same gap heights. Such erratic stress fluctuations are called rheological chaos; these simulations thus confirm results in [6] on the persistence of chaotic time series coupled with structure in confined plate gap simulations. Furthermore, these simulations generalize [6] in two significant directions: from a second-moment orientation tensor (5 components) to 65 component resolution of the PDF; and from imposed simple shear flow to full hydrodynamic coupling. Rheological and orientational chaos persists, along with irregular hydrodynamic fluctuations, in the interior of the cell. We turn now to spatial structure features across the plate gap, where the two models yield contrasting phenomena.

Figure 4 shows spatial morphology between the plates, for four fixed snapshots, in flow (top row), PDF (middle row), and stress (bottom row) features. The primary flow is a weakly nonlinear shear structure across the gap, with mild dynamic fluctuations. The most vivid non-Newtonian flow feedback is captured by the local Deborah number, \( \text{De}_{\text{loc}} \), in the top right panel. We recall from [4,17] that the local \( De \), if \( \partial f / \partial y = 0 \) and if \( \partial^2 v_x / \partial y^2 = 0 \), will produce a spectrum of unique, bi-stable and tri-stable monodomain responses, including chaotic attractors for \( 2.69 \leq De \leq 4.10 \), traditional kayaking (\( K_1 \)) orbits for \( 0 \leq De \leq 3.99 \) and tilted pairs of kayaking (\( K_{\pm}^2 \)) orbits for \( 2.53 \leq De \leq 2.69 \) and \( 4.10 \leq De \leq 4.65 \) (the role of spatial correlations in biasing the likelihood statistics of multiple monodomain attractors [32] is evident, yet this issue has not been explored in any systematic way).

Near each plate, for \( \mid y \mid \) between .8 and 1, there is a robust gradient layer with small dynamic fluctuations, even though \( \text{De}_{\text{loc}} \) is inside the chaotic range for sheared monodomains (fluctuating between 2.8 and 3.8, Figure 2, top right). This highlights the influence of confined wall anchoring to penetrate well into the shear gap and arrest dynamic tumbling and kayaking dynamics, confirmed by the \( y = 0.9 \) (near wall) director time series of Figure 1. Proceeding further into the shear gap, for \( \mid y \mid \) between .4 and .8, \( \text{De}_{\text{loc}} \) fluctuates in space and time between 3 and 5.5 (Figure 2, Row 2, Column 2), then above 4 in the Figure 4 snapshots. These values often lie outside the monodomain chaotic \( De \) range, so irregular dynamic fluctuations in \( \text{De}_{\text{loc}} \) appear to be responsible for the chaotic PDF time series at \( y = 0.6 \), Figure 1. Next, in the large interior gap layer for \( \mid y \mid \) between 0 and .4, \( \text{De}_{\text{loc}} \) experiences enormous amplitude fluctuations between qualitatively distinct laminar spatial profiles, with values ranging mostly within the chaotic monodomain range. This is indicative of a strong chaotic interior shear layer, but with spatial coherence at each fixed time.

These spatio-temporal features of \( \text{De}_{\text{loc}} \) are remarkably correlated with those of the PDF (Figure 4, Row 2) and stored stresses (Figure 4, Row 3). Namely, boundary wall layers
Figure 3: Time series of the first normal stress difference $N_1$ (left column) and shear stress $\tau_{xy}$ (right column) at the same gap heights and time interval of Figures 1, 2.
Figure 4: Primary velocity spatial profile $v_x$ (top left), $\partial v_x/\partial y$ (top right), $s$ (middle left), $\theta$ (middle right), $N_1$ (bottom left), and $\tau_{xy}$ (bottom right) across the plate gap ($-1 \leq y \leq 1$), at 4 snapshots $t = 2503$(solid line), 2506(dashed line), 2510(dot-dashed line), 2522(dotted line).
evince robust spatial profiles which fluctuate very little; a large interior gap layer with strong
temporal fluctuations between qualitatively different spatial structures; and a transition
layer between $|y| = .4$ and $.8$ with intermediate dynamic fluctuations among similar laminar
structures. The order parameter $s$ indicates intermittent defect generation, with twin defect
cores that form coincident with the strong local minima and strong gradients in $D_{\text{loc}}$. The
snapshots suggest the defect cores spawn, intensify, propagate, weaken and then melt during
this 20 time unit span. The polar angle exhibits strong spatio-temporal correlation between
transitions of the PDF peak direction in and out of the shear plane, defect events, and
structure in $D_{\text{loc}}$. The first normal stress difference, $N_1$, also appears highly correlated with
the above features. The shear stress $\tau_{xy}$ exhibits intriguing shear thinning and thickening
events.

Figure 5 provides spatio-temporal profiles of orientational, flow, and stress features across
the gap between times 2500 and 2575. Together, all simulations indicate intermittency asso-
ciated with spatially coherent, temporally chaotic phenomena. Thus, nematic polymer sus-
pensions driven by planar shear cells exhibit persistent orientational and rheological chaos
in a large interior cell layer, even with spatial heterogeneity due to plate anchoring condi-
tions and non-Newtonian hydrodynamic feedback. The spatial morphology in this flow-PDF
attractor is laminar, in contrast with spatio-temporal chaos in mesoscopic, imposed shear
simulations [6], at a presumptive higher Ericksen number regime or with much larger plate
separation relative to the persistence length of distortional elasticity. The transition between
these disparate spatio-temporal attractors poses an important gap to fill.

Effort sponsored by AFOSR grants F49620-02-1-0086, 03-1-0098, NSF grants DMS-
0204243, DMS-0308019, NASA URETI BIMat award No. NCC-1-02037, and the Army
Research Office.

References
3187 (2001).
Figure 5: Spatio-temporal features of orientational ($s$ top left, $\theta$ top right), flow ($v_x$ middle left, $\partial v_x/\partial y$ middle right), and stress ($N_1$ bottom left, $\tau_{xy}$ bottom right) variables versus $y$ between -1 and 1 and $t$ between 2500 and 2575.


