The influence of boundaries on shear banding in complex fluids

JM Adams\textsuperscript{1}, PD Olmsted\textsuperscript{2}, and SM Fielding\textsuperscript{3}

\textsuperscript{1}\textit{U Surrey (Physics)}, \textsuperscript{2}\textit{U Leeds (Physics & Astronomy)}, \textsuperscript{3}\textit{U Durham (Physics)}

1. Introduction and Background

2. Stress Selection

3. Instability and RheoChaos

4. Effect of Boundary Conditions

5. Summary
In the hatched area close to the non-equilibrium critical point, shear-banding along the gradient direction is observed. The shear bands are about 10 to 20 mm in height.

Wormlike Micelles

- Aligned, unaligned phases.
- Stress plateau, “phase separation”
- Near and far from nematic phases.
Wormlike Micelles

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- **Cates/Spenley/McLeish 1993** – Reptation/reaction + solvent viscosity. **Integral equation.**

- **Diffusive Johnson-Segalman model** [OR, PDO, CYDL *J Rheology* **44** (2000) 257]

\[
\nabla \cdot T = 0, \quad T = -pI + 2\eta D + \Sigma \\
(\partial_t + v \cdot \nabla) \Sigma - (\Omega \Sigma - \Sigma \Omega) - a(D\Sigma + \Sigma D) = D\nabla^2 \Sigma + 2\mu\tau D - \frac{1}{\tau} \Sigma
\]
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- **Two fluid models** based on JS-like advection \(a\) (Gordon-Schowalter derivative) [SMF & PDO Phys Rev E (2003); LP Cooke *et al.*, JNNFM 2005 & 2006.]
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**Rolie-Poly model;** Doi-Edwards theory for entangled polymers with convected constraint release (tune between monotonic and non-monotonic) [Likhtman & Graham *JNNFM* 2003; Adams & PDO *PRL* 2009].
Other systems?

**Colloidal suspensions**

**Onion surfactant phases**
Colloidal suspensions

Rod-like virus suspensions

Onion surfactant phases

Shear-thickening worms
Other systems?

Colloidal suspensions

Rod-like virus suspensions

Block Copolymer Micelles

Onion surfactant phases

Shear-thickening worms
Polybutadiene: 7.5 – 10% $10^6$ g/mol (entangled) + $10^3$ g/mol oligomer “solvent”.

- Monotonic flow curve + stress gradient? [Hu et al., J Rheology 2007; Adams and PDO, PRL 2009].
Stress selection: need gradient terms!!

![Diagram showing shear stress and strain rate relationships](image)

strain rate $\dot{\gamma}$

shear stress $\sigma$

Constitutive curve

Banded Stress

Unique D-independent stress determined by inhomogeneous terms.

$\sigma_{\text{tot}} = \sigma_p + \eta \dot{\gamma}$

$\sigma_p = -\tau - \left[ \sigma_p - \sigma_{p,\text{hom}}(\dot{\gamma}) \right] + D \nabla^2 \sigma_p$

Controls speed of interface formation and rheochaos.

$\dot{\gamma}_A, \dot{\gamma}_C$

Radulescu et al. EPL 63 (2003) 230

Fielding & PDO, PRL 92 (2004) 084502


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Unique $\mathcal{D}$-independent stress determined by inhomogeneous terms.

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\[ D_t \sigma_p = -\tau^{-1} [\sigma_p - \sigma_{p,\text{hom}}(\dot{\gamma})] + \mathcal{D} \nabla^2 \sigma_p \]
Stress selection: need gradient terms!!

- **Unique** $D$-independent stress determined by inhomogeneous terms.
  
  
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Shear Banding in curved geometries [PDO, Radulescu, Lu, J Rheology 2000].

\[ \nabla \cdot \mathbf{T} = 0 \Rightarrow T_{r\theta} \sim \frac{1}{r^2} \]

Diagram: Interface position

\[ \sigma = \sigma_{sel} \]

Outer cylinder: \[ \sigma = \Gamma(1+p)^2, r=1 \]

\( \gamma \)
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Shear Banding in curved geometries [PDO, Radulescu, Lu, J Rheology 2000].

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\begin{align*}
\text{Interface position} \\
\sigma = \sigma_{sel} \\
\text{Outer cylinder:} \\
\sigma = \Gamma/(1+p), \ r=1
\end{align*}

- Sloped “plateau”

![Graph](image)
Shear Banding in curved geometries [PDO, Radulescu, Lu, J Rheology 2000].

\[ \nabla \cdot \mathbf{T} = 0 \Rightarrow T_{r\theta} \sim \frac{1}{r^2} \]

\[ \text{Sloped "plateau"} \]

\[ \text{Outer cylinder: } \sigma = \frac{\Gamma}{(1+p)^2}, \, r=1 \]

\[ \text{Interface position} \]

[Salmon et al. PRL 2003 \( \Sigma^* = 64 \) Pa]
Shear banding in different geometries....

- Cylindrical Couette flow $\sigma(r) \sim \frac{1}{r^2}$: interface should lie at position for which $\sigma = \sigma_{coex}$ [Lu/Radulescu/PDO J Rheol 2000].


Recent non-locality experiments....

- **Rhodia group** [C Masselon, JB Salmon, A Colin PRL (2008)]
  Gradient terms necessary to fit to measurements in microchannels with strong stress gradients. **Diffusion length of order microns.**

![Graphs](image)

**FIG. 1.** Velocity profiles at (a) (○) $\Delta P = 200$, (▷) 300, (b) (□) 400, (◇) 500, and (△) 600 mbar; solid lines correspond to the modelized profiles according to Eq. (2) with the same fitting parameters for all of them and a standard deviation std = 83 $\mu$m s$^{-1}$ (CPCI-Sal).
Implications of Diffusion (non-local) terms

\[ \partial_t \sigma_p = f(\sigma_p, \dot{\gamma}) + D \nabla^2 \sigma_p \]

- **Stress selection** (non-universal).
- **Controls speed of interface motion** and related dynamics (total stress, banding profile evolution, ...).
  

- **Controls evolution of:**
  - complex spatial structure (rheo-chaos), [SM Fielding & PDO, PRL 92 (2004) 084502]
  - interfacial instabilities

- Requires a boundary condition on the microstructural variable!
FIG. 2. Shear stress relaxation in CTAT 1.35% on subjecting the sample to step shear rates of (a) 22.5 s\(^{-1}\), (b) 75 s\(^{-1}\), (c) 100 s\(^{-1}\), (d) 138 s\(^{-1}\), (e) 175 s\(^{-1}\) at 25°C. (f) shows the oscillations in the stress relaxation are found to decrease in amplitude and disappear completely at a temperature 

Consistent with deterministic (not stochastic) fluctuations?
Instabilities....

Exploding bands??!

[Decruppe/Lerouge/Berret PRL 2001]
Spatio-temporal structure

- **NMR (CTAB/NaSal)**

  [Callaghan et al. PRL 93 (2004) 268302]

- **Ultrasound (CTAB)**


  [Lerouge et al. PRL 2006]
**Calculations?**

- **Rheo-chaos** – couple banding to slow dynamical variable [Fielding & PDO PRL 2004].
- **Two dimensional instability in JS model** [Fielding PRL 2006, Wilson & Fielding 2006]
- **Taylor-Couette like instability in JS model** [Fielding PRE 2007]?

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**Figure 1:**

- **a)** Three-dimensional representation of velocity distribution over time and radial displacement across the gap.
- **b)** Two-dimensional velocity profiles at different times: 20s, 22s, 23.5s.
Boundary issues?

- Boundary conditions for structural variable (e.g. viscoelastic stress):

$$\partial_t \Sigma = \ldots + \mathcal{D} \nabla^2 \Sigma. \quad \nabla \Sigma = 0??$$
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$$\partial_t \Sigma = \ldots + D \nabla^2 \Sigma.$$  

$$\nabla \Sigma = 0??$$

Position of shear bands [Britton & Callaghan 1997]?
Boundary issues?

- Boundary conditions for structural variable (e.g. viscoelastic stress):

\[
\partial_t \Sigma = \ldots + D \nabla^2 \Sigma.
\]

\[\nabla \Sigma = 0??\]

- Position of shear bands [Britton & Callaghan 1997]?

- Correlation of wall slip with band motion? [Becu et al. PRL 2004].

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\(\delta\) (mm)

(a)

\(V_s\) (mm s\(^{-1}\))

(b)
Slip in triblock copolymer micelles

Velocity profiles & flow curves

Slip velocities
General boundary conditions

\[ \nabla \ \vec{v} \]

Prolate

Oblate

\[ \nabla \ \vec{v} \]

Homeotropic

Tangential

PDO et al. Boundaries and shear banding
General boundary conditions

\[ \mathbf{D}_T \hat{n} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = 0 \]

- **Prolate**:\[\nabla \mathbf{v}\]
- **Oblate**:\[\nabla \mathbf{v}\]
- **Homeotropic**:\[\nabla \mathbf{v}\]
- **Tangential**:\[\nabla \mathbf{v}\]

- Stress from bulk
- Anchoring potential \(W\)

**Characteristic length scales**
- **Interfacial width**: \(\ell = \sqrt{D_T \tau}\)
- **Surface anchoring length**: \(\xi = D_T \tau W\)

- Strong anchoring (Dirichlet BC): \(\Sigma = \Sigma_0\)
- Weak anchoring (Neumann BC): \(\nabla \Sigma = 0\)
General boundary conditions

\[ \mathbf{D}_T \hat{n} \cdot \nabla \Sigma + W \left( \Sigma - \Sigma_0 \right) = 0 \]

Anchoring potential \( W \)

Characteristic length scales

- Interfacial width: \( \ell = \sqrt{D_T} \)
- Surface anchoring length: \( \xi = \frac{D_T}{W} \)
General boundary conditions

\[ \mathbf{D} \tau \mathbf{\hat{n}} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = 0 \]

Anchoring potential \( W \)

Characteristics length scales

- Interfacial width \( \ell = \sqrt{D \tau} \)
- Surface anchoring length \( \xi = \frac{D \tau}{W} \)

\[ \frac{\xi}{\ell} \ll 1 \quad \text{Strong anchoring (Dirichlet BC)} \]

\[ \frac{\xi}{\ell} \gg 1 \quad \text{Weak anchoring (Neumann BC)} \]

PDO et al.  Boundaries and shear banding
Parametrize Dirichlet Boundary Condition

\[ \frac{\Sigma_0}{G} = \begin{pmatrix} \frac{2S}{3} & 0 & 0 \\ 0 & -\frac{S}{3} - b & 0 \\ 0 & 0 & -\frac{S}{3} + b \end{pmatrix} \]
Calculations

- 1D, Cylindrical Couette Geometry
  \[ q = \ln \frac{R_2}{R_1} \]

- Startup from various initial conditions, imposed average shear rate \( \langle \dot{\gamma} \rangle \).

- Models: DJS and Rolie-Poly/micelle.

- Dimensionless variables:
  \[ \hat{D} = \frac{D \tau}{R_1^2 q^2} \]
  \[ x = \frac{1}{q} \ln \left( \frac{r}{R_1} \right) \]
**Neumann BC in cylindrical Couette geometry**

- **Inverted bands** possible at low curvature
  - small \( p \equiv (R_2 - R_1)/R_1 \). destabilized at high curvature.
- **"Flatter"** plateau in flatter geometry.
  - [PDO, Radulescu, Lu, J Rheology 2000]
Hysteresis loop extends until interface “touch” the wall.
Neumann BC: hysteresis

- Hysteresis loop extends until interface “touches” the wall.

Neumann BC: hysteresis

- Hysteresis loop extends until interface “touches” the wall.
- Small D or other physics?

Unaligned BC (dJS model, \( q = 0.004, \hat{D} = 4.4 \times 10^{-5} \))

\[ \log_{10} \hat{\gamma} = \text{ramp up} \]
\[ \log_{10} \langle \hat{\gamma} \rangle = \text{ramp down} \]

... boundary conditions for which \( \Sigma_0 \) is one of these
values. For the DJS model with \( \epsilon = 0.05 \) and \( a = 0.3 \)
these values are...
Weak departure from high shear rate branch.

$\triangleright =$ ramp up

$\triangleleft =$ ramp down

$\Sigma_0$ is one of these values. For the DJS model with $\epsilon = 0.05$ and $a = 0.3$ these values are
Weak departure from high shear rate branch.
Weak departure from high shear rate branch.

Hysteresis only near low shear rate branch: “heterogeneous nucleation”?
BC flow-aligned \( (q = 0.004, \hat{D} = 4.4 \times 10^{-5}) \)
- Hysteresis near shear branch that the wall favors.
- Departs from unfavored constitutive shear branch (boundary layer).
Dirichlet BC (dJS, $q = 0.004, \dot{D} = 4.4 \times 10^{-5}$)

- Hysteresis near shear branch that the wall favors.
- Departs from unfavored constitutive shear branch (boundary layer).
- Similar in Rolie-Poly model.
Effect of Diffusion Coefficient $D$. 

\[ \begin{align*}
\log_{10}(\dot{\gamma}) &\quad \log_{10}(\dot{\gamma}) \\
-0.25 &\quad -0.15 &\quad -0.1 &\quad -0.05 &\quad 0 &\quad 0.65 &\quad 0.7 &\quad 0.75 &\quad 0.8 &\quad 0.85 &\quad 0.9 \\
\log_{10}(\dot{\gamma}) &\quad \log_{10}(\dot{\gamma}) \\
-0.24 &\quad -0.26 &\quad -0.28 &\quad -0.3 &\quad -0.32 &\quad -0.34 &\quad -0.28 &\quad -0.3 &\quad -0.32 &\quad -0.34 \\
\end{align*} \]

\( a) \ \Sigma_H \)

\( b) \ \Sigma_H \)

\( c) \ \Sigma_L \)

\( d) \ \Sigma_L \)

Homogeneous

$1.0 \times 10^{-4}$

$1.6 \times 10^{-5}$

$4.0 \times 10^{-6}$

$\theta$
Lack of hysteresis?

- 12% SDS/LAPD + 1% Salt (left) or 2.7% salt (right)

Couette Curvature vs BC: dJS Model

\[ \mathcal{D} = 10^{-3} \]

\[ \Delta R/R \]

\[ b) \quad \theta/° \quad 0.4 \quad 0.8 \quad 1.4 \quad 2.5 \quad 4.5 \quad 8.0 \quad 13.9 \quad 23.1 \quad 34.4 \]

\[ \Sigma_0 \text{ favors high shear rate} \]

\[ [Rossi, McKinley, & Cooke, JNNFM 2006] \]
Couette Curvature vs BC: dJS Model [Adams, Fielding, PDO JNNFM 2008]

\[ D = 10^{-3} \]

\[ \Sigma_0 \] favors high shear rate

[Rossi, McKinley, & Cooke, JNNFM 2006]

\[ \Sigma_0 \] favors low shear rate

[PDO et al. Boundaries and shear banding]
Larger $\mathcal{D} = 10^{-2}$ pushes interface away $q = \ln \frac{R_2}{R_1}$.

$\Sigma_0$ favors high shear rate

$\Sigma_0$ favors low shear rate
Larger $\mathcal{D} = 10^{-2}$ pushes interface away $q = \ln R_2/R_1$.

$\Sigma_0$ favors low shear rate

[Britton & Callaghan PRL 1997]
$\Sigma_0$ favors low shear rate. Anchoring length $\xi = D\tau/W$.

- $\star$ Large $\xi \sim$ Neumann.
- $\circ$ “In between”.
- $\blacktriangle$ Small $\xi \sim$ Dirichlet (anchored)
Dirichlet boundary conditions:

- Band position depends on stress gradient (Couette vs. cone & plate).
- “Heterogeneous nucleation” and asymmetric hysteresis when BC favors one phase; exploit to control switching?
- Lubricating/thickening boundary layers.
Summary

- **Dirichlet boundary conditions:**
  - Band position depends on stress gradient (Couette vs. cone & plate).
  - “Heterogeneous nucleation” and asymmetric hysteresis when BC favors one phase; **exploit to control switching?**
  - Lubricating/thickening boundary layers.

- **Mixed boundary conditions:**
  - The effective BC is a balance between anchoring length $\xi = \mathcal{D}\tau/W$ and strength of stress curvature (flow geometry).
  - “Transition” as a function of anchoring strength (weak signature in stress, weak dependence on applied shear rate).
  - In curved geometry one interface sits at selected stress.
Non-trivial slip constitutive relations [wormlike micelles]

Wall rheology ≠ bulk rheology.

<<, ▲ Smooth
□, ◇ Rough B: 100, 200μm gap
○ Rough A

\[ V_s \sim \sigma_w^{\alpha} \]
\[ \alpha = 2.6, 2.7, 3.5 \]
Non-trivial slip constitutive relations [microgel particles]

\[ V_s \sim (\sigma_w - \sigma_0)^2 \]

Elastohydrodynamic theory

[Meeker et al. PRL 2004, J Rheology 2008]
Side chain liquid crystalline polymers

[Fig. 1. Nonlinear rheology, in cone-plate geometry, at $T = 122^\circ C$, $T = 6^\circ C$.]

Shear stress vs time at different shear rates:
- $\dot{\gamma} = 12 s^{-1}$
- $\dot{\gamma} = 15 s^{-1}$
- $\dot{\gamma} = 17 s^{-1}$
- $\dot{\gamma} = 18 s^{-1}$
- $\dot{\gamma} = 19 s^{-1}$
- $\dot{\gamma} = 19.5 s^{-1}$
- $\dot{\gamma} = 20 s^{-1}$
- $\dot{\gamma} = 22 s^{-1}$

The inset shows the stationary shear stress vs shear rate.

Dependence of the inverse of the pseudoperiod.

Shear stress vs time for $\dot{\gamma}$:
- $\dot{\gamma} = 20 s^{-1}$
- $\dot{\gamma} = 22 s^{-1}$
- $\dot{\gamma} = 26 s^{-1}$
- $\dot{\gamma} = 40 s^{-1}$
- $\dot{\gamma} = 50 s^{-1}$

Evolution as a function of the applied shear rate of the two characteristic times of the period: $T_1$ and $T_2$, of the amplitude $A$ and of the maximum and minimum stress values of the oscillation. The dotted lines are guides to the eye.

Evolution vs shear rate of the stationary shear stress at various temperatures below and above the isotropic-nematic temperature:
- $T = 6^\circ C$
- $T = 1^\circ C$
- $T = 1^\circ C$
- $T = 6^\circ C$
- $T = 9^\circ C$
- $T = 14^\circ C$
- $T = 19^\circ C$.
Multiple anchoring states and stress fluctuations?
Multiple anchoring states and stress fluctuations?

Role of wall slip $v_2$ in stick-slip behaviour?

\[
\hat{n} \cdot \mathbf{T} = M(\Sigma, \ldots)\mathbf{v}_s
\]

\[
\mathcal{D}_T\hat{n} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = \Lambda \cdot \mathbf{v}_s
\]
Multiple anchoring states and stress fluctuations?

Role of wall slip $v_2$ in stick-slip behaviour?

$$\hat{n} \cdot T = M(\Sigma, \ldots)v_s$$

$$\mathcal{D}_T \hat{n} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = \Lambda \cdot v_s$$

Add independent surface transition/dynamics?
For the future....

- Multiple anchoring states and stress fluctuations?
- Role of wall slip $v_2$ in stick-slip behaviour?
  \[ \hat{n} \cdot T = M(\Sigma, \ldots) v_s \]
  \[ DT \hat{n} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = \Lambda \cdot v_s \]
- Add independent surface transition/dynamics?
- Concentration/depletion at surface...?
For the future....

- Microfluidic applications?

- Multiple anchoring states and stress fluctuations?
- Role of wall slip $v_2$ in stick-slip behaviour?

\[ \hat{n} \cdot T = M(\Sigma, \ldots)v_s \]

\[ \mathcal{D}_T \hat{n} \cdot \nabla \Sigma + W (\Sigma - \Sigma_0) = \Lambda \cdot v_s \]

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Role of wall slip $v_2$ in stick-slip behaviour?

$$\hat{n} \cdot T = M(\Sigma, \ldots) v_s$$

$$\mathcal{D}_T \hat{n} \cdot \nabla \Sigma + \mathcal{W}(\Sigma - \Sigma_0) = \Lambda \cdot v_s$$

Add independent surface transition/dynamics?

Concentration/depletion at surface...?

Microfluidic applications?

- Switch between viscosity branches ("transistor")?
Multiple anchoring states and stress fluctuations?

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- Microfluidic applications?
  - Switch between viscosity branches (“transistor”)?
  - Use intrinsic timescales of switching? [Adams & PDO, PRL 2009]
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