Outline


II. Experiments: Shear band formation kinetics in worms. Metastability / instability.

III. Theory: Initial stage of unstable banding kinetics.

[prelude: analogy with Cahn-Hilliard fluid-fluid demixing instability]

Our work: Non-local Johnson-Segalman model,

with 2-fluid coupling to concentration.

IV. Conclusions. Outlook.
Shear banding instability

- "Usual" steady shear: homogeneous

\[ \dot{\gamma} = \partial_y \nu \]

\[ \Sigma = \Sigma(\dot{\gamma}) \]

- But if underlying flow curve \( \Sigma_{xy}(\dot{\gamma}) \) has -ve slope...

...see shear-induced "phase separation"...

...steady state is banded

[Spenley, Cates, McLeish. '93]
[Olmsted, Goldbart. '90, '92]

- Here study initial instability...

Flow instabilities in the Johnson-Segalman model

Wormlike micelles: surfactant in H₂O (salt...)

- low surfactant concentration \( \rho \rightarrow 0 \)
  individual surfactant molecules

- \( \rho > \phi_{cmc} \): reversible assembly - spheres, worms, sheets...

- Semidilute \( \phi > \phi^* > \phi_{cmc} \): worms entangle

Dynamics: reptate \( \tau_d \)
break/recombine \( \tau_b \)

Rheology (Cates 87, 90)

Linear: maxwell

\[ G(t) = G_0 \exp \left( \frac{-t}{\tau_d} \right) \] if \( \tau_b \ll \tau_d \)

Non-linear:

\[ \sigma^{\text{micelles}} + \sigma^{\text{solvent}} = \sigma^{\text{BANDING!}} \]
Experiments: wormlike micelles

[Lerouge, Decruppe '01] [Lerouge et al. '00] [Berret '97] [Grand et al. '97]
[Berret, Porte '00] Below data: [Lerouge. Ph.D thesis, Univ. of Metz '00]

- $\Sigma_{xy}$, $\dot{\gamma}$ sweeps ("flow-curves")
  
  ![Graph of shear stress vs. shear rate for different conditions]
  
  - CTAB(0.3M)
  - $+$NaNO$_3$(1.79M)
  - $+$H$_2$O. 30°C

- $\dot{\gamma}$-jumps ("start-up") Metastable
  
  ![Graph of shear stress vs. time for different conditions with images of liquid layers]
  
  - CTAB(0.3M)
  - $+$NaNO$_3$(1.79M)
  - $+$H$_2$O. 30°C

Flow instabilities in the Johnson-Segalman model
Analogy? Cahn-Hilliard demixing instability \( \phi = 0 \)

2-fluid mixture of micelles (volume fraction \( \phi \)) and solvent

\[ \phi(y,t) = \bar{\phi} + \Re \exp(\omega t + iky) \]

Initial state = homogeneous + noise

Stable?

Dynamics: Cahn-Hilliard equation:

\[ \partial_t \phi = -\epsilon \Delta \frac{\Delta \phi}{\Delta \phi} \quad \text{free energy} \]

\[ F = \int [f_h(\phi) + \frac{\kappa}{2} \Delta \phi^2] \]

Gives growth rate \( w_k = -Dk^2 - \kappa k^4 \) sign? negative

with diffusion coefficient \( D = \frac{\partial^2 f_h}{\partial \phi^2} = \frac{\partial^2 \nu}{\partial \phi^2} \)

Figure 15.15: Diffusion de la lumière aux petits angles sous écoulement. Le taux de cisaillement imposé est 10 s\(^{-1}\). Les graphiques (a) et (b) correspondent respectivement aux plans d'observation (\( \theta, \phi \)) et (\( \theta, \nabla \phi \)).
Simplest transcription of CH theory $\rightarrow$ shear banding

\[ \text{homogeneous} + \text{noise} \]

\[ \left( \frac{\partial}{\partial t} \right) (\Sigma_{xy}) + \frac{\partial}{\partial x} (\Sigma_{yy}) e = e \]

\[ \text{stable?} \]

Force balance

\[ \rho \lambda \delta = \delta_x \Sigma_{xy} \]

Constitutive

\[ \Sigma_{xy} = \Sigma_{xy}(\delta_x) \]

\[ = \Sigma_{xy} + o(\lambda^2) \]

$\Rightarrow$ growth rate

\[ \omega_k = -\frac{\Sigma_{xy}(\delta_x)}{\rho} k^2 \]

\[ \Sigma_{xy} \quad \omega_k \quad \text{tue} \rightarrow \text{unstable} \]

\[ \Rightarrow \]

\[ \text{No } \kappa^x \text{??} \]

Diffusive Johnson-Segalman model

\[ \text{homogeneous} + \text{noise} \]

\[ \left( \frac{\partial}{\partial t} \right) \Sigma + \frac{\partial}{\partial x} (\Sigma) e = e \]

Dynamical equations:

1) Fluid velocity

\[ \rho \frac{\partial v}{\partial t} = \nabla \cdot \Sigma - \nabla p \quad \text{force balance} \]

2) Viscoelastic stress

\[ \Sigma = C(\dot{\epsilon}) \dot{\epsilon} + \eta(\dot{\epsilon}) \dot{\epsilon} \]

\[ \text{micellar} \quad \text{Newtonian} \]

\[ \text{SLIP} \quad \text{stretch} \quad \text{maxwell} \text{ tube} \quad \text{relaxation} \quad \text{mesh size?} \quad \text{interfaces} \]
Solve for time-independent...

\[ \Sigma_{xy} \]

Units:
\[ G(\phi = 0.11) = 1 \]
\[ \tau(\phi = 0.11) = 1 \]

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CPCI-Sal

Normalized shear stress \( \sigma G_0 \)

Critical concentration

Normalized shear rate \( \dot{\gamma} \tau_R \)
Solve for time-independent...

**Linear stability analysis:**

\[ w_k (\xi_1^2) = \frac{m_k}{B} \left( \xi_1^2 \right) + c \left( \xi_1^2 \right) \]

\[ \uparrow \quad \text{growth rate} \]

\[ \uparrow \quad \text{stability matrix} \]

\[ \sigma \phi = 0.11 \]

\[ \Delta \phi = 0.015 \]

--- unstable

Units:

\[ G(\phi = 0.11) = 1 \]
\[ r(\phi = 0.11) = 1 \]

--- spinodal

\[ \rightarrow \text{unstable, } w_k > 0 \quad \text{if } \Sigma_{xy}(\gamma) < 0 \]

--- unstable, spinodal.
Dynamics of $\dot{\gamma}_{\text{m}}$ & $\dot{\gamma}_{\text{rel}}$: 2-fluid model.

[de Gennes 76, Miether 93]

- Force balance for micelles

$$\frac{\gamma}{\rho} \dot{\gamma}_{\text{m}} = - \dot{\gamma}_{\text{rel}} + \nabla \cdot \nabla (\phi) \nabla \phi + 2 \nabla \cdot \nabla (\phi) \nabla \phi - \rho \frac{\partial F}{\partial \phi} - \rho \nabla p$$

Drag viscoelastic Newtonian (Rouse-)

$F = \int d\gamma \left[ f_\phi (\phi) + \frac{1}{2} \phi \nabla \phi^2 \right]$ osmotic

$\int d\gamma \left[ f_\phi (\phi) T \nabla \phi \right]$ elastic

- Force balance for solvent

$\gamma (1-\phi) \frac{\partial \gamma_{\text{s}}}{\partial t} = \gamma \dot{\gamma}_{\text{rel}} + 2 \nabla \cdot \nabla (\phi) \frac{\partial \gamma_{\text{s}}}{\partial t} - (1-\phi) \nabla p$

Drag Newtonian pressure

- Add $\rightarrow \dot{\gamma}_{\text{m}}$ force balance

- Subtract $\dot{\gamma}_{\text{rel}} = \frac{\partial \phi}{\partial t}$ continuity

Final dynamical equations

- Viscoelastic constitutive equation

$$\frac{\partial \gamma}{\partial t} = \frac{d-\gamma}{\delta \gamma}$$ as before (but $\gamma_{\text{m}} \rightarrow \gamma_{\text{m}}$

- Force balance

$$\frac{\partial \gamma}{\partial t} = \nabla \cdot \nabla (\phi) \nabla \phi + \nabla \cdot \nabla (\phi) \nabla \phi - \rho \frac{\partial F}{\partial \phi} - \rho \nabla p$$

- Continuity

$\frac{\partial \phi}{\partial t} = - \nabla \cdot (\gamma (1-\phi) \nabla \phi + \nabla \cdot \nabla (\phi) \nabla \phi + \nabla \cdot \nabla (\phi) \nabla \phi + \rho \frac{\partial F}{\partial \phi})$

Homogeneous constitutive curves as before

But now: fluctuations coupled (except for $\gamma_{\text{m}}$, $D$ fixed)

$M_{\text{m}} = \gamma_{\text{m}} (1-\gamma_{\text{m}})$

[Schmitt, Marques, Legueux; Helfand-Fredrickson]
Shifted spinodals:

\[ \Sigma_{xy}(\gamma) + \frac{C'(\phi)}{2} N_{yy}(\xi) = 0 \]

\[ \text{C.H. mechanical coupling} \]

\[ \Rightarrow \text{at } \Sigma_{xy}(\gamma) = 0 \text{ in uncoupled limit } \xi \rightarrow \infty \]

Coupling shifts it by \( O\left(\frac{C'(\phi)}{2}\right) = O\left(\frac{C'(\phi)}{f'(\phi)}\right) \)

Qualitatively 2 different types of system:

0. Far from C.H. \( \Rightarrow \text{mechanical, perturbed by } \phi \to (\delta Y, \delta \Sigma, \delta \phi) \)

0. Close to C.H. \( \Rightarrow \text{for low } \xi \): C.H. perturbed by flow \( (\delta x, \delta y, \delta \phi) \)

[Clarke, Mcleish, Milner, Onuki]
So far we've considered...

\[ \Sigma_{xy} \]

...fluctuations about intrinsic constitutive curve.

Can use these to define spinodal.

For slow \( \dot{\gamma} \) sweeps towards unstable region.

But: inside unstable region:

must consider \( \dot{\gamma} \) startup quenches...

\[ \Sigma_{xy} = \eta \dot{\gamma} + G(\phi) \chi_{xy} \]

"Instable" Maxwell time, \( \tau \)

But \( w^* = o(\frac{1}{\tau}) \)

time-scales comparable.

\[ \begin{array}{c}
\dot{\gamma} \\
\dot{\phi}
\end{array} \]

\( \Rightarrow \) explicitly consider time dependent background

\( \frac{\dot{w}}{w} (t) \)
Spinodals in $\phi - \dot{\gamma}$ space

Shear start-up type A; expect $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$

- Dispersion relation

- Eigenvector at peak of dispersion relation

Now consider shear start-up for

$\times$ a type A system [expect eigenvector $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$]

$\times$ a type B system [expect eigenvector $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$]

Find $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$ as expected
Shear start-up type B; expect $\left( \delta \gamma, \delta \sigma, \delta \phi \right)$

- Dispersion relation

- Eigenvector at peak of dispersion relation

Find $\left( \delta \gamma, \delta \sigma, \delta \phi \right)$ as expected
Conclusions

- Purely mechanical instability is enhanced by coupling to concentration
- Then has a selected wavevector $k^*$
- Two types of instability...
  - Extreme mechanical, slightly perturbed by $\phi$ coupling
  - Cahn-Hilliard, slightly perturbed by flow
- Smooth cross-over between these two types.
Extensions, outlook

- whole \( x, y \) plane
- first to find "static" \( S(x,t) \)
- later stages of unstable kinetics
- metastable kinetics
- steady state phase diagram
- other models, ideally microscopic
- Implications of unstable high \( \delta \) branch