Capillary Thinning & Breakup of Complex Fluids

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The Role of Fluid Rheology

- “Slimy”

\[ \tau_{yx} = \eta(\dot{\gamma}) \dot{\gamma}_{yx} \]

- “Sticky”

\[ \tau_{zz} - \tau_{rr} = \eta(\dot{\varepsilon}) \dot{\varepsilon}_{zz} \]

IMA Outline

• Brief introduction to rheological behavior and constitutive models

• The extensional viscosity of complex fluids
  □ …an independent material function

• Instrumentation for measuring filament breakup of Newtonian and Viscoelastic Fluids

• Concentration and molecular weight effects on extensional viscosity

• Memory of initial conditions

• Coupled filament evolution and mass (or heat) transfer
Extensional Rheometry

- Available techniques for measuring the extensional viscosity:
  - Ideal Elastic Liquids (Boger fluids)
  - Concentrated Solutions
  - ‘Low’ Viscosity Melts
  - Adhesives
  - Suspensions
  - Physical gels & colloidal systems
  - Paints, Foodstuffs, Dyes...

[Diagram showing a log-log plot with labels for different viscosity ranges and rheometric techniques, including Meissner Apparatus, Filament Stretching Rheometers, Zero-Shear Rate Viscosity [Pa.s], Capillary Breakup Rheometers, Opposed Jet Devices, Contraction Flows, and “Apparent Extensional Viscosity Indexers”]

[Numbers and scales for zero-shear rate viscosity ranging from $10^{-1}$ to $10^6$ Pa.s]
Application Areas

- Materials with time-varying properties; e.g. paints, adhesives, foodstuffs...
  - Rapid test time, small sample volume.
  - Simple pragmatic indexing application.
Physics of Complex Fluids: Dimensional Analysis

- Scale relative magnitude of each force governing fluid dynamical response of complex materials.
- Understand the operating space of a particular physical process (e.g. Ink-jetting, etc.)
- Understand the effects of formulation changes on resulting stability boundaries.

\[
\text{Reynolds Number} \quad \frac{\Omega}{\sigma} = \frac{\eta U}{\sigma}
\]

\[
\text{Deborah Number} \quad E_s = \frac{D e}{C a}
\]

\[
\text{Capillary Number} \quad C a = \frac{\text{Viscous Stress}}{\text{Surface Tension}} = \frac{\eta U}{\sigma}
\]

\[
E = \frac{D e}{R e} = \frac{\lambda \eta}{\rho \ell^2}
\]

\[
E_s = \frac{D e}{C a} = \frac{\lambda \sigma}{\eta \ell}
\]
A Primer on Dumbbell Kinetic Theory

- Canonical molecular model for polymer solutions

\[ F = H f(Q)Q \]

\[ f \approx \frac{1}{1 - Q^2/(Na)^2} \]

\[ L^2 = \frac{Q_{max}^2}{Q_{eq}^2} = 3N \]

**Fokker-Planck equation** (& closure approximations…Peterlin, Tanner)

**Upper-convected derivative**

**FENE-P Constitutive Equation**

\[ \frac{D A}{D t} - \nabla V^T \cdot A - A \cdot \nabla V = A_{(1)} = - \frac{1}{\lambda_1} [f(trA)A - I] \]

\[ \tau = \eta_s \dot{\gamma} + nk_BT [f(trA)A - I] \]

Lagrangian Formulation:

\[ \frac{D A}{D t} = \left( \nabla V^T \cdot A + A \cdot \nabla V \right) - \frac{1}{\lambda_1} [f(trA)A - I] \]
Consequences for Extensional Rheology

\[ \nabla \mathbf{v} = \frac{\dot{\varepsilon}_0}{2} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +2 \end{pmatrix} \]

- Large axial stresses ("Streamline tension")
- Transient extensional stretching of chains and tensile stress growth...

Evolution Eq:

\[ \frac{dA_{zz}}{d(t/\lambda_1)} = (2\lambda_1 \dot{\varepsilon}_0 - f(trA))A_{zz} + 1 \]

"High" $De > 1/2$:

Transient: $f \approx 1$:

\[ A_{zz} \approx \frac{2}{(2De - 1)} \left[ \exp \left( (1 - 1/2De)(\dot{\varepsilon}_0 t) \right) - 1 \right] \]

Steady state: $f \to 2De$:

\[ \tau_{zz} \approx 2n k_B T L^2 \lambda_1 \dot{\varepsilon}_0 \left( 1 - (2De)^{-1} + \ldots \right) \]

Kramers Bead-Rod Chain in Extensional Flow


Doyle, Shaqfeh, Spiegelberg, McKinley, *JNMFM* 1997
Capillary Breakup Extensional Rheometer (CABER)

- A quantitative version of the ‘thumb & forefinger’ test!
  - Original experimental and theoretical work of V. Entov & co-workers
  - Extensional equivalent of a ‘step-strain’ experiment

- Shape of $D_{mid}(t)$ curve and time to breakup provide information about extensional rheological properties of fluid at large strains.
  - Small sample volume, rapid test, useful for foods, dyes, consumer products...
CABER (Capillary Breakup Extensional Rheometer)

Early work by Bazilevsky, Entov & Rozhkov (1990)
Results for Simple Fluids

• Newtonian Fluids
  □ McKinley & Tripathi, *J Rheol.*, 2000

\[
\frac{R_{\text{mid}}}{R_0} = 0.0709 \frac{\sigma}{\eta_s R_0} (t_c - t)
\]

• Ideal Elastic Fluids
  □ Entov & Hinch, JNNFM, 1997

\[
\frac{R_{\text{mid}}}{R_0} = \left( \frac{GR_0}{\sigma} \right)^{1/3} \exp\left( -\frac{t}{3\lambda_1} \right)
\]

**Polystyrene Oil**

SM-1 (500 ppm $2 \times 10^6$ g/mol.

\[t_{\text{cap}} = \frac{\eta_0 R_0}{\sigma} \sim 8 \text{ sec}\]

\[2R_0 = 6 \text{ mm}\]
Capillarity-Induced Filament Breakup (summary of video)

PS Oil: Oligomeric styrene

\[ Bo = \frac{\rho g R_0^2}{\sigma} \approx 19 \]

\[ t^\ast = \left( \frac{\eta_0 R_0}{\sigma} \right) = 8.5 \text{s} \]

SM-1 Fluid: 0.05 wt% PS (\( M_w = 2 \times 10^6 \text{ g/mol.} \)) in oligomeric styrene

\[ t^\ast = 9.8 \text{s} \]
The Newtonian Fluid

- Plateau (1873); Rayleigh (1892)

\[ \sigma \]

\[ 2R_{mid}(t) \]

- Capillary velocity: \( \frac{\sigma}{\eta_s} \) [m / s]

- Axial Force Balance:

\[ 3\eta_s \left\{ \frac{-2}{R_{mid}(t)} \frac{dR_{mid}(t)}{dt} \right\} \sim \frac{\sigma}{R_{mid}(t)} \]

\textit{viscous stress} \hspace{1cm} \textit{capillary pressure}

Nonlocality (similarity solution; Papageorgiou, 1995)

\[ R_{mid}(t) = 0.0709 \frac{\sigma}{\eta_s} (t_c - t) \]


\[ 2R_{mid} \leq \sqrt{\frac{0.1 \sigma}{\rho g}} \]
Calibration Tests: Glycerin

- Use a well-characterized viscous Newtonian fluid to check the analytical solution.
Analysis of Visco-capillary Breakup: Glycerin

- Each breakup event well described by Newtonian analysis, but…
- Time to breakup monotonically decreases with each test:

\[ R_{mid}(t) = 0.0709 \frac{\sigma}{\eta_s(t)}(t_c - t) \]

- Glycerol (100%) is hygroscopic
  - Viscosity decreases with time
  - Surface tension ≈ constant
- Viscosity decreases until fluid is in equilibrium with ambient humidity
Other Classes of Complex Fluids

• Dilute Polymer Solutions
  ❑ Monodisperse polystyrene \( (M_w = 2, 7, 20 \times 10^6 \text{ g/mol}) \)

• Concentrated Polymer Solutions
  ❑ Entangled polystyrene solutions; \( M_w/M_e = 3 – 10 \)

• Associative Polymer (Physical Gels)
  ❑ Hydrophobically-modified Ethoxylated Urethanes (HEUR)

• Pressure Sensitive Adhesives

• Future Work
  ❑ Food stuffs & consumer products….yogurts; caramels, shampoo
  ❑ Paints and inks
  ❑ Suspensions
  ❑ Liquid crystals
Elasto-Capillary Necking: Hookean Dumbbells (Entov & Hinch, 1997)

- Kinematics
  \[ \dot{\epsilon} = -\frac{2v_r}{R} = -\frac{2}{R} \frac{dR}{dt} \]

- Constitutive Equation
  \[ \lambda_1 \frac{dA_{zz}}{dt} - 2\lambda_1 \dot{\epsilon} A_{zz} = -(A_{zz} - 1) \]

Combining Gives
  \[ \frac{d\ln A_{zz}}{d(t/\lambda_1)} - \frac{4d\ln R(t)}{d(t/\lambda_1)} = -1 \]

Conformation Tensor
  \[ A = \frac{\langle QQ \rangle}{Q_{eq}^2} \]

- Force balance – assuming axially uniform:
  \[ \text{Capillary Pressure} \approx \text{Elastic Stress} \]
  \[ \frac{\sigma}{R_{mid}(t)} \approx GA_{zz} = G\left(\frac{R_0}{R_{mid}(t)}\right)^4 \exp(-t/\lambda_1) \]

Elasto-Capillary Number
  \[ \frac{GR_0}{\sigma} = \frac{\eta_p R_0}{\lambda_1 \sigma} \equiv \frac{Ca}{De} \]
Dilute Polymer Solutions

- Increasing molecular weight delays elasto-capillary breakup
- Measured time-scale agrees quantitatively with Zimm relaxation time

- Important in many biological processes (saliva, spinning of spider silk)
THE EFFECT OF INITIAL CONDITIONS

- Fluid thread is formed by a rapid initial axial stretching (extensional 'step strain')
- Presence of nonzero initial axial stretch in the molecular conformation

\[ 3\eta_s \dot{\varepsilon}_{mid} = -G[A_{zz} - A_{rr}] + \frac{\sigma}{R_{mid}(t)} \quad + \text{ODEs for } A_{zz}(t), A_{rr}(t) \]

- Seek a solution in which all terms (viscous, elastic, capillary) contribute to filament evolution

- Constant stretching-rate solution:

\[ A_{zz}^0 = \left( \frac{\sigma}{GR_1} \right) \left( 1 - \frac{2\eta_s R_1}{\sigma \lambda_Z} \right) \]

- Initial condition directly (& dramatically) effects the time to breakup; a nonfading memory!
The Role of Fluid Rheology & Entanglements

- Increase concentration of polymer: chains become entangled \( (c^* \sim M_w^{-1/2}) \)
  - Concentrated high molecular weight polymer solution (5 wt% PS in TCP): \( N_e \sim 10 \)
  - Reasonably well-described by a single-mode nonlinear constitutive model (Giesekus…)

- Self-Similar Breakup of a Giesekus Fluid (Renardy, 1995; 2000)
  - shear-thinning but (bounded) strain-hardening in extensional viscosity.
  - Finite time breakup over a finite region of space:
    \[
    \frac{R_{mid}(t)}{R_0} = f(\alpha \eta_s) \frac{\sigma}{(\eta_0/\alpha)} (t_c - t)
    \]

\[
\begin{align*}
G_N^0 &= 95 \text{ Pa} & \lambda_1 &= 0.6 \text{ s} \\
\eta_0 &= 59 \text{ Pa.s} & \lambda_1 &= 0.6 \text{ s} \\
\eta_s &= 2.0 \text{ Pa.s} & \alpha &= 0.2
\end{align*}
\]
Elasto-Capillary Breakup of Entangled Solutions

- Finite extensibility of chains limited by distance between entanglements
- Extensional stresses reduced accordingly...

\[ t_{\text{cap}} = \frac{\eta_0 R_0}{\sigma} \approx 5.9 \text{s} \]
\[ \dot{\lambda}_1 = 0.60 \text{ s} \]

5 wt% PS (2 x10⁶ g/mol) in TCP

\[ \alpha \eta_s / \eta_p \approx 0.0068 \]

\[ Bo = \frac{\rho g R_0^2}{\sigma} \approx 3.1 \]
Filament Profile Close to Breakup

\[ t_{cap} = \eta_0 R_0 / \sigma \approx 5.9 \text{ s} \]
\[ \lambda_1 = 0.60 \text{ s} \]

\[ t-t_c = 6.23 \text{ s} \]

\[ t-t_c = 2.23 \text{ s} \]

\[ t-t_c = 1.23 \text{ s} \]

\[ t-t_c = 0.90 \text{ s} \]

\[ t-t_c = 0.57 \text{ s} \]

\[ t-t_c = 0.23 \text{ s} \]

\[ B_0 = \frac{\rho g R_0^2}{\sigma} \approx 3.1 \]

\[ g \]
Ongoing Work I: Associating Polymer Solutions

- **Hydrophobically-modified Ethoxylate-Urethane (HEUR) polymer**
  - Prepared by R.D. Jenkins; Union-Carbide (Singapore)
  - Used as an ‘associative thickener’ for paints etc… 2wt% in water

- Fails by a different mechanism:
  - Initial elastocapillary thinning
  - at a critical radius, thread ‘pinches off’...

- Concept of a critical stress
  - *Flower micelles* form a physically-cross-linked network (‘physical gel’):
    - Tensile stress grows as radius decreases:
      \[ \Delta \tau_{\text{network}} \sim \frac{\sigma}{R_{\text{min}}} \]
Conclusions

• In the past decade, filament rheometry has developed into a viable tool for measuring transient extensional viscosity of complex fluids.

• Interaction of experimentation, simulation and molecular modeling!
  - Good agreement with Brownian dynamics simulations, except at extremely high molecular weights.

• Filament Stretching Extensional Rheometers (FISER)
  - Impose a time scale \( t^* = 1/\dot{\varepsilon}_0 \)  \( \Rightarrow \) Hence vary \( De = \lambda\dot{\varepsilon}_0 \)
  - Mechanically difficult (\& expensive) to implement

• Capillary Breakup Extensional Rheometers (CABER)
  - Material selects its own time-scale for self-similar visco-elasto-capillary thinning:
  - Easy to realize, but analysis is more complex:
    \( \Rightarrow \) Timescales: capillary, elastic, mass transfer, heat transfer...

• Future work: other classes of complex ‘Non-Newtonian’ fluids
  - Consumer products...?